Alkaline-earth complexes supported by fluorinated ancillary ligands
Acknowledgements

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<th>Description</th>
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<tbody>
<tr>
<td>&lt;</td>
<td>less than</td>
</tr>
<tr>
<td>&gt;</td>
<td>more than</td>
</tr>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>1D, 2D</td>
<td>monodimensional, bidimensional</td>
</tr>
<tr>
<td>18-c-6</td>
<td>1,4,7,10,13,16-hexaoxacyclooctadecane</td>
</tr>
<tr>
<td>Å</td>
<td>Ångstrom</td>
</tr>
<tr>
<td>Ae</td>
<td>alkaline-earth</td>
</tr>
<tr>
<td>Anal.</td>
<td>analytically</td>
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<tr>
<td>au</td>
<td>atomic units</td>
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<tr>
<td>benzene-$d_6$</td>
<td>deuterated benzene</td>
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<tr>
<td>BDE</td>
<td>bond dissociation energy</td>
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<tr>
<td>br.</td>
<td>broad</td>
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<tr>
<td>ca.</td>
<td>circa</td>
</tr>
<tr>
<td>Calcd.</td>
<td>calculated</td>
</tr>
<tr>
<td>CCDC</td>
<td>Cambridge Crystallographic Data Centre</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>deuterated chloroform</td>
</tr>
<tr>
<td>$\varepsilon$-CL</td>
<td>$\varepsilon$-caprolactone</td>
</tr>
<tr>
<td>COSY</td>
<td>Correlation spectroscopy</td>
</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
</tr>
<tr>
<td>Cp$^*$</td>
<td>pentamethylcyclopentadienyl</td>
</tr>
<tr>
<td>C.N.</td>
<td>coordination number</td>
</tr>
<tr>
<td>dippNacNac</td>
<td>CH[CMeN(2,6-$i$-Pr$_2$C$_6$H$_3$)$_2$]$_2$</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>dichloromethane-$d_2$</td>
<td>deuterated dichloromethane</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DOSY</td>
<td>Diffusion-ordered NMR spectroscopy</td>
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<tr>
<td>e.g.</td>
<td>exempli gratia</td>
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<tr>
<td>Et</td>
<td>ethyl</td>
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<tr>
<td>equiv.</td>
<td>equivalent</td>
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<tr>
<td>et al.</td>
<td>et alia</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>g</td>
<td>grams</td>
</tr>
<tr>
<td>h</td>
<td>hours</td>
</tr>
<tr>
<td>HMBC</td>
<td>Heteronuclear multiple-bond correlation spectroscopy</td>
</tr>
<tr>
<td>HMQC</td>
<td>Heteronuclear multiple-quantum correlation spectroscopy</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>Ind</td>
<td>1,3-diisopropylindenide</td>
</tr>
</tbody>
</table>
List of Abbreviations

\[ i.e. \quad \text{id est} \]
\[ ^{1}\text{Pr} \quad \text{iso-propyl} \]
\[ J \quad \text{coupling constant} \]
\[ K \quad \text{Kelvin} \]
\[ k_{\text{app}} \quad \text{apparent rate constant} \]
\[ \text{KIE} \quad \text{kinetic isotope effect} \]
\[ \text{LA} \quad \text{lactide} \]
\[ \text{LUMO} \quad \text{Lowest Unoccupied Molecular Orbital} \]
\[ \{\text{LX}\}^{-} \quad \text{ancillary ligand} \]
\[ M \quad \text{molar concentration (mol/L) or metal} \]
\[ m \quad \text{multiplet} \]
\[ m- \quad \text{meta-} \]
\[ \text{Me} \quad \text{methyl} \]
\[ \text{MHz} \quad \text{Megahertrz} \]
\[ \text{min} \quad \text{minutes} \]
\[ \text{MS} \quad \text{mass spectrometry} \]
\[ \text{Mw} \quad \text{molecular weight} \]
\[ \text{n}^{\text{Bu}} \quad \text{n-Butyl} \]
\[ \text{NHC} \quad \text{N-heterocyclic carbene} \]
\[ \text{NMR} \quad \text{Nuclear Magnetic Resonance} \]
\[ \text{NOESY} \quad \text{Nuclear Overhauser Effect spectroscopy} \]
\[ o- \quad \text{ortho-} \]
\[ \text{OTf} \quad \text{triflate anion} \]
\[ p- \quad \text{para-} \]
\[ \text{PLA} \quad \text{poly(lactic-acid)} \]
\[ \text{Ph} \quad \text{phenyl} \]
\[ \text{ppm} \quad \text{parts-per-milion} \]
\[ \text{py} \quad \text{pyridine} \]
\[ \text{RE} \quad \text{rare-earth} \]
\[ \text{ROP} \quad \text{ring-opening polymerisation} \]
\[ T \quad \text{temperature} \]
\[ t \quad \text{time} \]
\[ \text{t}^{\text{Bu}} \quad \text{tert-butyl} \]
\[ \text{THF} \quad \text{tetrahydrofuran} \]
\[ \text{THF-}^{d_{8}} \quad \text{deuterated tetrahydrofuran} \]
\[ \text{TMSS} \quad \text{tetrakis(trimethylsilyl)silane} \]
\[ \text{TMC} \quad \text{trimethylene carbonate} \]
\[ \text{TON} \quad \text{turnover number} \]
\[ \text{toluene-}^{d_{8}} \quad \text{deuterated toluene} \]
\[ \text{TOF} \quad \text{turnover frequency} \]
Chapter 1: Heteroleptic Calcium Complexes: Stabilisation Methods and Applications in Homogeneous Catalysis
Chapter 2: Heteroleptic calcium complexes: stabilisation methods and applications in homogeneous catalysis

1.1. General introduction

Calcium was attested for the first time in 975 AD when the plaster of Paris (CaSO₄) was perceived as useful for treating bone fractures. Calcium was used by the Egyptians under the form of gypsum (CaSO₄·2H₂O) to construct the Great Pyramid of Gizeh and the plaster from Tutankhamun’s tomb. Moreover, a material derived from mixing sand and lime (based on CaCO₃) was used by the Romans in their constructions due to its higher resistance to humidity. As a matter of fact, the name ‘calcium’ comes from the Latin word calcis (lime in Latin) and was isolated by Sir Humphry Davy in 1808 by electrolysing a mixture of lime and HgO.¹

Beginning with the 20th century, the organometallic chemistry of alkaline-earth elements was dominated mostly by Grignard’s work on organomagnesium complexes.² It soon became evident that the chemistry of the heavier Ae* analogues (Ca, Sr, and Ba) was very different. This was reflected in the difficulties in synthesising complexes containing a Ca–C bond, which was hampered by extreme air, moisture and thermal sensitivity caused by their high reactivity. A major breakthrough was achieved in 1956 when Ziegler et al. reported the synthesis of CaCp₂;³ later in 1974 Stucky et al.⁴ published the polymeric molecular structure for the same complex. Nowadays, after the seminal work of Westerhausen,⁵ Grignard analogues of magnesium have become more common, albeit they are difficult to isolate and can promote ether degradations at temperatures as low as −35 °C.

Difficulties in manipulating complexes of calcium and its heavier analogues, strontium and barium, are related to their high oxophilicity, electrophilicity, polarisability and low electronegativities. Their high ionic radii (rCa²⁺ = 1.00 Å, rSr²⁺ = 1.18 Å, and rBa²⁺ = 1.35 Å)⁶ require high coordination numbers. In fact their size is more related to divalent (rYb²⁺ = 1.02 Å, rEu²⁺ = 1.17 Å, and rSm²⁺ = 1.22 Å) and trivalent (rNd³⁺ = 0.98 Å and rSm³⁺ = 0.96 Å) rare earths (lanthanides) than to those of their lighter Ae counterparts (rBe²⁺ = 0.45 Å, rMg²⁺ = 0.72 Å).⁶ Based on these resemblances in atomic properties, the coordination chemistry of divalent lanthanides (Ln²⁺) and heavy Ae elements is also comparable. However, Ln²⁺ elements are redox active and can easily oxidise in a +3 oxidation

¹ A list of abbreviations can be consulted at the beginning of the manuscript.
state \( (E^{°}_{\text{Yb}^{3+}/\text{Yb}^{2+}} = -1.05 \text{ V}, E^{°}_{\text{Sm}^{3+}/\text{Sm}^{2+}} = -1.55 \text{ V}, E^{°}_{\text{Eu}^{3+}/\text{Eu}^{2+}} = -0.35 \text{ V}) \), whereas alkaline-earths are essentially inert to electron transfer reactions. \(^\dagger\)

### 1.2. Application in homogeneous catalysis

#### 1.2.1. Foreword

In terms of applications in homogeneous catalysis, Lewis acid catalysts of type \( \text{ME}_x \) (\( E = \text{NTf}_2, \text{OTf} \)) based on calcium \(^8\) or rare earths \(^9\) have enjoyed an enormous success due to the fact that they are resistant towards air and moisture. On the other hand, well-defined complexes of type \([\text{LX}]\text{M}–\text{Nu}\) (\( \text{LX} = \text{ancillary ligand}; \text{M} = \text{RE or Ae}; \text{Nu} = \text{nucleophile group} \)) are more difficult to handle and require anaerobic working conditions. Progress was made in the field after the pioneering work of Marks, who demonstrated that complexes of type \([\text{Cp}^\bullet_2\text{Ln}–\text{Nu}]\) (\( \text{Ln} = \text{La, Nd, Sm, Yb, and Lu}; \text{R} = \text{H, } \eta^3–\text{C}_3\text{H}_5, \text{CH(SiMe}_3)_2, \text{and N(SiMe}_3)_2 \)) are excellent precatalysts for the hydroelementations (\textit{i.e.} (cyclo)hydroamination, \(^{10}\) hydrophosphination, \(^{11}\) hydrosilylation, \(^{12}\) and hydroboration \(^{13}\)) of alkenes. Detailed mechanistic investigations showed that the first step in the catalytic cycle (Scheme 2.1) is the catalyst formation (A) by displacement of the leaving group R with the substrate molecule \( \text{HX} \) (amines, phosphines, silanes, and boranes) \textit{via} \( \sigma \)-bond metathesis reactions, creating a M–X bond (\( X = \text{N, P, Si, B} \)).

![Scheme 2.1. Catalytic cycle for heterofunctionalisation reactions promoted by trivalent lanthanidocenes.](image_url)

Chapter 1: Heteroleptic Calcium Complexes: Stabilisation Methods and Applications Homogeneous Catalysis

The second step (often rate determining) consists in the insertion of the unsaturated moiety (from alkenes or alkynes) into the M–X bond to obtain the alkyl complex B. A second σ-bond metathesis reaction between B and a second HX molecule affords the catalyst regeneration which is simultaneous with the product release.

In these organic transformations, the Lewis acidity and the polarisability of the metal centre is of utmost importance; this can be easily observed, as for instance in Ln³⁺ metal complexes can easily undergo olefin insertion in M–C bonds and be effective precatalysts in ethylene polymerisation.¹⁴ The behaviour of alkaline-earth complexes is similar to that of divalent lanthanides and to date there are no such species that can promote the polymerisation of “unactivated” olefins.

1.2.2. The case of calcium complexes

A viable alternative to catalytic systems based on rare earth complexes is exemplified by calcium precatalysts. Calcium salts are biocompatible and the fact that they have a high earth crust abundance (3.4 wt%)¹⁵ makes the development of precatalysts using this element attractive. Even though lanthanidocene-mediated catalytic hydroelementation has now been known for over 25 years, the use of calcium complexes in homogeneous catalysis remained scarce until early 2000s when it witnessed a surge in popularity; this can also be tracked using the CCDC (Cambridge Crystallographic Data Centre) database: Figure 2.1 shows the number of crystallised calcium containing complexes in the period 1990–2013. For comparison, the number of crystallised calcium complexes in the same time span is comparable to that reported for magnesium, and essentially lower than seen for zinc or iron (i.e. 2148 and 2275, respectively in 2012).

![Figure 2.1](imageLink)  
*Figure 2.1. (left) Number of X-ray structures containing calcium reported over the 1999-2013 period according to a CCDC database search in august 2015. (right) Comparison between the number of X-ray structures of calcium (red), magnesium (blue), and zinc (green).*

In a recent review,¹⁶ Harder has named calcium a “sleeping beauty” in light of comparison with the omnipresent Grignard reagents. Indeed, this surge of calcium complexes may be seen as
representative of the “awakening” of this element, following the recent development of ligand platforms able to accommodate and stabilise the large ionic radius and high coordination numbers of this metal (C.N. = 4–7). The main aim of the following paragraphs is to present the application of calcium complexes in homogeneous catalysis with a particular emphasis on hydroelementation reactions.

1.2.3. Calcium mediated polymerisation catalysis

One of the main challenges that still troubles the chemical industry concerns the replacement of polluting non-degradable “plastics” with biodegradable ones. A viable solution consists in the preparation of polyesters such as polylactides. Nowadays, PLA production takes place on a large scale (~150 kilotons), typically by ROP of the bio-resourced lactide in the presence of the robust [Sn(Oct)]$_2$ and a protic co-initiator (H$_2$O, alcohols). In addition to issues related to the potential toxicity of tin(IV), the tin(II) precatalyst is unable to afford high activities and good control over ROP parameters, yielding mainly atactic\(^4\) polymers. For this reason, there is need for replacing this sluggish catalytic system with a more selective and active one.

This section will briefly summarise the catalytic systems in ROP reactions of LA (and other polar monomers such as TMC and ε-CL) based on neutral heteroleptic calcium complexes (Scheme 2.2). In addition, the activity of Ca catalysts in the polymerisation of activated olefins polymerisations will also be illustrated.

**Scheme 2.2.** Ring-opening (left) and styrene (right) polymerisation reactions promoted by calcium complexes.

1.2.3.1. Ring-opening polymerisation of cyclic esters

For the ROP of cyclic esters, Westerhausen and Feijen *et al.* have shown that the homoleptic compound Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ can be used both as an initiator and to generate *in situ* alkoxide-Ca species (upon addition of an alcohol) to polymerise L-lactide (L-LA) and ε-caprolactone (ε-CL) under

\(^4\) Atactic polylactides feature randomly distributed configurations of stereocentres.
living conditions.\textsuperscript{17} Chisholm \textit{et al.} showed that heteroleptic calcium complexes can be employed in polylactide synthesis and reported the catalytic activity of $\left(\text{DippNacNac}\right)\text{CaN(SiMe}_3\text{)}_2(\text{THF})$ (I) ($\text{DippNacNac} = \text{CH}[\text{CMeN}(2,6\cdotp\text{iPr}_2\text{C}_6\text{H}_3)]_2$).\textsuperscript{18a} Further progress was achieved by Chisholm and Mountford using the bulky $\{\text{Tp}^{\text{Bu}_3}\text{Ca–Nu}\}$ ($\text{Tp} = \text{trispyrazolylborate}$ (II); $\text{Nu} = \text{N(SiMe}_3\text{)}_2$, O-2,6-$\text{iPr}_2\text{C}_6\text{H}_3$, BH$_4$) who reported unprecedented activities for these complexes in d,L-LA polymerisation to give mainly heterotactic \textsuperscript{8} PLA.\textsuperscript{18,19} Interestingly, the stereoselectivity of the catalytic reaction was linked to the bulk of the ligand as the complex bearing a relatively less crowded Tp$^{\text{Bu}_3}$ afforded only atactic polymers. The most illustrative examples of heteroleptic calcium precatalysts in the ROP of cyclic esters are depicted in Figure 2.2.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{heteroleptic calcium complexes for the ROP of cyclic esters.png}
\caption{Heteroleptic calcium complexes for the ROP of cyclic esters.}
\end{figure}

\textsuperscript{8} Heterotactic polylactides have a perfect alternating sequence of the two enantiomers of LA (L-LA, D-LA, L-LA, etc.)
In addition, heteroleptic complexes bearing bulky ligand frameworks such as nitrogen tethered β-(diketiminates), β-diketonates, and β-(phosphinimino)methanides (II) were also tested in the ROP of cyclic esters. Sarazin and Carpentier reported on the use of calcium complexes supported by multidentate phenolato ligands (VII) for the ROP of L- and D,L-lactides. Also, calcium complexes stabilised by oxalamidinates (IV), pyrrolyl pincers (III), phosphorus-based pincer (V), polyethers, or a N^N^N^N macrocycle (VI) are active for the same purpose (Figure 2.2). In addition to heteroleptic complexes, neutral homoleptic, cationic, or open metallocene calcium species, are potent precatalysts in the polymerisation of cyclic esters.

### 1.2.3.2. Styrene polymerisation

Before 1990, for polymerisation reactions of activated olefins such as styrene or butadiene, catalytic systems based on alkaline-earths were essentially non-existent. In fact, the only reports in which styrene polymerisation is promoted by these metals mention the use of in situ generated barium precatalysts. Single-site precatalysts based on Ae elements became available with the development of a heteroleptic benzyl barocene by Harder and Brintzinger, albeit the resulting polymer was predominantly atactic and the metal complex suffered from kinetic lability in solution. For this reason, calcium complexes are more attractive as they are less prone to undergo Schlenk equilibria (vide infra). Harder et al. reported that a class of fluorenyl-benzyl-calcium heteroleptic complexes catalyse the formation of polystyrene in a syndioselective and living fashion (Figure 2.3). Subsequent studies on the same type of complexes proved that adding a bulky substituent in the 2- and 7- positions of the fluorenyl moiety increases the syndiotacticity of the resulting polystyrene. Homoleptic di(benzylamino)-calcium complexes can also catalyse to some extent the polymerisation of styrene, but yield only atactic polymers. Regarding the polymerisation of 1,3-butadiene (BD), Okuda’s bis(allyl)calcium is an effective precatalyst affording poly(BD) with narrow molecular weight distributions.

**The name heteroleptic complex implies the existence of at least two different ligands attached to the metal centre (two in the case of Ae complexes). By contrast, in the case of homoleptic complexes, the metal centre is bounded to identical ligands. Complexes of the type [CaNu]_2(THF)_n where the two anionic ligands are similar but where a donor solvent is also coordinated, are also (yet abusively) called homoleptic complexes.**
1.2.4. Hydroamination reactions

The addition of primary and secondary amines containing a N–H bond across unsaturated substrates (alkenes, alkynes or allenes) is an atom-efficient route for the production of valuable amines.\(^\text{41}\) This reaction has become very attractive as it can convert relatively inexpensive starting materials into building blocks in organic synthesis in the absence of any side-products. However, difficulties related to this process refer to a high activation barrier and a highly negative entropy which means the reaction equilibrium is shifted to the left (starting materials) when temperature rises. The utilisation of a catalyst is beneficial as it allows to decrease the activation barrier.\(^\text{41a}\) Traditional precatalysts in the intermolecular version of this reaction are based on late \(d\) block elements; however despite showing decent activities, the formation of the anti-Markovnikov addition product is not always certain.\(^\text{10c,42}\) For instance, literature data indicate that rhodium precatalysts are able to afford the anti-Markovnikov regioselectivity,\(^\text{43}\) in the case of iridium complexes, the Markovnikov products are generally obtained.\(^\text{44}\) On the other hand, catalytic systems based on oxophilic metals such as early transition metals\(^\text{45}\) or trivalent lanthanides,\(^\text{10}\) are sometimes more efficient and notably, they usually afford selectively the anti-Markovnikov product.

As heteroleptic Ae complexes of the type \([\{LX\}Ae–Nu]\) are able to undergo key reactions such as \(\sigma\)-bond metathesis and olefin insertion into the Ae–Nu bond, it soon became evident that they can be employed in C=C functionalisation reactions. To date, heteroleptic calcium complexes have been tested mostly in hydroamination catalysis; two benchmark reactions can be noted: intermolecular reaction between activated olefins (styrenics, and to a lesser extent conjugated dienes such as isoprene) and amines (pyrrolidine, benzylamine, etc.) and intramolecular hydroamination of aminoalkenes (Scheme 2.3).
Calcium based systems were also used in the intermolecular hydroamination of alkynes. For instance, Westerhausen et al. recently reported that the mixed K$_2$[Ca{N(H)Dipp}$_4$] (Dipp = 2,6-$^t$Pr$_2$C$_6$H$_3$) can catalyse the addition of benzylamine onto diynes. Moreover they also constitute suitable precatalysts for the additions of between amines to other electrophilic substrates such as carbodiimides or isocyanates.

1.2.4.1. Intermolecular hydroamination

Ae-catalysed intermolecular hydroamination of alkenes with an activated C=C bond was unknown until the group of Hill first reported that “homoleptic” complexes of the type Ae[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (Ae = Ca, Sr) are effective precatalysts in the reaction presented in Scheme 2.3 forming exclusively the anti-Markovnikov product. Further progress was achieved by Sarazin and Carpentier reporting unprecedented activities for the same type of reactions, this time employing the heteroleptic [{DippNacNac}CaN(SiMe$_2$H)$_2$](THF), (I) phenolato (VII) and iminoanilido (XII) precatalysts (Figure 2.4).
The reaction rates depend on the size of the metal centre and vary in the order Ca < Sr < Ba. Mechanistic investigations based on kinetic experiments for the iminoanilido-barium derivative revealed a first-order dependence in concentrations of each of the reaction components (amine, styrene and precatalyst) and this observation combined with a strong primary kinetic isotopic effect for the amines (KIE = 6.8, 7.3 at 313 and 333 K, respectively) was seen as an indicative of a non-insertive mechanism with a concerted six-centred transition state (Scheme 2.4–A). Subsequently, theoretical computations performed by Tobisch\(^51\) supported the feasibility of this mechanistic scenario, but suggested a more favourable \(\sigma\)-insertive pathway with a turnover limiting reversible C=C insertion into the Ae–Namide bond (Scheme 2.4–B).

**Scheme 2.4.** Proposed mechanisms for the intermolecular hydroamination of activated alkenes according to Sarazin and Carpentier (A)\(^50b\) and Tobisch (B).\(^51\)
1.2.4.2. Intramolecular hydroamination

In contrast to the intermolecular version, intramolecular hydroamination reactions are more entropically favourable, hence somewhat easier to achieve. For this reason, this field has enjoyed a wider popularity, with a larger number of suitable Ca precatalysts, as depicted in Figure 2.5.

Figure 2.5. Heteroleptic calcium precatalysts for intramolecular hydroamination of aminoalkenes.
The following trends were observed for intramolecular hydroamination reactions:

a) the formation of cyclic amines follows Baldwin’s ring closure rules, with formation of \( n\text{-exo-trig} \) (\( n = 5, 6, 7 \)) cyclisation products.  

b) cyclisation of the aminoalkenes \( \text{H}_2\text{C}=\text{CH}_2(\text{CH}_2)_n\text{C}(\text{R}_2)\text{CH}_2\text{NH}_2 \) is consistent with a beneficial Thorpe-Ingold effect in the substrate when the \( \text{R} \) group is bulky, with better activities being observed for \( \text{R} = \text{Ph} > \text{Cy} > \text{Me} \gg \text{H} \).

c) in contrast to intermolecular hydroaminations, for the family of large \( \text{Ae} \), the reaction rates are inversely proportional to the size of the metal centre, with the calcium precatalysts being the most active: \( \text{Ca} > \text{Sr} > \text{Ba} \).

According to catalytic studies performed by the groups of Hill, Sarazin and Carpentier, and Harder, the ubiquitous \( \{[\text{DippNacNac}]\text{CaN(SiMe}_2\text{R)}_2\}\text{(THF)} \) (\( \text{R} = \text{H, Me} \)) complexes display very good activities in the cyclisation reactions of aminoalkenes. Improvement of reaction rates can be achieved by employing iminoanilido ancillary ligands (XII) and substituting the \( \text{N(SiMe}_2\text{R)}_2^- \) with the more basic \( \text{CH(SiMe}_3)_2^- \). Other effective catalytic systems for this organic transformation include heteroleptic calcium complexes supported by multidentate phenolates (VII), triazenidois (XIII),aminotropoiminates (XIV), aminotroponates (XV), bis(imino)acenaphtenes (XVI), nitrogen-based pincers (XXI), bis(NHC)borates (XXII), and Cp-imidazolin-2-imines (XXIII). P. Roesky et al.  have reported that in an equimolar ratio of a heterobinuclear calcium-zirconium complex (XXIV) and \([\text{PhNMe}_2\text{H}]^+\cdot[B(\text{C}_6\text{F}_5)_3]^- \) promotes the cyclisation of primary and secondary aminoalkenes. The homoleptic complexes \( \text{Ca}[\text{E(SiMe}_3)_2\text{]}_2\text{(THF)}_2 \) (\( \text{E} = \text{N, CH} \)) catalyse the cyclisation of aminoalkenes, but their efficiency is lower in comparison to their heteroleptic counterparts.

Enantioselective intramolecular hydroaminations have been reported using calcium precatalysts stabilised by chiral tris(oxazolinyl)borates (XVII), bis(oxazolinyl)amides (XVIII), bis(oxazolinyl)ates (XIX), and aminoamides (XX), with ee\% values ranging from 10 to 50\%.

In order to study the reaction mechanism, kinetic experiments were performed by our group on \( \beta \)-diketiminate and iminoanilido supported barium complexes in the cyclisation reactions of 1-amino-2,2-dimethylpent-4-ene. In all cases, the determined reaction rate law was consistent with a first order in both precatalyst and aminoalkene concentrations. These findings, backed up by a mild kinetic isotopic effect (KIE) of 2.6 at 333 K and a considerable negative activation entropy (\( \Delta S^\ddagger = -206.0(6) \) J mol\(^{-1}\) K\(^{-1}\)) hints towards a well-ordered six-membered transition state. This type of mechanism was also detailed by Sadow et al. for a magnesium complex stabilised by a tris(oxazolinyl)borato ligand framework for which the same rate law was determined. The kinetic experiments performed by Hill et al. with the homoleptic \( \text{Ae}[\text{E(SiMe}_3)_2\text{]}_2\text{(THF)}_2 \) (\( \text{E} = \text{N, CH}; \text{Ae} = \text{Ca, Sr} \)) were consistent with the results of our group, although the authors specified that the high initial substrate concentrations inhibit
the catalytic turnover. Nevertheless, these data contrast with the experiments performed with trivalent lanthanides, for which it was determined that there was a zeroth order dependence on aminoalkene concentration.

In a very recent article, Tobisch provided computational data for the Ae-iminoanilido catalytic system developed by Sarazin and Carpentier. According to this study, the cyclisation reactions of aminoalkenes are likely to undergo a step-wise $\sigma$ insertion mechanism. The other alternative, a concerted six-membered transition state mechanism, was predicted to be energetically unfavourable with a $\Delta\Delta G^\ddagger$ value of 8 kcal mol$^{-1}$. The first order dependence on substrate concentration in the stepwise $\sigma$ insertion mechanism was justified by occurrence of a reversible olefin insertion in the Ae–N(SiMe$_3$)$_2$ bond.

### 1.2.5. Hydrophosphination reactions

Intermolecular hydrophosphination of alkenes is still considered to be one of the main challenges in heterofunctionalisation catalysis. For instance, the otherwise ubiquitous lanthanidocenes are only able to promote intramolecular hydrophosphination reactions. Precatalysts based on late transition metals have been reported to promote C–P bond formation but only under certain restraints limiting their applicability (e.g., presence of electron-withdrawing groups $\alpha$ to the olefin; addition of a basic co-catalyst: NEt$_3$). Alkaline-earth and rare earth complexes (Figure 2.6) have recently emerged as efficient precatalysts in alkene hydrophosphination catalysis. This is most probably due to the fact that soft elements like phosphorous are less likely to coordinate and poison the hard Lewis acidic metal centre.

![Figure 2.6](image.png)

**Figure 2.6.** Heteroleptic calcium precatalysts for the intermolecular hydrophosphination of activated alkenes.

Several alkaline-earth complexes known to catalyse intermolecular hydroamination reactions proved suitable precatalysts in the hydrophosphination of diphenylphosphine with styrene (Scheme 2.5). Anti-Markovnikov regioselectivity was observed in all cases in the absence of any side products.
Scheme 2.5. Hydrophosphination reactions promoted by Ae complexes.

The reaction rates are directly proportional to the size of the metal, the barium precatalysts emerging as being the most active. Hill et al. showed that [{D$_{2}$[NacNac}CaN(SiMe$_{3}$)$_{2}$](THF) can catalyse this transformation to some extent at high temperatures in benzene-d$_{6}$ affording a TOF of 0.5 h$^{-1}$.

Using a tridentate iminoimidinato ligand framework ({{N^N^N}N$^{-}$ XXV}, Cui et al. managed to stabilise a heteroleptic calcium complex [{N^N^N}Ca–Nu] (N^N = iminoanilido XII) in solvent-free conditions to obtain enhanced TOF values (Nu = N(SiMe$_{3}$)$_{2}$, TOF = 84 h$^{-1}$; Nu = CH(SiMe$_{3}$)$_{2}$, TOF = 152 h$^{-1}$).

Kinetic experiments performed with barium precatalysts supported by iminoanilido ligands lead to the conclusion that the reaction follows an overall second order law according to $r = k[HPPH]^{3}[styrene]^{4}[precatalyst]^{1}$. Experiments were also conducted with para-substituted styrenes and increasing activities were reported when the substituent was more electron-withdrawing (CF$_{3}$ > Cl > H > Me > $^{t}$Bu > OMe). These findings were in agreement with those reported by Marks and Hill for hydrophosphination reactions of alkenes and suggest a stepwise $\sigma$ insertive mechanism with a rate-determining step consisting in the insertion of the polarised C=C bond into the Ae–P bond. Homoleptic complexes of type [CaNu$_{2}$](THF)$_{n}$ (Nu = N(SiMe$_{3}$)$_{2}$, n = 2; Nu = PPh$_{2}$, n = 4) were also shown to be active in the hydrophosphination of carboimiides, diynes, and alkynes.

1.2.6. Hydrosilylation, hydroboration and hydrogenation of alkenes

The activity of heteroleptic calcium complexes has been tested also in other types of heterofunctionalisation catalysis. For instance Harder et al. have showed that some of the heteroleptic complexes previously evaluated in styrene polymerisation can also catalyse to some extent hydrosilylation reactions (Scheme 2.6–a). Interestingly, homoleptic di(benzyl-amino) Ae complexes were more active in this case. Cationic complexes can also be potent precatalysts in hydrosilylation catalysis; Okuda et al. have reported that a trinuclear cationic calcium hydride stabilised by a
tetradentate $N^4N^4N^4N^4$ macrocycle (VI) promoted the reaction between 1,1-diphenylethenylene and $\text{Ph}_2\text{SiH}_2$ to yield the anti-Markovnikov product.\textsuperscript{79}

The hydroboration of alkenes (Scheme 2.6–b) was also investigated by Harder; nevertheless it was regarded rather as a “Trojan horse” catalysis due to the fact that the calcium precatalyst is only responsible with the decomposition of the catecholborane to yield the active species under the form of $\text{B}_2\text{H}_6$.\textsuperscript{80} Still in relation with olefins, two of the isolated molecular calcium hydrides ($\{\text{DippNacNac}\text{CaH}\}_2$ and $\{[N^4N^4N^4N^4]\text{CaH}\}_2[\text{Ph}_3\text{SiH}_2]$)\textsuperscript{79,81} were active in the hydrogenation reaction of myrcene and 1,1-diphenylethenylene (Scheme 2.6–c).\textsuperscript{79,82}

![Scheme 2.6. Heterofunctionalisation reactions of olefins promoted by heteroleptic calcium complexes.](image)

1.3. Stabilisation pathways for heteroleptic calcium complexes

1.3.1. Schlenk equilibrium side reactions: the “nemesis” of Ae heteroleptic complexes

Ae heteroleptic complexes of type $\{\text{LX}\text{Ae–Nu}\}$ (LX = ancillary ligand; Nu = nucleophile) have displayed very encouraging results in heterofunctionalisation reactions (\textit{vide supra}, 1.2.4, 1.2.5, 1.2.6). Yet, besides the extreme air and moisture sensitivity, one of the main issues concerning the applicability of these complexes in catalysis is related to their kinetic lability in solution. The precatalysts (and catalysts) can be readily deactivated in solution through Schlenk equilibria side reactions (Scheme 2.7), a process which was previously documented for Grignard reagents using NMR techniques.\textsuperscript{83} The tendency to ligand redistribution can be attributed to the ionicity of the Ae–X bond (X = N, C), since heavy oxophilic elements are characterised by high polarisabilities, charge/size ratios (Ca > Sr > Ba), ionic bonding and high HOMO-LUMO gaps. Therefore one may assume that the propensity of the metal complexes to engage in Schlenk equilibria follows the Mg < Ca < Sr < Ba trend.
\[
2 \{[LX]_2 \text{Ae-Nu}\} \rightleftharpoons \{[LX]_2 \text{Ae}\} + 1/\text{n} \{\text{AeNu}_2\}_\text{n}
\]

Scheme 2.7. Ligand redistribution for kinetically labile alkaline-earth heteroleptic complexes.

This type of redistribution reaction leads to the formation of a mixture of homoleptic complexes possibly affecting the efficiency of the precatalyst. Studies performed on organomagnesium complexes have led to the conclusion that several aspects such as temperature, concentration, solvent, and size of the ligands have a considerable influence when it comes to the stability of heteroleptic complexes in solution. Indeed, adding dioxane over a standard RMgX solution drives the equilibrium completely to the right yielding \([\text{MgX}_2\]_dioxane\)_n as an insoluble salt. Schlenk equilibria are also related to the size and ionicity of the Ae metal centre. For instance \([\{\text{DppNacNac}\}_2\text{CaN(SiMe}_3)_2\}]_\text{(THF)}\) \text{Ia} (see Scheme 2.2) was inert towards redistribution; however \([\{\text{DppNacNac}\}_2\text{AeN(SiMe}_3)_2\}]_\text{(THF)}\) (Ae = Sr, Ba) which were observed by \textsuperscript{1}H NMR spectroscopy, eventually produce the “rearrangement” products \([\{\text{DppNacNac}\}_2\text{Ae}\}]_\text{and} [\text{AeN(SiMe}_3)_2\}_2\_\text{.}^\text{84}

In order to overcome issues concerning ligand scrambling in solution, two strategies have been proposed. They involve steric effects by using bulky ligands, and/or electronic stabilisation \textit{via} intramolecular coordination of tethered heteroatoms.

### 1.3.2. Bulky ancillary ligands

Steric effects are commonly employed to stabilise metal complexes in an unusual oxidation state or containing unstable bonds. For instance, the first compound containing a quintuple metal-metal bond was isolated using a bulky \(m\)-terphenyl derivative in the dichromium \([\{\text{C}_6\text{H}_5\text{-2,6-}(\text{C}_6\text{H}_3\text{-2,6-Pr}_3)_2\}]\text{Cr}_2\_\text{.}^\text{85}

More related to alkaline-earths, Hanusa reported the first and only example of intramolecular coordination of a diyne to calcium using the sterically encumbered \(\text{Cp}^+\) ligand.\textsuperscript{86} Harder employed the sterically demanding \textsuperscript{DppNacNac} ligand framework (as in \text{I}) to stabilise the first example of a molecular calcium hydride.\textsuperscript{81} It soon became evident that the same strategy can also be used to stabilise kinetically labile Ae heteroleptic complexes and researchers in the field have focused their efforts in this direction. The aim of this subchapter is to present families of bulky ancillary ligands which have been successfully utilised to stabilise heteroleptic compounds of the type \([\{LX\}_\text{Ca-Nu}\]_\text{.} In most cases, the nucleophile is a bulky \text{N(SiMe}_3)_2^-\_\text{, N(SiMe}_3\text{H}_2)_2^-\_\text{, or CH(SiMe}_3)_2^-\_\text{group. Aside from providing steric protection to the metal centre, these lipophilic moieties are frequently used because they can impart better solubility of complexes in hydrocarbon solvents. In addition, the Ca–X bond (X = C, N) can be easily displaced through \(\sigma\)-bond metathesis or acid-base reactions.\textsuperscript{80}
Chapter 1: Heteroleptic Calcium Complexes: Stabilisation Methods and Applications Homogeneous Catalysis

Perhaps the most eloquent example of steric stabilisation in Ae chemistry is represented by the class of β-diketiminate ligands, more specifically the ubiquitous \( \text{DippNacNac} \) ligand (as in I) which is also abundantly used with low-valent main group and transition metal chemistry. With Ae metals, this ligand was initially found to be efficient only in the case of calcium, since the strontium and barium analogues were found to be kinetically unstable in solution (\textit{vide infra}). \cite{84} \( \{\text{DippNacNac}\text{CaN(SiMe}_3\}_2\}(\text{THF}) \) was initially developed by Chisholm for lactide polymerisation and later employed as a precatalyst for hydroamination and hydrophosphination reactions. \cite{50,54,55} Similar ligand frameworks include the development of iminoanilides (as in V) \cite{74} and iminoamidinates (as in XX). \cite{74}

![Figure 2.7. Heteroleptic calcium complexes stabilised by bulky ancillary ligands.](image)

Another class of bulky supporting ligands is represented by tris(pyrazolyl)borates (and subsequent derivatives). \cite{88} These ligands are also suitable for alkaline-earths, with complexes of the type \( [\text{TpCa–Nu]} \) (\( \text{Tp} \) = tris(pyrazolylborate), II) enjoying a considerable success in ROP catalysis. \cite{18} Mountford and Westerhausen have extended these studies further and showed that the isoelectronic tris(pyrazolyl)methanides can be used as ancillary ligands to isolate Ae both heteroleptic and homoleptic complexes. \cite{89}

A most interesting aspect resides in the fact that the loss of steric bulk, for instance in the substitution of the large group \( \text{N(SiMe}_3\}_2 \) by smaller moieties like \( \text{BH}_4^- \), allows the coordination of an extra THF molecule (\textit{see in Figure 2.7}. \( \{\text{DippNacNac}\text{CaN(SiMe}_3\}_2\}(\text{THF}) \) I\textit{a} vs \( \{\text{DippNacNac}\text{CaBH}_4\}(\text{THF}) \) I\textit{b}). The same statement is also true for large ancillary ligands, as observed for the tris(pyrazolyl)borates (II) where substitution of the side-on \( '\text{Bu} \) group by \( '\text{Pr} \) decongests the metal centre resulting with the formation of the solvated complex (\textit{see in Figure 2.7} II\textit{a} vs II\textit{b}).
1.3.3. Stabilisation through electronic effects

1.3.3.1. Multidentate ligand frameworks

An alternative way to stabilise metal complexes is by providing electronic density through intramolecular coordination of heteroatoms. Intramolecular coordination also makes use of an entropically favourable chelating effect. For this, macrocycles such as crown ethers capable of hosting cations of different sizes are extremely valuable. With alkaline-earth metals, Ruhlandt-Senge et al. showed that 18-crown-6 can stabilise the monocationic \([\text{Ca}[\text{N(SiMe}_3)_2][18\text{-crown-6}]]^{+}\)[CPPh\(_2\)R]; Okuda et al. prepared a neutral heteroleptic complex \((\{O^O^O^O\text{CaN(SiMe}_3)_2\} \text{ capable of polymerising lactide using a polyether ligand (XXV). A tetradentate macrocyclic ligand (N^N^N^N VI) was used to stabilise the first cationic magnesium and calcium hydrides. Multidentate phenolato ligand systems (VII) have been employed to stabilise a variety of calcium heteroleptic complexes that have found extensive applications in the fields of ROP and heterofunctionalisation reactions. Other electron-donating ligands include the use of N and P based pincers (V, XVI) and chiral aminoamides.

![Figure 2.8. Heteroleptic calcium complexes stabilised by multidentate ancillary ligands.](image)

1.3.3.2. Carbene donors

Imidazol-2-ylidenes N-heterocyclic carbenes (NHC) (XXVI) behave as strongly donating two-electron \(\sigma\) donors by using an occupied sp\(^2\) orbital to coordinate to the metal centre, and therefore may
electronically stabilise Ae heteroleptic complexes. Hill et al. have reported on the synthesis of three coordinated \([\text{[NHC}]\text{Ae}(\text{N(SiMe}_3)_2)]\) (Ae = Ca, Sr, Ba), but the lability of the Ae–C\(_{\text{NHC}}\) bond in the presence of Lewis basic donors precluded their potential application in catalysis.\(^93\) Nevertheless, subsequent studies showed that complexes of the type \([\text{[H}_2\text{B(NHC)_2]}\text{AeN(SiMe}_3)_2])(\text{THF})\) (Ae = Ca, Sr) (XXII) are more robust and promote the cyclohydroamination of aminoalkenes.\(^62\) Similarly, \([\text{[HB(NHC)_3]}\text{CaN(SiMe}_3)_2]\) (XXV) has also been reported.\(^94\) Recently, the even stronger \(\sigma\) donors, cyclic(alkyl)(amino)carbenes (cAACs) (XXVII) have been used to prepare complexes of the type \([\text{[cAAC]}\text{Ae}(\text{N(SiMe}_3)_2)]\) (Ae = Sr, Ba).\(^95\) A schematic representation of these calcium is depicted in Figure 2.9.

![Figure 2.9. Heteroleptic Ae complexes stabilised by carbene ligands.](image)

**1.3.3. Secondary interactions**

According to several definitions found in chemistry textbooks, secondary or non-covalent interactions are much weaker than covalent bonds due to the fact no electrons are shared between the two involved elements. According to a recent review article by Ruhlandt-Senge et al., secondary interactions in organometallic complexes are described as an acceptor-donor motif formed between an electrophilic metal and a potential donor atom, rather than genuine bonding between the metal and a ligand.

These interactions are best detected by X-ray diffraction studies in these molecular structures where the metal centre has surprisingly low coordination numbers and is involved in heavily distorted geometries. Yet, there are certain difficulties in quantifying these interactions and the delineation of cut-off values is often debatable. Defining an interaction by taking into account the sum of the van der Waals radii between the donor atom and the metal is often considered to be incorrect with oxophilic elements; ionic radii are said to be more appropriate in these cases. For Ca···C\(_\pi\) interactions there is a common agreement that the value of the maximal distance between the two atoms should be fixed at ca. 3.1 Å.\(^97\) For Ca···F–C secondary interactions, the cut-off value defined by Plenio is also 3.1 Å.\(^98\) and it corresponds to the sum of the van der Waals radius for fluorine \((r_{\text{vdW}} \text{F} = 1.47 \text{ Å})\)\(^99\) and the ionic radii...
van der Waals radius for calcium (1.66 Å)\textsuperscript{11} according to Kollman.\textsuperscript{100} On the other hand, Ca⋯H–R (R = C, Si) agostic interactions are more difficult to describe due to the fact that hydrogen atoms are not always detected on Fourier electronic density maps obtained from X-ray diffraction and for this reason often only the Ca⋯R distances are reported. When a N(SiMe\textsubscript{3})\textsubscript{2} group is bound to a Ca centre,\textsuperscript{24a,26} a diagnostic feature of Ca⋯H–Si agostic bonding is the discrepancy between the two Ca–N–Si angles, and often only one Si–H moiety is tilted toward the metal (Figure 2.10).

**Figure 2.10.** Schematic representation of the coordination sphere of a calcium complex ([[[LO]CaN(SiMe\textsubscript{3})\textsubscript{2}]]\textsuperscript{2+} containing β-Si–H⋯Ca agostic interactions.

Reports describing the use of secondary interactions to stabilise Ca complexes are relatively scarce\textsuperscript{96}, however the most common are Ca⋯F–C, Ca⋯C\textsubscript{x}, and Ca⋯H–R (R = Si, C); they will be briefly described in the following section.

\textit{a) Ca⋯F–C interactions}

The use of M⋯F–C interactions to stabilise transition metal complexes are sometimes overlooked due to concerns related to C–F activation side reactions.\textsuperscript{101} Nevertheless, with oxophilic elements such as alkaline-earths, this is seldom the case and the only known examples of calcium mediated C–F bond activation have been reported by Hill and Xi.\textsuperscript{102} Perhaps this may be explained in terms of bond dissociation energies (BDE) as there is only a marginal difference between the values reported for C–F (123 kcal·mol\textsuperscript{-1}) and the resulting Ca–F (126 kcal·mol\textsuperscript{-1}) bonds.\textsuperscript{103} In a review article,\textsuperscript{98} Plenio has discussed the coordination properties of the C–F unit showing that oxophilic elements like group 1 and group 2 elements are preferred for this type of interaction. This is mostly due to the fact that this bond is highly polarised (C=δ+–Fδ−) and its poor coordination properties can be exploited in the presence of hard cations (\textit{e.g.} K\textsuperscript{+}, Ca\textsuperscript{2+}, Sr\textsuperscript{2+}, Ba\textsuperscript{2+}) through electrostatic interactions.\textsuperscript{104}

Ruhland-Senge and Caulton reported that electrophilic metals can be coordinatively saturated by employing the fluorine-enriched perfluoro-\textit{tert}-butoxo ligands.\textsuperscript{105,106} Sarazin and Carpentier reported that Ae⋯F contacts can be used to stabilise well-defined cations and estimated through DFT computations that the strength of these interactions amounted to \textit{ca.} 12–40 kcal mol\textsuperscript{-1}.\textsuperscript{32} In addition,

\textsuperscript{11} This value is an estimate based on the value for Na\textsuperscript{+} and K\textsuperscript{+}
such interactions have been observed in a number of alkaline-earth complexes structurally characterised previously reported in the literature (e.g. [[OC(CF$_3$)$_3$]$_2$Ca](DME)$_2$ (DME = dimethoxyethane), [[(RO)$_4$]Ae]$^+$·2[H$_2$N{B(C$_6$F$_5$)$_3$}]$_2$]$^-$ ([(RO)$_4$]H = 2-((1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)methyl)-1,1,1,3,3,3-hexafluoropropan-2-ol).\textsuperscript{32,47b,102a,106,107}

b) Ca···C\(_\pi\) interactions

Short contacts between Ca and \(\pi\) clouds are most common in metal complexes with anionic ligands such as indenyls,\textsuperscript{108} cyclopentadienyls,\textsuperscript{109} fluorenlys,\textsuperscript{110} or allyls.\textsuperscript{111} In contrast, neutral \(\pi\) complexes are far more challenging to synthesise and, to date, there are only a handful of reports which describe the interaction between Ae metals and arenes,\textsuperscript{112} or olefins.\textsuperscript{113} The interaction between Ae elements and neutral \(\pi\) donors is considered to be weak and mostly based on electrostatics. This is most probably due to the absence of d\(\pi^*\) donations from the Ae element to the \(\pi\) system. For this reason the Dewar-Chatt-Duncanson model described for transition metal-olefin compounds\textsuperscript{114} cannot be applied for such complexes.

c) Ca···H–R (R = Si, C) interactions.

Agostic interactions are best described as 3-centre 2-electron (3c–2e) bonds between C–H or Si–H moieties and metallic centres.\textsuperscript{115} They are often regarded as weak interactions (1–10 kcal mol\(^{-1}\)) according to DFT computations\textsuperscript{24a}) and are most easily observed using X-ray and neutron diffraction techniques (\textit{vide supra}).

Several molecular structures depicting Si–H\textsuperscript{24,107e} and C–H\textsuperscript{30a,84,116} agostic interactions with Ae (Ae = Ca, Sr, Ba) metals have already been reported (e.g. [[LO]$^3$CaN(SiMe$_3$H)$_2$] (VII\textit{a} in Figure 2.2); [[\textit{trans}-Sr(N(SiMe$_3$)$_2$)$_2$(µ-1,4-dioxane)]$_\infty$]).

Ae···H–Si agostic bonding can also be detected in solution using \(^1\)H NMR spectroscopy (Figure 2.11–\textit{top}) by measuring the \(^1J_{\text{Si–H}}\) coupling constant: values lower than 160 Hz usually indicate mild to strong interactions. Alternatively they can be detected by infrared (FTIR) spectroscopy by tracing the Si–H stretching vibration (\(\nu_{\text{Si–H}}\)) according to Figure 2.11 (bottom).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image.png}
\caption{Classification of the strength of Ae···H–Si interactions using \(^1\)H NMR (\textit{top}) and infrared (\textit{bottom}) spectroscopy.}
\end{figure}
1.4. Summary and outlooks

In summary, this first chapter highlights the prominent role of stable heteroleptic calcium complexes in homogeneous catalysis. Their applicability in these organic transformations is comparable to that reported for trivalent lanthanides as both classes of elements possess similar atomic properties and reactivity. Yet, the coordination chemistry of alkaline-earth elements is still considered to be in its infancy, therefore leaving opportunities to use new attractive precatalysts in homogeneous catalysis. Complexes of the type \([\{LX}Ca–Nu\] kinetically redistribute in solution, but this propensity can be overcome by using bulky or electron-donating ancillary ligands. Nevertheless, there is still the need to propose new ligand platforms that will allow the isolation of more efficient Ae precatalysts. The main objective of the next two chapters from this PhD thesis will be the synthesis and application in heterofunctionalisation catalysis of heteroleptic calcium complexes supported by two types of highly fluorinated ancillary ligands.

Hence, Chapter 2 will describe the catalytic activity of a heteroleptic calcium complex supported by a bulky fluorinated tris(indazolyl)borato ligand \(T_{\text{ind}}^F\) in hydroamination reactions. Chapter 3 will then explore the implementation of \(Ca\cdots H\text{--Si}\) and \(Ca\cdots F\text{--C}\) secondary interactions to yield kinetically inert \([\{LX}Ca–Nu\] complexes. Furthermore, the performance of the resulting complexes in the intermolecular hydrophosphination of styrene with diphenylphosphine will be presented.

Chapter 4 will illustrate that secondary interactions can be employed to stabilise synthetically challenging calcium-alkene complexes where the stabilising ligands contain tethered olefin moieties. It will be shown that olefin coordination to the metal centre is dominated mostly by electrostatic interactions and it is also dependent on steric effects. Using the same set of ligands, coordination of olefin tethers to other oxophilic metals such as strontium, ytterbium, will also be explored.

Chapter 5 will be focused on the attempts to synthesise calcium complexes featuring interactions between the metal centre and other \(\pi\) donors, for instance arenes, alkynes and allenes.
1.5. References

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Chapter 1: Heteroleptic Calcium Complexes: Stabilisation Methods and Applications Homogeneous Catalysis


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Chapter 1: Heteroleptic Calcium Complexes: Stabilisation Methods and Applications

Homogeneous Catalysis


Chapter 1: Heteroleptic Calcium Complexes: Stabilisation Methods and Applications Homogeneous Catalysis


Chapter 1: Heteroleptic Calcium Complexes: Stabilisation Methods and Applications Homogeneous Catalysis


Chapter 2: Early Steps in Homogeneous Catalysis. The Case of a Fluorinated Scorpionato Ligand.

A portion of this chapter has appeared in print:

Chapter 3: Early steps in homogeneous catalysis. The case of a fluorinated scorpionato ligand.

2.1. Introduction

This chapter is the result of a collaborative effort between our group and the group of Prof. Michel Etienne from Université Toulouse III Paul Sabatier. As part of this joint project (GreenLAkE, ANR-11-BS07-0009), the main goal was to devise new alkaline-earth complexes stabilised by fluorine-enriched ligand frameworks as precatalysts in hydroelementation reactions. Hence, in the following lines (and also in Annexure A), the catalytic activity of heteroleptic alkaline-earth complexes stabilised by fluorinated tris(indazolyl)borate is illustrated in the benchmark intramolecular hydroamination of 2,2-dimethylpent-4-en-1-amine. Note that all complexes presented herein were synthesised and characterised by our partners from Toulouse and reported in the PhD thesis of Dr. Nuria Romero.¹

2.1.1. On the benefits of using fluorine

Fluorinated compounds have enjoyed a wide popularity, especially as a result of extensive applications in medicinal chemistry.² In fact, fluorine atoms are key components in drugs as it was determined that this small and very electronegative atom can be used to increase binding affinities between a molecule and the targeted protein.³ Fluorine atoms are characterised by low polarisabilities, which means that fluorine-rich molecules have low surface energies and weak cohesive forces, hence increasing their volatility.⁴ In addition, owed to the strength of the C–F bond (BDE = 123 kcal·mol⁻¹) and hydrophobic nature of fluorine-containing groups (e.g. CF₃, C₆F₁₃), fluorocarbons are attractive as they display high thermal and moisture resistance. Such properties are highly valuable in chemical vapour deposition experiments (CVD) and for this reason, organometallic complexes containing fluorinated ligands have been extensively employed in this field.⁵⁶ For instance, Caulton et al. have shown that alkali salts of fluorinated alkoxides OCH(CF₃)₂⁻, OCMe(CF₃)₂⁻, or OCMMe₂CF₃⁻ are volatile and that their sublimation temperature is directly dependant on the fluorine content in the molecule.⁷ These studies were extended to heavy alkaline-earth elements by Ruhlandt-Senge et al. who reported that homometallic [{OC(CF₃)₃}₂Ae](THF)₄ (Ae = Ca, Sr, Ba) and heterobimetallic [{(OC(CF₃)₃)₃MAe}(THF)₄ (M = Na, K; Ae = Sr, Ba) sublimed easily and constituted potential CVD precursors.⁸ In relation with our work, it must be noted alkaline-earth complexes supported by bulky non-fluorinated tris(pyrazolylborate) ligands (Tp⁻) of type [{Tp}₂Ae] (Ae = Ca, Sr, Ba) display low melting points and have been used in atomic layer deposition experiments.⁹
2.1.2. Tris(pyrazolylborate) ligands

Pyrazolylborate-based ligand frameworks (Figure 3.1) have played an important role in the coordination chemistry of both main group and transition metals. This field has witnessed a surge in popularity after the seminal work by Trofimenko who, in a review article published in 1993, has nicknamed these ligands “scorpionates” as a result of their ability to “grab its prey with two identical claws [ = (pz*)₂]” and to “sting it with the sharp point of the curving tail”. More than 50 years after the publication of the first examples of this class of bulky ligands, these are still frequently employed; according to a CCDC database search, more than 100 molecular structures of organometallic complexes employing this set of ligands were reported in 2013 alone. With alkaline-earth elements, the groups of Chisholm and Mountford showed that [(Tp⁰⁸⁸)CaNu] (Tp = trispyrazolylborate; Nu = N(SiMe₃)₂, O-2,6-Pr₂C₆H₃, BH₄) are active in the ROP of lactides; however, reports describing the activity of similar complexes in heterofunctionalisation (= hydroelementation) catalysis are to date non-existent.

![Graphical representations of tris(pyrazolylborate) ligands “scorpionate” ligands.](image)

2.1.3. Targeted complexes

As previously described in Chapter 1, the catalytic activity of a complex is often highly dependent on the Lewis acidity of the metal centre. Due to their intrinsic electron-withdrawing nature, the use of fluorinated ligands with oxophilic elements is anticipated to make the metal centre more electrophilic and therefore it is expected to generate more active catalysts. This strategy has proved successful for ROP precatalysts supported by fluorinated aminoalkoxides. On the advantages of employing tris(indazolyl)borato ligands (Figure 3.2) instead of the more classical tris(pyrazolylborate)s, one may propose that the former is bulkier and has more positions available to increase the fluorine content of the molecule. The applicability of this ligand was tested by the groups of Etienne and Pérez for the silver-catalysed C–C bond formation between CH₄ and ethyl diazoacetate.
Chapter 2: Early Steps in Homogeneous Catalysis. The Case of a Fluorinated Scorpionato Ligand

Figure 3.2. Highly fluorinated \( \{T_{\text{ind}}^F \}^+ \) ligands introduced by Etienne and Pérez.\(^{15} \)

It was envisaged that Ae heteroleptic complexes stabilised by bulky scorpionato ligands with enclosed fluorinated moieties could make valuable candidates as precatalysts for heterofunctionalisation reactions. Our partners in Toulouse recently showed that the \( \{T_{\text{ind}}^F \}^+ \) ligand can also be used to synthesize the homoleptic \( \{T_{\text{ind}}^F \}_2 \text{Ca} \) and heteroleptic \( \{T_{\text{ind}}^F \}_2 \text{CaI} \) complexes.\(^{16} \)

It soon became apparent that the same type of heteroleptic complexes but with basic groups such as \( \text{N(SiMe}_3\}_2^- \) could be good precatalysts for heterofunctionalisation reactions.

\[
\{T_{\text{ind}}^F \}_2 \text{AeN(SiMe}_3\}_2 \text{(Ae = Ca (A), Sr (B))} \text{ were synthesised by reacting } \{T_{\text{ind}}^F \}_2 \text{TI} \text{ and Ae}[\text{N(SiMe}_3\}_2]_2 \text{ in pentane at room temperature in low (25% unoptimised – B) to moderate yields (67%–A) (Scheme 3.1). Their identity was confirmed through spectroscopic methods (NMR, FTIR). Perhaps the most interesting features of A and B relates to their molecular structure. Indeed, A represents a very rare case of a four-coordinate solvent-free complex with a bounded \( \kappa^3 \text{N} \)-ligand, the only other being \( \{T_p \}_2 \text{Ae(O-2,6-} \text{Pr}_2\text{C}_6\text{H}_3 \) reported by Chisholm et al.\(^{12} \) Complex B is unique as it remains the only solvent-free four-coordinate strontium complex structurally characterised to date. Details concerning the characterisation of these metal complexes can be found in the PhD thesis of Dr. Nuria Romero.\(^{1} \) All the results presented herein have been recently published\(^{18} \) and the corresponding research article is given in Annexure A.

Scheme 3.1. Synthesis of \( \{T_{\text{ind}}^F \}_{2} \text{CaN(SiMe}_3\}_2 \text{ (A) and } \{T_{\text{ind}}^F \}_{2} \text{SrN(SiMe}_3\}_2 \text{ (B).}\(^{1} \)
This chapter will describe chiefly the catalytic activity of A and B in the intramolecular hydroamination of aminoalkenes. Kinetic and mechanistic data will also be presented.

2.2. Hydroamination studies

2.2.1. Intramolecular hydroamination

The catalytic activity of \([\{\text{Tind}^F\}\text{CaN(SiMe}_3\}_2]\) (A) was screened in the standard intramolecular hydroamination of 2,2-dimethylpent-4-en-1-amine (S, Scheme 3.2). In all cases the cyclisation of the aminoalkene occurred according to Baldwin’s ring closure rules, leading to the 5-exo-trig product with 100% regioselectivity. The structure of precatalyst A and of other complexes C–H used for comparison purposes are represented in Figure 3.3.

\[
\text{[Ca]}
\]

\[
\text{S}
\]

\[
\text{HN}
\]

\[
\text{Scheme 3.2. Intramolecular hydroamination of 2,2-dimethylpent-4-en-1-amine (S) with Ca precatalysts.}
\]

Gratifyingly, A proved highly active in this ring-closure reaction. As observed from Table 3.1, complete conversion of 200 equiv of the aminoalkene can be achieved in as little as 16 minutes at room temperature (Table 3.1, entry 2). More remarkably, this precatalyst was capable of sustaining very high substrate loadings (up to 600 equiv, see Entry 4). The recorded turnover numbers (TON) are uncommon for this reaction, placing this precatalyst amongst the most productive ones reported to date. In terms of activity, the following discussion is to be considered qualitatively, considering the fact that multiple reaction conditions were used, no systematic kinetic monitoring was performed and that the reaction times were not always optimised. \([\{\text{Tind}^F\}\text{CaN(SiMe}_3\}_2]\) (A, Entries 1–4) outperforms the ubiquitous \([\{\text{DippNacNac}\}\text{CaN(SiMe}_2\}_2](\text{THF})\) (R = Me (C), entries 5–7; R = H (D), entry 8) and the calcium precatalysts based on multidentate phenolato ligands \([\{\text{LO}\}\text{CaN(SiMe}_2\}_2](\text{THF})\) (R = Me (F), entry 10; R = H (G), entry 11); higher turnover frequencies were reported only for \([\{\text{N}^\text{N}\}\text{CaCH(SiMe}_3\}_2](\text{THF})\) (H, entry 12). \([\{\text{Tind}^F\}\text{CaN(SiMe}_3\}_2]\) (A) was more active than calcium homoleptic complexes of the type \([\text{Ca[E(SiMe}_3\}_2]_2}(\text{THF})_2\) (E = N, entry 13; E = CH, entry 14), demonstrating the beneficial role of \(\{\text{Tind}^F\}^-\) (e.g. stabilisation against Schlenk equilibria side reactions; increase the reactivity of the Ca–Namide bond).
Table 3.1. Representative data for the intramolecular hydroamination of S catalysed by A–H.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Precatalyst</th>
<th>$[S]_0/ [Ca]_0$</th>
<th>Time (min)</th>
<th>T (°C)</th>
<th>Conv. (%)</th>
<th>TON</th>
<th>TOF (min$^{-1}$)</th>
<th>Ref</th>
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<tr>
<td>1$^a$</td>
<td>A</td>
<td>50:1</td>
<td>6</td>
<td>25</td>
<td>$&gt;99$</td>
<td>50</td>
<td>8</td>
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<tr>
<td>2$^a$</td>
<td>A</td>
<td>200:1</td>
<td>16</td>
<td>25</td>
<td>$&gt;99$</td>
<td>200</td>
<td>12</td>
<td>this work</td>
</tr>
<tr>
<td>3$^b$</td>
<td>A</td>
<td>400:1</td>
<td>27</td>
<td>25</td>
<td>85</td>
<td>340</td>
<td>12</td>
<td>this work</td>
</tr>
<tr>
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<td>A</td>
<td>600:1</td>
<td>18</td>
<td>25</td>
<td>57</td>
<td>342</td>
<td>19</td>
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</tr>
<tr>
<td>5</td>
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<td>C</td>
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<td>60</td>
<td>$&gt;99$</td>
<td>60</td>
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<td>93</td>
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<td>0.2</td>
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<td>&lt;2</td>
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<td>3 × 60</td>
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<td>50</td>
<td>0.166</td>
<td>23</td>
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<tr>
<td>14</td>
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<td>60</td>
<td>$&gt;99$</td>
<td>50</td>
<td>0.052</td>
<td>65</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 3.0 µmol of precatalyst, 1.2 mL of benzene-$d_6$. The conversion was determined by $^1$H NMR spectroscopy. [b] Reaction conditions: 3.0 µmol of catalyst, 1.8 mL of benzene-$d_6$. [c] Reaction conditions: 3.0 µmol of precatalyst, 1.7 mL of benzene-$d_6$. [d] Reaction conditions: 20 µmol of precatalyst, 0.4 mL of benzene-$d_6$. [e] Reaction conditions: 5.0 µmol of precatalyst, 1.2 mL of benzene-$d_6$. [f] Reaction conditions: 40 µmol of precatalyst, 0.4 mL of benzene-$d_6$. [g] The reaction conditions for this reaction were not optimised.

Figure 3.3. Selected Ae precatalysts in the intramolecular hydroamination of 2,2-dimethylpent-4-en-1-amine throughout this study.

Despite showing high productivity, A shows signs of decomposition when high substrate concentrations are used. This can be visually observed upon formation of an unidentified colourless precipitate. Catalyst deactivation can be ascribed to the reaction of A with moisture or other unidentified impurities from the substrate. In addition, decomposition of A can also be caused by a deleterious B–N cleavage. Degradations caused by B–N cleavages are not uncommon and have been reported before for tris(pyrazolyl)borate$^{24}$, hydrobis- and tris-(imidazol-2-ylidene-1-yl)borato
ligands. Precatalyst degradation was particularly troublesome in the case of \([\{T_{\text{ind}}\}SrN(SiMe_3)_2]\) (B) when all our attempts to promote the cyclisation of 2,2-dimethylpent-4-en-1-amine with this compounds were unsuccessful.

In order to elucidate the reaction mechanism, kinetic monitoring was performed using \(^1\text{H}\) NMR spectroscopy at 0 °C in toluene. Firstly, using different aminoalkene (S) concentrations (0.12 M, 0.24 M, and 0.31 M) with a constant amount of precatalyst (3.0 µmol), the conversion of the substrate was plotted against the reaction time (Figure 3.4). From the semi-logarithmic plot of monomer conversion vs. time, a linear dependence was observed between the monomer conversion and reaction time over 3 half-lives (Figure 3.5) with \(k_{\text{app}}\) values ranging from 0.0005±5.5 \(10^{-6}\) s\(^{-1}\) ([S]\(_0\) = 0.31 M ) to 0.0013±1.3 \(10^{-5}\) s\(^{-1}\) ([S]\(_0\) = 0.12 M). This equates to a first-order dependency upon substrate concentration and also suggests that, at high substrate concentrations, the coordination sphere of the metal centre might be saturated with aminoalkene donors, thus inhibiting the activity of the catalyst.

![Figure 3.4. Plot of substrate conversion (%) vs. reaction time (s) for the intramolecular hydroamination of 2,2-dimethylpent-4-en-1-amine catalysed by \([\{T_{\text{ind}}\}CaN(SiMe_3)_2]\) (A) at different substrate concentrations (0.12, 0.24 and 0.31 M). Reaction conditions: 0 °C, 3.0 µmol of precatalyst, total volume = 1.2 mL. The conversion was determined by \(^1\text{H}\) NMR.](image)

The influence in precatalyst concentration was studied using 3.60, 4.76 and 7.14 mM solutions of \([\{T_{\text{ind}}\}CaN(SiMe_3)_2]\) (A) in toluene and a constant amount of the aminoalkene (3.75 mmol). The logarithmic plot of \(k_{\text{app}}\) vs. precatalyst concentration indicated a linear dependence with a slope equal to 1.01±0.39 (Figure 3.6), indicating a first-order dependence in precatalyst.

* Room temperature reactions employing 50 or more equiv. of the substrate were too fast to be monitored by \(^1\text{H}\) NMR spectroscopy.
Figure 3.5. Plot of ln(S0/Sf) vs. reaction time (s) for the intramolecular hydroamination of 2,2-dimethylpent-4-en-1-amine (S) catalysed by [{Tind}F CaN(SiMe3)2] (A) at different substrate concentrations (0.12, 0.24 and 0.31 M). Reaction conditions: 0 °C, 3.0 µmol of precatalyst, total volume = 1.2 mL. The conversion was determined by 1H NMR.

Figure 3.6. Plot of ln(kapp) vs. ln([A]) for the intramolecular hydroamination of 2,2-dimethylpent-4-en-1-amine catalysed by [{Tind}F CaN(SiMe3)2] (A) at different catalyst concentrations (3.60, 4.76 and 7.14 mM). Reaction conditions: 0 °C, 3.75 mmol (0.44 M) of substrate, total volume = 1.25 mL.

Hence, the intramolecular hydroamination of 2,2-dimethylpent-4-en-1-amine catalysed by [{Tind}F CaN(SiMe3)2] follows the rate law given in equation (3.1).

\[ R_{\text{CHA}} = k[A]^1 [\text{aminoalkene}]^1 \]  \hspace{1cm} (3.1)

A first-order dependence in precatalyst and substrate concentrations in the cyclisation of aminoalkenes is not uncommon and has already been described for [{LO}CaN(SiMe3)2](THF) (5)\(^1\) and for the barium analogue of G, [{N^N}BaN(SiMe3)2](THF).\(^2\) However, it contrasts with previous studies performed on lanthanidocenes where a zeroth-order in substrate was reported.\(^2\)\(^6\),\(^27\) The rate law in equation (3.1) is compatible with two types of mechanisms: (i) one involving a six-membered
concerted transition state as proposed for instance for \([\{N^\text{N}\text{BaN(SiMe}_3\}_2]\text{(THF)}\) and a magnesium complex stabilised by a tris(oxazolinyl)borato ligand, and (ii) a stepwise \(\sigma\)-insertive mechanism which is more common for trivalent lanthanides. Tobisch provided theoretical computations for the ring-closure of 2,2-dimethylpent-4-en-1-amine catalysed by \([\{N^\text{N}\text{AeN(SiMe}_3\}_2]\text{(THF)}\) (Ae = Ca, Sr, Ba) and concluded that the \(\sigma\)-insertive mechanism was more energetically favourable than six-membered concerted transition state although the difference between the computed energies for the two pathways remained low (8 kcal mol\(^{-1}\)) and therefore no mechanism could be entirely rejected. Nevertheless, based on Tobisch’s calculations one can postulate that the cyclisation of the 2,2-dimethylpent-4-en-1-amine in the presence of \([\{T\text{ind}^F\text{CaN(SiMe}_3\}_2]\) (A) undergoes via a stepwise \(\sigma\)-insertive mechanism. The two types of mechanism for this organic transformation are represented in Scheme 3.3.

Scheme 3.3. Possible mechanisms for the intramolecular hydroamination of 2,2-dimethylpent-4-en-1-amine catalysed by \([\{T\text{ind}^F\text{CaN(SiMe}_3\}_2]\) (A).
2.2.2. Intermolecular hydroamination

Encouraged by our findings in the cyclisation reaction of 2,2-dimethylpent-4-en-1-amine promoted by \([\{T\text{ind}^F\}\text{CaN(SiMe}_3\text{)}_2]\) (A), we envisaged that the same precatalyst might be suitable for more challenging transformations. Consequently, A was tested in the intermolecular hydroamination of styrene with pyrrolidine (Scheme 3.4).

![Scheme 3.4. Attempted intermolecular hydroamination of styrene with pyrrolidine catalysed by \([\{T\text{ind}^F\}\text{CaN(SiMe}_3\text{)}_2]\) (A).](image)

Disappointingly, no conversion was detected at 60 °C even in the absence of solvent. Within seconds after mixing the reagents, the rapid formation of a colourless precipitate was observed, suggesting that catalyst decay had occurred. This experimental observation is consistent (both in neat and toluene solutions) with the behaviour of A when high concentrations of the aminooalkene were used (vide infra). This precipitate was formed in small amounts and was found to be largely insoluble in hydrocarbon solvents. Its identity could not be assessed by NMR (\(^1\text{H}, ^{19}\text{F}\)) techniques as all spectra were uninformative.

Calcium precatalysts for intermolecular hydroamination are very scarce and the only known examples are represented by Ca[E(SiMe\(_3\))]\(_2\)(THF)\(_2\) (E = N, CH)\(^{30}\) and the heteroleptic complexes C–E, G and H (see Figure 3.3)\(^{21,22,31}\). In group 2, barium complexes are known for their ability to catalyse intermolecular heterofunctionalisations\(^{21,22}\). For this reason, a hypothetical \([\{T\text{ind}^F\} \text{BaN(SiMe}_3\text{)}_2]\) would have been the best option choice, but judging from the fact that \([\{T\text{ind}^F\} \text{SrN(SiMe}_3\text{)}_2]\) (B) was unstable under intramolecular hydroamination conditions, the synthesis and catalytic activity of this barium complex in hydroelementation catalysis remained unexplored.

2.3. Conclusion remarks, side-works and perspectives

This preliminary chapter has shown that the heteroleptic calcium complex \([\{T\text{ind}^F\} \text{CaN(SiMe}_3\text{)}_2]\) (A) can be kinetically stabilised using a highly fluorinated bulky tris(indazolyl)borato ligand (T\(_{\text{ind}}^F\)). The presence of electron-withdrawing groups in the ancillary ligand and the low coordination number of calcium bolsters the catalytic activity of this metal complex in hydroelementation catalysis. This was demonstrated in the intramolecular hydroamination of 2,2-dimethylpent-4-en-1-amine where A was unusually active and productive, as compared to other Ae complexes. The cyclisation reaction
occurred with 100% regioselectivity and kinetic experiments indicate a first order dependence both in substrate and precatalyst concentrations. These findings are consistent with a recently published DFT computations on similar catalytic systems \((i.e. \{[\text{N}^\text{N}Ae\text{N}(\text{SiMe}_3)_2]\}(\text{THF}) (\text{Ae} = \text{Ca}, \text{Sr}, \text{Ba})^{22}\)), suggesting that most likely the reaction mechanism follows a stepwise \(\sigma\)-insertive pathway. The research article covering all synthetic and catalytic data can be found in Annexure A.

Despite the fact that A affords the ring-closure of aminoalkenes, this precatalyst has its own limitations. It was for instance unable to convert the addition of pyrrolidine onto styrene. This can be linked to the sensitivity of the metal complex under the given catalytic conditions, although the exact origin of the observed deactivation (precipitation) could not be ascertained. Hence, in order to successfully employ calcium precatalysts in highly challenging reactions such as intermolecular hydroamination or hydrophosphination of activated olefins, new ligand sets must be devised. We persisted in employing fluorinated ligand sets to enhance the catalytic activity of alkaline-earth complexes, and Chapter 3 will disclose the synthesis, characterisation and application in hydrophosphination catalysis of several heteroleptic calcium complexes stabilised by fluorinated aminoetheralkoxides.

Calcium and ytterbium have very similar atomic properties \((r_{\text{Ca}^{2+}} = 1.00 \, \text{Å}, \, r_{\text{Yb}^{2+}} = 1.02 \, \text{Å})^{32}\) and literature data show that heteroleptic complexes containing these two elements display comparable results in homogeneous catalysis.\(^{22,33}\) For this reason, in collaboration with the group of Prof. Alexander Trifonov from the Russian Academy of Sciences at Nizhny Novgorod, Russia, the catalytic activity of an ytterbium (II) complex supported by a bulky carbazol-9-y1 ligand was tested in intermolecular hydrophosphination catalysis. Preliminary catalytic tests conducted with this complex showed it is highly active in the benchmark reaction between styrene and diphenylphosphine, with TOF values reaching 23 turnovers per hour.\(^{34}\) Full results consisting of the synthesis and characterisation of the ytterbium complex (performed by our partners from Nizhny Novgorod) and featuring the catalytic application in hydrophosphination catalysis (the contribution of the author) can be found in the research article displayed Annexure B.
2.4. References

Chapter 2: Early Steps in Homogeneous Catalysis. The Case of a Fluorinated Scorpionato Ligand


Chapter 3: Alkaline-Earth Fluorinated Aminoetheralkoxides

A portion of this chapter has appeared in print:

Rosca, S.-C.; Roisnel, T.; Dorcet, V.; Carpentier, J.-F.; Sarazin, Y. “Potassium and Well-defined Neutral and Cationic Calcium Fluoroalkoxide Complexes: Structural Features and Reactivity” Organometallics, 2014, 33, 5630
Chapter 4: Alkaline-earth fluorinated aminoetheralkoxides

3.1. Introduction

As evoked in Chapter 2, highly fluorinated chemicals are widely applied in medicinal chemistry\(^1\) and when bounded with alkali or alkaline-earth elements, they can also serve as precursors in chemical vapour deposition experiments.\(^2,\,3,\,4\) In addition, fluorinated ligands are attractive for catalytic purposes as they increase the Lewis acidity of the metal centre, engendering more active catalysts for a variety of transformations.

Alkoxides are in general avoided as ancillary ligands for oxophilic Ae elements (Ae = Ca, Sr, Ba). Compared to O\(_{\text{phenolate}}\) in phenolato ligands, the O\(_{\text{alkoxide}}\) atom has an increased basicity, which results in the formation of oligomers through bridging oxygen atoms. For instance, reacting the simple 2-methoxyethanol with metallic calcium forms the large aggregate \([\text{Ca}(\text{OCH}_2\text{CH}_2\text{OMe})_{18}\text{(HOCH}_2\text{CH}_2\text{OMe})_2]_5\).\(^5\) Kim and Chung have recently shown that the degree of aggregation can be reduced by employing aminoetheralkoxides in combination with bulky \(\beta\)-diketonato ligands to yield solvent-free dinuclear and trinuclear strontium complexes (Figure 4.1).\(^6\) The only structurally characterised monometallic non-fluorinated alkoxide complex with Ae elements, \([\text{clox}\text{CaN(SiMe}_3)_2\text{(THF)}_3]_\text{clox} = \text{OC(C}_6\text{H}_5\text{)}\text{CH}_2\text{C}_6\text{H}_4\text{Cl}\), was reported by Hanusa, albeit THF solvent molecules are needed to fill the coordination sphere of the metal centre (Figure 4.1).\(^7\)

![Figure 4.1. Known Ae (Ca, Sr) non-fluorinated alkoxo complexes.\(^6,\,7\)](image_url)

One of the approaches to reduce the degree of aggregation in metal alkoxides was to introduce CF\(_3\) groups in the \(\alpha\) position of the O\(_{\text{alkoxide}}\) atom. The presence of the strongly electron-withdrawing moieties decreases the \(\pi\) donating ability of the oxygen atom and therefore reduces the bridging tendencies of the ligand. This strategy was validated when
HOC(CF₃)₂CH₂N(CH₃)CH₂CH₂N(CH₃)CH₂(CF₃)₂OH (ON²⁺NO) was used as a proteo-ligand for group 3, 4 and 13 metals (e.g. [{ON²⁺NO}Y(CH₃SiMe₃)](THF), [{ON²⁺NO}Al(O'Pr)], [{ON²⁺NO}Zr(CH₂Ph)₂]) resulting in efficient precatalysts for lactide and olefin polymerisation reactions. Despite promising results with early transition metals, reports describing the use of fluoroalkoxy ligands with large alkali or alkaline-earth metals remain scarce. Caulton and Ruhlandt-Senge have shown that the highly fluorinated {OC(CF₃)₃}⁻, {OCH(CF₃)₂}⁻, {OCMe(CF₃)₂}⁻, or {OCMe₂CF₃}⁻ can be used as ligands for the synthesis of K, Ca, Sr, Ba homobimetallic or heterobimetallic complexes (Figure 4.2–a). These fluorinated alkoxo complexes are stabilised by intramolecular Ae···F–C secondary interactions (as revealed through X-ray data) and are potential candidates for CVD. Other notable examples include [Ae(O₂CCF₃)₂]L₀.₅ (Ae = Sr, L = tetraglyme; Ae = Ba, L = triglyme, 12-crown-4, 15-crown-5, and 18-crown-6 ethers). In addition, Lewis acidic complexes, such as [{OC(CF₃)₃}₂Ca], have been successfully applied in the condensation reactions of 3-hydroxy-phenethylamine with aldehydes. According to studies performed by Chi et al., metal-fluoride interactions can also be employed to stabilise the solvent-free barium homoleptic complex [{RO²⁻}²Ba] ( [{RO²⁻}]H = HOC(CF₃)₂CH₂N(CH₂CH₂OMe)₂, Figure 4.2–b); however, these stabilising interactions are not present in the lighter strontium analogue [{RO²⁻}²Sr]. Our group has extended these studies and reported that a similar multidentate fluorinated aminoetheralkoxo ligand can be used to stabilise discrete dimeric Ae cations [{RO⁺}²Ae]⁺·₂[H₂N{B(C₆F₅)₃}²]⁻ (Ae = Ca, Sr, Ba; {RO⁺}H = HOC(CF₃)CH₂(1-aza-15-crown-5), Figure 4.2–c) accompanied by weakly coordinating anions. In these complexes, Ae···F–C interactions are present and actively contribute towards the stabilisation of the metal centre. According to DFT computations, they have a strength of approximately 30 kcal mol⁻¹.

![Figure 4.2. Known Ae (Ca, Sr, Ba) fluorinated alkoxo complexes containing intramolecular Ae···F–C interactions.](image-url)
The synthesis of the related solvated trifluoroacetates (TFAA) (e.g. \([\{\text{Ca}_2(\mu\text{-TFAA})_3(\text{THF})_4\}(\mu\text{-TFAA})_n]\)_n\)\(^{13}\), hexafluoracetates (HFA) (e.g. \([\text{trans-}[\text{Sr}(18\text{-crown-6})(\text{HFA})_2]\)]\(^{14}\) or hexafluoroacetylacetonates \([\text{Ae(HFacac)}_2(\text{diglyme})(\text{H}_2\text{O})_n]\) (Ae = Ca, Sr, \(x = 1\); Ae = Ba, \(n = 0\); HFacac = hexafluoroacetylacetonate)\(^{15}\) incorporating alkaline-earth metals was reported.

This chapter will explore new pathways for stabilising neutral alkaline-earth heteroleptic complexes, by employing electron-deficient fluorinated aminoetheralkoxo ligands. The use of such ligands serves several purposes, e.g. to prevent the aggregation of the resulting complexes and to provide additional stability towards the metal centre through Ae···F–C interactions.

In our quest to synthesise electron-deficient complexes for catalytic purposes, the preparation of well-defined Ae cations was also considered and details will be given Section 3.4. To date, there are no reports describing the use of group 2 cations in hydroelementation catalysis. Nevertheless, in a related context, studies by Roesky indicate that addition of \([\text{PhNMe}_2\text{H}]^+\cdot[\text{B}(\text{C}_6\text{F}_5)_4]^-\) to \([^{(\eta^5-\text{Cp})_2\text{ZnMe}}\] (ATI = \(N,\text{N}^\prime\)-disubstituted aminotroponiminate) improves the catalytic efficiency of the zinc complex in intramolecular hydroamination reactions.\(^{16}\) Such improvement was attributed to the formation of a cationic Zn complex. A similar beneficial effect was observed also for \([^{(\eta^5-\text{Cp})_2\text{ZnMe}}\] and \([\text{N}(\text{R}),\text{N}(\text{R})\text{-PLY}]\text{ZnMe}\) (R = Me, \(\eta^3\)-Pr, PLY = phenalenyl) which catalyse competently the cyclisation of aminoalkenes when combined with \([\text{PhNMe}_2\text{H}]^+\cdot[\text{B}(\text{C}_6\text{F}_5)_4]^-\).\(^{17,18}\) Very recently, a well-defined Zn cation \([\text{Zn}_2\text{Cp}_{3}^\text{+}]\cdot[\text{B}(\text{C}_6\text{F}_5)_4]^-\) was successfully employed to catalyse the same organic transformation.\(^{19}\)

En route to preparing neutral Ae complexes, the synthesis and characterisation of several potassium salts will be presented. In addition, this chapter will also feature the syntheses and characterisation of homoleptic complexes of the type \([\{\text{RO}\}_2\text{Ae}\] (\{\text{RO}\}^- = fluoroalkoxo ligand; Ae = Ca, Sr). Beyond their use in CVD experiments which were not explored here, such homoleptic complexes are also common side-products in the synthesis of Ae heteroleptic complexes, and as such their characterisation was not only necessary, but also valuable.

### 3.2. Potassium complexes as synthons for Ae (Ca, Sr) complexes

#### 3.2.1. Ligand synthesis

The proteo-ligands of interest here, noted \{RO\}^x\text{H} (\(x = 1\)–4) hereafter, are easily accessed by reacting the commercially available 2,2-bis(trifluoromethyl)oxirane with the relevant amine (Scheme 4.1), by adaptation of the synthetic protocol reported for similar compounds.\(^{11,20}\) This procedure is convenient

\[^*\] \{RO\}^x\text{H} was synthesised prior to this work and was already available in the laboratory. See Sarazin, Y.; Liu, B.; Roisnel, T.; Maron, L.; Carpentier, J.-F. J. Am. Chem. Soc. 2011, 133, 9069.
since the reactions are 100% atom-efficient, all starting materials are commercially available and the reaction products are obtained on multigram scales and in high yields (70–90%).

\[
\text{HNR}_2 + \text{Et}_2\text{O} \rightarrow \begin{align*}
\text{H} & \quad \text{O} \quad \text{O} \quad \text{F} \quad \text{CF}_3 \\
\text{O} & \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{F} \quad \text{CF}_3 \\
\text{O} & \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{F} \quad \text{CF}_3 \\
\text{O} & \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{F} \quad \text{CF}_3
\end{align*}
\]

Scheme 4.1. Synthesis of the proteo-ligands \{RO\}H (x = 1–4).

\{RO\}H (x = 1–4) proteo-ligands are fully soluble in common organic solvents and are isolated as colourless oils (except for \{RO\}H which is a colourless solid). They have been characterised by multinuclear NMR spectroscopy, mass spectrometry and elemental analysis. The molecular structure of \{RO\}H was determined by single-crystal X-ray diffraction studies after recrystallisation from a concentrated Et₂O solution. The \(^1\)H NMR spectra for all ligands are consistent with the proposed structure with the resonances for the OH proton being typically located around δ_H 6.5 ppm as a broad singlet. All other resonances can be easily attributed except for those corresponding to the aza-crown-ether methylene protons (for \{RO\}H and \{RO\}H) which form indiscernible multiplets. The \(^19\)F NMR spectra contain a single resonance (around δ_F -77 ppm) under the form of a sharp singlet, indicating that the CF₃ groups are equivalent in solution at room temperature. \(^1\)J_C-F and \(^2\)J_C-F determined from the \(^13\)C NMR spectra of the proteo-ligands have a value of approximately 287± 1 and 30±2 Hz, respectively.

3.2.2. Potassium complexes

This section aims to present the synthesis and characterisation of potassium complexes of type \{[RO\}K\} \(x = 1–3\). Relevant literature data indicate that such salts can be valuable precursors for the synthesis of Ae heteroleptic complexes through salt metathesis reactions (Scheme 4.2).

\[
\begin{align*}
\text{[RO}^\text{I}\text{]K}_4 & \quad \text{KN(SiMe}_3\text{R})_2 \\
\text{R} & = \text{H, Me} \\
\rightarrow & \quad 2 \text{[RO}^\text{I}\text{]CaN(SiMe}_2\text{R})_2]_{2+} + 4 \text{K}^+ \\
x & = 1–3
\end{align*}
\]

Scheme 4.2. Potassium complexes for salt metathesis pathways to neutral heteroleptic calcium complexes.

The multinuclear potassium complexes \{[RO\}K\} \(x = 3 (1), 2 (2), 1 (3)\) were obtained in moderate to high yields (78–93%) by reacting the proteo-ligands \{RO\}H \(x = 1–3\) with KN(SiMe₃)₂.
or KN(SiMe₂H)₂ in stoichiometric amounts (Scheme 4.3). Complexes \([\{RO^2\}K]_4\) (2) and \([\{RO^1\}K]_4\) (3) are readily soluble in hydrocarbons (pentane, benzene and toluene) and ethers (Et₂O, THF) while \([\{RO^1\}K]_2\) (1) is only partially soluble in dichloromethane. These complexes were characterised in the molecular solid state by X-ray crystallography and their purity was confirmed by combustion analysis. The analogous complex \([\{RO^4\}K]_2\) was synthesised prior to this work and was already available in the laboratory.

![Scheme 4.3. Synthesis of the potassium complexes \{RO\}K (x = 1–3).](image)

3.2.3. Solid-state characterisation

\([\{RO^1\}K]_4\) (1) was recrystallised from a concentrated dichloromethane solution at room temperature and its molecular structure is shown in Figure 4.3. It depicts a centrosymmetric dimer through O₉alkoxide bridging atoms with 8-coordinated potassium atoms. The structure features coordination from the nitrogen and oxygen atoms onto potassium while two K···F–C interactions (2.928(2) and 3.035(2) Å; average value: ~2.98 Å) ensure the filling of the coordination sphere of the metallic centre, thus resulting in a \(\mu_2:O^6,K^2\) chelate. These K···F–C contacts are shorter than the fixed cut-off values of 3.22
and are mostly based on electrostatic as they actually do not affect the integrity of the C–F bonds (C–F<sub>donating</sub> = 1.348 Å(avg) vs. C–F<sub>non-donating</sub> = 1.349 (avg)). The K···F–C distances are shorter to those found in [K(18-crown-6)][O(CF<sub>3</sub>)<sub>2</sub>C(CH<sub>2</sub>·Bu)GePh<sub>3</sub>]<sup>−</sup> (~3.24 Å),<sup>22</sup> and comparable to those in K[Cu(OC<sub>4</sub>F<sub>9</sub>)<sub>2</sub>] (~2.96 Å),<sup>23</sup> and [KAe(OC(CF<sub>3</sub>)<sub>3</sub>(THF))]<sub>4</sub> (Ae = Sr, ~2.94 Å; Ae = Ba, ~2.95 Å).<sup>2b</sup>

![Figure 4.3. ORTEP representation of the molecular structure of {RO<sup>3</sup>}K (1), recrystallised as the centrosymmetric dimer [{RO<sup>3</sup>}K]<sub>2</sub>. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): K(1)−O(15) = 2.630(2), K(1)−O(15′) = 2.682(2), K(1)−O(3) = 2.777(2), K(1)−O(6) = 2.821(2), K(1)−O(9) = 2.753(2), K(1)−N(12) = 2.990(2), K(1)−F(21) = 2.928(2), K(1)−F(23) = 3.035(2); K(1)−O(15)−K(1) = 92.65(5).

The molecular structure of [{RO<sup>2</sup>}K]<sub>4</sub> ([2]<sub>4</sub>), represented in Figure 4.4, was determined from single crystals isolated from a pentane solution at −30 °C. Changing the denticity of the ligand by removing a potential oxygen donor atom from the ligand set (in comparison with [1]<sub>2</sub>) results in the formation of a higher aggregate, since {RO<sup>2</sup>}K was recrystallised as the tetramer [2]<sub>4</sub>. The potassium and oxygen atoms are arranged in the shape of a heterocubane with a central K<sub>4</sub>O<sub>4</sub> core. This type of geometry around the potassium ions is not unusual and it has been reported for similar fluorinated sodium and potassium alkoxides.<sup>24,23,25</sup>

---

<sup>†</sup> The maximum distances for K···F interactions were fixed by Plenio at 3.47 Å (Chem. Rev. 1997, 97, 3363) which corresponds to the average of the sum of the ionic radius of potassium (2.00 Å) and van der Waals radius of fluorine (1.47 Å).
Figure 4.4. ORTEP representation of the molecular structure of \( \{RO^2\}K \) (2), recrystallised as the tetramer \([2]_4\). Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): K(1)–O(8) = 2.815(2), K(1)–O(20) = 2.642(1), K(1)–O(22) = 2.707(1), K(1)–O(41) = 2.707(1), K(1)–F(14) = 2.879(1), K(1)–F(25) = 3.076(1), K(1)–F(28) = 2.862(1), K(1)–F(50) = 3.155(1), K(1)–N(1) = 3.060(2), K(2)–O(22) = 2.639(1), K(2)–O(39) = 2.777(1), K(1)–O(42)–K(2) = 98.55(4); K(1)–O(42)–K(4) = 96.85(4), K(1)–O(20)–K(3) = 90.94(4), K(1)–O(41)–K(3) = 89.65(4), K(2)–O(22)–K(4) = 86.89(4).

All potassium atoms are distinct and each adopts a unique coordination pattern (C.N. = 7–9). Nevertheless several common features can be highlighted: (a) each K atom receives electronic density from a coordinated N side-arm atom, (b) the coordination sphere of each K atom is filled by K···F–C interactions (2.76–3.16 Å; average value: \( \approx 2.96 \) Å), and (c) from the two tethered methoxy potential donors, only one is coordinated to the K centre. This last aspect is certainly the most intriguing one with regards to the molecular structure, as it implies that multiple K···F–C interactions may have a stronger contribution towards the stability of the potassium complexes than the binding of additional O ether heteroatoms. In a review article, Ruhlandt-Senge et al. have already postulated that multiple secondary interactions might surpass donation from a single co-ligand such as ethers and amines. For instance, the molecular structure of \([\{C_5Me_3SiMe_2Ph\}Ba]_2\) is solvent-free and features two Ba···C \(_a\) interactions from the aryl ring per metal centre, despite the fact that coordinating solvents were used during synthetic procedures. This contrasts with \([\text{Cp}_3\text{Ba}]\), which in presence of THF, pyridine or bipyridine, crystallises as solvent adducts. Nonetheless, steric effects must also be taken into account as it is possible that the geometry around the potassium atoms is already overly congested, hampering the binding of the second OMe moiety on the side-arm).
X-ray data for \([2]_4\) indicates that coordination saturation of the potassium centres can be achieved through coordination from a single O_ether heteroatom in the ancillary ligand. Therefore substituting the non-coordinating CH_2CH_2OMe moiety with a simple Me group should not affect the stability of the potassium complex. To verify this hypothesis, \([RO^1]H\) was reacted with KN(SiMe_3)_2 to obtain the corresponding potassium salt \([RO^1]K\) (3). This compound recrystallised as a tetramer from a pentane solution at −30 °C (Figure 4.5), and is structurally similar to \([(RO^2]K)_4\) (\([2]_4\)). The tetrameric structure is arranged in a cubane-like geometry with a K_4O_4 central core. By contrast, the coordination numbers for the K atoms ranging from 6 to 8 are lower than in \([2]_4\). As postulated, coordination from a single O heteroatom is sufficient to ensure the stability of the potassium complex. Similarly to \([2]_4\), the coordination sphere of the metal centres is filled by K···F–C interactions with distances varying from 2.77–3.18 Å. From this perspective, it is undeniable that metal–fluoride interactions play a large a role in stabilising \([1]_2–[3]_4\). Their intensity can be gauged using bond valence sum analysis (BVSA).

**Figure 4.5.** ORTEP representation of the molecular structure of \([RO^1]K\) (3) recrystallised as the tetramer \([3]_4\). Only one of the two independent and comparable molecules found in the asymmetric unit is depicted. Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): K(1)–O(1) = 2.774(6), K(1)–O(13) = 2.666(5), K(1)–O(53) = 2.709(5), K(1)–O(73) = 2.708(5), K(1)–N(5) = 2.911(7), K(1)–F(11) = 2.908(7), K(1)–F(52) = 2.839(5), O(13)–K(2) = 2.744(5), K(2)–O(21) = 2.810(6), K(2)–O(33) = 2.658(5), K(2)–O(53) = 2.643(5), K(1)–O(13)–K(2) = 94.3(1), K(1)–O(53)–K(2) = 95.7(1), K(1)–O(53)–K(3) = 92.8(1), K(1)–O(73)–K(3) = 91.4(1), K(2)–O(33)–K(3) = 87.6(1), K(2)–O(53)–K(3) = 88.4(1), K(2)–O(13)–K(4) = 88.9(1), K(3)–O(73)–K(4) = 89.8(1).
Chapter 3: Alkaline-Earth Fluorinated Aminoetheralkoxides

3.2.4. Bond valence sum analysis

The contribution of donating atoms towards the coordination sphere of a metal centre can be estimated using bond valence sum analysis (BVSA). This mathematical concept was first introduced by Brown and Altermatt,\(^32\) and was later developed by O’Keefe and Brese.\(^33\) It is based on Pauling’s rules \(^34\) and postulates that the valence of an element consists of individual bond valences \(v\) that can be summed. The value of these bond valences depends on the interaction between the element and the neighbouring atoms and are calculated using Equation (4.1). In this equation, the values of \(R_{\text{Met-X}}\) and \(B\) depend on the pair of selected elements and have been previously tabulated for a large variety of atoms.\(^35\) A descriptive view of this complex process can be consulted in the referenced article.\(^36\) It is commonly accepted that for hard-hard or soft-soft pairs of atoms, \(B\) takes the value of 0.37 Å. The values of \(d_{\text{Met-X}}\) are determined experimentally using X-ray crystallography and represent the bond length between the two elements involved.

\[
v = \exp \left( \frac{R_{\text{Met-X}} - d_{\text{Met-X}}}{B} \right)
\]

Hence, owing to the molecular structures of \([1]_2\–[3]_4\), this model can be used to calculate the valence of the potassium atoms in these complexes. In order to do so, the bond valences for K and donating elements (O, N, F) have been determined. The calculations for \([\{\text{RO}^3\}\text{K}\]_4\ ([2]_4) are represented in Table 4.1, while the remaining data for \([1]_3\) and \([3]_4\) can be found in Annexure D. The values obtained for \([\{\text{RO}^3\}\text{K}\]_4\ ([2]_4) suggest a contribution of approximately 15% of the K···F–C interactions from the overall bonding pattern of the potassium complex. This value is very similar to that for \([\{\text{RO}^1\}\text{K}\]_4\ ([3]_4) (17%), Ruhlandt-Senge’s \([\text{K}(\text{PFTB})(\text{THF})]_4\) (PFTB-H = perfluoro-tert-butanol) (20%),\(^2b\) and is higher compared to that for \([\{\text{RO}^3\}\text{K}\]_2\ ([1]_2) (12%). This last feature was expected due to the fact that \([1]_2\) may be further stabilised by an extra oxygen donor in comparison with \([2]_4\). However, these values are inferior to those found in \([\text{K}[\text{OCPh}](\text{CF}_3)_2]\) (34%) and \([\text{K}[\text{OCMe}](\text{CF}_3)_2]\) (32%), a reasonable situation since the last two alkoxides do not contain binding amino moieties.\(^23\) The important conclusion that can be drawn is that the contribution of K···F interactions towards the coordination sphere of potassium increases as the number of potential \(\text{O}_{\text{ether}}\) heteroatoms decreases.
Table 4.1. Bond valence analysis calculations for $[\text{RO}_2]_4 \text{K}_4 ([2]_4)$.

<table>
<thead>
<tr>
<th>M</th>
<th>$d(\text{K–O})^a$</th>
<th>$d(\text{K–F})^a$</th>
<th>$d(\text{K–N})^a$</th>
<th>$v(\text{K–O})^b$</th>
<th>$v(\text{K–F})^b$</th>
<th>$v(\text{K–N})^b$</th>
<th>$\Sigma v$</th>
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</thead>
<tbody>
<tr>
<td>K(1)</td>
<td>2.642</td>
<td>2.863</td>
<td>3.060</td>
<td>0.252</td>
<td>0.095</td>
<td>0.115</td>
<td>1.229</td>
</tr>
<tr>
<td></td>
<td>2.707</td>
<td>2.879</td>
<td></td>
<td>0.211</td>
<td>0.091</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>2.707</td>
<td>3.076</td>
<td></td>
<td>0.211</td>
<td>0.053</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>2.815</td>
<td>3.156</td>
<td></td>
<td>0.158</td>
<td>0.043</td>
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<tr>
<td>$\Sigma$</td>
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<td></td>
<td></td>
<td>0.832</td>
<td>0.282</td>
<td>0.115</td>
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<tr>
<td>K(2)</td>
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<td>2.830</td>
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<td>K(3)</td>
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<td>0.115</td>
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<td>K(4)</td>
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<td>2.761</td>
<td>2.974</td>
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<td>0.125</td>
<td>0.145</td>
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</tr>
<tr>
<td>$\Sigma$</td>
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<td></td>
<td></td>
<td>0.971</td>
<td>0.198</td>
<td>0.145</td>
<td>1.314</td>
</tr>
</tbody>
</table>

| Contribution | 74% | 15% | 11% |

[a] Data from the X-ray structure of [2]₄. [b] Calculated using equation (4.1). $R_{\text{K–O}} = 2.132$, $R_{\text{K–F}} = 1.992$, $R_{\text{K–N}} = 2.260$; $B = 0.37$ as reported in the literature.³⁶

3.2.5. Characterisation by NMR spectroscopy

The $^1$H NMR spectra of alkali complexes $[\text{I}]_2–[3]_4$ in benzene-$d_6$ or dichloromethane-$d_2$ show the expected resonances for the proposed structures. As found for the proteo-ligands, only one singlet resonance was found in the $^{19}$F NMR spectra at around $\delta^{19}\text{F} –77$ ppm. This indicates that the fluorine atoms are equivalent and suggests that, at room temperature, the free rotation of the CF₃ groups is unhindered. Studies performed on potassium complexes on fluoro-macrocyclic cages indicate that K⋯F–C interactions can be detected in solution due to the fact that, upon complexation, the $^1J_{\text{C–F}}$ was reduced from 260.5 Hz (in the organic molecule) to 247.8 Hz (in the metal complex).³⁷ In our case, the values of $^1J_{\text{C–F}} (297 ± 1$ Hz) and $^2J_{\text{C–F}} (23 ± 1$ Hz) coupling constants in the complexes are only slightly different from those of the proteo-ligands ($^1J_{\text{C–F}} = 287 ± 1$ Hz and $^2J_{\text{C–F}} = 30 ± 2$ Hz). This slight variation cannot be seen as a sign of persistence of K⋯F–C secondary interaction in solution.
In the cases where X-ray crystallography indicates the formation of polymetallic structures, it is very useful to assess if the degree of aggregation is also retained in solution. For instance, in heterofunctionalisation catalysis, the degree of nuclearity of the precatalyst may have a direct influence on the mechanism. Even though potassium complexes \([1]_2-[3]_4\) were not synthesised for catalytic purposes, determining their nuclearity in solution offers an opportunity to validate the method which will be used in the work subsequently presented in this thesis.

In the last few years, PGSE NMR diffusion experiments have proven useful in determining the nuclearity of aggregated metal complexes in solution. The principle of the method is based on the comparison of the hydrodynamic radii for a given complex, which can be obtained both in solution and in the molecular solid state. It has been applied in our group for the study of related alkali metal complexes.\(^{38}\) Firstly, the hydrodynamic radius of the metal complex \((r_{H,X-ray})\) is calculated using the structural data obtained from the molecular solid-state structure according to equation (4.2), where \(a\) and \(b\) are the main and the minor semi-axes of the prolate ellipsoid respectively, and are calculated using literature procedures.\(^{39}\) Then, the hydrodynamic radius in solution \((r_{H,PGSE})\) is calculated using several mathematical equations (Stokes-Einstein (4.3),\(^{40}\) (4.4)–(4.6) and finally Chen (4.7)\(^{41}\)), with Si(SiMe\(_4\)) (TMSS) as the external standard. TMSS or SiMe\(_4\) (TMS) are widely applied as DOSY standards due to the fact that they have a spherical shape, which is a condition for the validity of the Stokes-Einstein equation. The diffusion coefficient of the metal complex is obtained from the plot of \(\ln(I/I_0)\) vs \(-\gamma^2\delta^2 G^2(\Delta - \delta/3)\) \(D_t\) \((I\) is the amplitude of the spin echoed signal, \(I_0\) is the intensity without gradient, \(\gamma\) is the gyromagnetic ratio, \(\delta\) is the duration of the gradient pulse, \(G\) is the strength of the gradient and \(\Delta\) is the diffusion time).\(^{42}\)

\[ r_{H,X-ray} = (a^2b)^{1/3} \quad (4.2)^{\dagger} \]

\[ D_t = \frac{k_B T}{c f_s^\text{met} \eta r_H} \quad (4.3)^{\ddagger} \]

\[ f_s^\text{met} = \frac{\sqrt{1 - \left(\frac{b}{a}\right)^2}}{\ln \left[1 + \sqrt{1 - \left(\frac{b}{a}\right)^2}\right]} \quad (4.4)^{**} \]

\(^{\dagger}\) \(r_{H,X-ray}\) is the hydrodynamic radius of the metal complex in the solid state and is determined using X-ray crystallography according to eq (4.2) where \(a\) and \(b\) are the main and the minor semi-axes of the prolate ellipsoid formed by the complex according to Perrin, F. J. Phys. Radium 1936, 7, 1.

\(^{\ddagger}\) \(k_B\) = Boltzmann constant, \(T\) = temperature (K), \(\eta\) = fluid viscosity, \(c^\text{met}\) = correction factor, \(r_H^\text{met}\) = hydrodynamic radius of the metal complex.

\(^{**}\) \(f_s^\text{met}\) is a correction factor and is determined using the \(a\) and \(b\) values from eqn (4.2).
Chapter 3: Alkaline-Earth Fluorinated Aminoetheralkoxides

According to the data provided in Table 4.2, the hydrodynamic radius in solution ($r_{H,P}GSE$) is in all cases very similar to the one obtained in the solid state ($r_{H,X-ray}$). This implies that the nuclearity of potassium complexes 1–3 observed in their molecular structure is preserved in solution.

**Table 4.2. Hydrodynamic radii in solution- ($r_{H,P}GSE$) and solid-state ($r_{H,X-ray}$) for complexes [1]$_2$–[3]$_4$.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Solvent</th>
<th>$D_1 [10^{-9} \text{m}^2 \text{s}^{-1}]$</th>
<th>$r_{H,P}GSE [\text{Å}]$</th>
<th>X-ray a [Å]</th>
<th>X-ray b [Å]</th>
<th>$r_{H,X-ray} [\text{Å}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[{RO_3K}]_2 [1]_2^c$</td>
<td>dichloromethane-$d_2$</td>
<td>3.60</td>
<td>5.66</td>
<td>5.28</td>
<td>4.60</td>
<td>5.04</td>
</tr>
<tr>
<td>$[{RO_2K}]_4 [2]_4$</td>
<td>benzene-$d_6$</td>
<td>0.88</td>
<td>5.74</td>
<td>7.65</td>
<td>4.65</td>
<td>6.48</td>
</tr>
<tr>
<td>$[{RO_1K}]_4 [3]_4$</td>
<td>benzene-$d_6$</td>
<td>0.77</td>
<td>6.45</td>
<td>5.59</td>
<td>5.23</td>
<td>5.46</td>
</tr>
</tbody>
</table>

[a] All NMR spectra were recorded at 298 K using 13.0–30.0 mM solutions of complex and of the external reference Si(SiMe$_3$)$_4$. [b] Average of the values of $D_1$ found for 3 or more separate peaks in the $^1$H PGSE NMR spectrum of the complex. [c] Measured in dichloromethane-$d_2$ due to lack of any solubility of the metal complex in hydrocarbon solvents.

A complementary method to determine the nuclearity of (poly)metallic complexes in solution is based on the approximation of their molecular weight (Mw) in solution. We have recently started to employ DOSY NMR to determine the nuclearity of metal complexes in solution based on correlation between the diffusion coefficient and its Mw. The formula weight of the complex can be readily obtained using diffusion-molecular weight analysis ($D_t$-Mw) according to literature procedures.$^{43}$ This method is very powerful since the degree of nuclearity of (poly)metallic complexes in solution can be estimated even in the absence of X-ray crystallographic data. More details concerning this technique will be given in Chapter 4.

$^\dagger$ $r_{H,solv}$ is the hydrodynamic radius for the chosen solvent and equals 2.68 Å for benzene-$d_6$ and 2.46 Å for dichloromethane-$d_2$ (Zuccaccia, D.; Macchioni, A. *Organometallics* 2005, 24, 3476); $r_{H,TMSS} = 4.28$ Å (TMSS is considered to be spherical).

$^\ddagger$ $D_1^{TMSS}$ = diffusion coefficient for TMSS, $f_s^{TMSS}$ = 1.00, $D_1^{met}$ = diffusion coefficient of the metal complex.

$^§§$ values of $r_{H,met}$ are deduced from this equation empirically by plotting $c^{met} r_{H,met}$ according to eqn (4.7).
3.3. Neutral heteroleptic and homoleptic Ae (Ca, Sr) fluorinated aminoetheralkoxo complexes

The present section is divided in two sections and will explore the synthesis and characterisation of Ae homoleptic (3.3.1) and heteroleptic (3.3.2) complexes bearing fluorinated aminoetheralkoxo ligands.

3.3.1. Alkaline-earth homoleptic complexes

Alkaline-earth homoleptic complexes of type Ae\[E(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}(THF)\textsubscript{2} (E = N, CH) are valuable in homogeneous catalysis, notably in ROP of cyclic esters, intermolecular olefin hydroamination and SiH-OH/NH dehydrocoupling reactions. In addition, some homoleptic complexes [Ae(OAr)\textsubscript{2}]\textsubscript{x}(S) supported by ArO– phenolato ligands can be used as precatalysts for ROP reactions and homoleptic complexes using fluoroalkoxo ancillary ligands are precursors for CVD. On the other hand, their formation can also come as a result of ligand redistribution reactions of Ae heteroleptic complexes. Therefore, besides their potential application in the abovementioned applications, their isolation is also important for establishing their NMR fingerprint in the mechanistic studies of hydroelementation reactions mediated by heteroleptic Ae complexes.

3.3.1.1. Synthesis

Homoleptic complexes can be easily accessed through protonolysis reactions, according to Scheme 4.4. Reaction of 2 equiv. of the proteo-ligand \{RO\textsuperscript{x}\}H (x = 1, 2, 3) with Ae\[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2}(THF)\textsubscript{2} in Et\textsubscript{2}O affords the formation of the desired Ae complexes [{RO\textsuperscript{x}}\textsubscript{2}Ae] (Ae = Ca, x = 3 (4), 2 (5), 1 (6); Ae = Sr, x = 3 (7), 2 (8), 1 (9)) in moderate to high yields (60–80%). Complexes 4–9 were isolated as air- and moisture sensitive solids which display solubility in hydrocarbons and ethers. Structural characterisation was carried out by multinuclear NMR spectroscopy and they can be also readily recrystallised, although the molecular structure of [{RO\textsuperscript{1}}\textsubscript{2}Ca] (6) was not determined as repeated crystallisation attempts only resulted in the formation of oils. The synthesis and characterisation for [{RO\textsuperscript{2}}\textsubscript{2}Sr] (8) has already been reported elsewhere.
Scheme 4.4. Synthesis of Ae (Ca, Sr) homoleptic complexes 4–[9]₂.

3.3.1.2. Solid-state characterisation

The molecular structure of [([RO]₃)₂Ca] (4) was obtained from single crystals grown from benzene at room temperature, and it is depicted in Figure 4.6. It features a monomeric arrangement with a formally 7-coordinate calcium atom in a distorted faced caped octahedral geometry. Besides coordination from O₃aloxide and N heteroatoms, the two {RO₃}⁻ ligands coordinate differently to the metal centre and act as κ¹–O and κ³–O donors. The coordination sphere of the metal centre is filled by one Ca···F (3.00 Å) contact which is taking preponderance over more powerful donors, i.e. the remaining O and N donors from the aza-crown ether moiety. For the Ca···F–C interactions, the cut-
The off value (3.13 Å) was fixed following the recommendations of Plenio (see 1.3.3.3. for details). The two Ca–O_{alkoxide} distances are fairly comparable (2.19 Å and 2.25 Å) and are expectedly narrower than Ca–O_{macrocyle} ones (avg. ~ 2.52 Å), considering that the latter bonds are dative.

Figure 4.6. (left) ORTEP representation of the molecular structure of [(RO\textsubscript{3})\textsubscript{2}Ca] (4). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and benzene solvent molecules are omitted for clarity. (right) Schematic representation of 4. Selected bond lengths (Å): Ca(1)–O(1) = 2.479(1), Ca(1)–O(21) = 2.187(1), Ca(1)–O(44) = 2.602(1), Ca(1)–O(41) = 2.475(1), Ca(1)–O(47) = 2.542(1), Ca(1)–O(61) = 2.246(1), Ca(1)–F(69) = 3.002(1); O(1)–Ca(1)–O(47) = 73.44(4), O(1)–Ca(1)–O(44) = 78.17(5), O(1)–Ca(1)–O(61) = 94.4(4), O(1)–Ca(1)–O(21) = 95.22(5), O(1)–Ca(1)–O(41) = 144.27(5).

The strontium analogue, [(RO\textsuperscript{1})\textsubscript{2}Sr] (7), was recrystallised as a mononuclear complex (Figure 4.7) at room temperature from a concentrated THF solution. The molecular structure features an eight-coordinate Sr atom arranged in a distorted bicapped trigonal prismatic geometry. Altogether, the coordination pattern of this metal complex is similar to that of 4, except for the two relatively weak Sr···F–C interactions (3.10 and 3.17 Å) that are now needed instead of one to fill the coordination sphere of the metal centre.

---

*** The maximum distances for Sr···F interactions were fixed at 3.30 Å (ionic $r_{dW}$ Sr (1.83 Å) + $r_{dWF}$ (1.47 Å) = 3.30 Å) according to Plenio H. *Chem. Rev.* 1997, 97, 3363.
Figure 4.7. (left) ORTEP representation of the molecular structure of $\left[\text{RO}_3\right]_2\text{Sr}$ (7). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and THF solvent molecule are omitted for clarity. (right) Schematic representation of 7. Selected bond lengths (Å): Sr(1)–O(45) = 2.426(1), Sr(1)–O(7) = 2.644(1), Sr(1)–O(10) = 2.663(1), Sr(1)–O(4) = 2.704(1), Sr(1)–O(15) = 2.423(1), Sr(1)–O(34) = 2.619(1), Sr(1)–F(53) = 3.166(1), Sr(1)–F(69) = 3.109(1); O(45)–Sr(1)–O(4) = 85.58(4), O(45)–Sr(1)–O(34) = 94.30(4), O(45)–Sr(1)–O(10) = 113.49(4), O(45)–Sr(1)–O(7) = 146.33(4), O(45)–Sr(1)–O(45) = 138.56(4).

Complex $\left[\text{RO}_3\right]_2\text{Ca}$ (5) was recrystallised from Et$_2$O (structure 5a) and also from pentane (structure 5b) solutions. Two polymorphs were hence characterised. The main difference between these two molecular structures is the geometry around the Ca centre as a result of a dangling CH$_2$CH$_2$OMe fragment (Figure 4.8). In 5a, the OMe group is bound to calcium, causing the metal centre to be 8-coordinate, in a slightly distorted octahedral geometry. By contrast with the molecular structure of $\left[\text{RO}_1\right]_2\text{Ca}$ (4), the coordination sphere in 5a is filled with only hard donors (O, N); there is no contribution from Ca···F–C interactions. The geometry around the Ca centre in 5b is different from that observed in 5a, as one OMe group from the ligand side-arm is not coordinated to the metal which results in a 7-coordinate Ca centre resting in a distorted capped trigonal prism arrangement. As observed from the bonding patterns of both molecular structures, the loss of one (hard) methoxy donor in 5b is compensated by a substantially stronger Ca–O_methoxy contact (5a: 2.669(1) Å vs 5b: 2.439(3) Å). The other metric parameters are in the range of those measured in $\left[\text{RO}_1\right]_2\text{Ca}$ (4).
Figure 4.8. (top) ORTEP and schematic representation of the molecular structure of \([\{RO\}^2]_2\text{Ca}\) (5a) recrystallised from an Et\(_2\)O solution. (bottom) ORTEP and schematic representation of the molecular structure of \([\{RO\}^2]\text{Ca}\) (5b) recrystallised from a pentane solution. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) for 5a: Ca(1)–O(1) = 2.221(1), Ca(1)–O(39) = 2.522(1), Ca(1)–O(35) = 2.459(1), Ca(1)–O(21) = 2.265(1), Ca(1)–O(15) = 2.669(1), Ca(1)–N(5) = 2.657(2), Ca(1)–N(32) = 2.772(1); O(21)–Ca(1)–O(19) = 89.2(1), O(1)–Ca(1)–O(15) = 124.73(1), O(21)–Ca(1)–O(21) = 144.2(1). Selected bond lengths (Å) for 5b: Ca(1)–O(1) = 2.223(3), Ca(1)–O(35) = 2.426(3), Ca(1)–O(15) = 2.439(3), Ca(1)–O(19) = 2.493(3), Ca(1)–N(5) = 2.715(3), Ca(1)–N(32) = 2.614(3); O(21)–Ca(1)–O(19) = 89.2(1), O(1)–Ca(1)–O(15) = 124.73(1), O(21)–Ca(1)–O(21) = 144.2(1).

Unfortunately, all attempts to crystallise \([\{RO\}^2]_2\text{Ca}\) (6) were unsuccessful. Yet, due to the fact that two alkoxo \(\{RO\}^+\) ligands are capable of ensuring a minimal coordination number of 6, it can be assumed that this calcium complex might remain monomeric in the solid state. The X-ray data of \([\{RO\}^2]\text{Sr}\) (9) indicate the formation of a dinuclear complex through bridging oxygen atoms (Figure 4.9). The two Sr centres are not equivalent: Sr(1) is formally 8-coordinate in a distorted octahedral geometry; Sr(2) features a formal coordination number of seven and is engaged in a distorted monocapped trigonal prism geometry. The Sr atoms in [9] do not reach coordinative saturation from N and O atoms alone, and therefore aggregation (three bridging oxygen atoms connect
the two strontium centres) and by Sr···F interactions (Sr(1)–F(16) = 2.898(1) Å; Sr(2)–F(51) = 2.749(1) Å) are also detected.

**Figure 4.9.** (left) ORTEP representation of the molecular structure of [[RO\(^1\)]\(_2\)]\(_2\)Sr\(_2\) ([9]\(_2\)). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. (right) Schematic representation of [9]\(_2\). Selected bond lengths (Å): Sr(1)–O(22) = 2.649(2), Sr(1)–O(29) = 2.370(2), Sr(1)–O(2) = 2.732(2), Sr(1)–O(9) = 2.536(1), Sr(1)–O(49) = 2.439(2), Sr(1)–N(25) = 2.739(2), Sr(1)–N(5) = 2.824(2), Sr(1)–F(16) = 2.898(1), Sr(2)–O(42) = 2.548(2), Sr(2)–O(69) = 2.306(2), Sr(2)–O(2) = 2.693(1), Sr(2)–O(9) = 2.445(2), Sr(2)–O(49) = 2.520(2), Sr(2)–N(45) = 2.791(3), Sr(2)–F(51) = 2.749(1); Sr(1)–O(2)–Sr(2) = 85.83(6), Sr(1)–O(9)–Sr(2) = 95.72(6), Sr(1)–O(49)–Sr(2) = 96.28(7).

3.3.1.3. NMR spectroscopy

The solution behaviour of alkaline-earth homoleptic complexes 4–[9]\(_2\) was studied using multinuclear NMR spectroscopy. NMR experiments were typically conducted in benzene-\(d_6\). Complex 4 is poorly soluble in hydrocarbons and was characterised in THF-\(d_8\) instead. The \(^1\)H NMR resonances at room temperature were in general complicated to interpret when ligands incorporating aza-crown-ether fragments were used (as in 4 and 7) as a result of overlapping signals. On the other hand, for Ae complexes bearing the \{RO\(^2\)\}\(^-\) ligand, that is, for 5 and 8, the \(^1\)H NMR spectra were well resolved at room temperature displaying only sharp resonances. For 6 and [9]\(_2\), the \(^1\)H NMR spectra in benzene-\(d_6\) at room temperature were characterised by well-separated but uninformative broad signals. This suggests that, at this temperature, 6 and [9]\(_2\) are involved in a fluxional process.

A similar behaviour was observed through \(^19\)F NMR spectroscopy. Depending on the denticity of the fluoroalkoxo ligands, sharp or broad resonances are observed. When the potentially tetradentate and tridentate proteo-ligands \{RO\(^2\)\}\(^-\)H and \{RO\(^3\)\}H were used, the homoleptic complexes 4, 5 and 7, 8
were found to contain a single sharp resonance each (ca. $\delta_{19F} - 77$ ppm); this indicates that the rotation of the CF$_3$ groups in these complexes is fast on the NMR timescale. $^{19}$F NMR spectroscopy indicated very broad resonances for 6 and [9]$_2$ which could not be resolved at low temperatures (193–267 K).

In order to explain the fluxional behaviour of 6 and [9]$_2$, two possible interpretations can be postulated: competitive coordination of OMe fragments from different {RO}$_1^-$ ligands on the NMR timescale (Scheme 4.5), or a monomer-dimer slow exchange. Such exchanges between different forms of aggregates are not uncommon and have been reported for example in Cu(I) complexes supported by $N,N',S,S'$ scorpionato ligands using DOSY NMR. Furthermore, upon coordination, the nitrogen atom from {RO}$_1^-$ becomes chiral and can cause the appearance of diastereotopic protons and magnetically inequivalent CF$_3$ groups, hence complicating the NMR spectra. From all these possibilities, it is believed that in [9]$_2$ a competitive coordination of OMe fragments is more probable. This is based on the fact that the bridging Ae–O$_{alkoxide}$ bond (BDE$_{Sr-O} = 101.9$ kcal mol$^{-1}$) is difficult to cleave in the absence of donor solvents.

![Scheme 4.5](image.png)

**Scheme 4.5.** Possible scenarios for the dynamic solution behaviour of [9]$_2$.

In relation with these observations, Chi et al. have also reported that [{RO}$_2$]$_2$Sr and [{RO}$_2$]$_2$Ba display a fluxional behaviour. Based on $^{19}$F VT NMR experiments it was implied that the fluxionality of these complexes might be ascribed to a cis-trans isomerisation process. Another possibility evoked by the authors refers to a reversible Ae···F–C binding at low temperature, which can result in an exchange between an isomer with a bicapped octahedron geometry (Ae···F–C interactions are present) to another isomer with a bicapped square antiprismatic geometry (there are no Ae···F–C interactions) (Scheme 4.6).
3.3.2. Heteroleptic alkaline-earth complexes

Heteroleptic calcium complexes have found numerous applications in homogeneous catalysis (see Chapter 1) and consequently, they have become a challenging target for synthetic coordination chemists in the last 10 years. Their synthesis is usually hampered by their extreme sensitivity towards moisture and air. Furthermore, they readily engage side reactions promoted by Schlenk equilibria (see 1.3.1). In the present section, the synthesis and characterisation of Ae (Ca, Sr) heteroleptic complexes will be described in detail. It will be discussed how the presence of Ca···F–C and Ca···H–Si interactions is beneficial in the kinetic stabilisation of these complexes.

3.3.2.1. Synthesis

Traditionally, Ae heteroleptic complexes can be synthesised using two methods: (a) salt metathesis reactions between one equiv. of isolated or in situ generated potassium alkoxide complexes and CaI$_2$ and (b) protonolysis reactions between the proteo-ligand and Ae[SiMe$_3$]$_2$(THF)$_2$ or Ae[SiMe$_2$H]$_2$(THF)$_n$ (Ae = Ca, n = 1; Ae = Sr, n = 2/3; Ae = Ba, n = 0) according to Scheme 4.7.$^{18,52}$
Scheme 4.7. Synthesis of Ae heteroleptic complexes via salt metathesis and protonolysis reactions.

The first attempts in our group to synthesise $\{RO^x\}AeN(SiMe_3R)_2$ (Ae = Ca, Sr, Ba; R = H, Me; $x = 1$–4) complexes with fluoroalkoxides made use of the proteo-ligand with the highest denticity, $\{RO^4\}H$ (see Scheme 4.1 for structure). This choice was motivated by the fact that the ligand with the most potential hard donors (O, N) should be more suited to stabilise Ae heteroleptic complexes. Consequently, $\{RO^4\}K_2$ was mixed with stoichiometric amounts of $K(SiMe_3)_2$ and $CaI_2$ in THF in the attempted preparation of $\{RO^4\}CaN(SiMe_3)_2$. Unfortunately, $^1H$ NMR spectroscopy indicated the formation of an intractable mixture of unidentified species. For this reason, the second synthetic route involving protonolysis reactions was tested. In this case, our experiments were conducted with $\{RO^3\}H$. For this experiment, a solution of the proteo-ligand in $Et_2O$ was added dropwise to a solution of $Ca[N(SiMe_3)_2]$ in $Et_2O$ at $–78\, ^\circC$ (Scheme 4.8).

Scheme 4.8. Attempts to synthesise the heteroleptic calcium complex $\{RO^3\}CaN(SiMe_3)_2$. 
The formation of the desired $[\{\text{RO}^3\}\text{CaN(SiMe}_3\text{)}_2])$ could not be attested by $^1\text{H}$ NMR spectroscopy. Multiple unidentified resonances were present where the SiCH$_3$ groups were expected to appear. Vinyl resonances were present at $\delta_{^1\text{H}}$ 6.4 ppm (Figure 4.10). Besides, the product obtained in this reaction was not $[\{\text{RO}^3\}^2\text{Ca}]$ (4), which we had previously synthesised. These observations rather suggest that, instead of $[\{\text{RO}^3\}\text{CaN(SiMe}_3\text{)}_2])$, a different product was formed as a result of deleterious C–O bond cleavages in the aza-crown ether moieties. The $^{19}\text{F}$ NMR spectrum of this product consisted in multiple resonances ranging from $\delta^{19}\text{F}$ $-74.4$ ppm to $\delta^{19}\text{F}$ $-79.2$ ppm (Annexure E). Due to the complexity of this spectrum, no conclusive information concerning the structure of the calcium complex could be obtained.

Figure 4.10. $^1\text{H}$ NMR spectrum (400.16 MHz) of the product of the reaction of Ca$[\text{N(SiMe}_3\text{)}_2]$ with $\{\text{RO}^3\}\text{H}$ (1 equiv) at 298 K in benzene-$d_6$.

Our assumption was later confirmed by X-ray data, which indicated the formation of a tetrameric calcium complex. The molecular structure of the product (Figure 4.11) features a Ca$_4$O$_6$ central core in a centrosymmetric arrangement with two types of Ca atoms.

Figure 4.11. (left) ORTEP representation of the molecular structure of the product isolated from the reaction of Ca$[\text{N(SiMe}_3\text{)}_2]$ with $\{\text{RO}^3\}$H (1 equiv). Hydrogen atoms are omitted for clarity. (right) Simplified representation of the Ca$_4$O$_6$ core showing the coordination sphere around the Ca atoms. Ellipsoids are drawn at the 50% probability level. Selected bond lengths: Ca(1)–O(23) = 2.156(1), Ca(1)–O(4) = 2.412(1), Ca(1)–O(53) = 2.272(1), Ca(1)–O(1) = 2.258(1), Ca(1)–O(31) = 2.359(1), Ca(2)–O(34) = 2.429(1), Ca(2)–O(53) = 2.408(1), Ca(2)–O(40) = 2.766(1), Ca(2)–O(31) = 2.337(1), Ca(2)–O(31) $^* = 2.424(1)$, Ca(2)–N(37) = 2.697(14), Ca(2)–F(46) = 2.759(1).
Those in terminal positions (Ca(1)) are 5-coordinated; they sit in a distorted trigonal bipyramidal geometry ($\tau = 0.77$) and are coordinatively saturated by oxygen donors only. By contrast, the Ca atoms in central positions (Ca(2)) are formally 8-coordinated and the geometry around the Ca centres is best described as distorted octahedral. The formation of a vinyl ether function OCH=CH$_2$ was detected from the value of the C–C bond lengths (avg. 1.31 Å) which are in the typical range for C$_{sp2}$ hybridised carbon atoms. Aside from benefiting from oxygen (6 atoms) and nitrogen (1 atom) donors, the coordination sphere of the Ca atoms is filled by a relatively strong Ca···F–C interaction (2.759 Å).

The arrangement consisting in a Ca$_4$O$_6$ compares well to that for the hydroxide-containing complexes [Ca$_2$(OMes)$_2$(µ-OMes)$_2$(OH)(THF)$_2$]$_2$ and [Ca$_2$(OMes)$_2$(µ-OMes)$_2$(OH)(en)$_2$.2PhMe reported by Ruhlandt-Senge et al. The problematic ability of strongly basic Ae-amides to cleave C–O functions in crown-ether moieties is not unheard of, and related phenomena were already mentioned by Hursthouse. In this study, Ba[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ was found to react with 18-crown-6 to yield [(Me$_3$Si)$_2$N][BaO(CH$_2$CH$_2$O)$_5$CH=CH$_2$](18-crown-6). In the proposed reaction mechanism, it was described that the C–O bond cleavage resulted from proton abstraction in the crown ether moiety by a silylamide anion, generating a vinyl ether residue. Studies performed by Westerhausen et al. showed that ether-solvated calcium complexes containing a Ca–C$_{aryl}$ bond often undergo such degradation reactions at ambient temperature.

Since {RO$_1$}H was unsuitable for the synthesis of calcium heteroleptic complexes, the remaining studies were conducted using the proteo-ligands of lower denticities {RO$_1$}H and {RO$_2$}H (Scheme 4.9).

Dropwise addition of a solution of the corresponding fluorinated aminoethanol in Et₂O to a cold solution of Ca[N(SiMe₂R)₂⁺]₂(THF)ₙ (R = H, Me; n = 1, 2) in Et₂O resulted in the formation of [[RO⁺]CaN(SiMe₂R)₂]₂ (x = 2, R = H ([10]₂), Me ([11]₂); x = 1, R = H ([12]₂), Me ([13]₂)) as white solids in 70-80% yields. Despite several attempts, the purity of [[RO⁺]CaN(SiMe₃)₂]₂ ([11]₂) did not exceed 90%, as homoleptic residues [[RO⁺]Ca]₂ (5) were always present. These complexes were stable in ether solutions at room temperature, with no signs of undesired Ca–O bond cleavages. Complexes [10]₂–[13]₂ are soluble in hydrocarbons and ethers, but they decompose within seconds in chlorinated solvents (CH₂Cl₂ and CHCl₃).

3.3.2.2. Solid-state and solution characterisation

The molecular structure of [[RO⁺]CaN(SiMe₂H)₂]₂ ([10]₂) was obtained after recrystallisation of the material from a concentrated Et₂O solution at room temperature; it is depicted in Figure 4.12. It features a centrosymmetric dimer with formally 7-coordinated Ca atoms in a distorted pentagonal bipyramidal geometry. Alongside hard donors (O, N), the coordination sphere of each Ca centre is filled by one close Ca···F–C contact (2.832(1) Å) and one β-Si–H···Ca agostic interaction, while THF solvent molecules (from the Ca[N(SiMe₂H)₂⁺](THF)₂) are absent from the metal coordination sphere. The Ca–O₇ distances (2.294(1) and 2.302(4) Å) are close to those observed in the homoleptic derivatives 4, 5a, and 5b (avg. 2.22 Å), and larger than the one reported in Hanusa’s [[clox]CaN(SiMe₃)₂](THF)₃ (2.087(4)).

![Figure 4.12.](image)

*Figure 4.12. (left) ORTEP representation of the molecular structure of [[RO⁺]CaN(SiMe₂H)₂]₂ ([10]₂). Hydrogen atoms (except the SiH ones) are omitted for clarity. Ellipsoids are drawn at the 50% probability level. (right) Schematic representation of ([10]₂). Selected bond lengths (Å) and angles (deg): Ca(1)–O(11) = 2.294(1), Ca(1)–O(11)° = 2.301(1), Ca(1)–O(25) = 2.419(1), Ca(1)–N(1) = 2.310(1), Ca(1)–N(22) = 2.596(1), Ca(1)–F(14) = 2.832(1), Si(1)–N(1)–Ca(1) = 103.27(7), Si(2)–N(1)–Ca(1) = 126.68(8), Ca(1)–O(11)–Ca(1)° = 104.62(4), Si(1)–N(1)–Si(2) = 130.0(1). Torsion angle: Ca(1)–H(1S)–Si(1)–N(1) = 5.1(9).*
Only one of the two OMe groups from the ligand coordinates to the Ca centre, in the way observed before in the molecular structure of the potassium salt \([\{RO^2\}_2K\] (2)). As postulated by Ruhlandt-Senge,\(^{26}\) multiple secondary interactions have a more stabilising effect than coordination from a single co-ligand, in this case a –OMe group. Subsequent studies presented in Chapter 4 will show that such complexes can be stabilised even if the proto-ligand has no O\(_{ether}\) potential donors and contains instead weakly donating moieties such as alkenes or alkynes.

\(\beta\)-Si–H···Ca agostic interactions are best estimated by measuring the Si–N–Ca angles in the molecular solid-state structure, obtained here by X-ray diffraction. The values of 103.27(7) ° and 126.68(8) ° in \([10]_2\) clearly indicate that one Si–H bond is pointing towards the metallic centre. (Figure 4.13).\(^{52}\) Since the hydrogen atoms were actually located on the Fourier electronic density difference map, another indication of the strength of \(\beta\)-Si–H···Ca agostic interactions is revealed by Ca···H and Ca···Si narrow distances (2.72(2) and 3.148(6) Å, respectively). Yet, upon coordination, the Si–H bond appears to be unaltered, as the Si(1)–H(1S) and Si(2)–H(2S) have almost identical values (1.45 Å) and fall in the reported range for Si–H distances.

![Figure 4.13. Schematic representation of \(\beta\)-Si–H···Ca agostic interactions in \([\{RO^2\}CaN(SiMe2H)_2]_2\) (\([10]_2\))](image)

The \(^1\)H NMR spectrum of \([\{RO^2\}CaN(SiMe2H)_2]_2\) (\([10]_2\)) recorded in benzene-\(d_6\) at room temperature (Figure 4.14) is in agreement with the formulated structure. The resonances for the methyl groups from the N(SiMe2H)_2 moiety are located at \(\delta_H\) 0.47 ppm and, due to coupling with SiH protons \((^1J_{Si-H} = 2.5\) Hz), the signal is split into a doublet. Furthermore, the NCH2CH2 and CH2(CF3)_2 protons are diastereotopic and form two AB systems that cannot be resolved due to signal overlap. The SiH protons resonate at \(\delta_H\) 4.88 ppm and the presence of \(^{29}\)Si satellites can be easily observed \((^1J_{Si-H} = 160\) Hz). As described in Chapter 1, the \(^1J_{Si-H}\) coupling constant is a useful tool to detect the strength of \(\beta\)-Si–H···Ae agostic interactions in solution. Yet, even if there is a significant \(\beta\)-Si–H···Ca interaction and the other SiH group does not interact with the metal centre, NMR spectroscopy can only detect the average \(^1J_{Si-H}\) for the two moieties due to the dynamic exchange that occurs on the NMR timescale. Cooling a NMR sample of \([10]_2\) down to 193 K in toluene-\(d_6\) did not have any effect. Yet, there are cases where the presence of \(\beta\)-Si–H···Ca interactions can be detected by \(^1\)H NMR
spectroscopy. For instance, the $^1$H NMR spectrum of the THF-free trinuclear [Ca{N(SiMe$_2$H)$_2$}]$_3$ at 183 K indicates values for $^1J_{Si-H}$ coupling constants ranging from 122 Hz to 152 Hz.$^{57}$ Another trinuclear calcium complex that will be presented in Chapter 4 also depicts strong $\beta$-Si–H···Ca agostic interactions in solution and, at room temperature, the $^1J_{Si-H}$ values varied from 132 to 161 Hz.

The $^{19}$F NMR spectrum of [10]$_2$ at 298 K consists in a single singlet resonance at $\delta_{19F}$ −77.6 ppm indicating the equivalency of the CF$_3$ groups. This is consistent with the observations from $^1$H NMR spectroscopy.

![Figure 4.14. $^1$H NMR spectrum (400.16 MHz) of [[RO$_2$]CaN(SiMe$_2$H)$_2$]$_2$ ([10]$_2$) at 298 K in benzene-$d_6$.](image)

Also consistent with previous observations from NMR spectroscopy, the FTIR spectrum of [10]$_2$ recorded in nujol at room temperature (Figure 4.15) reveals an absorption band for the SiH stretching vibration at 2015 cm$^{-1}$. This further confirms the mild nature of $\beta$-Si–H···Ca agostic interactions as SiH moieties involved in agostic interactions are typically located between $\delta$ 2000 and 1900 cm$^{-1}$.

![Figure 4.15. FTIR spectrum (nujol) of [[RO$_2$]CaN(SiMe$_2$H)$_2$]$_2$ ([10]$_2$).](image)
\[ \{\text{RO}_2\} \text{CaN(SiMe}_3\text{)_2}\} \_2 (\text{[11]_2}) \] was recrystallised as a dimer from a concentrated pentane solution at \(-30^\circ\text{C}\). Perhaps the most intriguing aspect of this X-ray structure (Figure 4.16) is that the Ca atoms remain 7-coordinate, in the absence of donation from SiH moieties. In comparison with \([\text{10}]_2\), the loss of donation by agostic contact is now compensated by the presence of a second Ca-\(\cdot\cdot\cdot\text{F}\_\text{C}\) interaction per Ca ion.

**Figure 4.16.** (left) ORTEP representation of the molecular structure of \([\{\text{RO}_2\} \text{CaN(SiMe}_3\text{)_2}\} \_2 (\text{[11]_2})\). Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50\% probability level. (right) Schematic representation of [11]2. Selected bond lengths (Å) and angles (deg): Ca(1)-O(1) = 2.332(1), Ca(1)-O(11) = 2.343(1), Ca(1)-O(29) = 2.375(1), Ca(1)-N(1) = 2.332(1), Ca(1)-N(22) = 2.719(1), Ca(1)-F(20) = 2.920(1), Ca(1)-F(15) = 3.113(1); Si(1)-N(1)-Si(2) = 121.48(9), Si(1)-N(1)-Ca(1) = 112.46(7), Si(2)-N(1)-Ca(1) = 125.64(8), Ca(1)-O(11)-Ca(1) = 105.64(5).

The Ca-\(\cdot\cdot\cdot\text{F}\_\text{C}\) distances in [11]2 (2.920(1) and 3.112(1) Å) are in line with those measured in [10]2 and 4; on the other hand, they are much longer than those in \([\{\text{DippNacNac}_{(CF}_3\text{)_2}\} \text{CaN(SiMe}_3\text{)_2}\} (\text{THF})_2\) (2.47 and 2.49 Å) and the cationic \([\{\text{RO}_4\} \text{Ca}\}^{+}[\text{H}_2\text{N}\{(\text{B(C}_6\text{F}_5\text{)}_3\}^{-}\] (2.664(3) and 2.681(4) Å). As seen in [10]2, one of the two CH\_2\_CH\_OMe tethers is not coordinated to the metal centre. [11]2 has limited solubility in benzene-\(d_6\) and consequently full characterisation in solution was performed in the potentially coordinating THF-\(d_8\). The corresponding \(^1\text{H}\) NMR spectrum (Figure 4.17) features resonances for the N(Si(CH\_3\text{)})\_2\text{C}\_2\text{ moiety at } \delta_{\text{H}} 0.05 \text{ ppm and with the exception of a signal overlap between the CH\_2(CF}_3\text{)}_2\text{ and NCH\_2 protons, the remaining resonances can be easily identified. Even though this spectrum was recorded using crystalline material, traces of } [\{\text{RO}_2\} \text{Ca}] (5) \text{ are present in low amounts (~10\%). Repeated recrystallisation did not improve the outcome and, as combustion analysis confirmed the purity of the complex, it can be concluded that a ligand redistribution reaction occurs upon dissolution of [11]2 in this solvent.}^{19}\text{F}\) NMR spectroscopy is in agreement with this
observation and besides a main singlet resonance at $\delta_{19F} \approx -81.7$ ppm, the signal corresponding to the CF$_3$ groups diagnostic of $[\{RO\}^2\text{Ca}\] (5)$ was also detected, confirming that the purity of $[11]_2$ in THF was approximately 90% under these conditions.

Figure 4.17. $^1$H NMR spectrum (400.16 MHz) of $[\{RO\}^2\text{CaN(SiMe}_3\}_2]_2 ([11]_2)$ at 298 K in THF-$d_8$.

The heteroleptic calcium complex $[\{RO\}^1\text{CaN(SiMe}_2\text{H})_2]_2 ([12]_2)$ was recrystallised from a concentrated Et$_2$O solution and its solid-state structure is illustrated in Figure 4.18.

Figure 4.18. (left) ORTEP representation of the molecular structure of $[\{RO\}^1\text{CaN(SiMe}_2\text{H})_2]_2 ([12]_2)$. Hydrogen atoms (except SiH ones) are omitted for clarity. Ellipsoids drawn at the 50% probability level. (right) Schematic representation of $[12]_2$. Selected bond lengths (Å) and angles (°): Ca(1)–O(17) = 2.311(1), Ca(1)–O(17)$^\prime\prime$ = 2.318(1), Ca(1)–O(2) = 2.408(1), Ca(1)–N(20) = 2.300(1), Ca(1)–N(5) = 2.571(1), Ca(1)–F(12)$^\prime\prime$ = 3.004(1), Ca(1)–H(2) = 2.99(2); Si(2)–N(20)–Si(1) = 128.16(8), Si(2)–N(20)–Ca(1) = 110.83(6), Si(1)–N(20)–Ca(1) = 120.49(7), Ca(1)–O(17)–Ca(1)$^\prime\prime$ = 105.03(4). Torsion angle: H(2)–Si(2)–N(20)–Ca(1) = 2.0(8).
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The molecular arrangement is very similar to the one observed for [10]$_2$ featuring formally 7-coordinated Ca atoms. On the other hand, the Ca···F–C distances (3.005(1) Å) are somewhat longer than in [10]$_2$ (2.833(1) Å). Another distinct feature concerns the β-Si–H···Ca agostic interactions, as the difference between the two Ca–N–Si angle values (10 °) is much narrower than that in [10]$_2$ (23°). This indicates that the two N(SiMe$_2$H)$_2^-$ moieties have an almost equal contribution when it comes to electron donation to the calcium centres.

The $^1$H NMR spectrum confirms the identity of [12]$_2$ and, as in [10]$_2$, the $^1$J$_{Si-H}$ coupling constant is 160 Hz. The fact that two quadruplets ($^2$J$_{F-F}$ = 9.2 Hz) are detected in the $^{19}$F NMR spectrum at 298 K of [12]$_2$ indicates that the CF$_3$ groups are now inequivalent (Figure 4.19). This is most probably due to the fact that in {RO}$^1^-$ the nitrogen atom is chiral, causing the CF$_3$ group to become magnetically distinct.

![Figure 4.19. $^{19}$F($^1$H) NMR spectrum (376.53 MHz) of [([RO]$^1$)CaN(SiMe$_2$H)$_2$]$_2$ ([12]$_2$) at 298 K in benzene-$d_6$.](image)

The molecular structure of [13]$_2$ is different from the previous ones described above, as the Ca atoms from the dimeric arrangement are now inequivalent. Ca(1) is formally 6-coordinate in a distorted octahedral geometry and is supported by a single Ca···F–C contact (3.08 Å). On the other hand, Ca(2) is formally 7-coordinated and two Ca···F–C secondary interactions (2.71 and 3.05 Å) contribute towards the coordinative saturation of the metal centre.
Figure 4.20. (left) ORTEP representation of the molecular structure of [[RO]\textsuperscript{1}]CaN(SiMe\textsubscript{3})\textsubscript{2} ([13])\textsubscript{2}. Hydrogen atoms and non-interacting benzene molecules are omitted for clarity. Ellipsoids are drawn at the 50% probability level. (right) Schematic representation of ([13])\textsubscript{2}. Selected bond lengths (Å) and angles (deg): Ca(1)–O(2) = 2.305(5), Ca(1)–N(1) = 2.353(7), Ca(1)–O(1) = 2.371(5), Ca(1)–O(12) = 2.397(6), Ca(1)–N(15) = 2.615(7), Ca(1)–F(26) = 3.084(6), Ca(1)–Ca(2) = 3.760(2), Ca(2)–O(1) = 2.317(5), Ca(2)–O(2) = 2.403(5), Ca(2)–N(31) = 2.370(7), Ca(2)–O(42) = 2.475(6), Ca(2)–N(45) = 2.627(7), Ca(2)–F(51) = 2.712(5), Ca(2)–F(22) = 3.056(6); Si(4)–N(31)–Si(3) = 121.6(4), Si(1)–N(1)–Si(2) = 119.7(4).

3.3.2.3. Bond valence sum analysis

The benefits in using BVSA have been illustrated in estimating the nuclearity of the potassium salts [1]\textsubscript{2}–[3]\textsubscript{4}. In the present section, only the factors for [[RO]\textsuperscript{2}]CaN(SiMe\textsubscript{3})\textsubscript{2} ([11])\textsubscript{2} will be displayed as an illustrative example (Table 4.3), whereas data for the remaining complexes can be found in Annexure D.

The data in Table 4.3 indicate that for [11]\textsubscript{2}, Ca···F–C interactions contribute ca. 4.5% to the overall coordination sphere of the Ca centres. A similar contribution of Ca···F–C interactions was calculated for [13]\textsubscript{2} (4.5%).

Table 4.3. Bond valence analysis calculations for [[RO]\textsuperscript{2}]CaN(SiMe\textsubscript{3})\textsubscript{2} ([11])\textsubscript{2}

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</table>

Contribution 54.5% 4.5% 41%

[a] Data from the X-ray structure of [11]\textsubscript{2}. [b] Calculated using Equation 1. R\textsubscript{Ca–O} = 1.967 Å, R\textsubscript{Ca–F} = 1.842 Å, R\textsubscript{Ca–N} = 2.14 Å; B = 0.37.
On the other hand, lower contributions were obtained for complexes \([10]_2\) (3.5%) and \([12]_2\) (2%) containing N(SiMe\(_2\)H)\(_2\) amides (see Annexure D for details). This most probably is the result of the fact that, in these cases, \(\beta\)-Si–H···Ca interactions have a direct contribution in saturating the coordination sphere of the Ca atoms, thereby reducing the need for Ca···F–C contacts. Although these figures are merely indicative, they provide evidence that Ae⁻ F–C interactions have a beneficial effect in the stabilisation of heteroleptic calcium complexes. The positive effect of these interactions will be further investigated in Chapter 4 for the synthesis of Ae heteroleptic complexes supported by neutral \(\pi\) donors.

### 3.3.2.4. Nuclearity in solution

The nuclearity in solution of the calcium complexes \([10]_2–[13]_2\) was determined by NMR diffusion-ordered spectroscopy (DOSY), using the method described for potassium complexes \([1]_2–[3]_4\) (see 3.2.5.). By comparing the values of hydrodynamic radii obtained in solution \(r_{\text{HPGSE}}\) with those obtained in the solid state \(r_{\text{HX-ray}}\) collated in Table 4.4, it can be concluded that these complexes retain their dimeric shape in solution. This information is of high value, since the knowledge of their nuclearity in solution could constitute an important preliminary step to the understanding of the mechanisms of heterofunctionalisation reactions promoted by these complexes.

**Table 4.4.** PGSE NMR measurements and X-ray crystallographic data for complexes \([10]_2–[13]_2\).\(^a\)

| Complex | \(D_i\) \((10^{-9} \text{ m}^2 \text{ s}^{-1})\) | \(r_{\text{HPGSE}}\) \([\text{Å}]\) | X-ray \(|a| \text{ Å} \quad b \text{ Å}\) | \(r_{\text{HX-ray}}\) \([\text{Å}]\) |
|---|---|---|---|---|
| \([\text{RO}_2\text{H}]\text{CaN(SiMe}_2\text{H)}_2\] \([10]_2\) | 0.65 | 6.14 | 7.6 | 4.78 | 6.39 |
| \([\text{RO}_2\text{H}]\text{CaN(SiMe}_3\text{)}_2\] \([11]_2\) | 1.33 | 5.25 | 6.93 | 4.48 | 5.89 |
| \([\text{RO}_1\text{H}]\text{CaN(SiMe}_2\text{H)}_2\] \([12]_2\) | 1.49 | 4.75 | 5.56 | 4.68 | 5.16 |
| \([\text{RO}_1\text{H}]\text{CaN(SiMe}_3\text{)}_2\] \([13]_2\) | 1.13 | 6.01 | 6.95 | 4.87 | 6.17 |

\[a\] All NMR spectra were recorded in benzene-\(d_6\) at 298 K using 13.0–30.0 mM solutions of complex and of the external reference Si(SiMe\(_3\))\(_4\). \[b\] Average of the values of \(D_i\) found for 3 or more separate peaks in the \(^1\text{H}\) PGSE NMR spectrum of the complex.

### 3.3.2.5. Short summary

This section presented the synthesis and characterisation of several calcium heteroleptic complexes using fluorinated aminoetheralkoxo ligands. Unexpectedly, only the proteo-ligands with the lowest denticity (\(\{\text{RO}_1\}\)H and \(\{\text{RO}_2\}\)H) yielded stable complexes. Attempts to use \(\{\text{RO}_3\}\)\(\) or \(\{\text{RO}_4\}\) were unsuccessful and lead to the formation of unidentified species or to crown-ether cleavage. The molecular structure of complexes \([10]_2–[13]_2\) was determined by X-ray diffractometry and the most relevant bond lengths and angle values are summarised in Table 4.5.
Table 4.5. Summary of metric data for heteroleptic calcium complexes [10]_2–[13]_2.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ca atom</th>
<th>Ca···F [Å]</th>
<th>Ca···Si [Å]</th>
<th>Ca···H–Si [Å]</th>
<th>Ca–N–Si [°]</th>
<th>N–Si–N [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[10]_2</td>
<td>Ca(1) = Ca(1)*</td>
<td>2.83</td>
<td>3.15</td>
<td>2.72</td>
<td>103.3</td>
<td>130.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.58</td>
<td>3.55</td>
<td></td>
<td>126.7</td>
<td></td>
</tr>
<tr>
<td>[11]_2</td>
<td>Ca(1) = Ca(1)*</td>
<td>2.92</td>
<td>3.37</td>
<td>–</td>
<td>112.5</td>
<td>121.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.11</td>
<td>3.60</td>
<td></td>
<td>125.6</td>
<td></td>
</tr>
<tr>
<td>[12]_2</td>
<td>Ca(1) = Ca(1)*</td>
<td>3.00</td>
<td>3.29</td>
<td>2.99</td>
<td>110.8</td>
<td>128.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.47</td>
<td>3.39</td>
<td></td>
<td>120.5</td>
<td></td>
</tr>
<tr>
<td>[13]_2</td>
<td>Ca(1)</td>
<td>3.08</td>
<td>3.42</td>
<td>–</td>
<td>114.4</td>
<td>119.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.62</td>
<td></td>
<td></td>
<td>125.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ca(2)</td>
<td>2.71</td>
<td>3.35</td>
<td>–</td>
<td>109.9</td>
<td>121.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.06</td>
<td>3.65</td>
<td></td>
<td>128.0</td>
<td></td>
</tr>
</tbody>
</table>

X-ray data indicated that for complexes [10]_2 and [12]_2 where the {RO_2}^- ligand was used, only one of the two methoxy donors is coordinated to the metal centre. The coordination sphere of the calcium atoms is however filled by multiple Ca···F–C and Ca···H–Si interactions. The molecular structures of complexes [11]_2 and [13]_2 demonstrate that the calcium atoms are already coordinatively saturated in the presence of a single OMe from the ligand side-arm. Furthermore, they indicate that the loss of electron density provided by SiH moieties can be compensated by an additional Ca···F–C contact.

The contribution of Ae···F–C interactions was estimated by using BVSA analysis with values ranging from 2% ([12]_2) to 4.5% ([13]_2). On the basis of X-ray and BVSA data, one can conclude that the complexes featuring Ca···H–Si agostic interactions, [10]_2 and [12]_2, receive less electronic density from CF_3 groups than [11]_2 and [13]_2. The Ca···H–Si agostic interactions can only be observed unambiguously by X-ray crystallography, whereas spectroscopic methods (NMR and FTIR) suggest that these interactions are weak (vide infra). By performing NMR DOSY experiments, it was concluded that complexes [10]_2–[13]_2 remain dimeric in solution in aromatic solvents.

As a perspective, fluoroalkoxo ligands with a single O_ether heteroatom are also suitable for the synthesis of heteroleptic complexes of the heavier Ae elements, such as strontium. This was illustrated by the reaction of {RO_1}H with Sr[N(SiMe_2H)_2]_2(THF)_2/3 to yield [{RO_1}SrN(SiMe_2H)_2]_2 ([14]_2) as an analytically pure solid. Furthermore, we next looked on using weaker donors than OMe groups (i.e. alkenes, alkynes) to stabilise Ae heteroleptic complexes. These experiments will be presented in Chapter 4.
Chapter 3: Alkaline-Earth Fluorinated Aminoetheralkoxides

3.4. Well-defined cationic Ae (Ae = Ca, Sr, Ba) complexes

3.4.1. Introduction

Cationic complexes of early transition and rare-earth elements are potent precatalysts in olefin polymerisation reactions. Their high activity in this transformation is most of the time linked to the high electrophilicity of the metal centre. Increasing the electrophilicity of the metal centre was also valuable in the case of zinc complexes for intramolecular hydroamination of aminoolkenes. In this case the catalytic activity of the charged neutral \( [\{\text{Pr}_2\text{ATI}\}\text{ZnMe}] \) (ATI = \( N,N'\)-disubstituted aminotroponiminate) was improved via cationisation of the neutral complex by addition of \( [\text{PhNMe}_2\text{H}][\text{B(C}_6\text{F}_5\text{)}_4\text{]} \). Furthermore isolated zinc cations such as \( [\text{Zn}_2\text{Cp}^*\text{]}^+\cdot[\text{B(C}_6\text{F}_5\text{)}_4\text{]}^- \) also catalyse efficiently this organic transformation. This strategy remains valid also in the case of Ae elements, where cationic systems employing these elements and paired with weakly coordinating anions (WCA) are extremely active in ROP of lactides. As the name implies, WCAs are “spectator” anions that have no or very weak interactions with the paired cation. In order to be weakly coordinating, an anion displays very low nucleophilicity and basicity and its negative charge is delocalised over a large surface in order to prevent potential electrophilic attacks. Several reported anions that fit in this category include: \( [\text{B(C}_6\text{F}_5\text{)}_3\text{]}^-, [\text{MeB(C}_6\text{F}_5\text{)}_3\text{]}^-, \) or \( [\text{B (3,5-(CF}_{3\text{)}_2\text{C}_6\text{H}_{4})}_4\text{]}^- \).

Alkaline-earth cationic complexes are characterised by extreme oxophilicity and electrophilicity and for this reason they are very difficult to synthesise. Mountford et al. have shown that a bulky tridentate tris(pyrazolyl)methanide ligand can stabilise Ca cations with additional donation from two coordinated THF molecules (Figure 4.21–a). Similarly, results in our group showed that other bulky ligands such as the bidentate \( \{\text{DippNacNac}\}^- \) can be used in this field, but the resulting Ae cations were stable only in the presence of pyridine donors (Figure 4.21–b). In this case, the two nitrogen donors and the large size of the ligand were not sufficient to stabilise such electrophilic metallic centres. Crown-ethers have also proved suitable co-ligands and Westerhausen et al. have described the isolation of \( [\{15\text{-crown}-5\}\text{CaCp}]^+\cdot[\text{THF}\text{CaCp}_3\text{]}^- \) (Figure 4.21–c). Itoh et al. have reported on the use of multidentate aminophenolato ligands to stabilise well-defined Ae cations, but due to their severe oxophilicity, the resulting complexes were isolated as \( \text{H}_2\text{O} \) or \( \text{MeOH} \) adducts (Figure 4.21–d). In contrast to Itoh’s findings, Sarazin and Carpentier showed that such Ae cations can be obtained free of any solvents if the WCA \( [\text{H}_2\text{N}\{\text{B(C}_6\text{F}_5\text{)}_3\}_2\}^- \) is employed (Figure 4.21–e).
Further progress showed that employing $[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ as a WCA, such cationic complexes can be isolated free of coordinated solvents. The choice of this aminoborane as a counter-ion became evident as it has better crystallisation properties (attributed to the presence of a dipole moment) than the ubiquitous $[\text{B}(\text{C}_6\text{F}_5)_4]$ and is very robust due to internal N–H···F interactions (Figure 4.22). In addition, the negative charge is delocalised over a very large volume (ca. 538 Å).

Figure 4.21. Reported well-defined calcium cations.

Figure 4.22. ORTEP (left) and schematic (right) representation of the $[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ anion.
Our group previously reported the molecular structure of a well-defined calcium cationic complex supported by a multidentate fluorinated alkoxide \( i.e \) \([\{\text{RO}^+\}\text{Ca}_{2}]^{2+} \cdot 2[\H_2\N\{\B(C_6\F_3)_3\}]^{-} \) (Figure 4.23). In this calcium complex, it was determined that besides coordination of the heteroatoms present in the crown-ether side-arm, the metal centre was further stabilised by an intramolecular Ca···F–C contact.

![Figure 4.23. Schematic representation of \([\{\text{RO}^+\}\text{Ca}_{2}]^{2+} \cdot 2[\H_2\N\{\B(C_6\F_3)_3\}]^{-} \) ](image)

It seemed to us that more electron-deficient metal complexes can be obtained by removing some of the heteroatoms from the ancillary ligand, that is, by using potential pentadentate (\([\{\text{RO}^3\}\] \)), tetradentate (\([\{\text{RO}^2\}\] \)) or even tridentate (\([\{\text{RO}^1\}\] \)) fluoroalkoxides. The present section describes the synthesis of well-defined Ae cations supported by low denticity fluoroalkoxides as ancillary ligands (3-5) and paired with the weakly coordinating anion \([\H_2\N\{\B(C_6\F_3)_3\}]^{-} \).

### 3.4.2. Synthesis

The synthesis of alkaline-earth cations can be carried out following two methods: \(^{12,67,68}\)

a) from double-protonated proteo-ligands; this synthetic pathway involves first the synthesis of double protonated ligands \([\{\text{RO}^+\}\H]^+ \cdot 2[\H_2\N\{\B(C_6\F_3)_3\}]^{-} \) and their subsequent reaction with \( \Ae[N(\SiMe_3)_2]_2 \) (\( \Ae = \Ca, \Sr, \Ba \)) (Scheme 4.10–Method A)

b) via protonolysis of \([\{\text{RO}^+\}\CaN(\SiMe_3\R)_2]_2 \) (\([1\text{O}]_2-[1\text{3}]_2 \)) neutral heteroleptic complexes; (described in 3.3.1.) upon reaction with \([\H(\OEi_2)_2]^+ \cdot 2[\H_2\N\{\B(C_6\F_3)_3\}]^{-} \) (Scheme 4.10–Method B).

![Scheme 4.10. Reaction pathways to synthesise well-defined Ae cations.](image)
Reaction of the proteo-ligands \({RO^x}H\) \((x = 1, 2, 3)\) with \([H(\text{OEt}_2)_2]^+\cdot[H_2N\{B(C_6\text{F}_5)_3\}]^-\) in \(\text{Et}_2\text{O}\) affords the double protonated acids \([(RO^x)HH]^+\cdot[H_2N\{B(C_6\text{F}_5)_3\}]^-\) \((x = 3 (15), 2 (16), 1 (17))\) in high yields according to Scheme 4.11. They are isolated as colourless solids after repeated precipitations from dichloromethane solutions upon addition of pentane.

**Scheme 4.11.** Synthesis of well-defined Ae (Ae = Ca, Sr) cations from doubly protonated proteo-ligands.

Well-defined alkaline-earth cations \([(RO^x)\text{Ae}]^+\cdot[H_2N\{B(C_6\text{F}_5)_3\}]^-\) \((\text{Ae} = \text{Ca}, x = 3 (18), 2 (19), 1 (21); \text{Ae} = \text{Sr}, x = 2 (20); \text{Ae} = \text{Ba}, x = 2 (22))\) are then isolable in moderate isolated yields (60–80%) by stoichiometric reactions of \([(RO^x)HH]^+\cdot[H_2N\{B(C_6\text{F}_5)_3\}]^-\) \((x = 1, 2, 3)\) with \(\text{Ae}[\text{N(SiMe}_3)\text{]_2\text{}}\)} using \(\text{C}_6\text{H}_5\text{Cl}\)} as a solvent (Scheme 4.11).

\(\text{††† THF-solvated precursors were avoided for these reactions due to possible coordination between the metal centre and solvent molecule.}\)
Alternatively, 19 and 21 can also be synthesised in moderate yields (70–80%) by using the parent heteroleptic complexes 10 and 13 as starting materials in the reaction with [H(OEt₂)₂]⁺·[H₂N·[B(C₆F₅)₃]₂]⁻ according to Scheme 4.12. The same issues regarding the removal of traces of diethyl ether were met; nevertheless, prolonged drying in vacuo at 40 °C did result in the isolation of pure colourless solids.

Complexes 18–20 are completely insoluble in hydrocarbons (pentane, benzene and toluene) and display very limited solubility in diethyl ether. On the other hand, they are soluble in THF. The Ae cations supported by the {RO¹⁻} ligand (Ae = Ca (21), Ba (22)) are soluble in dichloromethane. The alkaline-earth cations 18–22 were characterised by multinuclear NMR spectroscopy (¹H, ¹⁹F, ¹¹B, ¹³C) and the molecular structures (except for 21) of their H₂O adducts were determined by single crystal X-ray diffractometry.


Overall, the two different synthetic methods A and B afford the Ae cations in 18–22 in comparable yields (60–80%). Yet, Method A can be considered more advantageous as it avoids the synthesis of parent neutral heteroleptic complexes. The Ae cations in 18, 20, and 22 could only be obtained using Method A as the neutral [[{RO¹}CaN(SiMe₃)₂]₂, [{RO²}AeN(SiMe₃)₂]₂, and [{RO¹}BaN(SiMe₃)₂]₂ were not available. On the other hand, results from our laboratory show that only Method B could be

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¹¹¹ These reactions were performed initially in Et₂O, but the isolation of pure samples was hampered by removal of residual Et₂O which proved impractical, if not impossible.
used to synthesise the desired cations since the reaction of the double protonated proteo-ligands with metal amides was not always successful.

3.4.3. Characterisation in the solid state

The calcium cation \([\{RO\}_3Ca\}_2^+ \cdot 2[H_2N\{B(C_6F_5)_3\}_2]^- \cdot (H_2O)_2\) was recrystallised as the water adduct \([18 \cdot H_2O]_2\) from a concentrated solution in thoroughly dried dichloromethane (Figure 4.24). The undesired coordinated H_2O molecule probably is the expression of the extreme electron-deficiency and oxophilicity of the cationic calcium, even though the crystallisation process took place under the inert atmosphere of a glovebox and/or using passivated glassware.

Figure 4.24. (left) ORTEP representation of the dication \([\{RO\}_3Ca\}_2^+ \cdot 2[H_2N\{B(C_6F_5)_3\}_2]^- \cdot (H_2O)_2\) \(([18 \cdot H_2O]_2)\). Counter-ions, hydrogen atoms and non-coordinating solvent molecules omitted for clarity. O(31) and O(81) are encircled and represent the O atoms of coordinated water molecules. (right) Schematic representation of \([18 \cdot H_2O]_2\). Selected bond lengths (Å): Ca(1)–O(2) = 2.318(4), Ca(1)–O(1) = 2.405(4), Ca(1)–O(10) = 2.463(4), Ca(2)–O(4) = 2.471(4), Ca(1)–O(7) = 2.530(4), Ca(1)–N(1) = 2.687(5), Ca(1)–F(21) = 2.650(3), Ca(2)–O(1) = 2.302(4), Ca(2)–O(2) = 2.381(4), Ca(2)–O(81) = 2.421(4), Ca(2)–O(54) = 2.437(4), Ca(2)–O(60) = 2.474(4), Ca(2)–O(57) = 2.496(4), Ca(2)–N(51) = 2.682(4), Ca(2)–F(67) = 2.651(3). Ca(1)–O(2)–Ca(2) = 100.2(1), Ca(1)–O(1)–Ca(2) = 100.7(1).

Despite coordination of H_2O molecules, the structural features of this molecular structure are interesting and the following observations can be made: (a) both calcium atoms are formally 8-coordinate in a distorted bicapped octahedral geometry and (b) coordination saturation is achieved

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For instance, the reaction between the double protonated acid \([\{LO\}HH]^+ [A]^- \ ((LO)^- = \text{multidentate phenolato ligand}) \) and Sn[N(SiMe_3)_2]_2 did not give the expected \([\{LO\}Sn]^+ [A]^- \). The tin cation could be obtained, however, by reacting \([\{LO\}SnN(SiMe_3)_2]\) with \([H(OEt)_2]_2[H_2N\{B(C_6F_5)_3\}_2]\). Carpentier, J.-F.; Sarazin, Y, et al. unpublished results.
through one strong Ca···F–C contact (2.650(3) and 2.651(3) Å) from CF₃ groups carried by the opposite metal. The strength of these metal···fluoride interactions is similar to those reported in [{RO₃}⁺][H₂N{B(C₆F₅)₃}₂]⁻ (2.664(3) and 2.681(4) Å)¹² and superior to those found in the calcium neutral complexes 4, [10]₂·[13]₂ (avg. Ca···F–C ~ 2.9 Å). The increase in the strength of Ca···F–C interactions in the case of the cationic [18·H₂O]₂ compared to the neutral complexes is an indication that the metal centres are much more electron-deficient.

Similar difficulties were encountered in our attempts to obtain the molecular structure of [{RO₂}⁺][H₂N{B(C₆F₅)₃}₂]⁻·(H₂O)₂ (Figure 4.25). The crystallisation process was again plagued by traces of moisture leading to the formation of the water adduct [19·H₂O]₂ (Figure 4.25). Furthermore, the quality of the final refinement of the structure was somewhat limited (R₁ = 9.52%) and for this reason, the main discussion will be concentrated on connectivity features, without entering a detailed analysis of the metric parameters.

**Figure 4.25.** (left) ORTEP representation of one of the two non-equivalent dimeric cations in the asymmetric unit of [{RO₂}⁺][H₂N{B(C₆F₅)₃}₂]⁻·(H₂O)₂ ([19·H₂O]₂). Counter-ions, hydrogen atoms and non-coordinating solvent molecules omitted for clarity. O(91) and O(92) are encircled and correspond to the O atoms of coordinated water molecules. Ellipsoids are drawn at the 50% probability level. (right) Schematic representation of [19·H₂O]₂.

As in [18·H₂O]₂, the calcium atoms in the centrosymmetric [19·H₂O]₂ are formally 8-coordinate. Using a fluoroalkoxo ligand in a lower denticity (⟨RO⟩⁻ is potentially pentadentate while ⟨RO⟩⁻ is potentially tetradentate) affects the coordination pattern and an extra Ca···F–C contact (~ 3.0 Å) is hence needed to coordinatively saturate the metal centre. Comparing the molecular structure of [19·H₂O]₂ and those for the neutral heteroleptic complexes [10]₂ and [11]₂, it can be seen that in the case of the cationic complex, both OMe groups are now coordinated to the metal centre whereas a single OMe group was coordinated in [10]₂ and [11]₂. This experimental observation evidences the need of electrons for the calcium atoms in [19·H₂O]₂, denoting their high electrophilicity.
The molecular structure of \([\text{RO}_2^2\text{Sr}]_2^{+} \cdot 2\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2^- \cdot (\text{H}_2\text{O})_2 \cdot [\text{20-H}_2\text{O}]_2\) (Figure 4.26) confirms the formation of the cationic Sr complex, but once more the Sr cations achieve coordination saturation by trapping water molecules (O(11) and O(11)#1 in Figure 4.26). One truly remarkable feature of this molecular solid-state structure is the presence of short contacts between the metal centres and the fluorine atoms from the weakly coordinating anion \([\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2^- \cdot (\text{H}_2\text{O})_2\) (Sr···F_anion = 2.71 Å). This behaviour is extremely unusual; the only other example where this otherwise virtually non-coordinating WCA was found to coordinate to a metal was in \([\text{Tl}(\text{FeCp}_2)\]^{+} \cdot [\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2^- \cdot (\text{H}_2\text{O})_2\).  

Figure 4.26. (top) ORTEP plot and schematic representation of the dication in \([\text{RO}_2^2\text{Sr}]_2^{+} \cdot 2\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2^- \cdot (\text{H}_2\text{O})_2 \cdot [\text{20-H}_2\text{O}]_2\). Counter-ions, hydrogen atoms and non-coordinating solvent molecules omitted for clarity. O(11) and O(11)#1 are encircled and represent the O atoms of coordinated water molecules. Ellipsoids are drawn at the 50% probability level. (bottom) ORTEP representation of \([\text{20-H}_2\text{O}]_2\) depicting the interactions between the strontium atoms and the anions. Selected bond lengths (Å): Sr(1)–O(21) = 2.446 (1), Sr(1)–O(21)#1 = 2.464(1), Sr(1)–O(1) = 2.583(1), Sr(1)–O(11) = 2.595(1), Sr(1)–O(8) = 2.653(1), Sr(1)–N(5) = 2.686(1), Sr(1)–F(233) = 2.713(1), Sr(1)–F(27) = 2.946(1), Sr(1)–F(33) = 2.999(1); Sr(1)–O(21)–Sr(1) = 108.17(5). 

The molecular structure of \([\text{20-H}_2\text{O}]_2\) also features electron density donation from the CF_3 groups onto Sr (avg. Sr···C–F = 2.97 Å). These distances are longer than the Sr···F_anion ones (2.71 Å) and those reported for \([\text{RO}_2^2\text{Sr}]_2^{+} \cdot 2\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2^- \) (2.74 and 2.86 Å).  

Note, however, that in this
latter complex, there is only one Ae···F–C interaction per Sr atom owing to the presence of 4 O atoms in the tethered macrocycle. Other examples where Sr···F–C interactions are present include \([\{\text{HC(pz)}_3\}_2\text{Sr}\}^{2+}\cdot[\text{BF}_4]^{-}\) and \([\text{THF}]_6\text{Sr}_2[\text{N(H)}_2\text{C}_2\text{H}_5)_3\text{I}]\cdot\text{THF}\).\(^{75}\) Coordination of a WCA to an Ae centre has been reported before by Sadow in \([\{\text{HM}e_2\text{Si})_3\text{C}\}\text{Ca(THF)}_2]^+\cdot[\text{HB(C}_6\text{F}_5)_3\text{I}]^{-}\) where the Ca···F anion distances range from 2.41 to 2.44 Å.\(^{76}\)

Ae···F anion interactions were also observed in the molecular structure of the barium compound \([\{\text{RO}^1\}\text{Ba}_2]^\cdot2[\text{H}_2\text{N}\{\text{B(C}_6\text{F}_5)_3\}^2\cdot(\text{H}_2\text{O})_2\cdot(\text{22·H}_2\text{O})_2]\) illustrated in Figure 4.27. This is not surprising considering the fact that barium is larger than strontium\(^****\) and that the ligand with the lowest denticity (\({\text{RO}^1}\)\(^{-}\)) was used to prepare this compound.

**Figure 4.27.** (top) ORTEP plot and schematic representation of the dication in \([\{\text{RO}^1\}\text{Ba}_2]^\cdot2[\text{H}_2\text{N}\{\text{B(C}_6\text{F}_5)_3\}]^2\cdot(\text{H}_2\text{O})_2\cdot(\text{22·H}_2\text{O})_2\). Counter-ions, hydrogen atoms and non-coordinating solvent molecules omitted for clarity. O(21) and O(21)\(^#1\) are encircled and represent the O atoms of coordinated water molecules. Ellipsoids are drawn at the 50% probability level. (bottom) ORTEP plot of [22·H\(_2\)O]\(_2\) depicting the interactions between the Ba atoms and the anions. Selected bond lengths (Å): Ba(1)–O(13) = 2.6004(19), Ba(1)–O(13)\(^#1\) = 2.602(2), Ba(1)–O(2) = 2.680(2), Ba(1)–O(21) = 2.853(3), Ba(1)–N(5) = 2.959(2), Ba(1)–F(17) = 2.896(2), Ba(1)–F(112) = 2.917(8), Ba(1)–F(12) = 3.040(2), Ba(1)–F(111) = 3.207(1); Ba(1)–O(13)–Ba(1) = 110.15(7).

X-ray data for this Ba cation indicate that the barium centres are formally 9-coordinated in a distorted monocapped square antiprismatic geometry. One H\(_2\)O molecule is coordinated onto each

\(^{****}\) The ionic radii for Sr\(^{2+}\) and Ba\(^{2+}\) in a 9-coordinate environment are 1.31 and 1.47 Å, respectively according to Shannon, R. D. *Acta Cryst* 1976, A32, 751.
barium atom, further evidencing the high electrophilicity and oxophilicity of this metal complex. In addition to the further donation from heteroatoms present in the ancillary ligand (O, N), the coordination sphere of the Ba centres is completed by several short Ba···F–C interactions from the CF$_3$ groups (2.896(2) and 3.040(2) Å) and two Ba···F$_{\text{anion}}$ contacts (2.917(8) and 3.207(1) Å) with the fluorinated anion. The Ba···F–C from contacts the cationic part are comparable in strength (as assessed from contact distances) with those reported for similar barium cations: [(RO$_4$)Ba]$_2^+$·2[H$_2$N{B(C$_6$F$_5$)$_3$}]$^-$ (2.918(2) Å),$^{77}$ [(RO$_5$)Ba]$_2^+$·2[H$_2$N{B(C$_6$F$_5$)$_3$}]$^-$·(EtOH) (avg. 2.97 Å).$^{12}$ They are also commensurate with distances described in charge-neutral compounds, e.g. in Ba$_2$[hfacac]$_4$(Et$_2$O)$_x$ (2.77–3.09 Å)$^{78}$ and [(THF)$_2$Ba{N(H)-2,6-F$_2$C$_6$H$_3$}]$_x$ (2.87–2.90 Å),$^{79}$ but they are shorter, and hence more intense, than those in the homoleptic [(RO$_3$)$_2$Ba ] (3.13–3.21 Å).$^{11}$ Regarding Ae···F$_{\text{anion}}$ interactions, it can be highlighted that, in general, the number of these interactions is directly dependant on the size of the metal centre (that is, its electropositivity, polarisability and overall need for electronic density) since in the present case it varies in the order: Ba (2 contacts) > Sr (1 contact) > Ca (0 contacts).

### 3.4.4. NMR spectroscopy

To assess the purity of alkaline-earth cations [18]$_2$–[22]$_2$, NMR samples were run in THF-$d_8$, as this was the only solvent in which all complexes were fully soluble. Alternatively, the (very) weakly coordinating dichloromethane-$d_2$ could also be employed, but the resulting spectroscopic data were of moderate quality due to the limited solubility of the Ae cations in this solvent. The $^1$H NMR spectra of [18]$_2$–[22]$_2$ are consistent with the proposed formulations and can be interpreted easily. For instance, the NMR spectrum of [19]$_2$ in THF-$d_8$ at room temperature (Figure 4.28) features the characteristic resonances for the methylene resonances (NCH$_2$CH$_2$, CH$_2$(CF$_3$)$_2$ and CH$_2$OCH$_3$) at $\delta_{\text{HH}}$ 2.90, 2.94 and 3.78 ppm. The signal for OCH$_3$ is located at $\delta_{\text{HH}}$ 3.49 ppm, while the NH$_2$ hydrogens in the anion are found as a broad singlet at $\delta_{\text{HH}}$ 5.74 ppm.
Figure 4.28. $^1$H NMR spectrum (400.13 MHz) of $\{[\text{RO}_2]_2\text{Ca}\}^\pm_2\cdot\text{2[H}_2\text{N[B(C}_6\text{F}_5)_3]}_2^\pm$ ([19]$_2$) at 298 K in THF-$d_8$.

Despite the fact that the molecular structure of [19]$_2$ shows coordination of a H$_2$O molecule to calcium, no traces of water could be detected in the corresponding $^1$H NMR spectrum, suggesting that moisture contamination occurs during the recrystallisation process.

More information concerning the structure of these complexes in solution could be accessed from $^{19}$F NMR spectroscopy. The resonances for the C$_6$F$_5$ groups in the anion are located at $\delta_{19F} -133.1$ (o-C$_6$F$_5$), $-161.1$ (p-C$_6$F$_5$), and $-166.4$ (m-C$_6$F$_5$) ppm in all cases (including [H(OEt)$_2$]$_2\cdot\text{2[H}_2\text{N[B(C}_6\text{F}_5)_3]}_2^\pm$), confirming the identity, integrity and weakly-coordinating nature of the anion. These observations are also validated by $^{11}$B NMR spectroscopy; in all cases a peak around $\delta_{11B} -8.3$ ppm was identified.

The shape of the signals corresponding to the CF$_3$ groups from the same samples recorded both in THF-$d_8$ and dichloromethane-$d_2$ are informative. Taking the example of [19]$_2$, a sharp singlet was observed at $\delta_{19F} -79.7$ ppm when THF-$d_8$ was used. By contrast, when [19]$_2$ was dissolved in dichloromethane-$d_2$, the formation of a more convoluted pattern was observed (Figure 4.29). These observations suggest that Ca···F–C$_\text{ligand}$ interactions probably persist in dichloromethane-$d_2$ solutions and that the more complicated multiplet could arise from coupling between donating and non-donating fluorine atoms. This is in contrast with the solution behaviour of the Ca neutral heteroleptic complexes [10]$_2$–[13]$_2$ where no sign of Ca···F–C interactions could be detected in solution.

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Figure 4.29. $^{19}$F($^1$H) NMR spectra (376.53 MHz) of $[[\text{RO}_2\text{Ca}]_2]^+\cdot 2\text{H}_2\text{N}\{\text{B(C}_6\text{F}_5)_3\}_2]^-$ ([19]) at 298 K in THF-$d_8$ (top) and dichloromethane-$d_2$ (bottom).

3.4.5. Short summary

In this section, the synthesis and characterisation of several alkaline-earth cations supported by fluorinated aminoetheralkoxides with different denticities were presented. The data obtained from X-ray crystallography indicate the formation of the H$_2$O adducts of [18]$_2$-[22]$_2$, a clear indication of their extreme electrophilicity. The X-ray data indicate also that, in each example, all heteroatoms from the ancillary ligand are coordinated to the metal centre. In all cases, the coordination sphere is filled by Ae···F–C interactions. For the cations of the heavier strontium ([18]$_2$) and barium ([22]$_2$) elements, electron donation from the ancillary ligands was not sufficient to stabilise the metal centres. Consequently, the WCA [H$_2$N{B(C$_6$F$_5$)$_3$}]$_2^-$ contributes also to saturation of the coordination sphere of the Sr or Ba cations through the existence of short, extremely unusual Ae···F$_{\text{anion}}$ contacts.

Characterisation through spectroscopic methods corroborated with combustion analysis militates in favour of the purity of those cationic complexes. The chemical shifts for hydrogens and fluorine atoms in [H$_2$N{B(C$_6$F$_5$)$_3$}]$_2^-$ were found in all cases to be identical; this therefore rules out any possibility of lasting interaction between the cation and the anion in solution. On the other hand, the $^{19}$F NMR spectra recorded in dichloromethane-$d_2$ displayed a more complicated pattern for the CF$_3$ resonances. Even though it does not stand as a definitive proof, this unusual behaviour may be linked to the persistence of Ae···F–C$_{\text{ligand}}$ secondary interactions in solution.
3.5. Hydrophosphination catalysis

As presented in Chapter 1, very few calcium precatalysts have been tested in hydrophosphination reactions (Figure 4.30).80,81,82 A schematic representation of previous examples of calcium precatalysts in this organic transformation is illustrated in Figure 4.30 (see Chapter 1 for details).

![Figure 4.30. Known heteroleptic calcium precatalysts for the hydrophosphination of styrene with Ph3PH.](image)

This section presents the tests that were performed in order to determine the catalytic activity of the neutral heteroleptic [10]2, [12]2, [13]2, and the cationic [21]2; calcium complexes in the benchmark hydrophosphination of styrene with Ph3PH (Scheme 4.13). For these catalytic tests, [(RO)CaN(SiMe3)2]2 ([11]2) was not selected due to the fact that all attempts to isolate it free of homoleptic complexes were unsuccessful. All reactions proceeded with 100% regioselectivity, affording exclusively the anti-Markovnikov product.


Using conditions similar to those employed in the literature, all catalytic tests were performed at 60 °C directly in the NMR tube either using benzene-d6 as a solvent, or in neat conditions. Reactions catalysed by [10]2, [12]2 and [13]2 in benzene-d6 were relatively slow and full conversion could not be achieved even after 24 h by using 2 mol% precatalyst loadings (Table 4.6, Entries 1–3). On the other hand, running the reactions in neat conditions afforded improved activities and precatalysts [12]2 and...
could readily convert 100 equiv of styrene and Ph₂PH in 2 h (Table 4.6, Entry 6 and Entry 8) reaching high TOF values (45 h⁻¹). Due to its high activity and robustness under catalytic conditions, [[RO¹]CaN(SiMe₂H)₂]₂ ([12]₂) was selected for a more challenging test by employing 400 equiv. of the activated olefin and phosphine. Even under such conditions, ¹H NMR spectroscopy indicated a conversion of 26% after 2 h (TOF = 52 h⁻¹).


<table>
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<th>Entry</th>
<th>Precatalyst</th>
<th>[styrene]₀:[Ph₂PH]:[Ca]₀</th>
<th>t [h]</th>
<th>Conv. a (%)</th>
<th>TOF (h⁻¹)</th>
<th>Ref</th>
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<td>24</td>
<td>46</td>
<td>1.0</td>
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<tr>
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<td>1</td>
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<td>50</td>
<td>this work</td>
</tr>
<tr>
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<td>1</td>
<td>82</td>
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<td>24</td>
<td>55</td>
<td>1.3</td>
<td>this work</td>
</tr>
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</table>

[[a] Conversion determined by ¹H NMR spectroscopy [b] Reaction conditions: 10 µmol of precatalyst, 0.6 mL of benzene-d₆, T = 60 °C. [c] Neat reactions, T = 60 °C. [d] A = H₂N{B(C₆F₅)₃}₂. [e] T = 75 °C. [f] 10 µmol of catalyst, neat reactions, T = 60 °C. [g] T = 25 °C.]

As several reaction conditions were employed, comparison with the catalytic activity of other calcium complexes C, G–I (Figure 4.30) will be discussed in the simplest qualitative fashion. In this respect, [10]₂ (Table 4.6, Entry 1), [12]₂ (Table 4.6, Entry 2), [13]₂, (Table 4.6, Entry 3) display a
similar activity to Hill’s \(\{^{\text{Npp}}\text{NacNac}\}\text{CaN}({\text{SiMe}}_3)_2\)(THF) (C) (Table 4.6, Entry 11), but are outperformed by Cui’s \(\{[\text{N}^\text{N}^\text{N}]\text{CaN}({\text{SiMe}}_3)_2\](\text{THF})\) (I) (Table 4.6, Entry 14). Using similar reaction conditions, the activities of \([10]_2\), \([12]_2\) and \([13]_2\) (Table 4.6, Entries 1–3) were generally higher than those of the simple homoleptic complexes \(\text{Ca}[\text{N}({\text{SiMe}}_3)_2]_2(\text{THF})_n\) \((n = 0, 2)\) (Table 4.6, Entries 17 and 18). Recently, our laboratory described calcium complexes supported by iminoanilido ancillary ligands (\(\{[\text{N}^\text{N}]\text{CaN}({\text{SiMe}}_3)_2\](\text{THF})\) (G) and \(\{[\text{N}^\text{N}]\text{CaCH}({\text{SiMe}}_3)_2\](\text{THF})\) (H)) and their use in hydrophosphination catalysis in neat conditions. Based on the reported results (Table 4.6, Entries 12 and 13), the activity of \([10]_2\), \([12]_2\) and \([13]_2\) was generally lower compared to G and H.

Overall, the precatalysts bearing the \(\text{N}({\text{SiMe}}_2\text{H})_2^-\) group were slightly more active than those containing \(\text{N}({\text{SiMe}}_3)_2^-\); this is most probably due to the better kinetic stability and moisture resistance shown by the former complexes. In a recent contribution,\(^{82b}\) our group showed that H is more active than I due to the fact that the reaction between the metal complexes and \(\text{HPPH}_2\) is irreversible when a highly basic group (i.e. \(\text{CH}({\text{SiMe}}_3)_2^-\)) is employed obtaining the catalytic active species (\(\{[\text{N}^\text{N}]\text{Ca}(\text{PPH}_2)](\text{THF})\)). On these grounds alone, the calcium complexes incorporating the \(\text{N}({\text{SiMe}}_3)_2^-\) amide (\(pK_a\) (THF) 25.8 \(^{83}\)) were expected to be more active than those having the less basic \(\text{N}({\text{SiMe}}_2\text{H})_2^-\) amide (\(pK_a\) (THF) 22.6).\(^{83}\)

The activity of \(\{[\text{RO}]^1_2\text{Ca}^+\}_2[2\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3]\}_2^-\) ([21]2) was also tested in hydrophosphination catalysis, but the reaction was hampered by its low solubility in the styrene–\(\text{Ph}_2\text{PH}\) mixture; this was reflected by low turnover frequencies. (Table 4.6, Entry 10).

In order to propose a reaction mechanism for the hydrophosphination of styrene with \(\text{Ph}_2\text{PH}\), kinetic investigations are required. Even though such inquiries were not performed with \([10]_2\)–\([13]_2\), the following experiments might help postulating a mechanism for this organic transformation. In this respect, the kinetic rate law for this reaction would give an indication to assess the nature of the rate determining step (RDS). For instance, in the case of G, the rate law: \(R = k[\text{Ph}_2\text{PH}]^n[\text{styrene}]^m[\text{Ca}]^l\) suggested that the RDS of the reaction consisted of the insertion of the highly polarised double bond into the Ca–P bond. Comparison between reactions rates using \(\text{para}\)-substituted styrene derivatives with electron-withdrawing (\(\text{CF}_3\) or \(\text{Cl}\)) or electron-donating (Me, \(\text{tBu}, \text{OMe}\)) groups would be useful. Using electron-donating groups in the \(\text{para}\)-position tends to destabilise the growing negative charge on the \(\alpha\) benzylic carbon atom in the suggested transition state (Figure 4.31), while electron-withdrawing groups would have a stabilisation effect.\(^{82b}\)
Figure 4.31. Proposed transition state in a concerted-type mechanism for hydrophosphinination reactions promoted by \([\{LX]CaN(SiMe_3)_2\}](THF)\(^{32b}\)

3.6. Concluding remarks

This chapter introduced the use of fluorinated aminoetheralkoxo ligands for the synthesis of alkaline-earth heteroleptic complexes. It was showed that protonolysis reactions between the proteo-ligands \(\{RO^+\}H\ (x = 1, 2)\) and bulky metallic amides \(Ae[N(SiMe_2)R]_2\](THF)\(_n\) (Ae = Ca, Sr; R = Me, H; \(n = 0, 2/3, 1, 2\)) can afford the isolation of Ae heteroleptic complexes \([10]_2–[14]_2\) as analytically pure solids. Their molecular structure consists in all cases in a dimeric arrangement via bridging oxygen atoms, an arrangement which according to NMR diffusion experiments is also maintained in solution. Besides coordination from heteroatoms present in the ancillary ligands, X-ray data indicate that coordinative saturation is achieved through Ae···F–C and β-Si–H···Ae interactions. Perhaps more remarkable is that in cases where \(\{RO^+\}^–\) is employed as an ancillary ligand, one of the OMe groups is not coordinated, suggesting that multiple Ca···F–C interactions provide a better stabilisation than a single hard donor. Concerning Ca···F–C interactions, it was observed that they have a higher contribution towards the coordination sphere of the metal centre when the number of available heteroatoms from the ligand side-arm decreases. Ae···H–Si agostic interactions were observed through crystallography; nevertheless, the attempts to prove their existence using spectroscopic methods only gave mitigated success. Yet, complexes bearing the \(N(SiMe_2)H\)_2– moiety were found to be more kinetically stable than the ones bounded to a \(N(SiMe_3)_2\)– group.

As proof towards their extreme electrophilicity, \([\{RO^+\}Ae]_2^–2[H_2N\{B(C_6F_5)_3\}_2]–\ (x = 3, Ae = Ca ([18]_2); x = 2, Ae = Ca([19]_2), Sr ([20]_2); x = 1, Ae = Ba ([22]_2))\) could only be crystallised as H\(_2\)O adducts. Despite the presence of donors solvents, contribution of Ae···F–C\(_{ligand}\) interactions were observed in all cases, and the molecular structures of \([20]_2\) and \([22]_2\) also feature rare contacts between the weakly coordinating anion and the Ae cationic centre. Concerning Ae···F\(_{anion}\) interactions, it was observed that the tendency of the Ae metal to bind to the WCA varies with the size of the metal and ranges in the order: Ba > Sr > Ca. Nevertheless, new synthetic strategies must be devised in order to crystallise Ae cations \([18]_2–[20]_2\) and \([22]_2\) free of water contamination.
Our efforts in synthesising these metal complexes were rewarded when they were used as precatalysts in the hydrophosphination between styrene and Ph$_2$PH. Their TOF values are comparable with other similar calcium precatalysts and therefore range amongst the most active ones reported for this reaction. Kinetic experiments still need to be performed with [10]$_2$, [12]$_2$, and [13]$_2$ in order to be able to propose a detailed mechanistic scenario for these reactions.

In our pursuit to synthesise neutral Ae heteroleptic complexes, the potassium complexes [1]$_2$–[3]$_4$ were isolated and crystallised as tetramers (except [1]$_2$), forming cubane-like structures in the solid state. BVSA showed that, to a large extent, the alkali centres were actively supported by K···F interactions, which contributed to up to 17% of the total coordination sphere.

The synthesis and characterisation of alkaline-earth homoleptic complexes 4–[9]$_2$ was also reported. Since [(RO$_2$)$_2$Sr] and [(RO$_2$)$_2$Ba] can be used as CVD precursors, it makes sense to assume that 4–[9]$_2$ can be employed in the same field of application.

Based on our success in stabilising neutral heteroleptic and cationic alkaline-earth complexes with fluorinated aminoetheralkoxides, we concluded that Ae···F–C and Ae···H–Si interactions should be able to stabilise even more electron-deficient complexes, and Chapter 4 will describe the efforts paid in this aim.
3.7. References


63 Cushion, M. G.; Mountford, P. Chem. Commun. 2011, 47, 2276.


Chapter 4: Alkaline-Earth Heteroleptic Complexes
Supported by Aminoalkoxides with Olefin Pending Groups
Chapter 5: Alkaline-earth heteroleptic complexes supported by aminoalkoxides with olefin pending groups

4.1. Introduction

Metal-olefin complexes with late transition metals are abundant. In early transition metal chemistry, the coordination of an olefin onto the metal centre represents the first step in the homogeneous polymerisation of \( \alpha \)-olefins (e.g. ethylene, propylene, 1-hexene) and also in ubiquitous hydrogenation processes. Due to the absence of d–\( \pi^* \) back-donation, coordination of olefins onto d\(^0\) metals is difficult to achieve; computations suggest that the bonding between a d\(^0\) metal and an olefin is mostly based on electrostatic forces and van der Waals interactions. So far, only a handful of examples were observed for W, V, Zr, Ti, and Y by NMR spectroscopy and even fewer were characterised by X-ray diffractometry. The coordination of alkenes onto alkaline-earths is even less studied and, to date, literature data are restricted to Schumann’s tethered metallocene complexes \([\{C_5Me_4CH_2CH=CH_2\}_2Ae]\) (Ae = Ca, Sr and Ba; J–L in Scheme 5.1). P. Roesky et al. have also reported that a very similar barium-olefin complex can result from an intramolecular C–H activation when \([\text{Cp}^*\text{Ba}]\) is reacted in the melt with \([\text{Cp}^*\text{In}]\) (M in Figure 4.1). On the other hand, a number of Ae complexes with anionic \( \pi \) systems such as allyls (\([\{\eta^3-1,3-(\text{SiMe}_3)\text{C}_3\text{H}_3\}_2\text{Ca}\}(\text{THF})_2\), \([\{\eta^3-\text{C}_3\text{H}_5\}_2\text{Ca}\}(\text{triglyme-}\kappa^4)_2\)), indenyls (e.g. \([\text{Ind}_2\text{Ca}]\) (THF)_2) (N in Figure 4.1), cyclopentadienyls (e.g. \([\text{Cp}^*\text{Ca}]\), fluorenyls (e.g. bis(fluorenyl)barium-tetrakis(ammonia), O in Figure 4.1), have been structurally characterised.

Figure 5.1. Alkaline-earth complexes featuring interactions with \( \pi \) systems.
Ae-olefin complexes are relevant in catalysis and are intermediates in the catalytic cycle of the hydroelementation of alkenes (e.g. hydroamination, hydrophosphination), as illustrated in Figure 5.2.\textsuperscript{14,15} Furthermore, in the polymerisation of styrene promoted by heteroleptic benzyl calcium complexes (see 1.2.3.2), Harder \textit{et al.} surmised that the reaction mechanism involved coordination of the monomer to calcium in what was assumed to obey a coordination-insertion rather than an anionic mechanism.\textsuperscript{16}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{image}
\caption{Proposed calcium-olefin complexes as intermediates for intra- (left) and intermolecular (right) hydroamination reactions according to Tobisch.\textsuperscript{15}}
\end{figure}

In Chapter 3, it was seen that Ae···F–C and β-Si–H···Ae (Ae = Ca, Sr) secondary interactions play an important role towards the stabilisation of heteroleptic complexes of the type \([\{RO\}'\text{AeN(SiMe}_2\text{R}\}_2]_2 (x = 1, 2; R = H, Me).\textsuperscript{17}\) Moreover, it was shown that multiple Ca···F–C can be “more beneficial” (preferred) than the coordination of heteroatoms (i.e. O\textsubscript{ether} atoms) present in the ligand side-arms. Encouraged by these results, we envisaged that Ae heteroleptic complexes supported by fluorinated alkoxides could also be stable in the presence of weaker donors than OMe groups, such as vinylic moieties. The present chapter focuses on the synthesis and characterisation of Ae fluorinated alkoxo complexes that feature intramolecular M···alkene coordination.

\subsection*{4.2. Ligand design and synthetic strategy}

The proteo-ligands \([RO\}'\text{H} (x = 11, 12; Scheme 5.1) are related to the methoxy-containing \{RO\}'\text{H} and \{RO\}'\text{H}, except that the donating OMe moieties have now been replaced by vinylic groups. For synthetic reasons,\textsuperscript{*} \{RO\}'\text{H} was modelled bearing an \(^{1}\text{Pr} instead of Me group.

The commercially available allyl cyanide was reduced in the presence of LiAlH\textsubscript{4}/AlCl\textsubscript{3} (1:3) to yield the corresponding amine which was then used in a nucleophilic substitution reaction with 4-

\textsuperscript{*} The synthesis of \textit{N}-isopropylbut-3-en-1-amine was preferred in order to avoid the delicate use of methylamine which was necessary for the synthesis of \textit{N}-methylbut-3-en-1-amine.
bromo-1-butene using Et₃N as a base. N-isopropylbut-3-en-1-amine was isolated in quantitative yield after reacting 4-bromo-1-butene with a large excess of PrNH₂. Reaction of the freshly obtained primary amines with 2,2-bis(trifluoromethyl)oxirane afforded \{RO₁¹\}H and \{RO₁²\}H, respectively, in good yields (70–90%) according to Scheme 5.1. These newly synthesised proteo-ligands are colourless oils at room temperature and their identity was confirmed by spectroscopic methods and combustion elemental analyses. Their \(^1\)H NMR spectra in benzene-\(d_6\) are consistent with the proposed formulation and for each compound the vinylic moieties resonate as two multiplets around \(\delta_H 5.4\) (CH═CH₂) and 4.9 (CH═CH₂) ppm. \(^1\)F NMR spectroscopy indicates that the CF₃ groups are equivalent at room temperature, as singlet resonance were observed at \(\delta_{19F} –77.79\) and –77.10 ppm for \{RO₁¹\}H and \{RO₁²\}H, respectively.

![Scheme 5.1. Synthesis of proteo-ligands \{RO₁¹\}H and \{RO₁²\}H.](image)

In order to synthesise Ae heteroleptic complexes, our initial efforts focused on using Ca[N(SiMe₃)₂](THF)₂ or Ca[N(SiMe₃)₂] as precursors in protonolysis reactions with the corresponding olefin-tethered proteo-ligands. However, after work-up, only intractable oils could be isolated and all attempts to obtain crystalline materials from the reaction mixtures were unsuccessful.

A successful synthetic protocol consists in a dropwise addition of an Et₂O solution of \{RO₁¹\}H or \{RO₁²\}H to an excess of Ca[N(SiMe₂)₂](THF) (1.3 equiv) in Et₂O at –78°C, as depicted in Scheme 5.2. Following this protocol, the Ae-olefin complexes \([23]_{2}–[26]_{2}\) were isolated in moderate yields (40–70%). These complexes are extremely air- and moisture-sensitive; even freshly prepared NMR samples in benzene-\(d_6\) showed signs of hydrolysis within the first points of analysis.

\(^\dagger\) As the calcium methoxy complexes \([10]_{2}–[13]_{2}\) were inert towards redistribution reactions, the synthesis of homolectic complexes \([\{RO₁¹\}₂Ae]\) and \([\{RO₁²\}₂Ae]\) was averted.
Chapter 4: Alkaline-Earth Heteroleptic Complexes Supported by Aminoalkoxides with Olefin Pending Groups

4.3. Solid-state and solution characterisation

4.3.1. Alkaline-earth complexes with two olefin pending groups

Ae···C\_n secondary interactions are weak in nature, due to the fact that they lack dπ \rightarrow π^* back-donations. It is therefore expected that alkene coordination to Ae elements should not lead to a significant elongation of the C=C double bond, as observed in the case of other d^0 olefin complexes such as \([\text{Cp}_2\text{Zr(O(Me}_2\text{)CH}_2\text{CH}=(\text{CH}_2)_2]}^+\cdot[\text{MeB(C}_6\text{F}_5)_3]\)^\-. Ae···C\_n contacts are best detected using X-ray crystallography and, for this reason, our first efforts were directed in obtaining the solid-state molecular structures of [23]_2–[26]_2. Multinuclear NMR spectroscopy, FTIR spectroscopy and combustion C,H,N analysis were used to demonstrate the identity and purity of these complexes.
Single crystals from complex $[23]_2$ were obtained from a concentrated toluene solution at $-30$ °C. X-ray diffraction data revealed a dimeric arrangement with formally 8-coordinate calcium atoms in a distorted bicapped octahedral geometry (Figure 5.3). The presence of THF molecules was not observed, despite the fact that the THF-solvated Ca[N(SiMe$_2$H)$_2$]$_2$(THF) was employed as the starting material.

The most important aspect of this dimeric structure is that one alkene moiety from one ligand coordinates to Ca(1) with the $Si$ enantioface, whereas the other alkene binds to Ca(1)$^#$ with the $Re$ enantioface (this reflects the existence of an inversion centre in the dimeric molecule). This interaction is best regarded as an $\eta^2$ coordination with short contacts between vinylic carbon atoms and the metal centre (2.972(2) and 3.121(2) Å). These distances are similar to those in $[\{C_5Me_4CH_2CH_2CH=CH_2\}Ca]$ ($J$ in Figure 5.1) (2.941(2)–3.230(2) Å) reported by Schumann et al., albeit the coordination mode is different. In $[23]_2$, only one olefin moiety is coordinated and it displays a stronger contact of the internal carbon atom towards the calcium centre, that is, $d(Ca–C_{int}) < d(Ca–C_{ext})$; in Schumann’s example, both vinylic groups are coordinated to the metal centre in a

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Figure 5.3. (left) ORTEP representation of the molecular structure of $[\{RO^{12}\}CaN(SiMe_2H)_2]_2 ([23]_2)$ Hydrogen atoms (except $SiH$) are omitted for clarity. Ellipsoids are drawn at the 50% probability level. (right) Schematic representation of $[23]_2$. Selected bond lengths (Å) and angles (°): Ca(1)–O(11) = 2.302(1), Ca(1)–O(11)$^#$ = 2.31(1), Ca(1)–N(1) = 2.288(1), Ca(1)–N(22) = 2.597(1), Ca(1)–C(25) = 2.972(2), Ca(1)–C(26) = 3.121(2), Ca(1)–H(Si1) = 3.08(2), Ca(1)–H(Si2) = 3.33(3), Ca(1)–F(15) = 2.931(1), C(25)–C(26) = 1.327(3), C(29A)–C(30A) = 1.31(1); Ca(1)–N(1)–Si(1) = 119.6(1), Ca(1)–N(1)–Si(2) = 111.9(1), Ca(1)–O(11)–Ca(1)$^#$ = 103.9(6), Si(1)–N(1)–Si(2) = 127.4(1); Torsion angles: N(1)–Si(1)–H(Si2)–Ca(1) = 2.2(7), N(1)–Si(2)–H(Si1)–Ca(1) = 5.7(8).
dissymmetric fashion, with shorter Ca–C\text{ext} contacts ($d$(Ca–C\text{ext}) < $d$(Ca–C\text{int})). In [23]\textsubscript{2}, a hypothesis that may support the observed arrangement is that upon coordination, the C=C bond is polarised with a partial positive charge on C\text{ext} thus favouring a stronger Ca–C\text{int} binding. However, this would be in contrast with results from DFT for a similar calcium-olefin complex where a greater negative charge was determined for the C\text{ext} (−0.47 au) compared to C\text{int} (−0.28 au) (vide infra 4.5). The position of the alkene moiety towards Ca can also be described by the angle formed by Ca–C\text{olefin}(centroid) vector and that defining the vinyl alkene. A value of 73.1(1) ° was determined in the case of [23]\textsubscript{2}. The difference in C=C bond length between the coordinated and non-coordinated alkene moieties in [23]\textsubscript{2} is only marginal (coordinated C=C, 1.327(3); non-coordinated C=C, 1.31(1) Å), which suggests that the double bond remains essentially unaltered upon coordination.

The molecular structure of [23]\textsubscript{2} also shows that β-Si–H···Ca agostic interactions contribute towards the filling of the coordination sphere of the calcium centres. This was indicated by close Ca···H\textsuperscript{8} (3.08(2) and 3.33(3) Å) and Ca···Si (3.30(9) and 3.44(1) Å) contacts, when the N(1)–Si(1)–H(Si2)–Ca(1) and N(1)–Si(2)–H(Si1)–Ca(1) angles are both close to 0 ° (2.2(7) and 5.7(8) °). Furthermore, the difference of 7.7 ° between the two Ca–N–Si angles in [23]\textsubscript{2} (Ca–N–Si = 119.6(1) ° and 111.9(1) °) denotes the fact that the two β-Si–H···Ca agostic have a comparable intensity. This comes in contrast with the solid-state structure of [10]\textsubscript{2} (see 3.3.2) where the difference between the two interacting and non-interacting Ca–N–Si angles was significantly greater (23.6 °). The coordination sphere of the metal centre in [23]\textsubscript{2} is completed by one Ca···F–C interaction (2.931(1) Å). Overall, the coordination pattern around the calcium centres in [23]\textsubscript{2} is unique, and this complex represents the first example of a calcium compound where Ca···C\textpi, Ca···F–C, and β-Si–H···Ca secondary interactions are present and have a stabilising effect.

The $^1$H NMR spectrum of [{RO\textsubscript{12}}CaN(SiMe\textsubscript{2}H)\textsubscript{2}]\textsubscript{2} ([23]\textsubscript{2}) in benzene-$d_6$ at room temperature (Figure 5.4) shows the expected resonances and is consistent with the solid-state structure. Compared with the free ligand {RO\textsubscript{12}}H, the CH=CH\textsubscript{2} (H\textsubscript{int}) and CH=CH\textsubscript{2} (H\textsubscript{ext}) resonances are slightly shifted downfield (~ 0.3 ppm); those differences could highlight the interaction of the olefin with the metal centre. However, $^{13}$C{$^1$H} NMR spectroscopy depicts virtually identical chemical shifts for the vinylic moieties in [23]\textsubscript{2} compared to those found in the proteo-ligand, which does not support the previous hypothesis. Furthermore, the $^1$J\textsubscript{C,H} values (~154 Hz) taken from the $^{13}$C NMR spectrum of [23]\textsubscript{2} are identical to those in {RO\textsubscript{12}}H (154 Hz) and suggest a minimal change and no polarisation in the character of the C=C double bond. The $^{19}$F NMR spectrum of [23]\textsubscript{2} is similar to that of [10]\textsubscript{2} and features a sharp singlet at $\delta_{19F}$ = 76.69 ppm, indicating that all CF\textsubscript{3} groups are magnetically equivalent on the NMR timescale. Attempts to discern between the coordinating and non-coordinating vinylic

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\textsuperscript{8} The hydrogen atoms from the N(SiMe\textsubscript{2}H)\textsuperscript{2−} were located on the Fourier electronic density map.
groups in a toluene-$d_8$ solution did not produce any significant results and NMR spectroscopy indicates that the two vinylic moieties are magnetically equivalent on the NMR timescale, even at 193 K. These observations indicate that the Ca···olefin interaction is weak, or simply that the vinyl groups –the interacting one and the free one– do exchange very fast in solution.

Figure 5.4. $^1$H NMR spectrum (400.16 MHz) of [[RO]CaN(SiMe$_2$H)$_2$]$_2$ [23]$_2$ at 298 K in benzene-$d_6$.

The synthesis of [[RO]SrN(SiMe$_2$H)$_2$]$_2$ ([24]$_2$), the strontium analogue of [23]$_2$, was also carried out under identical reaction conditions (Et$_2$O, –78 °C) to those used for this calcium complex. The crude product is extremely soluble in hydrocarbons and, for this reason, all crystallisation and purification attempts were unsuccessful. The $^1$H NMR spectrum (Figure 5.5–top) of the crude product recorded in benzene-$d_6$ at room temperature indicates the existence of at least two sets of resonances, making the accurate assignment impossible.

Figure 5.5. $^1$H NMR spectra (400.13 MHz) of [[RO]SrN(SiMe$_2$H)$_2$]$_2$ [24]$_2$: (top) recorded in THF-$d_8$ at 298 K; (bottom) recorded in benzene-$d_6$ at 298 K.
The $^1$H NMR spectrum for $[24]_2$ recorded in THF-$d_8$ (Figure 5.5–bottom) is obviously simpler probably due to coordination of the solvent onto Ca and also depicts two sets of resonances. Furthermore, multiple resonances for the CF$_3$ groups were found in the $^{19}$F NMR spectra of the strontium complex both in THF-$d_8$ and benzene-$d_6$. From these experimental data, we could assess that the strontium complex $[24]_2$ was probably formed but no information could be gained concerning its purity and its structure.

4.3.2. Heteroleptic alkaline-earth complexes with one olefin group.

4.3.2.1. Characterisation of $\{[RO^{11}]CaN(SiMe_2H)_2\}_2 \{[25]_2\}$

X-ray data for $\{[RO^{12}]CaN(SiMe_2H)_2\}_2 \{[23]_2\}$ demonstrated that, apparently, electron density from a single olefin group is sufficient to stabilise the calcium atom. Hence, our reasoning was reconsidered accordingly. Subsequent experiments were performed using the proteo-ligand with a single alkene moiety, namely $[RO^{11}]H$.

Single crystals of $\{[RO^{11}]CaN(SiMe_2H)_2\}_2 \{[25]_2\}$ were obtained from a pentane solution at −30 °C. The molecular structure of $[25]_2$ (Figure 5.6) depicts a centrosymmetric arrangement around calcium, identical to that in $[23]_2$. This hardly comes as a surprise since the only difference between the two molecular structures is the replacement of the non-interacting CH$_2$CH$_2$CH=CH$_2$ in $[23]_2$ fragments with a simple $^1$Pr groups in $[25]_2$.

![Figure 5.6. (left) ORTEP representation of the molecular structure of $\{[RO^{11}]CaN(SiMe_2H)_2\}_2 \{[25]_2\}$. Hydrogen atoms (except SiH) are omitted for clarity. Ellipsoids are drawn at the 50% probability level. (right) Schematic representation of $[25]_2$. Selected bond lengths (Å) and angles (°): Ca(1)–O(1) = 2.309(2), Ca(1)–O(1)$^\#1$ = 2.309(2), Ca(1)–N(20) = 2.298(3), Ca(1)–N(12) = 2.658(3), Ca(1)–C(18) = 2.958(3), Ca(1)–C(19) = 3.102(3), Ca(1)–H(1) = 3.19(3), Ca(1)–H(2) = 3.12(3), Ca(1)–F(8) = 3.050(2), C(18)–C(19) = 1.305(4); Ca(1)–N(20)–Si(1) = 116.7(1), Ca(1)–N(20)–Si(2) = 128.1(1). Torsion angles: N(20)–Si(1)–H(1)–Ca(1) = 4.2(9), N(20)–Si(2)–H(2)–Ca(1) = 2.9(1).](image-url)
The distances between the carbon atoms in the alken moieties and the metallic centres (2.958(3) and 3.102(3) Å) in [25] match those found in [23]; and are also in the range of those reported by Schumann for [Ca(C₅Me₄CH₂CH=CH₂)₂]J (J in Figure 5.1) (2.941(2)–3.230(2) Å). The alkene moieties are coordinated to calcium using the Si-face (Ca(1)) and Re-face (Ca(2)) and the C=C distances (1.305(4) Å) again fall in the typical range of sp²-hybridised carbon atoms. The position of the olefin group in [25] is similar to that of [23] as illustrated by the angle between vector of the Ca–C(centroid) and the plane formed by the –CH₂=CH₂ plane (73.3(1) °). The small difference (1.4 °) between the two Ca–N–Si angles (Ca(1)–N(20)–Si(1) = 116.6(1) °, Ca(1)–N(20)–Si(2) = 115.2(1) °) in [25] militates in favour of two β-Si–H···Ca agostic interactions of comparable intensities within the same N(SiMe₂H)₂⁻ moiety. The nitrogen atoms from the ancillary ligands are coordinated to calcium. In this calcium complex, one Namine atom has an R absolute configuration, whereas the other one has an S configuration.

As determined by X-ray crystallography, [25] crystallised as a dimer. To establish if this dinuclearity is preserved in solution, this calcium complex was analysed by NMR diffusion techniques. In Chapter 3, it was described that the nuclearity of a metal complex can be determined by comparing the hydrodynamic radius in solution (rH,PGSE) to that obtained in the solid state (rX-Ray). In this case the value of rH,PGSE was calculated to 5.53 Å which is very close to that of rH,X-ray (5.13 Å). This suggests that the Ca complex retains its dimeric form in hydrocarbon solutions. Further details regarding these data can be found in Annexure G.

Another method for addressing the nuclearity in solution is based on the fact that the diffusion coefficient (Dₜ) relates to the molecular weight (Mw) according to Equation (5.1):²⁰,²¹

\[
\log Dₜ = \frac{1}{3} \log \text{Mw} + \frac{1}{3} \log \rho - \log \eta - \log \frac{162 \times \pi²}{K_B^3 \times T^3 \times N_A} \quad (5.1)^{*}
\]

Equation (5.1) depicts a linear correlation between log Dₜ and log Mw of a complex if dilute solutions are employed. By knowing the value of its diffusion coefficient, the molecular weight of an unknown sample can be estimated from a linear logarithmic plot between the molecular weights of several known compounds (used as calibrants) and their respective diffusion coefficients. For instance, Grubbs et al. reported that the molecular weights of polyurethanes can be determined using polystyrene molecules standards in this fashion.²⁰ Following the works of Williard,²¹ our group has recently shown that this method can be extended to coordination complexes and it was applied

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²° ρ is the volumic mass of the solvent; η is the viscosity of the solvent (kg·s⁻¹·m⁻³); k_B is Boltzmann’s constant (1.3806488 x 10⁻²³ m² kg s⁻² K⁻¹); T is temperature in K; N_A is Avogadro’s constant (6.022 x 10²³ mol⁻¹).
advantageously to estimate the molecular weight of a mixed yttrium–lithium “ate” complex\(^\text{22}\) and also for several tin amido- alkoxides\(^\text{23}\) and phenolates.\(^\text{24}\)

Even if the comparison between \(r_{\text{HPGSE}}\) and \(r_{\text{X-Ray}}\) is a good indicator to establish the nuclearity of a complex in solution, the results can thus be further confirmed using the \(D_t\)-Mw method associated to Eq (1). Hence, the molecular weight of \([\{\text{RO}^{11}\}\text{CaN(SiMe}_2\text{H)}_2\}_2\] \([25]\)_2 in solution was estimated to 845 g mol\(^{-1}\) using benzene (78 g mol\(^{-1}\)), naphthalene (128 g mol\(^{-1}\)), pyrene (202 g mol\(^{-1}\)) and TMSS (320 g mol\(^{-1}\)) as known calibrants (Figure 5.7).

\[
\text{Figure 5.7. Diffusion time–molecular weight (}D_t\text{–M.w.) analysis for }\text{[}\{\text{RO}^{11}\}\text{CaN(SiMe}_2\text{H)}_2\}_2\]\([25]\)_2.
\]

This experimental value (845 g mol\(^{-1}\)) is close to that for the dimeric form of \([25]\)_2 (929.3 g mol\(^{-1}\)) and it confirms that this complex retains its dinuclearity in hydrocarbons. At the time of writing this manuscript, the set of calibrants was extended and now includes compounds with high Mw (> 1500 g mol\(^{-1}\)). This will allow future experiments to be performed more accurately since the Mw of the complex will be inside the calibration area.

The \(^1\text{H NMR spectrum of }\text{[}\{\text{RO}^{11}\}\text{CaN(SiMe}_2\text{H)}_2\}_2\]\([25]\)_2 in benzene-\(d_6\) at room temperature contains broad resonances; hence, spectroscopic data for this complex were recorded at lower temperatures. The most explicit and informative results were obtained when measuring the spectrum at 263 K in toluene-\(d_8\) (Figure 5.8).
Despite the fact that crystalline material of [25]₂ was used, two sets of resonances in an equimolar ratio were identified. This behaviour seems to suggest the existence of two species with the same chemical composition. Consistent with the findings from ¹H NMR spectroscopy, the ¹³C{¹H} NMR spectrum of [25]₂ recorded in toluene-d₈ at 263 K also depicts two sets of resonances for the vinylic carbons that have very close chemical shifts to those obtained for the free proteo-ligand {RO¹¹}Η. In addition, ¹³C NMR spectroscopy shows that the ¹J_C–H coupling constants (~154 Hz) are nearly identical to those in the free proteo-ligand. These observations show that the C=C bond remains unaffected upon coordination to calcium, if coordination of the olefin to the metal persists in solution.

The ¹⁹F NMR spectrum of [25]₂ in toluene-d₈ at 263 K features what are likely four unresolved quadruplets in a ca. 1:1:1:1 ratio (Figure 5.9). This behaviour suggests that all CF₃ groups are magnetically inequivalent, possibly due to the chiral N_amine atoms. Upon further cooling the toluene solution, the signals broaden significantly at 233 K concomitantly with a recoalescence of these signals. Heating the NMR sample at 343 K results in the formation a large broad singlet, suggesting that all CF₃ groups are magnetically equivalent at this temperature.
In an attempt to elucidate the fluxional behaviour of [25]$_2$, variable temperature $^1$H NMR experiments were conducted; particular attention was paid to the $\delta_{1H}$ 4.7–6.4 ppm region where the resonances for vinylic and SiH hydrogen atoms are found. Starting from ambient temperatures, cooling a solution of [25]$_2$ in toluene-$d_8$ down to 263 K (Figure 5.10) results in a decoalescence of the $CH=CH_2$ (H$_{int}$) hydrogens, in two signals in a ca. 1:1.2 ratio at $\delta_{1H}$ 5.94 and 6.08 ppm. At temperatures > 293 K, these resonances coalesced, forming a single dominant species.

![Figure 5.10. Variable-temperature $^1$H NMR spectra (400.13 MHz) of [{RO}$^{11}$]CaN(SiMe$_2$H)$_2$]$_2$ ([25]$_2$) (vinylic and SiH region) recorded in toluene-$d_8$ at 193–343 K.](image-url)
All NMR data suggest that most likely there is an exchange process in [25]₂ between two species having the same chemical composition.†† For this exchange process several hypotheses can be postulated: (a) the existence of a pair of diastereoisomers arising from the presence of two stereogenic centres (N胺 atoms) (Scheme 5.3–a); if N胺→Ca coordination is retained in solution and since the complex remains dimeric, then the two N atoms are chiral.‡‡ (b) an olefin face exchange: coordination of the olefin with the Si-face followed by re-coordination using the Re-face (Scheme 5.3–b); this phenomenon was previously described for cationic Zr⁰ and Ti⁰-olefin complexes;⁵,⁶c (c) decoordination of one of the olefin moieties, followed by re-coordination using the same enantioface (Scheme 5.3–c); (d) a monomer-dimer equilibrium (Scheme 5.3–d); (e) exchange with the toluene solvent molecule. The latter assumption can be ruled out as the ¹H NMR spectrum of [25]₂ in the entirely non-coordinating methylcyclohexane-d₁₄ at 298 K is very similar to that obtained in toluene-d₈ at the same temperature.

Scheme 5.3. Possible exchange processes in \([\{\text{RO}\}^{\text{I}}\text{CaN(SiMe}_2\text{H})_2\}\)₂ ([25]₂). The influence of Ca···F–C and β-Si–H···Ca secondary interactions were omitted for clarity.

The ¹H NMR spectrum of recrystallised [25]₂ recorded in THF-d₈ (Figure 5.11) was easier to interpret and only consists of sharp resonances. Two sets of signals were observed for all hydrogens, except from the vinylic moieties, in an approximate ratio of 1.1:1. This ratio is very close to the one previously observed in toluene-d₈. Another observation is that the integration for the N(SiMe₂H)₂††

†† DOSY NMR experiments performed at room temperature (vide supra) informed that a single diffusion coefficient was present.

‡‡ These observations contrast with the behaviour of the related [12]₂. [[RO⁻¹]CaN(SiMe₂H)]₂ is dimeric in solution and the (RO⁻¹)⁻ ligand also employs a pro-chiral nitrogen atom. And yet, the NMR spectra (¹H, ¹⁹F) of [12]₂ clearly indicate that there are no signs of diastereoisomers in solution.
amido moiety is only half from what it was expected. This suggests that for each two \( \text{RO}^{11} \) ligands, there is a single amido group. No information could be extracted from this spectrum concerning the presence of \( \beta \)-Si–H···Ca agostic interactions in solution since the \( ^{29}\text{Si} \) satellites were not observed. In this respect a non-decoupled \( ^{29}\text{Si} \) NMR spectrum would be very informative.

Figure 5.11. \(^1\text{H} \) NMR spectrum (400.13 MHz) of \([ \text{RO}^{11}\text{CaN(SiMe}_2\text{H)}_2]_2 \) \( ^{25} \) in THF-\( d_8 \) at 298 K.

The \(^{19}\text{F} \) NMR spectrum of \( ^{25} \) consists of two sharp singlet resonances at \( \delta_{^{19}\text{F}} \) at –75.41 and –76.22 ppm also in a ca. 1.1:1 ratio. This suggests that in this coordinating solvent, there are two different types of \( \text{C(CF}_3\text{)}_2 \) groups where the \( \text{CF}_3 \) groups are magnetically equivalent, possibly due to the presence of two different species under these conditions. 2D DOSY NMR spectroscopy may help to discern if there are two different complexes in THF-\( d_8 \), but could not be recorded at the time of writing.

Adding excess of THF to \( ^{25} \) is expected to strongly modify the structure of this dimeric complex in solution. Saturating the coordination sphere of the calcium atoms may cause the displacement of the olefin (if they actually remain coordinated in solution) and may also cleave the Ca–Obridging bonds, resulting in the formation of a monomeric compound. The question about the structure of \( ^{25} \) in THF remains difficult to answer in the absence of support from X-ray structure analysis. All attempts to crystallise a “\( ^{25} \)” complex with coordinated THF molecules were unsuccessful due to its very high solubility in this solvent. Attempts to grow THF-solvated crystals by adding one equiv of THF vs. Ca to a concentrated pentane solution of \( ^{25} \) at –30 °C yielded crystals with the same cell parameters as those of \( ^{25} \). This is unsurprising in light of DFT data obtained subsequently (\textit{vide infra}, section 4.5) which showed that displacement of the two olefin moieties by two THF molecules is endergonic.
4.3.2.2. Characterisation of \([\{RO^{11}\}SrN(SiMe_2H)_2\}_2\) ([26]$_2$

\([\{RO^{11}\}SrN(SiMe_2H)_2\}_2\) also crystallised as a centrosymmetric dimer [26]$_2$, as shown in Figure 5.12. X-ray data indicate structural features similar to those of [25]$_2$. One noticeable difference is that now one extra Sr···F–C secondary interaction is present, taking the number of Sr···F–C interactions to two (Sr···F–C = 3.045(1) and 3.136(2) Å). The Sr···alkene distances (3.061(3) and 3.165(3) Å) in [26]$_2$ match well the ones reported by Schumann et al. in \([\{C_5Me_4CH_2CH=CH_2\}_2Sr\}] (2.99(2) and 3.20(2) Å, K in Figure 5.1). The M···alkene contacts are longer (ca. 0.083 Å) in [26]$_2$ than in the calcium analogues [23]$_2$ and [25]$_2$, a reflection of the larger size of the Sr$^{2+}$ ion (\(r_{Ca^{2+}} = 1.00\) Å, \(r_{Sr^{2+}} = 1.18\) Å). Also note that the difference in distances between Sr···alkene from [26]$_2$ and Ca···alkene from [25]$_2$ (avg. 0.083 Å) is narrower than the difference in ionic radii for the two elements (0.18 Å) suggesting stronger M···alkene interactions in the case of the Sr complex. The presence of β-Si–H···Sr interactions is assessed by the narrow Sr–N–Si angles (113.9 (1) and 111.7(1) °) and also by short Sr···H distances (3.09(3) and 3.16(3) Å).

![Figure 5.12.](image)

Our first concern regarding the solution behaviour of [26]$_2$ was to establish its nuclearity in solution. For this, as previously performed with calcium complexes [23]$_2$ and [25]$_2$ (vide supra), the
molecular weight of [26]$_2$ was estimated to 953 g mol$^{-1}$ which is very close to the theoretical value of the dimeric form (1024.4 g mol$^{-1}$). Furthermore, using the PGSE method, it was found that the $r_{\text{H,PGSE}}$ (5.89 Å) was very close to $r_{\text{H,X-ray}}$ (5.21 Å). In light of these experiments, it can be concluded that [26]$_2$ also remains dimeric in solution.

The $^1$H NMR spectrum of [\{RO$^{11}$\}SrN(SiMe$_2$H)$_2$]$_2$ ([26]$_2$) in toluene-$d_8$ (Figure 5.13) depicts broad resonances at 298 K, but is better resolved at 273 K when it reveals a single set of resonances. Since the only difference between [25]$_2$ (which featured two sets of resonances) and [26]$_2$ is the different metal (Ca in [25]$_2$, Sr in [26]$_2$), this variation in solution behaviour can be linked to the larger size of the Sr$^{2+}$ ion compared to Ca$^{2+}$. Nevertheless, the question concerning the appearance of a sole array of resonances in [26]$_2$ remains. The resonances for the H$_{\text{int}}$ ($\delta_H$ 6.24 ppm) and H$_{\text{ext}}$ (5.24 ppm) hydrogens are deshielded compared to those found for the proteo-ligand under identical conditions ($\delta_H$ 5.44 and 4.93 ppm, respectively).

![Figure 5.13. $^1$H NMR spectrum (400.13 MHz) of [\{RO$^{11}$\}SrN(SiMe$_2$H)$_2$]$_2$ ([26]$_2$) recorded in toluene-$d_8$ at 273 K.](image)

The $^{19}$F NMR spectrum in toluene-$d_8$ at 273 K shows two main resonances as two unresolved quadruplets and three broad singlets of weaker intensities (~15%). The fact that there are two quadruplets indicates a single type of C(CF$_3$)$_2$ group in which the CF$_3$ moieties are magnetically distinct. Nevertheless the presence of the broad singlets was unexpected. This spectrum can be consulted in Annexure E.
Chapter 4: Alkaline-Earth Heteroleptic Complexes Supported by Aminoalkoxides with Olefin Pending Groups

The $^1$H NMR spectrum of $[26]_2$ recorded in THF-$d_8$ (Figure 5.14) is simpler than in toluene-$d_8$, as the resonances are well-resolved in this solvent. Similarly to the NMR pattern of $[25]_2$, two sets of signals are identified in a 1.7:1 ratio.\(^\text{88}\) The fact that there are two sets of signals is certainly intriguing and again raises the question regarding the structure of these Ae-olefin complexes in THF-$d_8$. One N(SiMe$_2$H)$^-\text{amide}$ is found for each $\{\text{RO}^{11}\}^-$, contrasting the behaviour of $[25]_2$ in THF-$d_8$ when two $\{\text{RO}^{11}\}^-$ units were found for each amido group.

\[\text{Figure 5.14. $^1$H NMR spectrum (400.13 MHz) of } [[\text{RO}^{11}]\text{SrN(SiMe}_2\text{H)}_2]_2 ([26]_2) \text{ recorded in THF-$d_8$ at 273 K.}\]

The $^{19}$F NMR spectrum of $[26]_2$ in THF-$d_8$ (Annexure E) indicates the presence of two sharp singlets at $\delta_{^{19}F} -77.78$ and $-78.02$ ppm also in a 1.7:1 ratio, indicating that two distinct species exist in which the CF$_3$ moieties are magnetically equivalent. Based on these experimental data we are unable to assess the identity of these species and X-ray data is required in order to solve this matter. Future experiments needed to characterise this complex should include DOSY NMR in THF-$d_8$ in order to assess the nuclearity of this complex in the coordinating solvent. All attempts to crystallise $[26]_2$ in presence of THF were unsuccessful. Since the $^{29}$Si satellites overlap with other resonances, the assessment of the strength of $\beta$-Si–H···Sr agostic interactions cannot be performed using the $^1$H NMR spectrum in THF-$d_8$.

4.3.3. Short summary

Alkaline-earth heteroleptic complexes $[[\text{RO}^x]\text{AeN(SiMe}_2\text{H)}_2]_2$ ($x = 12$, Ae = Ca ($[23]_2$), $x = 11$, Ae = Ca ($[25]_2$), Sr ($[26]_2$)) were synthesised by protonolysis of Ae[N(SiMe$_2$H)$_2$]$_2$(THF)$_n$ (Ae = Ca, $n = 1$; Ae = Sr, $n = 2/3$) and the corresponding proteo-ligand. Their solid-state molecular structure depicts in

\[^{88}\] This ratio was determined by integrating the two CH(CH$_3$)$_3$ resonances. The other signals overlapped.
all cases one alkene moiety coordinated onto the Ae centre in a \(\eta^2\) fashion, although shorter contacts with the metal were observed with the internal carbon (C\(_{\text{int}}\)) from the alkene moiety. Consistently with previous findings in the literature,\(^8\) the interactions between alkenes and alkaline-earths seem weak. In fact, the coordinated C=C bond was completely unaltered with distances falling in the range expected for normal C\(_{sp^2}\)-hybridised atoms. Table 5.1 collates key metric parameters for these complexes.

**Table 5.1.** Summary of bond distances (Å) and angles (°) for complexes \([23]_2\), \([25]_2\), and \([26]_2\).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ae</th>
<th>Ae–C(_{\text{int}})</th>
<th>Ae–C(_{\text{ext}})</th>
<th>C(<em>{\text{int}})–C(</em>{\text{ext}})</th>
<th>Ae–F</th>
<th>Ae–Si</th>
<th>Ae–N–Si</th>
<th>N–Si–N</th>
</tr>
</thead>
<tbody>
<tr>
<td>([23]_2)</td>
<td>Ca(^a)</td>
<td>2.972(2)</td>
<td>3.121(2)</td>
<td>1.327(3)</td>
<td>2.931(1)</td>
<td>3.447(1)</td>
<td>3.307(9)</td>
<td>119.6(1)</td>
</tr>
<tr>
<td>([25]_2)</td>
<td>Ca(^a)</td>
<td>2.958(3)</td>
<td>3.102(3)</td>
<td>1.305(5)</td>
<td>3.050(2)</td>
<td>3.404(1)</td>
<td>3.381(1)</td>
<td>116.6(1)</td>
</tr>
<tr>
<td>([26]_2)</td>
<td>Sr(^b)</td>
<td>3.061(3)</td>
<td>3.165(3)</td>
<td>1.316(5)</td>
<td>3.045(1)</td>
<td>3.428(1)</td>
<td>3.477(1)</td>
<td>113.9(1)</td>
</tr>
</tbody>
</table>

\(^a\) Ionic radius: \(r_{\text{Ca}^{2+}} = 1.00\) Å; \(^b\) Ionic radius: \(r_{\text{Sr}^{2+}} = 1.18\) Å.

With the exception of \([\{\text{RO}_{12}\}\text{CaN(SiMe}_2\text{H)}_2\]_2\) \([23]_2\), the \(^1\)H NMR spectra of \([24]_2–[26]_2\) in aromatic solvents (benzene-\(d_6\), toluene-\(d_8\)) at 298 K displayed broad resonances. The \(^1\)H NMR data of \([23]_2\), \([25]_2\), and \([26]_2\) in toluene-\(d_8\) indicate that the chemical shifts for the vinylic moieties are deshielded compared to those for the corresponding proteo-ligands. However, \(^13\)C NMR spectroscopy in benzene-\(d_6\) confirms the retention of the sp\(^2\) character of C=C bond in solution: the \(^13\)C\(^{\text{\{1\}}\!\text{H}}\) NMR spectra of \([23]_2\), \([25]_2\), and \([26]_2\) indicate similar chemical shifts for the C\(_{\text{int}}\) and C\(_{\text{ext}}\) carbon atoms compared to those for the \{RO\(^{11}\)}H and \{RO\(^{12}\)}H proteo-ligands (Table 5.2). In addition, the \(^1\)J\(_{C-H}\) coupling constants for resonances from the alkene moieties are identical to those for the free proteo-ligands. According to DOSY NMR experiments performed with these Ae-olefin complexes, their solid-state dimeric structure is retained in weakly-coordinating solvents such as benzene-\(d_6\).

**Table 5.2.** \(^1\)H and \(^13\)C\(^{\text{\{1\}}\!\text{H}}\) NMR chemical shifts of the vinylic resonances for complexes \([23]_2\), \([25]_2\), and \([26]_2\) and their corresponding proteo-ligands in benzene-\(d_6\) at 298 K.

<table>
<thead>
<tr>
<th>Proteo-ligand/Complex</th>
<th>(^1)H NMR (ppm)</th>
<th>(^13)C NMR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{CH}=\text{CH}_2)</td>
<td>(\text{CH}=\text{CH}_2)</td>
</tr>
<tr>
<td>{RO(^{12})}H</td>
<td>5.46</td>
<td>4.92</td>
</tr>
<tr>
<td>{RO(^{11})}H</td>
<td>5.49</td>
<td>4.94</td>
</tr>
<tr>
<td>([{\text{RO}_{12}}\text{CaN(SiMe}_2\text{H)}_2]_2</td>
<td>5.81</td>
<td>5.18</td>
</tr>
<tr>
<td>([{\text{RO}_{12}}\text{CaN(SiMe}_2\text{H)}_2]_2</td>
<td>6.07</td>
<td>5.95</td>
</tr>
<tr>
<td>([{\text{RO}_{11}}\text{SrN(SiMe}_2\text{H)}_2]_2</td>
<td>6.20</td>
<td>5.28</td>
</tr>
</tbody>
</table>

\(^a\) Determined at 263 K in toluene-\(d_8\).
Better resolved spectra of $[23]_2$, $[25]_2$, and $[26]_2$ were obtained from THF-$d_8$ solutions, possibly due to coordination of solvent molecule(s) onto the metal centre. However, it is still unclear if one or two species co-exist in this solvent. DOSY NMR experiments must be performed to assess it.

Also, the FTIR spectra for complexes $[23]_2$, $[25]_2$, and $[26]_2$ were not recorded at the time of writing; this spectroscopy is a valuable tool to study the integrity of the C=C double bond upon coordination to Ae metals.

4.4. Probing Ae–Cπ interactions in solution

Single crystal X-ray diffractometry showed that one olefin moiety is coordinated to the metal centre in $[23]_2$, $[25]_2$, and $[26]_2$. On the other hand, $^{13}$C {$^1$H} NMR spectroscopy revealed that, upon coordination, the chemical shifts for the vinylic carbons remained mostly unaltered in comparison with the free alkene resonances in the pertaining proteo-ligands. This contrasts with the behaviour of other d$^0$ metal olefin complexes. For instance, Jordan et al. have reported that in $[\text{Cp}_2\text{Zr}(\text{OCMe}_2\text{CH}_2\text{CH}_2\text{CH}═\text{CH}_2)]^+\cdot[\text{B(C}_6\text{F}_5)_4]^−$ there is a divergent shift of approximately 20 ppm between the vinylic $^{13}$C resonances in the cationic zirconium complex and the free proteo-ligand: one signal shifts upfield and the other one shifts downfield, calling for a strong building up of charges on the coordinated C=C system. For Ae metals, comparing NMR spectroscopic data for the Ae complexes and the corresponding proteo-ligands does not provide information on the existence and intensity of Ae···Cπ interactions in solution.

Hence, this section presents our endeavours to study the Ae···Cπ interactions using NMR techniques based on scalar and through-space correlations. These studies were performed mainly on $[(\text{RO})^{11}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$ ($[25]_2$) because this complex is kinetically stable in solution and possesses a single olefin moiety per ligand.

4.4.1. 2D HMQC $^1$H–$^{15}$N spectroscopy

Our first attempts at studying the Ae–Colefin interaction in solution were based on heteronuclear correlation spectroscopy involving hydrogen and nitrogen nuclei. 2D HMQC $^1$H–$^{15}$N is typically employed for fingerprinting proteins. In the case of $[(\text{RO})^{11}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$ ($[25]_2$), it was hoped that the coordination of the alkene moiety onto calcium would result in a through-metal scalar correlation between the vinylic hydrogens and the nitrogen atom in $\text{N(SiMe}_2\text{H})_2^−$. In order to determine the adequate NMR parameters for this experiment, the 2D HMQC $^1$H–$^{15}$N spectra were

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*** Even though the $^1$H NMR spectrum of $[23]_2$ was easier to interpret, this calcium complex contains an additional olefin moiety which is not coordinated to the metal centre. Therefore, in order to simplify an already complicated situation, $[25]_2$ was chosen for the following experiments.
recorded for the proteo-ligand \{RO^{11}\}H in toluene-\textit{d}_8 at 263 K.\footnote{The 2D HMQC \textit{H}−\textit{N} NMR spectra for the \{RO^{11}\}H and [25]_2 were recorded at 263 K due to the fact that the \textit{H} NMR spectrum of the calcium complex was better resolved at this temperature.} In this spectrum, the scalar correlation between the nitrogen atom (\delta_{15N} = 37 ppm) and its neighbouring hydrogens (from methylene and \textit{i}Pr groups) was clearly detected. Unfortunately, using the same acquisition parameters, this method did not give the anticipated outcome for [25]_2; a single cross-peak correlation between the nitrogen atom from the amido group and the SiH moiety could be detected. All attempts to locate the nitrogen atom from the ancillary ligand were unsuccessful. The absence of this peak may tentatively be attributed to an exchange process involving the nitrogen atoms from the ancillary ligands, rendering detection of the relevant \textit{15N} resonances impossible on the different time-scales that were implemented. These 2D HMQC \textit{H}−\textit{15N} spectra can be found in Annexure H.

\subsection*{4.4.2. 2D \textit{H}−\textit{H} NOESY NMR spectroscopy}

Another NMR method that can offer an insight regarding the position of the alkene moiety with respect to the metal centre in solution is based on the Nuclear Overhauser Effect (NOE). By performing a 2D \textit{H}−\textit{H} NOESY spectrum, spatial correlations between hydrogen atoms, located within a distance of \textit{ca.} 5 Å, can be revealed in the absence of chemical bonds.\footnote{At 263 K, the NOESY spectrum of [25]_2 in toluene-\textit{d}_8 (Figure 5.15) illustrated negative intensity cross-peaks between the vinylic resonances (H\textit{int} and H\textit{trans}) and SiH hydrogens suggesting a close proximity (at a given time) between the alkene and N(SiMe\textit{2}H)_2 moieties.} At 263 K, the NOESY spectrum of [25]_2 in toluene-\textit{d}_8 (Figure 5.15) illustrated negative intensity cross-peaks between the vinylic resonances (H\textit{int} and H\textit{trans}) and SiH hydrogens suggesting a close proximity (at a given time) between the alkene and N(SiMe\textit{2}H)_2 moieties.

Figure 5.15. 2D \textit{H}−\textit{H} NOESY NMR spectrum (400.13, 40.55 MHz) of [[RO^{11}]CaN(SiMe\textit{2}H)_2]_2 ([25]_2) in toluene-\textit{d}_8 at 263 K (vinylic and Si-H region) describing exchange processes (red cross-peaks) and proximities correlations (blue cross-peaks).
Given the fact that the molecular structure of $[25]_2$ features a complicated dimeric arrangement, it is difficult to assess accurately whether this cross-peak correlation is indeed indicative of alkene coordination in solution. Oddly, no cross-peak correlations were detected for the SiH and H$_{cis}$ hydrogen atoms, even though they are positioned close to each other in the solid state (ca. 2.89 Å). Note however that the SiH resonance observed in this spectrum represents only the averaged value for the two SiH moieties in each N(SiMe$_2$H)$_2$– amide. Due to the fact that the SiH resonances are magnetically equivalent at 263 K, it would be impossible to discern which is in the proximity of H$_{trans}$. From this perspective, it would make sense to record the NOESY spectrum at –80 °C where the SiH are decoalesced (Figure 5.10). Importantly, the NOESY spectrum also shows that there are two positive cross-peak correlations (marked by red spots in Figure 5.15) for the vinylic hydrogens confirming the existence of an exchange process in $[25]_2$.

4.4.3. Comparison with a $^1$H–$^{171}$Yb HMBC NMR spectrum

We reasoned that a $^1$H–$^{43}$Ca HMBC spectrum with a scalar correlation between the vinylic hydrogens and calcium could provide undeniable evidence of alkene coordination in solution. However, due to its low natural abundance (0.135%) and its quadrupolar nucleus (I = 7/2), $^{43}$Ca NMR spectroscopy is very difficult to record. Relevant literature data indicate that such NMR experiments are usually performed in the solid state and often require NMR spectrometers with special probe heads. $^{28}$

On the other hand, it is well-known that the coordination chemistry of calcium is very close to that of ytterbium(II). The two elements have similar atomic properties (ionic radii: $r_{Yb^{2+}} = 1.02$ Å vs. $r_{Ca^{2+}} = 1.00$ Å, valence shells: Yb$^{2+}$ = [Ar] 4f$^{14}$, Ca$^{2+}$ = [Ar]). $^{171}$Yb has a good natural abundance (14.31%) and a nuclear spin I = ½, thus making it much more suitable for NMR spectroscopy. $^{29}$ Due to the close similarity of these two elements, a scalar correlation in the $^1$H–$^{171}$Yb HMBC spectrum of a putative $[\{RO\}^{11}]YbN(SiMe$_2$H)$_2$$_2$ between the vinylic hydrogens and the ytterbium atom could therefore provide an indication of alkene binding in this rare-earth complex. By extrapolation, it would support the surmise that the Ca···alkene interactions persist in solution in the cases of calcium complexes $[23]_2$ and $[25]_2$. Consequently, the synthesis of the ytterbium (II) analogue of $[25]_2$, $[\{RO\}^{11}]YbN(SiMe$_2$H)$_2$$_2$ ($[27]_2$) was envisaged. No report concerning the synthesis of the metallic precursor Yb[N(SiMe$_3$)$_2$$_2$](THF) was available in the literature, and only its molecular structure is known. $^{30}$ The synthesis of this ytterbium(II) precursor is similar to that of Ca[N(SiMe$_2$H)$_2$$_2$](THF). $^{31}$ It involves the transamination reaction of Yb[N(SiMe$_3$)$_2$$_2$](THF) with HN(SiMe$_2$H)$_2$ to give the Yb(II) homoleptic complex in high yields (81%). Yb[N(SiMe$_2$H)$_2$$_2$](THF) was then subjected to a reaction with $[RO]^{11}$H using the same conditions (Et$_2$O, –78 °C) as those previously employed for the calcium complex $[25]_2$. The formation of $[27]_2$ could be confirmed by $^1$H NMR spectroscopy (benzene-$d_6$), but
the spectrum was plagued by the presence of paramagnetic impurities. Attempts to purify the crude mixture allowed the isolation of small red crystals from a concentrated pentane solution of \([27]_2\) stored at \(-30^\circ\text{C}\). Nevertheless, the NMR data recorded in benzene-\(d_6\) for these crystals also showed contamination by paramagnetic impurities within the first point of analysis. This suggests that Yb\(^{2+}\) was oxidised to Yb\(^{3+}\) upon solvation in the NMR solvent.

The X-ray data of \([\{\text{RO}^{11}\}\text{Yb}(\text{SiMe}_2\text{H})_2]\)\(_2\) are similar to those of the calcium analogue \([25]_2\) and depicts a binuclear arrangement with an inversion centre (Figure 5.16). As in \([25]_2\), the alkene moieties from the ancillary ligands are coordinated onto the two ytterbium ions in a \(\eta^2\) fashion. Consistently with the solid-state behaviour of \([23]_2\), \([25]_2\), and \([26]_2\), the ytterbium exhibits shorter contacts with the internal vinylic carbon (Yb(1)–C(32) = 2.924(8)\(\text{Å}\)) than with the external one (Yb(1)–C(31) = 3.070(1) \(\text{Å}\)). The Yb···C_alkene distances compare well with similar ytterbium complexes that feature intramolecular olefin coordination e.g. \([\text{Yb}(\text{C}_5\text{Me}_4\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}=\text{CH}_2)_2]\)\(_2\) (2.905(3) and 3.182(3) \(\text{Å}\)),\(^{32}\) [\(\text{Yb}(\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)_2]\)\(_2\) (2.88(7)–3.13(7) \(\text{Å}\))\(^{33}\) Yb[\(\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{CH}=\text{CH}_2)\text{I}\)-\(\text{OEt}_2\) (2.98(2) \(\text{Å}\))\(^{34}\) but are longer than those in \([\text{Cp}^*_2\text{Yb}(\mu-\text{C}_2\text{H}_2)\text{Pt}(\text{PPh}_3)_2]\) (2.770(3)and 2.793(3) \(\text{Å}\))\(^{35}\) As in the case of the Ca analogue \([25]_2\), the metal centres are stabilised by rather weak Yb···F–C secondary interactions (2.973(5) \(\text{Å}\)). The metal centres are further stabilised by \(\beta\)-Si–H···Yb agostic interactions as depicted by the short Yb···Si (3.181(1) \(\text{Å}\), and Yb···H (2.72(7) \(\text{Å}\)) distances. The presence of a single \(\beta\)-Si–H···Yb agostic interaction per Yb\(^{2+}\) in \([27]_2\) was also attested to by the value of the Yb(1)–N(1)–Si(2) angle (104.2(3) \(^{\circ}\)), which is much narrower than that for Yb(1)–N(1)–Si(1) (126.8(3) \(^{\circ}\)).
**Figure 5.16.** (*left*) ORTEP representation of the molecular structure of $[[RO^{11}]_{2}YbN(SiMe_2H)_2]$ (27)$_2$. Hydrogen atoms (except SiH) are omitted for clarity. Ellipsoids are drawn at the 50% probability level. (*right*) Schematic representation of 27$_2$. Selected bond lengths (Å) and angles (°): Yb(1)–O(17) = 2.346(4), Yb(1)–N(1) = 2.320(5), Yb(1)–N(36) = 2.649(5), Yb(1)–C(32) = 2.924(8), Yb(1)–C(31) = 3.070(1), Yb(1)–H(2) = 2.72(7), Yb(1)–F(14) = 2.973(5), C(31)–C(32) = 1.317(10); Yb(1)–N(1)–Si(1) = 126.8(3), Yb(1)–N(1)–Si(2) = 104.2(3), Si(1)–N(1)–Si(2) = 129.0(3). Torsion angle: Yb(1)–N(1)–Si(2)–H(2) = 5.2(3).

We were also interested in studying the behaviour of metal-olefin complexes in the absence of β-Si–H···M agostic interactions. For this reason the synthesis of an ytterbium complex analogue of 27$_2$ bearing a N(SiMe$_3$)$_2$– amido group was prepared. Compared to Yb[N(SiMe$_2$H)$_2$]$_2$(THF), Yb[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ is a common precursor and has been more frequently used in protonolysis reactions. The synthesis of $[[RO^{11}]_{2}YbN(SiMe_2H)_2]$ (28)$_2$) was carried by reacting of $[RO^{11}]_2$H with Yb[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ according to Scheme 5.5.

**Scheme 5.5.** Synthesis of $[[RO^{11}]_{2}YbN(SiMe_2H)_2]$ (28)$_2$.

The $^1$H NMR spectrum of the crude product indicated broad resonances and some were located outside of the expected diamagnetic scale ($\delta_1$ 0–10 ppm). This suggests that the complex contained paramagnetic impurities, most probably as a result of traces of oxidation of Yb$^{3+}$ to Yb$^{3+}$. 

This precluded further characterisation by NMR techniques. The high propensity of this type of ytterbium(II) complexes for oxidation can be visually observed, as bright red solutions of [28]2 became entirely colourless in a matter of days.

Orange-red coloured crystals of [28]2 suitable for X-ray diffractometry were obtained upon recrystallisation of the crude mixture from a pentane solution at –30 °C. Its molecular structure (Figure 5.17) depicts the formation of a centro-symmetric dimer with a formally five-coordinate ytterbium atom. Unexpectedly, the olefin is not oriented toward the metal centre as the Yb···Calkene distances are long (5.17 and 5.76 Å) and exceed the sum of the van der Waals radii for the two elements (Σ rvdW(Yb, C) = 4.50 Å). This might be explained in terms of steric effects as the N(SiMe3)2– moiety is too bulky to allow the alkene to coordinate onto the metal. The molecular structure of [28]2 features a strong Yb···F–C interaction (2.710(3) Å), which is identical to that in the cationic complex [(RO)4][Yb(µ-F)2][H2N{B(C6F5)3}]2 (2.71(7) and 2.72(9) Å), but longer than in the mixed-valence complex [YbCp2][µ-F] (2.08(2) and 2.31(2) Å) and Sadows’s homoleptic [(HB(C6F5)3)]2Yb(S) (S = THF, x = 2, Yb···F–C = 2.47 Å; S = TMEDA, x = 1, Yb···F–C = 2.50 Å).

Figure 5.17. (left) ORTEP representation of the molecular structure of [(RO)4][YbN(SiMe3)2]2 ([28]2). Hydrogen atoms (except Si-H) are omitted for clarity. Ellipsoids are drawn at the 50% probability level. (right) Schematic representation of ([28]2). Selected distances (Å) and angles (°): Yb(1)–O(12) = 2.324(3), Yb(1)–N(1) = 2.324(3), Yb(1)–N22 = 2.679(4), Yb(1)–F(14) = 2.710(3), Yb(1)···C(25) = 5.178(6), Yb(1)···C(26) = 5.766(7), C(25)–C(26) = 1.297(8); Yb(1)–N(1)–Si(1) = 121.2(1), Yb(1)–N(1)–Si(2) = 114.6(2), Si(1)–N(1)–Si(2) = 124.6(2).

‡‡‡ Several values for the van der Waals radius of ytterbium have been proposed: (a) 2.42 Å according to Hu, S. Z.; Zhou, Z. H.; Tsai, K. R. Acta Phys.-Chim. Sin. 2003, 19, 1073; (b) 2.24 Å according to Hu, S.-Z.; Zhou, Z.-H.; Robertson, B. E. Z. Kristallogr. 2009, 224, 375 and (c) 2.80 Å according to Alvarez, S. Dalton Trans. 2013, 42, 8617. In this study, the value proposed by Alvarez is used (2.80 Å).
Due to the fact that even crystalline samples of $[27]_2$ and $[28]_2$ oxidise rapidly in solution, their use in $^1$H–$^{171}$Yb HMBC NMR experiments proved impossible. Yet, the fact that Ca$^{2+}$ and Yb$^{2+}$ have similar atomic properties, makes the obtained X-ray data valuable for comparison purposes with the calcium counterparts $[23]_2$ and $[25]_2$. It can be thought that alkene coordination onto Yb$^{2+}$ can be suppressed in the case of excessive steric constraints, since the bulky N(SiMe$_3$)$_2$– amido prevents its coordination in $[28]_2$ whereas the olefin does bond to the metal in $[27]_2$. In order to determine if this behaviour also applies to calcium complexes, the synthesis of $[[\text{RO}^{11}]\text{CaN(SiMe}_3)_2]$ was attempted. However, expectedly on account of the propensity of this type of Ca complexes to involve in deleterious Schlenk equilibria, it only yielded intractable oils that could not be characterised.

### 4.5. Computational data

In order to get an additional insight concerning the nature of Ca···alkene interactions our attention next focused on DFT calculations. The results presented in this section were obtained through a collaboration with Dr. Chiara Dinoi and Prof. Michel Etienne from Université Toulouse III Paul Sabatier as part of a joint project (GreenLAkE, ANR-11-BS07-0009).

All calculations were performed with $[[\text{RO}^{11}]\text{CaN(SiMe}_3\text{H}_2)]_2$ ($[25]_2$) since most spectroscopic data involved this calcium complex. First, the molecular structure of $[25]_2$ was optimised using the B3PW91 density functional. A triple-zeta 6-311G basis set augmented by a polarisation and a diffuse function was used for the Ca atom, while polarised all electron triple-zeta 6-311G(d,p) basis sets were used for Si, O, N, and F. Finally, for the carbon and hydrogen atoms, a polarised all electron double-zeta 6-31G(d,p) basis set was used. A comparison between the optimised and the experimental molecular structures of $[25]_2$ is depicted in Figure 5.18. The most important metric parameters are given in Table 5.3.

![Figure 5.18](Image)

**Figure 5.18.** Comparison between the X-ray (left) and B3PW91-computed optimised structure (right) for the $[[\text{RO}^{11}]\text{CaN(SiMe}_3\text{H}_2)]_2$ ($[25]_2$) complex with the 6-31G(d,p) basis set for the carbon atoms.
Gratifyingly, the optimised structure using the above method clearly indicates that the alkene moieties remain coordinated to the calcium centres. Furthermore, as reported in Table 5.3, the Ca···alkene interactions obtained using these DFT computations are in reasonably good agreement with those obtained experimentally (X-ray: 2.958(3) and 3.102(3) Å vs. DFT: 3.061 and 3.195 Å). The same is also true for the value of the C=C bond (X-ray: 1.305(4) vs. DFT: 1.339 Å). The magnitude of Ca···F–C and β-Si–H···Ca secondary interactions was also computed using DFT methods. The Ca···F–C and Ca···H–Si distances obtained using the B3PW91 density functional compare well with those determined experimentally in \([25]_2\). In addition, regarding β-Si–H···Ca agostic interactions, the values of the calculated Ca–N–Si angles (116.24 and 117.14 °) match well those measured from the X-ray data (115.2(1) and 116.7(1) °).

<table>
<thead>
<tr>
<th>Method</th>
<th>Ca–C int</th>
<th>Ca–C ext</th>
<th>C_{int}–C_{ext}</th>
<th>Ca···F</th>
<th>Ca···H</th>
<th>Ca–N–Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray</td>
<td>2.958(3)</td>
<td>3.102(3)</td>
<td>1.305</td>
<td>3.050(2)</td>
<td>3.19(3)</td>
<td>115.1(1)</td>
</tr>
<tr>
<td>DFT[a]</td>
<td>3.061</td>
<td>3.195</td>
<td>1.339</td>
<td>3.001</td>
<td>3.20</td>
<td>116.2</td>
</tr>
</tbody>
</table>

[a] performed using the B3PW91 density functional using 6-311 G (for Ca), 6-311 G (d,p) (for Si, O, N, F) and 6.31G (d,p) (for C, H) basis sets

To study in more details the interaction between the Ca atom and the olefin moiety, a natural population analysis (NPA) and a natural bonding order (NBO) analysis were carried out on \([{{\text{RO}}^{11}}\)CaN(SiMe$_2$H)$_2\]$_2$ for two different scenarios. In the first case, the alkene moiety is coordinated (as observed in the molecular structure of \([25]_2\)). Inversely, the second case explores the model where the alkene moiety is no longer coordinated onto calcium. In order to evaluate the electrostatic and covalent contributions to the Ca···alkene interaction, we were interested in both the natural charges and the possible interactions between “filled” (donor) Lewis-type NBOs and “empty” (acceptor) non-Lewis NBOs, quantified according to their energetic contribution computed at the second-order perturbation analysis. In the case where the alkene remains coordinated, no significant second-order interaction between the π-CC NBO and a vacant NBO on Ca was observed, ruling out a significant covalent character. On the other hand, comparing the natural charges in the structures with the coordinated and uncoordinated alkene moieties, it was observed that the charge separation between the carbon atoms of the olefin and the calcium centre decreases with the decoordination of the olefin. Indeed, in the structure depicting Ca···alkene interactions (Figure 5.19–left), the vinylic carbons and

§§§ Performed in the gaseous phase
the calcium atom are characterised by a natural charge of −0.28, −0.47 and +1.81 au, respectively. In the structure displaying no Ca···alkene interactions (Figure 5.19–right), these atoms are characterised by a natural charge of −0.23,−0.43 and +1.82 au, respectively. Taken globally, these results indicate that (i) the interaction of the olefin with the Ca\(^{2+}\) ion does exist, and (ii) it does not have any significant covalent character but instead features essentially an electrostatic component.

**Figure 5.19.** Natural charges in [25]\(_2\), with coordinated (left) and uncoordinated (right) olefin moiety.

Further on, the potential effect of THF molecules on the coordination sphere of calcium in [25]\(_2\) was also studied. Using using the BPE1BPE, wb97xd and B3PW91 density functionals with a polarised all electron double-zeta 6-31G(d,p) basis set for the carbon and hydrogen atoms, it was observed that coordination of the THF molecule to calcium is endergonic with a ΔG value of 3.8 (BPE1BPE), 3.7 (wb97xd) and 4.5 (B3PW91) kcal mol\(^{-1}\). These data are consistent with our experimental observations, as we were unable to isolate a THF-adduct from [25]\(_2\) (see 4.3.2.1.). The optimised structure of [25]\(_2\) in the presence of THF indicates that solvation of the complex would cause the displacement of the alkene moiety (Figure 5.20).

**Figure 5.20.** B3PW91 optimised structure for a hypothetical [(RO\(^{11}\)CaN(SiMe\(_2\)H)\(_2\)]\(_2\)(THF)\(_2\) using the 6-31G(d,p) basis set for the carbon and hydrogen atoms.
4.6. Probing coordination of substituted alkenes

In section 4.4.3, it was shown that the coordination of olefin dangling moieties onto ytterbium(II) may be altered by steric effects. Since the attempted isolation of \([\{\text{RO}^{11}\}\text{CaN(SiMe}_3\text{)H}_2\}_2\) failed, we persisted on studying how steric effects can influence the outcome of Ca···C\text{alkene} interactions by instead increasing the steric bulk of the ancillary ligand, using ligands bearing α,β-substituted alkenes.

For this study using the backbone of \{\text{RO}^{11}\}H, two types of new ancillary ligands were devised: one bearing a terminal methyl mono-substituted alke moiety –\{\text{RO}^{13}\}H– and the other one featuring a terminal dimethyl vinylidene group,\{\text{RO}^{14}\}H (Scheme 7). The synthesis of \{\text{RO}^{13}\}H involves two reaction steps. It begins with the conversion of the commercially available (Z)-pent-3-en-1-ol to (Z)-N-isopropylpent-3-en-1-amine in moderate yield (42%) via a modified Mitsunobu reaction.\(^{41}\) The resulting amine was then subjected to a reaction with 2,2-bis(trifluoromethyl)oxirane to yield the desired proteo-ligand \{\text{RO}^{13}\}H as a colourless oil (78%) (Scheme 5.6). \{\text{RO}^{14}\}H could be obtained by reacting first 5-bromo-2-methylpent-2-ene with a large excess of \(\text{iPrNH}_2\) (20 equiv). Subsequent reaction of the resulting secondary amine with 2,2-bis(trifluoromethyl)oxirane also affords \{\text{RO}^{14}\}H as a colourless oil (85%) (Scheme 5.6).

Complexes \([\{\text{RO}\}'\text{CaN(SiMe}_2\text{H}_2\}_2\) \((x = 13 ([29]_2), x = 14 ([30]_2))\) were obtained in moderate yields (50–60%) by reaction of the proteo-ligands and 1.3 equiv. of \text{Ca[N(SiMe}_3\text{)H}_2\}_2\text{(THF)} according to Scheme 5.7. Compounds \[29\]_2 and \[30\]_2 are very soluble in hydrocarbon solvents (pentane, benzene, and toluene). Analytically pure samples were obtained after recrystallisation from cold pentane or toluene solutions.
Scheme 5.7. Synthesis of \([\text{RO}^{13}]\text{CaN(SiMe}_2\text{H)}_2\)\text{2} (29)\text{2} and \([\text{RO}^{14}]\text{CaN(SiMe}_2\text{H)}_2\)\text{2} (30)\text{2}.

### 4.6.1. Characterisation of \([\text{RO}^{13}]\text{CaN(SiMe}_2\text{H)}_2\)\text{2} (29)\text{2}

The molecular structure of \([\text{RO}^{13}]\text{CaN(SiMe}_2\text{H)}_2\)\text{2} (29)\text{2} was obtained on crystals isolated by recrystallisation from a concentrated toluene solution at –30 °C and is illustrated in Figure 5.21. It features a dimeric structure with two non-equivalent formally 7-coordinate calcium atoms. The alkene moieties are coordinated onto the calcium centres, but the coordination pattern of the alkene is different from that in [25]2. It now depicts short interactions between calcium and internal vinylic carbon \((\text{Ca}(1)–C(3) = 2.933(1) \text{ Å}; \text{Ca}(2)–C(23) = 2.977(1) \text{ Å})\), whereas the Ca–C\text{ext} distances \((\text{Ca}(1)–C(2) = 3.334(2) \text{ Å}; \text{Ca}(2)–C(22) = 3.389(1) \text{ Å})\) are larger than the cut-off value imposed for Ca···C\text{π} interactions \((3.13) \text{ Å}^{12}\). In line with the other molecular structures of Ae heteroleptic complexes presented throughout this chapter, additional stabilisation in [29]2 is provided by one Ca···F–C secondary interaction per calcium \((\text{Ca}(1)–F(35) = 2.949(1) \text{ Å}; \text{Ca}(2)–F(15) = 2.834(1) \text{ Å})\). Agostic β-Si–H···Ca interactions are also present, as evidenced by short Ca···Si \((\text{Ca}(1)–Si(1) = 3.315(6) \text{ Å}; \text{Ca}(2)–Si(4) = 3.285(6) \text{ Å})\) and Ca···H \((\text{Ca}(1)–H(1) = 3.03(2) \text{ Å}; \text{Ca}(2)–H(4) = 2.98(2) \text{ Å})\) distances. Also, for each metal, one Ca–N–Si angle is narrower than the other \((\text{Ca}(1)–N(41)–Si(1) = 112.52(7), 119.18(8) ^{\circ}; \text{Ca}(2)–N(46)–Si(4) = 110.54(7), 122.06(8) ^{\circ})\).
Figure 5.21. (left) ORTEP representation of the molecular structure of \([\{\text{RO}\}^3\text{CaN(SiMe}_2\text{H)}_2\}^2 \text{[(29)]}_2\). Hydrogen atoms (except SiH) and the toluene solvent molecule are omitted for clarity. Ellipsoids are drawn at 50% probability level. (right) Schematic representation of [29]_2. Selected bond lengths (Å) and angles (°): Ca(1)–O(20) = 2.284(1), Ca(1)–O(40) = 2.319(1), Ca(1)–N(41) = 2.292(1), Ca(1)–N(6) = 2.623(1), Ca(1)–C(3) = 2.933(1), Ca(1)–C(2) = 3.334(2), Ca(1)–F(35) = 2.949(1), Ca(1)–H(1) = 3.03(2), C(2)–C(3) = 1.328(3), Ca(2)–O(20) = 2.308(1), Ca(2)–O(40) = 2.299(1), Ca(2)–N(46) = 2.295(1), Ca(2)–N(26) = 2.614(1), Ca(2)–C(23) = 2.977(1), Ca(2)–C(22) = 3.389(1), Ca(2)–F(15) = 2.98(2), C(22)–C(23) = 1.333(3); Ca(1)–N(41)–Si(1) = 112.52(7), Ca(1)–N(41)–Si(2) = 119.18(8), Si(1)–N(41)–Si(2) = 128.24(9), Ca(2)–N(46)–Si(3) = 122.06(8), Ca(2)–N(46)–Si(4) = 110.54(7), Si(3)–N(46)–Si(4) = 127.33(8). Torsion angles: Ca(1)–N(41)–Si(1)–H(1) = 7.3(8), Ca(2)–N(46)–Si(4)–H(4) = 5.3(8).

The $^1$H NMR spectrum of [29]_2 in benzene-$d_6$ displays broad resonances at room temperature, but better results can be achieved in toluene-$d_8$ at 263 K (Figure 5.22). As seen for the solution behaviour of [25]_2 in this solvent, two sets of resonances are again visible in a 1.2:1 ratio.

Figure 5.22. $^1$H NMR spectrum (400.16 MHz) of \([\{\text{RO}\}^3\text{CaN(SiMe}_2\text{H)}_2\}^2 \text{[29]}_2\) at 263 K toluene-$d_8$. 

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The vinylic hydrogens are found as two multiplets at $\delta_{1H} 5.92$ and 5.68 ppm, downfield compared to those in the free ligand ($\delta_{1H} 5.47$ and 5.19 ppm). The resonance for the SiH moiety is found at $\delta_{1H} 4.82$ ppm and features a $J_{Si-H}$ of 158 Hz indicating the mild nature of $\beta$-Si–H···Ca agostic interactions in solution. The $^{19}F$ NMR spectrum recorded at 283 K indicates the presence of two sets of quadruplets ($' J_{F}$ = 9.2 Hz). Increasing the temperature causes the $^{19}F$ resonances to merge, but full coalescence was not achieved even at 333 K, when degradation of the sample was ultimately observed. As described for [25]$_2$, due to the complexity of the molecular structure of [29]$_2$, the multiple sets of resonances cannot be unambiguously ascribed to a definite phenomenon and several hypotheses have been proposed (see section 4.3.2.). The $^{19}F$ and VT NMR data for [29]$_2$ can be consulted in Annexures E and F.

4.6.2. Characterisation of [[RO$^{14}$]CaN(SiMe$_2$H)$_2$]$_2$ ([30]$_2$)

The X-ray data for [[RO$^{14}$]CaN(SiMe$_2$H)$_2$]$_2$ ([30]$_2$) indicate that with the addition of a second methyl group in terminal position, coordination of the alkene onto the calcium atoms (Figure 5.23) is prohibited, as evidenced by the long Ca···C$_{alkene}$ distances (5.05 and 6.22 Å).

![Figure 5.23. (left) ORTEP representation of the molecular structure of [[RO$^{14}$]CaN(SiMe$_2$H)$_2$]$_2$ ([30]$_2$) Hydrogen atoms (except SiH) are omitted for clarity. Ellipsoids are drawn at 50% probability level. (right) Schematic representation of [30]$_2$. Selected bond lengths (Å) and angles (°): Ca(1)–O(1) = 2.2478(14), Ca(1)–O(1)$^{#1} = 2.333(1), Ca(1)–N(31) = 2.274(1), Ca(1)–N(12) = 2.562(1), Ca(1)–F(4) = 2.604(1), Ca(1)–F(4) = 2.604(1), Ca(1)–H(1) = 2.77(2), Ca(1)–C(19) = 5.052(2), Ca(1)–C(20) = 6.226(3); Ca(1)–N(31)–Si(1) = 104.93(9), Ca(1)–N(31)–Si(2) = 125.80(9). Torsion angles: Ca(1)–N(31)–Si(1)–H(1) = 9.7(8), Ca(1)–N(31)–Si(2)–H(2) = 8.1(8).

The absence of coordinating alkene donors in the coordination sphere of the calcium centre is instead compensated by an intense Ca···F–C interaction (2.604(1) Å), which is much stronger than

**** Recorded in benzene-$d_6$ at 298 K.
those in the related complexes [25]_2 (Ca···F–C = 3.050(2) Å) and [29]_2 (Ca···F–C = 2.834(1) and 2.949(1) Å). It even outclasses those measured in the cationic complexes \([\{\text{RO}_3\text{Ca}\}^+ \cdot 2\{\text{H}_2\text{N}\{\text{B(C}_6\text{F}_5)_3\}_2\}^- \cdot (\text{H}_2\text{O})_2 \text{~(2.65(3) Å) and ~([\{\text{RO}_4\text{Ca}\}^+ \cdot 2\{\text{H}_2\text{N}\{\text{B(C}_6\text{F}_5)_3\}_2\}^- \text{~(2.66(3) and 2.68(4) Å).} \])

The formally 6-coordinate calcium atoms gain additional stabilisation from β-Si–H···Ca agostic interactions, as indicated by the narrow Ca···Si (3.15(7) Å) and Ca···H (2.77(1) Å) distances. The presence of a single β-Si–H···Ca agostic contact per metal is also suggested by the two different Ca(1)–N(31)–Si(X) angles (X = 2, 125.80(9) and X = 1, 104.93(9) °).

The \(^1\text{H} \text{NMR spectrum of [30]_2 at 303 K in toluene-}d_8 \text{ depicts broad resonances for all methylene resonances (Figure 5.24). The CH=C(CH}_3}_2 \text{ hydrogen resonates at } \delta_{1\text{H}} 5.08 \text{ ppm and compares well with those from the proteo-ligand [RO}_14\text{H} (\delta_{1\text{H}} 4.95), whereas the characteristic signal for the SiH hydrogen is located at } \delta_{1\text{H}} 4.89. A ^1\text{J}_{\text{Si–H}} \text{ coupling constant of 156 Hz was found which is an indicative of mild of β-Si–H···Ca agostic interactions in solution. Low temperature NMR experiments were performed in order to obtain better resolved resonances, but cooling a sample of [30]_2 \text{ in toluene-}d_8 \text{ at 193 K did not bring any visible improvement to the spectrum. On the other hand, increasing the temperature to 333 K had a beneficial effect and the resonances were better resolved than at room temperature. These observations suggest the presence of two species with the same chemical composition as in [30]_2 \text{ that are involved in a fast exchange at 333 K.}

![Figure 5.24. \(^1\text{H} \text{NMR spectrum (400.16 MHz) of [\{\text{RO}_4\text{Ca}\}N(\text{SiMe}_2\text{H})_2\}_2 [30]_2 \text{ at 303 K toluene-}d_8.}

The \(^1\text{H} \text{NMR spectrum of [30]_2 \text{ at 303 K in toluene-}d_8 \text{ shows two partially coalesced broad singlets. VT NMR experiments performed in toluene-}d_8 \text{ show that they partially decoalesce at 263 K (only one of the two major peaks splits) and merge at 323 K. This behaviour contrasts with that observed for [29]_2 \text{ (signal coalescence could not be achieved at 333 K) and suggests that}
interconversion between two species (as postulated from the $^1$H NMR spectra of [30]$_2$) occurs at a rate higher than seen with [29]$_2$. Full NMR data for [30]$_2$ can be consulted in Annexures E and F.

Overall, the results presented in this section indicate that, as expected, substituting the terminal hydrogen atoms from the alkene moiety with methyl groups heavily influences the coordination of the alkene side-arm onto calcium (Figure 5.23). Hence, mono-methyl substitution changes the coordination mode of the alkene, as observed from the molecular structure of [29]$_2$ to what is best described as a $\eta^1$ mode, since only the internal carbon is bonded onto calcium. In similar d$^9$ olefin lanthanide (e.g. [C$_2$Me$_2$Si(Me)$_2$CH$_2$CH=CH$_2$]RE) (RE = Sm, Eu, Yb))$^{44}$ or Zr (e.g. [Cp$_2$ZrOCMe$_2$CH$_2$CH$_2$CH=CH$_2$]$^+$. [MeB(C$_6$F$_5$)$_3$]$^-$, (S,S,R)-(EBI)ZrOC(Me$_2$CH$_2$CH$_2$CH=CH$_2$)$^+$. [MeB(C$_6$F$_5$)$_3$]$^-6c$ complexes, the alkene interacts with the metal centre mainly via the C$_{exi}$ external carbon. In the case of the zirconium complexes, this was attributed to a delocalisation of the positive charge from the metal onto the internal vinylic carbon. In this Zr cationic complex, one may assume that the positive charge is dispersed onto the C$_{exi}$ atom. For [29]$_2$, another explanation is related to the steric hindrance caused by the Me group in the $\alpha$ position of the olefin which obstructs the coordination of the alkene onto the metal. Di-substitution of the terminal alkene hydrogens as in [30]$_2$ has an even more dramatic impact, since the olefin is no longer coordinated to the metal (Figure 5.25). In the absence of other factors, we propose that the inability of terminally di-substituted olefin to coordinate to calcium is linked to the increasingly cumbersome steric effects.

![Figure 5.25](image)

**Figure 5.25.** Representation of the coordination sphere of calcium in complexes [25]$_2$, [29]$_2$, and [30]$_2$ highlighting the interaction between the olefin moiety and the metal centre.

Perhaps one of the most interesting aspects which connects the molecular structures of [25]$_2$, [29]$_2$, and [30]$_2$ is the contribution of Ca···F–C secondary interactions towards the coordination sphere of the calcium centre. As previously described in Chapter 3 (see 3.2.4. and 3.3.2.), the influence of these secondary interactions can be gauged using bond valence sum analysis (BVSA). This mathematical model excludes here the potential influences of Ca···C$_x$ and $\beta$-Si–H···Ca secondary interactions and must therefore be seen in the simplest illustrative manner. BVSA calculations roughly indicate a 6%
contribution of Ca···F–C interactions in the case of [30]$_2$ with lower values being determined for [25]$_2$ (2%) and [29]$_2$ (3%). Expectedly, a higher contribution was estimated when no Ca···C$_\pi$ contacts are present, while complexes featuring Ca···C$_\pi$ interactions exhibit weaker Ca···F–C secondary interactions of comparable magnitude (2 and 3%). BVSA calculations for [25]$_2$, [29]$_2$, and [30]$_2$ are located in Annexure D.

4.7. Concluding remarks

This chapter illustrated for the first time that Ae···C$_\pi$, Ae···F–C, and β-Si–H···Ae secondary interactions can be used in tandem to stabilise otherwise largely electron-deficient heteroleptic Ae dimeric complexes of type [{RO$_x$}AeN(SiMe$_2$H)$_2$]$_2$ ($x$ = 12, Ae = Ca ([23]$_2$); $x$ = 11, Ae = Ca ([25]$_2$), Sr ([26]$_2$)). This can be achieved by reacting Ae[N(SiMe$_2$H)$_2$]$_2$(THF)$_n$ (Ae = Ca, $n$ = 1; Ae = Sr, $n$ = 2/3) with fluoroalkoxide proteo-ligands with alkene moieties. DOSY NMR experiments indicated that [23]$_2$, [25]$_2$, and [26]$_2$ remain dinuclear in hydrocarbon solution. These complexes have been structurally characterised, indicating that when steric constraints are small, the alkene moiety is coordinated to the metal centre in a η$^2$ fashion, or in a reduced η$^1$ fashion if some constraints are introduced such as a terminal methyl substituent. The Ae···alkene interaction is weak in nature and essentially based on electrostatics, as suggested by DFT calculations performed on the calcium complex [25]$_2$.

Ytterbium(II)-olefin complexes [{RO$_{11}$}YbN(SiMe$_3$R)$_2$]$_2$ (R = H ([27]$_2$), Me ([28]$_2$)) were synthesised in order to record their $^1$H–$^{171}$Yb NMR spectrum, which could potentially provide evidence for the persistence of Yb···alkene interactions in solution. Nevertheless, $^1$H NMR spectroscopy data for [27]$_2$ and [28]$_2$ indicated that these Yb(II) complexes were plagued by paramagnetic impurities. The molecular structures of [27]$_2$ and [28]$_2$ showed that the difference in steric bulk of the N(SiMe$_3$)$_2$ and N(SiMe$_2$H)$_2$ moieties can be a key factor towards the coordination of the alkene in these Yb(II), since X-ray data for [27]$_2$ clearly showed that the alkene moiety is coordinated onto Yb, whereas such interactions could not be detected in [28]$_2$.

In our attempts to coordinate terminal substituted alkene moieties onto calcium, it was shown that while mono-methyl substitution partially obstructs the coordination of the vinylic moiety, replacing both H$_{ext}$ hydrogens by Me groups prevents entirely coordination of the internal olefin onto the metal. These findings are relevant to catalysis, since for instance coordination of the C=C bond to calcium is one of the necessary steps in the catalytic cycle of intramolecular hydroamination of aminoalkenes. In light of these results, it can be suggested that substrates with terminal vinylidene moieties are unsuitable for this organic transformation. This can in particular be related to some experiments performed by Hill et al.. They showed that cyclisation of 2,2-diphenylhex-4-en-1-amine (Figure 5.26–b) promoted by homoleptic calcium complexes Ca[E(SiMe$_3$)$_2$]$_2$(THF)$_2$ (E = N, CH)
required forcing conditions (100 °C, 10–20 mol% precatalyst loadings) to achieve moderate conversions (60%), whereas conversion of 2,2-diphenylpent-4-en-1-amine (Figure 5.26–a) was achieved readily.\textsuperscript{45} Furthermore, experiments performed with the disubstituted aminoalkene 5-methyl-2,2-diphenylhex-4-en-1-amine (Figure 5.26–c) showed that the substrate was entirely unreacted after 24 h (20 mol% cat loading, 100 °C).\textsuperscript{45}

![Figure 5.26. Substrates tested in intramolecular hydroamination by Hill et al.\textsuperscript{45}](image)

Considering that alkenes proved to be suitable donors for calcium (and strontium), our subsequent efforts concentrated in evaluating the potential coordination of other π systems such as arenes, alkyne or arenes onto calcium. These results will be discussed in Chapter 5.
4.8. References


Chapter 5: Calcium Fluorinated Aminoalkoxides
Supported by Pending Arene, Alkyne and Allene Groups
Chapter 6: Calcium fluorinated aminoalkoxides supported by pending arene, alkyne and allene groups

5.1. Introduction

5.1.1. Calcium-arene complexes

The interaction between alkaline-earth metals and charge-neutral arenes has been so far studied mostly using computational methods.\(^1\) It was determined that the electrostatic contact between Ca\(^{2+}\) and benzene rings is likely to have bond energies between 73.8 and 81.3 kcal mol\(^{-1}\) with Ca–C\(_{\text{arene}}\) (centroid) distances varying from 2.35 to 2.47 Å.\(^{1b,g,j,k}\) Nevertheless, experimental reports describing such interaction between these d\(^0\) oxophilic elements and π clouds of neutral arene moieties are still very scarce, and literature data are restricted to a limited number of complexes. Niemeyer \textit{et al.} showed that Ca⋯C\(_{\text{arene}}\) η\(^6\) interactions can be observed in Ae (Ae = Ca, Sr, Ba) complexes supported by aryl-substituted triazenide ligands (P in Figure 6.1).\(^{2a}\) Recently, Westerhausen \textit{et al.} reported that the homoleptic calcium bis[N-(2,6-diisopropylphenyl)-N’-(2-pyridylmethyl)pivalamidinate] (Q in Figure 6.1) and the related calcium bis[N-diisopropylphenyl-N’-(8-quinolyl)pivalamidinate] (R in Figure 6.1) also display η\(^6\) interactions between the metal centres and Dipp units (Dipp = 2,6-diPr\(_2\)-C\(_6\)H\(_3\), Figure 6.1).\(^{2b,c}\) Ruhlandt-Senge \textit{et al.} reported that heterobimetallic ion-pairs of the type [Ca\(_2\)Odpp\(_3\)]\(^+\)·[LnOdpp\(_4\)]\(^-\) (Ln = Nd, Ho, Yb; Odpp = 2,6-diphenylphenolate) feature η\(^6\) interactions between the aryl rings and the calcium centres.\(^3\) The neutral [Ca\(_2\)Odpp\(_4\)](THF)\(_2\) was also reported to depict η\(^1\) and η\(^2\) Ca–C\(_{\text{aryl}}\) interactions. Other complexes that feature π interactions between an aryl rings and calcium include [ICA-η\(^1\),η\(^6\)-(Mes\(_2\)Cu)]\(_4\) reported by Westerhausen \textit{et al.}\(^4\) and [[DippNacNac]CaN(η\(^2\)-C\(_6\)H\(_3\))Ph](THF) by Hill \textit{et al.}\(^5\)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure61}
\caption{Known calcium complexes featuring η\(^6\) coordination of aryl rings.}
\end{figure}
5.1.2. Calcium-alkyne complexes

One of the earliest achievements in the synthesis of alkaline-earth complexes containing an Ae–C\(_\pi\) bond is the intermolecular coordination of 1,4-bis(trimethylsilyl)buta-1,3-diyne to [CaCp\(^*\)_2] reported by Hanusa et al.\(^6\) The interaction between Ae elements and C≡C triple bonds has been mostly observed in acetylides of the type \([\{LX\}Ae(C≡C_R)]_2(THF)_n\) (Ae = Ca, Sr, Ba; LX = Cp\(^{iPr}\), DippNacNac; R = Me, \(^t\)Bu, \(^i\)Bu, Ph, and SiPh\(_3\)); n = 0, 2).\(^7,8,9,10,11,12\) In these complexes, three types of coordination patterns were observed between the alkyne and the metal atoms: symmetrical (Figure 6.2–a), “side-on” (Figure 6.2–b) interactions, and “completely side-on” (Figure 6.2–c). In dinuclear Ae symmetric acetylides, the two Ae–C\(_\alpha–\pi\)C\(_\beta\) angles (\(\theta\) and \(\phi\)) are equal and there is no contribution of the \(\pi\) clouds towards the coordination sphere of the metal centre. On the other hand, in dinuclear Ae “side-on” acetylides, the C≡C moieties are tilted towards the opposite metal centre (Ae’) (\(\theta > \phi\)). In “completely side-on” Ae acetylides, the difference between \(\theta\) and \(\phi\) is close to 90°. Hill et al. proposed that the large difference between \(\theta\) and \(\phi\) may enhance dissipation of a negative charge over C\(_\alpha\) and C\(_\beta\) and can be considered as indicative of \(\pi\) donation towards the Ae centre.\(^8\) In this section, only completely side-on” Ae acetylides will be considered as examples of complexes involving “significant” Ae···C\(_\pi\) interactions.

![Figure 6.2](image)

Figure 6.2. Representation of symmetric, “side-on” Ae and “completely side-on”\([\{LX\}Ae(C≡CR)]_2\) acetylides (Ae = Ca, Sr, Ba; \{LX\} = monoanionic ancillary ligand).

Several examples of “completely side-on” calcium-alkyne complexes are known (Figure 6.3). Hill et al. reported the synthesis of \([\{DippNacNac\}Ca(C≡C–R)]_2\) (R = Ph, \(^p\)-tol) and \([\{DippNacNac\}Ca(C≡C–E)]_2\) (E = OMe, OPh, NMe\(_2\)).\(^8,10,11,12\) Similarly, Roesky et al. described the molecular structure of the THF-solvated analogue \([\{DippNacNac\}Ca(C≡C–Ph)]_2(THF)_2\).\(^10\) More

\(^*\) Cp\(^{Pr}\) = (\(^{Pr}\))\(_4\)C\(_5\)H
recently, Etienne and co-workers illustrated that a similar arrangement can also be found in \([\{\text{T}_{\text{ind}}\}^\text{F} \text{CaC}≡\text{C–Ph}\}]_2\) (\(\text{T}_{\text{ind}}^\text{F} = \text{fluorinated tris(indazolyl)}\text{borate}\)).\(^\text{13}\) Note that a single example of a “completely side-on” barium-alkyne is known and was reported by Westerhausen \(\text{et al.}\) using a phosphanide-based ligand.\(^\text{14}\)

**Figure 6.3.** Synthesised calcium acetylides featuring Ae···\(\pi\) contacts.\(^\text{8,10,11,12,13}\)

### 5.1.3. Calcium-allene complexes

The coordination chemistry of allenes has been mostly explored with transition metals\(^\text{15}\) and more prominently with gold.\(^\text{16}\) With oxophilic centres (e.g. in trivalent lanthanidocenes), metal–allene complexes have been postulated as intermediates in the intramolecular hydroamination reactions of aminoallenes.\(^\text{17}\) Nevertheless, to date, there is no report describing the interaction of heavy alkaline-earth elements with allenes. Furthermore, aminoallene hydroamination promoted by Ae complexes has not been yet disclosed.

### 5.2. Towards calcium-aryl complexes

#### 5.2.1. Synthetic strategy

In order to achieve intramolecular coordination of an aryl ring onto an Ae centre, our ligand design followed the model used for \(\{\text{RO}^1\}\)H,\(^\dagger\) but the donating OMe group was now replaced by a phenyl moiety. The synthesis of \(\{\text{RO}^{21}\}\)H was performed in a single step by quantitative reaction of the commercially available \(N\)-methyl-2-phenylethanamine with 2,2-bis(trifluoromethyl)oxirane. \(\{\text{RO}^{21}\}\)H is a colourless oil and was characterised by NMR spectroscopy, mass spectrometry and combustion analysis. Subsequently, a solution of \(\{\text{RO}^{21}\}\)H in \(\text{Et}_2\text{O}\) was added dropwise to an excess (1.3 equiv) of

\(^\dagger\) The analogue of \(\{\text{RO}^1\}\)H, where an \(^1\text{Pr}\) group is bounded to the nitrogen atom instead of a Me group, was not attempted at this point due to the fact that \(N\)-phenethylpropan-2-amine was not commercially available.
Ca[N(SiMe$_2$H)$_2$]$_2$(THF) in Et$_2$O at $-78 \, ^\circ \text{C}$ to yield [31]$_2$ (25% unoptimised synthesis) according to Scheme 6.1.

**Scheme 6.1.** Synthesis of {RO$^{21}$}H and [{RO$^{21}$}CaN(SiMe$_2$H)$_2$]$_2$(THF)$_2$ ([31]$_2$).

The product was analysed by $^1$H NMR spectroscopy in benzene-$d_6$ at room temperature (Figure 6.4). The presence of THF was detected in an approximately 1:1 ratio with respect to the calcium complex. Furthermore, the resonances for the CH$_2$ moieties from THF at $\delta$$_{1H}$ 1.35 and 3.64 ppm were slightly different from the ones from “free” THF ($\delta$$_{1H}$ 1.40 and 3.57 ppm), indicating that THF might be coordinated to the calcium atom.

**Figure 6.4.** $^1$H NMR spectrum (500.13 MHz) of [{RO$^{21}$}CaN(SiMe$_2$H)$_2$]$_2$(THF)$_2$ ([31]$_2$) recorded in benzene-$d_6$ at 298 K.

By contrast, 2D DOSY NMR showed that there was a substantial difference between the diffusion coefficients for the CH$_2$ resonances from THF (avg. 1.40·10$^{-9}$ m$^2$ s$^{-1}$) and the other resonances from...
the metal complex (avg 6.90×10^{-10} \text{ m}^2 \text{s}^{-1}). This implied that either the solvent molecules are not coordinated to the metal centre in solution, or that they are engaged in a fast coordination-decoordination exchange which cannot be detected on the NMR time-scale.\(^\ddagger\) The other resonances from the \(^1\text{H}\) NMR spectrum of [31]$_2$ are consistent with the formulated structure and are well resolved, except for the broad, overlapping methylene resonances (CH$_2$(CF$_3$)$_2$, NCH$_2$ and CH$_2$Ph) likely reflecting fluxionality of the metallacycle. The \(^{19}\text{F}\) NMR spectrum of [31]$_2$ contains two main broadened resonances in a 1.44:1 ratio: a large broad singlet at $\delta_{19\text{F}}$ = 75.77 ppm and two merged broad singlets between $\delta_{19\text{F}}$ = 76.54 and −77.18 ppm. Low temperature NMR experiments were not performed for this complex, but they are certainly needed in order to obtain better resolved \(^{19}\text{F}\) resonances.

Our assumption that THF was coordinated to the calcium centre in [31]$_2$ was confirmed by single-crystal X-ray diffraction studies. \([\{\text{RO}^{21}\}\text{CaN(SiMe}_2\text{H)}_2\}_2\] crystallised as a dimeric THF adduct from a cold pentane solution. The obtained molecular structure is illustrated in Figure 6.5. Unfortunately, as anticipated (competitive) coordination of THF onto the calcium atoms prevents the coordination of the arene onto Ca, as expressed by the long Ca···C$_\text{phenyl}$ distances (5.84–8.07 Å) which exceed the cut-off limit of 3.13 Å for Ca···C$_\pi$ interactions.\(^\ddagger\)

\[\text{Figure 6.5. (left) ORTEP representation of the molecular structure of } \{\{\text{RO}^{21}\}\text{CaN(SiMe}_2\text{H)}_2\}_2\text{(THF)}_2 \text{([31]$_2$). Hydrogen atoms (except SiH) are omitted for clarity. Ellipsoids are drawn at the 50% probability level. (right) Schematic representation of [31]$_2$. Selected bond lengths (Å) and angles (°): Ca(1)–O(21) = 2.3247(18), Ca(1)–O(21)$^\ddagger$ = 2.3283(18), Ca(1)–O(11) = 2.391(2), Ca(1)–N(1) = 2.314(2), Ca(1)–N(32) = 2.654(2), Ca(1)–H(1) = 2.9495(364), Ca(1)–F(29) = 3.0015(19); Ca(1)–N(21)–Si(1) = 112.52(14), Ca(1)–N(1)–Si(2) = 118.89(14), Si(1)–N(1)–Si2 = 128.18(15); Torsion angles: Ca(1)–N(21)–Si(1)–H(1) = 0.1(1)°, Ca(1)–N(21)–Si(2)–H(2) = 7.2(1)°.}\]

Aside from THF donors, the coordination sphere of the formally 7-coordinated calcium ions is filled by heteroatoms from the fluorinated aminoalkoxo ligands (N,O). Furthermore, Ca···F–C and β-Si–H···Ca secondary interactions also have a stabilising effect as depicted by the short Ca···F–C (3.001 (1) Å), Ca···H (2.95(3) Å), and Ca···Si (3.345(1) Å) distances and narrow Ca–N–Si angles (112.52(14)° and 118.89(14)°).

These observations are not unexpected in light of DFT calculations performed on this structure. After optimisation of a THF-free structure of [31]$_2$ using the wb97xd density functional, it was determined that the aryl rings are likely to coordinate in a reduced hapticity (towards $\eta^1$) fashion according to Figure 6.6.

![Figure 6.6. Optimised structure of THF-free $\{[RO^{21}]CaN(SiMe_2H)_2\}_2$ ([31]$_2$) using the wb97xd density functional.](image)

Nevertheless, addition of 2 equiv THF in this structure (with concomitant decoordination of the arene rings from the Ca atoms) is energetically-favoured with a $\Delta G$ value of $-21.3$ kcal mol$^{-1}$ ($\Delta E = -47.3$ kcal mol$^{-1}$). This comes in contrast with the behaviour of $\{[RO^{11}]CaN(SiMe_2H)_2\}_2$ ([25]$_2$) in which addition of THF is endergonic with $\Delta G$ values equal to 3.8, 3.7, 4.5 kcal mol$^{-1}$ using the BPE1BPE, B3PW91, and wb97xd functionals, respectively.

Donation from the THF molecules to calcium is certainly the most intriguing aspect of this molecular structure considering the fact that all attempts to crystallise a THF-adduct of the calcium-alkene complex [25]$_2$ were unsuccessful (see Chapter 4). This comes as a surprise since aryl groups are considered to be better donors than olefins. Therefore, we assume that a possible explanation can be related to steric effects; that is, the C$_6$H$_5$ groups combined with their side-arm are too bulky to coordinate to calcium, and that the THF molecule from the starting material Ca[N(SiMe$_2$H)$_2$]$_2$(THF)

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§ These theoretical calculations were performed in a joint collaboration with Dr. Chiara Dinoi (ANR GreenLAkE, ANR-11-BS07-0009)
fills the coordination sphere of the metal centres. If so, it would make sense to employ a THF-free calcium precursor, i.e Ca[N(SiMe2H)2]2, to enforce coordination of the arene rings (vide infra).

A second possibility is linked to the size of the alkyl group bonded to the nitrogen atom from the ancillary ligand. It is possible that due to their small size, methyl groups are unable to shield the metal centre from the binding of potential THF donors. On the other hand, in [{RO}1CaN(SiMe2H)2]2 ([13]2), one O_	ext{ether} donor is already present in the ligand side-arm and coordinates to the metal centre. Note that no THF molecule was coordinated to calcium in [13]2, although this can be justified by the fact that intramolecular coordination of O_	ext{ether} heteroatoms is favoured entropically. Perhaps the influence of the alkyl group bonded to N_	ext{amine} can be best observed in the Ae-olefin complexes [25]2 and [26]2, which are obtained free of THF despite having used the THF-containing Ca[N(SiMe2H)2]2(THF) as a starting material (Figure 6.7). It is possible that in this case the 'Pr group, due to its large size, it provides steric protection to the metal centre and precludes the coordination of donating solvents. Further experiments were performed to test this hypothesis (vide infra 5.2.2.2).

![Figure 6.7](image)

**Figure 6.7.** Representation of the coordination sphere in [13]2, [25]2, [30]2 and [31]2 highlighting the potential influence of the N-alkyl group on the coordination of O_	ext{ether}.

### 5.2.2. The case of trinuclear calcium complexes

#### 5.2.2.1. Characterisation of [{RO}21]CaN(SiMe2H)2]2(µ-Ca[N(SiMe2H)2]2) (32)

In order to assess whether THF contained in the starting material Ca[N(SiMe2H)2]2(THF) is responsible for the formation of the THF-adduct [31]2, the THF-free calcium precursor Ca[N(SiMe2H)2]2 was employed instead.19 The proteo-ligand {RO}21]H was reacted with Ca[N(SiMe2H)2]2 under reaction conditions identical to those for the synthesis of [31]2, according to Scheme 6.2.
Scheme 6.2. Attempted synthesis of the THF-free analogue of \([31]\). Synthesis of \([\{RO^{21}\}CaN(SiMe_2H)_2\]_2(\µCa[N(SiMe_2H)_2])_2\) (32).

Storage of a pentane solution of the crude reaction mixture at \(-30^\circ\mathrm{C}\) resulted in isolation of large amounts (62% yield) of single crystals suitable for X-ray diffraction. However, X-ray data indicated the unexpected formation of a trinuclear calcium complex, with two inequivalent \([RO^{21}\]CaN(SiMe_2H)_2 moieties that are bridged by a central Ca[N(SiMe_2H)_2]_2 moiety (Figure 6.8). Therefore, the formula that best describes this calcium complex is \([\{RO^{21}\}CaN(SiMe_2H)_2\]_2(\µCa[N(SiMe_2H)_2])_2\) (32).

Although the two terminal calcium atoms (Ca(2) and Ca(3)) are crystallographically inequivalent, they share some similarities: (a) both of them are formally 6-coordinate and lie in a distorted octahedral geometry; (b) the phenyl groups from the ancillary ligands are oriented away from the metallic centres; (c) the Si–H moieties from the central N(SiMe_2H)_2 groups have a substantial contribution towards the coordination saturation of the calcium atoms, as evidenced by short Ca(2,3)···H (Ca(2)···H(3Si) = 2.39(2) Å; Ca(3)···H(3Si) = 2.45(2) Å) and Ca(2,3)···Si distances (Ca(2)···Si(3) = 3.0859(7) Å; Ca(3)···Si(6) = 3.09(6) Å) and extremely narrow Ca–N–Si angles (Ca(2)–N(2)–Si(3) = 91.87(6) °; Ca(3)–N(3)–Si(7) = 92.28(7) °), and (d) no Ca(2,3)···F–C secondary interactions contribute to the coordination sphere of these two metals. On the other hand, the geometric arrangement around the central Ca(1) is different. In addition to coordination of heteroatoms (O, N), the coordination sphere of Ca(1) is filled by three Ca···F–C secondary interactions (Ca(1)–F(16) = 2.7401(14) Å, Ca(1)–F(36) = 3.0806(13) Å, Ca(1)–F(40) = 2.9492(15) Å).
Å). The heteroatoms around Ca(3) are fairly co-planar as expressed by the small value of the torsion angle N(29)–N(4)–N(3)–O(2) (14.40(4)°). A similar geometric arrangement was reported for strontium by Lappert et al. in the polymeric \(^{\text{trans}}\text{Sr}(N(SiMe}_3)_2\text{)}_2(\mu-1,4\text{-dioxane})_x^{,20}\) in this complex, the strontium atom lies in a square planar environment** formed by the nitrogen atoms from the amido moieties and oxygen atoms from the dioxane molecules.

Concerning the solution behaviour of 32 in benzene-\(d_6\) the first issue of interest was to determine whether or not the trinuclear arrangement of this calcium complex is retained. For this, 2D DOSY NMR spectroscopy was employed. Using the formula weight analysis described in Chapter 4 (see 4.3.2), the molecular weight of 32 in solution was estimated to 1201 g mol\(^{-1}\) which is very close to the theoretical value of 1278 g mol\(^{-1}\). These data indicate that 32 remains trinuclear in solution. Furthermore, this information was also validated using the PGSE method with \(r_{\text{H,PGSE}}\) (6.13 Å) being close to \(r_{\text{H,X-Ray}}\) (7.42 Å) (see Annexure G for details).

** This geometric arrangement was proposed taking into consideration only contributions from heteroatoms (N,O) and ignoring the potential influence of C–H···Sr agostic interactions.
The $^1$H NMR spectrum of $\text{[[(RO)}_2\text{CaN(SiMe}_2\text{H)}_2\text{]}_2 \ (\mu-\text{Ca}[\text{N(SiMe}_2\text{H)}_2\text{]}_2 \ (32)}$ in benzene-$d_6$ contains broad resonances at room temperature. By performing variable temperature NMR experiments in toluene-$d_8$, it was determined that the resonances are somewhat better resolved at 243 K (Figure 6.9). At this temperature, multiple resonances for the Si$CH_3$ moieties are observed between $\delta_{\text{H}}$ 0.29 and 0.72 ppm. Four resonances for the Si$H$ protons are located between $\delta_{\text{H}}$ 4.60 and 5.05 ppm. Furthermore two singlets corresponding to the N$CH_3$ moieties were identified at $\delta_{\text{H}}$ 2.31 and 2.36 ppm in an approximate 2:1 ratio. The $^{19}$F NMR spectrum of 32 recorded in benzene-$d_6$ at 298 K depicts a complicated arrangement with multiple quadruplet resonances corresponding to the CF$_3$ groups. These observations are in contrast with the molecular structure of 32 and suggest the existence of a mixture of isomers of 32 in solution and make the assignment of resonances to a given species difficult.

![Figure 6.9. $^1$H NMR (400.13 MHz) spectrum of $\text{[[(RO)}_2\text{CaN(SiMe}_2\text{H)}_2\text{]}_2 \ (\mu-\text{Ca}[\text{N(SiMe}_2\text{H)}_2\text{]}_2 \ (32)}$ in toluene-$d_8$ at 243 K.](image)

The presence of $\beta$-Si–H···Ca agostic interactions in solution was difficult to assess from the $^1$H NMR spectrum of 32 because the relevant $^{29}$Si satellites overlap with the various resonances for Si$H$ protons. Nevertheless the information could be obtained by performing a gated 2D $^1$H–$^{29}$Si HMQC experiment, which enabled the determination of the various $^1J_{\text{Si-H}}$ coupling constants (Figure 6.10).
Figure 6.10. $^1$H–$^{29}$Si gHMQC spectrum (400.13, 79.49 MHz) of \([\text{RO}_{21}^1\text{CaN(SiMe}_2\text{H})_2]_2(\mu-\text{Ca[HN(SiMe}_2\text{H})_2])\) (32) in benzene-$d_6$ at 298 K.

The suitability of this NMR experiment was recently demonstrated to determine the $^1J_{\text{Si-H}}$ in the homoleptic Ca[N(SiMe$_2$H)$_2$]$_2$. In the case of 32, the $^1$H–$^{29}$Si gHMQC spectrum reveals the presence of four different SiH moieties with $^1J_{\text{Si-H}}$ coupling constants ranging from 161 Hz (weak agostic interactions) to 132 Hz (very strong agostic interactions). These values are comparable to those observed in Ca[N(SiMe$_2$H)$_2$]$_2$ ($^1J_{\text{Si-H}} = 122–152$ Hz). They indicate that some of the observed $\beta$-Si–H···Ca interactions seen in the solid state are retained in solution.

The formation of the trinuclear calcium complex 32 could not be anticipated. However, considering the fact that Ca[N(SiMe$_2$H)$_2$]$_2$ is trimeric, it may be possible that complex 32 is only a reaction intermediate formed due to incomplete reaction according to Scheme 6.3. In this hypothesis only the “terminal” Ca-amides reacted with the proteo-ligand \{RO$_{21}^1$\}H, whereas the internal core one remained intact.

Scheme 6.3. Putative incomplete protonolysis between Ca[N(SiMe$_2$H)$_2$]$_2$ and \{RO$_{21}^1$\}H.
In order to test this assumption, 32 was reacted with one equiv of RO\textsuperscript{21}H in Et\textsubscript{2}O to observe whether [{RO\textsuperscript{21}}CaN(SiMe\textsubscript{2}H)\textsubscript{2}]\textsubscript{2} could be formed. However, only unidentifiable oils were obtained and we were unable to assess the identity of the resulting species.

5.2.2.2. Characterisation of [{RO\textsuperscript{22}}CaN(SiMe\textsubscript{2}H)\textsubscript{2}]\textsubscript{2}(\mu-Ca[N(SiMe\textsubscript{2}H)\textsubscript{2}]) (33)

A different strategy to enforce the coordination of the aryl moiety to calcium consisted in using a bulky alkyl moiety bonded to the N\textsubscript{amine} atom from the ancillary ligand. As previously discussed (vide supra), the difference in steric bulk between the Me and \textsuperscript{1}Pr group can be a decisive factor when it comes to coordination of THF (vide supra–Figure 6.7). Hence, our synthetic strategy involved the design of a new proteo-ligand using the pattern of {RO\textsuperscript{21}}H, but in which the Me group is replaced by a bulkier \textsuperscript{1}Pr moiety, namely{RO\textsuperscript{22}}H, and then to react it with Ca[N(SiMe\textsubscript{2}H)\textsubscript{2}]\textsubscript{2}(THF).

The synthesis of {RO\textsuperscript{22}}H was performed in two quantitative steps and involved first the reaction of the commercially available (2-bromoethyl)benzene with a large excess of \textsuperscript{1}PrNH\textsubscript{2}. Reaction of the obtained N-phenethylpropan-2-amine with 2,2-bis(trifluoromethyl)oxirane affords {RO\textsuperscript{22}}H as a colourless oil. The identity of this proteo-ligand is supported by NMR spectroscopy (\textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F). Subsequently, {RO\textsuperscript{22}}H was reacted with 1.3 equiv. of Ca[N(SiMe\textsubscript{2}H)\textsubscript{2}]\textsubscript{2}(THF) at –78 °C in Et\textsubscript{2}O, according to Scheme 6.4.

![Scheme 6.4. Synthesis of [{RO\textsuperscript{22}}CaN(SiMe\textsubscript{2}H)\textsubscript{2}]\textsubscript{2}(\mu-Ca[N(SiMe\textsubscript{2}H)\textsubscript{2}]) (33).](image)

After work-up, the crude mixture was recrystallised from a cold pentane solution at 4 °C. \textsuperscript{1}H NMR analysis in benzene-\textit{d}\textsubscript{6} of the resulting crystals indicated that the sample was partly hydrolysed as a significant amount of HN(SiMe\textsubscript{2}H)\textsubscript{2} was present. The rest of resonances are overlapped and broad
making signal attribution impossible. The remaining single crystals†† were analysed by X-ray diffractometry. The result was the formation of a trinuclear complex (Figure 6.11) very similar to \( \text{32, } [\text{(RO}^2\text{)}\text{CaN(SiMe}_2\text{H}_2\text{)}_2]_{\text{2}}(\mu-\text{Ca}[\text{N(SiMe}_2\text{H}_2\text{)}_2\text{]}_{\text{2}}) \) (\( \text{33} \)). The fact that this complex was crystallised free of THF molecules confirmed our hypothesis that the introduction of the larger 'Pr bonded onto the nitrogen atoms (instead of Me groups) shields the calcium atom from donor solvents. The molecular structure of \( \text{33} \) indicates that, as for \( \text{32} \), the phenyl rings are not coordinated to the calcium ions (Ca···C\text{arene} distances = 5.34–7.60 Å). Nevertheless, they have a different arrangement from that in \( \text{32} \), and seem to be folded in the direction of the metals. In \( \text{33} \), the three metals are inequivalent and feature different coordination patterns. The geometric arrangement around Ca(2) and Ca(3) is comparable to that for the terminal calcium atoms in \( \text{32} \) where \( \beta\text{-Si–H···Ca} \) agostic interactions play a large role in filling the coordination sphere of calcium. This was evidenced by the narrow Ca(2,3)···Si (3.11–3.21Å) and Ca(2,3)···H (2.46–2.75 Å) distances. The central calcium atom (Ca(1)) is supported by the two nitrogen atoms from amido moieties and two bridging O\text{alkoxide} atoms. In addition, the coordination sphere of Ca(1) in \( \text{33} \) is filled by two strong Ca···F–C secondary interactions (2.745(4) and 2.786(6) Å). This contrasts with the situation in \( \text{32} \), where three strong Ca···F–C secondary interactions were needed to ensure coordinative saturation of the central calcium atom.

Figure 6.11. (left) ORTEP representation of the molecular structure of \( [\text{(RO}^2\text{)}\text{CaN(SiMe}_2\text{H}_2\text{)}_2]_{\text{2}}(\mu-\text{Ca}[\text{N(SiMe}_2\text{H}_2\text{)}_2\text{]}_{\text{2}}) \) (\( \text{33} \)). Hydrogen atoms (except Si\text{H}) are omitted for clarity. Ellipsoids are drawn at the 50% probability level. (right) Schematic representation of \( \text{33} \). Selected bond lengths (Å) and angles (°):Ca(1)–O(53) = 2.282(4), Ca(1)–O(23) = 2.290(4), Ca(1)–N(66) = 2.464(5), Ca(1)–N(61) = 2.485(5), Ca(1)–F(52) = 2.745(4), Ca(1)–F(22) = 2.786(6), Ca(3)–O(53) = 2.307(4), Ca(3)–N(54) = 2.301(5), Ca(3)–N(66) = 2.509(5), Ca(3)–N(39) = 2.627(6), Ca(3)–H(6SI) = 2.46(6), Ca(3)–H(8SI) = 2.50(5), Ca(3)–H(4SI) = 2.75(5), Ca(2)–O(23) = 2.296(4), Ca(2)–N(24) = 2.300(6), Ca(2)–N(61) = 2.505(5), Ca(2)–N(9) = 2.621(5), Ca(2)–H(7SI) = 2.51(6), Ca(2)–H(5SI) = 2.57(6), Ca(2)–H(2SI) = 2.72(6); Ca(2)–N(24)–Si(1) = 127.5(3), Ca(2)–N(24)–Si(2) = 104.3(3), Ca(2)–N(61)–Si(5) = 93.8(2), Ca(2)–N(61)–Si(6) = 127.1(3), Ca(3)–N(54)–Si(3) = 125.5(3), Ca(3)–N(54)–Si(4) = 106.2(3), Ca(3)–N(66)–Si(7) = 125.3(2), Ca(3)–N(66)–Si(8) = 93.4(2), Si(1)–N(24)–Si(2) = 128.0(4), Si(3)–N(54)–Si(4) = 128.2(3), Si(5)–N(61)–Si(6) = 119.2(3), Si(7)–N(66)–Si(8) = 120.3(3).

†† Recrystallisation of \( \text{32} \) resulted in a small fraction of single crystals. No yield could be recorded for this reaction since after recording the \( ^1\text{H} \) and \( ^1\text{F} \) NMR spectra, the reaction vessel containing the crystalline material was exposed to air during sample preparation for X-ray analysis.
Normally, if the C₆H₅ groups were simply too bulky to coordinate to the metal centre in 33, then a geometric arrangement similar to that of \([\{RO^{34}\}CaN(SiMe₂H)₂]_2\) would have been expected \((see\ 4.6)\). The formation of complex 33 proves our earlier assumption that 32 was the product of an incomplete protonolysis reaction (Scheme 6.3) incorrect. Hence, considering that 32 and 33 both contain phenyl moieties in the ancillary ligands, it can be reasonably assumed that these Ph groups play a vital role in the construction of these trimetallic structures. For instance, one may assume that the synthesis of 32 and 33 can proceed via the desired Ca-aryl complexes which then further react with another equivalent of Ca[N(SiMe₂H)₂]₂(THF) to obtain the trinuclear species according to Scheme 6.5. In order to test this hypothesis, we propose the synthesis of \([\{RO^{32}\}CaN(SiMe₂H)₂]_2\) by reaction of \([\{RO^{22}\}Ca]^{11}\) with Ca[N(SiMe₂H)₂]₂(THF). Subsequently, we are aiming to react \([\{RO^{22}\}CaN(SiMe₂H)₂]_2\) with one equiv of Ca[N(SiMe₂H)₂]₂(THF) to observe whether this would lead to the formation of \([\{RO^{32}\}CaN(SiMe₂H)₂]_2(\mu-Ca[N(SiMe₂H)₂]₂)\).

**Scheme 6.5.** Possible formation of 32 and 33 via a Ca-aryl complex.

### 5.3. Calcium-alkyne complexes

Our strategy to coordinate an alkyne moiety to calcium is similar to that employed for the synthesis of calcium-olefin complex \([25]\)₂ and involves the placing of a –C≡C–Me moiety in the backbone of the fluoroalkohol proteo-ligand \{RO\}₃₂H.

The synthesis of \{RO\}₃₂H is closely related to that of \{RO\}₁₃H \((see\ 4.6)\). It involves the reaction of pent-3-yn-1-ol with of PPh₃, NBS and \(^3\)PrNH₂ to yield N-isopropylpent-3-yn-1-amine (~40%) using a modified Mitsunobu reaction.\(^{21}\) \{RO\}₃₂H is then obtained in high yields (~90%) by reacting N-isopropylpent-3-yn-1-amine with 2,2-bis(trifluoromethyl)oxirane. The identity of this ligand is supported by multinuclear NMR spectroscopy. \{RO\}₃₂H was then reacted with Ca[N(SiMe₂H)₂]₂(THF) to obtain the expected \([\{RO^{32}\}CaN(SiMe₂H)₂]_2\) \((\{34\})₂\) in 62% yield according to Scheme 6.6.

\(^{11}\) This calcium complex can be easily synthesised by reaction of two equiv of \{RO\}²₂H with Ca[N(SiMe₃)₂]₂.
Scheme 6.6. Synthesis of \([[\text{RO}]_{32}^2\text{CaN(SiMe}_2\text{H})_2]_2\) ([34]$_2$).

The $^1$H NMR spectrum of the isolated colourless solid in benzene-$d_6$ at room temperature indicates the formation of calcium complex in which the N(SiMe$_2$H)$_2$ moieties are present. As observed for [25]$_2$, the resonances are broad at 298 K; recording the $^1$H NMR spectrum at lower temperatures (193–283 K) in toluene-$d_8$ did not improve the quality of the spectrum. However, better results were obtained upon heating the sample in toluene-$d_8$ at 333 K (Figure 6.12). The $^{19}$F NMR spectrum of [34]$_2$ in toluene-$d_8$ at room temperature depicts multiple resonances corresponding to the CF$_3$ groups, which coalesce to a singlet resonances upon heating the sample at 333 K in toluene–$d_8$.

Figure 6.12. Stacked $^1$H NMR spectra (400.13 MHz) of \([[\text{RO}]_{32}^2\text{CaN(SiMe}_2\text{H})_2]_2\) ([34]$_2$): (top) recorded in toluene-$d_8$ at 333 K; (bottom) recorded in toluene-$d_8$ at 303 K.

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In an early attempt to synthesise a calcium-alkyne complex, an ancillary ligand containing a $-\text{C}≡\text{CH}$ moiety (\([[\text{OR}]_{31}]_\text{H}\)) was employed. Nevertheless, the $^1$H NMR data of the resulting calcium compound indicated the loss of the N(SiMe$_2$H)$_2$$^-$ amide, probably as a result of an acid-base reaction between the amido moiety and the acidic $-\text{C}≡\text{CH}$ proton ($pK_a \approx 25-26$).
Gratifyingly, $[34]_2$ recrystallised from a concentrated pentane solution at $-30 \, ^\circ C$. Its molecular structure (Figure 6.13) consists in a dinuclear calcium complex containing an inversion centre. The alkyne moieties are coordinated to the calcium atoms as illustrated by the short Ca⋯C\textsubscript{alkyne} contacts (Ca(1)–C(3) = 2.875(2) Å; Ca(1)–C(2) = 3.020(2) Å).

Figure 6.13. (left) ORTEP representation of the molecular structure of $[[\text{RO}_{32}]\text{CaN(SiMe}_2\text{H)}_2]_2$ ([34]$_2$). Hydrogen atoms (except SiH) are omitted for clarity. Ellipsoids are drawn at the 50% probability level. (right) Schematic representation of [34]$_2$. Selected bond lengths (Å) and angles (°): Ca(1)–O(20) = 2.305(1), Ca(1)–O(20)$^6$ = 2.364(1), Ca(1)–N(1) = 2.341(1), Ca(1)–N(6) = 2.618(1), Ca1–H1 = 2.65(3), Ca(1)–F(15) = 2.753(1), Ca(1)–C(3) = 2.875(2), Ca(1)–C(2) = 3.020(2), C(2)–C(3) = 1.199(3); Ca(1)–N(1)–Si(1) = 101.37(9), Ca(1)–N(1)–Si(2) = 131.6(1); Torsion angle Ca(1)–N(1)–Si(1)–H(1) = 0.6(11).

As for the calcium-olefin complex [25]$_2$, stronger interactions were observed between Ca$^{2+}$ and the internal carbons from the alkynyl moieties (Ca(1)–C(3)) compared to those formed between Ca$^{2+}$ and the external carbons (Ca(1)–C(2)). The Ca⋯C\textsubscript{alkyne} distances are shorter than the cut-off value for Ca⋯C\textsubscript{x} interactions (3.13 Å$^{32}$ and longer than those reported in other bridging calcium acetylides (2.53–2.82 Å$^{32}$). The coordination mode of the alkyne towards calcium in [34]$_2$ is unique (i.e. “non-acetylide”) and this complex represents the only “non-acetylide” example of a Ca–alkyne complex described to date. Compared to those in $[[\text{RO}_{13}]\text{CaN(SiMe}_2\text{H)}_2]_2$ (2.977(1) and 3.389(1) Å), the Ca⋯C\textsubscript{x} distances in [34]$_2$ are shorter, most probably due to the fact that the alkynes are better donors than alkenes. A schematic representation of [29]$_2$ and [34]$_2$ is illustrated in Figure 6.14.
The calcium ions in [34]2 are formally 7-coordinated and feature strong Ca···F–C secondary interactions (2.753(1) Å). Furthermore, β-Si–H···Ca agostic interactions also have a stabilising effect as illustrated by the short Ca(1)···H(1) (2.65(3) Å) and Ca(1)···Si(1) (3.134(8) Å) distances while the Ca(1)–N(1)–Si(1) angle is also very narrow (101.37(9) °). The pattern of Ca···F–C and β-Si–H···Ca secondary interactions in Ca···F–C in [34]2 differs from that in [29]2. For instance, the Ca···F–C interactions are more intense in [34]2 (2.753(1) Å) than in [29]2 (2.834(1) and 2.949(1) Å). Furthermore, in [34]2 the β-Si–H···Ca agostic interactions are dissymmetric as evidenced by the difference of the two Ca–N–Si angles (30.2 °), much larger than the discrepancies measured in [29]2 (6.66 and 11.52 °).

5.4. Towards calcium–allene complexes

Our strategy to synthesise a calcium complex featuring Ca···C_allene interactions is the same as that described for olefin and alkyne complexes [25]2 and [34]2 and involves grafting an allene onto the side-arm of the fluoroalkoxo ligand. For this, pent-3-yn-1-ol is reacted with CY2NH (1.8 equiv), (CH2O)₆ (2.5 equiv) and Cul (0.5 equiv) in a Crabbe reaction to yield penta-3,4-dien-1-ol. The resulting alcohol is then converted to N-isopropylpenta-3,4-dien-1-amine via a modified Mitsunobu reaction, in the presence of NBS, PPh₃, and PrNH₂. Reacting the synthesised secondary amine with 2,2-bis(trifluoromethyl)oxirane affords the desired proteo-ligand (RO¹⁴)H as a brown oil in a 20% overall yield. The synthetic procedure for (RO¹⁴)H is depicted in Scheme 6.7. The identity of this proteo-ligand is supported by NMR spectroscopy (¹H, ¹⁹F, ¹³C).
Scheme 6.7. Synthesis of \( \{RO^{4\text{I}}\}H \).

\( \{RO^{4\text{I}}\}H \) was reacted with \( \text{Ca}[\text{N(SiMe}_2\text{H)}_2]_2(\text{THF}) \) at \(-78^\circ C\). After work-up, a colourless solid was obtained. The \(^1\text{H} \) NMR spectrum of the crude mixture recorded in benzene-\( d_6 \) at room temperature indicates the presence of two sets of resonances (Figure 6.15—bottom). An overlap of this spectrum with that of \([34]_2 \) (recorded in identical conditions) clearly shows that one set of resonances belongs to the calcium-alkyne complex \( \{[RO^{3\text{I}}]_2\text{CaN(SiMe}_2\text{H)}_2\}_2 \). Since the second set of signals contains resonances which correspond to \( -\text{CH=CH=CH}_2 \), \(^1\text{Pr}, \) and \( \text{N(SiMe}_2\text{H)}_2^- \) moieties, it can be assumed that they belong to the putative \( \{[RO^{4\text{I}}]_2\text{CaN(SiMe}_2\text{H)}_2\}_2 \) (\([35]_2 \)).

Figure 6.15. Stacked \(^1\text{H} \) NMR spectra (400.13 MHz) for the crude product resulting from the reaction of \( \text{Ca}[\text{N(SiMe}_2\text{H)}_2]_2(\text{THF}) \) and \( \{RO^{4\text{I}}\}H \) (i.e. a mixture of \([34]_2 \) and possibly \([35]_2 \)):
- (bottom) recorded in benzene-\( d_6 \) at 298 K;
- (top) recorded in benzene-\( d_6 \) at 298 K after 12 hours.
Recording the $^1$H NMR spectrum after a further 12 h displayed only the resonances of $[34]_2$, as seen in Figure 6.15–top. This suggests that, at ambient temperature, $[35]_2$ isomerises to $[34]_2$ via a 1,3-hydride shift according to Scheme 6.8.

![Scheme 6.8. Postulated isomerisation from $[35]_2$ to $[34]_2$.](image)

Even though the isomerisation reaction of alkynes to allenes is well documented, reports describing the conversion of allenes to alkynes are scarce. Alkenes are often postulated as intermediates in the base-catalysed (KOH, NaNH$_2$, alkali-metal alkoxides in alcohols) isomerisation of alkenes. Prop-1-yne can be converted to propa-1,2-diene in the presence of catalytic CaH$_2$. Very recently, Mashima et al. reported that $[[N^\text{N}]\text{MgCH}_2\text{Ph}]_2$ ($[N^\text{N}]\text{H} = N^N\text{-}(1,2\text{-diphenylethyl})\text{-}N^2,N^2$-dimethylethane-1,2-diamine) can catalyse the isomerisation reaction of 3-phenyl-1-propyne to phenyllallene, which is then further isomerised to 1-phenyl-1-propyne.

### 5.5. Concluding remarks

Our efforts to coordinate $\pi$ systems such as arenes, alkynes or allenes to calcium in heteroleptic complexes of type $[(\text{RO})\text{CaN(SiMe}_2\text{H})_2]_2$ using fluorinated aminoalkoxo ligands, were illustrated.

It was shown that coordination of tethered aryl groups to calcium is prevented by coordination of the THF donors from the precursor $\text{Ca[N(SiMe}_2\text{H})_2]_2\text{(THF)}$, resulting with the formation of the THF adduct $[31]_2$. Subsequent attempts to use the THF-free $\text{Ca[N(SiMe}_2\text{H})_2]_2$ did not form the expected calcium-aryl complex, but instead yielded the trinuclear complex $32$. The molecular structure of $32$ features heavily distorted geometries around the terminal calcium atoms and indicates that $\beta$-$\text{Si-H}\cdots\text{Ca}$ agostic interactions are pivotal towards the stability of these species. The $^1J_{\text{Si-H}}$ coupling constants (132, 145 and 161 Hz) for $32$ were determined from a 2D HMQC $^1$H–$^{29}$Si spectrum and indicate that some $\beta$-$\text{Si-H}\cdots\text{Ca}$ interactions also persist in solution. DOSY NMR experiments showed that $32$ remains trinuclear in solution. Increasing the size of the alkyl group bonded to the $N_{\text{amine}}$ atom
from the ancillary ligand shields the metal centre from THF donors, and the reaction of \{RO^{22}\}_2H with Ca[N(SiMe_2H)_2]_2(THF) also results in the formation of a trinuclear calcium complex, 33. In order to answer the question regarding the formation of trinuclear complexes 32 and 33 additional work is required. For this, a useful experiment would be the reaction between the homoleptic calcium complex \{[RO^{31}]_2Ca\} with one equiv Ca[N(SiMe_2H)_2]_2(THF) to determine whether it leads to the formation 32.

Internal alkynes can also coordinate to calcium, as depicted by the molecular structure of \{[RO^{32}]CaN(SiMe_2H)_2\} \((34)_2\). The coordination mode of the alkyne moiety towards calcium is similar to the one found in \([25]_2\) and this interaction can be best described as a $\eta^2$ coordination. This complex represents the only example of a “non-acetylide” calcium complex featuring Ca···C_{alkyne} interactions. Furthermore this complex represents another example in which the calcium centre is stabilised by Ca···C_n, Ca···F–C, and β-Si–H···Ca secondary interactions.

Allene coordination to calcium was also attempted, however preliminary data indicate that Ca···allene species are unstable at room temperature and isomerise to alkyne complexes via a 1,3-hydride shift. Further NMR experiments are needed to establish the exact conditions to prevent this isomerisation reaction. The isolation and crystallisation of this calcium-allene complex certainly remains a very attractive prospect.
5.6. References


Experimental Part
Experimental Part

General procedures

All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glove-box (Jacomex; O₂ < 1 ppm, H₂O < 5 ppm) for catalyst loading. CaI₂ (Aldrich, 99.999% anhydrous beads), SrI₂ (Aldrich, 99.99% anhydrous beads), BaI₂ (Aldrich, 99.995% anhydrous beads), 2,2-bis(trifluoromethyl)oxirane (Apollo Scientific), 2-methoxy-N-methylethanamine (Aldrich), 1-aza-12-crown-4 (Alfa Aesar), N-methyl-2-phenylethanamine (Aldrich), isopropylamine (Acros), PPh₃ (Aldrich), NBS (Aldrich) and HPPh₂ (Strem Chemicals) were used as received. HN(SiMe₃)₂ (Acros) and HN(SiMe₂H)₂ (ABCR) were dried over CaH₂ and distilled prior to use. Styrene was dried and distilled over CaH₂ and stored over 3 Å molecular sieves. The compounds \{RO\}²H, Ca[N(SiMe₃)₂]₂, Sr[N(SiMe₃)₂]₂ (THF), Sr[N(SiMe₃)₂]₂ (THF)₂/₃, Ca[N(SiMe₃)₂]₂, Sr[N(SiMe₃)₂]₂ (THF)₂, Yb[N(SiMe₃)₂]₂(THF)₂, [H(OEt₂)]₂⁻[H₂N{(B(C₆F₅)₃)}₂]⁺, N-isopropylbut-3-en-1-amine, and di(but-3-en-1-yl)amine were prepared following literature protocols. [{T_{ind}}F]CaN(SiMe₃)₂ and [{T_{ind}}F]SrN(SiMe₃)₂ were synthesized by Dr. Nuria Romero and provided by Prof. Michel Etienne and Dr. Chiara Dinoi as part of a joint project (ANR-11-BS07-0009).

Solvents (THF, Et₂O, CH₂Cl₂, pentane and toluene) were purified and dried (water contents all below 10 ppm) over alumina columns (MBraun SPS). THF was further distilled under argon from sodium mirror/benzophenone ketyl prior to use. All deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 3 Å molecular sieves and were thoroughly degassed by several freeze-thaw-vacuum cycles.

NMR spectra were recorded on a Bruker spectrometer Avance III 400 MHz equipped with a BBOF pulsed field-gradient probe or a Bruker spectrometer Avance 500 MHz equipped with a dual pulse field gradient probehead. All ¹H and ¹³C chemical shifts were determined using residual signals of the deuterated solvents and were calibrated vs. SiMe₄ (δ 0 ppm). ²⁹Si{¹H} chemical shifts were determined against Si(Si(CH₃)₃)₄. ¹⁹F{¹H} chemical shifts were determined by external reference to an aqueous solution of NaBF₄. ¹¹B chemical shifts were determined against BF₃·Et₂O. Coupling constants are given in Hertz.

Assignment of the signals was carried out using 1D (¹H, ¹³C{¹H}) and 2D (COSY, edited HSQC and HMBC) NMR experiments. NOESY spectra were recorded using a 800ms mixing time. ¹H,¹⁵N HMQC spectra were recorded using different coupling constants from 4 to 16 Hz. PGSE NMR
Experiments were carried out using a bipolar gradient pulse stimulated echo sequence. Each experiment was performed on a 0.1 M solution at 298 K using a spectral width of 4807 Hz, a 90° pulse width of 11.5 µs, a diffusion delay time of 0.05 s, and a total diffusion-encoding pulse width of 0.0016 s. The diffusion encoding pulse strength was arrayed from 0 to 35 G·cm⁻² over 12 or 16 increments with 4 dummy scans and 8 scans per increment.

X-ray diffraction data were collected at 150 K using a Bruker APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A combination ω and Φ scans was carried out to obtain at least a unique data set. The crystal structures were solved by direct methods, and remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares based on $F^2$ (programs SIR97 and SHELXL-97). The SiH atoms could be found from the Fourier difference analysis. Carbon-, oxygen-, and nitrogen-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom contributions were calculated, but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance.

Elemental analyses were performed on a Carlo Erba 1108 Elemental Analyzer instrument at the London Metropolitan University by Stephen Boyer and were the average of a minimum of two independent measurements. ESI mass spectra were recorded on a Bruker MicrOTOF-Q II spectrometer with a QqoaTOF geometry. FTIR spectra were recorded between 400 and 4000 cm⁻¹ as nujol mulls in KBr plates on a Shimadzu IRAffinity-1 spectrometer.

**Syntheses of secondary amines**

The secondary amines employed in this study were obtained following two synthetic methods:

*Method A (starting from alkyl bromides):* Adapting from literature procedures, a mixture of 20 equiv of PrNH₂ and 1 equiv of the appropriate alkyl bromide (typically 10 mmol) was heated at 50 °C overnight forming a white precipitate. Then, H₂O (20 mL) was added to the reaction mixture. After separation of the two layers, the organic fraction was acidified by addition of aqueous HCl 5% until pH = 3. The two layers were separated and the aqueous phase was back-extracted with Et₂O (2 × 100 mL). The aqueous phase was then neutralised by slow addition of concentrated aqueous NaOH until pH = 12. To this solution, Et₂O (100 mL) was then added. The organic phase was separated and the aqueous phase was again extracted with Et₂O (3 × 50 mL). The combined organic layers were dried on MgSO₄ for 2 h. Removal of the solvent allowed the isolation of the secondary amine which was used without further purification.
Experimental Part

**Method B (starting from alcohols):** Adapting from literature procedures, the appropriate alcohol (typically 25 mmol, 1 equiv) was mixed with PPh₃ (1 equiv) in dry THF (10 mL). After cooling the solution at –18 °C, NBS (1 equiv) was added over a period of 1 min. The reaction mixture was stirred at this temperature for 5 min. iPrNH₂ (2.4 equiv) was then added with a syringe and stirring was continued at –18 °C for another 10 min. The cold bath was then removed and the reaction mixture was heated to reflux (80 °C) for 1 h. Most of the resulting PPh₃=O and succinimide precipitated by adding pentane (50 mL). After filtration, the mother liquor was kept and the precipitate was washed with pentane (3 × 25 mL) and pentane:Et₂O (10 mL of a 5:1 v/v mixture). The liquid fractions were then combined, concentrated and dried over MgSO₄. From this point, the acidic work-up described in Method A was employed to isolate the secondary amine. The amine was used without further purification.

**N-phenethylpropan-2-amine** Method A was used (91% yield). ¹H NMR (benzene-d₆, 400.13 MHz, 298 K): δ 7.19–7.14 (m, 2H, m-C₆H₅), 7.13–7.09 (m, 1H, p-C₆H₅), 7.09–7.05 (m, 2H, o-C₆H₅), 2.75–2.70 (m, 2H, NCH₂CH₂), 2.66–2.56 (overlapping m, 3H, NCH₂CH₂ and CH(CH₃)₂), 0.92 (d, 6H, J₃H-H = 6.2 Hz, CH(CH₃)₂), 0.87 (br s, 1H, NH) ppm.

**N-isopropylpent-3-en-1-amine** Method B was used (56% yield). ¹H NMR (benzene-d₆, 400.13 MHz, 298 K): δ 2.69–2.57 (overlapping m, 3H, NC₃H₂CH₂, and C₆H₁₃(CH₃)₂), 2.13–2.01 (m, 2H, NCH₂CH₂), 1.54 (t, 3H, J₂H-H = 2.6 Hz, C=CHCH₃), 0.93 (d, 6H, J₃H-H = 6.2 Hz, CH(CH₃)₂), 0.89 (br s, 1H, NH) ppm.

**N-isopropylpenta-3,4-dien-1-amine** Method B was used (38% yield). ¹H NMR (benzene-d₆, 400.13 MHz, 298 K): δ 5.08 (quint, 1H, J₃H-H = 6.8 Hz, H₂C=C=CH₂), 4.63–4.57 (m, 2H, H₂C=C=CH₂), 2.69–2.49 (overlapping m, 3H, NCH₂CH₂, and CH(CH₃)₂), 2.13–2.01 (m, 2H, NCH₂CH₂), 0.95 (d, 6H, J₃H-H = 6.2 Hz, CH(CH₃)₂), 0.79 (br s, 1H, NH) ppm.
Experimental Part

Syntheses of proteo-ligands

**{RO}^1H**: A solution of 2-methoxy-N-methylethanamine (3.53 g, 40 mmol) was added dropwise to a solution of 2,2-bis(trifluoromethyl)oxirane (6.78 g, 37.6 mmol) in Et₂O (100 mL) at 0 °C. The reaction mixture was warmed slowly to room temperature and stirred for two days. The resulting solution was concentrated to ca. 80 mL and extracted with a saturated solution of NaHCO₃ in water (2 × 250 mL). The aqueous layer was back-extracted with Et₂O (100 mL). The organic phases were combined and dried over MgSO₄. After filtration, removal of the volatiles in vacuo afforded {RO}^1H as a yellow oil. Yield 8.0 g (79%). ¹H NMR (CDCl₃, 500.13 MHz, 298 K): δ 6.61 (s, 1H, OH), 3.46 (t, 2H, ³JHH = 5.0 Hz, NCH₂CH₂), 3.35 (s, 3H, OCH₃), 3.01 (s, 2H, CH₂C(CF₃)₂), 2.82 (t, 2H, ³JHH = 5.0 Hz, NCH₂CH₂), 2.48 (s, 3H, NCH₃) ppm. ¹³C(¹H) NMR (CDCl₃, 125.75 MHz, 298 K): δ 123.57 (q, ¹JC = 286.7 Hz, CF₃), 77.62 (hept, ²JC = 31.4 Hz, C(CF₃)₂), 69.84 (NCH₂CH₂), 58.83 (OCH₃), 58.44 (CH₂C(CF₃), 54.96 (NCH₂CH₂), 42.83 (NCH₃) ppm. ¹⁹F(¹H) NMR (CDCl₃, 376.52 MHz, 298 K): δ −78.11 (s, 6F, CF₃) ppm. Elemental analysis for C₈H₁₉F₆NO₃ (269.18 g·mol⁻¹): theoretical, C 35.7%, H 4.9%, N 5.20%; found C 34.2%, H 4.7%, N 5.1%. Mass spectrometry ESI [M + Na⁺] (C₈H₁₉F₆NO₃Na) m/z theoretical: 292.0748; found 292.0746.

**{RO}^2H**: A solution of bis(2-methoxyethyl)amine (2.91 g, 21.9 mmol) in Et₂O (100 mL) was added dropwise to a solution of 2,2-bis(trifluoromethyl)oxirane (3.74 g, 20.8 mmol) in Et₂O (300 mL) at 0 °C. The reaction mixture was warmed slowly to room temperature and stirred vigorously for 36 h. The resulting solution was concentrated to ca. 80 mL and extracted with a saturated solution of NaHCO₃ in water (2 × 250 mL). The aqueous layer was back-extracted with Et₂O (100 mL). The organic phases were combined and dried over MgSO₄. After filtration, removal of the volatiles in vacuo afforded {RO}²H as a yellow oil. Yield 4.75 g (73%). ¹H NMR (benzene-ｄ₆, 400.13 MHz, 298 K): δ 6.72 (s, 1H, OH), 3.07 (s, 2H, CH₂C(CF₃)₂), 3.04–2.96 (overlapping m, 10H, OCH₃ and NCH₂CH₂), 2.55 (t, 4H, ³JHH = 5.1 Hz, NCH₂CH₂) ppm. ¹³C(¹H) NMR (benzene-ｄ₆, 100.62 MHz, 298 K): δ 124.43 (q, ¹JC = 287.6 HZ, CF₃), 73.99 (hept, ²JC = 28.3 HZ, C(CF₃)₂), 70.13 (NCH₂CH₂), 58.39 (OCH₃), 54.70 (NCH₂CH₂), 53.92 (CH₂C(CF₃)₂) ppm. ¹⁹F(¹H) NMR (benzene-ｄ₆, 376.52 MHz, 298 K): δ −77.37 (s, 6F, CF₃) ppm. Elemental analysis for C₁₆H₃₂F₁₂NO₃ (313.24 g·mol⁻¹): theoretical, C 38.3%, H 5.5%, N 4.5%; found C 38.7%, H 5.0%, N 4.4%. Mass spectrometry ESI [M + Na⁺] (C₁₆H₃₂F₁₂NO₃Na) m/z theoretical: 336.1010; found 336.1009.

**{RO}³H**: A solution of 1-aza-12-crown-4 (0.49 g, 2.81 mmol) in Et₂O (5 mL) was added dropwise at 0 °C to a solution of 2,2-bis(trifluoromethyl)oxirane (0.55 g, 3.05 mmol) in Et₂O (5 mL). The reaction mixture was warmed slowly
Experimental Part

to room temperature and stirred for two days. The volatiles were then evaporated under reduced pressure to afford [RO\textsuperscript{1}]H as a colourless solid. Yield 0.88 g (88%). X-ray quality crystals were obtained by slow concentration of a solution of the title compound in Et\textsubscript{2}O. \textsuperscript{1}H NMR (benzene-\textit{d}\textsubscript{6}, 500.13 MHz, 298 K): \(\delta\) 6.80 (s, 1H, OH), 3.34--3.20 (m, 12H, OCH\textsubscript{2} all crown-ether moieties), 2.79 (s, 2H, CH\textsubscript{2}C(CF\textsubscript{3})\textsubscript{2}), 2.41--2.31 (m, 4H, NCH\textsubscript{2}CH\textsubscript{2}) ppm. \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (benzene-\textit{d}\textsubscript{6}, 125.75 MHz, 298 K): \(\delta\) 124.61 (q, \(J_{CF}= 288.2\ Hz, CF\textsubscript{3}\)), 73.97 (hept, \(J_{CF}= 28.3\ Hz, C(CF\textsubscript{3})\textsubscript{2}\)), 70.60, 70.39, 69.05 (all crown-ether moieties), 57.85 (CH\textsubscript{2}C(CF\textsubscript{3})\textsubscript{2}), 55.68 (NCH\textsubscript{2}CH\textsubscript{2}) ppm. \textsuperscript{19}F\{\textsuperscript{1}H\} NMR (benzene-\textit{d}\textsubscript{6}, 376.52 MHz, 298 K): \(\delta\) –77.21 (s, 6F, CF\textsubscript{3}) ppm. Elemental analysis for C\textsubscript{12}H\textsubscript{19}F\textsubscript{2}NO\textsubscript{4} (355.27 g·mol\textsuperscript{-1}): theoretical, C 40.5%, H 5.4%, N 3.9%; found C 40.7%, H 5.3%, N 4.0%. Mass spectrometry ESI [M + Na\textsuperscript{+}] (C\textsubscript{12}H\textsubscript{19}F\textsubscript{2}NO\textsubscript{4}Na) \textit{m/z} theoretical: 378.1116; found 378.1112.

\[
\text{RO}\textsuperscript{[H]}: \quad \text{Following the protocol described for the synthesis of [RO\textsuperscript{3}]H, N-}
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isopropylbut-3-en-1-amine (2.26 g, 19.96 mmol) was reacted with 2,2-bis(trifluoromethyl)oxirane (3.95 g, 21.95 mmol) to yield [RO\textsuperscript{1}]H as a colourless oil. Reaction time: 7 days. Yield 5.15 g (88%). \textsuperscript{1}H NMR (toluene-\textit{d}\textsubscript{6}, 400.13 MHz, 263 K): \(\delta\) 6.53 (s, 1H, OH), 5.47 (ddt, 1H, \(J_{HH}^{\text{trans}} = 15.8\ Hz, J_{HH}^{\text{cis}} = 11.2\ Hz, J_{HH} = 6.9\ Hz, CH=CH\textsubscript{2}\)), 5.01--4.92 (m, 2H, CH=CH\textsubscript{2}), 2.78, 2.29 (ABq, 2H, \(J_{AB} = 15.6\ Hz, CH\textsubscript{2}C(CF\textsubscript{3})\textsubscript{2}\)), 2.79 (s, 2H, CH\textsubscript{2}C(CF\textsubscript{3})\textsubscript{2}), 2.55 (hept, 1H, \(J_{HH} = 6.6\ Hz, CH(CH\textsubscript{3})\textsubscript{2}\)), 2.26--2.19 (m, 1H, NCH\textsubscript{2}HCH\textsubscript{2}), 1.99--1.88 (m, 1H, NC(H)HCH\textsubscript{2}), 1.88--1.73 (m, 2H, NCH\textsubscript{2}CH\textsubscript{2}), 0.62 (d, 3H, \(J_{HH} = 6.7\ Hz, CH(CH\textsubscript{3})\textsubscript{2}\)), 0.56 (d, 3H, \(J_{HH} = 6.6\ Hz, CH(CH\textsubscript{3})\textsubscript{2}\)) ppm. \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (toluene-\textit{d}\textsubscript{6}, 100.62 MHz, 263 K): \(\delta\) 135.59 (CH=CH\textsubscript{2}), 124.45 (q, \(J_{CF} = 287.1\ Hz, CF\textsubscript{3}\)), 117.21 (CH=CH\textsubscript{2}), 72.06 (hept, \(J_{CF} = 28.9\ Hz, C(CF\textsubscript{3})\textsubscript{2}\)), 51.67 (CH\textsubscript{2}C(CH\textsubscript{3})\textsubscript{2}), 50.44 (NCH\textsubscript{2}CH\textsubscript{2}), 48.87 (CH\textsubscript{2}C(CF\textsubscript{3})\textsubscript{2}), 32.95 (NCH\textsubscript{2}CH\textsubscript{2}), 18.27 (CH\textsubscript{2}C(CH\textsubscript{3})\textsubscript{2}), 17.12 (CH\textsubscript{2}C(CH\textsubscript{3})\textsubscript{2}) ppm. \textsuperscript{19}F\{\textsuperscript{1}H\} NMR (toluene-\textit{d}\textsubscript{6}, 376.47 MHz, 263 K): \(\delta\) –77.10 (m, 6F, CF\textsubscript{3}) ppm. Elemental analysis for C\textsubscript{13}H\textsubscript{21}F\textsubscript{2}NO (293.25 g·mol\textsuperscript{-1}): theoretical, C 45.0%, H 5.8%, N 4.8%; found C 44.9%, H 5.5%, N 4.8%. Mass spectrometry ESI [M + Na\textsuperscript{+}] (C\textsubscript{13}H\textsubscript{21}F\textsubscript{2}NO\textsubscript{Na}) \textit{m/z} theoretical: 316.1112; found 316.1109.

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\text{RO}^{[2]}\text{H}: \quad \text{Di(but-3-en-1-yl)amine (2.21 g, 17.65 mmol) was reacted with 2,2-bis(trifluoromethyl)oxirane (3.49 g, 19.38 mmol) to yield [RO}^{[2]}\text{H} as a colourless oil. Reaction time: 2 days. Yield 5.00 g (93%). \textsuperscript{1}H NMR (benzene-\textit{d}\textsubscript{6}, 400.13 MHz, 298 K): \(\delta\) 6.36 (s, 1H, OH), 5.46 (ddt, 2H, \(J_{HH}^{\text{trans}} = 17.1\ Hz, J_{HH}^{\text{cis}} = 10.4\ Hz, J_{HH} = 6.8\ Hz, CH=CH\textsubscript{2}\)), 4.97--4.87 (m, 4H, CH=CH\textsubscript{2}), 2.63 (s, 2H, CH\textsubscript{2}C(CF\textsubscript{3})\textsubscript{2}), 2.24 (t, 4H, \(J_{HH} = 7.4\ Hz, NCH\textsubscript{2}CH\textsubscript{2}\)), 1.80 (q, 4H, \(J_{HH} = 7.2\ Hz, NCH\textsubscript{2}CH\textsubscript{2}\)) ppm. \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (benzene-\textit{d}\textsubscript{6}, 100.63 MHz, 298 K): \(\delta\) 135.32 (CH=CH\textsubscript{2}), 124.32 (q, \(J_{CF} = 287.6\ Hz, CF\textsubscript{3}\)), 117.10 (CH=CH\textsubscript{2}), 72.43 (hept, \(J_{CF} = 29.2\ Hz, C(CF\textsubscript{3})\textsubscript{2}\)), 53.62 (NCH\textsubscript{2}CH\textsubscript{2}), 52.63 (CH\textsubscript{2}C(CF\textsubscript{3})\textsubscript{2}), 31.05 (NCH\textsubscript{2}CH\textsubscript{2}) ppm. \textsuperscript{19}F\{\textsuperscript{1}H\} NMR (benzene-\textit{d}\textsubscript{6}, 376.49 MHz, 298 K): \(\delta\) –77.79 (s,
Experimental Part

6F, CF₃) ppm. Mass spectrometry ESI [M + Na⁺] (C₁₂H₁₇F₄NO₂Na) m/z theoretical: 328.11120; found 328.1110.

{RO₁³}H: (Z)-N-isopropylpent-3-en-1-amine (0.37 g, 2.90 mmol) was reacted with 2,2-bis(trifluoromethyl)oxirane (0.67 g, 3.77 mmol) to yield {RO₁³}H as a colourless oil. Reaction time: 2 days. Yield 0.70 g (78%). ¹H NMR (benzene-d₆, 400.13 MHz, 298 K): δ 6.54 (s, 1H, OH), 5.55–5.40 (m, 1H, CH=C(CH₂)CH₃), 5.24–5.13 (m, 1H, CH=C(H)CH₃), 2.99–1.74 (overlapping m, 7H, CH₂(CF₃)₂, NCH₂CH₂, NCH₂CH₂ and CH(CH₃)₂), 1.47 (d, 3H, 3JH-H = 6.8 Hz, CH=C(H)CH₃), 0.59 (d, 6H, 3JH-H = 4.5 Hz, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (benzene-d₆, 100.63 MHz, 298 K): δ 126.91 (CH=C(H)CH₃), 126.66 (CH=C(H)CH₃), 124.52 (q, 1JC-F = 287.6 Hz, CF₃), 72.29 (hept, 2JC-F = 29.2 Hz, C(CF₃)₂), 51.97 (CH(CH₃)₂), 51.13 (NCH₂CH₂), 49.23 (CH₃C(CF₃)₂), 26.27 (NCH₂CH₂), 18.28 (CH(CH₃)₂), 12.79 (HC=C(H)CH₃) ppm. ¹⁹F{¹H} NMR (benzene-d₆, 376.47 MHz, 298 K): −77.12 (s, 6F, CF₃) ppm.

{RO₁⁴}H: N-isopropyl-4-methylpent-3-en-1-amine (1.44 g, 10.19 mmol) was reacted with 2,2-bis(trifluoromethyl)oxirane (3.20 g, 12.23 mmol) to yield {RO₁⁴}H as a colourless oil. Reaction time: 2 days. Yield 2.78 g (85%). ¹H NMR (benzene-d₆, 400.13 MHz, 298 K): 6.58 (s, 1H, OH), 4.99–4.92 (m, 1H, CH=C(CH₂)CH₃), 3.00–1.72 (overlapping m, 7H, CH₂C(CF₃)₂, NCH₂CH₂, NCH₂CH₂ and CH(CH₃)₂), 1.63 (CH=C(CH₃)CH₃), 1.48 (CH=C(CH₃)CH₃), 0.62 (d, 6H, 3JH-H = 4.5 Hz, CH(CH₃)₂) ppm. ¹³C{¹H} NMR (benzene-d₆, 100.63 MHz, 298 K): δ 134.21 (CH=C(CH₃)₂), 124.54 (q, 1JC-F = 287.7 Hz, CF₃), 121.19 (CH=C(CH₃)₂), 72.28 (hept, 2JC-F = 29.2 Hz, C(CF₃)₂), 51.98 (CH(CH₃)₂), 51.49 (NCH₂CH₂), 49.26(CH₃C(CF₃)₂), 27.54 (NCH₂CH₂), 25.73 (CH=C(CH₃)CH₃), 18.32 (CH(CH₃)₂), 17.66 (CH=C(CH₃)CH₃) ppm. ¹⁹F{¹H} NMR (benzene-d₆, 376.47 MHz, 298 K): −77.05 (s, 6F, CF₃) ppm.

{RO₂¹}H: N-methyl-2-phenylethanimine (1.24 g, 9.17 mmol) was reacted with 2,2-bis(trifluoromethyl)oxirane (1.98 g, 11.00 mmol) to yield {RO₂¹}H as a colourless oil. Reaction time: 2 days. Yield 2.34 g (81%). ¹H NMR (benzene-d₆, 400.13 MHz, 298 K): δ 7.15–7.09 (m, 2H, m-C₆H₅), 7.08–7.02 (m, 1H, p-C₆H₅), 6.89–6.84 (m, 2H, o-C₆H₅), 6.20 (s, 1H, OH), 2.47 (br s, 2H, CH₂C(CF₃)₂), 2.37–2.28 (overlapping m, 4H, NCH₂CH₂ and NCH₂CH₂), 1.80 (s, 3H, NCH₃) ppm. ¹³C{¹H} NMR (benzene-d₆, 125.77 MHz, 298 K): δ 138.85 (i-C₆H₅), 128.90 (m-C₆H₅), 128.77 (o-C₆H₅), 126.82 (p-C₆H₅), 124.21 (q, 1JC-F = 285.6 Hz, CF₃), 72.12 (hept, 2JC-F = 29.1 Hz, C(CF₃)₂), 60.18 (NCH₂CH₂), 54.59 (CH₃C(CF₃)₂), 44.24 (CH₃), 33.75 (NCH₂CH₂) ppm. ¹⁹F{¹H} NMR (benzene-d₆, 376.49 MHz, 298 K): δ −78.13 (s, 6F, CF₃) ppm.
**Experimental Part**

**{RO}^{22}H:** N-phenethylpropan-2-amine (0.87 g, 5.33 mmol) was reacted with 2,2-bis(trifluoromethyl)oxirane (1.13 g, 6.13 mmol) to yield {RO}^{22}H as a colourless oil. Reaction time: 2 days. Yield 1.35 g (74%). $^1$H NMR (benzene-d$_6$, 400.13 MHz, 298 K): $\delta$ 7.20–7.13 (m, 2H, m-C$_6$H$_5$), 7.11–7.05 (m, 1H, p-C$_6$H$_5$), 7.00–6.95 (m, 2H, o-C$_6$H$_5$), 6.43 (s, 1H, OH), 3.00–1.72 (overlapping m, 7H, CH$_2$C(CF$_3$)$_2$, NCH$_2$CH$_2$, NCH$_2$CH$_2$ and CH(CH$_3$)$_2$), 0.63 (d, 6H, $^3$J$_{H-H}$ = 6.5 Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C$[^1]$H NMR (benzene-d$_6$, 125.77 MHz, 298 K): $\delta$ 139.10 (i-C$_6$H$_5$), 128.97 (m-C$_6$H$_5$), 128.86 (o-C$_6$H$_5$), 126.79 (p-C$_6$H$_5$), 124.51 (q, $^1$J$_{CF}$ = 288.1 Hz, CF$_3$), 72.17 (hept, $^2$J$_{CF}$ = 29.0 Hz, C(CF$_3$)$_2$), 35.50 (NCH$_2$CH$_2$), 18.30 (CH(CH$_3$)$_2$) ppm. $^{19}$F$[^1]$H NMR (benzene-d$_6$, 376.49 MHz, 298 K): $\delta$ –77.16 (s, 6F, CF$_3$) ppm.

**{RO}^{12}H:** N-isopropylpent-3-yn-1-amine (1.35 g, 10.75 mmol) was reacted with 2,2-bis(trifluoromethyl)oxirane (2.32 g, 12.90 mmol) to yield {RO}^{12}H as a colourless oil. Reaction time: 2 days. Yield 2.60 g (79%). $^1$H NMR (benzene-d$_6$, 400.13 MHz, 298 K): $\delta$ 6.53 (s, 1H, OH), 3.12–2.04 (overlapping m, 5H, CH$_2$C(CF$_3$)$_2$, NCH$_2$CH$_2$, and CH(CH$_3$)$_2$), 1.95 (br s, NCH$_2$CH$_2$), 1.52 (s, 3H, C=–C–H$_3$), 0.64 (d, 6H, $^3$J$_{H-H}$ = 6.7 Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C$[^1]$H NMR (benzene-d$_6$, 100.63 MHz, 298 K): $\delta$ 124.49 (q, $^1$J$_{CF}$ = 287.8 Hz, CF$_3$), 78.09 (C=–C–), 76.27 (C=C–C–CH$_3$), 72.65 (hept, $^2$J$_{CF}$ = 29.1 Hz, C(CF$_3$)$_2$), 51.95 (CH(CH$_3$)$_2$), 50.30 (NCH$_2$CH$_2$), 49.20 (CH$_2$C(CF$_3$)$_2$), 18.93 (NCH$_2$CH$_2$), 18.23 (CH(CH$_3$)$_2$), 3.06 (C=–C–H$_3$) ppm. $^{19}$F$[^1]$H NMR (benzene-d$_6$, 376.47 MHz, 298 K): –77.08 (s, 6F, CF$_3$) ppm.

**{RO}^{41}H:** N-isopropylpenta-3,4-dien-1-amine (0.63 g, 5.05 mmol) was reacted with 2,2-bis(trifluoromethyl)oxirane (1.17 g, 6.50 mmol) to yield {RO}^{41}H as a colourless oil. Reaction time: 2 days. Yield 1.17 g (72%). $^1$H NMR (benzene-d$_6$, 400.13 MHz, 298 K): $\delta$ 6.46 (s, 1H, OH), 4.82 (quint, 1H, $^3$J$_{H-H}$ = 6.8 Hz, H$_2$C=C=CH), 4.61–4.55 (m, 2H, H$_2$C=C=CH), 3.00–1.92 (overlapping m, 5H, CH$_2$C(CF$_3$)$_2$, NCH$_2$CH$_2$, and CH(CH$_3$)$_2$), 1.80 (br s, 2H, NCH$_2$CH$_2$), 0.57 (d, 6H, $^3$J$_{H-H}$ = 5.5 Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C$[^1]$H NMR (benzene-d$_6$, 100.63 MHz, 298 K): $\delta$ 209.32 (H$_2$C=C=CH), 124.47 (q, $^1$J$_{CF}$ = 287.4 Hz, CF$_3$), 18.17 (H$_2$C=C=CH), 75.41 (H$_2$C=C=CH), 72.26 (hept, $^2$J$_{CF}$ = 29.0 Hz, C(CF$_3$)$_2$), 52.09 (CH(CH$_3$)$_2$), 50.71 (NCH$_2$CH$_2$), 49.16 (CH$_2$C(CF$_3$)$_2$), 27.40 (NCH$_2$CH$_2$), 18.22 (CH(CH$_3$)$_2$) ppm. $^{19}$F$[^1]$H NMR (benzene-d$_6$, 376.47 MHz, 298 K): –77.07 (s, 6F, CF$_3$) ppm.
Syntheses of complexes

\[ [\{RO\}^3K] \text{ (1): KN(SiMe}_3\text{)}_2 \text{ (56 mg, 0.56 mmol) was added in solid portions} \]

with a bent finger to a solution of \{RO\}^3H (100 mg, 0.56 mmol) in Et\(_2\)O (10 mL). A white precipitate formed immediately. The reaction mixture was stirred overnight at room temperature. The volatiles were removed in vacuo and the resulting solid was washed with pentane (4 × 5 mL) to yield 1 as a colourless solid (88 mg, 80%). The product displayed poor solubility in hydrocarbon and ether solvents and was soluble only in CH\(_2\)Cl\(_2\). X-ray quality crystals were obtained by recrystallisation from a concentrated CH\(_2\)Cl\(_2\) solution at room temperature. \(^1\)H NMR (dichloromethane-\(d_2\), 500.13 MHz, 298 K): \(\delta\) 3.73–3.51 (m, 12H, all crown ether), 2.71 (overlapping m, 6H, NCH\(_2\)CH\(_2\) and CH\(_2\)C(CF\(_3\))\(_2\)) ppm. \(^{13}\)C\([\{\text{H}\}]\) NMR (dichloromethane-\(d_2\), 125.75 MHz, 298 K): \(\delta\) 127.81 (q, \(J_{C-F} = 298.2\) Hz, CF\(_3\)), 67.14, 66.63, 66.25 (all crown ether), 59.88 (CH\(_2\)C(CF\(_3\))\(_2\)), 54.80 (NCH\(_2\)CH\(_2\)) ppm. The resonance for C(CF\(_3\))\(_2\) was not observed. \(^{19}\)F\([\{\text{H}\}]\) NMR (dichloromethane-\(d_2\), 376.52 MHz, 298 K): \(\delta\) –78.41 (s, 6F, CF\(_3\)) ppm. Elemental analysis for C\(_{12}\)H\(_{18}\)F\(_6\)KNO\(_3\) (393.36 g·mol\(^{-1}\)): theoretical, C 36.6%, H 4.6%, N 3.6%; found C 36.6%, H 3.8%, N 3.8%.

\[ [\{RO\}^3K] \text{ (2): KN(SiMe}_3\text{)}_2 \text{ (0.10 g, 0.59 mmol) was added in solid portions} \]

with a bent finger to a solution of \{RO\}^3H (0.18 g, 0.59 mmol) in Et\(_2\)O (5 mL). The reaction mixture was stirred overnight at room temperature. The volatiles were removed in vacuo to obtain a colourless solid. Extraction with pentane (20 mL) and evaporation of the volatiles afforded 2 as a colourless solid (0.16 g, 78%). X-ray quality crystals were obtained by recrystallisation from a concentrated pentane solution. \(^1\)H NMR (benzene-\(d_6\), 300.13 MHz, 298 K): \(\delta\) 3.23 (t, 4H, \(J_{\text{H-H}} = 5.1\) Hz, NCH\(_2\)CH\(_2\)), 3.07 (s, 6H, OCH\(_3\)), 3.00 (s, 2H, CH\(_2\)C(CF\(_3\))\(_2\)), 2.78 (t, 4H, \(J_{\text{H-H}} = 5.1\) Hz, NCH\(_2\)CH\(_2\)) ppm. \(^{13}\)C\([\{\text{H}\}]\)NMR (75.46 MHz, benzene-\(d_6\), 25°C): \(\delta\) 127.61 (q, \(J_{C-F} = 297.2\) Hz, CF\(_3\)), 82.43 (hept, \(J_{C-F} = 22.8\) Hz, C(CF\(_3\))\(_2\)), 69.20 (NCH\(_2\)CH\(_2\)), 58.19 (OCH\(_3\)), 57.92 (NCH\(_2\)CH\(_2\)), 53.77 (CH\(_2\)C(CF\(_3\))\(_2\)) ppm. \(^{19}\)F\([\{\text{H}\}]\)NMR (benzene-\(d_6\), 376.52 MHz, 298 K): \(\delta\) –77.17 (s, 6F, CF\(_3\)) ppm. Elemental analysis for C\(_{10}\)H\(_{16}\)F\(_6\)KNO\(_3\) (351.33 g·mol\(^{-1}\)): theoretical, C 34.2%, H 4.6%, N 4.0%; found C 34.3%, H 4.7%, N 4.1%.

\[ [\{RO\}^3K] \text{ (3): KN(SiMe}_3\text{)}_2 \text{ (0.55 g, 3.20 mmol) was added in solid portions} \]

with a bent finger to a solution of \{RO\}^3H (0.90 g, 3.34 mmol) in Et\(_2\)O (30 mL). The reaction mixture was stirred overnight at room temperature. The volatiles were removed in vacuo to yield 3 as a colourless solid (0.95 g, 93%). X-ray quality crystals were obtained by recrystallisation from a concentrated pentane solution at room temperature. \(^1\)H NMR (benzene-\(d_6\), 400.13 MHz, 298 K): \(\delta\) 3.03 (s, 3H, OCH\(_3\)), 2.92 (t, 2H, \(J_{\text{H-H}} = 4.6\) Hz, NCH\(_2\)CH\(_2\)), 2.75 (s, 2H, CH\(_2\)C(CF\(_3\))\(_2\)), 2.32 (br, 2H, NCH\(_2\)H), 2.17
Experimental Part

([RO₃]₂Ca) (4): Ca[N(SiMe₃)₂]₂ (0.07 g, 0.21 mmol) was added in portions with a bent finger to a solution of [RO₃]H (0.15 g, 0.42 mmol) in Et₂O (7 mL). After 10 min of reaction, a colourless precipitate formed. The reaction mixture was stirred overnight at room temperature. The colourless precipitate was filtered off, washed with pentane (3 × 3 mL) and dried in vacuo to afford 4 as a colourless powder (0.10 g, 67%). X-ray quality crystals were obtained by recrystallisation from a concentrated benzene solution at room temperature. ¹H NMR (benzene-d₆, 500.13 MHz, 298 K): δ 3.67–3.09 (m, 12H, all crown ether), 2.81 (s, 2H, CH₂(CF₃)₂), 2.53 (br s, 4H, NCH₂CH₂) ppm. ¹³C [¹H] NMR (benzene-d₆, 125.75 MHz, 298 K): δ 69.79, 68.91, 67.76 (all crown ether), 60.15 (CH₂(CF₃)₂), 56.82 (NCH₂CH₂) ppm. The resonances for C(CF₃)₂ and CF₃ were not observed. ¹⁹F [¹H] NMR (dichloromethane-d₂, 376.52 MHz, 298 K): δ −77.42 (s, 12F, CF₃) ppm. Elemental analysis for C₅₆H₆₀CaF₁₂N₂O₈ (748.61 g·mol⁻¹): theoretical, C 38.5%, H 4.8%, N 3.7% was not performed at the time of writing the manuscript.

([RO₃]₂Ca) (5): Ca[N(SiMe₃)₂]₂ (0.20 g, 0.56 mmol) was added in solid portions with a bent finger to a solution of [RO₂]H (0.90 g, 3.34 mmol) in Et₂O (20 mL). The reaction mixture was stirred overnight at room temperature. The volatiles were removed in vacuo and the resulting oil was stripped with pentane (4 × 4 mL) to afford 5 as a colourless solid (0.27 g, 72%). X-ray quality crystals were obtained by recrystallisation from a concentrated benzene solution at room temperature. ¹H NMR (benzene-d₆, 500.13 MHz, 298 K): δ 3.17 (s, 6H, OCH₃), 3.06 (t, 4H, J₁H₂H = 5.1 Hz, NCH₂CH₂), 2.79 (s, 2H, CH₂(CF₃)₂), 2.46 (NCH₂CH₂) ppm. ¹³C [¹H] NMR (125.75 MHz, benzene-d₆, 25°C): δ 127.27 (q, J₁C₆ = 297.1 Hz, CF₃), 82.59 (hept, J₁C₂F = 25.2 Hz, C(CF₃)₂), 69.37 (NCH₂CH₂), 59.07 (OCH₃), 53.89 (CH₂(CF₃)₂), 55.79 (NCH₂CH₂) ppm. ¹⁹F [¹H] NMR (benzene-d₆, 376.53 MHz, 298 K): δ −78.36 (s, 12F, CF₃) ppm. Elemental analysis for C₅₆H₆₀CaF₁₂N₂O₈ (665.54 g·mol⁻¹): theoretical, C 36.1%, H 5.0%, N 4.2%; found C 35.8%, H 5.2%, N 4.2%.
Experimental Part

\[\text{[RO}\text{I}]_2\text{Ca} (6): \text{Ca}[\text{N(SiMe}_3)_2]\text{]}_2 (0.24 \text{ g, 0.67 mmol}) was added in portions with a bent finger to a solution of \{RO\text{I}\}H (0.36 \text{ g, 1.33 mmol}) in Et\(_2\text{O}\) (20 mL). The reaction mixture was stirred overnight at room temperature. The volatiles were removed in vacuo and the resulting oil was stripped with pentane (4 × 5 mL) and washed with the same solvent (3 × 2 mL) to afford 6 as a colourless solid (0.22 g, 57%). \textsuperscript{1}H NMR (benzene-\textit{d}_6, 400.13 MHz, 298 K): \(\delta\) 3.30 (br s, 3H, OCH\(_3\)), 3.19 (br s, 2H, NCH\(_2\)CH\(_2\)), 2.69 (br s, 2H, CH\(_3\)C(CF\(_3\))\(_2\)), 2.47 (br s, 2H, NCH\(_2\)CH\(_2\)), 2.20 (br s, 3H, NCH\(_3\)) ppm. \textsuperscript{13}C[\textsuperscript{1}H]NMR (125.75 MHz, benzene-\textit{d}_6, 25°C): \(\delta\) 126.44 (q, \textsuperscript{1}J_{\text{CF}} = 295.2 Hz, CF\(_3\)), 82.57–79.77 (m, C(CF\(_3\))\(_2\)), 70.47 (OCH\(_3\)), 43.84 (NCH\(_3\)) ppm. \textsuperscript{19}F[\textsuperscript{1}H] NMR (benzene-\textit{d}_6, 376.52 MHz, 298 K): \(\delta\) –77.37 (br s, CF\(_3\)), –78.98 (s, CF\(_3\)) ppm. Elemental analysis for C\(_{16}\)H\(_6\)CaF\(_2\)N\(_2\)O\(_4\) (576.43 g·mol\(^{-1}\)): theoretical, C 33.3%, H 4.2%, N 4.9%; found C 32.1%, H 4.7%, N 4.7%.

\[\text{[RO}\text{I}]_2\text{Sr} (7): \text{Sr}[\text{N(SiMe}_3)_2]\text{]}_2 (0.08 \text{ g, 0.21 mmol}) was added in solid portions with a bent finger to a solution of \{RO\text{I}\}H (0.15 g, 0.42 mmol) in Et\(_2\text{O}\) (10 mL). A colourless precipitate formed instantaneously. The reaction mixture was stirred overnight at room temperature. The colourless precipitate was filtered off, washed with pentane (4 × 3 mL) and dried in vacuo to afford 7 as a colourless solid (87 mg, 46%). X-ray quality crystals were obtained by recrystallisation from a concentrated THF solution at room temperature. \textsuperscript{1}H NMR (THF-\textit{d}_8, 400.16 MHz, 298 K): \(\delta\) 3.93–3.72 (m, 12H, all crown ether), 2.85 (br s, 4H, NCH\(_2\)CH\(_2\)), 2.72 (s, 2H, CH\(_3\)C(CF\(_3\))\(_2\)) ppm. \textsuperscript{13}C[\textsuperscript{1}H]NMR (THF-\textit{d}_8, 100.62 MHz, 298 K): \(\delta\) 127.62 (q, \textsuperscript{1}J_{\text{CF}} = 295.8 Hz, CF\(_3\)), 80.94–79.92 (m, C(CF\(_3\))\(_2\)), 70.44 (NCH\(_2\)CH\(_2\)), 68.39 (all crown ether), 61.56 (CH\(_2\)C(CF\(_3\))\(_2\)), 58.42 (NCH\(_2\)CH\(_2\)), 43.84 (NCH\(_3\)) ppm. \textsuperscript{19}F[\textsuperscript{1}H] NMR (THF-\textit{d}_8, 376.52 MHz, 298 K): \(\delta\) –77.37 (s, 12F, CF\(_3\)) ppm. Elemental analysis for C\(_{20}\)H\(_{36}\)SrF\(_2\)N\(_2\)O\(_8\) (796.15 g·mol\(^{-1}\)): theoretical, C 36.2%, H 4.58%, N 3.5% was not performed at the time of writing the manuscript.

\[\text{[RO}\text{I}]_2\text{Sr} (9): \text{Sr}[\text{N(SiMe}_3)_2]\text{]}_2 (0.41 \text{ g, 1.00 mmol}) was added in solid portions with a bent finger to a solution of \{RO\text{I}\}H (0.54 g, 2.00 mmol) in Et\(_2\text{O}\) (20 mL). The reaction mixture was stirred overnight at room temperature. The volatiles were removed in vacuo and the resulting oil was stripped with pentane (4 × 7 mL) to afford 9 as a colourless solid (0.45 g, 72%). X-ray quality crystals were obtained by recrystallisation from a concentrated Et\(_2\text{O}\) solution at –30 °C. \textsuperscript{1}H NMR (benzene-\textit{d}_6, 500.13 MHz, 298 K): \(\delta\) 3.41–2.98 (overlapping m, 5H, OCH\(_3\), NCH\(_2\)CH\(_2\)), 2.68 (br s, 2H, CH\(_2\)C(CF\(_3\))\(_2\)), 2.56–2.28 (m, 2H, NCH\(_2\)), 2.19 (s, 3H, NCH\(_3\)) ppm. \textsuperscript{13}C[\textsuperscript{1}H]NMR (125.75 MHz, benzene-\textit{d}_6, 25°C): \(\delta\) 126.83 (q, \textsuperscript{1}J_{\text{CF}} = 295.8 Hz, CF\(_3\)), 82.57–79.77 (m, C(CF\(_3\))\(_2\)), 70.47 (OCH\(_3\)), 68.99, 68.55, 68.39 (all crown ether), 61.56 (CH\(_2\)C(CF\(_3\))\(_2\)), 57.51 (NCH\(_2\)CH\(_2\)), 43.84 (NCH\(_3\)) ppm. \textsuperscript{19}F[\textsuperscript{1}H] NMR (THF-\textit{d}_8, 376.52 MHz, 298 K): \(\delta\) –77.37 (s, 12F, CF\(_3\)) ppm. Elemental analysis for C\(_{20}\)H\(_{36}\)SrF\(_2\)N\(_2\)O\(_8\) (796.15 g·mol\(^{-1}\)): theoretical, C 36.2%, H 4.58%, N 3.5% was not performed at the time of writing the manuscript.
Experimental Part

60.23 (CH₂C(CF₃)₂), 59.46 (NCH₂CH₂), 58.54 (NCH₂CH₂), 43.34 (NCH₃) ppm. ¹⁹F¹[H] NMR (benzene-d₆, 376.52 MHz, 298 K): δ −76.15 to −78.67 (m, 12F, CF₃) ppm. Elemental analysis for C₁₉H₃₂F₁₂N₂O₄Sr (624.06 g·mol⁻¹): theoretical, C 30.8%, H 3.9%, N 4.5% was not performed at the time of writing the manuscript.

[(RO)²CaN(SiMe₃H)₂] (10): A solution of {RO²}H (0.18 g, 0.57 mmol) in Et₂O (10 mL) was added at −78 °C over a period of 1 h to a solution of Ca[N(SiMe₃H)₂]₂(THF) (0.28 g, 0.76 mmol) in Et₂O (10 mL). The mixture was warmed to room temperature and stirred overnight, and the volatiles were removed under vacuum. The resulting powder was stripped with pentane (3 × 4 mL) and dried in vacuo to give analytically pure 10 as an off-white powder (0.22 g, 79%). Single-crystals of 10 suitable for X-ray diffraction crystallography were obtained by recrystallisation from Et₂O at room temperature. ¹H NMR (benzene-d₆, 400.13 MHz, 298 K): δ 4.88 (m, 2H, J₁Si-H = 162 Hz, SiH), 3.22–3.14 (m, 2H, NCH₂CH₂), 3.03–2.89 (overlapping m, 12H, OCH₃), 2.47 (d, 2H, J₁H-H = 12.4 Hz, NC(CH₃)) ppm. ¹³C¹[H]NMR (100.62 MHz, benzene-d₆, 25°C): δ 125.84 (q, J_C-F = 250.1 Hz, CF₃), 79.30 (hept, J₂C-F = 25.7 Hz, C(CF₃)₂), 69.35 (NCH₂CH₂), 59.46 (OCH₃), 55.45 (CH₂C(CF₃)₂), 53.45 (NCH₂CH₂), 5.02 (SiCH₃) ppm. ¹⁹F¹[H] NMR (376.52 MHz, benzene-d₆, 25°C): δ −77.64 (s, 6F, CF₃) ppm. ²⁹Si¹[H] NMR (benzene-d₆, 79.49 MHz, 298 K): δ −25.1 ppm. FTIR (nujol in KBr plates): δSi-H = 2016 (s) cm⁻¹. Elemental analysis for C₁₄H₃₀CaF₆N₂O₄Si₂ (484.64 g·mol⁻¹): theoretical, C 34.7%, H 6.2%, N 5.8%; found C 34.4%, H 6.4%, N 5.7%.

[(RO)²CaN(SiMe₃)₂] (11): A solution of {RO²}H (0.23 g, 0.73 mmol) in pentane (10 mL) was added at −78 °C over a period of 1 h to a solution of Ca[N(SiMe₃)₂]₂(THF) (0.44 g, 0.88 mmol) in pentane (10 mL). The mixture was warmed to room temperature and stirred overnight, and the volatiles were removed under vacuum. The resulting powder was stripped with pentane (3 × 4 mL) and dried in vacuo to give a brown powder which was dissolved in toluene (5 mL). Layering of the resulting solution with pentane (15 mL) resulted in the formation of a brown oil with a higher density than the rest of the solution. The oil was separated and the remaining solution was stored in a freezer at −30 °C to afford 11 as colourless crystals (50 mg, 13%; not optimised). ¹H NMR (THF-d₆, 500.13 MHz, 298 K): δ 3.70 (t, J₂H-H = 5.3 Hz, 4H, NCH₂CH₂), 3.63 (s, 6H, OCH₃), 2.85–2.80 (overlapping m, 6H, NCH₂CH₂ and CH₂C(CF₃)₂), 0.05 (s, 18H, SiCH₃) ppm. ¹³C¹[H] NMR (THF-d₆, 125.73 MHz, 298 K): δ 127.24 (q, J₁C-F = 292.0 Hz, CF₃), 82.33 (hept, J₂C-F = 25.9 Hz, C(CF₃)₂), 70.31 (NCH₂CH₂), 61.16 (OCH₃), 56.23 (CH₂C(CF₃)₂), 53.68 (NCH₂CH₂), 5.92 (SiCH₃) ppm. ¹⁹F¹[H] NMR (THF-d₆, 376.45 MHz, 298 K): δ
Experimental Part

−81.78 (s, 6F, CF₃) ppm. Elemental analysis for C₁₆H₃₄CaF₆N₂O₂Si₂ (512.69 g·mol⁻¹): theoretical, C 37.5%, H 6.7%, N 5.5%; found C 37.6%, H 6.5%, N 5.6%.

13C{¹H} NMR (benzene-d₆, 125.75 MHz, 298 K): δ 125.70 (q, JₙCH = 290.8 Hz, C(CF₃)₂), 125.46 (q, JₚCH = 289.6 Hz, C(CF₃)₂), 79.66 (hept, JₐCH = 25.3 Hz, C(CF₃)₂), 69.53 (NCH₂CH₂), 60.90 (OCH₃), 59.75 (NCH₂CH₂), 58.43 (CH₂C(CF₃)₂), 45.70 (NCH₃), 6.43 (SiCH₃) ppm. ¹⁹F{¹H} NMR (benzene-d₆, 376.52 MHz, 298 K): δ −37.39 (q, 3F, JₕF = 9.4 Hz, CF₃), −75.14 (q, 3F, JₕF = 9.4 Hz, CF₃) ppm. ²⁹Si{¹H} NMR (benzene-d₆, 79.49 MHz, 298 K): δ −14.3 ppm. Elemental analysis for C₁₆H₃₄CaF₆N₂O₂Si₂ (440.59 g·mol⁻¹): theoretical, C 32.7%, H 6.0%, N 6.4%; found C 32.3%, H 6.0%, N 6.2%.

[[RO⁺]Ca(N(SiMe₂)₂] (12): A solution of {RO⁺}H (0.15 g, 0.55 mmol) in Et₂O (10 mL) was added at −78 °C over a period of 1 h to a solution of Ca[N(SiMe₂)₂](THF) (0.28 g, 0.74 mmol) in Et₂O (10 mL). The reaction mixture was warmed to room temperature and stirred overnight, and the volatiles were removed under vacuum. The resulting powder was stripped with pentane (3 × 4 mL) and dried in vacuo to give pure 12 as an off-white powder (0.18 g, 73%). Single-crystals of 12 suitable for X-ray diffraction crystallography were obtained by recrystallisation from Et₂O at room temperature. ¹H NMR (benzene-d₆, 400.13 MHz, 298 K): δ 4.86 (m, 2H, JₙSiH = 162 Hz, SiH₃), 3.12 (s, 3H, OCH₃), 2.84–2.61 (overlapping m, 4H, NCH₂CH₂ and NCH₂CH₂), 2.51 (ABq, 2H, JₓAB = 0.12, JₖCH = 15.1 Hz, CH₂C(CF₃)₂), 2.03 (s, 3H, NCH₃), 0.45 (d, 12H, JₕCH = 2.5 Hz, SiCH₃) ppm. ¹³C{¹H} NMR (benzene-d₆, 100.62 MHz, 298 K): δ 125.92 (q, JₙCF = 289.9 Hz, CF₃), 125.36 (q, JₚCF = 290.1 Hz, CF₃), 79.45 (hept, JₐCF = 25.8 Hz, C(CF₃)₂), 69.39 (NCH₂CH₂), 60.15 (OCH₃), 59.26 (CH₂C(CF₃)₂), 58.60 (NCH₂CH₂), 43.28 (NCH₃), 5.09 (SiCH₃), 4.82 (SiCH₃) ppm. ¹⁹F{¹H} NMR (benzene-d₆, 376.52 MHz, 298 K): δ −37.39 (q, 3F, JₕF = 9.4 Hz, CF₃), −75.14 (q, 3F, JₕF = 9.4 Hz, CF₃) ppm. ²⁹Si{¹H} NMR (benzene-d₆, 79.49 MHz, 298 K): δ −25.4 ppm. FTIR (nujol in KBr plates): ʋ̃Si-H = 2015 (s) cm⁻¹.

[RO⁺]Ca(N(SiMe₂)₂] (13): A solution of {RO⁺}H (0.34 g, 1.26 mmol) in Et₂O (15 mL) was added at −78 °C over a period of 1 h to a solution of Ca[N(SiMe₂)₂] (0.45 g, 1.26 mmol) in Et₂O (20 mL). The reaction mixture was warmed to room temperature and stirred overnight, and the volatiles were removed under vacuum. The resulting powder was stripped with pentane (3 × 4 mL) and dried in vacuo to give 13 as a yellow powder (0.42 g, 71%). Single-crystals suitable for X-ray diffraction crystallography were obtained by recrystallisation from a concentrated benzene solution. ¹H NMR (benzene-d₆, 500.13 MHz, 298 K): δ 3.03 (overlapping m, 5H, OCH₃ and NCH₂CH₂), 2.39 (ABq, 2H, JₓAB = 14.8 Hz, CH₂C(CF₃)₂), 2.12 (s, 3H, NCH₃), 2.02 (m, 2H, NCH₂CH₂), 0.35 (s, 18H, SiCH₃) ppm. ¹³C{¹H} NMR (benzene-d₆, 125.75 MHz, 298 K): δ 125.70 (q, JₙCF = 290.8 Hz, C(CF₃)₂), 125.46 (q, JₚCF = 289.6 Hz, CF₃), 79.66 (hept, JₐCF = 25.3 Hz, C(CF₃)₂), 69.53 (NCH₂CH₂), 60.90 (OCH₃), 59.75 (NCH₂CH₂), 58.43 (CH₂C(CF₃)₂), 45.70 (NCH₃), 6.43 (SiCH₃) ppm. ¹⁹F{¹H} NMR (benzene-d₆, 376.52 MHz, 298 K): δ −37.39 (q, 3F, JₕF = 9.4 Hz, CF₃), −75.14 (q, 3F, JₕF = 9.4 Hz, CF₃) ppm. ²⁹Si{¹H} NMR (benzene-d₆, 79.49 MHz, 298 K): δ −14.3 ppm. Elemental analysis for
C_{13}H_{30}CaF_{6}N_{2}O_{2}Si_{2} (468.64 g·mol⁻¹; theoretical, C 35.9%, H 6.5%, N 6.0); satisfactory results could not be obtained in spite of repeated attempts.

[\{RO\}^{4}]SrN(SiMe_{2}H)_{2} (14): A solution of \{RO\}^{4}H (0.16 g, 0.61 mmol) in Et_{2}O (10 mL) was added at −78 °C over a period of 1h to a solution of Sr[N(SiMe_{2}H)_{2}]_{2}(THF)_{2/3} (0.32 g, 0.80 mmol) in Et_{2}O (10 mL). The reaction mixture was warmed to room temperature and stirred overnight. After removal of the volatiles in vacuo, the resulting oil was stripped with pentane (3 × 6 mL) and dried in vacuo to give pure 14 as an off-white powder (0.28 g, 95%). {\textsuperscript{1}}H NMR (benzene-d_{6}, 400.13 MHz, 298 K): δ 4.94 (s, 2H, {\textsuperscript{1}}J_{Si-H} = 158 Hz, SiH_{3}, 3.00 (s, 3H, OCH_{3}), 2.84–2.61 (overlapping m, 4H, NCH_{2}CH_{2} and NCH_{2}CH_{3}), 2.47 (ABq, 2H, Δ{\textdelta}_{AB} = 0.16, {\textsuperscript{2}}J_{AB} = 15.2 Hz, CH_{2}C(=CF_{2})) ppm. {\textsuperscript{19}}F({\textsuperscript{1}}H) NMR (benzene-d_{6}, 376.52 MHz, 298 K): δ −77.16 (q, 3F, {\textsuperscript{4}}J_{F-F} = 9.1 Hz, CF_{3}), −77.39 (q, 3F, {\textsuperscript{4}}J_{F-F} = 9.1 Hz, CF_{3}) ppm. Elemental analysis for C_{13}H_{30}CaF_{6}N_{2}O_{2}Si_{2}: theoretical, C 29.5%, H 5.4%, N 5.7%; found C 29.3%, H 4.3%, N 5.5%.

**General procedure for the synthesis of \{\{RO\}^{x}\}HH\}^{+}[H_{2}N[(B(C_{x}F_{3})_{3}]_{2}]^{-}**: The following procedure was followed for the three title compounds. The proteo-ligand \{RO\}^{x}H (x = 1–3) was reacted in Et_{2}O at room temperature with an equimolar amount of [H(OEt_{2})_{2}]^{+}[H_{2}N[(B(C_{x}F_{3})_{3}]_{2}]^{-}. Evaporation of the solvent followed by dissolution in CH_{2}Cl_{2} and precipitating with pentane (4 times) afforded the desired compounds cleanly and near quantitatively. Single crystals were grown by slow concentration of CH_{2}Cl_{2} solutions or by layering CH_{2}Cl_{2} solutions with pentane.

\{\{RO\}^{4}\}HH\}^{+}[H_{2}N[(B(C_{x}F_{3})_{3}]_{2}]^{-} (15): {\textsuperscript{1}}H NMR (dichloromethane-d_{2}, 500.13 MHz, 298 K): δ 8.08 (s, 1H, OH), 5.89–5.51 (overlapping m, 3H, NH_{2} and NH'), 4.25–3.42 (overlapping m, 18H, OCH_{2} moieties, NCH_{2}CH_{2} and CH_{2}C(=CF_{2})) ppm. {\textsuperscript{13}}C({\textsuperscript{1}}H) NMR (dichloromethane-d_{2}, 100.62 MHz, 298 K): δ 149.26, 147.36, 140.54, 138.07, 136.10 (all C_{x}F_{3}), 121.95 (q, {\textsuperscript{1}}J_{CF} = 289.1 Hz, CF_{3}), 74.56 (hept, {\textsuperscript{3}}J_{CF} = 30.9 Hz, C(CF_{3})_{2}), 71.26, 70.32, 64.60, 60.09 (all crown ether), 52.50 (CH_{2}C(=CF_{2}) ppm. {\textsuperscript{19}}F({\textsuperscript{1}}H) NMR (dichloromethane-d_{2}, 376.52 MHz, 298 K): δ −77.35 (s, 6F, CF_{3}), −132.95 (d, 12F, {\textsuperscript{3}}J_{F-F} = 18.8 Hz, o-F), −160.24 (t, 6F, {\textsuperscript{3}}J_{F-F} = 20.3 Hz, p-F), −165.75 (t, 12F, {\textsuperscript{3}}J_{F-F} = 19.3 Hz, m-F) ppm. {\textsuperscript{11}}B NMR (dichloromethane-d_{2}, 128.38 MHz, 25°C): δ −8.31 ppm. Elemental analysis for C_{46}H_{22}B_{2}F_{36}N_{2}O_{4} (1396.26 g·mol⁻¹): theoretical, C 41.3%, H 1.6%, N 1.5%; found C 41.4%, H 1.5%, N 2.2%.
\[
[RO^2]HH]^+ [H_2N(B(C_6F_3)_3)_2]^+ (16): 1^H NMR (dichloromethane-\text{d}_2, 400.13 MHz, 298 K): \delta 65.67 (s, 2H, NH2), 3.87 (s, 2H, CH_2C(CF_3)_2), 3.79 - 3.70 (m, 4H, NCH_2CH_2), 3.67 - 3.56 (m, 4H, NCH_2CH_2), 3.46 (s, 6H, OCH_3) ppm.
\]

The signals for OH and NH could not be observed. \(^1^C\) NMR (dichloromethane-\text{d}_2, 100.62 MHz, 298 K): \delta 149.53, 147.14, 140.80, 138.33, 135.88 (all C\_F\_3), 121.96 (q, \(J_{C\_F} = 289.0\) Hz, CF\_3), 74.19 (hept, \(J_{C\_F} = 31.2\) Hz, C(CF\_3)_2), 64.61 (NCH\_2CH\_2), 59.97 (OCH\_3), 58.06 (NCH\_2CH\_2), 53.23 (CH\_2C(CF\_3)_2) ppm. \(^1^F\) \(^1^H\) NMR (dichloromethane-\text{d}_2, 376.52 MHz, 298 K): \delta -77.61 (s, 6F, CF\_3), -132.96 (d, 12F, 
\(J_{F\_F} = 17.9\) Hz, o-F), -160.24 (t, 6F, \(J_{F\_F} = 20.3\) Hz, p-F), -165.77 (t, 12F, \(J_{F\_F} = 19.5\) Hz, m-F) ppm.

\(^1^B\) NMR (dichloromethane-\text{d}_2, 128.38 MHz, 25\(^\circ\)C): \delta -8.34 ppm. Elemental analysis for C\_9\_H\_9\_B\_3\_F\_3\_N\_2\_O\_2 (1354.23 g\cdot mol\(^{-1}\)):
theoretical, C 40.8\%, H 1.5\%, N 2.1\%; found C 40.6\%, H 1.4\%, N 2.2%.

\[
[RO^2]HH]^+ [H_2N(B(C_6F_3)_3)_2]^+ (17): 1^H NMR (dichloromethane-\text{d}_2, 400.13 MHz, 298 K): \delta 5.70 (br, 2H, NH2), 3.88 - 3.71 (overlapping m, 4H, CH\_2C(CF\_3)_2 and NCH\_2CH\_2), 3.58 (t, 2H, \(J_{H\_H} = 4.6\) Hz, NCH\_2CH\_2), 3.49 (s, 3H, OCH\_3), 3.22 (s, 3H, NCH\_3) ppm. The signals for OH and NH could not be observed. \(^1^C\) NMR (75.46 MHz, dichloromethane-\text{d}_2, 25\(^\circ\)C): \delta 149.99, 146.83, 141.28, 138.85, 138.00, 135.56 (all C\_F\_3), 121.90 (q, \(J_{C\_F} = 289.3\) Hz, CF\_3), 73.83 (hept, \(J_{C\_F} = 31.5\) Hz), 63.92 (NCH\_2CH\_2), 61.26 (OCH\_3), 60.07 (CH\_2C(CF\_3)_2), 55.49 (NCH\_2CH\_2), 46.17 (NCH\_3) ppm. \(^1^F\) \(^1^H\) NMR (dichloromethane-\text{d}_2, 376.52 MHz, 298 K): \delta -77.80 (s, 6F, CF\_3), -132.95 (d, 12F, \(J_{F\_F} = 17.3\) Hz, o-F), -160.24 (t, 6F, \(J_{F\_F} = 20.3\) Hz, p-F), -165.76 (t, 12F, \(J_{F\_F} = 19.2\) Hz, m-F) ppm. \(^1^B\) NMR (dichloromethane-\text{d}_2, 128.38 MHz, 25\(^\circ\)C) \delta -8.34 ppm. Elemental analysis for C\_9\_H\_9\_B\_3\_F\_3\_N\_2\_O\_2 (1310.17 g\cdot mol\(^{-1}\)):
theoretical, C 40.3\%, H 1.2\%, N 2.4%; found C 40.3\%, H 1.1\%, N 2.3%.

\[
2[H_2N(B(C_6F_3)_3)_2]^+ (18): \ [RO^3]Ca^+ [H_2N(B(C_6F_3)_3)_2]^+ (132 mg, 0.09 mmol) was added in solid portions with a bent finger to a solution of Ca[N(SiMe\_3)_2] (34 mg, 0.09 mmol) in C\_8\_H\_8\_Cl (5 mL). Stirring was continued at room temperature for two days. The solution was evaporated in \textit{vacuo} and the resulting colourless solid was purified by precipitation from CH\_2Cl\_2 with pentane (3 times). The final colourless powder was dried in \textit{vacuo} to afford analytically pure 18 (96 mg, 70%). \(^1^H\) NMR (THF-\text{d}_8, 400.13 MHz, 298 K): \delta 5.74 (br, 2H, NH2), 4.06 - 3.93 (m, 8H, OCH\_2 moieties), 3.93 - 3.82 (m, 4H, OCH\_2 moieties), 3.12 - 2.75 (overlapping m, 6H, NCH\_2CH\_2 and CH\_2C(CF\_3)_2) ppm. \(^1^C\) \(^1^H\) NMR (THF-\text{d}_8, 100.62 MHz, 298 K): \delta 150.08, 147.69, 141.39, 138.85, 136.36 (all C\_F\_3), 126.99 (q, \(J_{C\_F} = 292.8\) Hz, CF\_3), 72.36, 71.16, 70.75 (all OCH\_2 moieties), 59.51 (CH\_2C(CF\_3)_2), 54.01 (NCH\_2CH\_2) ppm; the resonance for C(CF\_3)_2 was not detected. \(^1^F\) \(^1^H\) NMR
Experimental Part

(THF-\textit{d}_8, 376.52 MHz, 298 K): $\delta$ $-79.49$ (s, 6F, $CF_3$), $-133.13$ (d, 12F, $^3J_{F,F} = 18.4$ Hz, $o$-F), $-161.14$ (t, 6F, $^3J_{F,F} = 20.2$ Hz, $p$-F), $-166.44$ (t, 12F, $^3J_{F,F} = 19.3$ Hz, $m$-F) ppm. $^{11}$B NMR (THF-\textit{d}_8, 128.38 MHz, 25°C) $\delta$ $-8.31$ ppm. Elemental analysis for C_{36}H_{36}B_2CaF_{36}N_{20}O_4 (1434.33 g·mol\textsuperscript{-1}): theoretical, C 40.2%, H 1.4%, N 2.0%; found C 40.1%, H 1.3%, N 2.1%.

Method A. \{[RO\textsuperscript{3}]Ca\textsuperscript{+}[H_2N(B(CF_3)_3)_2]\}\textsuperscript{2+} (19): Method A. \{[RO\textsuperscript{3}]HH\}\textsuperscript{+}[H_2N{(B(CF_3)_3)_2}]\textsuperscript{-} (0.15 g, 0.11 mmol) was added in solid portions with a bent finger to a solution of Ca[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2} (37 mg, 0.11 mmol) in C\textsubscript{6}H\textsubscript{5}Cl (10 mL). The stirring was continued at room temperature for two days. The solution was evaporated under vacuum and the resulting colourless solid was purified by repeated precipitation from CH\textsubscript{2}Cl\textsubscript{2} with pentane (3 times). Drying under vacuum to constant weight afforded 19 as a colourless powder (97 mg, 63%).

Method B. [H(OEt\textsubscript{2})\textsubscript{2}]\textsuperscript{+}[H_2N{(B(CF_3)_3)_2}]\textsuperscript{-} (97 mg, 0.08 mmol) was added in solid portions to a solution of 10 (40 mg, 0.08 mmol) in Et\textsubscript{2}O (10 mL). A colourless precipitate formed after a few min. The stirring was continued overnight at room temperature. The solution was then filtered to isolate a solid which was purified by precipitation from CH\textsubscript{2}Cl\textsubscript{2} with pentane (3 times). The title compound was isolated as a colourless powder after drying \textit{in vacuo} (85 mg, 75%). \(^1\)H NMR (THF-\textit{d}_8, 500.13 MHz, 298 K): $\delta$ 5.74 (br, 2H, NH\textsubscript{2}), 3.78 (t, 4H, $^3J_{H,H} = 4.8$ Hz, NCH\textsubscript{2}CH\textsubscript{2}), 3.49 (s, 6H, OCH\textsubscript{3}), 2.94 (s, 2H, CH\textsubscript{2}C(CF\textsubscript{3})\textsubscript{2}), 2.90 (t, 4H, $^3J_{H,H} = 5.1$ Hz, NCH\textsubscript{2}CH\textsubscript{2}) ppm. \(^{13}\)C\{\(^1\)H\} NMR (THF-\textit{d}_8, 125.75 MHz, 298 K): $\delta$ 149.90, 148.01, 141.18, 139.23, 138.64, 136.70 (all C\textsubscript{F\textsubscript{3}}), 127.06 (q, $^1J_{C,F} = 292.0$ Hz, C\textsubscript{F\textsubscript{3}}), 70.87 (NCH\textsubscript{2}CH\textsubscript{2}), 60.26 (OCH\textsubscript{3}), 56.89 (CH\textsubscript{2}C(CF\textsubscript{3})\textsubscript{2}), 54.41 (NCH\textsubscript{2}CH\textsubscript{2}) ppm; the resonance for C(CF\textsubscript{3})\textsubscript{2} was not observed. \(^{19}\)F\{\(^1\)H\} NMR (THF-\textit{d}_8, 376.52 MHz, 298 K): $\delta$ $-79.68$ (s, 6F, $CF_3$), $-133.13$ (d, 12F, $^3J_{F,F} = 18.4$ Hz, $o$-F), $-161.14$ (t, 6F, $^3J_{F,F} = 20.2$ Hz, $p$-F), $-166.44$ (t, 12F, $^3J_{F,F} = 19.3$ Hz, $m$-F) ppm. \(^{11}\)B NMR (THF-\textit{d}_8, 128.38 MHz, 25°C): $\delta$ $-8.35$ ppm. Elemental analysis for C\textsubscript{36}H\textsubscript{36}B\textsubscript{2}CaF\textsubscript{36}N\textsubscript{20}O\textsubscript{4} (1392.29 g·mol\textsuperscript{-1}): theoretical, C 39.7%, H 1.3%, N 2.0%; found C 39.6%, H 1.3%, N 2.1%.

\{[RO\textsuperscript{3}]Sr\textsuperscript{+}[H_2N(B(CF_3)_3)_2]\}\textsuperscript{2+} (20): Method A. \{[RO\textsuperscript{3}]HH\}\textsuperscript{+}[H_2N{(B(CF_3)_3)_2}]\textsuperscript{-} (0.300 g, 0.11 mmol) was added in solid portions with a bent finger to a solution of Sr[N(SiMe\textsubscript{3})\textsubscript{2}]\textsubscript{2} (0.090 g, 0.22 mmol) in Et\textsubscript{2}O (10 mL). A colourless precipitate formed almost instantly. Stirring was continued at room temperature for two days. The solution was evaporated under vacuum and the resulting colourless solid was purified by precipitation from CH\textsubscript{2}Cl\textsubscript{2} with pentane (3 times). Drying under vacuum to constant weight afforded 20 as a colourless powder (0.18 g, 57%). \(^1\)H NMR (THF-\textit{d}_8, 500.13 MHz, 298 K): $\delta$ 5.74 (br, 2H, NH\textsubscript{2}), 3.78 (t, 4H, $^3J_{H,H} = 4.8$ Hz, NCH\textsubscript{2}CH\textsubscript{2}), 3.49 (s, 6H, OCH\textsubscript{3}), 2.93 (s, 2H, CH\textsubscript{2}C(CF\textsubscript{3})\textsubscript{2}), 2.87 (t, 4H, $^3J_{H,H} =$
Experimental Part

4.9 Hz, NCH₂CH₂) ppm.¹³C{¹H} NMR (d₆, 125.75 MHz, 298 K): δ 149.89, 147.98, 141.18, 139.21, 138.62, 136.67 (all C₆F₃), 127.31 (q, J_{C,F} = 293.7 Hz, CF₃), 71.16 (NCH₂CH₂), 59.76 (OCH₃), 57.79 (CH₂C(CF₃)₂), 54.90 (NCH₂CH₂) ppm. The resonance for C(CF₃)₂ was not observed.¹⁹F NMR (THF-d₈, 376.52 MHz, 298 K): δ −79.66 (s, 6F, CF₃), −133.13 (d, 12F, J_{F,F} = 18.4 Hz, α-F), −161.14 (t, 6F, J_{F,F} = 20.2 Hz, p-F), −166.44 (t, 12F, J_{F,F} = 19.3 Hz, m-F) ppm. Elemental analysis for Ca[N(SiMe₃)₂] (1440.84 g·mol⁻¹): theoretical, C 38.3%, H 1.3%, N 1.9% was not performed at the time of writing the manuscript.

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\text{[\{RO¹\}Ca⁺}[\text{H₂N}\{\text{B(C₆F₃)₃}\}]₂\text{]}\quad (21): \text{ Method A.}
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\text{[\{RO¹\}HH⁺}[\text{H₂N}\{\text{B(C₆F₃)₃}\}]₂\text{]}\quad (200 mg, 0.15 mmol) was added in solid portions to a solution of Ca[N(SiMe₃)₂] (54 mg, 0.15 mmol) in C₆H₆Cl (5 mL). Stirring was continued at room temperature for two days. The volatile fraction was evaporated under vacuum to give a solid which was purified by precipitation from CH₂Cl₂ with pentane (3 times). The colourless powder was dried in vacuo to afford analytically pure 21 (164 mg, 80%).

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\text{Method B. [H(OEt₂)]⁺}[\text{H₂N}\{\text{B(C₆F₃)₃}\}]₂\text{]}\quad (76 mg, 0.06 mmol) was added in solid portions to a solution of 13 (30 mg, 0.06 mmol) in Et₂O (10 mL). A colourless precipitate formed within a few min. Stirring was continued overnight at room temperature. The solution was filtered out and the colourless solid was purified by precipitation from CH₂Cl₂ with pentane (3 times). The crude sample contained residual Et₂O which could not be removed. The powder was dried in vacuo to afford 21 (66 mg, 76%) as a colourless powder.¹H NMR (THF-d₆, 400.13 MHz, 25°C): δ 5.74 (br, 2H, NH₂), 3.78 (t, 2H, J_{H,H} = 5.2 Hz, NCH₂CH₂), 3.55 (s, 3H, OCH₃), 2.90–2.70 (overlapping m, 4H, NCH₂CH₂ and CH₂C(CF₃)₂), 2.38 (s, 3H, NCH₃) ppm.¹³C{¹H} NMR (THF-d₆, 100.62 MHz, 298 K): δ 150.08, 147.71, 141.40, 138.87, 136.39 (all C₆F₃), 126.88 (q, J_{C,F} = 293.8 Hz, CF₃), 71.53 (NCH₂CH₂), 61.21 (OCH₃), 60.01 (CH₂C(CF₃)₂), 58.92 (NCH₂CH₂), 43.66 (NCH₃) ppm; the resonance for C(CF₃)₂ was not detected.¹⁹F{¹H} NMR (THF-d₆, 376.52 MHz, 298 K): δ −79.16 (s, CF₃), −133.13 (d, 12F, J_{F,F} = 17.7 Hz, α-F), −161.15 (t, 6F, J_{F,F} = 20.2 Hz, p-F), −166.45 (t, 12F, J_{F,F} = 19.0 Hz, m-F) ppm.¹¹B NMR THF-d₆, 128.38 MHz, 25°C): δ −10.21 ppm. Elemental analysis for C₆H₆B₂CaF₆N₂O₂ (1348.24 g·mol⁻¹): theoretical, C 39.2%, H 1.0%, N 2.1%; found C 39.2%, H 1.1%, N 2.2%.

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\text{[\{RO¹\}Ba⁺}[\text{H₂N}\{\text{B(C₆F₃)₃}\}]₂\text{]}\quad (22): \text{[\{RO¹\}HH⁺}[\text{H₂N}\{\text{B(C₆F₃)₃}\}]₂\text{]}\quad (0.20 g, 0.15 mmol) was added in solid portions to a solution of Ba[N(SiMe₃)₂] (0.07 mg, 0.15 mmol) in Et₂O (10 mL). Within min, a fine precipitate formed. Stirring was continued overnight. After filtration, the white precipitate was washed dissolved in CH₂Cl₂ (2 mL) and precipitated by dropwise addition of pentane (15 mL). This procedure was repeated three times to
afford analytically pure 22 (0.11 g, 52%).$^1$H NMR (dichloromethane-$d_2$, 400.13 MHz, 25°C): $\delta$ 5.67 (br, 2H, NH$_2$), 3.84–3.74 (m, 2H, CH$_2$), 3.48 (s, 3H, OCH$_3$), 3.10–2.77 (overlapping m, 3H, NCH$_2$CH$_2$ and C(H)HC(CF$_3$)$_2$), 2.56 (d, 1H, $^3$J$_{H-H}$ = 14.1 Hz, C(H)HC(CF$_3$)$_2$), 2.35 (s, 3H, NCH$_3$) ppm. $^{19}$F{$^1$H} NMR (dichloromethane-$d_2$, 376.52 MHz, 298 K): $\delta$ −75.51 to −77.44 (m, 6F, CF$_3$), −132.87 (d, 12F, $^3$J$_{F-F}$ = 17.7 Hz, CH=CF$_2$), −160.11 (t, 6F, $^3$J$_{F-F}$ = 20.2 Hz, p-F), −165.65 (t, 12F, $^3$J$_{F-F}$ = 19.0 Hz, m-F) ppm. Elemental analysis for C$_{4}$H$_{14}$B$_{2}$F$_{3}$N$_{2}$O$_{2}$Sr (1395.78 g·mol$^{-1}$): theoretical, C 37.8%, H 1.0%, N 2.0% was not performed at the time of writing the manuscript.

$\text{[\{RO}^{12}\text{\}CaN(SiMe$_{2}$H)$_{2}$]}$ (23) A solution of $\{\text{RO}^{12}\}$H (0.18 g, 0.58 mmol) in diethyl ether (10 mL) was added at −78 °C over a period of 1 h to a solution of Ca[N(SiMe$_{2}$H)$_{2}$]$_{2}$(THF) (0.29 g, 0.77 mmol) in diethyl ether (10 mL). The reaction mixture was warmed to room temperature and, after stirring for 1 h, volatiles were removed under vacuum. The resulting oil was stripped with pentane (3 × 4 mL) and recrystallisation from the same solvent at −30 °C afforded 23 as colourless crystals (0.13 g, 52%). $^1$H NMR (benzene-$d_6$, 400.16 MHz, 298 K): $\delta$ 5.81 (ddt, 4H, $^3$J$_{H-H}$ (trans) = 17.2 Hz, $^3$J$_{H-H}$ (cis) = 10.4 Hz, $^2$J$_{H-H}$ = 6.8 Hz, CH=CH$_2$), 5.24–5.14 (m, 8H, CH=CH$_2$), 4.93 (s, 4H, $^1$J$_{Si-H}$ = 158 Hz, SiH), 2.76–2.50 (overlapping m, 12H, NCH$_2$CH$_2$ and CH$_2$C(CF$_3$)$_2$), 1.91 (q, 8H, $^3$J$_{H-H}$ = 6.7 Hz, NCH$_2$CH$_2$), 0.43 (d, $^3$J$_{H-H}$ = 2.5 Hz, 24H, SiCH$_3$). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 100.63 MHz, 298 K): $\delta$ 136.32 (CH=CH$_2$), 125.73 (q, $^1$J$_{C-F}$ = 290.1 Hz, CF$_3$), 119.09 (CH=CH$_2$), 79.30 (hept, C(CF$_3$)$_2$), $^2$J$_{C-F}$ = 26.0 Hz), 53.94 (CH$_2$C(CF$_3$)$_2$), 53.84 (NCH$_2$CH$_2$), 28.63 (NCH$_2$CH$_2$), 4.69 (s, SiCH$_3$) ppm. $^{19}$F{$^1$H} NMR (benzene-$d_6$, 376.53 MHz, 298 K): $\delta$ −76.68 (s, CF$_3$). Elemental analysis for C$_{4}$H$_{14}$B$_{2}$F$_{3}$N$_{2}$O$_{2}$Sr (476.66 g·mol$^{-1}$): theoretical, C 40.3%, H 6.3%, N 5.9%; found C 40.3%, H 6.3%, N 5.8%.

$\text{[\{RO}^{14}\text{\}CaN(SiMe$_{2}$H)$_{2}$]}$ (25) A solution of $\{\text{RO}^{14}\}$H (0.24 g, 0.82 mmol) in diethyl ether (10 mL) was added at −78 °C over a period of 1 h to a solution of Ca[N(SiMe$_{2}$H)$_{2}$]$_{2}$(THF) (0.40 g, 1.06 mmol) in diethyl ether (10 mL). The reaction mixture was warmed to room temperature and, after stirring for 1 h, volatiles were removed under vacuum. The resulting oil was stripped with pentane (3 × 2 mL) and washed with the same solvent (2 × 2 mL) to afford 25 as a colourless powder (250 mg, 66%). Crystals suitable for X-ray diffractometry were obtained from a pentane solution at −30 °C. This complex features two sets of resonances: A and B. $^1$H NMR (toluene-$d_8$, 400.13 MHz, 263 K): $\delta$ 6.28–6.09 (m, 1H, CH=CH$_2$ (A)), 6.01–5.87 (m, 1H, CH=CH$_2$ (B)), 5.45 (d, 1H, $^3$J$_{H-H}$ (cis) = 9.6 Hz, CH=C(H)H$_{cis}$ (A)), 5.35 (d, 1H, $^3$J$_{H-H}$ (cis) = 10.0 Hz, CH=C(H)H$_{trans}$ (B)), 5.29 (d, 1H, $^3$J$_{H-H}$ (trans) = 18.0 Hz, CH=C(H)H$_{trans}$ (A)), 5.27 (d, 1H, $^3$J$_{H-H}$ (trans) = 18.0 Hz, CH=C(H)H$_{trans}$ (B)). 4.81 (s, 4H, $^1$J$_{Si-H}$ = 160 Hz, SiH (A + B)), 2.99, 2.19 (ABq, 2H, $J_{AB} =$
Experimental Part

15.4 Hz, CH₂(CF₃)₂ (A + B)), 2.95–2.84 (m, 2H, CH(CH₃)₂ (A + B)), 2.88, 2.31 (ABq, 2H, Jₐb = 15.6 Hz, CH₂(CF₃)₂ (A or B)), 2.83–2.74 (m, 1H, NCH(H)CH₂ (A)), 2.52–2.41 (m, 1H, NCH(H)CH₂ (B)), 2.27–2.10 (m, 1H, NC(H)HCH₂ (B) and NC(H)HCH₂ (A)), 2.04–1.82 (overlapping m, 4H, NCH₂CH₂ (B) and NCH₂CH₂ (A)), 1.05 (d, 3H, Jₕ-H = 6 Hz, CH(CH₃)(CH₃) (A or B)), 0.90 (d, 3H, Jₕ-H = 6.1 Hz, CH(CH₃)(CH₃) (A or B)), 0.59 (d, 3H, Jₕ-H = 6.3 Hz, CH(CH₃)(CH₃) (A or B)), 0.41 (overlapping m, 27H, SiCH₃ (A + B) and CH(CH₃)(CH₃) (A or B)) ppm. ¹³C[¹H] NMR (toluene-d₆, 100.62 MHz, 263 K): δ 136.37 (CH=CH₂ (A)), 136.27 (CH=CH₂ (B)), 121.95 (CH=CH₂ (A)), 120.66 (CH=CH₂ (B)), 53.19 (NCH₂CH₂ (A)), 51.73 (NCH₂CH₂ (B)), 51.17 (CH(CH₃)₂ (A or B)), 50.16 (CH₂(CF₃)₂ (A or B)), 49.41 (CH(CH₃)₂ (A or B)), 49.23 (CH₂(CF₃)₂ (A or B)), 30.76 (NCH₂CH₂ (A or B)), 30.13 (NCH₂CH₂ (A or B)), 20.71 (CH(CH₃)(CH₃) (A or B)), 18.48 (CH(CH₃)(CH₃) (A or B)), 16.29 (CH(CH₃)(CH₃) (A or B)), 14.31 (CH₂(CF₃)₂ (A or B)), 4.67(SiCH₃ (A or B)), 4.53 (SiCH₃ (A or B)) ppm. The resonances for C(CF₃)₂ and CF₃ were not detected. ¹⁹F[¹H] NMR (toluene-d₆, 376.47 MHz, 263 K): δ −76.29 (br s, 6F, CF₃), −76.95 (q, Jₑ-F = 9.2 Hz, 6F, CF₃), −77.22 (br s, 6F, CF₃), −77.36 (br s, 6F, CF₃) ppm.

Elemental analysis for C₁₅H₃₀CaF₆N₂OSi₂ (464.65 g mol⁻¹): theoretical, C 38.7%, H 6.5%, N 6.0%; satisfactory results could not be obtained in spite of repeated attempts.

\[ [\text{RO}^{11}]\text{SrN(SiMe₃)₂} (26) \] A solution of \{RO^{11}\}H (0.35 g, 0.61 mmol) in diethyl ether (10 mL) was added at −78 °C over a period of 1 h to a solution of Sr[N(SiMe₃)₂]₂(THF)₂₃ (0.40 g, 1.06 mmol) in diethyl ether (10 mL). The reaction mixture was warmed to room temperature and, after stirring for 1 h, volatiles were removed under vacuum. The resulting oil was stripped with pentane (3 × 6 mL) and washed with the same solvent (2 × 2 mL) to afford 26 as a colourless powder (127 mg, 49%). Crystals suitable for X-ray diffractometry were obtained from a pentane solution at −30 °C. ¹H NMR (benzene-d₆, 400.16 MHz, 298 K): δ 6.30–6.11 (m, 1H, CH=CH₂), 5.39 (d, 1H, Jₕ-H (cis) = 10.1 Hz, CH=C(H)H₂), 5.22 (d, 1H, Jₕ-H (trans) = 17.8 Hz, CH=C(H)H₂), 4.86 (s, 4H, Jₕ-H = 160 Hz, SiH₂), 2.97, 2.16 (ABq, 2H, J₂ₚ = 15.6 Hz, CH₂(CF₃)₂), 2.83 (hept, 1H, Jₕ-H = 6.4 Hz, CH(CH₃)₂), 2.63 (t, 1H, Jₕ-H = 12.0 Hz, NCH(H)CH₂), 2.12–1.99 (m, 1H, NC(H)HCH₂), 1.99–1.76 (m, 2H, NCH₂CH₂), 0.99–0.83 (m, 6H, CH(CH₃)₂), 0.46 (d, 12H, Jₕ-H = 2.9 Hz, SiCH₃) ppm. ¹³C[¹H] NMR (benzene-d₆, 125.77 MHz, 298 K): δ 138.98 (CH=CH₂), 121.17 (CH=CH₂), 79.76 (hept, Jₑ-F = 25.5 Hz, C(CF₃)₂), 51.93 (NCH₂CH₂), 50.38 (NCH₂CH₂), 49.28 (CH(CH₃)₂ or CH₂C(CF₃)₂), 49.25 (CH(CH₃)₂ or CH₂C(CF₃)₂) 30.24 (NCH₂CH₂), 19.52 (CH(CH₃)(CH₃), 14.87 (CH(CH₃)(CH₃), 4.70 (SiCH₃) ppm; the resonances for C(CF₃)₂ were not detected. ¹⁹F[¹H] NMR (benzene-d₆, 376.49 MHz, 298 K): δ −75.24, −76.13, −76.45 (all minor singlets), −76.91 (q, Jₑ-F = 7.8 Hz, 3F, CF₃), −77.42 (m, 6F, CF₃) ppm. Elemental analysis for C₁₅H₃₀CaF₆N₂OSi₂ (512.20 g mol⁻¹): theoretical, C 35.2%, H 5.9%, N 5.5%; found C 35.2%, H 6.0%, N 5.4%.

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Yb[N(SiMe₂H)₂]₂(THF): HN(SiMe₂H)₂ (66 mg, 0.5 mmol) was added dropwise over a period of 2 min to a solution of Yb[N(SiMe₃)₂]₂(THF)₂ (0.13 g, 0.20 mmol) in THF (10 mL) cooled at 0 °C. The reaction mixture was stirred at this temperature for 1.5 h. After removal of the volatiles in vacuo, the resulting brown oil was stripped with pentane (3 × 5 mL) to afford the title compound as a brown solid (86 mg, 85%). ¹H NMR (benzene-d₆, 400.13 MHz, 298 K): 5.29–4.64 (m, 2H, Si–H), 3.56 (br s, 2H, CH₂CH₂O), 1.64 (br s, 2H, CH₂CH₂O), 0.44 (br s, 12H, SiCH₃).

[[RO¹¹]YbN(SiMe₂H)₂] (27): A solution of {RO¹¹}H (55 mg, 0.18 mmol) in diethyl ether (5 mL) was added at −78 °C over a period of 1 h to a solution of Yb[N(SiMe₂H)₂]₂(THF) (0.12 g, 0.25 mmol) in diethyl ether (4 mL). The reaction mixture was warmed to room temperature and, after stirring for 1 h, volatiles were removed under vacuum. The resulting oil was stripped with pentane (3 × 2 mL) and recrystallisation from the same solvent afforded 27 as red crystals in a very small amount. NMR investigations were precluded owing to the presence of paramagnetic impurities.

[[RO¹¹]YbN(SiMe₃)₂] (28): A solution of {RO¹¹}H (99 mg, 0.34 mmol) in diethyl ether (4 mL) was added at −78 °C over a period of 1 h to a solution of Yb[N(SiMe₃)₂]₂(THF)₂ (0.22 g, 0.34 mmol) in diethyl ether (6 mL). The reaction mixture was warmed to room temperature and after stirring for 1 h the volatiles were removed under vacuum. The resulting oil was stripped with pentane (3 × 2 mL) and recrystallisation from the same solvent afforded 28 as orange-red crystals in a very small amount (ca. 10 mg, 5%). NMR investigations were precluded owing to the presence of paramagnetic impurities. Elemental analysis for C₁₇H₃₄F₆N₂O₅Si₂Yb (626.15 g mol⁻¹): theoretical, C 32%, H 5.5%, N 4.5%; satisfactory results could not be obtained despite repeated attempts.

[[RO¹³]CaN(SiMe₂H)₂] (29): A solution of {RO¹³}H (94 mg, 0.31 mmol) in diethyl ether (6 mL) was added at −78 °C over a period of 1 h to a solution of Ca[N(SiMe₂H)₂]₂(THF) (0.15 g, 0.40 mmol) in diethyl ether (7 mL). The reaction mixture was slowly warmed to room temperature and, after stirring for 1 h, volatiles were removed under vacuum. The resulting oil was stripped with pentane (3 × 4 mL) and was finally dissolved in 3 mL of this solvent. Storage of this pentane solution at −30 °C resulted in the precipitation of a colourless precipitate. Filtration and drying in vacuo of the precipitate afforded 29 as a colourless powder (76 mg, 52%). The complex was recrystallised from toluene at −30 °C. This complex features two sets of signals which could be discerned and only the identity of the hydrogen atoms was clearly established. ¹H NMR (benzene-d₆, 400.13 MHz, 298 K): δ 5.91–5.75 (m, 1H, CH=CH(H)CH₃), 5.68–5.47 (m, 1H, CH=CH(H)CH₃), 4.88 (s, 2H, CH₃), 1.58 Hz, SiH), 3.08–2.86
Elemental analysis for C$_{16}$H$_{32}$CaF$_{6}$N$_{2}$SiO$_{2}$ (478.68 g·mol$^{-1}$): theoretical, C 40.1%, H 6.7%, N 5.8% was not performed at the time of writing the manuscript.

Experimental Part

A solution of [RO$^{4}$]CaN(SiMe$_{2}$H)$_{2}$ (30): A solution of [RO$^{3}$]H (0.13 g, 0.42 mmol) in diethyl ether (8 mL) was added at ~78 °C over a period of 1 h to a solution of Ca[N(SiMe$_{2}$H)$_{2}$]$_{2}$(THF) (0.20 g, 0.53 mmol) in diethyl ether (6 mL). The reaction mixture was warmed to room temperature and, after stirring for 1 h, volatiles were removed under vacuum. The resulting oil was stripped with pentane (3 x 4 mL) and recrystallisation from the same solvent at ~30 °C afforded 30 as colourless crystals (106 mg, 51%). $^1$H NMR (benzene-$d_6$, 500.13 MHz, 298 K): δ 5.11–5.06 (m, 1H, CH=CH(CH$_3$)$_2$), 4.97 (s, 2H, $^1$J$_{5,5}$ = 156 Hz, SiH), 3.06 (hept, 1H, $^1$J$_{6,6}$ = 6.6 Hz, CH(CH$_3$)$_2$), 2.99–1.97 (overlapping m, 6H, NCH$_2$CH$_2$, NCH$_2$CH$_2$, and CH$_2$C(CF$_3$)$_2$), 1.65 (s, 3H, CH=CH(CH$_3$)$_2$CH$_3$), 1.55 (s, 3H, CH=CH(CH$_3$)$_2$CH$_3$), 1.05–0.66 (m, 6H, CH(CH$_3$)$_2$), 0.43 (d, 12H, $^1$J$_{4,4}$ = 2.8 Hz, SiCH$_3$) ppm. $^{13}$C [$^1$H] NMR (benzene-$d_6$, 125.77 MHz, 298 K): δ 135.55 (CH=CH(CH$_3$)$_2$), 125.76 (q, $^1$J$_{C,F}$ = 288.8 Hz, CF$_3$), 119.53 (CH=CH(CH$_3$)$_2$), 78.82 (hept, $^2$J$_{C,F}$ = 25.9 Hz, C(CF$_3$)$_2$), 52.75 (CH$_2$C(CF$_3$)$_2$), 52.55 (CH(CH$_3$)$_2$), 50.53 (NCH$_2$CH$_2$), 27.91 (NCH$_2$CH$_2$), 25.62 (CH=CH(CH$_3$)$_2$CH$_3$), 17.96 (CH(CH$_3$)$_2$), 17.80 (CH=CC(CH$_3$)$_2$) ppm. $^{19}$F [$^1$H] NMR (benzene-$d_6$, 376.47 MHz, 298 K): −77.05 (s, 6F, CF$_3$) ppm. $^{19}$F [$^1$H] NMR (benzene-$d_6$, 376.47 MHz, 298 K): −76.69 (br s, 3F, CF$_3$), −77.06 (br s, 3F, CF$_3$) ppm. Elemental analysis for C$_{17}$H$_{34}$CaF$_{6}$N$_{2}$SiO$_{2}$ (492.70 g·mol$^{-1}$): theoretical, C 41.4%, H 7.0%, N 5.7% was not performed at the time of writing the manuscript.
Experimental Part

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{\{\text{RO}^{21}\}}\text{Ca(N(SiMe}_2\text{H})_2\}}\text{]}(\text{THF}) \quad (31): \text{A solution of } {\{\text{RO}^{21}\}}\text{H} \quad (0.13 \text{ g}, \quad 0.40 \text{ mmol}) \text{ in diethyl ether (12 mL) was added at } -78 \ ^\circ \text{C over a period of 1 h to a solution of Ca[N(SiMe}_2\text{H})_2\}}\text{]}(\text{THF}) \quad (0.20 \text{ g}, \quad 0.53 \text{ mmol}) \text{ in diethyl ether (10 mL). The reaction mixture was warmed to room temperature and, after stirring for 1 h, volatiles were removed under vacuum. The resulting oil was stripped with pentane (3 x 4 mL) and recrystallisation from the same solvent at } -30 \ ^\circ \text{C afforded 31 as colourless crystals (112 mg, 54\%).} {\text{H NMR (benzene-d}_6\text{, 500.13 MHz, 298 K): } \delta \quad 7.15-7.12 \text{ (m, 4H, }} \text{C}_6\text{H}_5\text{), 7.08-7.04} \text{ (m, 2H, } p-\text{C}_6\text{H}_5\text{), 7.04-6.99} \text{ (m, 4H, } \alpha-\text{C}_6\text{H}_3\text{), 4.94} \text{ (s, 4H, } J_{\text{Si-H}} = 157 \text{ Hz, SiH}, \text{ 3.67-3.61} \text{ (m, 4H, OCH}_2\text{CH}_2\text{), 3.16-2.40} \text{ (overlapping m, 12H, } \text{C}_6\text{H}_5\text{)}\text{CH}_2\text{, NCH}_2\text{CH}_2\text{ and NCH}_2\text{CH}_2\text{), 2.37} \text{ (s, 6H, } \text{CH}_3\text{), 1.37-1.33} \text{ (m, 4H, OCH}_2\text{CH}_2\text{), 0.38} \text{ (d, 24H, } J_{\text{Si-H}} = 3\text{Hz, SiCH}_3\text{) ppm.} {\text{C}}^{1}\text{H NMR (benzene-d}_6\text{, 125.77 MHz, 298 K): } \delta \quad 138.63 \text{ (}\iota-\text{C}_6\text{H}_5\text{), 129.04} \text{ (}\text{m-C}_6\text{H}_5\text{), 128.87} \text{ (}\alpha-\text{C}_6\text{H}_5\text{), 126.93} \text{ (}\text{p-C}_6\text{H}_5\text{), 125.84} \text{ (s, } J_{\text{CF}} = 288.9 \text{ Hz, CF}_3\text{), 79.72} \text{ (hept, } J_{\text{CF}} = 25.8 \text{ Hz, C(CF}_3)_2\text{), 68.94} \text{ (OCH}_2\text{CH}_2\text{), 61.48} \text{ (CH}_2\text{C(CF}_3)_2\text{), 57.36} \text{ (NCH}_2\text{CH}_2\text{), 44.12} \text{ (CH}_3\text{), 28.99} \text{ (NCH}_2\text{CH}_2\text{), 25.44} \text{ (OCH}_2\text{CH}_2\text{), 4.74} \text{ (SiCH}_3\text{) ppm.} {\text{F}}^{1}\text{NMR (benzene-d}_6\text{, 376.49 MHz, 298 K): } \delta \quad -75.77 \text{ (br s, CF}_3\text{), } -76.53 \text{ to } -77.30 \text{ (m, CF}_3\text{) ppm.} {\text{Si}}^{29}\text{NMR (benzene-d}_6\text{, 79.49 MHz, 298 K): } \delta \quad -23.7 \text{ ppm. Elemental analysis for C}_2\text{H}_3\text{F}_5\text{CaF}_6\text{N}_2\text{O}_2\text{Si}_2\text{ (565.78 g mol}^{-1}\text{): theoretical, C 45.6\%, H 6.6\%, N 4.9\%; found C 45.2\%, H 6.6\%, N 4.9\%.}
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{\{\text{RO}^{21}\}}\text{Ca(N(SiMe}_2\text{H})_2\}}\text{]}(\mu-\text{Ca[N(SiMe}_2\text{H})_2\}}\text{]} \quad (32): \text{A solution of } {\{\text{RO}^{21}\}}\text{H} \quad (0.16 \text{ g}, \quad 0.50 \text{ mmol}) \text{ in diethyl ether (10 mL) was added at } -78 \ ^\circ \text{C over a period of 1 h to a solution of Ca[N(SiMe}_2\text{H})_2\}}\text{]}(\text{THF}) \quad (0.15 \text{ g}, \quad 0.50 \text{ mmol}) \text{ in diethyl ether (10 mL). The reaction mixture was warmed to room temperature and after stirring for 1 h the volatiles were removed under vacuum. The resulting oil was stripped with pentane (3 x 4 mL) and recrystallisation from the same solvent at } -30 \ ^\circ \text{C afforded 32 as colourless crystals (131 mg, 62\%).} \]
Experimental Part

Hydrogen, C 176 Hz, C 3

Elemental analysis for C42H84Ca3F12N6O2Si8 (1278.07 g·mol⁻¹): theoretical, C 39.5%, H 6.6%, N 6.6%; found C 39.6%, H 6.7%, N 6.4%.

A solution of {RO22}H (0.11 g, 0.32 mmol) in diethyl ether (8 mL) was added at −78 °C over a period of 1 h to a solution of Ca[N(SiMe2H)2]2(THF) (0.15 g, 0.41 mmol) in diethyl ether (7 mL). The reaction mixture was warmed to room temperature and after stirring for 1 h the volatiles were removed under vacuum. The resulting oil was stripped with pentane (3 × 4 mL) and recrystallisation from the same solvent at −4 °C afforded the title compound as colourless crystals (unoptimised synthesis). Informative NMR analysis was precluded by high fluxionality of the complex at room temperature.

A solution of {RO31}H (0.15 g, 0.48 mmol) in diethyl ether (12 mL) was added at −78 °C over a period of 1 h to a solution of Ca[N(SiMe2H)2]2(THF) (0.24 g, 0.63 mmol) in diethyl ether (8 mL). The reaction mixture was warmed to room temperature and after stirring for 1 h the volatiles were removed under vacuum. The resulting oil was stripped with pentane (4 × 4 mL) and washed with the same solvent (2 × 3 mL) to afford 34 as a colourless powder (0.15 g, 62%). Crystals suitable for X-ray diffractometry were obtained from a cold pentane solution at −30 °C. 1H NMR (benzene-d6, 400.13 MHz, 298 K): δ 4.93 (s, 2H, SiH), 3.27–1.84 (overlapping m, 7H, CH2C(CF3)2, NCCH2CH3, NCH2CH2 and CH(CH3)2), 1.71 (s, 3H, C≡C–CH3), 0.64 (d, 6H, 3JH-H = 6.7 Hz, CH(CH3)2), 0.46 (d, 12H, 3JH-H = 2.3 Hz, SiCH3) ppm. 13C{1H} NMR (benzene-d6, 100.63 MHz, 298 K): δ 78.97 (hept, 2JCF = 29.1 Hz, C(CF3)2), 77.92 (C≡C–CH3), 51.55 (CH(CH3)2), 50.88 (NCH2CH3), 49.02 (CH2C(CF3)2), 22.74 (NCH2CH3), 18.23 (CH(CH3)2), 4.83(SiCH3), 4.20 (C≡C–CH3) ppm. The resonances for C≡C–CH3 and CF3 were not detected. 19F{1H} NMR (benzene-d6, 376.47 MHz, 298 K): −76.18 (br s, 6F, CFS), −77.44, −78.04, −78.22, −78.84 (all minor resonances) ppm. Elemental analysis for C16H30CaF6N2OSi (476.66 g mol⁻¹): theoretical, C 40.3%, H 6.3%, N 5.9%; satisfactory results could not be obtained in spite of repeated attempts.

Attempted preparation of [(RO41)CaN(SiMe3H)2] (35): A solution of [RO41]H (0.14 g, 0.44 mmol) in diethyl ether (5 mL) was added at −78 °C over a period of 1 h to a solution of Ca[N(SiMe2H)2]2(THF) (0.21 g, 0.56 mmol) in diethyl ether (6 mL). The reaction mixture was warmed to room temperature and, after stirring for 1 h, volatiles were
removed under vacuum. The resulting oil was stripped with pentane (4 x 4 mL). The crude mixture was dissolved in pentane (3 mL) and cooled at −30 °C. After 1 h, a colourless solid precipitated. After filtration, the precipitate was dried in vacuo. A 1H NMR spectrum recorded of the colourless solid indicated a mixture of the title compound with complex 34.

Miscellaneous compounds

{ROH}H: A solution of diethylamine (1.16 g, 15.86 mmol) was added via syringe to a solution of 2,2-bis(trifluoromethyl)oxirane (3.13 g, 17.38 mmol) in Et2O (10 mL). The reaction mixture was stirred at room temperature for two days. The volatiles were then evaporated under reduced pressure to afford {ROH}H as a colourless solid. Yield 3.55 g (89%). 1H NMR (benzene-d6, 400.16 MHz, 298 K): δ 6.67 (s, 1H, OH), 2.51 (s, 2H, CH2C(CF3)2), 2.09 (q, 3JH–H = 7.2 Hz, 4H, NC2H3), 0.51 (t, 3JH–H = 7.2 Hz, 6H, NCH2C2) ppm.

19F{1H} NMR (benzene-d6, 376.49 MHz, 298 K): δ −77.76 (s, 6F, C2F3) ppm. The NMR chemical shifts are consistent with the ones previously reported in the literature.

1a [{RO}K]: To a solution of {RO}H (0.24 g, 0.82 mmol) in Et2O (15 mL) was added in solid portions with a bent finger KN(SiMe3)2 (0.16 g, 0.82 mmol). The reaction mixture was stirred at room temperature overnight. Volatiles were removed under vacuum and the resulting oil was stripped with pentane (3 x 3 mL) to afford the title compound as a colourless oil. All attempts to obtain the title compound as a solid or recrystallisation from various solvents failed. Yield 0.23 g (85%). 1H NMR (benzene-d6, 400.13 MHz, 298 K): δ 5.86 (ddt, 3JH–H (trans) = 17.3 Hz, 3JH–H (cis) = 10.3 Hz, 3JH–H = 6.8 Hz, 1H, CH=CH2), 5.10 (d, 1H, 3JH–H (trans) = 17.3 Hz, CH=CH2), 5.03 (d, 1H, 3JH–H (cis) = 10.3 Hz, CH=CH2), 2.94 (hept, 3JH–H = 6.4 Hz, CH(CH3)2), 2.64 (s, 2H, CH2C(CF3)2), 2.58 (t, 2H, 3JH–H = 7.6 Hz, NCH2CH2), 2.20 (q, 2H, 3JH–H = 7.2 Hz, NCH2CH2), 0.92 (d, 6H, 3JH–H = 6.8 Hz, CH(CH3)2), ppm.

13C{1H} NMR (benzene-d6, 100.62 MHz, 298 K): δ 137.73 (CH=CH2), 127.65 (q, 3JCF = 294.4 Hz, CF3), 115.67 (CH=CH2), 81.31 (m, C(CF3)2), 56.95 (CH2C(CF3)2), 51.45 (NCH2CH2), 51.32 (CH(CH3)2), 33.60 (NCH2CH2), 18.20 (CH(CH3)2) ppm. 19F{1H} NMR (benzene-d6, 376.47 MHz, 298 K): δ −75.47 (s, 6F, CF3) ppm.

{RO}H: To a solution of {RO}H (0.21 g, 0.67 mmol) in Et2O (10 mL) was added in solid portions with a bent finger KN(SiMe2)2 (0.11 g, 0.65 mmol). The reaction mixture was stirred at room temperature overnight. Volatiles were removed under vacuum and the resulting oil was stripped with pentane (3 x 4 mL) to afford the title compound as a colourless oil. In a matter of days, the oil crystallised and the title compound could be isolated as off-white crystals. Yield (161 mg, 72%).
NMR (benzene-\textit{d}_6, 400.13 MHz, 298 K): \( \delta \) 5.79 (ddt, 2H, \( J_{\text{H-H}} \) (\textit{trans}) = 17.4 Hz, \( J_{\text{H-H}} \) (\textit{cis}) = 9.9 Hz, \( J_{\text{H-H}} = 6.7 \) Hz, \( \text{CH} = \text{CH}_2 \)), 5.13–5.01 (m, 4H, \( \text{CH} = \text{CH}_2 \)), 2.76 (s, 2H, \( \text{CH}_2\text{C(CF}_3\text{)_2} \)), 2.62 (t, 4H, \( J_{\text{H-H}} = 6.4 \) Hz, \( \text{NCH}_2\text{CH}_2 \)). 2.06 (q, \( J_{\text{H-H}} = 6.4 \) Hz, 4H, \( \text{NCHCH}_2 \)) ppm. \(^{13}\text{C} \) \(^{1}\text{H} \) NMR (benzene-\textit{d}_6, 100.63 MHz, 298 K): \( \delta \) 137.70 (\( \text{CH} = \text{CH}_2 \)), 127.78 (q, \( J_{\text{C-F}} = 291.3 \) Hz, \( \text{CF}_3 \)), 116.01 (\( \text{CH} = \text{CH}_2 \)), 81.58 (hept, \( J_{\text{C-F}} = 22.4 \) Hz, \( \text{C(CF}_3\text{)_2} \)), 61.03 (\( \text{CH}_2\text{C(CF}_3\text{)_2} \)), 53.12 (\( \text{NCH}_2\text{CH}_2 \)), 29.79 (\( \text{NCH}_2\text{CH}_2 \)) ppm. \(^{19}\text{F} \) \(^{1}\text{H} \) NMR (benzene-\textit{d}_6, 376.49 MHz, 298 K): \( \delta \) –75.86 (s, 6F, \( \text{CF}_3 \)) ppm. Elemental analysis for \( \text{C}_{38}\text{H}_{6}_4\text{F}_{24}\text{K}_4\text{N}_4\text{O}_4 \) (1373.42 g·mol\(^{-1}\)) theoretical, C 42.0%, H 4.7%, N 4.1%; found C 42.1%, H 4.6%, N 4.2%

\[ \text{[RO}^{31}\text{K]} \]: To a solution of \{RO\}^{31}\text{H} (0.10 g, 0.33 mmol) in Et\text{2}O (10 mL) was added in solid portions with a bent finger KN(SiMe\text{3})\text{2} (0.060 g, 0.33 mmol). The reaction mixture was stirred at room temperature overnight. Volatiles were removed under vacuum with the formation of a colourless sticky solid. Stripping with pentane (3 × 3 mL) afforded the title compound as a colourless solid (0.080 g, 69%). The complex was recrystallised from a concentrated pentane solution at –30 °C. \(^{1}\text{H} \) NMR (benzene-\textit{d}_6, 400.13 MHz, 298 K): \( \delta \) 7.21–7.14 (m, 2H, \( m\text{-C}_6\text{H}_5 \)), 7.12–7.03 (overlapping m, 3H, \( p\text{-C}_6\text{H}_5 \) and \( o\text{-C}_6\text{H}_5 \)), 2.66–2.45 (overlapping m, 6H, \( \text{CH}_2\text{C(CF}_3\text{)_2} \), \( \text{NCH}_2\text{CH}_2 \), \( \text{and NCH}_2\text{CH}_2 \)), 2.17 (s, 3H, \( \text{NCH}_3 \)) ppm. \(^{19}\text{F} \) \(^{1}\text{H} \) NMR (benzene-\textit{d}_6, 376.49 MHz, 298 K): \( \delta \) –76.44 (s, 6F, \( \text{CF}_3 \)) ppm.

\[ \text{[RO}^{32}\text{K]} \]: To a solution of \{RO\}^{32}\text{H} (0.13 g, 0.44 mmol) in Et\text{2}O (10 mL) was added in solid portions with a bent finger KN(SiMe\text{3})\text{2} (0.080 g, 0.44 mmol). The reaction mixture was stirred at room temperature overnight. Volatiles were removed under vacuum and the resulting oil was stripped with pentane (3 × 3 mL) to afford the title compound as colourless solid. The complex was recrystallised from a concentrated pentane solution at –30 °C. Yield 50 mg (33%). \(^{1}\text{H} \) NMR (benzene-\textit{d}_6, 400.13 MHz, 298 K): \( \delta \) 2.93 (hept, 1H, \( J_{\text{H-H}} = 6.8 \) Hz, \( \text{CH(CH}_3\text{)}\text{2} \)), 2.78 (t, 2H, \( J_{\text{H-H}} = 6.5 \) Hz, \( \text{NCH}_2\text{CH}_2 \)), 2.72 (s, 2H, \( \text{CH}_2\text{C(CF}_3\text{)_2} \)), 2.44–2.33 (m, 2H, \( \text{NCH}_2\text{CH}_2 \)), 1.60 (t, 3H, \( J_{\text{H-H}} = 2.3 \) Hz, \( \text{C} = \text{C–CH}_3 \)), 0.92 (d, 6H, \( J_{\text{H-H}} = 6.5 \) Hz, \( \text{CH(CH}_3\text{)}\text{2} \)) ppm. \(^{13}\text{C} \) \(^{1}\text{H} \) NMR (benzene-\textit{d}_6, 100.63 MHz, 298 K): \( \delta \) 127.72 (q, \( J_{\text{C-F}} = 291.3 \) Hz, \( \text{CF}_3 \)), 78.15 (\( \text{C} = \text{C–CH}_3 \)), 76.98 (\( \text{C} = \text{C–CH}_3 \)), 57.31 (\( \text{CH}_2\text{C(CF}_3\text{)_2} \)), 51.88 (\( \text{CH(CH}_3\text{)}\text{2} \)), 51.56 (\( \text{NCH}_2\text{CH}_2 \)), 18.24 (\( \text{CH(CH}_3\text{)}\text{2} \)), 3.06 (\( \text{C} = \text{C–CH}_3 \)) ppm. \(^{19}\text{F} \) \(^{1}\text{H} \) NMR (benzene-\textit{d}_6, 376.47 MHz, 298 K): –77.32 (s, 6F, \( \text{CF}_3 \)) ppm. Elemental analysis for \( \text{C}_{17}\text{H}_{16}\text{F}_2\text{KNO} \) (343.35 g·mol\(^{-1}\)) theoretical, C 42.0%, H 4.7%, N 4.1%; found C 40.2%, H 4.4%, N 4.1%. 

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[Ca₂[RO⁹](µ-{RO⁹})₂(OH)]₂: To a solution of {RO⁹}H (0.25 g, 1.00 mmol) in diethyl ether (15 mL) Ca[N(SiMe₃)]₂ (0.18 g, 0.5 mmol) was added in solid portions with a bent finger. The reaction mixture was stirred for two days at room temperature. Removal of the volatiles followed by stripping with pentane (3 × 4 mL) and subsequent recrystallisation from pentane at −30 °C affords the formation the title compound as colourless crystals (0.12 g, 44%).

1H NMR (toluene-d₈, 400.13 MHz, 263 K): δ 3.02 (s, 4H, C₆H₂C(CF₃)₂ (terminal)), 2.83–2.67 (overlapping m, 16H, C₆H₂CH₃ (terminal) and C₆H(C(H))CH₃ (bridging)), 2.61–2.50 (m, 8H, C(H)HCH₃ (bridging)), 1.04 (t, 12H, 3J_H-H = 7.1 Hz, CH₃CH₃ (terminal)), 0.75 (t, 24H, 3J_H-H = 7.0 Hz, CH₂CH₃ (bridging)) ppm.

19F{¹H} NMR (toluene-d₈, 376.47 MHz, 263 K): δ −74.28 (s, 6F, C₆F₃ (terminal)), −78.05 (s, 12F, C₆F₃ (bridging)) ppm.

Elemental analysis for C₄₈H₇₄Ca₄F₃₆N₆O₈ (1707.41 g·mol⁻¹): theoretical, C 33.8%, H 4.4%, N 4.9%; found C 33.6%, H 4.4%, N 4.8%.

**Typical procedure for hydroamination reactions.** In a glovebox, the appropriate amount of precatalyst was loaded in an NMR tube. All subsequent operations were carried out on a vacuum manifold using Schlenk techniques. The required amount of benzene-d₆ was added with a syringe to the precatalyst, followed by addition of 2,2-dimethylpent-4-en-1-amine. The NMR tube was immersed in an oil bath set at the desired temperature and the reaction time was measured from this point. The reaction was terminated by addition of “wet” benzene-d₆ to the reaction mixture. The conversion was determined by 1H NMR spectroscopy.

**NMR monitoring of hydroamination reactions.** In a glovebox, the appropriate amount of precatalyst was loaded in an NMR tube. All subsequent operations were carried out on a vacuum manifold using Schlenk techniques. The required amount of toluene-d₈ was added with a syringe to the precatalyst, followed by addition of 2,2-dimethylpent-4-en-1-amine. The NMR tube was then then cooled in a bath at 0 °C (reaction times were measured from this point) and maintained at this temperature until it was inserted into the probe of a Bruker AM 500 NMR spectrometer preset at 0 °C. Data points were recorded as soon as possible after this, and it typically took altogether about 5 min to record the first of these. The reaction kinetics were monitored (using the multi_zgvd command; D1= 0.2 s; DS = 0; NS = 4 or more) over the course of 3 or more half-lives on the basis of amine consumption by comparing the relative intensities of resonances diagnostic of substrate and product. The conversion was determined by 1H NMR spectroscopy.

**Typical procedure for hydrophosphination reactions.** In the glove-box, the precatalyst was loaded in an NMR tube. All subsequent operations were carried out on a vacuum manifold using Schlenk techniques. The required amount of solvent was added with a syringe to the precatalyst, followed by
addition of styrene and HPPh₂. The NMR tube was immerged in an oil bath set at the desired
temperature and the reaction time was measured from this point. The reaction was terminated by
addition of “wet” benzene-\textit{d₆} to the reaction mixture. The conversion was determined by \textsuperscript{1}H NMR
spectroscopy.
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General Conclusion and Perspectives
General conclusion and perspectives

The main objective of this PhD thesis was the synthesis of alkaline-earth heteroleptic complexes stabilised by ancillary ligands with a high fluorine content and to test their catalytic applicability in homogeneous catalysis, notably in hydroamination and hydrophosphination reactions.

Through a collaboration with Prof. Michel Etienne and Dr. Chiara Dinoi from Université Toulouse III Paul Sabatier (GreenLAkE, ANR-11-BS07-0009), the activity of a calcium heteroleptic complex supported by fluorinated tris(indazolyl)borato ligand ([{T\text{ind}}^\text{F}]CaN(SiMe\text{3})\text{2}]) was tested in the intramolecular hydroamination of 2,2-dimethylpent-4-en-1-amine. It was showed that, for the first time, a calcium complex is able to sustain very high loadings of the substrate (600 equiv) with remarkable TON (342) and TOF (19 min$^{-1}$) values, assessing the beneficial role of the fluorinated ligand. Kinetic studies performed with [{T\text{ind}}^\text{F}]CaN(SiMe\text{3})\text{2}] indicated a first order dependence in both substrate and precatalyst concentrations.

We next synthesised Ae heteroleptic complexes using fluorinated aminoetheralkoxo ligands. These complexes are stable against Schlenk redistribution reactions and crystallise as dimers. In all presented examples, X-ray data indicated that, aside coordination of the N and O heteroatoms from the ligand, intramolecular Ae⋯F–C secondary interactions granted greater stability. Furthermore, complexes employing the N(SiMe\text{2}H)\text{2} amido group displayed intramolecular $\beta$-Si–H⋯Ae stabilising agostic interactions. Remarkably, crystallographic data showed that multiple secondary interactions can have a more stabilising effect than coordination from a single hard donor such as an oxygen atom.

The activity of the charged-neutral [{RO}$^+$CaN(SiMe\text{2}R)\text{2}]\text{2} ($x = 2, R = H (\text{[10]}_2); x = 1, R = H (\text{[12]}_2)$ and Me (\text{[13]}_2)) was evaluated in the benchmark hydrophosphination of styrene with diphenylphosphine. These three precatalysts showed comparable activities (TOF = 40–50 h$^{-1}$) that are in the top range of those known for this reaction.

The possibility to use fluorinated aminoetheralkoxo ligands in order to synthesise highly oxophilic and electrophilic alkaline-earth cations paired with weakly coordinating anions was probed. Such cations could be generated cleanly, but as a sign of their extreme electrophilicity, they were all crystallised as water adducts. Apart from intramolecular Ae⋯F–C\text{ligand} interactions, X-ray data indicated that these complexes also featured Ae⋯F$\text{anion}$ interactions from the WCA [H$_\text{2}$N{B(C$_\text{6}$F$_\text{5}$)$_\text{3}$}]$^-$.

The number of Ae⋯F$\text{anion}$ interactions varies with the size and electropositivity of the metal in the order: Ba > Sr > Ca.

The synthesis of Ae–olefin (vinyl) complexes supported by fluorinated aminoalkoxo ligands, with a general formula [{RO}$^+$AeN(SiMe\text{2}H)\text{2}]\text{2}, was described. For the first time, it was showed that the
combined effects of Ae···C, Ae···F–C, and β-Si–H···Ae secondary interactions can lead to the stabilisation of electron-deficient Ae heteroleptic complexes. According to crystallographic and spectroscopic studies, the Ae···C olefin interactions are rather weak, as the metric parameters of the C=C double bond are mostly unaffected upon coordination to the Ae metal. DFT computations performed by our collaborator in Toulouse are in agreement with these experimental observations and indicate that the Ae···C olefin are exclusively based on electrostatic contributions. In order to determine whether the interaction between the olefin and the Ae metal persists in solution, a similar Yb(II)–olefin complex was synthesised. Unfortunately, paramagnetic impurities in the Yb–olefin complex precluded spectroscopic characterisation, notably $^{171}$Yb NMR and $^1$H–$^{171}$Yb HMBC NMR. X-ray data showed that, in the case of Yb(II) complexes, the utilisation of a bulky $N(SiMe_3)_2$–amido group blocks the coordination of the alkene to the metal, indicating the importance of steric effects in these complexes.

In order to study the influence of steric effects upon Ae···C olefin interactions, the coordination of terminally methyl-substituted alkene moieties onto calcium was considered. Substitution of one H$_{ext}$ as in (H$_{ext}$)(Me)C=CH– affects the coordination properties of the alkene which interacts with calcium only with the C$_{int}$ atom. Substituting both H$_{ext}$ hydrogen atoms as in Me$_2$C=CH– prevented entirely the coordination of the alkene moiety onto calcium.

Based on our success in synthesising Ae heteroleptic featuring intramolecular olefin coordination, our next aim was to assess the potential coordination properties of other π systems, i.e. arenes, alkynes and allenes. All attempts to coordinate aryl rings onto calcium in the same manner as that described for alkenes were unsuccessful, and resulted either in the formation of THF-solvated bimetallic adducts or THF-free trinuclear complexes. The bonding pattern in the trinuclear complexes indicate a large contribution of very strong β-Si–H···Ca agostic interactions towards the coordinative saturation of the metals. Spectroscopic data showed that these agostic interactions also persist in solution. On the other hand, coordination of internal alkynes to calcium was achieved and complex [{RO$_3$CaN(SiMe$_2$H)$_2$}]$_2$ ([34]) is the only “non-acetylide” alkaline-earth complex described to date, featuring interactions with the π cloud of an alkyne moiety. The coordination of allenes to calcium was also attempted; however, preliminary spectroscopic data showed that such complex is thermodynamically unstable and readily isomerises to the Ca-alkyne complex [34].

As an overall outlook of this work, it was shown that all calcium heteroleptic complexes of the type [{RO}$^+$CaN(SiMe$_2$H)$_2$}]$_2$ are stabilised by a pattern of Ca···F–C and β-Si–H···Ca secondary interactions. The evaluation of the relative strength of these secondary non-covalent interactions vs. that of strong donors when the ancillary ligand contains hard donors (i.e. N$_{amide}$ and O$_{ether}$) or weak donors (i.e. –CH=CH$_2$, –CH=CHMe, –CH=CMe$_2$, and –C≡C–Me), or if the coordination sphere of calcium is filled by a THF solvent molecule. The aforementioned calcium complexes are represented
in Figure A and their selected metric parameters involving these secondary interactions are collected in Table A.

![General Conclusion and Perspectives](image)

**Figure A.** Heteroleptic calcium complexes described in this work, featuring Ca···F–C and β-Si–H···Ca secondary interactions.


<table>
<thead>
<tr>
<th>Complex</th>
<th>Donor</th>
<th>Ca···F</th>
<th>Ca···H</th>
<th>Ca···Si</th>
<th>Ca–N–Si</th>
<th>N–Si–N</th>
</tr>
</thead>
<tbody>
<tr>
<td>[{RO1}CaN(SiMe2H)2]2</td>
<td>OMe</td>
<td>3.004(1)</td>
<td>2.99(2)</td>
<td>3.294(5)</td>
<td>110.8(6)</td>
<td>128.2(8)</td>
</tr>
<tr>
<td>[{RO21}CaN(SiMe2H)2]2</td>
<td>THF</td>
<td>3.001(1)</td>
<td>2.95(3)</td>
<td>3.346(1)</td>
<td>112.5(1)</td>
<td>128.2(1)</td>
</tr>
<tr>
<td>[{RO11}CaN(SiMe2H)2]2</td>
<td>CH=CH2</td>
<td>3.050(2)</td>
<td>3.12(3)</td>
<td>3.381(6)</td>
<td>115.2(1)</td>
<td>128.1(1)</td>
</tr>
<tr>
<td>[{RO13}CaN(SiMe2H)2]2</td>
<td>CH=C(H)Me</td>
<td>2.949(1)</td>
<td>3.03(2)</td>
<td>3.316(6)</td>
<td>112.5(7)</td>
<td>128.2(9)</td>
</tr>
<tr>
<td>[{RO14}CaN(SiMe2H)2]2</td>
<td>CH=CMe2</td>
<td>2.604(1)</td>
<td>2.72(7)</td>
<td>3.153(7)</td>
<td>104.9(9)</td>
<td>129.2(1)</td>
</tr>
<tr>
<td>[{RO32}CaN(SiMe2H)2]2</td>
<td>–C≡C–Me</td>
<td>2.753(1)</td>
<td>2.65(3)</td>
<td>3.134(8)</td>
<td>101.3(9)</td>
<td>126.4(1)</td>
</tr>
</tbody>
</table>

[a] The position of the hydrogen atom was determined on the Fourier electron density map [b] This complex is not centrosymmetric and features different bond distances and angles for the two calcium centres. [c] The CH=CMe2 moiety does not interact with calcium.
The metric parameters from Table A indicate shorter Ca····F–C, Ca····H and Ca····Si distances, translating into stronger interactions, in the case of calcium complexes employing weak donors, compared to other complexes that feature coordination from O_{ether} atoms to calcium. This shows that, provided the Ae····π_{donor} complexes can be made and stabilised, the strength of Ca····F–C and β-Si–H····Ca secondary interactions is, as expected, directly affected by the nature of the donating moiety from the ligand side-arm.

Yet, several questions remained unanswered and require further synthetic work. For instance, the crystallisation of well-defined Ae cations (see 3.4.) free of water contamination is highly desirable to study the influence of Ca····F–C secondary interactions towards the coordinative saturation of the metal centre. In addition, Chapter 4 showed that the behaviour of [[RO^{11}]AeN(SiMe_{2}H)_{2}]_{2} (Ae = Ca ([25]_{2}, Sr ([26]_{2})) in THF-d_{8} is enigmatic. For this reason, additional NMR experiments are needed to elucidate the structure of these complexes in the coordinating NMR solvent. In Chapter 5, the unexpected formation of trinuclear complexes [[RO^{x}]N(SiMe_{2}H)_{2}]_{2}(μ-Ca[N(SiMe_{2}H)_{2}]_{2}) (x = 21 (32), 22 (33)) was presented, yet we could not conclude how these complexes are actually formed. This needs to be elucidated.

The collective results gathered in this PhD thesis demonstrate that secondary interactions can be used to effect the stabilisation of highly oxophilic and electrophilic metal centres. Keeping this in mind, the synthesis of heteroleptic calcium complexes employing highly basic C(SiMe_{2}H)_{2}–moiety of type [[RO^{x}]AeC(SiMe_{2}H)_{2}]_{2} can be envisaged, as they can serve two purposes. Firstly, they are expected to show very high activity in hydroelementation (and other types of) catalysis. Furthermore, a putative [[RO^{11}]AeC(SiMe_{2}H)_{2}]_{2}, an analogue of [25]_{2}, can serve as a model to study whether insertion of the C=C double bond into the Ca–C_{alkyl} bond is achievable (Scheme A). From this perspective, a positive result can open a new pathway towards the use of calcium precatalysts in olefin polymerisation reactions.

![Scheme A](image_url)

Scheme A. Putative insertion of a C=C double bond into a Ca–C_{alkyl} bond.

The results described in this PhD thesis showed that alkene coordination to calcium can be performed in an intramolecular fashion, thanks to the driving force of chelation. Nevertheless, using a
suitable proteo-ligand, one can propose the synthesis of calcium complexes in which “free” olefins such as norbornene or 1-hexene are coordinated to the metal centre.

Further work in this field can concentrate on employing fluoroalkoxy ligands for other challenging synthetic targets. The synthesis of molecular Ae hydrides (Scheme B–a), fluorides (Scheme B–b), hydroxides (Scheme B–c) or phosphides (Scheme B–d) can be envisaged by reacting complexes of the type \([\{\text{RO}\}\text{AeN(SiMe}_2\text{H)}_2\] with the appropriate reagent. As nicknamed by Harder, molecular calcium hydrides are “worker bees” in calcium chemistry, and previous examples displayed high reactivity towards unsaturated substrates (e.g. alkenes, ketones or nitriles).\(^*\) The synthesis of a molecular calcium hydride using fluoroalkoxy ligands with olefin pending groups would serve as a model to investigate whether the C=C double bond can insert into the Ca–H bond. Calcium hydroxides are also important and H. Roesky indicated that they may be used in sol-gel coating experiments.\(^†\) Calcium phosphide complexes featuring alkene coordination from the ligand side-arm to the metal would be attractive for spectroscopic purposes and also to model intermediates in hydrophosphination catalysis. A \(^1\text{H}–^{31}\text{P}\) HMQC NMR spectrum of a putative \([\{\text{RO}\}^1\text{AePPh}_2]\) could perhaps assess whether there are through-metal scalar correlations between the vinylic protons and the phosphorus atom, therefore providing a vital clue concerning the presence of Ca···alkene interactions in solution.

![Scheme B](image)

**Scheme B.** Proposed synthesis of heteroleptic Ae hydrides, fluorides, hydroxides and phosphides starting from \([\{\text{RO}\}^1\text{AeN(SiMe}_2\text{H)}_2\]专业化。
Annexures
Annexures

Annexure A: Research article published in a collaboration with the group of Prof. Michel Etienne

Abstract: Heteroleptic silylamido complexes of the heavier alkaline earth elements calcium and strontium containing the highly fluorinated 3-phenyl hydrotetrasilindazoylborate \( \left[ \text{F}_2\text{TP}^{\text{Ph}}\text{SiMe}_3\right] \) ligand have been synthesized by using salt metathesis reactions. The homoleptic precursors \( \left[ \text{AE}(\text{N} = \text{Ca}, \text{Sr})\text{SiMe}_3\right] \) were treated with \( \left[ \text{H}\left[ \text{F}_2\text{TP}^{\text{Ph}}\text{SiMe}_3\right] \right] \) in pentane to form the corresponding heteroleptic complexes \( \left[ \text{F}_2\text{TP}^{\text{Ph}}\text{SiMe}_3\right] \text{AE}(\text{N=Ca, Sr})\text{SiMe}_3\right] \). Compounds 1 and 3 are inert towards intermolecular redistribution. The molecular structures of 1 and 3 have been determined by using X-ray diffraction. Compound 3 exhibits a S=MeSi agostic distortion. The synthesis of the homoleptic THF-free compound \( \left[ \text{Ca}\text{NSiMe}_3\text{H}_2\right] \) (4) by transamination reaction between \( \left[ \text{Ca}\text{NSiMe}_3\text{H}_2\right] \) and HNSiMe\(_3\)H\(_2\) is also reported. This precursor constitutes a convenient starting material for the subsequent preparation of the THF-free complex \( \left[ \text{F}_2\text{TP}^{\text{Ph}}\text{SiMe}_3\text{H}_2\right] \) (5). Compound 5 is stabilized in the solid state by a Ca–H–Si–H agostic interaction. Complexes 1 and 3 have been used as precatalysts for the intramolecular hydroamination of 2,2-dimethylpentene-4-en-1-amine. Compound 1 is highly active, converting completely 200 equivalents of aminoalkene in 16 min with 0.50 mol% catalyst loading at 25 °C.

Introduction

The synthesis of nitrogen-containing molecules through metal-catalyzed hydroamination of C–C multiple bonds offers a perfectly atom-economic route to the production of fine chemicals.\(^{11}\) Whereas the catalytic activity of transition metal and rare earth complexes for the addition of a N–H bond across C–C multiple bonds has been largely described in the literature,\(^{11,21}\) the use of alkaline earth (AE) metal complexes as hydroamination catalysts is only now starting to emerge.\(^{22-24}\) AE metals are abundant, oxophilic, and redox-inactive in their cat-ionic form. They are characterized by a wide range of ionic radii and cation charge densities (Mg\(^{2+}\) = 0.72 Å; Ca\(^{2+}\) = 1.00 Å; Sr\(^{2+}\) = 1.18 Å; Ba\(^{2+}\) = 1.35 Å for six-coordinate ions)\(^{25}\). Their chemistry is therefore largely governed by electrostatic and steric factors, featuring highly ionic and essentially non-directional bonding. One consequence is the dynamic Schlenk equilibrium that redistributes ligands in a heteroleptic complex \( [L_X(AeX)]^+ + [L_X)(Me)]^+ \) yielding a mixture of the two homoleptic species \( [L_X)(Ae)]^+ \) and \( [AlX]^+ \) (Scheme 1). This equilibrium is often problematic for catalysis, and its control by the appropriate choice of ligands remains a challenge in this chemistry.

\[ 2[L_X)(AeX)]^+ = [L_X)(Me)]^+ + [AeX]^+ \]  

Scheme 1. Schlenk-type equilibrium with heteroleptic Ae complexes.

Intermolecular hydroamination reactions are extremely challenging and only a limited number of reports involving Ae catalysts are available in the literature.\(^{26-28}\) By contrast, the entropically favored intramolecular version of this process has been investigated in more detail: both homo and heteroleptic alkaline earth complexes are competent cyclohydroamination precatalysts and, in general, the activity trend observed for such reactions is Ca > Sr > Ba; on the other hand, no definitive trend in their reactivity with respect to the nature of the ancillary ligands emerges so far. With the readily available homoleptic compounds \( [M](\text{NSiMe}_3)^2\text{H}_2\text{j}(\text{thf})\text{j} (\text{M} = \text{Ca, Sr, Ba; x = 0 or 2}) \), the THF-free complexes displayed lower catalytic activity.

\[ \text{Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201405454.} \]
than their THF-containing analogues, except in the case of substrates with secondary amine functionalities; moreover, the stromium systems were less active than their calcium counterparts.12,13 For the heteroleptic Ae species, very bulky ancillary donating ligands, capable of stabilizing the oxophilic metal center while providing the steric protection needed to prevent the Schlenk equilibrium, were employed. The catalytic activities of the heteroleptic silylimidate [diketiminate derivatives (BDIMINSI=Me2,Me)],[thf] (BDIMINSI=Me2,Me)H2[C(Me)=N-2,6-Di(Ph)C6H4]2, M = Ca, x = 0 or 1; M = Sr, x = 1) proved useful insight into the mechanism of the reaction.14,15 The Ca precatalyst exhibited better catalytic performance than its Sr analogue. In contrast, the hydroboration and triis(indenylidene)-1-yl)borate complexes, containing C-based donors instead of N-based donors in the trispa ligand, resulted in the Sr silylimidate complexes performing better than their Ca counterparts. With the N-bound aminotroponimidinate or 2,5-bis-(N-aryl)iminomethyl)pyrrolidyl Ca and Sr silylimidate complexes, the activity of the catalysts decreased with increasing atomic number of the metal.16,17 Asymmetric versions of these reactions have also been reported.18,19 Some of us have recently described new Ca, Sr, and Ba heteroleptic [(LO)AE(n=SiMe2Me)x][thf] (R = H, Me) complexes bearing different types of N- and O-based amino-phenolate ligands (LO). The rates for the cyclohydroamination reactions decreased with increasing atomic number of the metal.20 For a given ligand framework and metal center, complexes that contain (NSiMe2Me)n were much better precatalysts than those containing (NSiMe2Me)n. Heteroleptic silylimidate complexes [(N=N)(AE(n=SiMe2Me)x)][thf] 1 (R = Ca; Sr, x = 2) containing the bulky imino-amidine ligand (N=n=6) also catalyzed the cyclohydroamination reaction efficiently, with rates increasing in the order Ba < Sr < Ca.21

We became interested in stabilizing electron-deficient heteroleptic alkene earth complexes [L,MeWX] while maintaining their reactivity. Our strategy is based on the use of highly fluoro- raditris(indenylidene)borate ligands (F2,Tp3Ph,39)22,23 that combine two fundamental properties: 1) The steric hindrance, which would avoid Schlenk-type redistributions and 2) the electron-withdrawing ability, which would enhance the polarity, hence the reactivity of the Ae-X bond.24 Two differently substituted ligands, (F2,Tp3Ph,39)R = CF3, n = 21, and R = Ph, n = 12, have been tested on Ca, the phenyl-based ligand providing the best compromise in terms of steric protection and electron-withdrawing properties (Scheme 2).

![Scheme 2. The 3-Ph substituted hydrotris(indenylidene)borate ligand (R- reactive ligand).](image)

Earlier reports have shown that sterically encumbered, differently substituted tris(pyrazolyl)borates (Tp) coordinate Ca2+ with the formation of heteroleptic TpCaX complexes.25 A four-coordinate amido complex (Tp3PhCa(NiSMe2Me)x) was obtained with Tp3Ph, whereas a five-coordinate THF adduct (Tp3PhCa(NiSMe2Me)x)[thf] was obtained with Tp3Ph.26 These amido complexes were shown to catalyze the ring-opening polymerization of lactide,27 but to our knowledge they have not been tested for hydroamination reactions.

We report here the synthesis of heteroleptic calcium and strontium silylimidate complexes (F2,Tp3Ph,39)AE(n=SiMe2Me)x) (Ae = Ca, Sr), which are inert to intermolecular redistribution in solution. The synthesis of the heteroleptic THF-free compound (CaSiMe2Me)x by a transamination reaction between (CaSiMe2Me)x and HSiMe2Me is also reported. This precursor has then been used for the preparation of (F2,Tp3Ph,39)AE(n=SiMe2Me)x, which exhibits a Ae—Si—H agostic distortion. The catalytic activity of these amido complexes for the intramolecular hydroamination of 2,2-dimethylpent-4-en-1-amine is described. (F2,Tp3Ph,39)AE(n=SiMe2Me)x is highly active, converting completely 200 equivalents of aminobutane in 16 min at 25 °C.

**Results and Discussion**

**Synthesis and characterization of** (F2,Tp3Ph,39)AE(n=SiMe2Me)x

Treatment of (Tf2n=SiMe2Me)x with an excess of (CaSiMe2Me)x in pentane provided the heteroleptic (F2,Tp3Ph,39)CaSiMe2Me)x (1) in 67% yield. Compound 1 was characterized by standard analytical/spectroscopic techniques, and the solid-state structure was analyzed by single-crystal X-ray diffraction (see below). The 1H NMR spectrum in [D6]benzene shows four signals (δ = 144.30, 151.59, 153.83, and 163.15 ppm) corresponding to the four benzene fluorine atoms of (F2,Tp3Ph,39). The 13C NMR spectrum displays one singlet for the Me groups of the (SiMe2Me)n amido ligand (δ = 23.34 ppm) and three multiplets (δ = 7.54, 7.32, and 7.23 ppm) for the aromatic protons of (F2,Tp3Ph,39). From the equivalence of the three indazolyl groups of (F2,Tp3Ph,39) in solution, a time-averaged C3 symmetry can be inferred for 1. The synthesis and purification of 1 proved to be challenging due to the involvement of an equilibrium process as summarized in Scheme 3 and Figure 1.

The heteroleptic compound (CaSiMe2Me)x was treated with (Tf2n=SiMe2Me)x in [D6]benzene affording 1 quantitatively over a period of 30 h (Figure 1a–c). After evaporation of the solvent and re-dissolution in [D6]benzene, however, we observed the reappearance of the characteristic signals of (Tf2n=SiMe2Me)x together with those of 1 (Figure 1d), evidencing that the reverse reaction had occurred according to the equilibrium process in Scheme 3. The (Tf2n=SiMe2Me)x is less soluble than 1 in [D6]benzene and its precipitation displaced the equilibrium towards the formation of the reactants.

The isolation of complex 1 was therefore achieved by carrying out the reaction in pentane. Due to their poor solubility,
Figure 1. $^{19}$F NMR spectroscopic monitoring of the reaction of [Ca(N(SiMe$_3$)$_2$)$_2$]$\parallel$ with [(F$_2$-Tp)$^{39}$] in D$_2$-benzene; a) Pure [(F$_2$-Tp)$^{39}$];

b) 1:1 reaction mixture over a period of 3 h t = 0 (F$_2$-Tp)$^{39}$; c) Reaction mixture over a period of 30 h;
d) 1:1 reaction mixture after evaporation and re-dissolution in D$_2$-benzene.

[(F$_2$-Tp)$^{39}$] and complex 1 precipitated leaving [Ca(N(SiMe$_3$)$_2$)$_2$]$\parallel$ and [N(SiMe$_3$)$_2$]$\parallel$ in solution. Following a simple filtration of the reaction mixture, complex 1 was then separated from [(F$_2$-Tp)$^{39}$] by extraction with a toluene/ pentane (1:3) mixture. The whole process was facilitated by using an excess of [Ca(N(SiMe$_3$)$_2$)$_2$]$\parallel$ that further displaced the equilibrium towards the products. Compound 1 was finally isolated in 67% yield. Complex 1 is very air and moisture sensitive; small traces of air or water lead to immediate decomposition, with the formation of an unidentified white precipitate and HNSiMe$_3$. As a result of the presence of the bulky (F$_2$-Tp)$^{39}$ ligand, compound 1 was found to be inert towards the Schlenk equilibrium. Indeed, heating a [D$_2$-benzene] solution of 1 at 60°C over a period of 2 h did not result in any apparent decomposition nor in ligand redistribution.

Addition of THF to a [D$_2$-benzene] solution of 1 suggested the formation of a mixture of THF amido species [F$_2$-Tp$^{39}$N(H)Ca(N(SiMe$_3$)$_2$)$_2$]$\parallel$ and [F$_2$-Tp$^{39}$N(H)Ca(N(SiMe$_3$)$_2$)$_2$]$\parallel$. Concentration under vacuum yielded, on the basis of $^{1}$H and $^{19}$F NMR spectroscopies, what we suggest is [F$_2$-Tp$^{39}$N(Ca(N(SiMe$_3$)$_2$)$_2$)](THF) (see below) as the major compound together with free indazole.

An ORTEP drawing of the solid state molecular structure of 1 is given in Figure 2 along with selected bond lengths and angles. Compound 1 has a monomeric structure where the Ca atom is four-coordinate in a distorted tetrahedral geometry. The B1, C1, and N7 (amido) atoms are almost collinear (165°). The distortion of the tetrahedron is such that Ca1-N5a bond lengths are longer for N2 and N4 (2.5084(14) and 2.4989(16) Å) than for N6 (2.4566(15) Å) and the angle N2-Ca1-N4 (71.79(5)°) is smaller than those involving N6 (83.13(5)° and 85.49(5)°). These parameters are comparable to those observed for the homoleptic complex [F$_2$-Tp$^{39}$]Ca, even though the latter exhibits one inverted indazolyl ring. Despite this distortion and the low coordination number, complex 1 does not show any agostic-type interaction involving the hexamethyldisilamido group.

The Ca1-N7 bond (2.2342(15) Å) is shorter than the Ca-N bond, bonds of related 4-coordinate complexes [BDBCa(N(SiMe$_3$)$_2$)$_2$]($\parallel$thf)$_2$] [26], [N(CH$_3$)$_2$Ca(SiMe$_3$)$_2$]$_2$[N(CH$_3$)$_2$] [27], and [LX][Ca(N(SiMe$_3$)$_2$)$_2$] [28], where LX = CH$_3$C(=O)CH$_3$, CH$_3$C(=O)CH$_3$, and CH$_3$C(=O)CH$_3$, respectively. This can be ascribed to the presence of the electron-withdrawing fluorinated [F$_2$-Tp$^{39}$] ligand in 1.

Four-coordinate Ca complexes are not common. Only two four-coordinate Ca complexes bearing $\kappa$-N-bound ligands have been previously described: The alkoxide species [Tp$^{39}$Ca(O-2,6-iPr$_2$-C$_6$H$_3$)$_2$], with the 2,6-substituted tris (pyrazolyl)borate ligand, [29] and the abovementioned [LX][Ca(N(SiMe$_3$)$_2$)$_2$] complex, containing the tridentate b-diketiminate ligand LX. [30]
The one-pot procedure employed for the synthesis of several tri(pyrrozolyl)borate Ca amido complexes has not successful for the synthesis of THF or EtO to a 1:1 mixture of [K(NSiMe₃)₃]₂, CaL₂, and [KF₂⁺,Tp²⁻,η⁵] provided the heteroleptic compounds [Tp₂⁺,Tp²⁻,η⁵]Ca(NSiMe₃)₂[Li] in extremely low yields (L = THF, x = 2, 1a; L = EtO, x = 1, 1b, 4%) yield. Several byproducts either containing the (Tp₂⁺,Tp²⁻,η⁵) ligand or resulting from B-N bond cleavage were observed in all cases. After extraction with a 1:3 toluene/pentane mixture, compound 1a yielded [Tp₂⁺,Tp²⁻,η⁵]Ca(NSiMe₃)₂[thf] (1c) in 7% yield. Attempts to crystallize 1a resulted in crystals of the indazolate complex [Tp₂⁺,Tp²⁻,η⁵]Ca(thf)₂(thf) (2). The X-ray molecular structure of 2 (Figure 3) features two coasted THF molecules and an η¹-indazolate ligand arising from fragmentation of the [Tp₂⁺,Tp²⁻,η⁵] group by B-N bond cleavage. The 3-phenylindazolate ligand directs its phenyl group syn to the boron of the Tp₂⁺,Tp²⁻,η⁵, with Ca–N (2.40(3) Å) significantly shorter than Ca–N (2.469(3) Å). Coordination-induced B–N bond cleavage of tri(pyrrozolyl)borates and hydrobisis- and tri(pyrrozolyl)borates have been observed previously. Ca–N bond cleavage in a tris(3-phenylpyrazolyl)methanide complex of calcium has also been reported.[26]

The strontium analogue of 1 has also been similarly synthesized. [Tp₂⁺,Tp²⁻,η⁵]Sr(NSiMe₃)₂[Li] (3) was isolated in 25% yield upon reaction of [THF₂⁺,Tp²⁻,η⁵] with an excess of [Sr(NSiMe₃)₂][Li] in pentane (Scheme 3). The ¹H and ¹³C NMR spectra for 3 are qualitatively similar to those for 1. A single ¹H NMR resonance for the Si–CH₃ groups was observed at all temperatures between 298 and 183 K in [D₆]toluene. An X-ray crystal structure has been obtained for 3 for which an ORTEP drawing is given in Figure 4 along with selected bond lengths and angles. Complex 3 has a monomeric structure and the metal center is only four-coordinate, a truly remarkable feature for such a large metal as strontium. Only two heteroleptic four-coordinate Sr amido complexes have been previously described: the [B(Dipp)Sr(NSiMe₃)₂][thf][27] and the [Pt(N₂)[Sr(NSiMe₃)₂][thf][28] amides, containing the η¹-Bound (η-diketiminate) and imino-anilide ligand, respectively. Compound 3 is therefore the first heteroleptic four-coordinate Sr complex bearing a tripodal η¹-Bound ligand. Unlike the Ca analogue 1, the coordination sphere in 3 is strongly distorted and the geometry around Sr is best described as a trigonal bipyramid with a seemingly vacant equatorial coordination site (Figure 5).

N₅, one of the indazolate nitrogen, and N₇, the amido nitrogen, occupy the apical positions (N₇–Sr–N₅ 106.84(10)°) being significantly less obtuse than Sr–N₇–N₁ (126.74(10)°). The distance Sr–C₆₄ (2.996(3) Å) is slightly longer than the sum of the covalent radii of Sr and C (2.71 Å)[29] and is significantly shorter than Sr–C₂ (ca. 3.81 Å). A similar barium complex of formula [Tp₂⁺,Ba(NSiMe₃)₂][thf][30] has also been described. It shows the favored η¹(N₂,N₄,A) coordination mode of the Tp ligand and...
Annexure A

Figure 5. Different geometrical environments for complexes 1 (left) and 3 (right) highlighting the coordination polyhedra (distorted tetrahedron versus trigonal bipyramid, respectively) in shaded gray.

differently from compound 3, it is six-fold coordinated with two molecules of THF completing the coordination sphere of the barium center.

Other Sr complexes featuring an asymmetrical arrangement of the \((\text{NISiMe}_3)\)\(^{1-}\) ligand have been previously described\(^{25,32,42-44}\), although the difference between the two Sr-N-Si angles is in all cases smaller than that observed in 3. The Sr1-N5 bond trans to the amido is significantly longer (2.672(16) \(\text{Å}\)) than Sr1-N1 and Sr1-N3 (2.612(16) and 2.578(16) \(\text{Å}\)), those two being in a range typical of \((\text{Tp}^*\text{Sr})\) complexes\(^{45,46}\). The Sr1-N7 bond (2.421(18) \(\text{Å}\)) is slightly shorter than the related bond length reported for the four-coordinate complexes \((\text{BBDiSiN})(\text{NISiMe}_3)\)\((\text{thf})^{18}\) and \((\text{[NiNOSi(NISiMe}_3)\]})\((\text{thf})^{15}\) 2.446(2) and 2.463(2) \(\text{Å}\), respectively), outlining the electron-withdrawing properties of the fluorinated \(\text{F}_{1,2}\) \(\text{Tp}^*\text{Sr}\) ligand.

Synthesis and characterization of bis(dimethylsilylamido) calcium complexes \([\text{LX}]\text{Ca}[\text{SiMe}_3\text{H}_3]\)\((\text{LX}) = \text{NISiMe}_3\text{H}_3, \text{F}_{1,2}\text{Tp}^*\text{Ca}^{16,19}\)

As reported for lanthanides\(^{20,30-32}\) and Ae complexes,\(^{22}\) the replacement of \((\text{NISiMe}_3)\)\(^{1-}\) by \((\text{NISiMe}_3)\)\(^{2-}\) can impart a stabilizing effect by the formation of internal \(\text{P-Si-H}\) agostic interactions. Whereas \([\text{Ca}(\text{NISiMe}_3\text{H}_3)]\)\((\text{thf})\) was known, its THF-free analogue \([\text{Ca}(\text{NISiMe}_3\text{H}_3)]\)\((\text{tmt})\) is a potentially very attractive starting material for Ca chemistry. We first describe the synthesis and properties of 4 before presenting those of \([\text{F}_{1,2}\text{Tp}^*\text{Ca}(\text{NISiMe}_3\text{H}_3)]\) (5).

Following a similar procedure to that used for the synthesis of \([\text{Ca}(\text{NISiMe}_3\text{H}_3)]\)\((\text{thf})\)\(,^{20,25}\) transmission between \(\text{HN(SiMe}_3\text{H}_3)\) in pentane at 0°C yielded the pure homoleptic \([\text{Ca}(\text{NISiMe}_3\text{H}_3)]\) (4) in 87% yield (Scheme 4). Compound 4 is a highly air and moisture-sensitive white solid for which satisfactory elemental analyses were obtained. Despite numerous attempts, we were unable to crystallize 4.

Compound 4 is fluxional as revealed by a variable-temperature \(^1\text{H}\) NMR spectroscopic study in the 358-183 K range (Figure 6). According to this dynamic process, we propose that complex 4 is a trinuclear Ca species of the type \([\text{Ca}(\text{NISiMe}_3\text{H}_3)]\)\((\text{tmt})\), displaying a linear array of three calcium atoms, bridged by four \((\text{NISiMe}_3\text{H}_3)\) units and framed by two terminal symmetrical \((\text{NISiMe}_3\text{H}_3)\)\(^{1-}\) ligands as depicted in Figure 7. For comparison purposes, the diffusion coefficients of 4 and \([\text{Ca}(\text{NISiMe}_3\text{H}_3)]\)\((\text{tmt})\) were measured by using DOSY NMR spectra in \([\text{D}_2]\text{toluene at 298 K. The values obtained (D) = 0.6x10^{-9} and 1.0x10^{-6} \text{m}^2 \text{s}^{-1} for 4 and }[\text{Ca}(\text{NISiMe}_3\text{H}_3)]\)\((\text{tmt})\), respectively) indicate that 4 has a higher nuclearity than \([\text{Ca}(\text{NISiMe}_3\text{H}_3)]\)\((\text{tmt})\). A diffusion molecular weight analysis against a series of reference compounds (D-4v) yielded a molecular weight of 906 g mol\(^{-1}\) fully consistent with the trinuclear structure (913 g mol\(^{-1}\)) proposed for 4 (see the Supporting Information).

In the fast exchange limit (358 K, Figure 6), two resonances for the S-H and the \(\text{SiH}_2\) groups were observed at \(\delta = 4.48\) and 0.37 ppm, respectively (1:6 ratio, label A'). A first exchange
process was revealed upon cooling the sample below 338 K in which each of the SiH and SiCH₃ split to give two resonances (A and A', Figure 6) in a 1:2 ratio ($\Delta G_{190}$ ≈ 69 kJ mol⁻¹). Upon further cooling, line-broadening occurred only for each of the more shielded signals A' characteristic of a second exchange process; below 253 K, the A' signals of the SiH and SiCH₃ groups split into four and eight separate resonances B-E, Figure 6), respectively ($\Delta G_{190}$ ≈ 40 kJ mol⁻¹). In the slow exchange limit (183 K), the ¹H NMR spectrum showed five types of SiMe₃H signals, (A and B-E, Figure 6) in a 2:1:1:1:1 ratio. They correspond to five inequivalent SiMe₃H groups, likely dependent on the presence of different [Si–Si–H] agostic interactions with C₆.

Evidence for [Si–Si–H] agostic interactions in 4 came from a [¹H-²⁹Si] HMQCD 2D NMR experiment at 183 K. Figure 8 shows the correlations between five different [²⁹Si] signals at δ = -23.7,

-15.3, -14.0, -13.9, and -11.8 ppm and the H₆, H₅, H₄, and H₃ protons, respectively ($\nu_{HH}$= 152, 146, 143, 147, and 122 Hz, respectively). δ$_{HH}$ coupling constants in the range 140–160 Hz suggest mild agostic interactions [29,28]. For SiH₆, a stronger Ca-[Si–Si–H] interaction is reflected by the lower δ$_{HH}$ value of 122 Hz [29,28,29]. The presence of Si–H agostic interactions was further corroborated by solid-state IR spectroscopy: whereas ν$_{HH}$ of HCl(SiMe₃)H₃ is found at 2122 cm⁻¹, three ν$_{HH}$ absorptions are observed for 4 in the region 1900 to 2030 cm⁻¹. The lowest ν$_{HH}$ at 1905 cm⁻¹, significantly lower than that for [Ca(NSSiMe₃)H₃][THF] · 2H₂O, most likely reflects a stronger Ca-[Si–Si–H] interaction. The presence of three ν$_{HH}$ frequencies in the Si–H stretching modes region has also been reported for homocyclic TMEDA- or THF-coordinated Ca complexes containing the [C(SiMe₃)H₃]²⁻ ligand [29,28].

Overall, exchange of terminal and bridging amido groups in 4 affords a single set of resonances in the fast exchange limit (A', Figure 6). By decreasing the temperature, the resonances for the terminal and bridging groups of the [N(SiMe₃)H₃]²⁻ ligands split into two signals in a 1:2 ratio (A and A'). At lower temperature, finally, the separation of the bridging SiH and SiCH₃ signals (A') into four well-defined peaks with a ratio 1:1:1:1 (B-E) reflects the four different types of bridging [N(SiMe₃)H₃]²⁻ groups with significant [Si–Si–H] agostic interactions for the E sites (Figure 7). From the NMR spectroscopic data, there is no way to assign which resonance corresponds to the non-equivalent B, C, and D sites in Figure 7.

With the exception of the agostic interactions, the only previous example of a trinuclear homoleptic Ca complex is [Ca$_{3}$(but₂p)$_{6}$H$_{6}$] [30], which exhibits a similar variable-temperature ¹H NMR behavior. Trinuclear homoleptic Mg compounds displaying two different ligand environments in a 1:2 ratio for the terminal and bridging positions are more common [30,31]. Trinuclear divalent lanthanide complexes of composition Ln[μ-NSSHMe$_{2}$]$_{3}$[Ln(NSSHMe$_{2}$)$_{3}$][H(bis)] (Ln = Sm, Eu, Yb) and Eu have been also described. As in the case of complex 4, the coordinately unsaturated and electron-deficient Ln(IIs) centers favor the formation of close Ln-[Si–Si–H] agostic interactions involving all of the SiHMe₃ groups. Extensive Eu-[Si–Si–H] secondary interactions, finally, have also been reported very recently for the donor-free, mixed-valence, trinuclear complex (Eu)$_{3}$[μ-NSSHMe$_{2}$] [Eu$_{3}$(NSSHMe$_{2}$)$_{3}$][H(bis)] [32].

Complex 4 has been used as a precursor for the synthesis of the heteroleptic compound [Eu$_{3}$(TP$_{3}$)$_{3}$][Ca(NSSiMe$_{3}$)H$_{3}$] (5). Treatment of [TTF$_{2}$-TP$_{3}$(TP$_{3}$)] with an excess of 4 in pentane over a period of 2 days, followed by extraction with a 1:3 toluene/pentane mixture, provided 5 in 37% yield (Scheme 5).

![Scheme 5. Synthesis of complex 5.](image)

Compound 5 was characterized by elemental analysis, NMR, and IR spectroscopies. In the ¹H NMR spectrum at 298 K, the SiH resonance of 5 (δ = -4.17 ppm) is significantly upfielded with respect to the free amine (δ = -4.92 ppm). In the ¹H-²⁹Si HMQCD 2D NMR spectrum, the SiH resonance is observed at δ = -24.1 ppm as a doublet with $\Delta$ν$_{HH}$ = 159 Hz. As observed above for 4, this time-average value is indicative of a mild (140–160 Hz) to weak (160–170 Hz) agostic interaction [29,28]. No decoupling of the SiH signal was observed by variable-temperature ¹H NMR from 298 to 193 K in [D$_{3}$]toluene. The solid-state IR data confirmed the presence of a [Si–Si–H] agostic interaction. Compound 5 exhibited one ν$_{HH}$ absorption at 2044 cm⁻¹ and a second remarkably low band at 1888 cm⁻¹, characteristic of a Ca-[Si–Si–H] interaction.

The solid-state structure of 5 was determined by X-ray diffraction (Figure 9). The metal center is four-coordinate, an uncommon feature for Ca complexes, with a short Ca–N$_{amide}$ distance (Ca–N$_{amide}$ = 2.68 Å), barely longer than that of 1. Ex-
amination of the Ca[N(SiMe3)2]2 fragment strongly supports the presence of an agnostic Ca−Si−H contact, as the two SiMe3H moieties are clearly non-equivalent. This is reflected by the difference between the obtuse Ca1–N7–Si1 and much more acute Ca1–N7–Si2 angles (134.99(13) and 97.62(10)°, respectively), corresponding to a much shorter Ca1−Si2 distance (3.003(3) Å) with respect to Ca1−Si1 (3.655(1) Å). Interestingly, the agnostic hydrogen H2a has been unambiguously localized (Ca1−H2a = 2.41(2) Å), affording a nearly planar Ca1N7Si2H2a core (torsion angle 6.5°). Similar geometric features have been noted for other heteroleptic silylamidomithocene and tris(dimethylsilyl) methylcalcium complexes, which also exhibit β-Si−H agnostic interactions. The presence of this interaction is likely to confer a certain degree of stability, since 5 appeared significantly less reactive towards air and moisture than 1.

Attempts at synthesizing the THF adduct of 5 were less successful. The treatment of [(THF)3Ca(TpMe3)] with [Ca(N(SiMe3)2)2(thf)] in pentane over a period of 2 days provided, after extraction with a 1:3 toluene/pentane mixture, [(THF)2Ca(TpMe3)(N(SiMe3)2)2(thf)] (6) as the major compound in 36% yield. Despite numerous attempts, it proved impossible to fully purify and analytically characterize 6; crystals of 6 suitable for X-ray diffraction could not be obtained. In addition to 6, 1H and 13C NMR spectroscopies revealed the presence of several unidentified species containing (F5Cp)2TpMe3. The 27Al NMR spectrum of 6 (and the other species) shows four signals for the benzo fluorines of (F5Cp)2TpMe3. The 1H NMR spectrum of 6 shows SiH and SiCH3 resonances at δ = 4.69 and 0.01 ppm, respectively, as well as THF signals whose integration is in accord with a mono adduct. In the 1H NMR 2D NMR spectrum, the Si−H resonance is observed at δ = –24.1 ppm with JSiH = 160 Hz. Addition of some drops of THF to a D2 benzene solution of 5 led to similar spectra and behavior.

Cyclohydroamination catalysis

Our efforts towards the synthesis of 1 were rewarded upon examination of its catalytic performance for the cyclohydroamination of 1-amino-2,2-dimethyl-4-pentene (5) (Scheme 6), a common model aminoalkene for which abundant data are available in the literature. Representative results are gathered in Table 1.

![Scheme 6. Cyclohydroamination reaction of 5 catalyzed by 1.](image)

Table 1. Representative data for the cyclohydroamination of 5 catalyzed by 1 at 25 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[1][5]</th>
<th>t [min]</th>
<th>Conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1H</td>
<td>1:50</td>
<td>6</td>
<td>99</td>
</tr>
<tr>
<td>2H</td>
<td>1:200</td>
<td>16</td>
<td>99</td>
</tr>
<tr>
<td>3H</td>
<td>1:400</td>
<td>27</td>
<td>85</td>
</tr>
<tr>
<td>4H</td>
<td>1:600</td>
<td>18</td>
<td>57</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 3.0 μmol of precatyst, 1.2 mL of D2 benzene.  
[b] Reaction conditions: 3.0 μmol of catalyst, 1.8 mL of D2 benzene.  
[c] Reaction conditions: 3.0 μmol of catalyst, 1.7 mL of D2 benzene.  
[d] The conversions were determined by 2H NMR spectroscopic monitoring.

In all cases, the ring-closure of 5 proceeded according to Baldwin's rules (5-exo-trig) leading to the exclusive formation of 2,4,4-trimethylpyrrolidine. Virtually complete conversion of 50 and 200 equivalents of 5 was observed within 6 and 16 min, respectively, at room temperature (turnover number, TON = 50 and 200); apparent turnover frequency, TOF, 50 min = 8 and 12 min–1). This reactivity highlights the highly effective catalytic activity of 1, which, although comparable with the [NNi(Ca(thf))] systems (X = N(SiMe3)2 or CH(SiMe3)2)(32) outperforms that of the homoleptic complexes [Ca(N(SiMe3)2)](thf), (x = 0 or 2) or [Ca(CH(SiMe3)2)(thf)](11) as well as that of the heteroleptic bis(silylamido-2,4-pyrazolato-2,5,3-methylamine, cyclophosphazene, 1,3-diketiminate-based amido species. Therefore, compound 1 represents one of the most efficient precatysts reported to date for the cyclohydroamination of 5. When large loadings of 400 and 600 equivalents of aminoalkene were used, the conversion peaked at 85 and 57% after 27 and 18 min, respectively (TON = 340 and 342, TOF, 50 min = 12 and 19 min–1).

These results were found quite reproducible and can be ascribed to catalyst decomposition, consistently with the observed formation of an unidentified white precipitate during...
the catalytic runs. Such catalyst decay at higher substrate loadings may be due to either the very high sensitivity of these Ae species towards residual impurities (moisture or other unidentified factors) contained in the substrate/solvent or intrinsic decomposition pathways of complex 1 (or species derived thereof) under the catalytic conditions. Kinetic monitoring was performed by $^1$H NMR spectroscopy at 0°C since at 25°C complex 1 was found too active for reliable measurements. Substrate consumption followed first-order kinetics; no induction period was observed (Figure 10). The semi-logarithmic plots of monomer conversion versus reaction time were linear over 3 half-lives, with the apparent rate constants $k_{app}$ values ranging from 0.0005 to 0.0013 s$^{-1}$ for 125 and 50 equivalents of 5, respectively (with $k_{app} = k[1]$ expressed in s$^{-1}$, in which $k$ is the reaction rate constant in 1 mol$^{-1}$s$^{-1}$, see below). The reaction rates decreased when higher substrate concentrations were used, pointing to a possible catalyst inhibition by the product.

First-order dependence upon substrate concentration has also been observed for other heavier Ae-based catalytic systems,\textsuperscript{11,12,14} although reaction rates with zeroth-order in substrate\textsuperscript{12,14} or inversely proportional to substrate concentration may also be possible.\textsuperscript{11,12,14}

To determine the effect of the precatalyst concentration upon the reaction rate, the cyclohydroamination of 5 was performed at 0°C with initial concentrations [1], varying from 3.60 to 7.14 mM. The linear plot of $\ln k_{app}$ versus $\ln[1]$ had a slope of 1.05 suggesting first-order dependence upon precatalyst concentration (see the Supporting Information). Thus, the rate law for the cyclohydroamination of the aminolefine S catalyzed by 1 is given in Equation (1).

$$r = k[1][S]$$  \hspace{1cm} (1)

Catalytic systems based on heavier alkaline earth metals that feature such a kinetic rate law are uncommon. Examples include the imino-enolide 8a-amido, and -alkyl precatalysts.\textsuperscript{19} The same rate law was also established for Mg-based precatalysts supported by tris(oxazolyl)phenylborate\textsuperscript{70} or phenoxo-amine ligands.\textsuperscript{71} This rate law is consistent with a mechanism implying a fast $\alpha$-insertive pathway followed by rate-limiting aminolysis, as recently computed for both intra- and intermolecular hydroamination.\textsuperscript{72-76}

Alternatively, it may also be accounted for by the interaction between two substrate molecules and the metal center, with the formation of a six-membered transition state involving concerted ring-closure and proton transfer, as the turnover-liming step\textsuperscript{77} DFT computations performed on $	ext{[Cp}^+\text{Ag}]^+$ alkyloxazolyl)borate (TOB) and arildo-imine-Ae complexes suggested that the latter scenario may be significantly more energy demanding, and therefore less realistic.\textsuperscript{78} $	ext{[Cp}^+\text{Ag}]^+$ cyclopentadienyl-\text{bitoxazolyl}borate (TTOB) = tris(oxazolyl)borate.\textsuperscript{79-81}

The stromium analogue 3 was also evaluated in the intramolecular hydroamination reaction of 5, displaying a much lower catalytic activity than its Ca analog.\textsuperscript{82} The reaction with 50 equivalents of the aminolefine at 25°C only provided a conversion of 10% in 7 min. Signs of catalyst decomposition were noted with also the formation of a white precipitate at the bottom of the NMR tube within seconds after the reactants were mixed. Apparently, the active species in the stromium case decomposes much faster than in the calcium case.\textsuperscript{83}

Conclusion

The synthesis and characterization of the silylamido complexes $\text{[F}_{2}T_{2}P_{4}^{\text{SiMe}}\text{Me}_2\text{Ar(NMe)}_2]$ (R = SiMe$_3$-Ca, Sr, R = SiMe$_3$H, Ae = Ca) supported by the bulky, highly fluorinated, hydrotris(inda- zolyl)borate ligand $\text{[F}_{2}T_{2}P_{4}^{\text{SiMe}}\text{Me}_2]$ have been detailed. These heteroleptic complexes, free of ethereal ligands, are inert in solution, showing a remarkable inertness towards Schlenk equilibria. The solid-state structure of $\text{[F}_{2}T_{2}P_{4}^{\text{SiMe}}\text{Me}_2\text{NNSiMe}_2\text{Me}_2]$ (3) displays an agnostic interaction between the electron-deficient Sr$^{2+}$ center and one of the Si-CH$_3$ groups of the (N(NSiMe)$_2$)$_2$ ligand. The synthesis of the new homoleptic diamido complex $\text{[Ca(NSiMe}_2\text{H})_2]}_2$ (4) has been described. On the basis of its fluxional behavior, a trinuclear structure with additional [F-Si-H] agnostic interations has been proposed for 4. This precursor has enabled the synthesis of the heteroleptic THF-free compound $\text{[F}_{2}T_{2}P_{4}^{\text{SiMe}}\text{Me}_2\text{Ca(NSiMe}_2\text{H})]}_2$ 5, also stabilized by a [F-Si-H] agnostic contact.

Complex 1 proved to be particularly efficient for the catalytic cyclohydroamination of 1-aminoo-2,2-dimethyl-4-pentene, representing one of the most active precatalysts reported to date for this reaction. However, the activity of 1 seems limited by catalyst degradation over time with large substrate loadings (much higher than those reported in the literature), a feature apparently even more obvious for the stromium analogue 3.

Despite stability issues largely due to B-N bond cleavage, the highly fluorinated ligand $\text{[F}_{2}T_{2}P_{4}^{\text{SiMe}}\text{Me}_2]$ forms well-defined heteroleptic Ca and Sr silylamido complexes. Its electron-withdrawing properties coupled to the bulky trihal scaffold enhance the polarity and hence the reactivity of the Ae-N bond yet avoiding Schlenk-type redistributions. This is remarkable since there are only few ligands capable of preventing scrambling equilibria during catalysis, especially in the case of Sr.\textsuperscript{[12,32]}
Experimental Section

All operations were performed with rigorous exclusion of air and moisture, using standard Schlenk, high-vacuum, and glovebox techniques under Ar (0.1–0.3 atm; H₂O ≤ 1 ppm). All solvents were dried and distilled under Ar (THF over Na/benzophenone; acetonitrile over diisopropylamine; toluene over Na; pentane over CaH₂) and further degassed by freeze-pump-thaw cycles and stored in sealed ampoules in the glovebox. THF (v-THF) was prepared as previously reported.¹⁾²⁾ CaH₂ and SrH₂ (Alcohol; anhydrous beads; ~10 mesh, 99.99% trace metal basis) were used as received. H₂N(CH₂)₉NH₂ (97%) was dried over activated 3 Å molecular sieves. H₂N(CH₂)₉NH₂ was distilled over CaH₂. The substrate 1-amino-2,2-dimethyl-4-pentene (5) was prepared according to literature methods.³⁾⁴⁾ K(Ni(SiMe₃)₂)₂ (KNSMe₂) was prepared from KH and H₂NiCl₂ by following the same procedure used for KNi(SiMe₃)₂.⁵⁾⁶⁾ CaNi(SiMe₃)₂ (3) and SrNi(SiMe₃)₂ (4) were synthesized from KNi(SiMe₃)₂, and either CaH₂ or SrH₂ according to literature procedures.⁷⁾⁸⁾ [CaNi(SiMe₃)₂] (8) was prepared as previously reported.⁹⁾¹₀⁾¹¹⁾

Unless stated otherwise, NMR spectra were recorded by using J. Young valve NMR tubes at 299 K using Bruker DPX 300 (9, 300.13; ³⁵⁾¹²⁾ 282.38 MHz, Avance II 4000 (H, 400.16; ³⁵⁾¹²⁾ 376.69 MHz, Avance 300 (H, 300.13, ³⁵⁾¹²⁾ 282.38 MHz, Avance 400 (H, 400.13; ³⁵⁾¹²⁾ 376.48; ³⁵⁾¹²⁾ 100.63 MHz). Avance 500 (H, 500.33; ³⁵⁾¹²⁾ 79.49; ³⁵⁾¹²⁾ 125.82 MHz) spectrometers. Chemical shifts for ¹H NMR were determined using residual proton signals in the deuterated solvents and reported versus SiMe₄. Chemical shifts for ¹³C NMR spectra were taken of the solvent referenced to SiMe₄. ¹³C NMR spectra were referenced versus external CFCℓ and SiMe₄, respectively.¹²⁾¹³⁾¹⁴⁾¹⁵⁾¹⁶⁾¹⁷⁾¹⁸⁾¹⁹⁾²⁰⁾²¹⁾²²⁾²³⁾²⁴⁾²⁵⁾²⁶⁾²⁷⁾²⁸⁾²⁹⁾³⁰⁾³¹⁾³²⁾³³⁾³⁴⁾³⁵⁾³⁶⁾³⁷⁾³⁸⁾³⁹⁾⁴⁰⁾⁴¹⁾⁴²⁾⁴³⁾⁴⁴⁾⁴⁵⁾²⁾⁴⁶⁾⁴⁷⁾⁴⁸⁾⁴⁹⁾⁵⁰⁾⁵¹⁾⁵²⁾⁵³⁾⁵⁴⁾⁵⁵⁾⁵⁶⁾⁵⁷⁾⁵⁸⁾⁵⁹⁾⁶⁰⁾⁶¹⁾⁶²⁾⁶³⁾⁶⁴⁾⁶⁵⁾⁶⁶⁾⁶⁷⁾⁶⁸⁾⁶⁹⁾⁷⁰⁾⁷¹⁾³²⁾³³⁾³⁴⁾³⁵⁾³⁶⁾³⁷⁾³⁸⁾³⁹⁾⁴⁰⁾⁴¹⁾⁴²⁾⁴³⁾⁴⁴⁾⁴⁵⁾²⁾⁴⁶⁾⁴⁷⁾⁴⁸⁾⁴⁹⁾⁵⁰⁾⁵¹⁾⁵²⁾⁵³⁾⁵⁴⁾⁵⁵⁾⁵⁶⁾⁵⁷⁾⁵⁸⁾⁵⁹⁾⁶⁰⁾⁶¹⁾⁶²⁾⁶³⁾⁶⁴⁾⁶⁵⁾⁶⁶⁾⁶⁷⁾⁶⁸⁾⁶⁹⁾⁷⁰⁾⁷¹⁾³²⁾³³⁾³⁴⁾³⁵⁾³⁶⁾³⁷⁾³⁸⁾³⁹⁾⁴⁰⁾⁴¹⁾⁴²⁾⁴³⁾⁴⁴⁾⁴⁵⁾²⁾⁴⁶⁾⁴⁷⁾⁴⁸⁾⁴⁹⁾⁵⁰⁾⁵¹⁾⁵²⁾⁵³⁾⁵⁴⁾⁵⁵⁾⁵⁶⁾⁵⁷⁾⁵⁸⁾⁵⁹⁾⁶⁰⁾⁶¹⁾⁶²⁾⁶³⁾⁶⁴⁾⁶⁵⁾⁶⁶⁾⁶⁷⁾⁶⁸⁾⁶⁹⁾⁷⁰⁾⁷¹⁾³²⁾³³⁾³⁴⁾³⁵⁾³⁶⁾³⁷⁾³⁸⁾³⁹⁾⁴⁰⁾⁴¹⁾⁴²⁾⁴³⁾⁴⁴⁾⁴⁵⁾²⁾⁴⁶⁾⁴⁷⁾⁴⁸⁾⁴⁹⁾⁵⁰⁾⁵¹⁾⁵²⁾⁵³⁾⁵⁴⁾⁵⁵⁾⁵⁶⁾⁵⁷⁾⁵⁸⁾⁵⁹⁾⁶⁰⁾⁶¹⁾⁶²⁾⁶³⁾⁶⁴⁾⁶⁵⁾⁶⁶⁾⁶⁷⁾⁶⁸⁾⁶⁹⁾⁷⁰⁾⁷¹⁾³²⁾³³⁾³⁴⁾³⁵⁾³⁶⁾³⁷⁾³⁸⁾³⁹⁾⁴⁰⁾⁴¹⁾⁴²⁾⁴³⁾⁴⁴⁾⁴⁵⁾²⁾⁴⁶⁾⁴⁷⁾⁴⁸⁾⁴⁹⁾⁵⁰⁾⁵¹⁾⁵²⁾⁵³⁾⁵⁴⁾⁵⁵⁾⁵⁶⁾⁵⁷⁾⁵⁸⁾⁵⁹⁾⁶⁰⁾⁶¹⁾⁶²⁾⁶³⁾⁶⁴⁾⁶⁵⁾⁶⁶⁾⁶⁷⁾⁶⁸⁾⁶⁹⁾⁷⁰⁾⁷¹⁾³²⁾³³⁾³⁴⁾³⁵⁾³⁶⁾³⁷⁾³⁸⁾³⁹⁾⁴⁰⁾⁴¹⁾⁴²⁾⁴³⁾⁴⁴⁾⁴⁵⁾²⁾⁴⁶⁾⁴⁷⁾⁴⁸⁾⁴⁹⁾⁵⁰⁾⁵¹⁾⁵²⁾⁵³⁾⁵⁴⁾⁵⁵⁾⁵⁶⁾⁵⁷⁾⁵⁸⁾⁵⁹⁾⁶⁰⁾⁶¹⁾⁶²⁾⁶³⁾⁶⁴⁾⁶⁵⁾⁶⁶⁾⁶⁷すこと。
Annexure A

\[ \text{SiH}_4 \] 4.74 s (2H, SiH\(_2\)), 4.41 s (2H, SiH\(_2\)), 4.36 s (2H, SiH\(_2\)), 0.64 s (2H, SiH\(_2\)), 0.61 s (2H, SiH\(_2\)), 0.43 s (2H, SiH\(_2\)), 0.39 s (2H, SiH\(_2\)), 0.38 s (2H, SiH\(_2\)), 0.34 s (2H, SiH\(_2\)), 0.24 s (2H, SiH\(_2\)).

\[ \text{NMR (D}_2\text{COO}: \text{D} = 100 \text{°C}) \]

- 13C: \( \delta = \ldots \) ppm
- 1H: \( \delta = \ldots \) ppm

Synthesis of \([\text{Fe}_{12}\text{P}_{7}\text{TPP}_{5}\text{S}_{5}\text{C}_{2}\text{CaSiMe}_{2}H_{2}]^{2+}\) (SI: \([\text{Fe}_{10}\text{P}_{7}\text{TPP}_{5}\text{S}_{5}\text{C}_{2}\text{CaSiMe}_{2}H_{2}]^{2+}\))

- 0.259 g, 0.256 mmol, \( \text{CaSiMe}_{2}H_{2} \), 0.117 g, 0.384 mmol, and \( \text{H} \) were combined in a flask. The white slurry was stirred at room temperature for 2 days, during which time it changed color to dark gray. After filtration and washing with pentane, the solid was extracted with a toluene-pentane (1:3 v/v) mixture and filtered. After removal of volatiles under vacuum, compound 5 was obtained as a white solid (0.095 g, 37%, un-optimized yield). Crystals suitable for X-ray diffraction analysis were obtained from a saturated toluene-pentane solution at 40 °C.

NMR-scale cyclohydroamination reactions

In a glovebox, the appropriate amount of catalyst (1 or 3) was weighed in an NMR tube, and the substrate dissolved in \( \text{D}_2\text{COO} \) was then added. The tube was sealed, vigorously shaken, and immersed into an oil bath at the desired temperature.

Kinetics of the cyclohydroamination reaction

In a glovebox, the appropriate amount of precatalyst was weighed in an NMR tube. The substrate and \( \text{D}_2\text{COO} \) (1.7, 1.7, or 1.8 mL) were then added to the NMR tube. The tube was rapidly sealed and vigorously shaken, then cooled in a bath at 0 °C (reaction times were measured from this point) and maintained at this temperature until it was inserted into the probe of a Bruker AM 500 NMR spectrometer preset at 30 °C. Data points were recorded as soon as possible after this, and it typically took altogether about 5 min to record the first of these. The reaction kinetics were monitored using the multi-aged command (11 = 0.2 s, DS = 0; N = 4 or more) over the course of 3 or more half-lives on the basis of amine consumption, by comparing the relative intensities of resonances diagnostic of substrate and product.

X-ray diffraction crystallography

The data for crystals of 1 and 2 were collected on a Gemini Ultra diffractometer equipped with an APEX II detector and an Oxford Cryosystem N2 gas stream low-temperature device. Graphite monochromatized MoK\(_\alpha\) radiation was used for collecting diffraction data at a temperature of T = (180 ± 2) K. The data for crystals of 3 were collected on a Bruker D8 diffractometer equipped with an APEX II detector and an Oxford Cryosystem N2 gas stream low-temperature device. Multi-layer monochromatized micro-focus MoK\(_\alpha\) radiation was used for collecting diffraction data at a temperature of T = (193 ± 2) K. The structure was solved by direct methods using SHELXL2016 and refined by means of least-squares procedures on \( F^2 \) with the aid of the program SHELXL-2016 included in the software package WinGX version 1.83z. All non-hydrogen atoms were anisotropically refined. All hydrogen atoms were geometrically placed and refined by using a riding model. In the last cycles of refinement a weighting scheme was used, where weights were calculated from the following formula:

\[ w = \frac{1}{[(\sigma(F^2))^2 + (0.0380P)^2 + 1.258P]} \]

where \( P = F^2 - (2F^2) \). For complex 2, a disorder between two molecules of THF was treated using the PART command in SHELX-97. For complex 2, the check cif presents one Alert Level A about a low theta full; the reason is due to incomplete scans, possibly based on erroneously assumed higher than actual symmetry for the final measurement strategy determination. Ellipsoid plots were drawn at the 30% probability level. Relevant collection and refinement data are summarized in the Supporting Information.

Acknowledgements

Financial support from the ANR (GreenAir project; contract number ANR-11-BSV7-0009) is gratefully acknowledged. The assistance of Dr. Remy Brousse with the X-ray diffraction crystallography and Dr. Christian Biani with the NMR spectroscopy measurements is also acknowledged.

Keywords: agostic interactions · alkaline earth metals · cyclohydroamination · ligands · metathesis

Annexure B: Research article published in a collaboration with the group of Prof. Alexander Trifonov
ComPLEXES 6–8 are highly air- and moisture-sensitive crystals, well soluble in aliphatic and aromatic hydrocarbons. As evidenced by NMR spectroscopy, complexes 6–8 are diamagnetic, in line with the divalent oxidation state of the ytterbium atom.

Complex 6 crystallizes with two crystallographically independent molecules in the asymmetric unit as established by an X-ray diffraction study. The solid-state structure of 6 reveals that introduction of an additional Lewis base group (e.g., OMe) into one of the aryl substituents of the NCN core leads to a dramatic change in the coordination mode of the aminate ligand (Figure 1). In fact, in complex 6, the bistetradenate aminate ligand adopts a classic $\mu^2$-$\eta^2$:O$_2$p$_2$-arene fashion. $\mu^2$-$\eta^2$:O$_2$p$_2$-arene coordination to ytterbium has been previously documented for Yb(III) complexes with bulky guanidinate and aminate ligands$^{13,15}$ while, to our knowledge, $\mu^2$-$\eta^2$:O$_2$p$_2$-arene coordination fashion is described here for the first time. Besides the tridentate aminate ligand, the Yb(III) center in 6 is bound to one mononuclear [N(SiMe$_3$)$_2$]$^+$ group and the oxygen atom of the THF molecule. The formal coordination number of Yb(II) in 6 is thus seven. The Yb–N$_{NCS}$ and Yb–N$_{amidine}$ distances in 6 (2.452(2) and 2.695(3) Å) are expectedly longer compared to those in the related six-coordinated Yb(II) complexes with $\mu^2$-$\eta^2$:O$_2$p$_2$-arene coordination ([BuNC(phen)$_2$]$_2$Yb(μ-H)$_2$] (2.329(3), 2.420(4) Å)$^{16}$, [BuNC(phen)$_2$]$_2$Yb(μ-SCH$_2$Ph)$_2$] (2.386(4), 2.409(4) Å)$^{17}$, and [Cy$^5$NC(NH)$_2$]$_2$Yb(μ-$\eta$)] (2.300(3), 2.426(4) Å)$^{18}$). No other examples of seven-coordinate Yb(II) complexes featuring $\mu^2$-$\eta^2$:O$_2$p$_2$-arene coordination of the aminate ligand are known so far, limiting possible comparisons. The Yb–N$_{amidine}$ bond length in 6 (2.260(2) Å) is noticeably shorter than those in seven-coordinate Yb(II)–amidine complexes [Na(THF)$_2$][Cu$_2$Yb$_2$(N(SiMe$_3$)$_2$)$_2$] (2.41(2) Å)$^{19}$ and [(Me$_2$Si)$_2$N]Yb$_2$(μ-DAC)$_2$] (2.413(4)–3.44(3) Å)$^{20}$. The Yb–C$_{amidine}$ distances fall into a rather large range (2.886(2)–3.57(3) Å, average = 3.05(3) Å)$^{21}$. The Yb–O coordination bonds in complex 6 have similar lengths: Yb(1A)–O(1A) = 2.485(2) Å and Yb(1A)–O(1SA) = 2.458(2) Å.

In the $^1$H NMR spectrum of 6 recorded in toluene-$d_8$, the methyl hydrogens of the aminate isopropyl groups appear as a broadened multiplet at δ 1.27–1.33 ppm overlapping with the β-CH$_2$ hydrogens of the THF molecule, and the methine hydrogens of the isopropyl groups give one broad multiplet at δ 3.66 ppm. The α-CH$_3$ THF hydrogens appear as a broadened multiplet at δ 3.28 ppm. A singlet at δ 3.51 ppm is assigned to

Figure 1. Molecular structure of [2-MeOCH$_2$NC(Ph)$_2$N(SiMe$_3$)$_2$][Yb(THF)$_2$] (6). Only one of the two independent molecules is shown. Hydrogen atoms, methyl fragments of the Ph groups, and methylene fragments of the THF molecule are omitted for clarity. Thermal ellipsoids drawn at the 50% probability level. Bond lengths (Å) and angles (deg): Yb(1)–N(3) 2.506(2), Yb(1)–N(2) 2.452(2), Yb(1)–O(15) 2.458(2), Yb(1)–O(1) 2.483(2), Yb(1)–C(6) 2.886(3), Yb(1)–C(7) 2.94(1), Yb(1)–C(8) 3.08(1), Yb(1)–C(21) 3.04(3), Yb(1)–C(9) 3.13(3), Yb(1)–C(10) 3.15(3), Yb(1)–N(2) 3.47(2), Yb(1)–N(3) 3.50(3), N(1)–C(1) 1.29(3), N(2)–C(1) 1.37(3), N(3)–Yb(1)–N(2) 122.4(7), N(3)–Yb(1)–O(15) 107.0(7), N(2)–Yb(1)–O(15) 115.5(7), N(3)–Yb(1)–O(11) 119.7(7), N(2)–Yb(1)–O(11) 134.0(6), O(11)–Yb(1)–O(1) 131.8(6).
the methoxy group hydrogens of the amminate ligand, while the signals arising from the aromatic hydrogens of the 2-methoxyphenyl and 2,6-dinitrophenyl moieties give rise to a multiplet in the region δ 6.30-6.80 ppm. The methyl hydrogens of the styliamid ligand appear as a characteristic sharp, high-field shifted singlet at δ 0.24 ppm. Variable temperature 1H and 13C NMR spectra of complex 6 in the range −60 to 50 °C were recorded in toluene-d8 and THF-d8, however, they did not provide informative clues about the actual arené coordination mode in solution, notably if the N-d coordination observed in the solid state is maintained.

The X-ray diffraction studies of complexes 7 and 8 (Figures 2 and 3) revealed a very unusual χ coordination of the central five-membered ring of 1,3,6,8-tetra-t-butylcarbazol-9-yl ligands to the Yb(II) centers. Unlike lanthanide complexes of unsubstituted[13] or 1,8-difluoro-9-t-butyl carbazol-9-yl ligands that feature metal–ligand π-interaction through the amide N-donor, the ytterbium atoms in 7 and 8 are disposed above the pyrrolid ring (Yb–centroid distances = 2.517(5) Å in 7 and 2.545(7) Å in 8) along the Yb–Namine bond (7, 2.490(3); 8, 2.393(3) Å), bonding of the ytterbium center with two neighboring pyrrolid carbons are detected in both complexes. The lengths of these Yb–C bonds (7, 2.675(4) and 2.708(3) Å; 8, 2.670(4) and 2.840(4) Å) are comparable to those observed in related Yb(II) cyclopentadienyl complexes for comparison, see [C(4,4)Me2Yb[N(SiMe3)]2]; Yb–C average = 2.75(2) Å, 2(C4,4)Me2Yb[N(SiMe3)]2[THF]; Yb–C = 2.675(4)–2.727(4) Å[2]. Moreover, two somewhat longer contacts between the ytterbium center and the two remaining distal carbons of the pyrrolid ring are detected (7, 2.085(3) and 3.047(3) Å; 8, 2.899(4) and 2.979(4) Å). These distances just slightly longer than the analogous Yb–C bonds in the bis(benzylidenyl)-ytterbium complex (C5H4)2Yb(THF)2 (2.825(4)–2.952(7) Å[2]). Curiously, the difference of coordination numbers of the metal centers in 7 and 8 does not affect much the Yb–C distances (average Yb–C bond length: 7, 2.854(3); 8, 2.856(4) Å) while, at the same time, the Yb–Namine distance in 8 (2.631(3) Å) is substantially longer than in 7 (2.490(3) Å). Overall the geometric parameters of complexes 7 and 8 suggest χ′-coordination of the 1,3,6,8-tetra-t-butylcarbazol-9-yl ligands with a noticeable tilting toward the χ′-fashion, as observed in (C5H4)2Yb(THF); (1n = Sm, Yb) complexes.[20,23] The Yb–Namine bond lengths in 7 and 8 (2.389(3) and 2.332(3) Å, respectively) fall in the range of values normally measured in Yb(II) complexes with terminal N(SiMe3)2 ligands.[13,14,15] In complex 7, the short contacts Yb(1)–N(1) (3.146(11) Å) and Yb(1)–N(1′) (2.841(4) Å), together with noticeable distortion of the geometry around the nitrogen (Si(1′)–N(1)–Yb(1)–Si(1′)) 103.3(2), Si(2′)–N(2)–Yb(1)–Si(2′) 128.0(2)° and silicon (C(29)–Si(1′)–N(1)–N(2)) 107.5(3)° atoms are indicative of an agostic interaction between the metal center and one of the methyl groups of the uylamide ligand.[27] In complex 8, which contains a more coordinatively saturated Yb(II) center, no such agostic interaction was observed.

In the 1H NMR spectrum of 7 recorded in CD2Cl2 solution at ambient temperature, the Yb(II) groups of the carbazolyl ligand give rise to a slightly broadened singlet at δ 1.48 ppm, the aromatic hydrogens of the carbazolyl moiety appear as two doublets at δ 7.59 and 8.23 ppm (JYb-H = 1.4 Hz). A sharp, high-field shifted singlet at δ 0.37 ppm corresponds to the uylamide ligand. The hydrogens of the THF molecule give two slightly broadened singlets at δ 1.27 and 3.53 ppm.
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NMR spectrum of 8 is similar to that of 7 with the only difference being the integral intensity of the signals corresponding to the THF hydrogen.

Hydrophosphination Catalysis. Ytterbium(II) complexes 5–7 were investigated as catalyst precursors in the hydrophosphination reaction between styrene and Ph₂PH or Ph₂PH₂, chosen as model reactions. Representative results are reported in Table 1. All reactions were found to be regiospecific.

### Table 1. Hydrophosphination of Styrene with Ph₂PH and Ph₂PH₂ Catalysts by Yb(II)–Amide Complexes 5–7

<table>
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<th>Entry</th>
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<th>Phosphone</th>
<th>Time (h)</th>
<th>Conversion [%]</th>
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<td>Ph₂PH</td>
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<td>27</td>
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<td>55</td>
</tr>
<tr>
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<td>6 (2.0)</td>
<td>Ph₂PH</td>
<td>0.25</td>
<td>17</td>
</tr>
<tr>
<td>4</td>
<td>6 (2.0)</td>
<td>Ph₂PH</td>
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<td>7</td>
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<tr>
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<td>8</td>
<td>15</td>
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<td>60</td>
<td>61</td>
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<tr>
<td>11</td>
<td>(Me₅Si)₂N₂Yb(THPF)₃</td>
<td>2</td>
<td>22</td>
<td></td>
</tr>
</tbody>
</table>

*Reaction conditions: neat substrates in a 1:1 ratio, 60 °C. Conversion determined by 1H NMR spectroscopy in C₆D₆.*

Forming exclusively the anti-Markovnikov addition product. Complex 7 was found to be the most productive over the series (compare entries 2, 4, and 6), although all three complexes featured performance of the same magnitude. The catalytic activity of 5–7 in the hydrophosphination of styrene with diphenylphosphine, especially that of 7, is remarkable and is commensurate to that which we recently disclosed for an Yb(II)–amide complex supported by an amido–imine ligand.²⁸ Notably, the performance of 5 and 7 is clearly superior to that of the simple precursor [(Me₅Si)₂N₂]Yb-(THPF)₃ (entry 11). The reactivity of phosphinophosphate with 7 proved considerably lower than that of diphenylphosphine (entries 9–10). Of note, only the primary hydrophosphination product was formed in the latter reactions with Ph₂PH₂, i.e., no PhCH₂CH₂Ph₂PPh₂ eventually resulting from subsequent reaction of PhCH₂CH₂PPh₂ with styrene was observed.

Besides experiments using 50 equiv of styrene and Ph₂PH, the limit of complex 7 was evaluated by increasing the substrates loading up to 100 and 200 equiv (with [styrene]/[Ph₂PH] = 1:1). The neat reaction using 100 equiv of substrates reached 92% conversion after 4 h at 60 °C. However, in the presence of 200 equiv of substrates, only 15% conversion was observed after 8 h, suggesting catalyst decay. Actually, in the experiments performed over 2 h at such low catalyst loadings, we noticed that the color of the solution gradually changed from deep red to pale yellow: this is consistent with an oxidation of Yb(II) to Yb(III). This hypothesis is also corroborated by the observation of broad resonances in all NMR spectra of the crude reaction mixtures, diagnostic of paramagnetic Yb(III) species, especially at high styrene concentrations.²⁹ This putative oxidation of divalent ytterbium with styrene, in the presence of phosphine (or amine, vide infra), is reminiscent of our recent results with related divalent lanthanide systems.²⁸

More detailed kinetic data about this reaction were sought after using 7 as a catalyst, with relatively large catalyst loadings (>10 mol%) to prevent as much as possible problems connected to the above-mentioned catalyst decay. To determine the partial order in Ph₂PH₂, its conversion over time was studied using a large excess of styrene, at three different [phosphine]/[7] ratios (see the Supporting Information, Figures S6–S8). In all cases, similar values of kₚ were obtained (0.107 s⁻¹, 0.133 s⁻¹, and 0.125 s⁻¹), that is, 0.120 ± 0.013 s⁻¹, thus suggesting a zeroth order dependence on phosphine. Another interesting observation in these experiments is the induction period which was observed in all cases. In fact, the larger the amount of Ph₂PH₂, the shorter the induction period: 3 equiv, 98 h; 7 equiv, 81 h; 15 equiv, 36 h (data obtained by extrapolation of least-squares linear regression lines, see Figures S6–S8). This may suggest that the Yb(II)–amide complex reacts with the phosphine to produce the real catalytic species, tentatively assigned as a Yb(II)–PPh₂ species. Unfortunately, attempts to prepare this putative phosphine species, through independent reactions of Ph₂PH with 7, have been unsuccessful thus far.

In order to determine the partial order in the catalyst, the conversion of the phosphine was studied using a large excess of styrene at different catalyst concentrations (over a 10-fold range, in the range 0.25–65 mM) while maintaining the total volume of reactants and solvent constant. The apparent rate constants (kₚ) were thus determined for substrate conversion below 70% (see the Supporting Information Table S1). The plot of ln(1/kᵣ) vs ln([7]) gave a straight line (R² = 0.957) with a slope of 0.5 corresponding to the apparent kinetic order for the precatlyst (Figure 4; see also Figure S9).

![Figure 4. Plot of ln(1/kᵣ) vs ln([7]) for the intermolecular hydrophosphination of styrene and Ph₂PH catalyzed by 7 at different catalyst concentrations (0.25, 1.50, 2.50, 4.00, 45.0, and 65.0 mM). Reaction conditions: 60 °C, [styrene]₀ = 1.34 M, [styrene]/[Ph₂PH] = 100:1, C₆D₆ + Ph₂PH + styrene = 0.66 mL.](image-url)

Further experiments were conducted to determine the partial order in styrene, using a constant concentration of the catalyst and the phosphine and varying the concentration of styrene in the reaction mixture in a 10-fold range (in the range 0.33–2.61 M).³⁰ Similar treatment as that performed above gave an apparent partial order in styrene of 0.72 (R² = 0.986). However, because of the narrow concentration range (due to
experimental constraints,\(^\text{20}\) a substantial error exists, and the values are also quite consistent with a partial first-order on styrene (\(R^2 = 0.962; \text{see Figures S10} - \text{S12 and Table S2})). Since a first order is usually observed for intramolecular hydrophosphination of styrene with group 3 and 4 divalent metals,\(^\text{11,12,28}\) we assume this is also the case here.

On the basis of previous results with related Yb(II) catalytic systems,\(^\text{26}\) we anticipated to find a zeroth order for Ph$_2$P=H and a first order for styrene and the catalyst, respectively. In fact, the data with 7 are consistent with a zeroth order in phosphine and a first order in styrene but indicate a 0.5 order for the catalyst, suggesting that the precatalyst (putatively a Yb(III)-phosphate) has a dimeric association in solution or is involved in a reversible dimer–monomer aggregation phenomenon. In order to obtain additional evidence for a dimeric structure of the real catalytic species in solution, the NMR-nuclide reactions of complexes 5–7 with equimolar amounts of Ph$_2$P=H (CD$_2$Cl$_2$ r.t.) were found to occur with the release of amine and formation of precipitates, albeit the $^{31}$P and $^{195}$Yb spectra of the reaction mixtures turned out to be uninformative. In particular, no coupling patterns were observed in the $^{31}$P and $^{195}$Yb spectra.

**Hydroamination Catalysis.** Complexes 5–7 have been also investigated briefly in the intermolecular hydroamination of styrene and pyridine. Experiments were performed in neat reagents, using a 2 mol loading of the precatalyst at 60 °C. Representative results are reported in Table 2. In all cases, only the anti-Markovnikov hydroamination product was observed. As for hydrophosphination reactions, complexes 7 proved to be the most productive, with nearly complete conversion after 31 h of reaction, somewhat better than with 6, and much better than with 5 or the simple precursor $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Yb(THF)}]$. In fact, with the latter complexes 5 and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Yb(THF)}]$, the color of the reaction mixture turned from red to yellow within minutes, indicating rapid catalyst decay (oxidation); in these cases, and in contrast to the hydroamination reactions conducted with 6 and 7 (see Figure S13), the NMR spectra of the crude reaction mixtures featured rather broad resonances, indicating the presence of Yb(III) species; also, formation of an unidentified precipitate was noticed when $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Yb(THF)}]$ was used as a catalyst precursor. It is important to note that the yet unidentified species resulting from the oxidation of 5 under the reaction conditions is (are) not active (or at least significantly less than 5). This provides indirect evidence that the true active species in these hydroamination reactions are indeed dimeric ytterbium species.

The catalytic performance of precatalysts 6 and 7 are remarkable since with another Yb(II)–amide complex supported by an aminoacetic anilido–imine ligand,\(^\text{29}\) no hydroamination took place under the same conditions; this complex employed decomposed (likely oxidized) in the presence of styrene and pyridine (also evidenced by the rapid color change from purple to light yellow concurrent with the formation of a precipitate), and only the starting reagents were observed.\(^\text{30}\)

### CONCLUSIONS

The amine elimination reactions of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Yb(THF)}]$ with amidine 2-MeO$_2$C$_6$H$_3$NH$_2$(S$_{\text{Me}}$) = $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Ph(THF)}]$ and 1,3,6,8-tetra-tert-butylcarbazol pro-ligands allowed for the synthesis of new heteroleptic Yb(II) amido complexes which were isolated in high yields. The solid state structures of complexes 6–8 revealed profound changes of coordination modes of conventional ligands provoked by modification of their denticity and steric bulkiness. The introduction of an additional Lewis base group (i.e., OMe) into one of the aryl substituents of the amidinate ligand leads to an unprecedented $\eta^2$-N$_2$C$_6$H$_4$-OPh aren coordination, instead of the classic $\eta^1$-N$_2$A mode. Similarly, replacing a simple carbazol-9-yl by 1,3,6,8-tetra-tert-butylcarbazol-9-yl ligand results in the switch of coordination mode from $\sigma$ to $\kappa$.

The Yb(II)–amide complexes 5–7 all proved able to promote intermolecular hydroamination of styrene under mild conditions; however, their catalytic performances are quite contrasted. The carbazol-9-yl-Yb(II)–amide revealed superior abilities for both hydrophosphination and hydroamination, as compared to amidinate 5 and 6. This can be tentatively related to the lower (formal) coordination number of complex 7, as in this type of catalysis, activity tends to increase as the coordination number of the catalyst decreases. The high activity of complex 7 in hydrophosphination is commensurate to that of a recently reported (amido-imine)Yb(II)–amide,\(^\text{48}\) but it is remarkable that it also promotes efficiently the addition of pyridine onto styrene, while the (amido-imine)Yb(II)–amide proved completely unable to do so, due to rapid decomposition/oxidation in the presence of these reagents. This clearly evidences that the reactivity and stability of those classes of divalent lanthanide complexes can be largely tuned with appropriate ligand frameworks. Research along these lines is currently under progress in our laboratories.

### EXPERIMENTAL SECTION

**General Considerations.** All experiments were performed in evacuated tubes, using standard Schlenk-flasks or glass-techniques, with rigorous exclusion of traces of moisture and air. After drying over KOH, THF and DME were purified by distillation from lithium/benzophenone/tert-butyliodide and benzophenone/hexamethyldisilazane (HMDS) and condensed in a vacuum prior to use. $\text{Yb}((\text{OMe})_2)_{\text{e}}$ was prepared according to literature procedure.\(^\text{19}\) Ph$_2$SiH$_2$ was purchased from Aldrich and was prepared from SiH$_4$ and condensed in a vacuum prior to use. (Ph$_3$CH)$_2$ was purchased from Acros and were used without additional purification. Styrene and pyridine were purchased from Aldrich or Acros and were vacuum-distilled over CaH$_2$ and then were degassed by freeze–pump–thaw methods. Diphenylphosphine and phenylphosphine were purchased from Aldrich and used as received.

**Instruments and Measurements.** NMR spectra were recorded on a Bruker DXP 200 or Bruker Avance DRX-400 spectrometer. Chemical shifts for $^1$H and $^{13}$C($^1$H) spectra were referenced internally using the residual solvent resonances and are reported relative to TMS. Lanthanide metal analysis was carried out by complexometric
### Table 3. Crystallographic Data and Structure Refinement Details for 6–8

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[1,3,6,8-BisC₆H₄(N₂)N(C₆H₅)Br₂(THF)](7). A solution of 1,3,6,8-
BisC₆H₄(N₂)N(C₆H₅)Br₂ (0.053 g, 1.29 mmol) in toluene (10 mL) was added to a solution of [Me₃Si(N₂)N(C₆H₅)Br₂(THF)] (0.020 g, 1.29 mmol) in toluene (15 mL) at room temperature. The reaction mixture was stirred at 70 °C for 3 days, volatiles were removed in a vacuum, the solid residue was dissolved in benzene (20 mL), and the resulting solution was centrifuged. Slow concentration of the benzene solution at room temperature and prolonged cooling of the concentrated solution at -30 °C resulted in the formation of complex 7 as bright orange crystals. The mother liquid was decanted, and the crystals were washed with cold benzene and dried in a vacuum for 30 min. The yield was isolated in 70% yield (0.558 g, 6.76 mmol). 

**Acknowledgments:**...
Inorganic Chemistry

Annexure B

hexane. Complex 8 was isolated in 85% yield (1.040 g, 1.20 g mol). "H NMR (400 MHz, CDCl3, 293 K): / = 0.57 (s, 18H, SiMe3), 1.27 (br m, 8H, ρ-CH2 THF), 1.48 (s, CH2, Si(CH3)2), 3.53 (s, Br, CH2, Si(CH3)2), 7.59 (d, J = 1.4 Hz, 2H, CH2, CH2-N), 8.23 (d, J = 1.4 Hz, 2H, CH2, CH2-N). "C NMR (100 MHz, CDCl3, 293 K): 35.3 (s, SiMe2), 24.7 (s, ρ-CH2 THF), 30.1 (s, CH2, Si(CH3)2), 34.4 (s, C, CH2), 54.7 (s, C, CH2), 69.3 (s, ρ-CH2 THF), 114.3 (s, C, CH2-N), 120.0 (s, CH2, CH2-N), 124.6 (s, C, CH2-N), 131.7 (s, C, CH2-N), 135.6 (s, C, CH2-N), 1620 (s, C, CH2-N) ppm. Elem.


Hydrophosphination/Hydroamination Experiments. In a typical hydrophosphination experiment, the complex was loaded in an NMR tube in the glovebox. Styrene and Ph3P were then added in and the reaction time started after heating the NMR tube at 60 °C in a preheated oil bath. After the desired reaction time, CD2Cl2 was added to the reaction mixture, and the "H NMR spectrum was recorded shortly after at regular time intervals. Conversion was determined by integrating the remaining styrene and the newly formed addition product.

X-Ray Crystallography. The X-ray data for 6–8 were collected on a Smart Apex diffractometer (graphite monochromated, MoKα radiation, ω-scan technique, λ = 0.71073 Å, T = 100(2) K). The structures were solved by direct methods and were refined on F2 using the SHELXTL package.12 All non-hydrogen atoms were found from Fourier synthesis of electron density and were refined anisotropically. All hydrogen atoms were placed in calculated positions and were refined in the riding model. SADABS13 was used to perform anode-detector scaling and absorption corrections. The X-ray data for complex 6 were refined using the HKL9S method. The details of crystallographic collection, and refinement data are shown in Table 3, and corresponding CIF files are available as Supporting Information. CCDC-959665 (6), -969365 (7), and -969367 (8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via fax: +44 1223 336037. (b) Zienk, W.; Befus, S.; Trzeciak, T.; Zaborski, T. J. Org. Chem. 2006, 71, 8259–8266.

ASSOCIATED CONTENT

Supporting Information

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Inorganic Chemistry

(29) NMR spectra turned out impossible to integrate when the styrene concentration was higher than 2.61 M.
(30) At very high styrene concentration (4.61 M), the NMR spectra featured very broad resonances, making the integration difficult and inaccurate.
(33) Seldén, G. M. SADABS v2.01, Bruker/Siemens Area Detector Absorption Correction Program. Bruker, Madison, WI, 1998.
INTRODUCTION

Calcium is a large (c_{calcium} = 1.00 Å), electropositive, and amorphous metal that forms d complexes. Heteroleptic (LX)-Ca(Nu)(S) complexes (LX = ancillary monooxamino ligand; Nu = monoanionic macrocyclic; S = solvent) are of interest for catalysis, but they are labile and readily engage in deleterious Schlenk equilibria. As a result, the coordination chemistry of calcium has been regarded as challenging. Yet, after Hanusa’s seminal efforts,1 it has experienced a surge of interest and synthetic strategies that enable the utilization of calcium complexes for applications in polymerization, fine chemical catalysis, and material science have been devised.5 Westerhausen et al.6 has enabled Roesky’s6 and Harder’s6 to prepare a collection of heteroleptic [Cg(NacNac)(Ca)(S)] complexes, while Hill used the ubiquitous [Cg(NacNac)(Ca)(SMe2)](TFHP) to catalyze a variety of reactions.8 Nevertheless, in spite of these major achievements along with some others,9 the need for new ligand platforms and routes to robust heteroleptic calcium complexes remains.

In a landmark article, Ruhlbrand-Senge discussed that secondary (nonoxidative) interactions such as M⋯S, M⋯P, and agostic bonds are, in some cases, key for the stabilization of alkane-earth (AE = Ca, Sr, Ba) complexes.10 For instance, AE⋯H⋯Si agostic interactions allow the synthesis of...
stable \((\text{LX})\text{Ar(N(SiMe}_{3}H)}_{2}\text{(S)}\text{)}\text{ complexes. This strategy has proved valuable to isolate heteroleptic complexes,}\text{ but the benefits are limited in catalysis, for instance when the N(SiMe}_{3}H)}_{2}\text{ amide is replaced by another reactive group prior to entering the catalytic cycle, or because of the intrinsic (detrimental) reactivity of the Si–H moiety.}\text{ Intramolecular Ae–F interactions between the metal atom and ancillary ligand are attractive, because they are both strong and permanent features of the complex. Fluorinated alkoxide ligands have been used to prepare volatile compounds suitable for metal organic chemical vapor deposition.}\text{ We have in the past employed fluorinated alkoxo ligands bearing CF}_{3}\text{ groups in positions α to the O}_{\text{alkoxo}}\text{ atom to synthesize group 3, 4, and 15 precatalysts for the polymerization of α-olefins and lactide.}\text{ These alkoxides are comparable to phenoxo in terms of electronic properties, and the steric bulk and electron-withdrawing effect of the α-CF}_{3}\text{ prevent the formation of polynuclear species. Well-defined cationic Ae complexes of the type }\left[\text{RO}_{X}^+\text{Ar}^+\right]\text{ }(X^-)\text{, where }\left[\text{RO}_{X}^+\right]\text{ is a fluorinated alkoxide bearing a 1-aza-15-crown-5 tether and }X^-\text{ is a weakly coordinating anion, are stable thanks to strong (ca. 30 kcal mol}^{-1}\text{) intramolecular Ae–F interactions,}\text{ but attempts to prepare the parent charge-neutral }\left[\text{RO}_{X}^-\text{Ar(N(SiMe}_{3}H)}_{2}\right]\text{ complexes failed because of kinetic lability, leading to ligand redistribution in solution. We report here the use of fluorinated alkoxide }\left[\text{RO}_{X}^+\right]^-\text{ ligands with aminooether tethers for the synthesis of heteroleptic calcium amide complexes }\left[\text{RO}_{X}^+\text{Ca(N(SiMe}_{3}H)}_{2}\right](x = 1–3; R = H, Me; Chart 1). It is shown that Ae–F interactions help toward the stabilization of these species. Their performance as catalysts in the intermolecular hydrophosphination of styrene is illustrated, and their ability to act as precursors for highly electron-deficient }\left[\text{RO}_{X}^+\text{Ca}^+\right]^+\text{[X}^-\text{]}\text{ is presented.}
Annexure C

Organometallics

RESULTS AND DISCUSSION

Synthesis of Potassium and Calcium Charge-Neutral Complexes. The protio ligands [RO\textsubscript{4}H\textsuperscript{+}] are prepared in high yields by an equimolar reaction of the appropriate amine with 2,2-bis(trifluoromethyl)aniline\textsuperscript{213} react with KN(SiMe\textsubscript{3})\textsubscript{2} or KN(Si(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2} in diethyl ether to afford the corresponding solvent-free potassium salts [RO\textsubscript{4}K\textsuperscript{+}]\textsubscript{2} (\textit{k} = 1 \textsubscript{(1)}, 2 \textsubscript{(2)}, 3 \textsubscript{(3)}) in satisfactory yields (Scheme 1). Complexes 1–3 have been fully characterized; they form a dimer or tetramer in the molecular solid state, and their polymeric structure persists in solution in aromatic solvents (vide infra). These complexes failed to react cleanly with 1:1 mixtures of CaH\textsubscript{2} and KN(SiMe\textsubscript{3})\textsubscript{2} to give heterocyclic amidino calcium complexes during salt metathesis reactions (R = H, Me), and one-pot reactions of [RO\textsubscript{4}H\textsuperscript{+}]\textsubscript{2} with 2 equiv of KN(Si(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2} were also unsuccessful. Analytically pure samples of the targeted heteroleptic complexes [RO\textsubscript{4}H\textsuperscript{+}]Ca(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2} (k = 1, R = Me, \textit{x} = 2, R = H, \textit{x} = 3, R = Me, \textit{x} = 3, R = H, \textit{x} = 2, R = H, \textit{x} = 3, R = H, \textit{x} = 3, R = H, \textit{x} = 3) were eventually obtained in moderate yields by protonolysis of Ca(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2} or Ca(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2}(THF)\textsubscript{2} or Ca(N(Si(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2}(THF)\textsubscript{2} with the protio ligand (Scheme 1). Whereas we anticipated that the protio ligand of highest denticity should also yield heterocyclic ligands, we were unable to obtain [RO\textsubscript{4}H\textsuperscript{+}]Ca(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2} for R = H, Me; this was reminiscent of the difficulties encountered in our attempts at making [RO\textsubscript{4}H\textsuperscript{+}]Cu(N(SiMe\textsubscript{3})\textsubscript{2})\textsubscript{2} (13). The identities of 4–7, which all form solvent-free binuclear dimers in the solid state regardless of the nature of the starting material, have been authenticated by structural analysis and NMR spectroscopy, and their purity was corroborated by combustion analyses. Complexes 5–7 are soluble in common nonpolar organic solvents (ethers, hydrocarbons) and decompose within minutes in chlorinated solvents (CD\textsubscript{3}CN, CDCl\textsubscript{3}). Their NMR data were recorded in benzene-d\textsubscript{6}; 4 is only sparingly soluble in hydrocarbons, and THF-d\textsubscript{4} was used as the NMR solvent.

Two organoamidoalkoxide compounds 4 and 5 are less stable than the congeneric tetramethylidyldiisilazide 5 and 7; in particular, 4 rapidly shows signs of decomposition in solution. This was tentatively attributed to the presence of sterically demanding Ca–H–Si interactions in 5 and 7, although their existence could not be firmly demonstrated by spectroscopic methods.

The [RO\textsubscript{4}H\textsuperscript{+}] NMR spectra for the potassium complexes 1–3 and the calcium complexes 4 and 5 exhibit a single, sharp singlet for the Cf\textsubscript{4} groups typically in the range \textit{d}_\text{CF}_{4} = -77.2 to -81.8 ppm, indicating the equivalence of all Cf\textsubscript{4} moieties in solution for these complexes. On the other hand, two quartets of equal intensity are detected in the spectra of the Ca complexes 6 (centered at -73.4 and -75.1 ppm; \textit{J}_{\text{Ca}-\text{H}} = 9.4 Hz) and 7 (centered at -76.5 and -76.8 ppm; \textit{J}_{\text{Ca}-\text{H}} = 9.4 Hz), indicating that the CF\textsubscript{4} groups are in these cases nonequivalent. Hence, the [RO\textsubscript{4}H\textsuperscript{+}] NMR spectra for 4–7 recorded at 25 °C provided no evidence for the metal–F intramolecular interactions detected in all these complexes in the molecular solid state (vide infra). Attempts to observe splitting of the resonances by recording low-temperature data (down to -80 °C) did not improve on this situation; evidently the Cf\textsubscript{4} groups are highly fluxional, rotating and exchanging positions too easily for NMR detection methods. In their H NMR spectra, complexes 5 and 7 exhibit a resonance at \textit{d}_\text{H} = 4.88 and 4.86 ppm, respectively, assigned to the SiH moieties. These chemical shifts and the corresponding \textit{J}_{\text{Si}-\text{H}} coupling constant (162 Hz in both cases) do not provide compelling evidence for the presence of intramolecular Ca–H–Si interactions; again, low-temperature NMR brought no improvement, and decoalescence of the resonance that could potentially be expected did not occur at -80 °C. Consistent with this, the FTIR spectra of 5 and 7 show a unique, symmetric absorption band for Si–H stretching at \textit{f} = 2016 and 2015 cm\textsuperscript{-1}, i.e. in the region expected for SiH moieties not interacting with a metal center; As–H–Si contacts (As = Ca–Ba) are characterized by a band at lower energy, typically 1900–1980 cm\textsuperscript{-1}, depending on the strength of the interaction and identity of the metal. The 29Si{[\textsubscript{13}C]} NMR data for 5 and 7 (\textit{\delta}_{\text{Si}} = -25.1 and -25.4 ppm, respectively) are comparable to those for related [LO]Ca(N(SiMe\textsubscript{3})\textsubscript{2}]THF\textsubscript{2} aminooxo phenolate complexes.\textsuperscript{9}

Solid-State Structural Investigations. Single crystals of 1–7 were grown typically from concentrated hydrocarbon (toluene, benzene, and/or pentane) or diethyl ether solutions, and their structures were determined by X-ray diffraction studies.

The complex [RO\textsubscript{4}H\textsuperscript{+}]K\textsubscript{1} (1) recrystallized as the centrosymmetric dimer \textit{K}_{2} where each metal atom is 9-coordinated and the two K atoms are directly bridged through the O\textsubscript{alkoxide} atoms (Figure 1). The coordination sphere on each metal is...
Figure 2. (left) ORTEP representation of the molecular structure of (BO$_4$)$_3$K$_2$ (2), recrystallized as the tetramer [2]$_4$. Hydrogen atoms are omitted for clarity. (right) Simplified representation of the K$_2$O$_4$ heterocubane in [2]$_4$, showing the coordination sphere around K atoms and the atom-numbering scheme. Color scheme: F atoms, green; K atoms, purple; C atoms, black; O atoms, red; N atoms, blue. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): K(1)–O(8) = 2.815(2), K(1)–O(20) = 2.642(1), K(1)–O(22) = 2.707(1), K(2)–O(1) = 2.707(1), K(1)–F(14) = 2.879(1), K(1)–F(25) = 3.807(2), K(1)–F(28) = 2.802(1), K(1)–F(50) = 3.355(2), K(1)–N(1) = 3.060(2), K(2)–O(22) = 2.690(1), K(2)–O(30) = 2.777(1), K(2)–O(41) = 2.800(1), K(2)–O(70) = 2.690(1), K(2)–F(38) = 2.830(1), K(2)–F(44) = 3.138(1), K(2)–F(45) = 2.857(1), K(2)–N(33) = 2.970(2), K(3)–O(20) = 2.627(1), K(3)–O(44) = 2.620(1), K(3)–O(67) = 2.738(2), K(3)–O(70) = 2.773(3), K(3)–F(74) = 2.861(1), K(3)–F(75) = 3.28(2), K(3)–N(60) = 3.060(2), K(4)–O(20) = 2.692(1), K(4)–O(22) = 2.692(1), K(4)–O(70) = 2.599(1), K(4)–O(88) = 2.708(2), K(4)–F(15) = 2.761(1), K(4)–F(17) = 2.962(1), K(4)–N(65) = 2.976(1).

Figure 3. (left) ORTEP representation of the molecular structure of (BO$_4$)$_3$K$_3$ (3), recrystallized as the tetramer [3]$_4$. Only one of the two independent and comparable molecules found in the asymmetric unit is depicted. Hydrogen atoms are omitted for clarity. (right) Simplified representation of the K$_2$O$_4$ heterocubane in [3]$_4$, showing the coordination sphere around K atoms and the atom-numbering scheme. Color scheme: F atoms, green; K atoms, purple; C atoms, black; O atoms, red; N atoms, blue. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): K(1)–O(1) = 2.774(6), K(1)–O(13) = 2.660(5), K(1)–O(33) = 2.709(5), K(1)–O(73) = 2.708(5), K(1)–N(1) = 3.061(2), K(2)–O(11) = 2.906(7), K(2)–F(35) = 2.839(5), O(13)–K(2) = 2.744(5), K(2)–O(21) = 2.810(6), K(2)–O(33) = 2.658(5), K(2)–O(53) = 2.643(5), K(2)–N(15) = 2.918(7), K(4)–O(2) = 2.777(6), F(17)–K(1) = 3.180(7), O(33)–K(3) = 3.069(5), K(3)–O(41) = 2.734(5), K(3)–O(53) = 2.677(5), K(3)–O(73) = 2.709(5), K(3)–N(45) = 2.875(6), K(3)–F(50) = 2.925(3), K(3)–F(77) = 2.931(5), K(3)–F(76) = 3.011(6), O(13)–K(4) = 2.631(5), O(33)–K(4) = 2.681(5), K(4)–O(61) = 2.765(6), K(4)–O(73) = 2.625(3), K(4)–N(60) = 2.921(6), F(30)–K(4) = 3.020(7), F(32)–K(4) = 3.081(7), K(1)–K(4) = 3.780(2), K(2)–K(3) = 3.710(2), K(2)–K(4) = 3.707(2).

with each of the metal atoms, and therefore they both act overall as a μ$_2$κ$_4$κ$_4$ chelate. The K(1)–K(1)$^{109}_{90}$ distance of 3.94 Å is much shorter than that in elemental potassium (4.54 Å) and smaller than double the van der Waals radius of potassium (r$_{vdw}$ = 2.75 Å); this coincides with a narrow K(1)–O(15–)

K(1)$^{90}_{90}$ angle of 92.6°. Similar or even stronger geometric constraints were for instance seen in the complex K$_2$Ru$_2$(CO)$_{12}$([PF$_6$]$_2$)$_4$·4Bu$_2$C$_6$H$_4$O$_2$ (K–K = 3.60 Å, $\angle$(K–O–K) = 78.3°)$^{18}$ in the potassium calix[4]arene complex {([calix[4]O]$_2$K$_2$)[μ-K]$_2$[THF]$_{16}$}. K–K = 3.27 Å, $\angle$(K–O–K...K) = 180°.
The complex $[\text{RO}_4]^-$ also recrystallized as the tetramer $[\text{RO}_4]^-$ (2) with a central $\text{K}_2\text{O}$ core adopting a slightly distorted cubic arrangement where each metal atom is adjacent to three $\text{O}_{\text{alkali}}$ atoms (Figure 2). The formation of heterocubanes is well-known for alkali-metal alkoxides, as for instance seen in $[\text{MOC}n\text{F}_4]^-$ (M = Na, K). Each metal atom engages in two to four nonequivalent K-F interactions with neighboring CF$_4$ groups (average distance K-F ($\bar{A}$)): K(1), 2.99; K(2), 2.94; K(3), 3.05; K(4), 2.86; the limit for significant K-F interactions was set at 3.23 $\bar{A}$, and the coordination sphere is completed by the $\text{N}_{\text{side}}$ amine atom and only one $\text{O}_{\text{alkali}}$ atom, with total coordination numbers varying from 7 to 9. The other metric parameters around the metals in [2]$_4$ are unexceptional. Note that, for each metal, the bonding of only one of the two $\text{OMe}$ moieties in the amineoxide tether is required to ensure coordinative saturation, as the addition of multiple K-F interactions turns out to be more stabilizing than the coordination of the second $\text{OMe}$, a possibility already suggested by Ruhland-Senge. As a matter of fact, the second methoxy does not interact with any metal atom in the crystal lattice, and the coordination spheres about the metal atoms in [2]$_4$ actually resemble closely those in [X]$_3$K, also a heterocubane obtained upon recrystallization of $[\text{RO}_4]^-$ (2) where the dangling CH$_3$CH$_2$OMe fragment is replaced by a simple methyl group on the N atom (Figure 3). The heterocubane structure imposes short K-K distances (ca. 3.00-4.00 $\bar{A}$ and narrow K-O-K angles in these two complexes. Formation of tetramers [2]$_4$ and [3]$_4$ with the ligands $[\text{RO}_4]^-$ and $[\text{RO}_4]^-$, in contrast to the dimer seen with $[\text{RO}_4]^-$ in [2], and with $[\text{RO}_4]^-$, is linked to the lower intrinsic coordinating ability of these ligands.

The molecular structure of the dimeric calcium complex [S]$_2$ depicted in Figure 4 shows a peculiar arrangement about the metal atoms. The positions of the SiH$_4$ hydrogen atoms were not idealized but were determined from the electron density map in this work, which features an inversion center. The metal atoms are 3-coordinated and, if Ca-H-Si is taken into account, 7-coordinated. The large discrepancies between the two Ca-N-Si angles (103.3 and 126.7°) and corresponding Ca-Si distances (3.15 and 3.58 $\bar{A}$ to Si(1) and Si(2), respectively) suggest that the Si(1)-H(15) moieties are involved in agnostic bonding with the metal atoms. The coplanarity of Ca(1)-N(1)-Si(1)-H(15) is in agreement with this interpretation. Yet, one may also note that Si(2) and H(25) also fit in this very plane, even if other metric parameters do not support the claim of Ca-H(25)-Si(2) agnostic interactions. Pertinent metric parameters for [S]$_2$ and other related calcium complexes are collected in Table 1.

The structural features presented here may indeed argue in favor of (at least) Ca-H(15)-Si(1) agnostic bonding, but spectroscopic methods did not provide supporting evidence (vide supra), and we are unable to conclude as to the existence of such agnostic bonding on the basis of these experimental data. There is no ambiguity regarding the Ca(1)-F(14) interaction characterized by a short distance of 2.83 $\bar{A}$ between these two atoms, even if the intensity of this secondary interaction is weaker than that detected in $[\text{Py}^2\text{NaCl}_{2}$], $\text{CaN(SiMe}_{3})_2$ (TTF), $\text{CaF} - 2.47$ and $2.49$ $\bar{A}$, and in the cationic complex $[\text{RO}_4]^-$ (2), $\text{CaF} - 2.64$ and $2.68$ $\bar{A}$. Expectedly, the Ca-N$_{\text{alkyl}}$ bond length is much shorter than the Ca-N$_{\text{alkane}}$ length (2.60 $\bar{A}$), whereas the bridging $\text{O}_{\text{alkali}}$ atoms are also substantially closer to the metal atoms (ca. 2.50 $\bar{A}$) than the sole $\text{O}_{\text{alkane}}$ atom involved in the coordination sphere of the metal (Ca(1)-O(25) = 2.42 $\bar{A}$). Remarkably, in line with the above observations on [2]$_4$, the other methoxy side arm (v.i., O(29)) in [S]$_2$ does not interact with any metal atom, as coordinative saturation is fulfilled by the N(SiMe$_3$)$_2$ moiety and a Ca-F secondary interaction in addition to the ancillary ligand.

The geometry of the centrosymmetric dimer [4]$_2$ is similar to that in [S]$_2$ (Table 1), except that the potential Ca-H-Si agnostic interaction in the latter is now replaced by a second, albeit weaker, Ca-F contact. The metal atoms in [4]$_2$ are 7-coordinated, with relatively intense (Ca-F(20) = 2.92 $\bar{A}$) and loose (Ca-F(15) = 3.11 $\bar{A}$) secondary interactions, while the rest of the coordination sphere is occupied by the ancillary ligand. The metric parameters about the metal in [4]$_2$ are comparable to those measured in [S]$_2$, and again one of the $\text{O}_{\text{alkane}}$ atoms (v.i., O(25)) is not interacting with the metal atoms. On the other hand, the geometric features around the N$_{\text{alkyl}}$ atoms are different; the Si-N-Si angle of 121.3° is narrower than that in [S]$_2$ (120.0°), and the difference between the two types of Ca-N-Si angles in [4]$_2$ (112.5 and 126.6°) is not as great as in [S]$_2$. These observations, as well as the coordination of a second F atom to achieve a coordination number of 7, seem to imitate in favor of a Ca-H-Si agnostic interaction in [S]$_2$ in the solid state. The bonding pattern in the centrosymmetric dimer $[\text{RO}_4]^-$ $\text{CaN(SiMe}_{3})_2$ (2), which matches that in [S]$_2$, except for the fact that the dangling, noncoordinating CH$_3$CH$_2$OMe side arm

Figure 4. ORTEP representation of the molecular structure of $[\text{RO}_4]^-$Ca(N(SiMe$_3$)$_2$)$_2$ (2). Hydrogens (except SiH) are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths ($\bar{A}$) and angles (deg): Ca(1)-O(11) = 2.29(1), Ca(1)-O(14) = 2.30(2), Ca(1)-N(1) = 2.31(3), Ca(1)-O(25) = 2.41(1), Ca(1)-N(22) = 2.59(1), Ca(1)-F(14) = 2.83(1), Si(1)-N(1)-Ca(1) = 103.27(7), Si(3)-N(1)-Ca(1) = 126.69(8), Ca(1)-O(11)-Ca(1) = 104.03(3), Si(1)-N(1)-Si(2) = 130.03(9).

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Table 1. Summary of Metric Data for the Heteroleptic Calcium Complexes \([4\text{b}]_{2}\) 

<table>
<thead>
<tr>
<th>complex</th>
<th>Ca atom</th>
<th>Ca–F ((\text{Å}))</th>
<th>Ca–S ((\text{Å}))</th>
<th>Ca–N–Si (deg)</th>
<th>N–Si–N (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{RO}<em>2\text{F}]\text{Ca}[\text{N(SiMe}</em>{3}\text{)}]<em>{2}) (\left(\text{E}</em>{2}\right))</td>
<td>Ca(1) = Ca(1)(^{19})</td>
<td>2.92</td>
<td>3.37</td>
<td>112.5</td>
<td>123.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.11</td>
<td>3.60</td>
<td>125.6</td>
</tr>
<tr>
<td>([\text{RO}<em>2\text{F}]\text{Ca}[\text{N(SiMe}</em>{3}\text{)}]<em>{2}) (\left(\text{E}</em>{3}\right))</td>
<td>Ca(1) = Ca(1)(^{19})</td>
<td>2.83</td>
<td>3.15</td>
<td>103.3</td>
<td>130.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.38</td>
<td>3.58</td>
<td>126.7</td>
</tr>
<tr>
<td>([\text{RO}<em>2\text{F}]\text{Ca}[\text{N(SiMe}</em>{3}\text{)}]<em>{2}) (\left(\text{E}</em>{4}\right))</td>
<td>Ca(1)</td>
<td>3.08</td>
<td>3.42</td>
<td>114.4</td>
<td>119.7</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>3.62</td>
<td>125.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ca(2)</td>
<td>2.71</td>
<td>3.15</td>
<td>109.9</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>3.06</td>
<td>3.65</td>
<td>128.0</td>
</tr>
<tr>
<td>([\text{RO}<em>2\text{F}]\text{Ca}[\text{N(SiMe}</em>{3}\text{)}]<em>{2}) (\left(\text{E}</em>{5}\right))</td>
<td>Ca(1) = Ca(1)(^{19})</td>
<td>3.00</td>
<td>3.29</td>
<td>110.8</td>
<td>128.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.47</td>
<td>120.5</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5. ORTEP representation of the molecular structure of \([\text{RO}_2\text{F}]\text{Ca}[\text{N(SiMe}_{3}\text{)}]_{2}\) \(\left(\text{E}_{2}\right)\). Hydrogen atoms (except SiH\(_3\)) are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (\(\text{Å}\)) and angles (deg): Ca(1)–O(11) = 2.33 \(\pm\) 0.02, Ca(1)–N(11) = 2.33 \(\pm\) 0.02, Ca(1)–F(15) = 1.31 \(\pm\) 0.02, Ca(1)–O(11)\(^{19}\) = 2.34 \(\pm\) 0.02, Ca(1)–O(20)\(^{19}\) = 2.37 \(\pm\) 0.02, Ca(1)–F(20)\(^{19}\) = 2.90 \(\pm\) 0.05, Si(1)–N(11)–Si(2) = 121.4 \(\pm\) 0.6, Si(1)–N(11)–Ca(1) = 112.4 \(\pm\) 0.7, Si(2)–N(11)–Ca(1) = 125.6 \(\pm\) 0.8, Ca(1)–O(11)–Ca(1)\(^{19}\) = 103.6 \(\pm\) 0.5.

that was in \([\text{S}]\) has now been replaced by a simple methyl group. As can be seen in Figure 6 and in Table 1, this bears no incidence on the coordination about the metal atoms. There is one Ca–F secondary interaction for each metal in \([\text{S}]\) with a corresponding distance of 3.00 \(\text{Å}\).

The arrangement is different in \([\text{RO}_2\text{F}]\text{Ca}[\text{N(SiMe}_{3}\text{)}]_{2}\) \(\left(\text{E}_{2}\right)\), displayed in Figure 7. Here, the two calcium atoms are not equivalent (Table 1). The atom Ca(1) is 6-coordinated, having only one Ca–F interaction (with F(26), 3.08 \(\text{Å}\)) the atom Ca(2) is 7-coordinated as found in \([\text{A}]_{2}\) with two Ca–F contacts of 2.71 and 3.06 \(\text{Å}\). The CaO\(_2\) central core is not symmetrical, and the interaction of a single F atom on Ca(1) generally induces slight deviations from symmetry throughout the dimer. Note, however, that the values of the two N–Si–N angles are very close.

Figure 6. ORTEP representation of the molecular structure of \([\text{RO}_2\text{F}]\text{Ca}[\text{N(SiMe}_{3}\text{)}]_{2}\) \(\left(\text{E}_{2}\right)\). Hydrogen atoms (except SiH\(_3\)) are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (\(\text{Å}\)) and angles (deg): Ca(1)–N(20) = 2.80 \(\pm\) 0.03, Ca(1)–O(17) = 2.31 \(\pm\) 0.01, Ca(1)–O(17)\(^{19}\) = 2.31 \(\pm\) 0.01, Ca(1)–O(17)\(^{19}\) = 2.08 \(\pm\) 0.01, Ca(1)–N(5) = 2.37 \(\pm\) 0.01, Ca(1)–F(12)\(^{19}\) = 3.00 \(\pm\) 0.05, Si(2)–N(20)–Si(1) = 128.1 \(\pm\) 0.8, Si(2)–N(20)–Ca(1) = 110.8 \(\pm\) 0.6, Si(1)–N(20)–Ca(1) = 120.4 \(\pm\) 0.7, Ca(1)–O(17)–Ca(1)\(^{19}\) = 103.0 \(\pm\) 0.4.

**NMR Diffusion Measurement Experiments.** The nuclearity of the potassium complexes 2 and 3 and calcium complexes 4–7 in solution was assessed by pulse gradient spin–echo (PGSE) NMR spectroscopy, following protocols developed for related alkaline and alkaline-earth complexes. 24 All measurements were performed at 298 K, using 13.0–30.0 mM solutions in benzene-\(d_{12}\). 25 The validity of the method was assessed using Si(SiMe\(_3\))\(_4\) (TMSS) as a reference. From the PGSE experiments, the translational coefficient \(D\) was acquired for all compounds from the plot of \(\ln(U)U\) vs \(\gamma^2\delta^3G^3(\Delta - \delta)/3\Delta\) (see the Experimental Section for details). The values of the hydrodynamic radius of the metal complexes \(\eta_{\text{cular}}\) thus determined are collected in Table 2. 

For all complexes, the value of the hydrodynamic radius determined from the solid-state structures (ellipsoidal model) 26 matches well that estimated by PGSE experiments, suggesting that they maintain their polymeric structure in aromatic hydrocarbons.

These measurements also confirmed that the heteroleptic complexes \([\text{RO}_2\text{F}]\text{Ca}[\text{N(SiMe}_{3}\text{)}]_{2}\) \(\left(\text{R} = \text{H, Me}\right)\) do not decompose entirely or in part to a mixture of homoleptic
Annexure C

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Figure 7. ORTEP representation of the molecular structure of $[\text{RO}^\text{a}_3\text{Ca}(\text{NC(SiMe})_3)_2\text{]}\text{]}_2$. Hydrogen atoms and noninteracting benzene molecules are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ca(1)–O(2) = 2.305(5), Ca(2)–N(1) = 2.83(317), Ca(1)–O(1) = 2.371(5), Ca(1)–O(1)[6] = 2.389(6), Ca(1)–N(15) = 2.031(5), Ca(1)–P(16) = 3.084(6), Ca(1)–Ca(3) = 2.780(3), O(1)–Ca(2) = 2.317(5), O(2)–Ca(2) = 2.84(5), F(22)–Ca(2) = 2.056(6), Ca(2)–N(31) = 2.370(7), Ca(2)–O(1)[42] = 2.475(6), Ca(2)–N(45) = 2.62(7), Ca(2)–F(31) = 2.71(5), Si(4)–N(31)–Si(5) = 121.6(4), Si(1)–N(1)–Si(6) = 119.7(4).

species $[\text{RO}^\text{a}_3\text{Ca}]_2$ and $\text{Ca}(\text{NC(SiMe})_3)_2$, as a single diffusion coefficient was measured in all cases. 1

Bond Valence Analysis. The contribution of secondary interactions (K–F and Ca–F) to the coordination sphere of the metal atoms can be estimated using bond valence sum analysis (BVSA). This theoretical model, first introduced by Brown and Altermatt 2 and later developed by O’Keefe and Bresee, 3 makes use of bond distances obtained from single-crystal X-ray diffraction to assign the contribution of each neighboring atom toward the metallic center through traditional interactions and secondary interactions. Bond valences ($u$) were calculated for each environment in the complexes $[\text{RO}^\text{a}_3\text{Ca}]_2$, $[\text{RO}^\text{a}_3\text{Ca}]_2$, and $[\text{RO}^\text{a}_3\text{Ca}(\text{NC(SiMe})_3)_2]_2$ using eq 1, with experimental bond lengths $d_{\text{Obs}}$ and tabulated bond lengths $R_{\text{tab}}$:

$$u = \exp\left[\frac{d_{\text{Obs}} - d_{\text{tab}}}{\theta}\right]$$

where $X = \text{O}, \text{F}, \text{N}$; $M = \text{K}, \text{Ca}, \text{B} = 0.37$; $R_{\text{K-O}} = 2.132, R_{\text{Ca-F}} = 1.992, R_{\text{Ca-N}} = 2.260$; $R_{\text{Ca-F}} = 1.967, R_{\text{Ca-N}} = 1.842, R_{\text{Ca-N}} = 2.140$. 16,20

For the calcium complex $[\text{RO}^\text{a}_3\text{Ca}]_2$ (Table 3), coordinative saturation is not reached if only coordination of the N and O side atoms is considered. Further extension by inclusion of the Ca–F interactions affords near coordinative saturation ($\sum \theta = 1.959$), and in this case the mean contribution of Ca–F 2 interactions to the overall coordination sphere approaches 4%. 20

For $[\text{RO}^\text{a}_3\text{Ca}]_2$ the mean contribution of K–F interactions to the coordination sphere (averaged over the four metal atoms) amounted to a considerable 18% (see the Supporting Information). This value compares well with the average values determined for $[\text{RO}^\text{a}_3\text{K}]_4$ (17%) (see the Supporting Information) and Rahldaht-Serge’s $[\text{KPTFB}(\text{THF})_2]_{20}$ (20%) PFBT = perfluoro-tetra-butoxide). 16,20 Higher K–F contributions were found in the tetrameric alkoxide $\text{KOC}([\text{Ph}(\text{CF}_2)]_{14}$ (34%) and $\text{KOCMe}(\text{CF}_2)]_{14}$ (32%), respectively, 16,20 which is unsurprising, as the K atoms are not supported by side N/O atoms in these compounds.

Synthesis of Calcium Cations. Cationic calcium complexes devoid of coordinated solvent are rare because of their intrinsic sensitivity, but they present an interest in catalysis owing to their high electronegativity. 16 The compounds $[\text{RO}^\text{a}_3\text{Ca}]_2$ $[\text{H}_2\text{N}(\text{B}(\text{CF}_2)_2)]_2$ 16 $[\text{RO}^\text{a}_3\text{Ca}]_2$ $[\text{H}_2\text{N}(\text{B}(\text{CF}_2)_2)]_2$ 16 (9) and $[\text{RO}^\text{a}_3\text{Ca}]_2$ $[\text{H}_2\text{N}(\text{B}(\text{CF}_2)_2)]_2$ 16 (10) were obtained as colorless solids by equivolume reactions of $\text{Ca}(\text{NC(SiMe})_3)_2$, with the appropriate doubly acidic compounds $[\text{RO}^\text{a}_3\text{H}(\text{THF})]_2$ 16 $[\text{H}_2\text{N}(\text{B}(\text{CF}_2)_2)]_2$ 16 $(x = 1–3); these are prepared by treatment of $[\text{RO}^\text{a}_3\text{H}]_2$ with Bochmann’s acid, $\text{H}(\text{OEt})_2$ 16 $[\text{H}_2\text{N}(\text{B}(\text{CF}_2)_2)]_2$ 16 (6) see the Supporting Information) in dichlorobenzene (Scheme 2). Solvents such as THF must be avoided because of the risk of coordination onto the metal, and hence the standard synthetic precursor $\text{C}(\text{NC(SiMe})_3)_2$ (THF), should not be used. Alternatively, 9 and 10 were also prepared by addition of Bochmann’s acid to 5 and 6, respectively, but this is less convenient, as it entails the preliminary synthesis of the charge-neutral heteroleptic parent complexes. The choice of the counterion $\text{H}_2\text{N}(\text{B}(\text{CF}_2)_2)$ 16 was prompted by synthetic considerations. This large ($538 \text{ Å}^3$), 16 weakly coordinating anion possesses a dipolar moment which provides good crystallization properties, and indeed salts of this anion are known to crystallize more easily than with the spherical, more conventional $\text{B}(\text{CF}_2)_2$ 16 borate derivative. 16

The compositions of 8–10 were authenticated by NMR spectroscopy, and their purity was confirmed by microanalytical measurements. They are poorly soluble in nonpolar solvents.

Table 2. PGSE NMR Measurements and X-ray Crystallographic Data for Complexes 2–7

<table>
<thead>
<tr>
<th>complex</th>
<th>$\Delta \psi^a (10^{-6} \text{ m}^2 \text{ s}^{-1})$</th>
<th>$\tau_{\text{NMR}}$ (Å)</th>
<th>X-ray</th>
<th>$\sigma$ (Å)</th>
<th>$\theta$ (Å)</th>
<th>$\tau_{\text{NMR}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RO$^\text{a}_3\text{Ca}$]$_2$</td>
<td>(12)</td>
<td>0.88</td>
<td>5.74</td>
<td>7.65</td>
<td>4.65</td>
<td>6.68</td>
</tr>
<tr>
<td>[RO$^\text{a}_3\text{Ca}$]$_2$</td>
<td>(13)</td>
<td>0.77</td>
<td>6.45</td>
<td>5.89</td>
<td>5.23</td>
<td>5.47</td>
</tr>
<tr>
<td>[RO$^\text{a}_3\text{Ca}$]$_2$</td>
<td>(14)</td>
<td>1.33</td>
<td>5.25</td>
<td>6.95</td>
<td>4.48</td>
<td>5.99</td>
</tr>
<tr>
<td>[RO$^\text{a}_3\text{Ca}$]$_2$</td>
<td>(15)</td>
<td>1.13</td>
<td>6.01</td>
<td>6.97</td>
<td>4.87</td>
<td>6.17</td>
</tr>
<tr>
<td>[RO$^\text{a}_3\text{Ca}$]$_2$</td>
<td>(16)</td>
<td>0.65</td>
<td>6.14</td>
<td>7.60</td>
<td>4.78</td>
<td>6.51</td>
</tr>
<tr>
<td>[RO$^\text{a}_3\text{Ca}$]$_2$</td>
<td>(17)</td>
<td>1.49</td>
<td>4.75</td>
<td>5.56</td>
<td>4.68</td>
<td>5.25</td>
</tr>
</tbody>
</table>

*All NMR spectra were recorded in C$_2$D$_2$ at 298 K using 13.0–30.0 mM solutions of complex and of the external reference Si(SiMe)$_3$ (TMSS).

**Average of the values of D, found for three or more separate peaks in the H NMR spectrum of the complex. Calculated according to $\tau_{\text{NMR}} = (\psi/4\pi)^{0.5}$ where $\sigma$ and $\theta$ respectively, the major and minor semiaxes of the ellipsoid formed by the complex, are determined from the solid-state structures.

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and we found that they could only be dissolved in THF. $^{19}$F and $^{11}B$ NMR in THF-$d_8$ tested the integrity of the anion, but the existence of Ca–F interactions could not be proved by NMR spectroscopy owing to the mandatory use of this coordinating solvent. Attempts to grow single crystals of 8–10 suitable for X-ray diffraction studies were thwarted by their extreme sensitivity (electrophilicity) and affinity for water. Attempts using various crystallisation techniques only afforded crystals of the water adducts [(RO$_2$)$_2$Ca(H$_2$O)$_2$]$\cdot$2H$_2$N-B-(C$_6$F$_5$)$_2$H]$\cdot$[(HO$_2$)$_2$]$_2$ and [(RO$_2$)$_2$Ca(H$_2$O)$_2$]$\cdot$2H$_2$N-B-(C$_6$F$_5$)$_2$H]$\cdot$[(HO$_2$)$_2$]$_2$, where the water molecules presumably came from the moisture background level. Unsatisfactory refinement (final R = 9.52%) precludes precise discussion of the metric parameters in [9-H$_2$O]$_2$ (Figure 8), but several features can nonetheless be mentioned with confidence: (i) each asymmetric unit contains four anions and two structurally non-identical dications of the general formula [(RO$_2$)$_2$Ca(H$_2$O)$_2$]$_2$ and Ca–F interactions (ca. 2.70–2.75 Å) are seen in only one of these, (ii) each of the four metal atoms is coordinated by a molecule of water, (iii) there is no contact between the cations and the anions, and (iv) unlike what is found in the charge-neutral parents, for each [RO$_2$]$_2^-$ ligand the coordination of both OCH$_2$ moieties onto the metal centers is seen. Evidently these observations point at the greater need for electron density in these cationic complexes, as highlighted by their ability to bind water from surrounding traces of moisture. Even with the more chelating and electron-donating ligand [RO$_2$]$_2^-$, the Ca cations trapped residual water during the recrystallization of 8 in dichloromethane to afford the adduct [8+H$_2$O]$_2$. The structure of the dimeric cationic fragment depicted in Figure 9 shows the presence of a coordinated water molecule and a strong intramolecular Ca–F–C interaction (C$\equiv$C–F(21) = 2.668(3) Å; Ca(2)–F(77) = 2.651(3) Å) between each of the metal atoms and CF$_3$ groups of the ligand; there is no contact with the counterion. All attempts to grow water-free crystals of these species proved unsuccessful; note that under the same experimental conditions, the cationic [RO$_2$]$_2$Ca$_2$H$_2$N[B(C$_6$F$_5$)$_2$]$_2^-$ where the ligand [RO$_2$]$_2^-$ contains one more O$_{aryl}$ atom than does [RO$_2$]$_2^-$ (see Chart 1), crystallized without binding water.\textsuperscript{59}

**Hydrophosphination Catalysis.** Well-defined heteroleptic calcium complexes have emerged as potent precatayysts in atom-efficient hydroamination reactions such as hydro-amination and hydrophosphination of amines.\textsuperscript{57} Yet, reports of calcium complexes in the hydrophosphination reactions of activated amines are confined to the use of precataysts bearing bulky [PH$_3$P$(Nac)$_2$]$_2^-$,\textsuperscript{22} tridentate amidoamines,\textsuperscript{32} and imino-anilide ligands.\textsuperscript{50} The fluorinated aralkyl calcium complexes 5–7 catalyze competitively the addition of diphenylphosphine across the C=O vinyl bond in styrene under mild conditions (Table 4). Complex 4 was not included in this screening, as we found it was not sufficiently stable under catalysis conditions. Characteristically for these calcium systems (and their heavier alkaline-earth congeners), this hydrophosphination reaction proceeds with strict 100% anti-Markovnikov regiose...
Figure 9. ORTEP representation of the dication in [(BO$_3$)$_2$.Ca(H$_2$O)$_2$]$_2$[H$_2$N(NC$_2$H$_4$)$_2$.H$_2$O](H$_2$O)$_2$, showing the coordinating H$_2$O molecules and Ca$^{2+}$ contacts. Counterions, hydrogen atoms, and noncoordinating solvent molecules are omitted for clarity. O(31) and O(81) are O atoms of coordinated water molecules.


catalytic activity at 60 °C. With as little as 1 mol % catalyst loading, the turnover numbers and frequencies observed with 5–7 for catalysed reactions performed in the presence of solvent (entries 3–5) or with neat substrates (entries 6–11), apparent TOF = 90 mol$_\text{amine}$ mol$_\text{cat}$⁻¹ h⁻¹ compare well with those reported with other calcium-based precatalysts$^{30,34,35}$ and place them among some of the most efficient systems reported to date for this challenging reaction.$^{36–37}$ Valuably, these complexes featured the same catalytic performances when higher substrate loadings were used (see e.g. entry 11). Under comparable conditions (entries 1–5), complexes 5–7 are generally more active than the simple bis(amido) complexes Ca(N(SiMe$_3$)$_2$)$_2$(THF)$_2$ and Ca(N(SiMe$_3$)$_2$)$_2$(entries 1 and 2), showing the beneficial role of the fluorinated alkoxides.

Precatalysts with the N(SiMe$_3$)$_2$H$_2$ moiety perform somewhat better than those having a N(SiMe$_3$)$_2$ group. This observation, which is counterintuitive on the basis of π$_\text{N}$ considerations alone, is explained by the reduced stability of compounds 4 and 6 in solution (signs of decomposition of the metal complexes can be observed in a matter of hours under catalysis conditions), while on the other hand, complexes 5 and 7 are visually more stable (the first signs of decomposition occurring only after 24 h). This is tentatively attributed to the presence of Si–H moieties in 5 and 7, which can impart stabilization to the metal through weak Ca$^{2+}$–H–Si interactions. With zinc, the higher catalytic activity of cationic complexes with respect to their neutral analogues has been observed for the cylo-hydroamination of aminoalkenes.$^{38}$ We found instead that 9 and 10 do not catalyze well the addition of HPPH$_2$ to styrene (entry 12), possibly because they are hampered by their limited solubility.

**Conclusion**

Potassium and heteroleptic calcium complexes supported by monoanionic fluorinated alkoxide ligands of varying dentity afford unusual coordination patterns in the solid state, forming polymeric species which remain aggregated in solution. The calcium complexes 4–7 represent new additions to the small family of kinetically inert heteroleptic Ca mono(alkoxide) complexes, the most prominent example being Hanusa’s Ca(dca)[X](THF)$_2$ (dca = OC$_2$H$_4$CH$_2$CH$_2$Cl; X = I, x = 4; X = N(SiMe$_3$)$_2$, x = 3).$^{35}$ Both potassium and calcium complexes are stabilized by a pattern of intramolecular M–F secondary interactions which contribute significantly to reach coordinative saturation around the metal atom. In addition, although definitive evidence for agostic Ca$^{2+}$–H–Si interactions could not be found, it is undeniable that the [Ca(N(SiMe$_3$)$_2$)$_2$]$_2$ complexes 5 and 7 are less labile than their [Ca(N(SiMe$_3$)$_2$)$_2$]$_2$ derivatives 4 and 6. The heteroleptic complexes 4–7 can serve as synthetic precursors to solvent-free discrete cationic Ca complexes which exhibit extreme

Table 4. Hydrophosphinylation of Styrene with Pb$_2$Ph$_2$ Catalyzed by the Calcium Amide Complexes 5–7 and Cationic Complex 10

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>[styrne]$_2$</th>
<th>[HPPH]$_2$</th>
<th>C$_2$H$_4$</th>
<th>TOF (mol$<em>\text{cat}$⁻¹ mol$</em>\text{amine}$⁻¹ h⁻¹)</th>
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<td>1$^a$</td>
<td>Ca(N(SiMe$_3$)$_2$)$_2$(THF)$_2$</td>
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<td>24</td>
<td>53</td>
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<td>24</td>
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<td>1.3</td>
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<td>3$^a$</td>
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<td>83</td>
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<td>(RO$_2$)$_2$Ca(N(SiMe$_3$)$_2$)$_2$(6)</td>
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<td>50</td>
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<td>44</td>
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<td>52</td>
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<td>8</td>
<td>2.0</td>
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*Conversion determined by $^1$H NMR spectroscopy. *Conditions: 10 μmol of precatalyst, [C$_2$H$_4$] = 16.67 mM, 0.6 mL of C$_2$D$_2$ at 60 °C. *Conditions: 10 μmol of precatalyst, no solvent, 60 °C.
Annexure C

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(RO)₂C≡CH[N(SiMe₃)₂] (5). A solution of (RO)₂C≡CH (0.34 g, 1.26 mmol) in Et₂O (15 mL) was added at -78 °C over a period of 1 h to a solution of Ca(N(SiMe₃)₂)₂ (0.45 g, 2.66 mmol) in Et₂O (20 mL). The reaction mixture was warmed to room temperature and stirred overnight, and the volatiles were removed under vacuum. The resulting powder was stripped with pentane (3 × 4 mL) and dried in vacuo to give 6 as a yellow powder (0.62 g, 71%). Single crystals of 6 suitable for X-ray diffraction crystallography were obtained by recrystallization from Et₂O at room temperature. H NMR (CD₂Cl₂, 400.13 MHz, 25 °C) δ 8.48 (m, 2H, J = 162 Hz, SHF), 3.2–3.14 (m, 2H, 2H, OCH₂OCH₂), 3.03–2.89 (overlapping m, 12H, CH₂OCH₂, CH₂OCH₂), and NCH₂CH₂), 2.47 (d, 2H, J = 12.4 Hz, NCH(N)), 0.47 (d, 13H, J = 5.5 Hz, Si(CH₃)₃), 1.21 (s, 18H, NCSi(CH₃)₂) ppm. ¹³C(CD₂Cl₂) NMR (100.62 MHz, CD₂Cl₂, 25 °C) δ 125.84 (q, J = 290.1 Hz, CF₂), 79.30 (broad, J = 25.5 Hz, CH(CF₃)), 69.35 (CH₂OCH₂), 59.46 (OCH₃), 55.45 (CH₂C(F₃)), 53.45 (NCH₂CH₂), 5.02 (CH₂OCH₂), 2.06 (Si(CH₃)₃), 1.30 (s, 18H, NCSi(CH₃)₂) ppm. ³¹P(CD₂Cl₂) NMR (192.6 MHz, CD₂Cl₂, 25 °C) δ -77.64 (s, 66P, CF₃) ppm. ¹⁹F(CD₂Cl₂) NMR (376.52 MHz, CD₂Cl₂, 25 °C) δ -113.57 (s, 66F, CF₃) ppm. ²⁹Si(CD₂Cl₂) NMR (79.49 MHz, 25 °C) δ -25.1 ppm. FTIR (Nujol in KBr plates): ν = 1644 cm⁻¹. Anal. Calc. for C₁₄H₁₃F₁₀NₐO₆: C, 46.1; H, 3.1; N, 5.8. Found: C, 46.4; H, 3.6; N, 4.7.

(RO)₂C≡CH[N(SiMe₃)₂] (6). A solution of (RO)₂C≡CH (0.34 g, 1.26 mmol) in Et₂O (15 mL) was added at -78 °C over a period of 1 h to a solution of Ca(N(SiMe₃)₂)₂ (0.45 g, 2.66 mmol) in Et₂O (20 mL). The reaction mixture was warmed to room temperature and stirred overnight, and the volatiles were removed under vacuum. The resulting powder was stripped with pentane (3 × 4 mL) and dried in vacuo to give 6 as a yellow powder (0.62 g, 71%). Single crystals of 6 suitable for X-ray diffraction crystallography were obtained by recrystallization from Et₂O at room temperature. H NMR (CD₂Cl₂, 400.13 MHz, 25 °C) δ 3.03 (overlapping m, 12H, CH₂OCH₂, CH₂OCH₂), 2.39 (Abg 2H, J = 0.8 Hz, CH₂C(F₃)), 2.12 (s, 3H, NCH₂), 2.02 (m, 2H, NCH₂CH₂), 0.33 (s, 18H, NCSi(CH₃)₂) ppm. ¹³C(CD₂Cl₂) NMR (100.62 MHz, CD₂Cl₂, 25 °C) δ 125.46 (q, J = 290.1 Hz, CF₂), 79.66 (broad, J = 25.5 Hz, CH(CF₃)), -77.3 Hz (s, 6F, J = 9.4 Hz, CH₂OCH₂), -67.1 Hz (s, 6F, J = 9.4 Hz, CH₂OCH₂), 58.34 (CH₂C(F₃)), 45.70 (NCH₂), 6.34 (Si(CH₃)₃), 1.30 (s, 18H, NCSi(CH₃)₂) ppm. ¹⁹F(CD₂Cl₂) NMR (376.52 MHz, CD₂Cl₂, 25 °C) δ -78.39 (s, 6F, J = 9.4 Hz, CH₂OCH₂), -64.9 Hz (s, 6F, J = 9.4 Hz, CH₂OCH₂), 70.87 (CH₂OCH₂), 60.26 (OCH₃), 56.99 (CH₂C(F₃)), 54.41 (NCH₂CH₂) ppm. The resonance for (CF₃)₃CH₂CH₂ was not observed. ²⁹Si(CD₂Cl₂) NMR (79.49 MHz, 25 °C) δ -83.1 ppm. Anal. Calc. for C₁₄H₁₃F₁₀NₐO₆: C, 46.1; H, 3.1; N, 5.8. Found: C, 46.4; H, 3.6; N, 4.7.

[RO2]2C≡CH[N(H)(NMe3)2] (9). Method A. [RO2]2C≡CH[N(H)(NMe3)2] (0.25 g, 0.711 mmol) was added to [5 mL] with a bent glass finger to a solution of Ca(NHMe3)₂ (0.07 mg, 0.011 mmol) in CDCl₃ (10 mL). The stirring was continued at room temperature for 2 days. The solution was evaporated under vacuum, and the resulting colorless solid was purified by repeated recrystallization from Et₂O with pentane (three times). Drying under vacuum at constant weight afforded 9 as a colorless powder (57 mg, 63%).

Method B. H[N((NHMe3)2](C≡CH)2] (0.07 mg, 0.008 mmol) was added in portions to a solution of 5 (0.40 g, 0.008 mmol) in Et₂O (10 mL). A colorless precipitate formed within a few minutes. Stirring was continued overnight at room temperature. The solution was filtered, and the colorless solid was purified by repeated recrystallization from Et₂O with pentane (three times). Drying under vacuum at constant weight afforded 5 as a colorless powder (57 mg, 63%).

H[N((NHMe3)2](C≡CH)2] (0.07 mg, 0.008 mmol) was added in portions to a solution of 5 (0.40 g, 0.008 mmol) in Et₂O (10 mL). A colorless precipitate formed within a few minutes. Stirring was continued overnight at room temperature. The solution was filtered, and the colorless solid was purified by repeated recrystallization from Et₂O with pentane (three times). Drying under vacuum at constant weight afforded 5 as a colorless powder (57 mg, 63%).

H[N((NHMe3)2](C≡CH)2] (0.07 mg, 0.008 mmol) was added in portions to a solution of 5 (0.40 g, 0.008 mmol) in Et₂O (10 mL). A colorless precipitate formed within a few minutes. Stirring was continued overnight at room temperature. The solution was filtered, and the colorless solid was purified by repeated recrystallization from Et₂O with pentane (three times). Drying under vacuum at constant weight afforded 5 as a colorless powder (57 mg, 63%).
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Supporting Information

Text, figures, tables, and CIF files giving details of the synthesis and characterization of $\text{[RO}_{3}\text{H}]^{+}$, $\text{[RO}_{4}\text{H}]^{+}$, and $\text{[RO}_{5}\text{H}]^{+}$; X-ray structures of $\text{[RO}_{3}\text{H}]^{+}$, $\text{[RO}_{4}\text{H}]^{+}$, and $\text{[RO}_{5}\text{H}]^{+}$; X-ray data for $\text{[RO}_{4}\text{H}]^{+}$; and bond valence analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

minimum and maximum distances defined by Plessix, even if we are aware that this may be somewhat restrictive.

(22) The limit for Ca-F interactions was set at 3.13 Å, as recommended by Plessix.


(25) Measurements for [BrO$_2$H$^+$][SiMe$_3$]$_2$ could not be performed in benzenes-d$_6$, owing to the poor solubility of the complex in this solvent. The diffusion coefficient ($D = 360 \times 10^{-10}$ m$^2$ s$^{-1}$) measured in dichloromethane-d$_2$ shows that the complex remains dimeric in this solvent ($r_{\text{C1-C1}} = 5.66$ Å, $r_{\text{Si-Si}} = 5.04$ Å).

(26) The following values were determined for TMSS (considered spherical): D$_{\text{Dichloromethane-d$_2$}}$ = $(1.0750-1.0830) \times 10^{-10}$ m$^2$ s$^{-1}$ (depending on the concentration of TMSS that was used) and $r_{\text{Si-Si}}$ = 5.04 Å, using $r_{\text{Dichloromethane-d$_2$}}$ = 4.8223 Å, using $r_{\text{Dichloromethane-d$_2$}}$ = 1.00 and $r_{\text{Dichloromethane-d$_2$}}$ = 4.28 Å. The value of $r_{\text{Si-Si}}$ was calculated according to $r_{\text{Si-Si}} = (R/2)^2(1 + 0.695(r_{\text{Dichloromethane-d$_2$}}/r_{\text{Dichloromethane-d$_2$}})^2)$ using $r_{\text{Dichloromethane-d$_2$}} = 2.68$ Å as found in Zuccacce, D.; Macchioni, A. Organometallics 2005, 24, 3476.

(27) Partial or total decomposition to [BrO$_2$H$^+$]Ga and Ca(\text{N(SiMe$_3$)$_2$})$_2$ would have resulted in the detection of three and two clearly distinct diffusion coefficients, respectively.


(34) These crystals were grown by recrystallization from saturated dichloromethane (mixture level < 5 ppm) solutions prepared and stored in a glovebox with a moisture level lower than 4 ppm. Crystallization outside the glovebox and/or using silica gel glassware or Teflon vials gave the same outcome.


Annexure D: Bond valence sum analysis

Table I. Bond valence analysis calculations for $[\{RO\}_3K]_4 ([I]_2)$

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<th>M</th>
<th>$d$(K-O)$^a$</th>
<th>$d$(K-F)$^a$</th>
<th>$d$(K-N)$^a$</th>
<th>$\nu$(K-O)$^b$</th>
<th>$\nu$(K-F)$^b$</th>
<th>$\nu$ (K-N)$^b$</th>
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Contribution

|          | 77% | 12% | 11% |

Table II. Bond valence analysis calculations for $[\{RO\}_1K]_4 ([4]_2)$

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Contribution

|          | 67% | 16% | 17% |
Table III. Bond valence analysis calculations for \([\{RO^2\}CaN(SiMe_2H)_2\]_2 ([10]_2)

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Contribution 56% 3% 41%

Table IV. Bond valence analysis calculations for \([\{RO^1\}CaN(SiMe_2H)_2\]_2 ([12]_2)

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Contribution 52% 2% 46%

Table V. Bond valence analysis calculations for \([\{RO^1\}CaN(SiMe_3)_2\]_2 ([13]_2)

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Contribution 50% 4% 46%
Table VI. Bond valence analysis calculations for \([\{RO^{13}\}CaN(SiMe_3)_2\}]_2 ([29]_2)

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Table VII. Bond valence analysis calculations for \([\{RO^{14}\}CaN(SiMe_3)_2\}]_2 ([30]_2)

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Annexure E: $^{19}$F NMR spectra.

Figure I. $^{19}$F NMR spectrum (376.53 MHz) of the product of the reaction of Ca[N(SiMe$_3$)$_2$]$_2$ with {RO$_3$}H (1 equiv) at 298 K in benzene-$d_6$.

Figure II. $^{19}$F NMR spectrum (376.53 MHz) of [{RO$_{11}$}CaN(SiMe$_2$H)$_2$]$_2$ [26]$_2$ at 263 K toluene-$d_8$. 
Figure III. $^{19}$F NMR spectrum (376.53 MHz) of $[\{\text{RO}^{11}\} \text{CaN(SiMe}_2\text{H)}_2]_2 [26]_2$ at 263 K THF-$d_8$.

Figure IV. $^{19}$F NMR spectrum (376.53 MHz) of $[\{\text{RO}^{13}\} \text{CaN(SiMe}_2\text{H)}_2]_2 [29]_2$ at 263 K toluene-$d_8$. 
Figure V. $^{19}$F NMR spectrum (376.53 MHz) of $[(RO)^{14}\text{CaN(SiMe}_3\text{H)}_2]_2$ [30]$_2$ at 303 K toluene-$d_8$
Annexure F: Variable Temperature NMR spectra.

**Figure VI.** Stacked $^{19}$F NMR spectra (376.50 MHz) of $[^{[\text{RO}^{\text{11}}]}\text{CaN(SiMe}_2\text{H)}_2]_2$ ([25]$_2$) recorded in toluene-$d_8$ at 193–343 K.

**Figure VII.** Stacked $^1$H NMR spectra (400.13 MHz) of $[^{[\text{RO}^{\text{11}}]}\text{CaN(SiMe}_2\text{H)}_2]_2$ ([25]$_2$) recorded in THF-$d_8$ at 193–333 K.
Figure VIII. Stacked $^{19}$F NMR spectra (376.50 MHz) of $\left[\{RO^{11}\}CaN(SiMe_2H)_2\right]_2$ ($\{25\}_2$) recorded in THF-$d_8$ at 193–333 K.

Figure IX. Stacked $^1$H NMR spectra (400.13 MHz) of $\left[\{RO^{11}\}CaN(SiMe_2H)_2\right]_2$ ($\{29\}_2$) recorded in toluene-$d_8$ at 193–343 K.
Figure X. Stacked $^{19}$F NMR spectra (376.53 MHz) of $[\{\text{RO}^{13}\}\text{CaN(SiMe}_2\text{H)}_2\}_2$ $([29]_2)$ recorded in toluene-$d_8$ at 193–333 K.

Figure XI. Stacked $^1$H NMR spectra (400.13 MHz) of $[\{\text{RO}^{13}\}\text{CaN(SiMe}_2\text{H)}_2\}_2$ $([30]_2)$ recorded in toluene-$d_8$ at 193–343 K.
**Figure XII.** Stacked $^{19}$F NMR spectra (376.53 MHz) of $[({RO}^{14})\text{CaN(SiMe}_2\text{H})_2]_2$ ($[30]_2$) recorded in toluene-$d_8$ at 193–343 K.

**Figure XIII.** Stacked $^1$H NMR spectra (400.13 MHz) of $[({RO}^{32})\text{CaN(SiMe}_2\text{H})_2]_2$ ($[34]_2$) recorded in toluene-$d_8$ at 193–343 K.
Figure XIV. Stacked $^{19}$F NMR spectra (376.53 MHz) of $\left\{\text{RO}^{32}\text{CaN(SiMe}_{3}\text{H})_{2}\right\}_{2}$ ([$34]_2$) recorded in toluene-$d_8$ at 193–333 K.
Annexure G: Diffusion NMR experiments.

Table VIII. PGSE NMR measurements and X-ray crystallographic data for complexes $[23]_2$, $[25]_2$, $[26]_2$ and $32$.

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<th>$D_t$ \textbf{(10$^{-9}$ m$^2$ s$^{-1}$)}</th>
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<th>$X$-ray</th>
<th>$r_{H,X-ray}$ [Å]</th>
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<tr>
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<td>5.22</td>
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<td>$[{RO^{11}}]\text{CaN(SiMe}_2\text{H)}_2 \text{]_2 ([25]_2}$</td>
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<td>$[{RO^{11}}]\text{SrN(SiMe}_2\text{H)}_2 \text{]_2 ([26]_2}$</td>
<td>0.68</td>
<td>5.89</td>
<td>5.45</td>
<td>4.77</td>
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<td>$[{RO^{22}}]\text{CaN(SiMe}_2\text{H)}_2 \text{]_2$ ($\mu$-\text{Ca}[N(SiMe}_2\text{H)}_2 \text{]) (32}$</td>
<td>0.56</td>
<td>6.13</td>
<td>9.74</td>
<td>4.31</td>
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</table>

[a] All NMR spectra were recorded in benzene-$d_6$ at 298 K using 13.0–30.0 mM solutions of complex and of the external reference Si(SiMe$_3$)$_4$. [b] Average of the values of $D_t$ found for 3 or more separate peaks in the $^1$H PGSE NMR spectrum of the complex.

**Figure XV.** Diffusion time–molecular weight ($D_t$–M.w.) analysis for $[\{RO^{11}\}]\text{SrN(SiMe}_2\text{H)}_2 \text{]_2 ([26]_2)$.}
Figure XVI. Diffusion time–molecular weight ($D_t$–M.w.) analysis for $\left\{\text{RO}^{21}\right\}\text{CaN(SiMe}_2\text{H}_2\right\}_2\left(\mu\text{-Ca[N(SiMe}_2\text{H}_2\right\}_2)\left(32\right)$. 

![Graph showing relationship between log $D_t$ and log Mw for different molecules.](image_url)
Annexure H: $^1$H–$^{15}$N HMQC spectra

**Figure XVII.** $^1$H–$^{15}$N HMQC spectrum (400.13, 40.55 MHz) of [{RO}$^{11}$]CaN(SiMe$_2$H)$_2$$_2$ ([25]$_2$) recorded at 263 K in toluene-$d_8$.

**Figure XVIII.** $^1$H–$^{15}$N HMQC spectrum (400.13, 40.55 MHz) of {RO$^{11}$}H recorded at 263 K in toluene-$d_8$. 
Annexure I: Miscellaneous molecular structures

**Figure XIX.** ORTEP representation of the molecular structure of \([\{RO^{12}\}K]_4\). Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): K(1)–O(1) = 2.635(2), K(1)–O(1)* = 2.765(2), K(1)–N(5) = 3.031(3), K(1)–F(1) = 3.062(2), K(1)–F(2) = 2.928(2), K(1)–C(18) = 3.192(4), K(1)–C(19) = 3.148(4), C(12)–C(13) = 1.327(4), C(8)–C(9) = 1.292(8).

**Figure XX.** (left) ORTEP representation of the molecular structure of \([\{RO^{12}\}K]_4\). Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. (right) Zoom view of one K₄O₄ core. Selected bond lengths (Å): K(1)–O(13) = 2.659(1), K(1)–O(43) = 2.749(1), K(1)–O(103) = 2.798(1), K(1)–N(9) = 3.174(2), K(1)–F(45) = 2.851(1), K(1)–F(17) = 2.880(1), K(1)–F(107) = 2.955(1), K(1)–F(111) = 3.213(1), K(1)–C(1) = 3.418(3), K(1)–C(12) = 3.447(2), K(1)–C(2) = 3.463(3).
Figure XXI. ORTEP representation of the molecular structure of \([\{RO^{12}\}K]_4\). Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): K(1)–O(41) = 2.630(1), K(1)–O(1) = 2.688(1), K(1)–O(61) = 2.726(1), K(1)–F(68) = 2.758(1), K(1)–F(65) = 2.804(1), K(1)–F(45) = 3.215(1), K(1)–F(111) = 3.213(1), K(1)–C(1) = 3.418(3), K(1)–C(12) = 3.447(2), K(1)–C(2) = 3.463(1), C(18)–C(19) = 1.178(3).

Figure XXII. (left) ORTEP representation of the molecular structure of \([Ca_2\{RO^0\}(\mu-\{RO^0\})_2(\text{OH})]_2\). Hydrogen atoms (except OH) are omitted for clarity. Ellipsoids are drawn at the 50% probability level. (right) Schematic representation of \([Ca_2\{RO^0\}(\mu-\{RO^0\})_2(\text{OH})]_2\). Selected bond lengths (Å) and angles (°): Ca(1)–O(1) = 2.135(1), Ca(1)–O(21) = 2.281(1), Ca(1)–O(0) = 2.353(1), Ca(1)–N(12) = 2.650(1), Ca(1)–F(4) = 2.757(1); Ca(1)–O(1)–Ca(2) = 103.24(4), Ca(1)–O(0)–Ca(2) = 104.02(5), Ca(1)–O(0)–Ca(2) = 104.66(4).
Chimie organométallique des complexes alcalino-terreux à base de ligands fluorés
Chimie organométallique des complexes alcalino-terreux à base de ligands fluorés

1. Introduction


Les difficultés dans la manipulation des complexes de calcium et de ses analogues plus lourds, strontium et baryum, sont principalement liées à leur grande oxophilie, électrophilie, polarisabilité et leur faible electronegativité. Leurs rayons ioniques (\(r_{\text{Ca}^{2+}} = 1.00 \, \text{Å}, \ r_{\text{Sr}^{2+}} = 1.18 \, \text{Å}, \ et \ r_{\text{Ba}^{2+}} = 1.35 \, \text{Å}\)) requièrent un nombre de coordination élevé. En fait, leurs tailles sont plus proches de celles des lanthanides (terres rares) divalents (\(r_{\text{Yb}^{2+}} = 1.02 \, \text{Å}, \ r_{\text{Eu}^{2+}} = 1.17 \, \text{Å}, \ et \ r_{\text{Sm}^{2+}} = 1.22 \, \text{Å}\)) et trivalents (\(r_{\text{Nd}^{3+}} = 0.98 \, \text{Å} \ and \ r_{\text{Sm}^{3+}} = 0.96 \, \text{Å}\)) que de celle du magnésium ou béryllium (\(r_{\text{Be}^{2+}} = 0.45 \, \text{Å}, \ r_{\text{Mg}^{2+}} = 0.72 \, \text{Å}\)).

Les sels de calcium sont biocompatibles et abondants dans la croûte terrestre (3.4 pt%). En outre, la chimie de coordination du calcium n’en est encore qu’à ses balbutiements et laisse l’opportunité d’utiliser de nouveaux précatéyseurs en catalyse homogène. Les complexes hétéroleptiques de type \([\{\text{LX}\}\text{Ca–Nu}]\) ont été largement appliqués en polymérisation par ouverture d’esters cycliques. Ce sont aussi d’ excellents précatéyseurs en hydroélementation, (cyclo)hydroamination, hydrophosphination et hydrosilylation d’alcènes. Néanmoins, ces complexes ont tendance à se redistribuer cinétiquement en solution (Schéma 1). Cette tendance peut être surmontée en utilisant des ligands ancillaires encombrés ou électrodonneurs. Cependant, il est encore nécessaire de proposer nouvelles plateformes de ligands qui pourraient permettre l’ isolation de précatéyseurs de Ca encore plus efficaces.


La stabilisation des complexes de calcium peut aussi être obtenue en utilisant des interactions secondaires, telles que Ca···F–C, Ca···Cₓ ou Ca···H–R (R = Si, C). Ces interactions sont
particulièrement bien détectées en diffraction de rayons-X. Dans ce cas, les structures moléculaires ont un centre métallique avec un nombre de coordination étonnamment bas et possèdent des géométries profondément déformées. L’objectif principal de cette thèse est d’étudier et d’augmenter ces interactions secondaires afin de rendre cinétiquement inertes les complexes de type \([LX]_{\text{Ca-Nu}}\). En outre, les performances des complexes résultats en hydroamination et hydrophosphination d’alcènes seront présentées.

2. Premières avancées en catalyse homogène. Cas d’un ligand scorpionate floruré

Cette section présente les premiers travaux conduits durant les premiers mois de mon doctorat en collaboration avec le groupe du Prof. Michel Etienne de l’Université Toulouse III Paul Sabatier., en tant que partie d’un projet commun (GreenLAkE, ANR-11-BS07-0009). L’objectif principal était de concevoir des nouveaux complexes alcalino-terreux stabilisés par des ligands enrichis en fluor utilisés comme précatalyseurs en réactions d’hydroélementation.

À cause de leur nature électro-attractrice, l’utilisation de ligands fluorés avec des éléments oxophiles tendrait à rendre le centre métallique plus électrophile et par conséquent tendrait à générer des catalyseurs plus actifs. À cet égard, l’activité de \([T_{\text{ind}}^{F}]_{\text{CaN(SiMe}_3)_{2}}\) (A) en hydroamination intramoléculaire de la 2,2-dimethylpent-4-en-1-amine (S) (Schéma 2) a été testée. La synthèse et la caractérisation de A a été reportée dans les travaux de thèse du Dr. Nuria Romero.  

![Schéma 2. Hydroamination intramoléculaire de la 2,2-dimethylpent-4-en-1-amine (S) avec \([T_{\text{ind}}^{F}]_{\text{CaN(SiMe}_3)_{2}}\) (A)](image)

A a montré une grande activité pour cette réaction de fermeture de cycle et le produit cyclisé (2,4,4-trimethylpyrrolidine) a été obtenu avec 100% de régiosélectivité. Comme présenté dans le Tableau 1, la conversion complète de 20 équivalents d’aminoalcène peut être obtenue en à peine 16 minutes à température ambiante (Tableau 1, entrée 2). De manière encore plus remarquable, ce
précatalyseur a été capable de maintenir une très grande charge de substrat (600 équivalents, cf entrée 4). Les TON enregistrés sont peu communs pour cette réaction, classant ce précatalyseur parmi les plus efficaces reportés à ce jour.

Tableau 1. Données représentatives pour l’hydroamination intramoléculaire de S catalysée par A.

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<th>([S]_0/ [Ca]_0)</th>
<th>Temps (min)</th>
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<td>&gt;99</td>
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<td>25</td>
<td>&gt;99</td>
<td>200</td>
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</tbody>
</table>

[a] Conditions de réaction: 3.0 µmol de précatalyseur, 1.2 mL de benzène-\(d_6\). La conversion est déterminée par spectrométrie RMN \(^1\)H. [b] Conditions de réaction: 3.0 µmol of catalyst, 1.8 mL of benzène-\(d_6\). [c] Conditions de réaction: 3.0 µmol de précatalyseur, 1.7 mL de benzène-\(d_6\).

Les mesures cinétiques indiquent une dépendance au premier ordre des concentrations en substrat et en précatalyseur. Ces observations sont en accord avec une étude DFT publiée récemment sur des systèmes catalytiques similaires \(i.e.\) \([N^N]AeN(SiMe_3)_2](THF) (Ae = Ca, Sr, Ba) \(^9\)), laissant ainsi probablement suggérer un mécanisme réactionnel passant par une étape d’insertion \(\sigma\).

**3. Complexes aminoetheralcoolates fluorés des métaux alcalino-terreux**

Les alcoolates sont en général prohibés comme ligand auxiliaire pour les alcalino-terreux (Ca, Sr, Ba). En effet, les atomes O\(_{\text{alcoolate}}\) ont une basicité plus importante que les atomes O\(_{\text{phenolate}}\) présents dans les ligands de type phénolates, ce qui provoque une oligomérisation des complexes par les atomes d’oxygène pontants. Une des stratégies pour réduire ce degré d’agréagation est l’introduction de groupements CF\(_3\) en position \(\alpha\) de l’atome O\(_{\text{alcoolate}}\). La présence de ces substituants fortement électroattracteur décroît l’effet \(\pi\) donneur de l’atome d’oxygène et ainsi la capacité pontante du ligand. Les protéo-ligands d’intérêt, notés \{RO\(^x\)\}H \((x = 1–4^\ast)\) ci-après, ont facilement été obtenus en faisant réagir le 2,2-bis(trifluoromethyl)oxirane, disponible commercialement, avec l’amine correspondante (Schéma 3), par adaptation d’un protocole reporté pour des produits similaires.

3.1. Complexes neutres

Traditionnellement, les complexes hétéroélectriques d’alcalino-terreux peuvent être synthétisés par deux méthodes: (a) Réaction de métathèse entre un équivalent d’alcoolate de potassium, isolé ou généré in situ, et CaI₂ et (b) réaction de protonolyse entre le protéo-ligand et les complexes Ae[N(SiMe₃)₂]₂(THF)₂ ou Ae[N(SiMe₂R)₂]₂(THF)ₙ (Ae = Ca, n = 1; Ae = Sr, n = 2/3; Ae = Ba, n = 0) tel que décrit dans le Schéma 4. 

La réaction du sel de potassium [{RO₄}K] (obtenu par la réaction de {RO₄}H avec KN(SiMe₃)₂) avec une quantité stochiométrique de KN(SiMe₃)₂ et CaI₂ dans le THF n’a pas permis d’obtenir le complexe attendu [{RO₄}CaN(SiMe₃)₂]₂, formant plutôt un mélange d’espèces. Pour cette raison, la deuxième voie synthétique passant par des réactions de protonolyse a été testée. Dans ce cas, nos expériences ont été menées avec {RO₃}H. La formation du complexe désiré [{RO₃}CaN(SiMe₃)₂] n’a pas été observée par spectroscopie RMN ¹H. La cristallographie par rayons-X a révélé un produit différent, résultant de la rupture de la liaison C–O dans la couronne éthérée. Des résultats plus concluants ont été obtenus en utilisant des protéo-ligands à plus faible denticité ({RO₁}H et {RO₂}H). L’addition d’une solution de l’amine-thio-alcool fluoré correspondant dans Et₂O sur une solution refroidie de Ca[N(SiMe₂R)₂]₂(THF)ₙ (R = H, Me; n = 1, 2) dans Et₂O a permis de former...
[[RO\textsuperscript{3}]\text{CaN(SiMe}_{2}R\text{)}_{2}] (x = 2, R = H ([10]\text{)}_{2}, \text{Me} ([11]\text{)}_{2}; x = 1, R = H ([13]\text{)}_{2}, \text{Me} ([14]\text{)}_{2}) sous la forme de solides avec 70-80\% de rendements (Schéma 5).

La structure moléculaire des complexes [10]\text{)}_{2}–[13]\text{)}_{2} a été déterminée. Les données radiocristallographiques indiquent que pour les complexes [10]\text{)}_{2} et [12]\text{)}_{2} dans lesquels le ligand \{RO\textsuperscript{3}\}– a été utilisé, seulement un des deux donneurs de méthoxy est coordiné au centre métallique. En effet, la sphère de coordination des atomes de calcium est complétée par de multiples interactions Ca...F–C et Ca...H–Si. Les structures moléculaires des complexes [11]\text{)}_{2} et [13]\text{)}_{2} démontrent quant à elles que les atomes de calcium sont déjà coordinativement saturés en présence d’un seul groupement OMe provenant du bras latéral du ligand. Par ailleurs, elles révèlent que la perte de densité électronique fournie par les groupements SiH peut être compensée par un contact Ca...F–C supplémentaire. La contribution des interactions Ae...F–C a été estimée en utilisant l’analyse de la somme des liaisons de valence avec des valeurs allant de 2\% ([12]\text{)}_{2}) à 5\% ([13]\text{)}_{2}). Grâce à la réalisation d’expériences de spectroscopie RMN DOSY, nous avons pu conclure que les complexes [10]\text{)}_{2}–[13]\text{)}_{2} restent dimériques en solution dans des solvants aromatiques.

### 3.2. Complexes cationiques

Accroître le caractère électrophile d’un centre métallique est une stratégie couramment utilisée pour augmenter l’activité catalytique de complexes employant des éléments de début de transition\textsuperscript{13} et des terres rares,\textsuperscript{14} notamment pour les réactions de polymérisation d’oléfines. Cette approche a également été validée dans le cas des complexes de zinc dans lesquels la cationisation de [[(\text{Pr})\text{2}ATI]ZnMe] (ATI = aminotroponiminate \text{N,N}’-disubstitué) avec [\text{PhNMe}_{2}H]\textsuperscript{+}[\text{B(C}_{6}\text{F}_{5})\text{4}] s’est
avérée bénéfique pour l’hydroamination intramoléculaire des aminoalcènes.\textsuperscript{15} Notre groupe a précédemment décrit la synthèse d’un complexe cationique bien défini de calcium portant un alcoolate fluoré multidente, \textit{i.e.} $[\{RO_4\}Ca]_2^+ \cdot 2[H_2N\{B(C_6F_5)_3\}]_2^-$. Ce complexe était très actif dans la polymérisation par ouverture de cycle des lactides.\textsuperscript{16} Nous avons supposé que des complexes métalliques plus électro-déficients pouvaient être obtenus en ôtant quelques hétéroatomes du ligand auxiliaire, à travers l’utilisation d’éventuels fluoroalcoolates pentadentes ($[\{RO_3\}]^-$), tétradentes ($[\{RO^2\}]^-$) ou même tridentes ($[\{RO_1\}]^-$).

La synthèse de cations alcalino-terreux a pu être réalisée en suivant deux méthodes : (a) \textit{via} des protéo-ligands bis-protonés : cette voie de synthèse implique tout d’abord la synthèse de ligands doublement protonés $[[\{RO^x\}]H][H_2N\{B(C_6F_5)_3\}]_2^-$ puis une réaction consécutive avec $\text{Ae}[N(SiMe_3)_2]_2$ (Ae = Ca, Sr, Ba) (Schéma 6–Méthode A), et (b) \textit{via} protonolyse de $[[\{RO^y\}]\text{CaN}(SiMe_2R)_2]_2$ ([10]$_2$–[13]$_2$), les complexes hétéroleptiques neutres, avec $[\text{H(OEt}_2]_2\text{][H}_2N\{B(C_6F_5)_3\}]_2^-$ (Schéma 6–Méthode B).

Schéma 6. Chemins réactionnels pour la synthèse de cations Ae bien définis.

Comme preuve de leur extrême électrophilie, les espèces $[[\{RO^y\}]\text{Ae}]_x^2+ \cdot 2[H_2N\{B(C_6F_5)_3\}]_2^-$ ($x = 3$, Ae = Ca ([18]$_2$); $x = 2$, Ae = Ca ([19]$_2$), Sr ([20]$_2$); $x = 1$, Ae = Ba ([22]$_2$)) ont été cristallisées sous forme d’adduits de H$_2$O bien que des Schlenck aient été utilisés ainsi qu’une manipulation en boîte à gants. Malgré la présence de solvants donneurs, une contribution des interactions Ae⋯F–C ligand a été observée dans tous les cas et les structures moléculaires de [20]$_2$ et [22]$_2$ présentent également des contacts rares entre l’anion faiblement coordiné et le centre cationique Ae. Concernant les interactions Ae⋯F$_\text{anion}$, il a été observé que la tendance du métal Ae à se lier à l’anion varie avec la taille du métal et se classe selon l’ordre : Ba > Sr > Ca.

3.3 Catalyse d’hydrophosphination

Tous nos efforts de synthèse de ces complexes de calcium ont été récompensés lorsqu’ils ont été utilisés comme pré-catalyseurs dans la réaction d’hydrophosphination modèle entre le styrène et Ph$_2$PH (Schéma 7).
Résumé


<table>
<thead>
<tr>
<th>Entrée</th>
<th>Précatalyseur</th>
<th>[styrène]₀:[Ph₂PH]:[Ca]₀</th>
<th>t [h]</th>
<th>Conv. a (%)</th>
<th>TOF (h⁻¹)</th>
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<td>[(RO)₂CaN(SiMe₃H)₂]₂ ([10]₂)</td>
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<td>24</td>
<td>46</td>
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<td>[(RO)₁CaN(SiMe₃)₂]₂ ([13]₂)</td>
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<td>24</td>
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</tr>
<tr>
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<td>50:50:1</td>
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<td>6 c</td>
<td>[(RO)₁CaN(SiMe₃H)₂]₂ ([12]₂)</td>
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<td>[(RO)₁Ca]⁺2[A⁻] ([21]₂)</td>
<td>50:50:1</td>
<td>2</td>
<td>8</td>
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</table>

[a] Conversion déterminée par spectroscopie RMN ³¹H. [b] Conditions opératoires : 10 µmol de pré-catalyseur, 0.6 mL de benzène-d₆, T = 60 °C. [c] Réaction sans solvant, T = 60 °C. [d] A = H₂N[B(C₆F₅)₃]₂.
4. Complexes hétéroleptiques alcalino-terreux supportés par des donneurs π

Dans la section précédente, nous avons décrit que les interactions secondaires du type Ae···F–C et Ae···H–Si (Ae = Ca, Sr) jouent un rôle primordial dans la stabilisation des complexes hétéroleptiques \([\text{RO}^x]_{\text{Ae}}N(\text{SiMe}_2R)_2 \) (x = 1, 2; R = H, Me) qui, sans elles, sont sujets à des réactions d’équilibre de Schlenk. De plus, il a été montré que de multiples interactions Ca···F–C peuvent prédominer sur la coordination d’hétéroatomes (i.e. atomes O_{éther}) présents sur le bras latéral du ligand. Conforté par nos résultats précédents, nous avons envisagé que les complexes Ae hétéroleptiques supportés par des alcoolates fluorés pourraient être stables en l’absence de tout autre atome O_{éther} et en introduisant, à la place, des faibles donneurs π, i.e. des groupements alcène, alcyne, allène ou aryle.

4.1. Complexes alcalino-terreux d’oléfines

Pour cette étude, les protéo-ligands \{\text{RO}^{11}\}H et \{\text{RO}^{12}\}H, contenant une fonction vinyle, ont été synthétisés en suivant un mode opératoire similaire à celui décrit pour \{\text{RO}^x\}H (x = 1–4). Ainsi, \{\text{RO}^{11}\}H et \{\text{RO}^{12}\}H ont pu être mis en réaction avec Ae\{N(\text{SiMe}_2H)_2\}_2(\text{THF})_n (Ae = Ca, n = 1; Ae = Sr, n = 2/3) pour obtenir les complexes \([\text{RO}^x]_{\text{Ae}}N(\text{SiMe}_2H)_2 \) (x = 12, Ae = Ca ([23]_2; x = 11, Ae = Ca ([25]_2), Sr ([26]_2)) attendus, comme indiqué sur le Schéma 8. Le complexe pur \([\{\text{RO}^{12}\}SrN(\text{SiMe}_2H)_2\] ([24]_2) n’a pas pu être isolé, tous les essais de recristallisation s’étant révélés infructueux.

![Schéma 8. Synthèse des complexes Ae [23]_2–[26]_2.](image-url)
Les structures moléculaires à l’état solide des complexes [23]₂, [25]₂ et [26]₂ montrent, dans tous les cas, qu’un des substituants alcène est coordonné de façon η² au centre métallique Ae. Des contacts ont été observés entre le métal et l’atome de carbone interne (C_int) † du groupement alcène. En accord avec de précédents exemples de la bibliographie, les interactions entre alcènes et les alcalino-terreux sont faibles. En effet, malgré la coordination, la double liaison C=C n’est pas du tout impactée, avec des distances entre C_int et C_ext dans la moyenne de ce qui est attendu pour des atomes hybridés C_sp². En outre, la spectroscopie RMN ¹H confirme le caractère sp² de la double liaison C=C en solution, la constante de couplage ¹J_C−H pour la résonance du groupement alcène étant identique à celle trouvée dans le ligand libre. De plus, les spectres RMN ¹³C{¹H} pour [23]₂, [25]₂, et [26]₂ montrent des résonnances très similaires pour les atomes de carbones C_int et C_ext, comparées à celles obtenues pour {RO¹¹}H et {RO¹²}H. Toutes ces données indiquent que la coordination du groupement alcène sur l’atome Ae est probablement faible et principalement basée sur des forces électrostatiques. Concernant [25]₂, la spectroscopie RMN (¹H, ¹³C, ¹⁹F) montre l’existence de deux isomères du complexe de calcium, présentant un échange lent dans le toluène-d₈ à 263 K. Cet échange a ensuite été confirmé par spectroscopie RMN 2D ¹H−¹H NOESY avec l’observation d’une corrélation entre les deux jeux de résonances vinyliques.

Dans l’objectif de vérifier si le motif alcène est coordonné au centre métallique en solution, différentes expériences RMN -2D ¹H−¹⁵N HMQC NMR- ont été menées sur le complexe [25]₂. Malheureusement, aucune corrélation entre les atomes N_amide and SiH n’a été observée.

De par les propriétés atomiques comparables des cations Ca²⁺ et Yb²⁺ (rayons ioniques: r_Yb²⁺ = 1.02 Å, r_Ca²⁺ = 1.00 Å), une corrélation inter-pic entre Yb et les signaux vinyliques du spectre HMBC ¹H−¹⁷¹Yb pour le complexe [[RO¹¹]YbN(SiMe₃R)₂]₂ (R = H ([27]₂), Me ([28]₂)) permettrait d’obtenir des information pour les complexes de calcium. Néanmoins, les données RMN du proton des complexes [27]₂ et [28]₂ ont montré que ces complexes de Yb(II) sont contaminés par des impuretés paramagnétiques rendant la lecture des spectres difficiles. Les structures moléculaires de [27]₂ et [28]₂ suggèrent qu’une interaction M···alcène dépend des effets stériques. La différence de l’encombrement stérique entre N(SiMe₃)₂⁻ et N(SiMe₂H)₂⁻ pourrait être un facteur important du fait que les données cristallographiques pour [27]₂ montrent clairement la coordination de la partie alcène à l’ytterbium, à l’instar du complexe [28]₂ où la coordination n’est pas observée.

† Les abréviations pour les protons et carbones vinyliques sont utilisées suivant ce qui suit.
Schéma 9. Synthèse des complexes \([\{RO^{11}\}YbN(SiMe_2R)_2\_2\] (R = H (27)\_2), Me ([28]\_2)).

L’effet des effets stériques sur la coordination de l’alcène au centre métallique a été ensuite étudié. Pour cela, nos efforts se sont orientés vers l’exploration des propriétés de coordination de motifs alcènes méthyl-substitués en position terminale (Schéma 10).


Comme observé dans la structure du complexe [29]\_2, la présence d’un groupement méthyle sur le motif alcène a affecté le modèle de coordination, conduisant à une coordination du type \(\eta^1\). La double
substitution des deux protons \( H_{ext} \) par des groupements méthyles a un effet plus prononcé, empêchant la coordination du motif alcène à l’atome de calcium.

4.2. Étude d’autres systèmes \( \pi \)

La coordination d’autres systèmes \( \pi \) (\textit{e.g.} arènes, alcynes or allènes) au calcium a aussi été envisagée. Pour cette étude, les protéo-ligands suivants ont été synthétisés par réaction du 2,2-bis(trifluoromethyl)oxirane avec l’amine appropriée (Figure 1).

![Protéo-ligands](image1)

\textbf{Figure 1.} Protéo-ligands envisagés pour l’étude de la coordination de groupement arène, alcyne ou allène au calcium.

Malgré nos efforts pour coordonner des groupements aryle de la même façon que les alcènes, nous n’avons pas obtenu le résultat escompté. Au lieu de cela, nous avons observé la formation du complexe \([31]_2\) contenant deux molécules de THF dans la sphère de coordination ou les complexes trinucléaires de calcium \(32\) décrits dans le Schéma 11.

![Synthèse de \([31]_2\) et 32](image2)

\textbf{Schéma 11.} Synthèse de \([31]_2\) et 32.
Le complexe trinucléaire 32 présente une géométrie fortement distordue autour de l’atome de calcium, ce qui indique que les interactions agostiques $\beta$-Si–H···Ca sont la clé de la stabilité de ces espèces. Les constantes de couplage $^{1}J_{\text{Si-H}}$ (132, 145 and 161 Hz) déterminées dans le spectre 2D HMQC de $^{1}H$–$^{29}$Si pour le complexe 32 indiquent que les interactions agostiques $\beta$-Si–H···Ca existent également en solution.

Les différentes tentatives de synthèse d’un complexe hétéroleptique de calcium avec des interactions Ca···alcyne ont été infructueuses pour les alcynes terminaux, probablement à cause du caractère acide du proton –C≡CH (pKa ~ 25-26). En revanche, les alcynes liés de façon intramoléculaire peuvent être coordonnés au calcium, comme il est représenté dans le Schéma 12 pour le complexe $\left[[\text{RO}]^{31}\text{CaN(SiMe}_{2}\text{H}_{2}]{\text{(THF)}}_{2}\right]$.$^{[34]_{2}}$.

**Schéma 12. Synthèse de $[34]_{2}$.**

Le suivi par RMN de la coordination d’allènes au calcium a montré l’instabilité de cette fonction, qui s’isomérise à température ambiante pour former des alcynes (Schéma 13).

**Schéma 13. Réaction d’isomérisation proposée du $[35]_{2}$ à $[34]_{2}$.**
5. Références

Abstract

The catalysed additions of amines or phosphines across unsaturated substrates (alkenes, alkynes or allenes) constitute atom-efficient routes for the production of valuable fine chemicals such as amines and phosphines. For these reactions, heteroleptic alkaline-earth complexes have emerged as promising precatalysts. This PhD thesis describes the synthesis and characterisation of a series of alkaline-earth complexes of type \([\{\text{RO}\} \text{AeN(SiMe}_2\text{H)}_2]\) supported by fluorinated aminoalkoxides (\(\{\text{RO}\} = \text{fluorinated aminoalkoxide}; \text{Ae} = \text{Ca, Sr}\)). X-ray diffraction studies show that these complexes heavily involve \(\text{Ae} \cdots \text{F} \cdots \text{C}\) and \(\beta\)-\(\text{Si} \cdots \text{H} \cdots \text{Ae}\) secondary interactions to achieve kinetic stabilisation. Remarkably, these so-called secondary, non-covalent interactions can be more beneficial towards the stabilisation of the metallic species than the coordination of ethers onto the metal centre. Furthermore, fluorinated aminoalkoxo ligands were used to prepare rare examples of Ae heteroleptic complexes featuring intramolecular coordination from \(\pi\) donors (i.e. alkenes and alkynes). For the first time, Ae complexes stabilised by a combination of \(\text{Ae} \cdots \text{C}_2\), \(\text{Ae} \cdots \text{F} \cdots \text{C}\) and \(\beta\)-\(\text{Si} \cdots \text{H} \cdots \text{Ae}\) interactions were described. The structural and electronic features of these unique complexes were probed by crystallographic, spectroscopic and computational (DFT) methods. The utilisation of aryl-containing ligands resulted in the formation of trinuclear complexes featuring a unique pattern of strong \(\beta\)-\(\text{Si} \cdots \text{H} \cdots \text{Ca}\) agostic interactions. Some of these calcium heteroleptic complexes were tested in the hydrophosphination of styrene and \(\text{HPPh}_2\). They displayed high activities (TOF \(\approx 50 \text{ h}^{\text{−1}}\)) under mild conditions with 100% regioselectivity towards the anti-Markovnikov addition product. In collaboration with Prof. M. Etienne and Dr. C. Dinoi from the Laboratoire de Chimie de Coordination (Toulouse), a heteroleptic calcium complex supported by a fluorinated tris(indazolyl)borate was used in the intramolecular hydroamination of 2,2-dimethylpent-4-en-1-amine, and it displayed excellent performances.

Résumé

L’addition catalysée des amines ou phosphines sur des substrats insaturés (alcènes, alcynes ou allènes) constitue une méthode efficace pour la production d’amines et phosphines à hautes valeurs ajoutées. Pour ces réactions, les complexes hétéroélectrophiles des métaux alcalino-terreux ont émergé comme des précurseurs efficients. Cette thèse décrit la synthèse de complexes des alcalino-terreux supportés par des ligands aminoalcoolates fluorés de type \([\{\text{RO}\} \text{AeN(SiMe}_2\text{H)}_2]\) (\(\{\text{RO}\} = \text{aminoalcoolate fluoré}; \text{Ae} = \text{Ca, Sr}\)). Des études par diffraction de rayons X montrent que ces complexes utilisent des interactions \(\text{Ae} \cdots \text{F} \cdots \text{C}\) et \(\beta\)-\(\text{Si} \cdots \text{H} \cdots \text{Ae}\) pour être cinétiquement inertes. Étonnamment, la somme de ces interactions non-covalentes dites secondaires est prédominante par rapport à la coordination d’éthers sur le centre métallique. En outre, les ligands aminoalcoolates fluorés ont été utilisés pour préparer de rares exemples de complexes Ae hétéroélectrophiles impliquant la coordination intramoléculaire de donneurs d’électrons \(\pi\) (i.e. alcènes et alcynes). Ainsi, pour la première fois, des complexes Ae stabilisés par des combinaisons d’interactions \(\text{Ae} \cdots \text{C}_2\), \(\text{Ae} \cdots \text{F} \cdots \text{C}\) et \(\beta\)-\(\text{Si} \cdots \text{H} \cdots \text{Ae}\) ont été synthétisés. La nature de ces interactions a été sondée par des moyens spectroscopiques, cristallographiques et calculatoires (DFT). En revanche, nos efforts pour obtenir des complexes Ca-aryles ont conduit à la formation de complexes trinucléaires originaux présentant des interactions secondaires \(\beta\)-\(\text{Si} \cdots \text{H} \cdots \text{Ca}\) extrêmement fortes. Certains de ces complexes de calcium ont ensuite été testés en catalyse d’hydrophosphination du styène avec la diphénylphosphine. Ils ont démontré des activités remarquables (TOF \(\approx 50 \text{ h}^{\text{−1}}\)) en conditions douces, ainsi qu’une régiosélectivité de 100% vers la formation du produit d’addition anti-Markovnikov. En collaboration avec le Pr. M. Etienne et le Dr C. Dinoi du Laboratoire de Chimie de Coordination (Toulouse), un précatalyseur hétéroélectrophile de calcium supporté par un ligand tris(indazolyl)borate fluoré a été utilisé pour l’hydroamination intramoléculaire du 2,2-diméthylpent-4-en-1-amine, et a fait preuve d’une activité catalytique parmi les plus élevées à ce jour.