



Alkaline-earth metals : coordination chemistry and catalytic applications

Hanieh Roueindeji

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Matière Molécules et Matériaux

Spécialité : Chimie Moléculaire et Macromoléculaire

Par

Hanieh ROUEINDEJI

**Métaux Alcalino-terreux: Chimie de Coordination
et Applications Catalytiques**

Thèse présentée et soutenue à « Rennes », le « 4 Novembre 2020 »

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To my wonderful parents

The two angels, who gave in to their desires, endured hardships and protected me from troubles and misfortunes so that I could reach the position where I stand now.

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“Try not to become a person of success, but rather try to become a person of value.”

– *Albert Einstein*

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Liste of Abbreviations

Ad	Adamantyl
Ae	alkaline-earth
benzene- <i>d</i> ₆	deuterated benzene
CCDC	Cambridge Crystallographic Data Centre
CDCl ₃	deuterated chloroform
Cp	cyclopentadienyl
C.N.	coordination number
BDI ^{dipp}	β-Diketiminato
DFT	Density functional theory
DiPP	2,6-diisopropylphenyl
DOSY	Diffusion-ordered NMR spectroscopy
EDG	electron donating group
Et	ethyl
EWG	electron withdrawing group
FTIR	Fourier transform infrared spectroscopy
g	grams
h	hours
ⁱ Pr	iso-propyl
<i>J</i>	coupling constant
<i>k</i> _{app}	apparent rate constant
<i>m</i> -	<i>meta</i> -
Me	methyl
MS	mass spectrometry
NMR	Nuclear Magnetic Resonance
<i>o</i> -	<i>ortho</i> -
<i>p</i> -	<i>para</i> -
Ph	phenyl
ppm	parts-per-million
T	temperature
t	time
^t Bu	tert-butyl
THF- <i>d</i> ₈	deuterated tetrahydrofuran
TMSS	tetrakis(trimethylsilyl)silane
toluene- <i>d</i> ₈	deuterated toluene
TOF	turnover frequency

Chapter 1

Chemistry of the large alkaline-earth metals: synthesis and homogeneous catalysis

Chapter 1: Chemistry of the large alkaline-earth metals: synthesis and homogeneous catalysis

1.1 Introduction

The heavy alkaline-earth organometallic chemistry was inspired mostly by Victor Grignard's investigations on magnesium chemistry in 1900. Grignard (Nobel Prize in 1912) showed that through the treatment of an organic halide with magnesium metal in diethylether, the organomagnesium halides might be prepared.¹ Later, the heavy group 2 congeners (Ca, Sr, Ba) showed more reactivity, although their chemistry involved significant synthetic challenges.² The chemistry of alkaline-earth metals (Ae = Ca, Sr, Ba) is attractive since these metals are relatively less harmful to humans, environmentally benign and have economic (relatively inexpensive and easily accessible) advantages compared with the late transition metals (Figure 1.1).

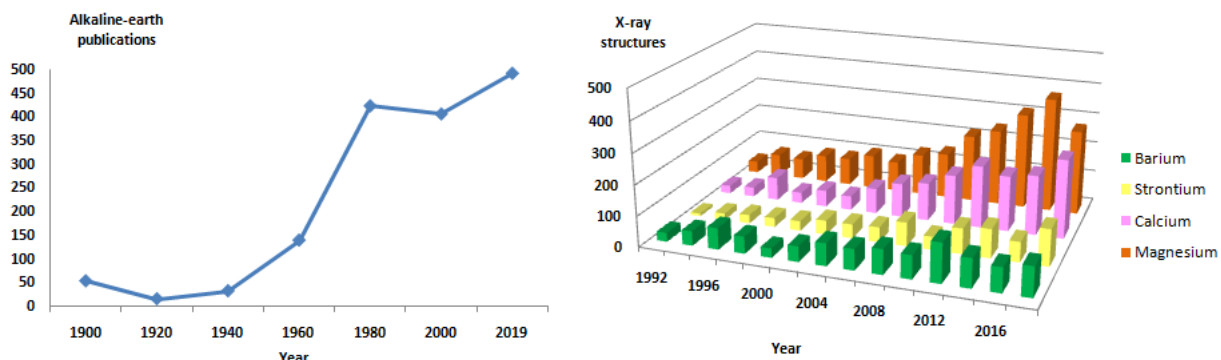


Figure 1.1. Growing interest for alkaline-earth chemistry: (*left*) Number of publications reported over the period 1900-present on “alkaline-earth metal chemistry” (source: SciFinder, June, 2020). (*right*) Number of alkaline earth structures published from 1990 to 2018 (source: CCDC database, June, 2020).

In 1956, there was an important breakthrough reported by Ziegler *et. al.* about the synthesis of $\text{Ca}(\text{C}_5\text{H}_5)_2$.³ In 1991, Cloke and Lappert reported the structurally characterized dialkyl species of calcium $[\text{Ca}\{\text{CH}(\text{SiMe}_3)_2\}_2\cdot(\text{dioxane})_2]$ in which the presence of the solvent prevented the oligomerization of the complex.⁴ Later on, $[\text{Ca}\{\text{C}(\text{SiMe}_3)_3\}_2]$ was prepared through salt metathesis chemistry by Eaborn *et. al.*⁵ They showed the importance of the steric demand of the metal center and also the effectiveness of the methyl groups to give enhanced solubility. The

application of the bulky silylamido ligand $\{\text{N}(\text{SiMe}_3)_2\}^-$ was reported to successfully avoid the oligomerization and to provide the isolated monomeric and dimeric complexes.⁶ These compounds have an excellent solubility in hydrocarbons which is one of the reasons for their popularity (beside their bulkiness, low nucleophilicity and low basicity due to the SiMe_3 effect in α position).

Generally, the high reactivity of Ae complexes is related to the large ionic radii strong electropositivity of the metal and ionic bonding (Table 1.1).^{7,8,9} Their large ionic radius and electrophilicity give them a strong tendency for high coordination numbers (typically 6 or more). Their large ionic radius also requires either sterically demanding ligands or co-ligating molecules (like small coordinating (solvent) molecules), in order to prevent their aggregation, to provide kinetic stability and to maintain their solubility. The heavy Ae metals can be compared to trivalent lanthanides ($r_{\text{La}^{3+}} = 1.03 \text{ \AA}$; $r_{\text{Nd}^{3+}} = 0.98 \text{ \AA}$; $r_{\text{Sm}^{3+}} = 0.96 \text{ \AA}$). Like group 3 (Ln^{+3} lanthanides) metal complexes, Ae^{2+} complexes have an electronic configuration of $s^0 d^0$, and the hard, oxophilic cations from both of these families preferably interact with hard *O*- or *N*-based donor ligands (Table 1.1).¹⁰ Alkaline-earth metals are known to have the single oxidation state of (2+), so they are not active for oxidative addition. Due to the highly ionic character of Ae complexes, such molecules generally display strong basicity (like Ae alkyls or amides) and in some circumstances, high nucleophilicity, depending on the Ae / ligand pair (similar to alkali metal compounds). Furthermore, similar to group 3 metals, the Ae metal center is Lewis acidic (compared to transition metals).¹¹ Finally, Ae metal complexes are highly air- and moisture-sensitive and thus require careful handling under inert atmosphere conditions.

Table 1.1. Selected properties of alkaline-earth metals.⁷⁻¹⁰

Element		Ionic radius $\text{\AA}$ (CN = 6)	Electronegativity	Redox potential (V) (M^{2+} / M)
	Be	0.45	1.576	-1.97
	Mg	0.72	1.293	-2.36
	Ca	1.00	1.00	-2.84
	Sr	1.18	0.95	-2.89
	Ba	1.35	0.89	-2.92

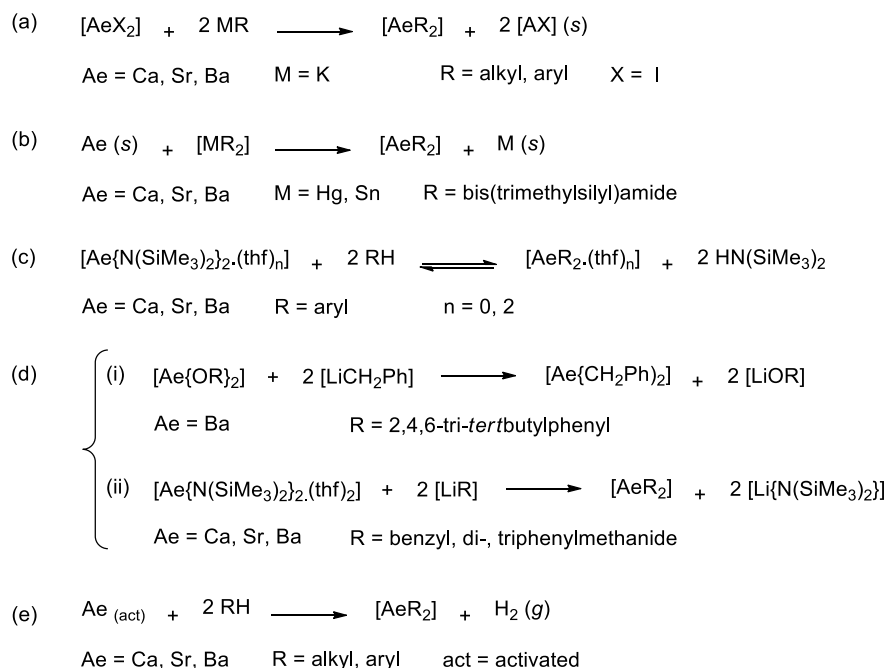
The large Ae metals have had numerous applications including, synthetic chemistry, solid-state applications and polymer chemistry.¹² Ae alkoxides have been investigated to prepare chemical vapor deposition (CVD) source reagents and sol-gel work.¹³ There have been developments in asymmetric aldol, Michael, Mannich, and related reactions.¹⁴ The broad interest in Ae organometallic molecular compounds is now mainly driven by their potential in homogeneous catalysis.

1.2 Synthesis of molecular organometallic alkaline-earth complexes

Molecular Ae organometallic complexes include Ae–C bond by definition, but nowadays, they have been extended as metal bonding to other atoms (e.g. O, N, P, H, S). Difficulties encountered in establishing the synthetic protocols of Ae complexes are essentially due to the high reactivity/instability of the final compounds. Large radius of the Ae²⁺ cation, oxophilicity together with high electropositivity and empty *d*-orbitals are at the origin of difficulties in dealing with heavy Ae metals and their complexes (including high reactivity, sensitivity to hydrolysis and ligand scrambling). Both homoleptic and heteroleptic organometallic Ae compounds have been developed due to the growing interest of their chemistry. In this section, we will describe the synthetic approaches implemented for the preparation of these compounds.^{7,15}

1.2.1 Homoleptic alkaline-earth complexes

In the case of homoleptic Ae complexes, the metal center is bound to two identical monoanionic ligands. By extension, solvated complexes of the type [Ae{L₂}.(solv.)_{*n*}] (L = a monoanionic ancillary ligand, solv. = solvent such as thf, Et₂O, dme (dimethoxyethane), tmeda (tetramethylethylenediamine), thp (tetrahydropyran)) are also referred to as homoleptic complexes. The most successful synthetic routes to Ae homoleptic complexes include (a) salt metathesis, (b) redox transmetallation, (c) protonolysis, (d) metal exchange and (e) direct metallation (Scheme 1.1).



Scheme 1.1. Established synthetic methodologies for the isolation of organometallic Ae complexes.

(a) Salt metathesis

This method has allowed the isolation of various Ae complexes (especially calcium).^{5,16} However, the isolation of the product is not straightforward. Salt metathesis is affected by several items including the Ae halide, the solvent, the alkali metal and the ligand. Under non-optimized conditions, the reaction is incomplete and leads to the formation of a mixture of products and/or of ‘ate’ complexes which are difficult to detect and eliminate. For instance, Okuda co-workers reported the isolation of the potassium tris(allyl)strontiate ‘ate’ complex $\text{K}[\text{Sr}(\text{C}_3\text{H}_5)_3]$ during their attempt to prepare bis(allyl)strontium $[\text{Sr}(\text{C}_3\text{H}_5)_2]$.¹⁷ Salt metathesis is typically conducted in thf to ensure the solubility of the reactants. The mixture of organopotassium reagents ($[\text{KR}]$) with the Ae iodides ($[\text{AeI}_2]$) is advantageous for purification issues, since KI nicely precipitates and enables an easy extraction. For instance, Hanusa and co-workers reported the reaction of $[\text{K}\{\text{C}_5\text{H}_5\}]$ with CaI_2 in thf to provide the calcium complex $[\text{Ca}\{\text{C}_5\text{H}_5\}_2 \cdot (\text{thf})_2]$.^{16a} Also, Panda *et. al.* reported heavier Ae metal complexes $[\text{Ae}\{(\text{Ph}_3\text{CN}=\text{CH})\text{C}_4\text{H}_3\text{N}\}_2 \cdot (\text{thf})_n]$ (Ae = Ca, Sr, (n = 2); Ba, (n = 3)) from salt metathesis of potassium salt with metal diiodides AeI_2 in 2:1 molar ratio in thf.^{16h}

(b) Redox transmetallation

Redox transmetallation is a route toward organometallic compounds involving in particular organometallic complexes of Hg¹⁸ or Sn.¹⁹ The reaction time depends on the metal size and it is shorter for Ba than for its lighter analogues. Although the purification of the product upon filtration of the unreacted reagent is straightforward, the toxicity of Hg and Sn is yet a significant drawback. The Ae bis(trimethylsilyl)amides $[Ae\{N(SiMe_3)_2\}_2.(thf)_n]$ (Ae = Ca, Sr, Ba) were thus synthesized by Sullivan *et. al.* from $[Hg\{N(SiMe_3)_2\}_2]$ in tetrahydrofuran,^{18a} and by Westerhausen from bis[bis(trimethylsilyl)amido]tin(II) ($[Sn\{N(SiMe_3)_2\}_2]$).^{19a}

BiPh₃ provided a more benign way to access Ae compounds by redox transmetallation. The related process referred to as “redox transmetallation/ligand exchange” was conducted as a one-pot procedure ($Ae + 2/3 BiPh_3 + 2HR$, R = ligand).²⁰ Ruhlandt-Senge *et. al.* thus prepared different homoleptic BaR₂ complexes (R = bis(trimethylsilyl)amide, phenyl(trimethylsilyl)amide, pentamethylcyclopentadienide, fluorenyl, 2,6-diisopropylphenolate, 3,5-diphenylpyrazolate).

(c) Protonolysis

This method involves the reaction of the $[Ae\{N(SiMe_3)_2\}_2.(thf)_n]$ with an acidic substrate and the liberation of the amine ($HN(SiMe_3)_2$; $pK_{a(DMSO)} = 25.8$).²¹ The availability and solubility of the heavy Ae metal bis(bis(trimethylsilyl)amides) $[Ae\{N(SiMe_3)_2\}_2.(thf)_n]$ (Ae = Ca, Sr, Ba; n = 0, 2) in various solvents along with the easy removal of the liberated amine ($HN(SiMe_3)_2$), are the advantages of this synthetic pathway. However, the organic substrate needs to be more acidic than the latter free amine ($pK_a < 26$). The relatively high pK_a of the parent amine allows the use of a wide range of organic substrates to prepare the Ae organometallic complexes such as β -diketimines ($[BDI^{DiPP}\{AeN(SiMe_3)_2\}_2.(thf)_n]$ (Ae = Ca, n = 1; Sr, Ba, n = 2) and iminoanilides ($[N^N^{DiPP}\{AeN(SiMe_3)_2\}_2.(thf)_n]$ (Ae = Ca, n = 1; Sr, Ba, n = 2). Hill *et. al.* reported the preparation of heavier Ae diphenylphosphides ($[Ae\{PPh_2\}_2.(thf)_n]$, (Ae = Ca, Sr (n = 4); Ba (n = 1.5)) by protonolysis of the corresponding bis(trimethylsilyl)amides.^{21b}

(d) Metal exchange

The metal exchange reaction is based on the switch of ligands from one metal to another (based on the HSAB theory). The separation of the two solid products recovered is the key challenge and thus requires a difference in their solubility. Therefore, the careful choice of the ligands is very important. Two different alternatives to this reaction have been reported as shown in

Scheme 1.1, including (i) the reaction of Ae alkoxide with benzyllithium and (ii) the treatment of the Ae bis(di(trimethylsilyl)amides with a lithium reagent.²² Harder *et. al.* thus prepared dibenzylbarium from the reaction of bis(bis-trimethylsilylamide) ($[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{thf})_2]$) or bis(2,4,6-tri-tert-butyl phenolate) ($[\text{Ba}\{\text{OC}_6\text{H}_2\text{-}2,4,6\text{-}^t\text{Bu}_3\}_2]$) with ($[\text{Li}\{\text{CH}_2\text{Ph}\}\cdot(\text{tmeda})]$).^{11g}

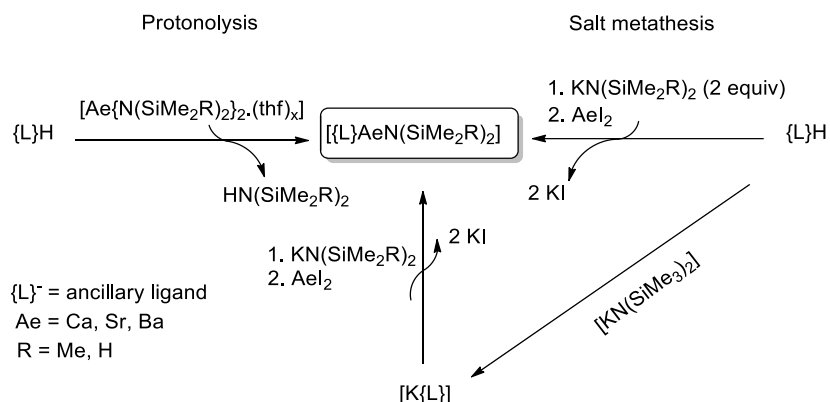
(e) Direct metallation

Application of this direct metallation method offers distinct advantages compared to the other synthetic routes. First, simple commercially available reagents can be used. Besides, the only byproduct formed is dihydrogen gas which facilitates the purification workup and easily provide high purity products. Generally, this synthetic route requires oxide-free metal surface. However, it highly depends on the pK_a of the substrate used. The ligands with very low pK_a can react under reflux.²³ For ligands with relatively higher pK_a this method requires activation of the metal. There are several ways to accomplish these requirements including: (i) the reduction of the Ae metal iodides with potassium or lithium naphthalide;^{12h,12i,24} (ii) the use of distilled metal;^{4,25} (iii) the addition of a small quantity of iodine; (iv) the activation of the metal by anhydrous ammonia.²⁶ Lappert *et. al.* thus reported the preparation of strontium and calcium complexes (e.g. $[\text{Sr}\{\text{OAr}\}_2\cdot(\text{thf})_4]$, $[\text{Sr}\{\text{OAr}\}_2]$ ($\text{Ar} = \text{C}_6\text{H}_2^t\text{Bu}_2\text{-}2,6\text{-Me-}4$) and $[\text{Ca}(\text{CH}(\text{SiMe}_3)_2\cdot(\text{thf})_3)]$ through activation of the metals by co-condensation with toluene.⁴

1.2.2 Heteroleptic alkaline-earth complexes

Heteroleptic complexes refer to the presence of two different monoanionic ligands bound to the metal centre. They have shown encouraging results as precatalysts for different types of organic transformations (e.g. hydroelementation and polymerization reactions). Ae heteroleptic complexes are traditionally synthesized through (only) two different pathways including: (a) salt metathesis and (b) protonolysis (Scheme 1.2).²⁷

The salt metathesis reaction is carried out through the combination of the Ae-halide and an equimolar mixture of the potassium precursor, which can be pre-isolated as $[\text{K}\{\text{L}_n\}]$. The protonolysis reaction is usually implemented from an equimolar mixture of the proligand ($\{\text{L}_n\}\text{H}$) and the metallic precursor such as ($[\text{Ae}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{thf})_2]$ or $[\text{Ae}\{\text{N}(\text{SiMe}_2\text{H})_2\}_2\cdot(\text{thf})_n]$ ($\text{Ae} = \text{Ca}$, $n = 1$; Sr , $n = 2/3$; Ba , $n = 0$) and related alkyl precursors.

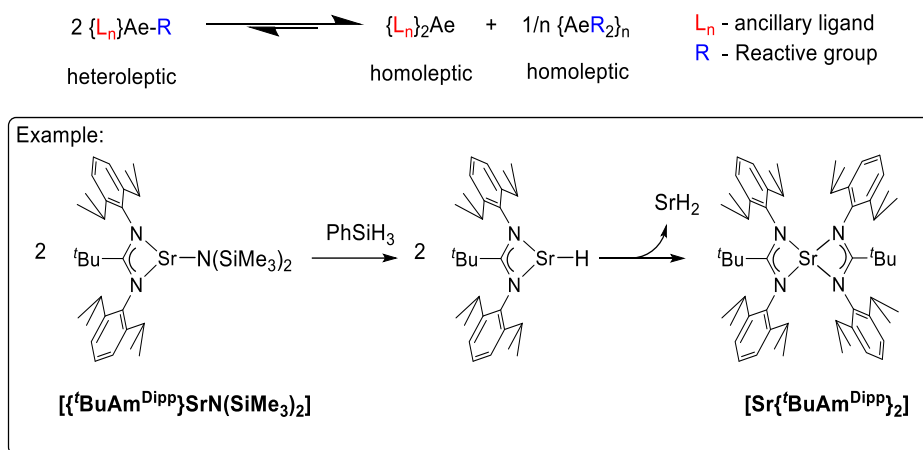


Scheme 1.2. Synthesis of Ae heteroleptic complexes by protonolysis and salt metathesis reactions.

1.3 Schlenk equilibrium

Heteroleptic Ae complexes of the type $[\{L_n\} AeR]$ (L_n = ancillary monoanionic ligand, R = monoanionic nucleophilic and/or basic reactive group) are not only highly air- and moisture-sensitive (reaction of the metal with oxygen or water giving oxides or hydroxides), but they can also be deactivated in solution through ligand redistribution reactions named Schlenk equilibrium, after the eponymous reaction leading to the formation of MgR_2 and MgX_2 from two equivalents of $RMgX$ (X = halide). Schlenk equilibrium leads to the formation of the corresponding thermodynamically more stable mixture of homoleptic species $[\{L_n\}_2 Ae]$ and $[AeR_2]$. This mixture shows less efficiency in catalysis and makes the kinetic / mechanistic analysis impossible along with possible raising solubility problem (the homoleptic species with less solubility). The homoleptic complexes could be catalytically active; however in some cases the application of the heteroleptic complex is necessary: If the ancillary ligand ($\{L_n\}$) is used to give solubility to the heteroleptic complex $[\{L_n\} AeR]$, the ligand scrambling leads to precipitation of the homoleptic $[AeR_2]$ complex. Secondly, if the ancillary ligand is used to give a special reactivity or selectivity to the heteroleptic complex (e.g. as an enantioselective catalyst), the homoleptic complex does not fulfill this objective. (Scheme 1.3). This undesirable side reaction is one of the main challenges of Ae chemistry and stems from the kinetic lability of the complex in solution. The propensity of the Ae complexes to engage in Schlenk equilibria increases upon descending in group 2 ($Mg < Ca < Sr < Ba$) according to the size and electropositivity of the metal center. As the metal size increases, the Ae–ligand bond strength

decreases and the ligand exchange becomes more difficult to control. Other parameters affect the probability of this redistribution including, temperature, concentration, the nature of the solvent and of the ligand.



Scheme 1.3. Ligand redistribution for kinetically labile Ae heteroleptic complexes, known as Schlenk equilibrium, with example of homoleptic complex of $[\text{Sr}\{^t\text{BuAm}^{\text{DiPP}}\}_2]$.²⁸

Harder and co-workers have reported the heteroleptic Sr amidinate $[\{^t\text{BuAm}^{\text{DiPP}}\}\text{SrN}(\text{SiMe}_3)_2]$ prepared from $\{^t\text{BuAm}^{\text{DiPP}}\}\text{H}$ (DiPP = 2,6-diisopropylphenyl). All attempts to convert this heteroleptic complex into the corresponding hydride complex $[\{^t\text{BuAm}^{\text{DiPP}}\}\text{SrH}]$ failed due to the Schlenk equilibrium which gave the homoleptic complex $[\text{Sr}\{^t\text{BuAm}^{\text{DiPP}}\}_2]$ after precipitation of SrH_2 . $[\text{Sr}\{^t\text{BuAm}^{\text{DiPP}}\}_2]$ the first reported monomeric, Lewis base free bis-amidinate strontium complex). Subsequently, the use of a much bulkier amidine $\{p\text{TolAm}^{\text{Ar}^\ddagger}\}\text{H}$ ($\text{Ar}^\ddagger = 2,6\text{-Ph}_2\text{CH-4-}i\text{Pr-phenyl}$) prevented the ligand scrambling (Scheme 1.3).²⁸

Hill *et al.* showed that among the heteroleptic compounds of $[\{\text{BDI}^{\text{DiPP}}\}\text{Ae}\{\text{N}(\text{SiMe}_3)_2\} \cdot (\text{thf})_n]$ ($\text{Ae} = \text{Ca}$, $n = 1$; Sr , Ba , $n = 2$), only the Ca derivative is stable and resists intermolecular ligand transfer of the ancillary ligand (BDI^{DiPP}) between the metal centers in the solution.²⁹ For the β -diketiminato calcium complex $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(\text{SiMe}_3)_2\} \cdot (\text{thf})]$ of Chisholm³⁰ and the calcium complexes bearing substituted fluorenyl ligands of Harder and co-workers (Figure 1.2),³¹ the Schlenk equilibrium shifts

completely towards the heteroleptic compounds and their structures in solution are identical to those observed in the solid state.

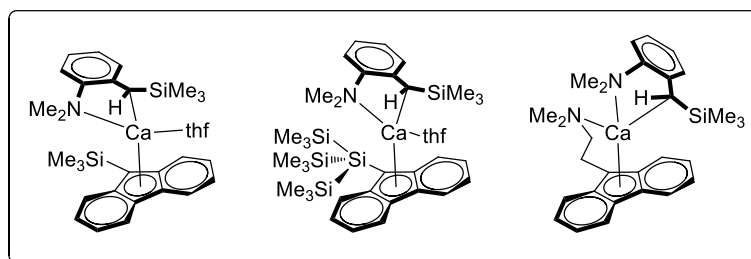


Figure 1.2. Heteroleptic benzylcalcium complexes with fluorenyl ligands.³¹

1.4 Stabilization of heteroleptic alkaline-earth complexes

In order to overcome issues concerning ligand scrambling in solution of Ae heteroleptic complexes, different strategies have been proposed.³² In Ae heteroleptic complexes of the type $[\{L_n\}AeR]$, the coligand (R) is usually a bulky $N(SiMe_3)_2^-$, $N(SiMe_2H)_2^-$, or $CH(SiMe_3)_2^-$ group that provides steric protection, stabilization of the negative charge, low nucleophilicity and better solubility to the complex in hydrocarbon solvents. It is also the reactive coligand of the initial precatalyst in catalytic cycles (Figure 1.3).

	$-N(SiMe_2H)_2$	$-N(SiMe_3)_2$	$-CH(SiMe_3)_2$
pK_a	22.6	25.8	40-45
Reactivity	→		
Stability	←		

Figure 1.3. Different reactivity and stability trends for the reactive R ligand in $[\{L_n\}AeR]$ complexes.

According to the ionic character of the Ae metals, the synthetic approaches implemented to overcome Schlenk equilibrium rely on steric effects (kinetic stability) by using bulky ligands, and/or electronic stabilization (thermodynamic effect) via intramolecular coordination of tethered heteroatoms. Steric stabilization of heteroleptic complexes lies in the implementation of ligands sufficiently voluminous to be able to encapsulate the metal center and provide kinetic stabilization against ligand scrambling. Indeed, the use of such ligands develops stable Ae complexes even under the relatively harsh catalytic conditions. The thermodynamic stability of the complexes relies on the tendency of the metal to selectively form a specific complex and is

related to the metal-ligand bond energies. The thermodynamic stability is represented by the formation constant. The higher the value of the formation constant (K_f), the greater the stability of the complex. ($K_f = \frac{[ML]}{[M][L]}$)

Consequently, a large number of multidentate and bulky ancillary ligands have been developed for the stabilization of heteroleptic complexes.

1.4.1 Bulkiness and/or electronic effect of the ligands toward the stabilization of alkaline-earth heteroleptic complexes

This section presents examples of families of bulky ancillary ligands that have been successfully used to stabilize Ae heteroleptic complexes through the encapsulation of the metal center. The β -diketiminato ligand ($\text{BDI}^{\text{DiPP}} = \text{H}_2\text{C}\{\text{C}(\text{Me})\text{N}-2,6-(i\text{Pr})_2\text{C}_6\text{H}_3\}_2$), was first used as a ligand in 1968 to prepare a nickel complex.³³ It is a typical *N,N*-chelating ancillary that stabilizes effectively calcium (and magnesium) complexes through the formation a six-membered metallacycle (Figure 1.4).^{34,35}

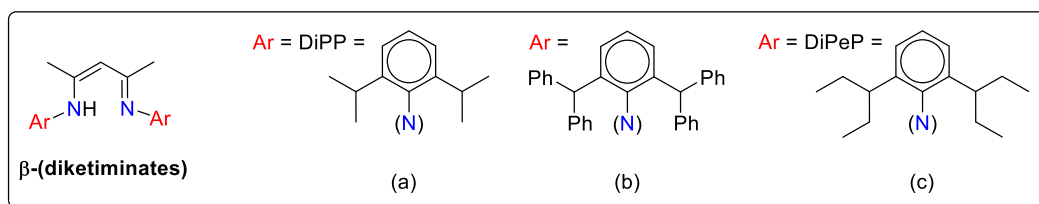


Figure 1.4. Bulky β -diketiminato ligands.³⁴⁻³⁶

The extremely sterically hindered 2,6-bis-(diphenylmethyl)-*p*-tolyl-substituted β -diketiminato ligand of Hill, was used to stabilize the monomeric Ae hydride complexes (Figure 1.4, b).³⁶ Harder and co-workers introduced a bulky and inert version of the $\{\text{BDI}^{\text{DiPP}}\}^-$ ligand in which the isopropyl groups are replaced by isopentyl moieties, $\{\text{BDI}^{\text{DiPeP}}\}^-$, and prepared the related heteroleptic Ae (Ae = Ca, Sr, Ba) amide complexes upon direct deprotonation of $\{\text{BDI}^{\text{DiPeP}}\}\text{H}$ with either $[\text{Ae}\{\text{N}(\text{SiMe}_3)_2\}_2]$ or $[\text{Ae}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{thf})_2]$ (Figure 1.4, c).^{34j} Iminoanilides^{37,38} and iminoamidinates are also among the most effective and widely used bidentate ancillary ligands towards stable heteroleptic Ae complexes. Other bidentate monoanionic ligands include bis(imino)acenaphtene³⁹ and aminotroponimate⁴⁰ (Figure 1.5).

Tridentate ancillary ligands displaying encapsulating ability have been used towards the isolation of stable heteroleptic Ae complexes. Tris(pyrazolyl)borates^{30,41} and their subsequent derivatives, imino-amidates,⁴² bis(imino)carbazoles,⁴³ and iminophenolates⁴⁴ are bulky ligands within this category (Figure 1.6). Roesky co-workers have also reported *N*-based pincers for the preparation of stabilized Ae complexes (Figure 1.6, **XI**).⁴⁵

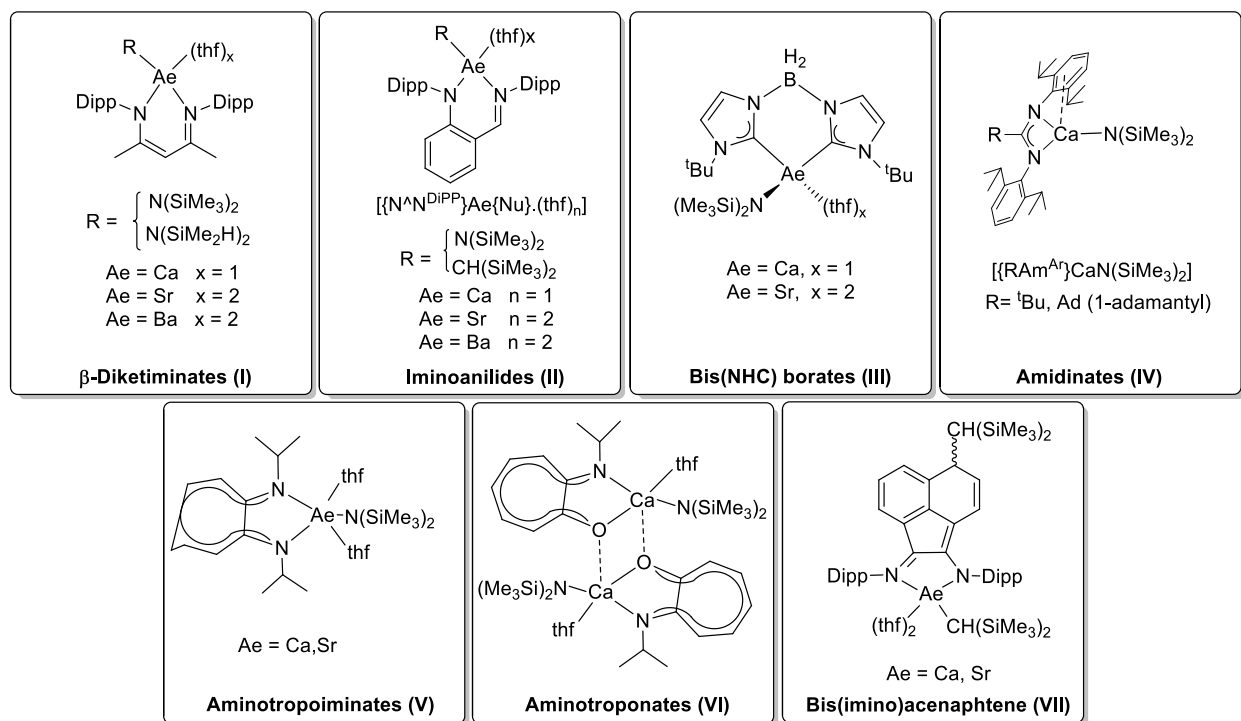


Figure 1.5. Bidentate monoanionic ancillary ligands used to stabilize heteroleptic Ae metal complexes (DiPP = 2,6-*i*Pr₂-C₆H₃).³⁶⁻⁴⁰

The large ionic radius of the Ae metals coupled with their high electropositivity and oxophilicity, gives them strong affinity for high coordination number or formation of bridged, aggregated, polynuclear species. Therefore, the synthesis of low coordinate Ae complexes with lower nuclearity is challenging. In order to overcome this problem, an alternative way is to use ligands which provide electronic density through coordination of the metal center with the heteroatoms of the ligand. Application of the secondary interactions is another efficient strategy for the stabilization of the Ae complexes.

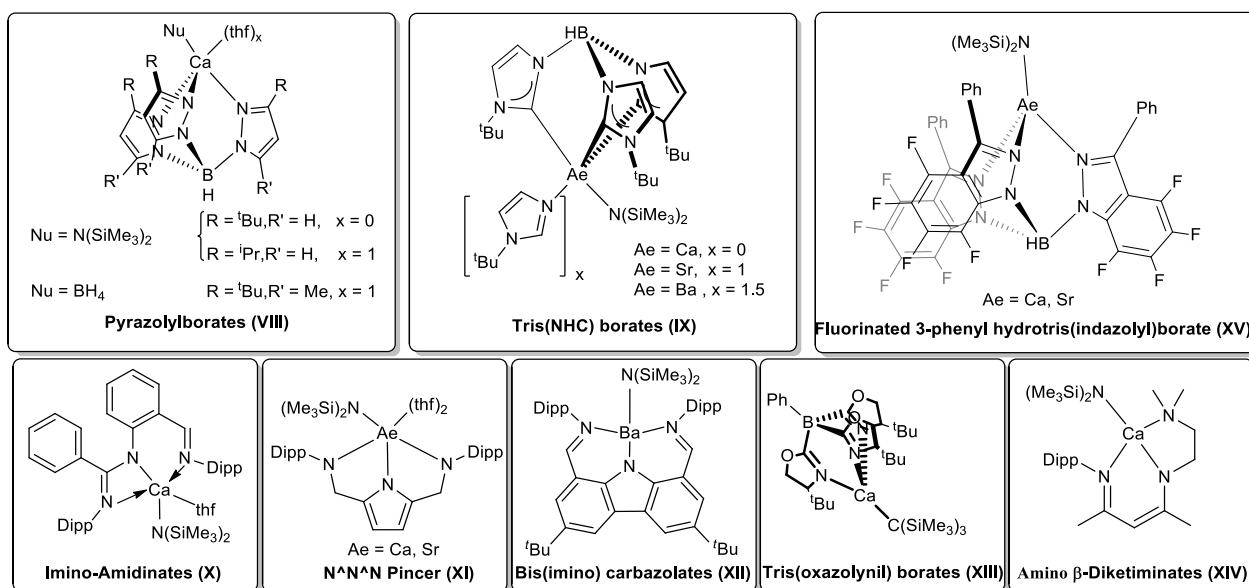


Figure 1.6. Tridentate monoanionic ancillary ligands ($\text{Dipp} = 2,6\text{-}i\text{Pr}_2\text{-C}_6\text{H}_3$).⁴¹⁻⁴⁵

Heteroleptic Ae complexes can be stabilized through additional electron density provided by the metal intramolecular coordination to heteroatoms. Neutral (thf, dme, tmeda) or monoanionic multidentate ligands have been developed. One can cite the macrocycles (typically crown ethers or aza-crown ethers) and the monoanionic ligands containing several heteroatoms such as neutral, half-crown ether [$\{\text{O}^{\wedge}\text{O}^{\wedge}\text{O}^{\wedge}\}\text{AeNu}$] of Okuda *et. al.* including a tetradentate polyether ligand,⁴⁶ or more importantly, the corresponding *N*-based tetradentate monoanionic macrocyclic ligand ($\text{N}^{\wedge}\text{N}^{\wedge}\text{N}^{\wedge}\text{N}$)⁴⁷ that are capable of stabilizing the Ae metal center (Figure 1.7, **XVII** and **XVIII**). Several multidentate phenolates have been prepared and used to synthesize a variety of Ae stabilized complexes that have shown reactivity in ring-opening polymerization and hydroelementation reactions (Figure 1.7, **XVI**). We have also investigated the preparation of multidentate heteroleptic Ca-fluoroalkoxides and their catalytic activity for hydrophosphination reactions (Figure 1.7, **XX**).^{34h}

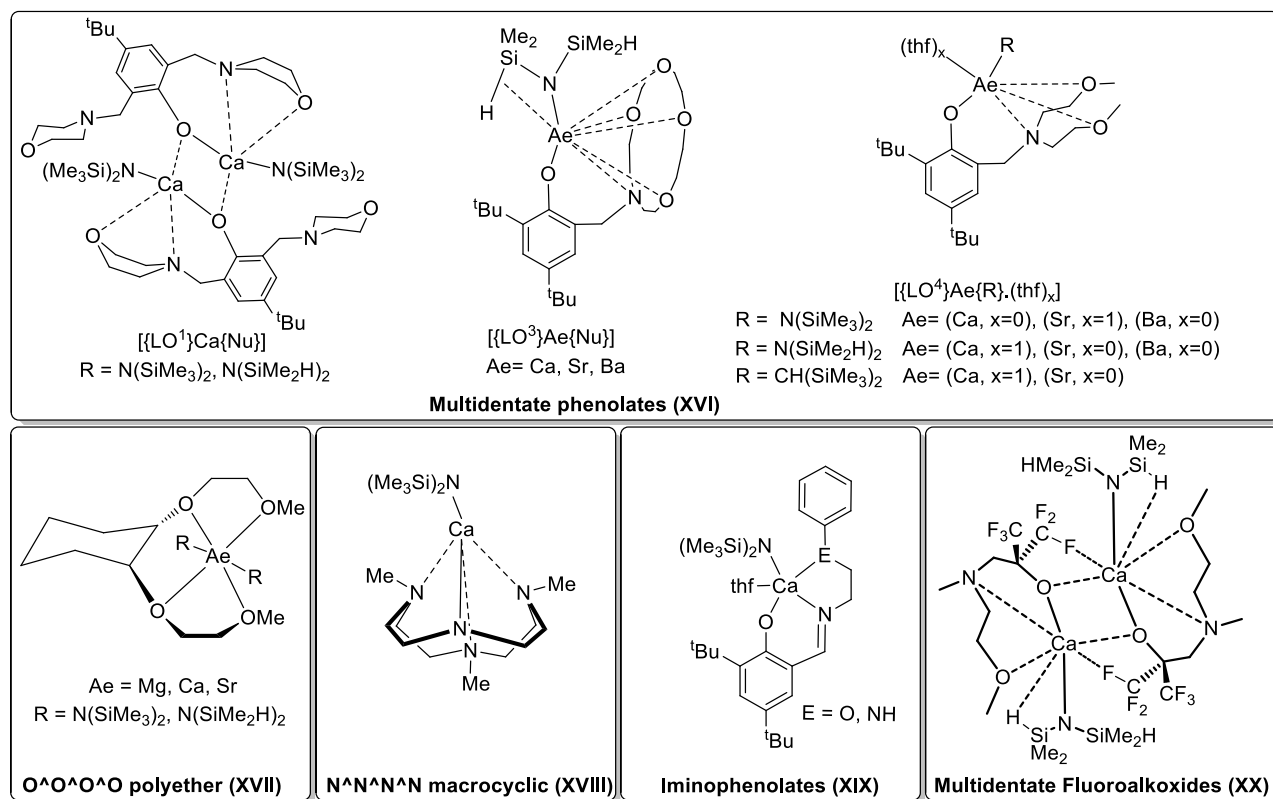


Figure 1.7. Heteroleptic Ae complexes stabilized by multidentate ancillary ligands.^{34h,46-47}

1.4.2 Secondary interactions

Due to their low charge/size ratio and electron deficiency, large Ae metals have a high tendency to form aggregated, oligonuclear structures.^{8,48,49} A common remedy is the use of ligands that could provide secondary/non-covalent interactions to saturate the coordination sphere of the metal center and therefore to reduce the nuclearity of the final structure.⁷ However, secondary interactions are weaker than covalent primary interactions since they do not involve any electron sharing. Ruhlandt-Senge and co-workers described this type of interactions as an acceptor-donor motif between the electron deficient metal center and a donor atom or group of atoms that contains an electron density with a neutral charge⁷, for instance (a) $M \cdots C\pi$,^{28,34h,50} (b) $M \cdots H-R$ ($R = Si, C$)^{27,41f,51} and (c) $M \cdots F-C$.⁵² Due to the highly electropositive Ae metals, such secondary/non-covalent interactions can be considered as electrostatic interactions. Bond valence sum analysis (BVSA) offers a method to calculate the contribution of the secondary interactions in coordination sphere of the metal. The application of this method is described in Chapter 2 of this manuscript.

(a) $\text{Ae} \cdots \text{C}\pi$ secondary interactions

The short $\text{M} \cdots \text{C}\pi$ secondary contacts between the metal and the π clouds are divided into two main categories: (i) interactions with anionic fragments (such as indenyls⁵³, cyclopentadienyls,⁵⁴ fluorenyls,^{31,55} benzyls,⁵⁶ cyclooctadienyls⁵⁷ and allyls^{46,58}), and (ii) interactions with neutral π complexes (aryls^{17b,18b,59} and olefins^{48a,50c,60}). The $\text{M} \cdots \text{C}\pi$ interactions of Ae metals with neutral π donors are mostly electrostatic. There is a model named Dewar-Chatt-Duncanson which explains the transition metal-alkene chemical bonding. This model explains the increase of the C–C bond length based on the metal electron back-donation from its d orbital into the empty π^* antibonding molecular orbital of the C=C double bond. However, this could not be applied for the Ae (d^0 metal) complexes, since there is no $d-\pi^*$ back-donation from the d^0 -Ae metal to the π system.

$\text{Ae} \cdots \text{C}\pi$ interactions are common in Ae chemistry especially with larger analogues. For instance, Westerhausen *et al.* reported the bis(phenylamide) Ae complexes. While there is no observable $\text{Ca} \cdots \text{C}(\pi)$ interaction in $[\text{Ca}\{\mu\text{-N}(\text{H})\text{Ph}\}_2(\text{thf})_2]_4$, barium complex $([\text{Ba}\{\text{NH}(\text{Ph})\}_2(\text{thf})_{1.5}]_\infty)$ shows six $\text{Ba} \cdots \text{C}(\pi)$ interactions in the solid state.⁶¹ In our group, we have developed the coordination of alkenes to the Ae metals (with an $\text{Ae} \cdots \text{C}\pi$ interaction) using fluorinated alkoxides (Figure 1.8).^{50b}

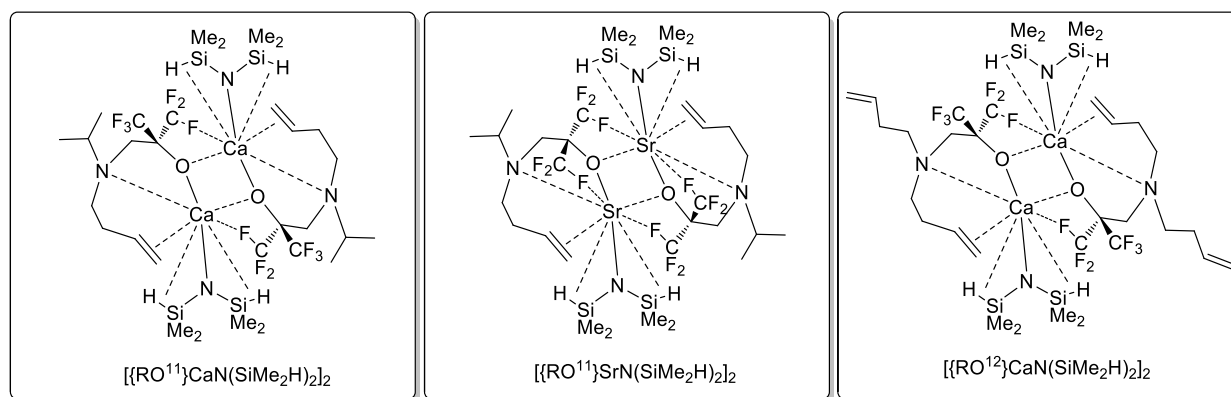


Figure 1.8. Heteroleptic Ae complexes including fluorinated alkoxo ligands with secondary interactions ($\text{Ae} \cdots \text{C}\pi$, $\text{Ae} \cdots \text{H-Si}$ and $\text{Ae} \cdots \text{F-C}$).^{48b}

(b) $\text{Ae} \cdots \text{H-R}$ ($\text{R} = \text{Si}, \text{C}$) anagostic interactions

The term “agostic” was first proposed by Brookhart and Green. Agostic interactions are best described as 3-centre 2-electron ($3c-2e$) bonds between C–H moieties and metallic centers

without cleavage of C–H bond.⁶² Scherer and McGrady proposed a more general definition for agostic interaction as the distortion of the organometallic moiety that brings the C–H bond close to the metal center.⁶³ The agostic interaction is commonly proved by the elongation of the C–H bond^{34b,64} and rather short contact of M...H.⁶⁵ This includes the donation of the electron density from the occupied molecular orbital of the C–H toward the unoccupied orbital of the metal center, completed by the back-donation (for non- d^0 metal centers) into the C–H unoccupied orbital. Lengthening of the C–H bond will occur according to the strong back-donation.⁶⁰

Brookhart *et al.* called the $M\cdots C-H$ interaction with covalent 3c–2e bonding as agostic interaction and all other situations which lack these characteristics, are considered as anagostic interactions. They have assigned the spectroscopic and structural features to distinguish between agostic and anagostic interactions as follows: agostic interaction: $\delta(^1H) < 0$ ppm, $d(M-H) = 1.8-2.3$ Å, $(M-H-C) = 90-140^\circ$; anagostic interaction (usually higher comparatively): $\delta(^1H) > 0$ ppm, $d(M-H) = 2.3-2.9$ Å, $(M-H-C) = 110-170^\circ$.⁶⁶ The $^1J_{C-H} = 50-100$ Hz, is reported for both type of $M\cdots C-H$ interactions, while for *ca.* 125 Hz no interaction exists. The X-ray crystal structure provides an estimation of the hydrogen position. The FTIR spectroscopy is applied to illustrate the weakening of the C–H band with a low-frequency shift observed ($M\cdots H-C$ secondary interaction: $\nu_{C-H} = 2700-2350$ cm⁻¹). In the absence of the interaction, the stretching wavenumber is higher than 2700 cm⁻¹.

Natural bond order (NBO) analysis of the orbitals shows the agostic interaction works as a donation of electron density from C–H to the empty d -orbital of the metal center. Nevertheless, they are relatively weak (1–10 kcal mol⁻¹, as established by DFT).^{34b,64c,67} For Ae metals that are incapable of back-donation from the metal atom (d) orbital to the C–H group (σ^*), this interaction is mostly electrostatic and is referred to as anagostic interaction. The DFT calculations for Ae complexes highlight an important electrostatic component and only a weak covalent character.²⁷ Ae...H–C anagostic interaction is present in bis(trimethylsilyl)amides of Ae metals ($[Ae\{N(SiMe_3)_2\}_2]_2$) (with two bridging and one terminal ligand per metal), and the formal interaction numbers significantly increases upon descending group 2 metals ($N(Ca\cdots H-C) = 4$, $N(Ba\cdots H-C) = 6$). Several Ae molecular complexes showing Ae...C–H interactions have been reported^{34b,64} (e.g. Ae...H–C interaction : $[\{N(2,4,6-Me_3C_6H_2)(SiMe_3)\} Ae\{PMDTA\}_2]$ (M = Sr, Ba), (PMDTA = N,N,N',N'',N''' -

pentamethyldiethylenetriamine). Also, Bochmann *et al.* reported the homoleptic $[\text{Ca}\{\text{N}(\text{CH}_2\text{-2-O-3,5-(tBu)}_2\text{-C}_6\text{H}_2\}_2\text{-}\{\text{CH}_2\text{CH}_2\text{NMe}_2\}\}_2]$ complex with $\text{Ca}\cdots\text{H-C}$ interactions (2.37 and 2.41 Å).^{64c} Sarazin and Carpentier have reported the barium boryloxide complex $[\text{Ba}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)_2]$ featuring the lowest coordination number for barium and for which the presence of the anagostic $\text{Ba}\cdots\text{H}_3\text{C}$ interactions are vital to stabilize this compound.⁶⁸

The $\text{M}\cdots\text{H-Si}$ interaction proved to be efficient to stabilize the metal center and Si-H moiety is an excellent spectroscopic probe.^{27,49a,50a,69} Later this interaction was called anagostic for Ae metal complexes as well. The anagostic interaction between the Ae metal and Si-H is mostly electrostatic as well as $\text{Ae}\cdots\text{C-H}$ interaction. However the C-H bond is considered to be nonpolar covalent, while the Si-H is polar covalent bond. Silicon is larger than carbon and had greater polarizability. Since, the hydrogen in the Si-H moiety has a hydridic character (partly negative charged), the $\text{Ae}\cdots\text{H-Si}$ interaction is strong.

Inspired by the investigations of Anwender,^{65,70} $\text{N}(\text{SiMe}_2\text{H})_2^-$ was used to provide kinetically inert Ae heteroleptic complexes through the secondary interaction of the metal center with the Si-H moiety. Our group has for instance reported Si-H anagostic interactions in several cases, such as $[\{\text{LO}^3\}\text{CaN}(\text{SiMe}_2\text{H})_2]$ ($\{\text{LO}^3\}\text{H} = (2\text{-}\{(1,4,7,10\text{-tetraoxa-13-azacyclopentadecan-13-yl)-methyl}\}\text{-4,6-di-}i\text{-tert-butylphenol})$), Ae heteroleptic complexes containing a β -diketiminato ancillary ligand and $\text{N}(\text{SiMe}_2\text{H})_2^-$ as the reactive ligand (including the Si-H moiety) $[\{\text{BDI}^{\text{DiPP}}\}\text{Ae}\{\text{N}(\text{SiMe}_2\text{H})_2\} \cdot (\text{thf})_x]$ ($\text{Ae} = \text{Ca}$ ($x = 1$), Sr ($x = 2$), Ba ($x = 2$)). Figure 1.9.^{27,32,38}

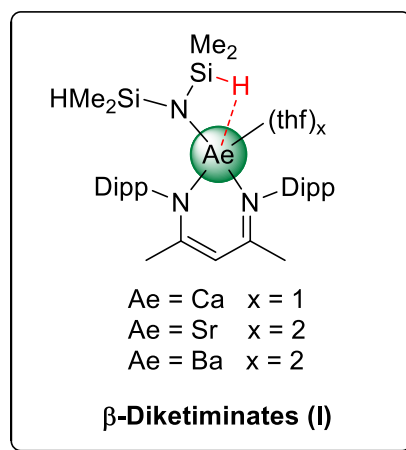


Figure 1.9. Heteroleptic Ae precatalysts including $\text{Ae}\cdots\text{H-Si}$ anagostic interactions ($\text{DiPP} = 2,6\text{-}i\text{Pr}_2\text{-C}_6\text{H}_3$).³⁸

The presence and strength of $\text{Ae} \cdots \text{H-Si}$ anagostic interactions is generally demonstrated by X-ray diffraction and/or by spectroscopic analyses. The $^1J_{\text{Si-H}}$ coupling constants (in ^1H NMR spectroscopy) with the values around 130–140 Hz indicate a strong interaction, while 140–160 Hz is considered as mild $\text{Ae} \cdots \text{H-Si}$ secondary interaction. For *ca.* 170 Hz no interaction exists. Also, in FTIR spectroscopy, Si–H bands ($\nu_{\text{Si-H}}$) are above 2100 cm^{-1} (for $\text{HN}(\text{SiMe}_2\text{H})_2$, the stretching wavenumber is 2120 cm^{-1}) while for the interacting Si–H with the metal center, the stretching wavenumber is in the range of $1850\text{--}2000 \text{ cm}^{-1}$ (Table 1.2).

Table 1.2. Classification of the strength of $\text{Ae} \cdots \text{H-Si}$ interactions using ^1H NMR (top; in solution) and FTIR (bottom; in solid state) spectroscopies.

Item \ Strength	Strong	mild	Weak
$^1J_{\text{Si-H}}$ (^1H NMR) Hz	130–140	140–160	160–170
$\nu_{\text{Si-H}}$ (FTIR) cm^{-1}	1900–1950	1950–2050	2050–2100

(c) $\text{Ae} \cdots \text{F-C}$ secondary interactions

In 1983, Glusker *et. al.* reported that C–F bonds provide stabilizing interactions with alkali and Ae metals.⁷¹ Plenio *et. al.* extended these investigations with further observing the interactions to relate ^{19}F NMR shifts, and studied by DFT calculations of the binding energy of a $\text{Li}^+ \cdots \text{F-C}$ interaction.⁷² The C–F bond is highly polarized and the C–F dipole ($\text{C}^{+\delta}$ and $\text{F}^{-\delta}$) interacts electrostatically with approaching charges involving a charge-dipole interaction.⁷³ Therefore, highly electropositive and electrophilic elements like group 1 and group 2 metals are preferred for this type of interaction.⁷⁴ $\text{Ae} \cdots \text{F-C}$ noncovalent interactions contribute to the stabilization of the Ae complexes. These interactions with the metal center limit the tendency of the metal to coordinate to additional co-ligands.

Fluorinated alkoxide ligands (with CF_3 groups in α -position to the O-alkoxide) were used to stabilize Ca complexes by $\text{Ca} \cdots \text{F-C}$ secondary interactions, thereby preventing the formation of polymeric species (e.g. $[\{\text{RO}^2\}\text{CaN}(\text{SiMe}_2\text{R})_2]_2$, $[\{\text{RO}^1\}\text{CaN}(\text{SiMe}_2\text{R})_2]_2$, $\text{R} = \text{H}, \text{Me}$) (Figure 1.9).^{50,52e,34h,60b} Also, we reported the first solvent-free cationic Ae complexes $[\{\text{RO}^3\}\text{Ae}]^+[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ ($\{\text{RO}^3\}\text{H} = 2\text{-(1,4,7,10-tetraoxa-13-azacyclo-pentadecan-13-yl)methyl-1,1,1,3,3,3-hexafluoropropan-2-ol}$) (Ae = Ca, Sr, Ba) using the amino-ether

fluoroalkoxide ancillary ligand with high denticity and strong $\text{Ae} \cdots \text{F}-\text{C}$ secondary interactions (e.g. $\text{Ca}-\text{F} = 2.681(4), 2.664(3) \text{ \AA}$, Figure 1.10).⁷⁵ There are also other examples in the literature. For instance, Deacon synthesized calcium complex of $[\text{Ca}(p\text{-HC}_6\text{F}_4\text{N}(\text{CH}_2)_2\text{NR}_2)_2 \cdot (\text{thf})_2]$ ($\text{R} = \text{Me}$ or Et) through the protonolysis of $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2(\text{thf})_2\}]$ with the N,N -dialkyl- N' -2,3,5,6-tetrafluorophenylethane-1,2-diamines and showed the presence of $\text{Ae} \cdots \text{F}-\text{C}$ secondary interactions in this compound.^{52c} Hill reported a calcium homoleptic fluorinated bis-amido complex with $\text{Ca} \cdots \text{F}-\text{C}$ secondary interactions ($2.489(3), 2.468(2) \text{ \AA}$; Figure 1.10).^{52a}

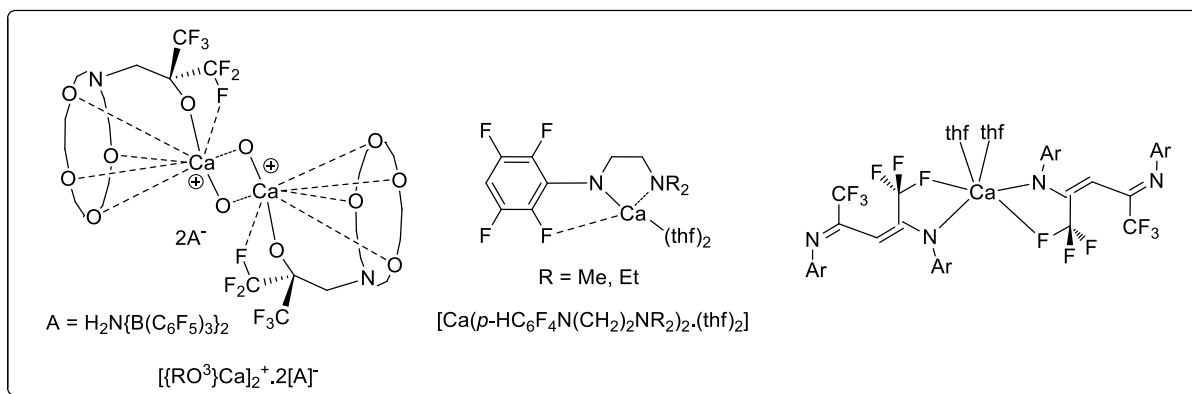


Figure 1.10. Solvent-free cationic calcium complex (left), homoleptic calcium complexes of $[\text{Ca}(p\text{-HC}_6\text{F}_4\text{N}(\text{CH}_2)_2\text{NR}_2)_2 \cdot (\text{thf})_2]$ (middle) and fluorinated bis-amido complex containing trifluoromethyl coordination (right).

Schelter *et al.* reported the cerium and uranium complexes using fluorinated diarylamines. $\text{HN}(\text{SiMe}_3)(\text{C}_6\text{F}_5)$, $\text{HN}(\text{C}_6\text{H}_5)(\text{C}_6\text{F}_5)$, $\text{HN}(\text{C}_6\text{F}_5)_2$ and $\text{HN}(\text{C}_6\text{H}_5)(3,5\text{-bis(trifluoromethyl)phenyl})$ successfully fulfilled the coordination environment of f-metals through multiple $\text{C}-\text{F}$ interactions (Figure 1.11).⁷⁶ The $\text{C}-\text{F}$ interactions were evidenced by ^{19}F NMR.

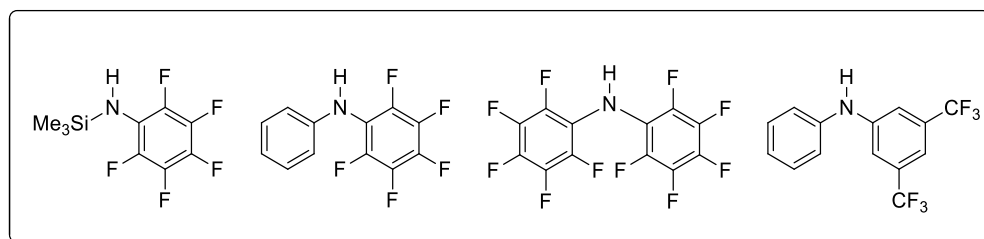


Figure 1.11. Fluorinated arylamides used for preparation of stable cerium and uranium complexes.⁷²

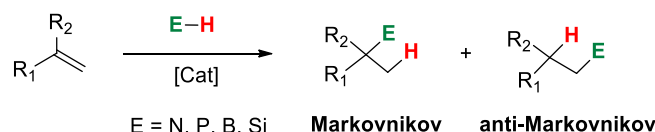
They have studied the electron density of the *ortho*-fluorine atoms in two different types of ligands (HN(SiMe₃)(C₆F₅) and HN(SiMe₃)(*o*-F-C₆H₄)). The DFT calculations revealed that removal of the *para*- and *meta*-fluorine atoms from HN(SiMe₃)(C₆F₅) ligand could lead to a more electronegative *ortho*-fluorine atom in HN(SiMe₃)(*o*-F-C₆H₄) ligand. Therefore, the C–F interactions with the metal center become stronger.

1.5 Application of alkaline-earth metal complexes in homogeneous catalysis

Over the last two decades, the organometallic chemistry of Ae metals has developed rapidly,^{12,15b,77} mainly due to their enormous potential in homogeneous catalysis⁷⁸ including polymerization (e.g. of cyclic esters^{21a,27,41,44,46,47,63c,75,79} and styrenes^{112g,31,55b,58e,80}), hydroelementation reactions and dehydrocoupling reactions. This section presents the most common Ae-mediated reactions.

1.5.1 Hydroelementation reactions

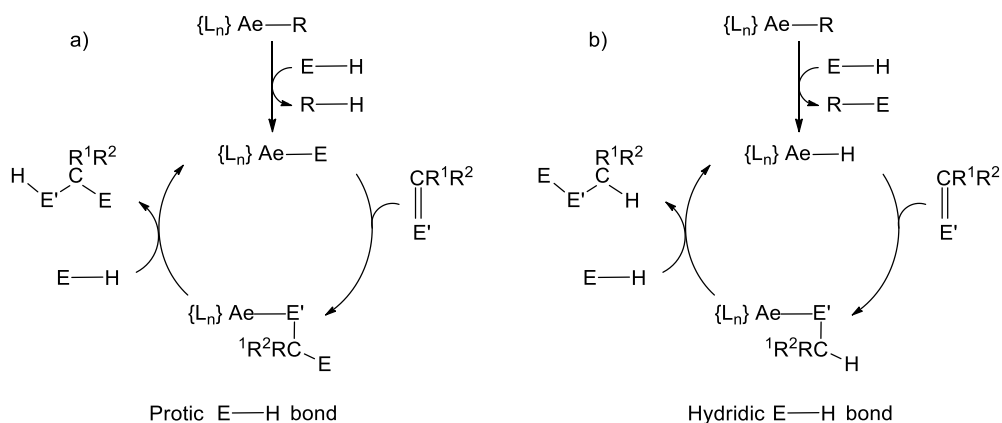
Hydroelementations of unsaturated substrates such as alkenes, alkynes and allenes are atom-economical methods toward the formation of C–E bonds, where E is a heteroatom such as N, P, B or Si (Scheme 1.4). These 100% atom-efficient reactions are attractive since it converts the starting materials into useful building blocks in organic synthesis, with no side-product. Ae-based complexes have proven to be excellent catalysts for the hydroelementation of some olefinic substrates.



Scheme 1.4. Intermolecular hydroelementation reactions of olefins.

Based on the Dewar-Chatt-Duncanson model, in the case of transition metals, the $\pi \rightarrow d$ donation leads to the alkene electrophilic activation and decreases the electron density on the C=C bond. However, a strong $d \rightarrow \pi^*$ back-donation could reduce this activation. Therefore, the transition metals that are mostly used in catalysis are not prone to $d \rightarrow \pi^*$ back-donation (Pd, Pt, Au).⁸¹ On the contrary, for the Ae metals, the alkene activation is accomplished by an

electrostatic interaction with the Lewis acidic metal, involving metal-induced polarization of the C–C double or triple bond. The protic E–H bonds engage in protonolysis to result in metal–E fragments in catalytic cycle (E = amines (HNR₂), phosphines (HPR₂)). They include the insertion of the unsaturated bond into the metal–E bond that occurs *via* a highly polarized four-centered transition state. The hydridic E–H bonds undergo σ -bond metathesis to yield metal–hydrides as catalytic active species (E = Si, B, hydrosilanes (HSiR₃), boranes (e.g. B_nH_{n+4}, B_nH_{n+6} pertaining substrates, pinacolborane)). This system is appropriate for the hydrogenation, hydrosilylation and hydroboration of multiply bonded substrates. Such catalytic cycles can be applied to different types of heterofunctionalization reactions (Scheme 1.5).



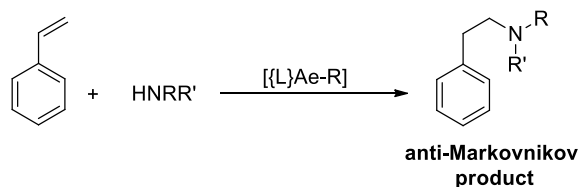
Scheme 1.5. Hydroelementation catalytic cycles including (a) the addition of a protic E–H fragment (amines or phosphines), (b) the addition of a hydridic E–H fragment (hydrosilane, borane) to a C = E'. (R¹R²C = E' = unsaturated moiety)

1.5.1.1 Hydroamination reactions

The addition reaction of N–H bond of primary or secondary amines onto olefinic double bond(s) leads to the formation of the substituted amines.⁸² This type of reaction has been one of the interesting topics over the past decade.⁸³ These organic products are particularly valuable for industrial applications such as in pharmaceutical and fine chemical areas.^{84,85,86} There are generally two types of hydroamination benchmark reactions conducted by Ae metal complexes: (a) inter- and (b) intra-molecular hydroamination reactions.

(a) Intermolecular hydroamination

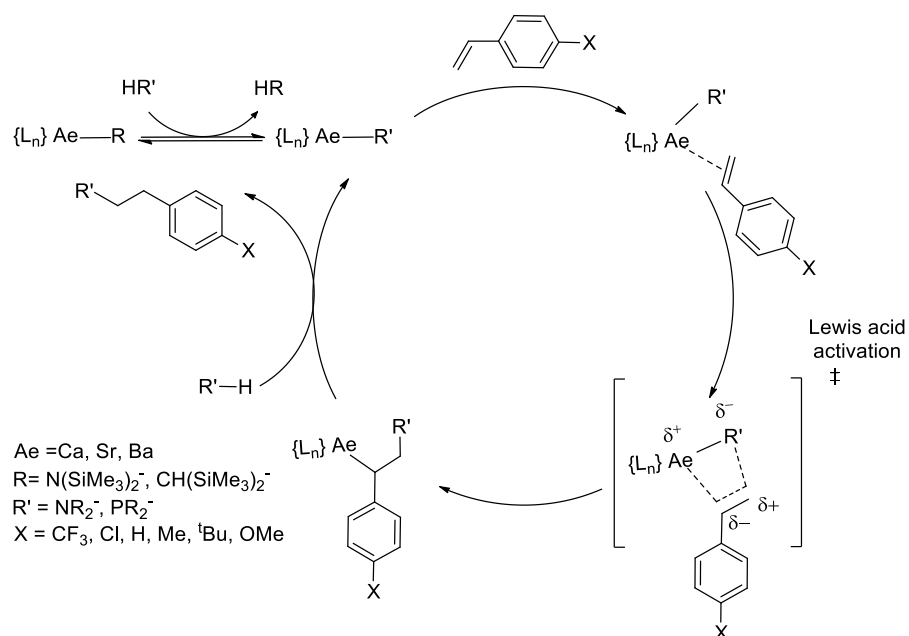
The intermolecular hydroamination reaction takes place between an activated olefin (due to the stabilization of the negative charge) such as styrene, and to a lesser extent conjugated dienes such as isoprene, and an amine (pyrrolidine, benzylamine, etc.; Scheme 1.6).



Scheme 1.6. Intermolecular hydroamination reactions promoted by Ae complexes.

One needs to overcome the high activation energy considering that both substrates are electron-rich and that the coupling is not favorable from the kinetic point of view. To get over the activation barrier, Ae catalysts have been used to induced polarization on the π system which leads to C=C bond insertion into the metal–N bond (Scheme 1.7).⁸⁷

Hydroamination reactions have been investigated previously using lanthanide complexes and early transition metals.⁸⁸ Intermolecular hydroamination of activated alkenes catalyzed by Ae complexes was reported for the first time by Hill and co-workers. The homoleptic complexes employed were of the type $[\text{Ae}\{\text{N}(\text{SiMe}_3)_2\}_2]$ and $[\text{Ae}\{\text{CH}(\text{SiMe}_3)_2\}_2(\text{thf})_2]$, (Ae= Ca, Sr).⁸⁹ The reactivity of the Ae metals in intermolecular hydroamination was later confirmed by DFT calculations from Tobisch to follow the trend of (Ca < Sr < Ba).⁹⁰ Later, this type of heterofunctionalization reaction was investigated through the use of new Ae heteroleptic complexes such as the heteroleptic β -diketiminato (**I**), iminoanilido (**II**) and phenolato (**XV**) precatalysts.^{37,38}



Scheme 1.7. General proposed mechanism for Ae-catalyzed hydroamination and hydrophosphination reactions of activated olefins.

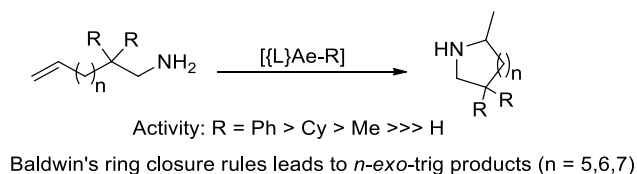
Intermolecular hydroamination proceeds with anti-Markovnikov regioselectivity. The 2,1-insertion is related to the organization of the transition state and formation of the $\text{R}'\text{-C}$ bond ($\text{R}' = \text{N, P}$). During the 2,1-insertion of $\text{C}=\text{C}$ into the $\text{Ae-R}'$ bond the phenyl group may stabilize the adjacent anionic center which is not possible in 1,2-insertion. The 2,1-regioselectivity is also the consequence of the relative position of the aromatic ring to the metal center in the transition state and the interaction of Ae metal with the $\text{C}(\pi)$ reduces the activation energy.

The alkyl ligand $\{\text{CH}(\text{SiMe}_3)_2\}^-$ in Ae heteroleptic complexes shows an even greater activity than their amido analogues, since the alkyl is more basic to start the deprotonation of the amine and generate the active species (e.g. $[\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{Ba}\{\text{CH}(\text{SiMe}_3)_2\} \cdot (\text{thf})_2]$ complex is more active than $[\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)_2\} \cdot (\text{thf})_2]$).

(b) Intramolecular hydroamination

The intramolecular hydroamination of an aminoalkene is more favorable from the entropy point of view compared to intermolecular hydroamination. The formation of a chelating amidoalkene needs less energy than the binding of styrene. Therefore, intramolecular hydroamination has less

steric requirements and the calcium complex provides superior rates of reaction than its heavier analogues under identical conditions (the cyclization is less thermodynamically favorable for the heavier Ae metals). The double bond has effective interaction with a more compact Ae centre that favors the insertive cyclization; Therefore calcium is the most and barium is the least efficient analogue in cyclohydroamination catalysis. Various types of Ae-based precatalysts have been implemented for cyclohydroamination (Scheme 1.8).



Scheme 1.8. Intramolecular hydroamination reactions promoted by Ae complexes.

Following the initial studies in 2005, a number of calcium-based precatalysts have been synthesized in order to conduct this reaction. Hill, Roesky and also our group,^{37,38} used complexes that bear β -diketimines (**I**), iminoanilides (**II**) and other Ae precatalysts such as N[^]N[^]N pincer, aminotropoiminate, Cp-imidazolin-2-imine^{40b,45,91}, bis(imino)acenaphthene, bis(NHC) borate, triazenide^{16g,92,93} (Figure 1.12). Considering the catalytic studies of Hill,^{3,34a} complete cyclohydroamination of 1-amino-2,2-dimethyl-4-pentene was achieved in the presence of the calcium stable heteroleptic complex containing a β -diketiminato ancillary ligand [$\{BDI^{DiPP}\}Ca\{N(SiMe_3)_2\} \cdot (thf)$]. According to the Baldwin's ring closure rules, the intramolecular hydroamination results in the formation of *n*-exo-trig products (*n* = 5, 6, 7).⁹⁴ Interestingly, this is in contrast with those reported for the alike intermolecular reaction.

The computational study provided by Tobisch suggests a stepwise σ -insertion mechanism for cyclohydroamination of the aminoalkene.⁹⁰ Based on the Thorpe-Ingold effect, the geminal groups favor the reactive conformation of the aminoalkene by decreasing the conformational freedom.^{95,96}

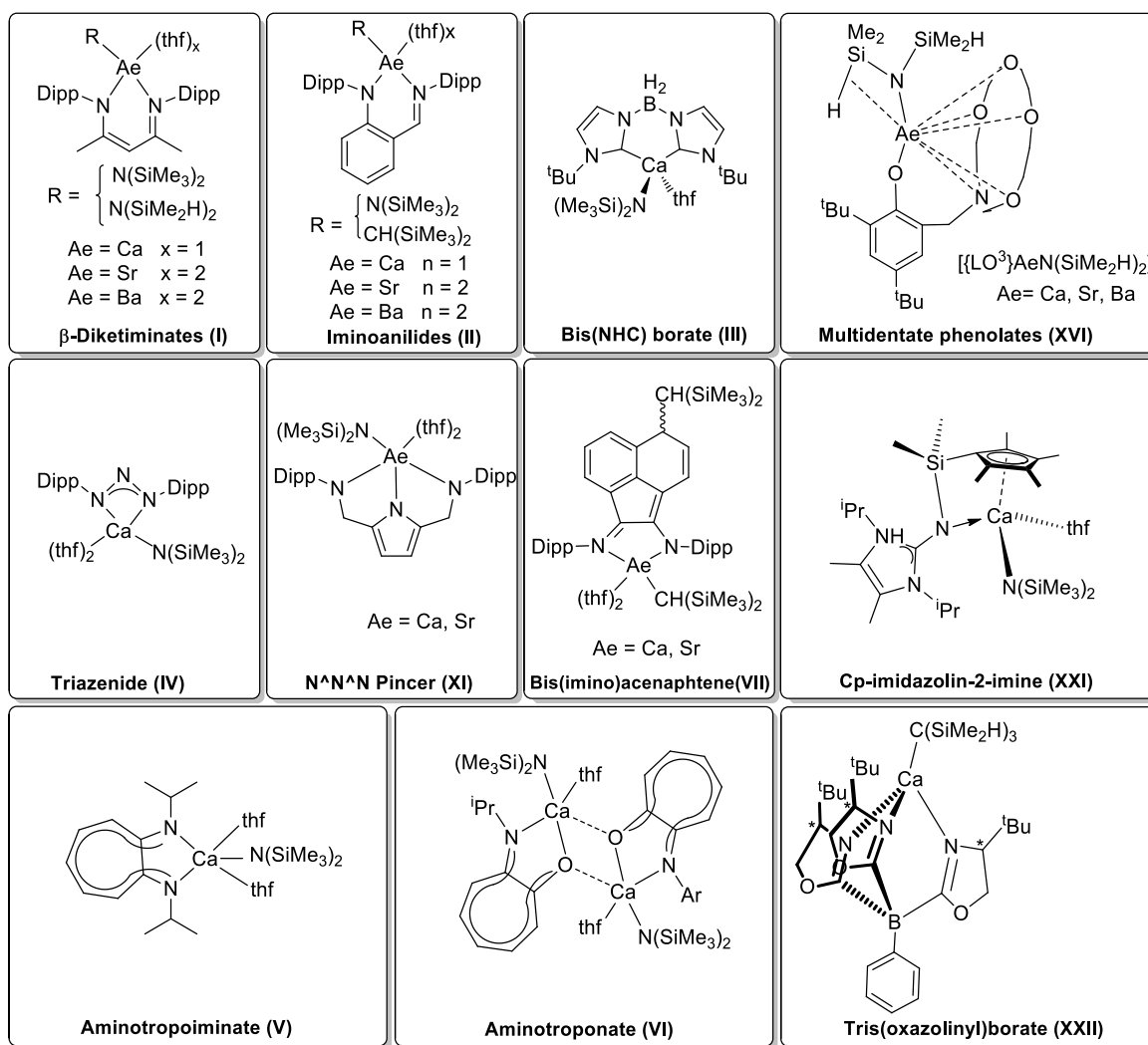


Figure 1.12. Heteroleptic Ae precatalysts for the intramolecular hydroamination of aminoalkenes. (DiPP = 2,6-*i*Pr₂-C₆H₃)^{16g,37,38,40b,45,91-93}

1.5.1.2 Hydrophosphination reactions

Over the recent years, the formation of a C–P σ -bond through the addition of the P–H bond into a C–C multiple bond, has attracted efforts from organometallic chemists. The metal-mediated C–P σ -bond formation can be classified into general categories as follows:

- phosphination, that is the cross-coupling reaction of a C–X bond (C_{sp2} or C_{sp3}, X = halide) with P–H (primary or secondary phosphines) generally in the presence of a base and releasing a secondary or tertiary phosphine with HX;⁹⁷
- P-hydroelementation reactions that (depending on the number of the oxygen atoms involved) are divided into three subdivisions as:

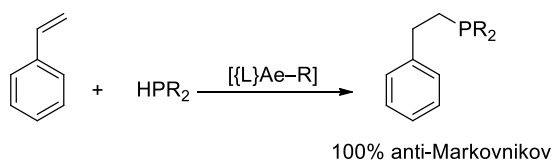
(b-1) hydrophosphination (sometimes referred to as hydrophosphanylation) which involves a phosphine HPR_2 , with no oxygen atom);

(b-2) hydrophosphinylation that is the addition of a pentavalent P–H species (phosphine oxide: HP(O)R_2 or HP(O)(OR)R') across a C–C multiple bond;

(b-3) hydrophosphonylation in which substrates with three oxygen atoms are involved (HP(O)(OR)_2).^{78c}

Hydrophosphination is a controlled addition of primary or secondary phosphines to an unsaturated C–C bond (first metal-catalyzed hydrophosphination was reported in 1990 with platinum⁹⁸). Hydrophosphination is an atom economic tool to prepare organo-phosphorous compounds. Generally, in comparison to hydroamination reactions, Ae-mediated hydrophosphination is not often explored.

The hydrophosphination reaction was originally conducted by catalysts based on palladium,⁹⁹ platinum,¹⁰⁰ nickel.¹⁰¹ Later on, other metals such as copper,¹⁰² iron,¹⁰³ tin¹⁰⁴ and more oxophilic ones like titanium/zirconium,¹⁰⁵ divalent lanthanides^{42,106} and Ae^{37,38,107} have also been applied. According to Pearson's hard and soft acid and base (HSAB) theory,¹⁰⁸ oxophilic Ae metals are hard elements; hence there is less possibility for the Ae compounds to be deactivated upon coordination by soft phosphines (comparing to late transition metals). Cui and coworkers catalyzed the intermolecular hydrophosphination of alkenes with the active $[\{\text{N}^{\wedge}\text{N}^{\wedge}\text{N}\}\text{Ca}\{\text{N}(\text{SiMe}_3)_2\} \cdot (\text{thf})]$ complex under mild conditions (Figure 1.6, X).⁴² Their tridentate iminoamidinato ligand featured an imine arm to stabilize the large ionic radius of the calcium anion.



Scheme 1.9. Hydrophosphination of styrene promoted by Ae complexes.

Hill *et al.* examined the performance of the β -diketiminato calcium complex $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(\text{SiMe}_3)_2\} \cdot (\text{thf})]$ precatalyst. The final products are consistent with an anti-

Markovnikov *syn* addition of the P–H bond across the least hindered unsaturated C–C bond of the substrate. Westerhausen and co-workers extended the hydrophosphination reactions to alkynes (like phenyl substituted alkynes) and dienes catalyzed effectively by $[(\text{thf})_4\text{Ca}(\text{PPh}_2)_2]$ complex.¹⁰⁹ They also investigated the intermolecular hydrophosphorylation (Pudovik reaction) of alkynes $\text{R}^1\text{--C}\equiv\text{C--R}^2$ ($\text{R}^1 = \text{H, alkyl, Ph}$; $\text{R}^2 = \text{alkyl, Ph, COOMe, SiMe}_3, \text{Si}(\text{iPr})_3$) with HP(=O)R^2 substrates (e.g. bis(2,4,6-trimethylphenyl)phosphane oxide (dimesitylphosphane oxide, $\text{Mes}_2\text{P(O)H}$)).¹¹⁰ Recent developments in hydrophosphination catalysis by Ae complexes have shown their very good efficiency in the reactions with activated alkenes. Intermolecular alkene hydrophosphination reactions have been successfully conducted using iminoanilides (**II**), fluoroalkoxides, phenolates (**XVI**) and a bis(imino)carbazolate (**XII**).^{37,38,107,111}

Based on these investigations, the catalytic activity was shown to increase with the metal size, $\text{Ba} > \text{Sr} > \text{Ca}$. Conducting the experiment with *para*-substituted styrene indicated that a more electron-withdrawing substituent on styrene increases the activity ($\text{CF}_3 > \text{Cl} > \text{H} > \text{Me} > \text{tBu} > \text{OMe}$). This means that an electron-withdrawing group has a stabilization effect through the decrease of the charge on the α benzylic carbon atom in the suggested transition state (General proposed mechanism Scheme 1.8).³⁷

1.5.1.3 Hydrosilylation and hydroboration reactions

The catalytic hydrosilylation of olefins is of great importance in the production of organosilicons by the addition of a Si–H function to unsaturated C=C bonds.¹¹² Hydrosilylation catalysis implicates the generation of Ae-hydride intermediates. Harder *et. al.* have used metal benzyl complexes of group 1 and 2 for hydrosilylation reactions of styrene derivatives with arylsilanes (Figure 1.13, **XXIII**).¹¹³ Recently, they have used the $[\text{Ae}\{\text{DMAT}\}_2(\text{thf})_2]$ complexes ($\text{Ae} = \text{Ca, Sr}$; $\text{DMAT} = 2\text{-dimethylamino-}a\text{-trimethylsilylbenzyl}$) for efficient catalytic reduction of imines with phenylsilane that revealed the increasing trend descending in the second group column ($\text{Ca} < \text{Sr} < \text{Ba}$).¹¹⁴ Harder has also reported the reactivity of molecular calcium hydride $[\{\text{BDI}^{\text{DiPP}}\}(\text{thf})\text{Ca}\{\mu\text{-H}\}]_2$ in the catalytic hydrosilylation reaction of 1,1-diphenylethylene (1,1-DPE) (Figure 1.13).^{78a,115} Cationic complexes have also shown their potential to mediate hydrosilylation reactions. Okuda *et. al.* have reported the application of a calcium hydride cation $[\text{CaH}]^+$ stabilized by a macrocyclic polyamine ligand ($\text{Me}_4\text{TACD} = 1,4,7,10\text{-tetramethyl-}$

1,4,7,10-tetraazacyclododecane) for the hydrosilylation of ethylene, olefins and styrene derivatives.

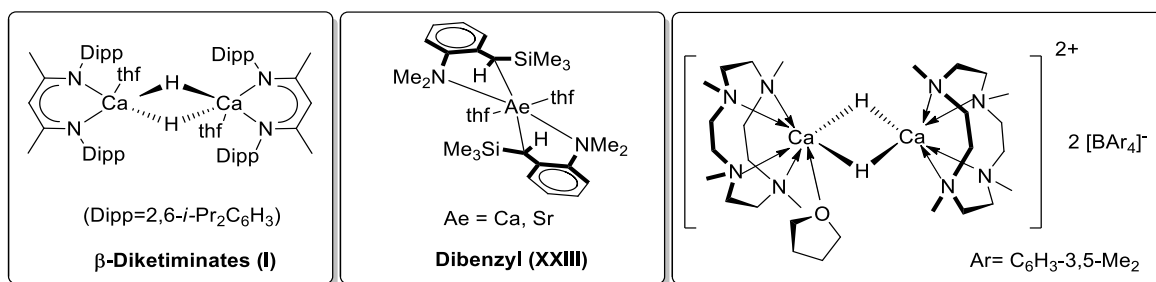
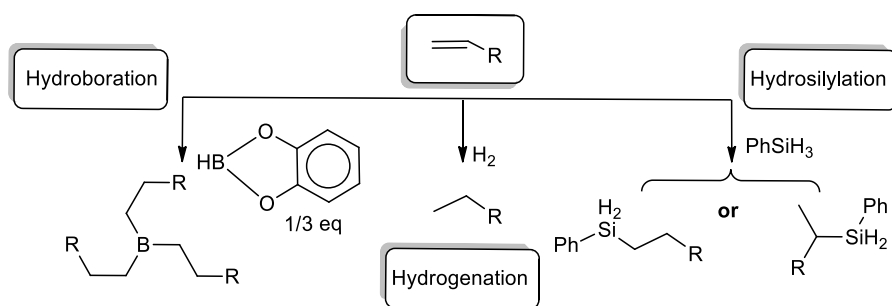
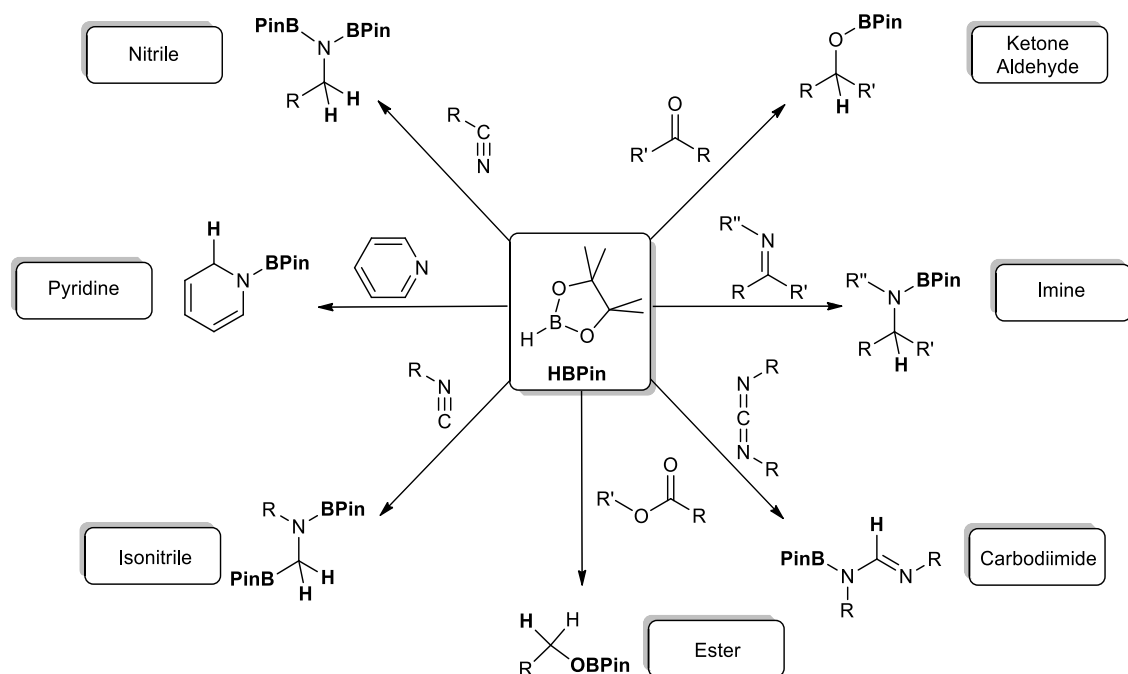


Figure 1.13. Molecular calcium hydride $[\{\text{BDI}^{\text{Dipp}}\}(\text{thf})\text{Ca}\{\mu\text{-H}\}]_2$, $[\text{Ae}\{\text{DMAT}\}_2(\text{thf})_2]$ (Ae = Ca, Sr) and macrocyclic polyamido complex applied for hydrosilylation.¹¹²⁻¹¹⁵



Scheme 1.10. Heterofunctionalisation reactions of olefins promoted by heteroleptic Ae complexes.

Harder and co-workers have investigated the hydroboration of diphenylethylene with catecholborane (HBcat) using the organocalcium catalysts.¹¹⁶ However, the calcium-hydride mediated the decomposition of the catecholborane. Therefore, (Ph₂CHCH₂)₃B was produced instead of Ph₂CHCH₂OBCat. The Hill group has also used the less electron-withdrawing pinacol borane (HBpin), which is less prone to decomposition, in the hydroboration of several unsaturated substrate such as ketones, aldehydes,¹¹⁷ imines,¹¹⁸ carbodiimides,¹¹⁹ isonitriles,¹²⁰ pyridines¹²¹ or nitriles.¹²² Sadow has reported the hydroboration of esters with pinacolborane by organomagnesium precatalyst.¹²³ (Scheme 1.11)



Scheme 1.11. Hydroboration reactions of different unsaturated functions.¹¹⁶⁻¹²³

1.5.1.4 Hydrogenation reactions

The first Ae metal catalyzed alkene hydrogenation reaction was reported by Harder *et al.* in 2008.^{58d,124,125} Okuda and co-workers prepared a cationic calcium hydride catalyst and reported the hydrogenation of unactivated alkenes (Scheme 1.13).^{47,126} Hill *et al.* reported the hydrogenation by the solvent-free β -diketiminate calcium hydride [$\{\text{BDI}^{\text{DiPP}}\}\text{CaH}\}_2$.^{34f} Alkene hydrogenation has a reverse relationship with the number of substituents on the double bond while conjugation in the ring system makes it more feasible (Figure 1.14).

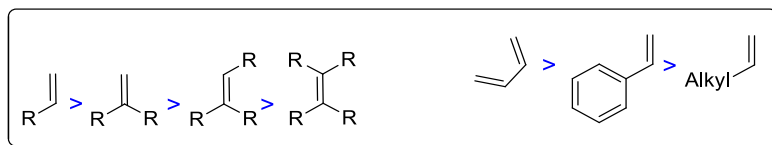
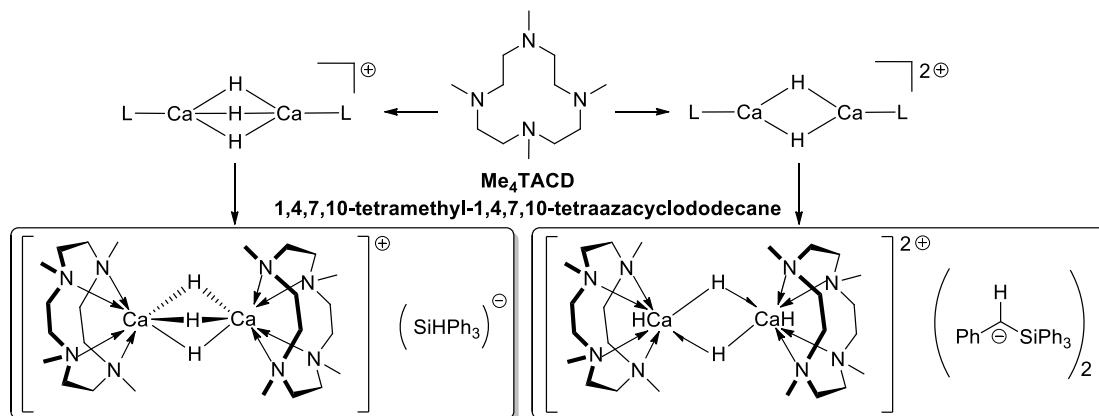


Figure 1.14 Reactivity order for hydrogenation of alkene.

Harder and co-workers have reported the catalytic hydrogenation of alkenes by $[\text{Ae}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (Ae = Ca, Sr, Ba), tolerating ether functional group (Ba the most active metal).¹²⁷ They have also investigated the hydrogenation of alkenes using 1,4-cyclohexadiene

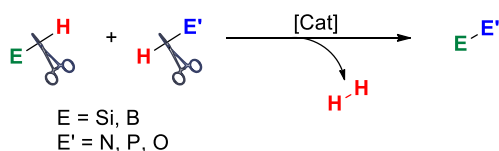
(1,4-CHD) as a H source, and showed that the metal hydride species $[\{N(\text{SiMe}_3)_2\}_2\text{AeH}]$ (Ae = Ca, Sr, Ba) act as catalyst for alkene hydrogenation.¹²⁸ Their results showed $[\text{Ba}\{N(\text{SiMe}_3)_2\}_2]$ is the most active catalyst. Lately Harder *et. al.* showed the catalyst activities increase along the series $[\text{Ae}\{N(\text{SiMe}_3)_2\}_2] < [\text{Ae}\{N(\text{TRIP})(\text{DiPP})\}_2] < [\text{Ae}\{N(\text{TRIP})_2\}_2]$ (Ae = Ca, Sr, Ba) (TRIP = $\text{Si}(\text{iPr})_3$, DiPP=2,6-diisopropylphenyl) and with metal size (Ca < Sr < Ba). Highly active $[\text{Ba}\{N(\text{TRIP})_2\}_2]$ is able to reduce unactivated internal alkenes.¹²⁹



Scheme 1.12. Cationic hydride catalyst featuring a tetraamine ligand used in hydrogenation reaction.¹²⁴

1.5.2 Cross-dehydrocoupling reactions

Since the 1980s, dehydrocoupling has been used as an efficient method for the cross metathesis allowing the formation of E–E or E–E' bonds, in which both elements are of the main group (either electronegative like N, O, P, or electropositive like B, Si; Scheme 1.13).¹³⁰ E'–H type reagents (amine, alcohol, phosphine) are usually commercially available or easily accessible precursors. They can be activated by a metal center through catalysis, since they have weak E'–H bond dissociation enthalpies.¹³¹



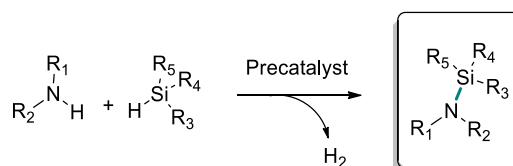
Scheme 1.13. Dehydrocoupling reaction.

This type of reactions is highly atom economic, with dihydrogen being the only by-product, therefore it is considered as a clean method through which the byproduct could be recycled as a subsequent energy source.¹³² There are two major groups for this type of reaction: homocoupling (E–E bond formation) and heterocoupling (E–E' bond formation).

Various Ae metal complexes have been applied in particular for the preparation of N–Si and N–B bonds (silazanes and aminoboranes respectively) through dehydrocoupling reactions that will be described in the following part.

1.5.2.1

Traditionally, the Si–N bond has been formed either through aminolysis of chlorosilane or *via* metalation (Li, Na, K) of the amine.^{133,134} However, these reactions are not atom-economic due to the formation of inorganic salts (LiCl, NaCl, KCl) or HCl byproducts in stoichiometric amounts; this is a major drawback especially for industrial applications. Cross-dehydrocouplings through metal-catalyzed homogeneous catalysis are considered efficient methodologies for the chemoselective N–H/H–Si coupling of amines and hydrosilanes (Scheme 1.14).^{135,136,137,138}



Scheme 1.14. Catalytic cross dehydrocoupling reaction N–H / H–Si.

Silazanes find several applications. They can serve as amine protecting agents.^{139,140,141,142} are also known to be silylating agents which are effective as alcohol protecting groups.¹⁴³ In the field of polymers, polysilazanes are established precursors for ceramics of the type Si₃N₄, which are valuable for their excellent resistance to corrosion, stability at high temperature (> 1000 °C) and long term durability.^{144,145,146} Cross dehydrocoupling of N–H/H–Si has been catalyzed with a magnesium precatalyst (To^MMgMe, To^M = tris(4,4-dimethyl-2-oxazolinyl)phenylborate) by Sadow *et al.*¹⁴⁷ We have reported a similar mechanism with barium iminoanilide complex [$\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)_2\} \cdot (\text{thf})_2$] supported by a mechanistic study as well as DFT calculations.¹⁴⁸ The azametallacyclopropane calcium complex (Ca(η^2 -Ph₂CNPh)(hmpa)₃) (Figure

1.15, XXV) has been synthesized and used for the amine dehydrogenative silylation by Harder.¹⁴⁹

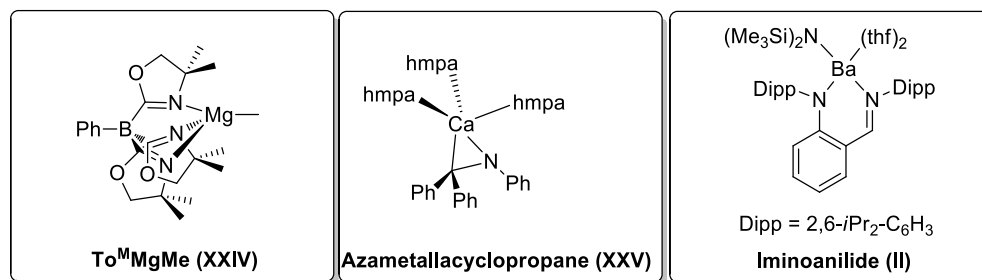
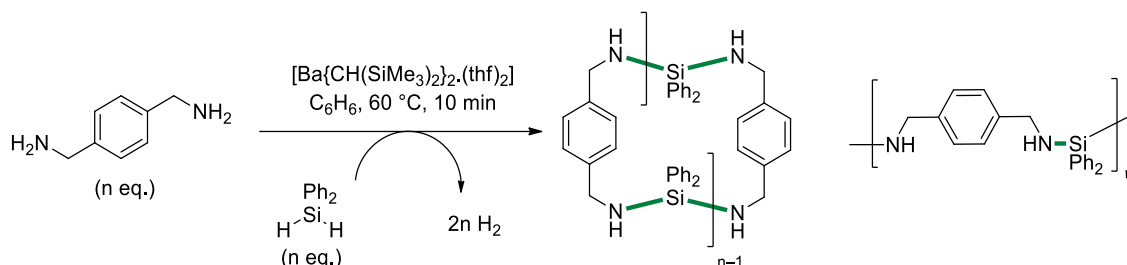


Figure 1.15. Ae precatalysts for cross dehydrocoupling of N H/H Si.¹⁴⁷⁻¹⁴⁹

Hill and co-workers have applied Ae complexes of [Ae{N(SiMe₃)₂}]₂ (M = Mg, Ca, Sr) as precatalysts for cross dehydrocoupling of amines and hydrosilanes.¹⁵⁰ Calcium complex is much more active than the magnesium amide and the corresponding strontium complex. Ae homoleptic complexes featuring the bulky amido group N(SiMe₃)₂ as a ligand have shown a high reactivity in catalysis of N H/H Si cross-dehydrocoupling. In our group the reactivity of the barium homoleptic precatalysts [Ba{N(SiMe₃)₂}.(thf)₂] and [Ba{CH(SiMe₃)₂}.(thf)₂] have been highlighted for the first time in this type of coupling. [Ba{E(SiMe₃)₂}.(thf)₂] (E = N, CH) are more efficient than [{N^{DiPP}}Ba{E(SiMe₃)₂}.(thf)₂] (E = N, CH) complexes (where {N^{DiPP}} = {ArN(o-C₆H₄)C(H)=NAr} with Ar = 2,6-*i*Pr₂-C₆H₃) bearing an iminoanilide ligand, and alkyl precatalysts show better efficiency than amido analogues (due to its more basicity). It has been proved that barium outperforms its calcium and strontium analogues from activity and selectivity point of view (Ca < Sr < Ba).^{148,151} This is related to the size and the electron density of the metal center. Barium is more accessible as the metal center and the Ae–N bond is weaker upon going down the group 2 metals. This has been also established *via* DFT calculations.

Recently Hill and Manners reported the synthesis of ferrocene-containing polycarbosilazanes (such as FeCp(Cp(SiPh(NHBn)₂)) (Bn = CH₂(C₆H₅)), and Fe(Cp(SiPh(NHBn)₂))₂) through dehydrocoupling of silanes and amines catalyzed by different types of Ae complexes including [Ae(N(SiMe₃)₂)₂}.(thf)₂] (Ae = Ca, Sr, Ba) and [Ae(CH(SiMe₃)₂)₂}.(thf)_x] (Ae = Ca, Sr x = 2; Ba, x = 3).¹⁵² As shown by our group, [Ba{CH(SiMe₃)₂}]₂}.(thf)₂] proved the most effective precatalyst

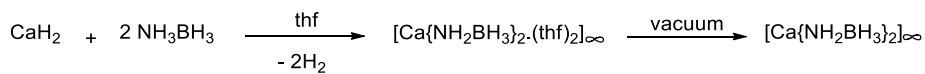
for the synthesis of linear or cyclic polycarbosilazanes resulting from the dehydropolymerization of *p*-xylylenediamine ($\text{H}_2\text{N}^{\wedge}\text{NH}_2$) and Ph_2SiH_2 (Scheme 1.15).¹⁵³



Scheme 1.15. Dehydropolymerization of Ph_2SiH_2 and $\text{H}_2\text{NCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2$ catalyzed by $[\text{Ba}\{\text{CH}(\text{SiMe}_3)_2\}_2.(\text{thf})_2]$.¹⁵³

1.5.2.2

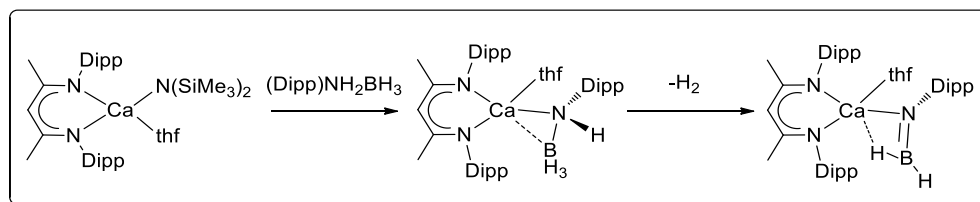
Due to the possible use of amine-borane adducts (especially NH_3BH_3) as a hydrogen-storage source containing high hydrogen content (19.6 wt%),^{77c,132a,154} the main group metal amidoboranes have attracted intense attention since they have high potential to serve as hydrogen storage materials for clean energy applications. Burrell and co-workers have reported the first Ae amidoborane in 2007 as $[\text{Ca}\{\text{NH}_2\text{BH}_3\}_2.(\text{thf})_2]_\infty$ polymer that eliminates coordinated thf under vacuum (Scheme 1.16).¹⁵⁵



Scheme 1.16. Synthesis of the first calcium amidoborane.¹⁵⁵

The elimination of molecular hydrogen in salt-like early main group amidoboranes (like LiNH_2BH_3 , NaNH_2BH_3 and $\text{Ca}(\text{NH}_2\text{BH}_3)_2$) has advantages over neutral NH_3BH_3 including: (a) lower hydrogen release temperature (120 °C–170 °C for $[\text{Ca}\{\text{NH}_2\text{BH}_3\}_2]$); (b) no contamination with borazine ($\text{B}_3\text{H}_6\text{N}_3$, a cyclic compound in which the three BH units and three NH units alternate) as by-product); (c) the dehydrogenation process is less exothermic than for NH_3BH_3 (3–5 $\text{kJ}\cdot\text{mol}^{-1}$ compared to 22.5 $\text{kJ}\cdot\text{mol}^{-1}$). Since 2008, Harder and co-workers have studied the amidoboranes based on the Ae heteroleptic complexes containing large β -diketiminato ligand.¹⁵⁶ Harder has also investigated the substitution on nitrogen which reveals the following trends: the

increase in the steric bulk increases the length of the Ca–N bond and the decomposition temperature related to H₂ release; the B–N bond length is not affected from the nitrogen substitution.¹⁵⁷ The β -diketiminato-supported calcium complex ($[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2(\text{thf})]$) was reacted with aminoborane ((DiPP)NH₂BH₃, DiPP = 2,6-*i*Pr₂-C₆H₃), and after elimination of H₂, the resulting monomeric calcium amidoborane was isolated with a borylamide anion (RN=BH₂[−]) in which the B–H hydride atom interacts with the calcium atom (Scheme 1.17).



Scheme 1.17. Calcium amidoborane complex containing a large β -diketiminato ligand (DiPP = 2,6-*i*Pr₂-C₆H₃).¹⁵⁷

Hill *et. al.* demonstrated that $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2(\text{thf})]$ reacts with *t*-BuNH₂BH₃ to form the corresponding primary amidoborane ($[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{(\text{t-Bu})\text{NHBH}_3\}(\text{thf})]$, Figure 1.16). They have proposed a metal-mediated mechanism for the catalyzed dehydrocoupling of the aminoboranes based on his investigations, as presented in Scheme 1.18.¹⁵⁸ This mechanism shows the formation of the amido-borane catalytic species from the precatalyst and Me₂NH.BH₃, followed by first a β -elimination of the Me₂N=BH₂ product. Once formed, Me₂N=BH₂ can again react with the amido-borane species by insertion into the metal–N bond followed by a δ -elimination to afford the cyclic product obtained.

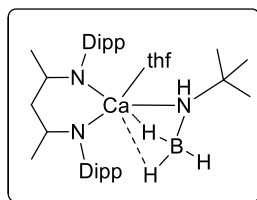
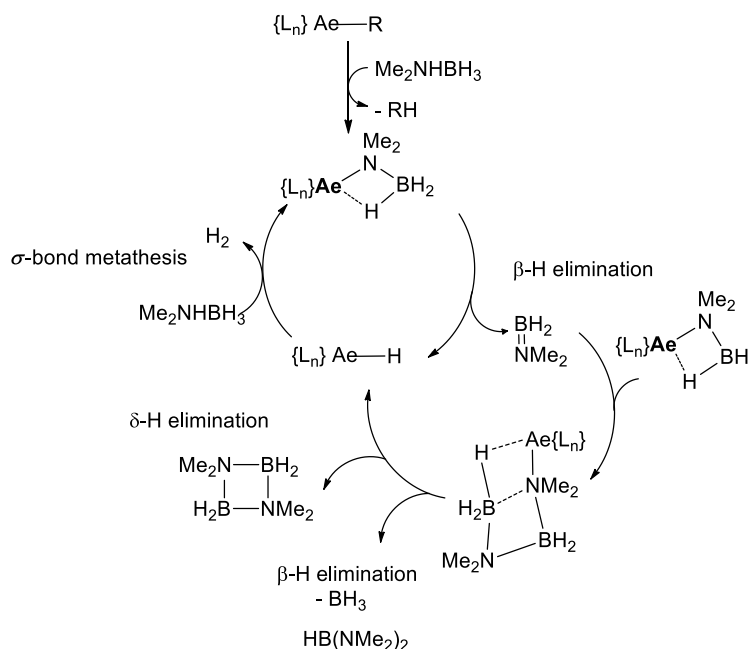


Figure 1.16. β -diketiminato calcium *tert*-butylamidoborane ($[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{(\text{t-Bu})\text{NHBH}_3\}(\text{thf})]$) (DiPP = 2,6-*i*Pr₂-C₆H₃).¹⁵⁸

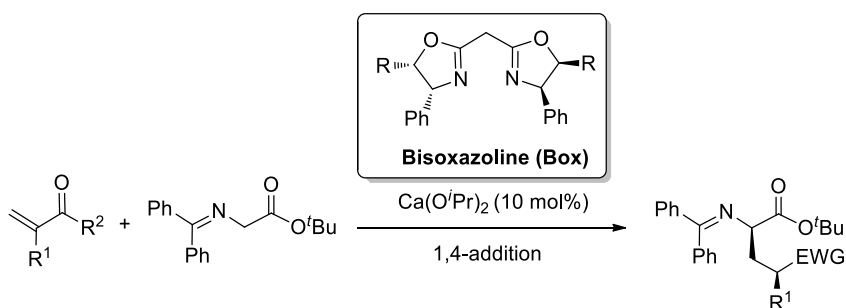


Scheme 1.18. Mechanism of the s-block-catalyzed release of dihydrogen through aminoborane dehydrocoupling ($\{Ln\} = \{BDI^{Dipp}\}^-$, (DiPP = 2,6-*i*Pr₂-C₆H₃)).¹⁵⁸

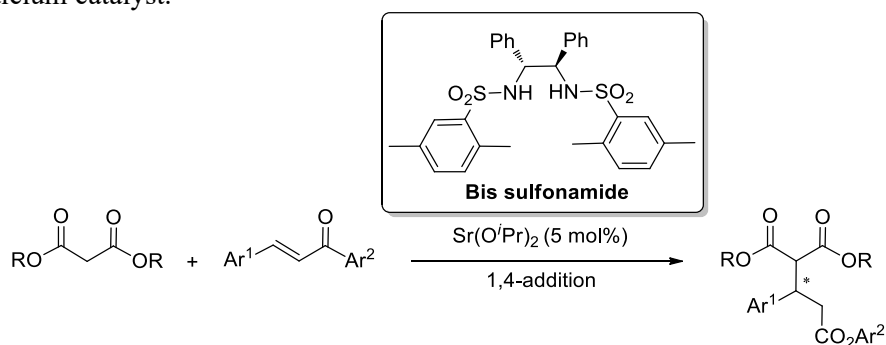
1.5.3 Enantioselective catalysis

The low electronegativity of Ae metals is the reason for strong Brønsted basicity of their counteranions and leads to their activity in deprotonation. Their Brønsted basicity increases upon descending down the group, hence the barium-associated bases show the highest Brønsted basicity (Ba > Sr > Ca). Both the Lewis acidity and the Brønsted basicity are important characteristics to give them the potential to provide acid-base catalysts. Due to the large ionic radius of Ae metals, flexible coordination geometries are possible for their chiral modifications. The tuning of the chiral ligand structure allows the preparation of some enantioselective metal catalysts. In 1998 Shibasaki and Yamada reported that the chiral barium complexes are suitable catalysts for asymmetric aldol reactions.¹⁵⁹ Kobayashi *et. al.* have used chiral bisoxazoline (Box) derivatives to promote catalytic asymmetric 1,4-addition reactions with high diastereo- and enantioselectivities (Scheme 1.19). Moreover, they have reported asymmetric 1,4-addition reactions with high enantioselectivities catalyzed by chiral strontium-bis-sulfonamide (Scheme 1.20) and chiral barium-BINOLate (BINOL = 1,1'-Bi-2-naphthol) complexes (Scheme 1.21). Kobayashi has also revealed that pyridinebisoxazolines (Pybox) served as excellent ligands for

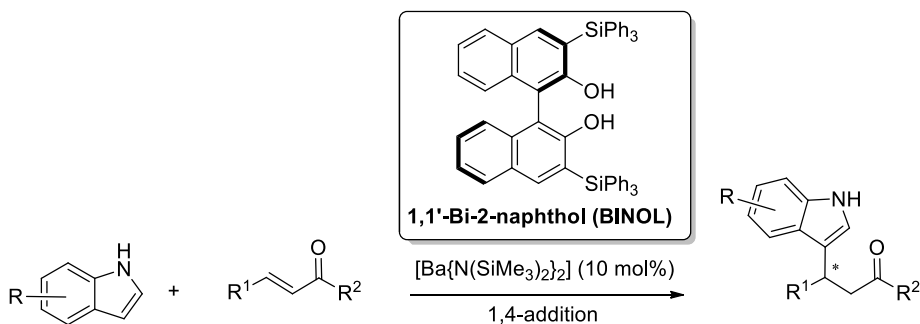
calcium compounds in 1,4-addition reactions and Mannich reactions with enantioselective protonation (Scheme 1.22).^{160,161,162} Kazmaier has also investigated this type of reactivity.¹⁶³



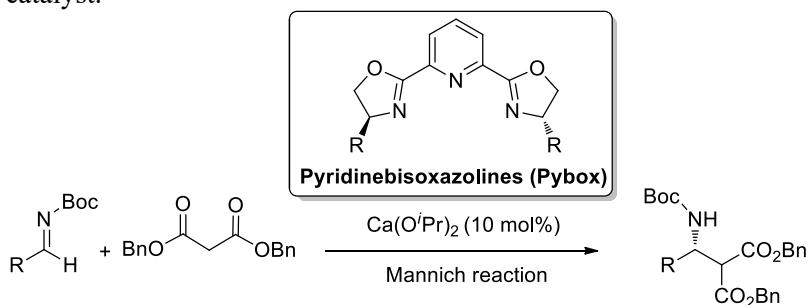
Scheme 1.19. Asymmetric 1,4-addition of a Schiff base of a glycine ester with acrylate derivatives using a chiral (Box) calcium catalyst.



Scheme 1.20. Asymmetric 1,4-addition of a malonate using a chiral (bissulfonamide) strontium catalyst.



Scheme 1.21. Asymmetric 1,4-addition of indole derivatives with chalcone derivatives using a chiral (BINOLate) barium catalyst.



Scheme 1.22. Asymmetric Mannich reaction of a malonate using a chiral (Pybox) calcium catalyst.

Harder *et. al.* investigated the enantioselective hydrosilylation and intramolecular hydroamination of alkenes using chiral Ca-catalyst including bisoxazoline (BOX) [$\{(S)\text{-Ph-BOX}\}\text{CaN}(\text{SiMe}_3)_2(\text{thf})_2$].¹⁶⁴ Ward co-workers used chiral heteroleptic calcium complexes bearing bis(oxazolinyphenyl)amine (BOPA) ligand for the enantioselective hydroamination of aminoolefins (Figure 1.17).¹⁶⁵ However, the stereoselective catalysis by Ae metals has not been much developed and there is still a lot to be explored.

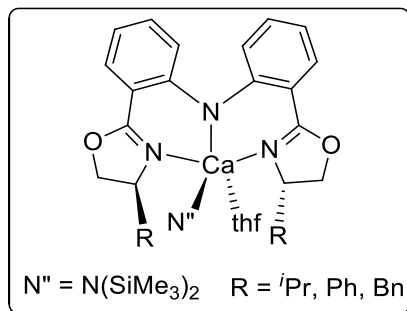


Figure 1.17. Structure of calcium heteroleptic complex including bis(oxazolinyphenyl)amine (BOPA) ligand [$\{\text{R-BOPA}\}\text{CaN}(\text{SiMe}_3)_2\} \cdot (\text{thf})$].

1.6 Summary

In conclusion, this chapter points out the characteristics and applications of Ae organometallic compounds in homogeneous catalysis. According to their features such as their large ionic radii, electropositive and oxophilic nature, the heteroleptic complexes of the type $[\{L_n\}AeR]$ undergo Schlenk equilibrium, hence, their stability in solution is of great importance considering their kinetic lability and ligand scrambling. This kinetic redistribution problem can be overcome by using a suitable ligand that has different qualities to coordinate to the metal center or provide suitable interactions to stabilize the complex through its bulkiness, denticity, heteroatoms and/or secondary interactions. Thus, there is still the need to design appropriate ligand platforms that will result in stable Ae organometallic compounds. Moreover, their other major field of interest is in their application in original catalytic reactions.

My PhD research has been developed in these two directions. Hence, as presented in Chapter 2, fluorinated aryl ligands have been used for the stabilization of low-coordinate calcium and barium complexes (both homoleptic and heteroleptic) through $Ae \cdots F-C$ secondary interactions. Several compounds have been synthesized and characterized *via* X-ray diffraction, NMR and FTIR spectroscopies and structural analysis was further complemented by DFT calculations. Finally, the reactivity of some of the resulting heteroleptic Ae complexes has been evaluated through the benchmark hydrophosphination reaction of styrene with diphenylphosphine. According to the proposed mechanisms for hydrophosphination reaction by Ae metals, during the initial protonolysis, the amide ($N(C_6F_5)_2^-$) will be replaced by the phosphide (PPh_2^-) to create the catalyst (active species). Therefore, the importance of the role of $N(C_6F_5)_2^-$ will not be to stabilize the active species in the catalytic cycle. However, one of the challenges in hydrophosphination reactions is to avoid the formation of the $[Ae\{PPh_2\}_2]$ species which precipitates and affects the catalytic turnovers. The comparable pK_a of $N(C_6F_5)_2^-$ ($pK_a = 23.97$) and (PPh_2^-) ($pK_a = 22.9$) limits the formation of $[Ae\{PPh_2\}_2]$ species in the solution.

Chapter 3 will illustrate the design of new iminoaniline and amidine prolignands for the preparation of the corresponding barium heteroleptic complexes. The corresponding multidentate monoanionic ligands have been shown to provide the required bulkiness around the barium center to provide stable original Ae derivatives. The $N(SiMe_2H)_2^-$ group has been used as the reactive coligand, and it is shown that it contributes to the stability of the precatalysts through

favorable Ba $\cdots$ H–Si secondary interactions. The performance of the resulting complexes have then been examined in different benchmark intermolecular hydrophosphination reactions.

1.7 References

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Chapter 2

Low-coordinate alkaline earth fluoroarylamides containing $\text{Ae} \cdots \text{F}-\text{C}$ secondary interaction

A portion of this chapter has appeared in print:

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Chapter 2: Low-coordinate alkaline earth fluoroarylamides containing $\text{Ae}\cdots\text{F}\cdots\text{C}$ secondary interactions

2.1 Introduction

The main objective of the work described in this chapter was to prepare and study new, low-coordinate Ae complexes (Ae = Ca, Sr, Ba) stabilized by fluorine-enriched ligand and without coordinated solvent. Hence, the role of weak $\text{Ae}\cdots\text{F}\cdots\text{C}$ secondary interactions towards the stabilization of the sought compounds was probed. The catalytic activity of the resulting complexes was illustrated in the benchmark intermolecular hydrophosphination of styrene with diphenylphosphine.

2.1.1 Hard donor ligands for Ae metals

The low charge/size ratio of Ae metals gives them a tendency for high coordination numbers or for the formation of aggregated structures. The utilization of bulky, multidentate ligands improves the kinetic stability of the complex. The key to the stabilization of heavier Ae heteroleptic complexes is to control over the Schlenk equilibrium by means of ancillary ligand. The ligand could be bi- or multidentate to prevent the ligand scrambling in the solution thereby improving the thermodynamics. Furthermore, applying the bulky ligand leads to encapsulating the metal center through steric hindrance in order to avoid the formation of homoleptic species ultimately improving the kinetics. Achieving this goal is more challenging for larger Ae metals. According to the electropositive character of the Ae metals, they form hard ions which preferentially bind to the hard donor atoms like oxygen and nitrogen; hence ligands such as alkoxides and phenoxides (*O*-donors) and amides (*N*-donors) tend to be the most suitable to generate Ae complexes, while softer donor atoms like phosphorus (P) and sulfur (S) are not commonly encountered.

2.1.1.1 *N*-based ancillary ligands

As previously mentioned in chapter 1, the ionic and weak nature of the bonds between the ligand and Ae metals easily leads to ligand exchange in solution. Ae complexes used in molecular catalysis are mostly heteroleptic compounds of the type $[\{\text{L}\}\text{Ae}-\text{R}]$, in which R is the reactive ligand (such as amide, alkyl, alkoxide, hydride) and L is an ancillary ligand that controls the

coordination sphere and influences the Lewis acidity of the metal. The ancillary ligand is usually bi- or multidentate. Simple alkoxides are usually avoided since they lead to the formation of insoluble oligomers. Over the years, nitrogen-based ligands have emerged as a better option to generate stable and soluble well-defined Ae complexes.¹

The most well-known bidentate *N*-donor ligand used to successfully stabilize heteroleptic Ae complexes is the β -diketiminate $\{\text{BDI}^{\text{Dipp}}\}^-$ ($\{\text{BDI}\} = [\text{H}_2\text{C}\{\text{C}(\text{Me})\text{N}-2,6-(i\text{Pr})_2\text{C}_6\text{H}_3\}_2]$). This ancillary ligand has been largely used for the preparation of both main group and transition metal complexes and allows tuning the steric and electronic properties of the complex. In particular, it was very efficient in affording a stable four-coordinate complex of calcium, namely the ubiquitous ($[\{\text{BDI}^{\text{Dipp}}\}\text{CaN}(\text{SiMe}_3)_2(\text{thf})]$ (Dipp= 2,6-*i*Pr₂-C₆H₃) (Figure 2.1, I).² The strontium and barium analogues were found to be kinetically unstable in solution.³

The presence of the solvent in the coordination sphere of the metal center increases the coordination number and the steric hindrance. It also reduces the Lewis acidity of the metal center. These are major drawbacks for potential applications in homogeneous catalysis. Therefore, the removal of this coordinated solvent is a valuable strategy to obtain electrophilic complexes that will display enhanced performances as molecular catalysts.

Hill and co-workers have used the solvent-free calcium complex $[\{\text{BDI}^{\text{Dipp}}\}\text{CaN}(\text{SiMe}_3)_2]$ (Figure 2.1, II) to prepare the solvent-free calcium hydride $[\{\text{BDI}^{\text{Dipp}}\}\text{CaH}]_2$.⁴ In the $[\{\text{BDI}^{\text{Dipp}}\}\text{CaN}(\text{SiMe}_3)_2]$ complex, there are intramolecular ($\text{Ca}\cdots\text{C} = 2.964(4) \text{ \AA}$) and intermolecular contacts ($\text{Ca}\cdots\text{C} = 2.999(5) \text{ \AA}$) between the metal center and the methyl group of the hexamethyldisilazide moiety that create a tetrameric structure in the crystals of the solid state. This Ca-hydride is in turn much more active than its thf adduct $[\{\text{BDI}^{\text{Dipp}}\}\text{CaH}(\text{thf})]_2$ ⁵ in order to generate Ca-alkyl species *via* a consecutive polarized C=C insertion into a Ca–H bond and deprotonation pathway ($[\{\text{BDI}^{\text{Dipp}}\}\text{CaR}]_2$, Scheme 2.1).^{2h,6,7,8,9,10}

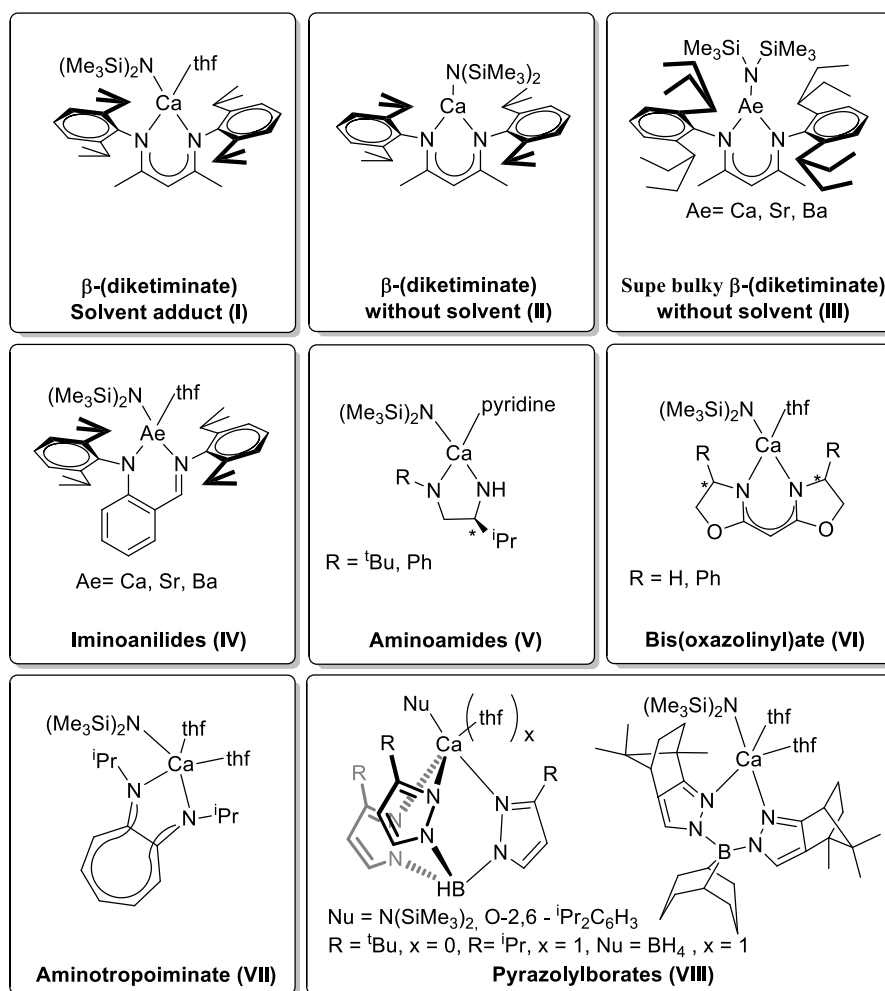
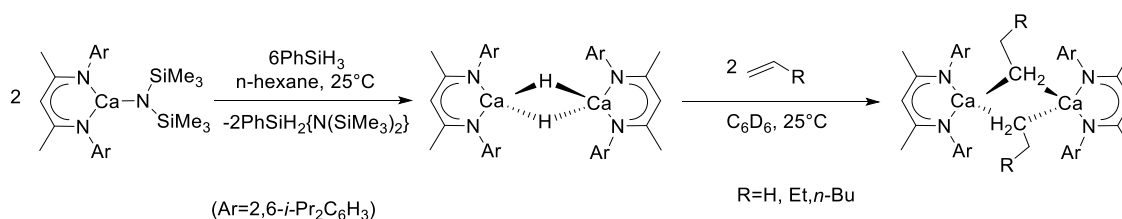


Figure 2.1. Examples of Ae complexes bearing chelating N-based ligands.^{2,4,12,13,14,15,16,17,18,19}



Scheme 2.1. Synthesis of Ca-alkyl from solvent-free $[\{\text{BDI}^{\text{DIPP}}\}\text{CaN}(\text{SiMe}_3)_2]$ complex.^{2h,6,7,8,9,10}

Hill *et. al.* recently reported the reactions of dimeric β -diketiminato magnesium and calcium hydrides ($[(\text{BDI})\text{MgH}]_2$ and $[(\text{BDI})\text{CaH}]_2$) with a β -diketiminato magnesium cation paired with the weakly coordinating anion ($[(\text{BDI})\text{Mg}]^+[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$) that provided ionic multimetallic

hydride derivatives. They have been subsequently used for hydrosilylation of 1-hexene and diphenylacetylene.¹¹

Beyond Hill's seminal β -diketiminato ligand, Harder and co-workers used a very bulky β -diketiminato ligand of $\{\text{BDI}^{\text{DIPeP}}\}^-$ ($\text{CH}[\text{C}(\text{Me})\text{N-DIPeP}]_2$, DIPeP = 2,6-di-*iso*-pentylphenyl) to prepare solution stable heteroleptic Ae complexes through direct deprotonation of the proligand $\{\text{BDI}^{\text{DIPeP}}\}\text{H}$ with $[\text{Ae}\{\text{N}(\text{SiMe}_3)_2\}_2]$ or $[\text{Ae}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{thf})_2]$ (Ae = Ca-Ba; Figure 2.1, **III**).¹² Among the heavy alkaline-earth metals, this bulky β -diketiminato $\{\text{BDI}^{\text{DiPP}}\}^-$ ligand enabled the calcium derivative to be stable against ligand exchange in solution, while the heavy barium alike complex prepared with this latter ligand ($\{\text{BDI}^{\text{DIPeP}}\}^-$) as $[\{\text{BDI}^{\text{DIPeP}}\}\text{BaN}(\text{SiMe}_3)_2]$ was very stable even at 140°C for two weeks.

The sterically hindered iminoanilide $\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}^-$ ($\{\text{N}^{\wedge}\text{N}\} = [\text{DippN}(o\text{-C}_6\text{H}_4)\text{C}(\text{H})=\text{NDipp}]$) with the similar concept of bidentate ligand, was used by our group to prepare the calcium complex of $[\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2\cdot(\text{thf})]$ and its congeneric Sr and Ba complexes; they were used to catalyze olefin hydroamination and hydrophosphination reactions (Figure 2.1, **IV**).^{13,14,15} We could also mention other effective catalytic calcium precatalysts supported by nitrogen-based ligands such as aminoamides (Figure 2.1, **V**),¹⁶ chiral bis(oxazolinyl)ates (Figure 2.1, **VI**),¹⁷ aminotroponimate (Figure 2.1, **VII**)¹⁸ and tris(pyrazolyl)borates (Figure 2.1, **VIII**).¹⁹

2.1.1.2 O-based ancillary ligands

As mentioned in chapter 1, one of the Ae-based catalytic systems effective for organic transformations includes heteroleptic complexes supported by multidentate *phenolates* (*O*-donors). There are several contributions by our group in this area, and many stable and effective heteroleptic complexes of Ae metals have been prepared such as Ae-aminophenolato catalysts illustrated in Figure 2.2. The behavior of these ether-phenolato complexes has been studied in different catalytic reactions like intermolecular hydrophosphination of activated alkenes and Ae-mediated inter- and intramolecular alkene hydroaminations.^{13,20}

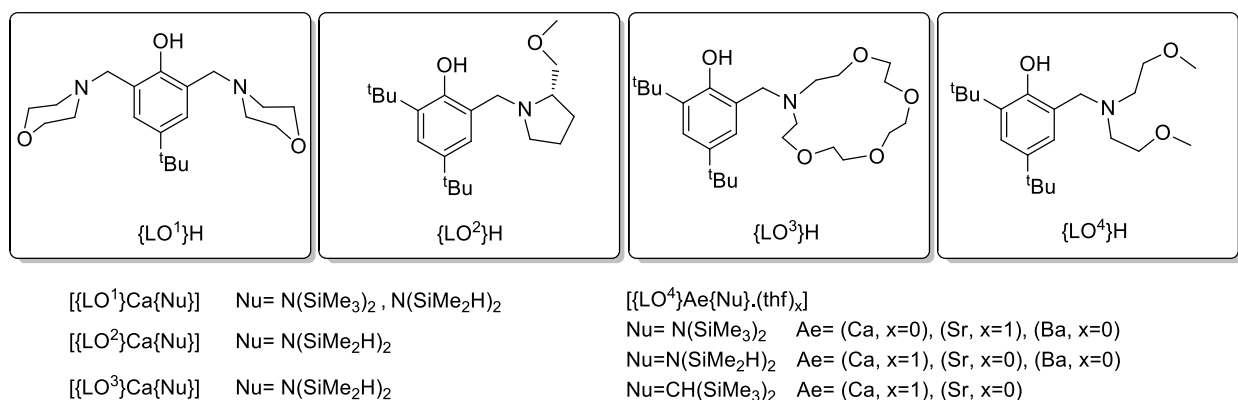


Figure 2.2. Multidentate aminophenol proligands and their related Ae heteroleptic complexes $[\{LO^n\}Ae\{Nu\} \cdot (thf)_x]$.^{13,20}

One could also refer to the heteroleptic amido complex $[\{ONO\}CaN(SiMe_3)_2 \cdot (thf)]$ that has been prepared and applied in the ring-opening polymerization (ROP) of lactide; it showed better performance than its homoleptic bis(amido) precursor $[Ca\{N(SiMe_3)_2\}_2 \cdot (thf)_2]$ (Figure 2.3).²¹ This highlights the valuable effect of the phenoxy-iminophenolate ligand framework in terms of activity/productivity.

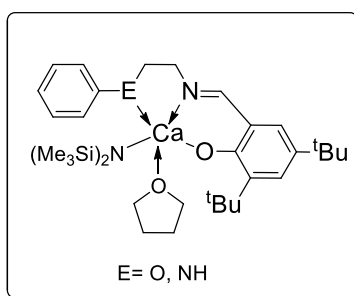
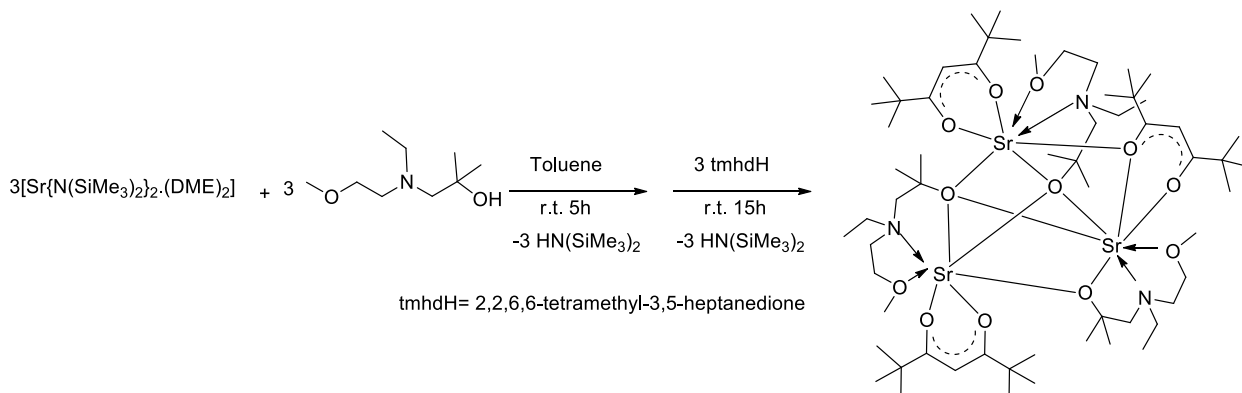


Figure 2.3. Heteroleptic Ae complexes $[\{ONO\}CaN(SiMe_3)_2 \cdot (thf)]$ prepared from multitdentate phenolates.²¹

In the case of *alkoxides* as other type of *O*-donor ligands, because of the high Lewis basicity and donating ability of the oxygen atoms, highly aggregated (and often insoluble) structures and complex mixtures often result from the propensity of *O*-based ligands to act as bridging ligands.²² For instance, one of the largest aggregations for alkoxide complexes in the literature is the first molecular calcium dialkoxide $[Ca_9(OCH_2CH_2OMe)_{18}(HOCH_2CH_2OMe)_2]$ that is

prepared from calcium fillings and 2-methoxyethanol.²³ The molecular structure includes three 6-coordinate and six 7-coordinate calcium atoms.

The work of Kim and Chung *et. al.* exemplifies monometallic non-fluorinated Ae alkoxide complexes. These authors succeeded in reducing the degree of aggregation down to three through utilization of β -diketonates and aminoetheralkoxides and they prepared the solvent-free heteroleptic strontium-alkoxide complexes (Scheme 2.2).²⁴



Scheme 2.2. Synthesis of trimeric heteroleptic strontium complex including β -diketonates and donor functionalized alkoxide.²⁴

Hanusa reported another monometallic complex with calcium [$\{\text{clox}\}\text{CaN}(\text{SiMe}_3)_2(\text{thf})_3$] (clox = $\text{OC}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}_6\text{H}_4\text{Cl}$), obtained from potassium alkoxide and calcium iodide. Some coordinated thf is present to satisfy the coordination sphere of the metal center in the monomeric structure (Figure 2.4).²⁵

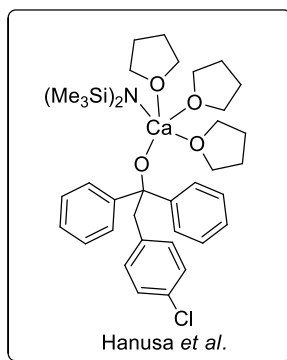


Figure 2.4. Calcium non-fluorinated alkoxo complex.²⁵

Recently, in our group, the two-coordinate barium complex $[\text{Ba}\{\text{OB}(\text{CH}(\text{SiMe}_3)_2)_2\}_2]$ bearing the very bulky boryloxide $\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{BO}^-$ has been synthesized.^{26,27} In the boryloxide, the geometry of the oxygen π orbitals enables the delocalization of its lone pairs in the vacant $2p_z$ orbital at boron. Therefore, the electron density on the oxygen is reduced in comparison with classical alkoxides and, correspondingly, it decreases the propensity of the oxygen to act as a bridging atom between several metal centers. This has proved a beneficial characteristic that limits the formation of bridged polynuclear species and aggregations in Ae chemistry (Figure 2.5).

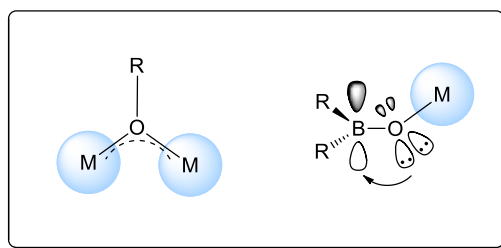


Figure 2.5. Schematic representation of the electronic differences between metal alkoxide (left) and boryloxide (right).

Besides, the presence of the boron atom in the α position of oxygen adds space between the metal and the R groups of the ligand. This relative distance allows the use of two very large R groups to avoid the aggregation of the complexes (Figure 2.6). Hence, bulky boryloxides have been utilized as proligands to prepare low coordinate, soluble and highly electrophilic barium complexes.

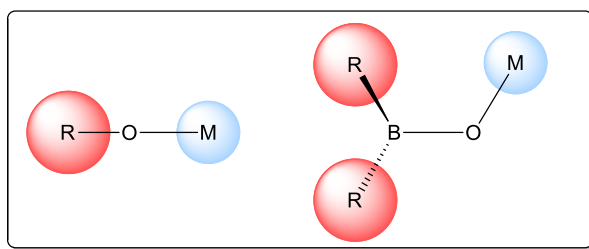
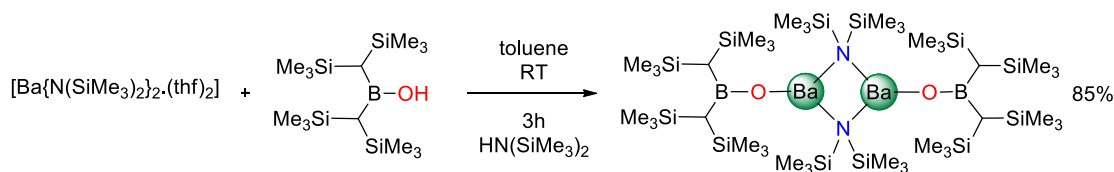


Figure 2.6. Schematic representation of the steric differences between alkoxide and boryloxide.

As shown recently in our group, the equimolar reaction of $\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{BOH}$ with $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{thf})_2]$ affords the heteroleptic dimer $[\text{Ba}\{\mu\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2$ (Scheme 2.3). The effect of the delocalization of N -electrons into antibonding σ ($\text{Si}-\text{C}^*$) orbitals

in $\text{N}(\text{SiMe}_3)_2^-$ is more limited than that of the partial delocalization of O -electrons into the empty p_z orbital at boron in the boryloxide. Therefore, the two hexamethyldisilazide groups are taking the bridging positions between the two metal centers. For further stabilization of the coordinatively unsaturated barium complex $[\text{Ba}(\text{OBR}_2)_2]$, $\text{Ba}\cdots\text{H}_3\text{C}$ anagostic bonds have been shown to play an important role.^{26,27}



Scheme 2.3. Synthesis of heteroleptic barium boryloxide complex $[\text{Ba}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2$.^{26,27}

2.1.2. On the benefits of using fluorinated ligands

Based on the strong C–F bond ($\text{BDE} = 123 \text{ kcal}\cdot\text{mol}^{-1}$), and also on the hydrophobic nature of fluorine, the fluorocarbons have high moisture and thermal tolerance. The possibility to establish an $\text{Ae}\cdots\text{F}-\text{C}$ secondary interaction could also decrease the need of the metal for the presence of the co-ligand and thereby gives stable complexes with less ligands and relatively lower molecular weights. Fluorine atoms have a tight binding of their valence electrons, low polarizability which results in low surface energies and weak cohesive forces between fluorocarbon molecules.²⁸ Therefore, they are suitable chemical vapor deposition (CVD) precursors for inorganic nanomaterials.^{22,29} There are some structurally simple fluorinated alcohols used for this purpose such as $\text{Me}_2(\text{CF}_3)\text{COH}$, $\text{Me}(\text{CF}_3)_2\text{COH}$, $\text{Ph}(\text{CF}_3)_2\text{COH}$ or $(\text{CF}_3)_3\text{COH}$.^{30,31} The electrostatic nature of the $\text{Ae}\cdots\text{F}-\text{C}$ interaction gives extra electron density and a better satisfied coordination sphere of the Ae metal center and therefore significantly contributes to the stabilization of the complexes. Noteworthy, fluorine is active in NMR spectroscopy, thereby providing valuable structural information. Finally, the $\text{M}\cdots\text{F}-\text{C}$ interaction is often detected in the X-ray structure of metallic complexes.

In organofluorine compounds, the C–F bond is highly polarized ($\text{C}^{\delta+}-\text{F}^{\delta-}$) because of the electronegativity difference between carbon and fluorine (2.5 vs 4.0), so fluorine interacts electrostatically with its environment. Fluorine is a Pearson-type hard donor and coordinates to

hard metal cations (*e.g.* K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+}).³² In 1983, based on the analysis of crystal structures, Glusker concluded that: “We believe that the C–F bond is capable of significant, if not prominent, interactions with both alkali metal cations and proton donors.” He also mentioned the possibility of the same interaction with alkaline earth metals.³³ Later, Plenio extended this investigation to solution by NMR spectroscopy analysis, in order to enlighten whether this interaction is just the result of the packing forces in the crystal or if the $M\cdots F-C$ interaction could really affect the stability of the complex.³⁴ These studies demonstrate that the stability of the Ae complexes with partially fluorinated ligands is significantly higher than that of alike hydrogenated Ae complexes, thereby evidencing the interaction of the metal with the F–C bond.³⁵ All these experimental data indicate that fluorine is an efficient donor for the coordination sphere of hard metal ions. DFT calculations indicated strong intramolecular interactions between the Ae metal ion and the fluorine atoms in the fluoroalkoxide cationic complexes of $[\{RO^4\}Ae]^+[H_2N\{B(C_6F_5)_3\}_2]^-$ (Ae = Mg, Ca, Sr, Ba) (Figure 2.7).^{20c} In the case of the calcium complex, the crystal structure shows relatively short distances for $Ca\cdots F-C$ interactions in the range 2.664(3)–2.681(4) Å.

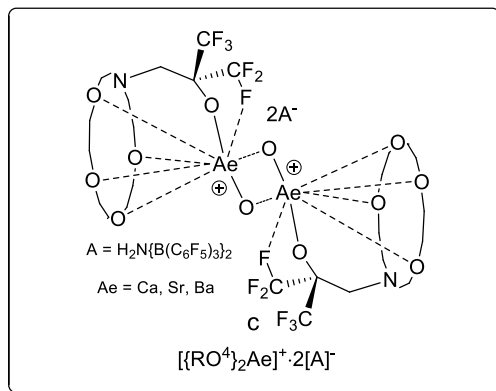


Figure 2.7. Fluorinated alkoxo complex containing intramolecular $Ae\cdots F-C$ interactions.^{20c}

The usually accepted significant “threshold” for $Ae\cdots F-C$ interaction is defined according to Table 2.1 based on the Plenio’s studies.³⁶

Table 2.1. Ae...F–C interaction parameters according to Plenio.

Ae metal	r_{ion}^a	d_{min}^b	d_{max}^c
Ca ²⁺	1.06	2.53	3.13
Sr ²⁺	1.26	2.73	3.30
Ba ²⁺	1.52	2.99	3.48

^a r_{ion} [Å] is the ionic radius of the metal ion (according to Shannon ³⁷)

^b d_{min} [Å] is the sum of the ionic radius of the respective metal ion (r_{ion}) and the van der Waals radius of fluorine (1.47 Å).

^c d_{max} [Å] is the maximum metal-fluorine distance considered in Plenio's study and it is the sum of the van der Waals radii of fluorine (1.47 Å) and the ionic van der Waals radii by Kollman.

In order to provide Ae...F–C interaction within the complex, it is necessary to have fluorinated ligands such as CF₃ or C₆F₅. These ligands have electron-withdrawing effect that reduces the propensity for the formation of polymetallic species.

2.1.2.1 Fluorinated alkoxides

In order to decrease the degree of aggregation, fluorinated groups like CF₃ are introduced in α position of the O_{alkoxide} atom to generate fluoroalkoxides. CF₃ is an electron-withdrawing moiety which generates intra- and intermolecular repulsions and also decreases the bridging of the oxygen atom by reducing its π donating ability.^{38,39} This strategy is applied in chemical vapor disposition (CVD) to provide volatile material precursors.⁴⁰ Caulton and Ruhlandt-Senge have used highly fluorinated alkoxides to synthesize K, Ca, Sr and Ba homo- and heterobimetallic complexes (ligands: {OC(CF₃)₃}⁻, {OCH(CF₃)₂}⁻, {OCMe(CF₃)₂}⁻, or {OCMe₂CF₃}⁻).^{30,31} Based on X-ray crystallographic data, it can be seen that some stabilization of the resulting low-coordinated species (coordination number = 6–8) is accomplished by Ae...F–C secondary interactions, while the degree of nuclearity decreases. For example, Ruhlandt *et al.* reported highly volatile Ae species based on the perfluorotertbutoxide (PFTB) ligand. The isolated complexes [Ae(PFTB)₂(d)_x]; (d = thf, dimethoxyethane, or diglyme) (for example d = thf, x = 4, Ae = Ca, Sr, Ba) show coordination numbers between six and eight.³⁸

The studies of Chi *et al.* have shown a monomeric solvent-free barium homoleptic complex that has a 10-coordinate environment [$\{\text{RO}^2\}_2\text{Ba}$] ($[\{\text{RO}^2\}\text{H}] = \text{HOC}(\text{CF}_3)_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OMe})_2$, Figure 2.8).⁴¹ In this complex, the ligands consist of oxygen and nitrogen atoms and also involve additional fluorine-to-barium contacts from the

trifluoromethyl groups (CF_3) of the aminoalkoxide ligands with distances of 3.212(3)–3.132(2) Å.

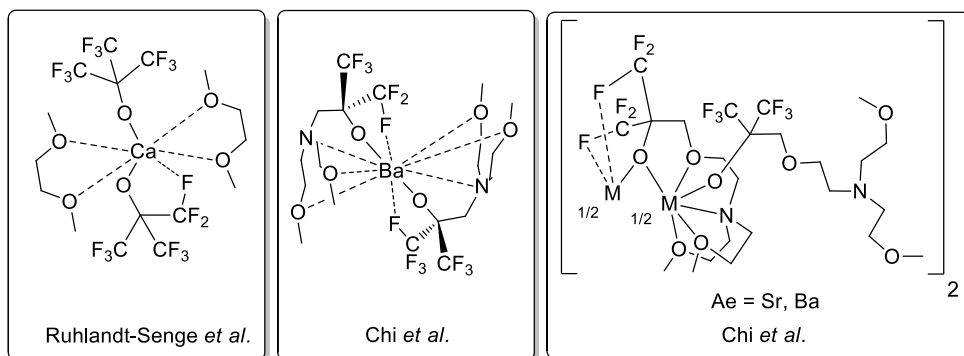


Figure 2.8. Reported Ae (Ca, Sr, Ba) fluoroalkoxo complexes containing intramolecular $\text{Ae} \cdots \text{F}-\text{C}$ interactions.^{38,39,41}

Several fluoroalkoxides have been designed and successfully previously used in our group to prepare alkaline-earth complexes.^{42,43,44,45} Some of the related ligands possessed a methoxy or even an olefinic dangling side-arm (Figure 2.9). These solvent-free complexes owe their stability to the intramolecular, non-covalent $\text{Ae} \cdots \text{C}\pi$, $\text{Ae} \cdots \text{F}-\text{C}$, and anagostic $\text{Ae} \cdots \beta\text{-Si}-\text{H}$ interactions.

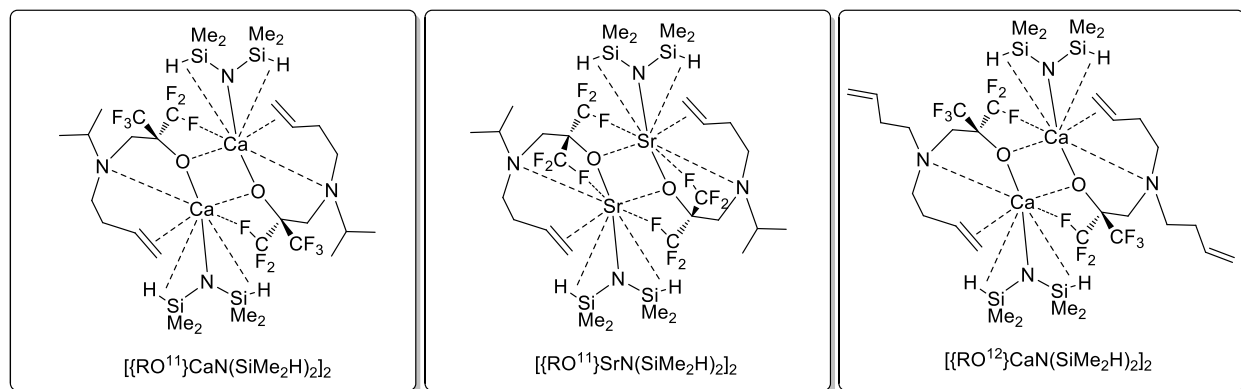
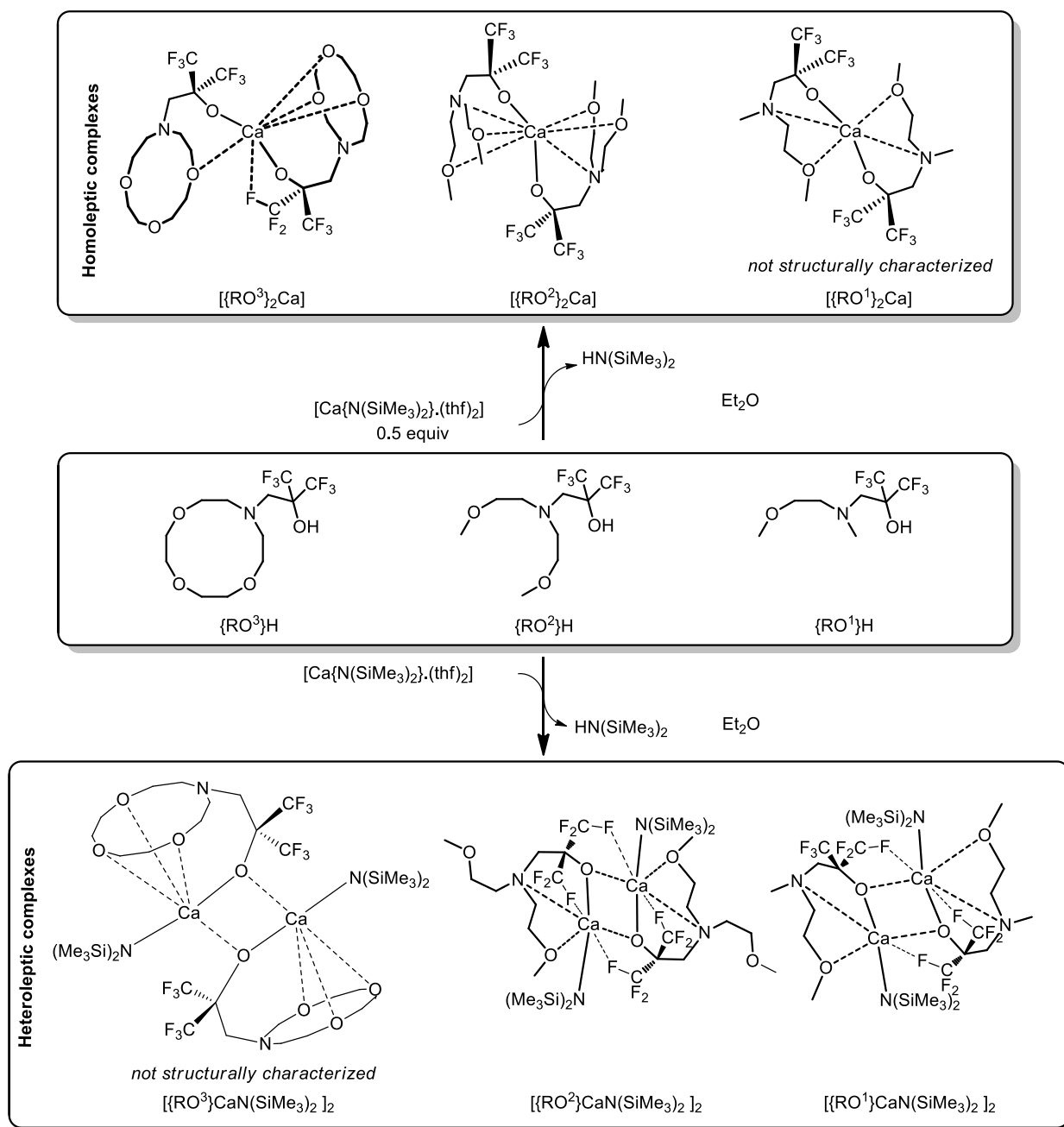


Figure 2.9. Some fluoroalkoxo heteroleptic complexes containing unsaturated $\text{C}=\text{C}$ bond.⁴⁵

Fluorinated aminoetheralkoxides have been used to prepare alkaline-earth heteroleptic complexes featuring $\text{Ae} \cdots \text{F}-\text{C}$ secondary interactions (Scheme 2.4). However, some of these solvent-free heteroleptic calcium complexes were extremely air and moisture sensitive and got hydrolyzed even at the first point of NMR analysis, thus precluding their complete characterization.



Scheme 2.4. Some fluoroalkoxide ligands and their related fluoroalkoxo homoleptic and heteroleptic calcium complexes.⁴³

2.1.2.2 Fluorinated arylamides

The fluorinated amides are interesting ligands. They protect the reactive metal center sterically and they may also provide the complex with $\text{Ae} \cdots \text{F}-\text{C}$ interactions for further stabilization of the structure in the absence of coordinated Lewis base. The fluorinated arylamide $\text{N}(\text{C}_6\text{F}_5)_2^-$ was prepared in 1960,⁴⁶ but it has been applied as ligand only at the beginning of this century. Several types of U(III), U(IV) and Ce(III) (i.e. lanthanide/actinide hard metals) complexes including fluorinated arylamides, such as $\text{N}(\text{C}_6\text{F}_5)_2^-$, $\text{N}(\text{SiMe}_3)(o\text{-F-C}_6\text{H}_4)^-$ and $\text{N}(\text{SiMe}_3)(\text{C}_6\text{F}_5)^-$, have been studied by Schelter and co-workers.⁴⁷ Metal $\cdots \text{F}-\text{C}$ interactions have been examined by ^{19}F NMR spectroscopy and computational studies. Using $\text{N}(\text{SiMe}_3)(o\text{-F-C}_6\text{H}_4)^-$ ligand instead of $\text{N}(\text{SiMe}_3)(\text{C}_6\text{F}_5)^-$, gives a more electron rich *ortho*-fluorine atom that leads to a larger C–F bond dipole and therefore, a stronger $\text{Ln} \cdots \text{F}-\text{C}$ interaction (Figure 2.10, **IX**, **X**, **XI**). With the less fluorinated ligand ($\text{N}(\text{SiMe}_3)(o\text{-F-C}_6\text{H}_4)^-$), a more accessible and less sterically hindered complex is expected.

As reported by Schelter *et al.*, DFT calculations have shown that in $\text{N}(\text{SiMe}_3)(o\text{-F-C}_6\text{H}_4)^-$, the *ortho*-fluorine atom is more electron rich than in $\text{N}(\text{SiMe}_3)(\text{C}_6\text{F}_5)^-$ due to the larger electron density on the *ortho*-fluorine atom in $\text{HN}(\text{SiMe}_3)(o\text{-F-C}_6\text{H}_4)$ ligand (Figure 2.11).

The fluorine atoms with relatively more electron density in $\text{N}(\text{SiMe}_3)(o\text{-F-C}_6\text{H}_4)^-$, provide a larger C–F bond dipole, and as a result the $\text{M} \cdots \text{F}-\text{C}$ interaction is stronger; however, it is less sterically hindered and the metal center is thus more accessible.^{47c} Another point to consider is the fact that the high number of electron withdrawing fluorine atoms in the amide $\text{N}(\text{SiMe}_3)(\text{C}_6\text{F}_5)^-$ decreases the basicity of this amide as a ligand compared to $\text{N}(\text{SiMe}_3)(o\text{-F-C}_6\text{H}_4)^-$, which could result in a lower reactivity in catalysis.

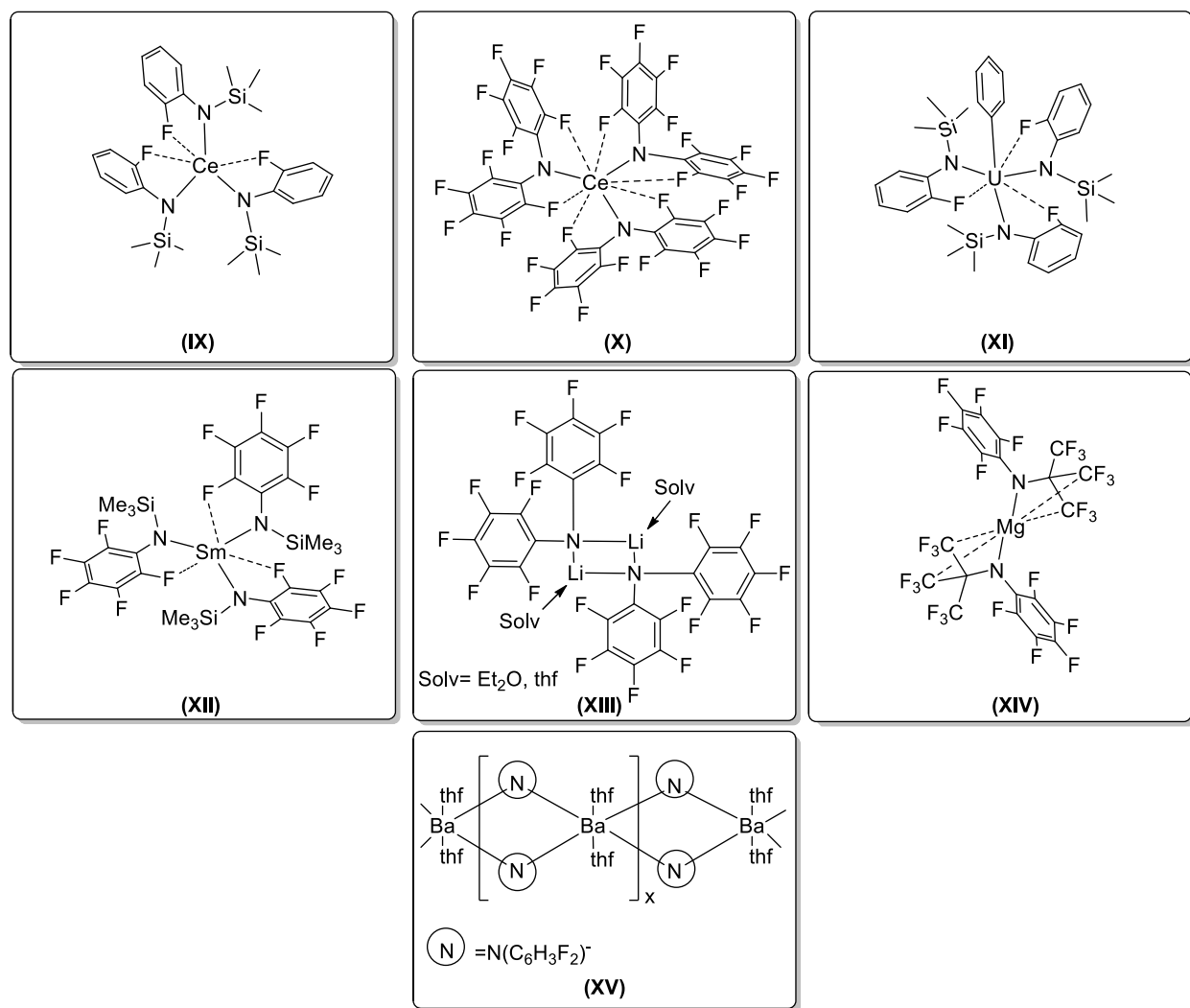


Figure 2.10. Examples of homoleptic fluorinated arylamido complexes.^{47,48,50,51,53}

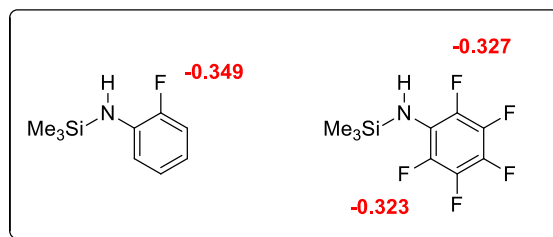


Figure 2.11. Charges on fluorine atoms calculated by DFT computation.^{47c}

Watkin and co-workers have prepared homoleptic complexes using highly fluorinated ligands and highly electrophilic lanthanide metals in which the multiple $\text{Ln}\cdots\text{F}-\text{C}$ interactions ($\text{Ln} = \text{Nd}, \text{Sm}$) were studied by X-ray diffraction analysis (Figure 2.10, **XII**).⁴⁸ They also introduced the use of $\text{N}(\text{C}_6\text{F}_5)_2$ ligand to transition metal chemistry. The resulting complexes exhibited secondary interactions between the fluorine atom in *ortho* positions and the electrophilic metal center as in $[\text{Co}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2]\cdot(\text{py})_2$.⁴⁹ The structure of dinuclear lithium complexes bearing the $\text{N}(\text{C}_6\text{F}_5)_2^-$ ligand along with diethyl ether or thf, $[\text{Li}\{\text{N}(\text{C}_6\text{F}_5)_2\}(\text{solv})]_2$, has been reported by Sundermeyer and co-workers and depicts short intramolecular $\text{Li}\cdots\text{F}-\text{C}$ interactions (Figure 2.10, **XIII**).⁵⁰ They have also reported the preparation of thermally stable and volatile lithium and magnesium complexes from the $\text{N}(\text{C}_6\text{F}_5)(\text{C}(\text{CF}_3)_3)^-$ amide which are believed to be useful in applications such as lithium electrolytes (Figure 2.10, **XIV**).⁵¹ In a further investigation on main group metals, the authors have reported the homoleptic species $\text{Al}[\text{N}(\text{C}_6\text{F}_5)_2]_3$ and $\text{Ga}[\text{N}(\text{C}_6\text{F}_5)_2]_3$ along with their complete characterization.⁵² Using 2,6- $\text{F}_2\text{-C}_6\text{H}_3\text{-NH}_2$, Westerhausen *et al.* have prepared multinuclear solvated Ae complexes that feature intra- and intermolecular $\text{Ae}\cdots\text{F}-\text{C}$ secondary interactions as in $[(\text{thf})_5\text{Ca}_2\{\text{N}(\text{H})\text{-2,6-}\text{F}_2\text{C}_6\text{H}_3\}_4\cdot 2(\text{thf})]$, $[(\text{thf})_6\text{Sr}_2\{\text{N}(\text{H})\text{-2,6-}\text{F}_2\text{C}_6\text{H}_3\}_3\text{I}\cdot(\text{thf})]$ and $[(\text{thf})_2\text{Ba}\{\text{N}(\text{H})\text{-2,6-}\text{F}_2\text{-C}_6\text{H}_3\}]_\infty$ (Figure 2.10, **XV**).⁵³

2.1.3 Objective

Our objective is to design Ae complexes in which the ligand could sufficiently stabilize the metal without requiring the presence of the additional Lewis bases (i.e. solvents like thf). This chapter thus describes the synthesis and characterization of Ae complexes supported by fluorinated arylamides $\text{N}(\text{C}_6\text{F}_5)_2^-$ and $\text{N}(\text{o-F-C}_6\text{H}_4)_2^-$.

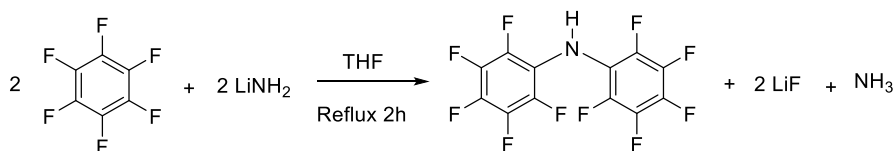
To earn a better understanding of the nature of $\text{Ae}\cdots\text{F}-\text{C}$ contacts, we have first investigated the use of $\text{HN}(\text{C}_6\text{F}_5)_2$, since it is the most fluorinated proligand and therefore it should give a complex with a less accessible metal center. On the other hand, $\text{HN}(\text{o-F-C}_6\text{H}_4)_2$ is expected to provide a more accessible and less sterically hindered site. Application of these two fluorinated arylamides should then prevent the aggregation of the resulting Ae complexes. The fluorinated arylamides provide a robust core including several various potential sites for $\text{Ae}\cdots\text{F}-\text{C}$ secondary interactions to satisfy the coordination sphere of the metal center. Furthermore, $\text{HN}(\text{C}_6\text{F}_5)_2$ and $\text{HN}(\text{o-F-C}_6\text{H}_4)_2$ have a different number of fluorine atoms that could change the Lewis acidity of the metal center and influence the structure and catalytic activity of the resulting complex.

The results presented herein are mainly focussing on the preparation of heteroleptic Ae complexes including bulky ligand frameworks such as β -diketiminates (derived from $\{\text{BDI}^{\text{DiPP}}\}\text{H}$), iminoanilide (from $\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{H}$) and in association with a recent work from our group (PhD thesis E. Le Coz), boryloxide (from $\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{BO}\}\text{H}$) along with fluorinated amides. Both calcium and barium homoleptic complexes have been prepared in order to probe the differences in the bond lengths and the influence of $\text{Ae}\cdots\text{F}-\text{C}$ secondary interactions according to the size of the metal center. Structural analysis of the bonding patterns has been performed by spectroscopic and crystallographic methods, supported by complementary DFT computations and bond valence sum analysis. Besides, the potential of the resulting calcium heteroleptic complexes to act as molecular catalysts has been assessed on benchmark reactions, such as the hydrophosphination of styrene with diphenylphosphine.

2.2 Synthesis of Ae fluoroarylamides

2.2.1 Synthesis of decafluorodiphenylamine

The fluorinated proligand (HNX_2) of interest here is prepared based on the reported procedure ($\text{X} = \text{C}_6\text{F}_5$) from commercially available reagents. The perfluorinated diarylamine $\text{HN}(\text{C}_6\text{F}_5)_2$ was prepared from hexafluorobenzene and LiNH_2 on a multigram scale and in 42% yield (Scheme 2.5), in agreement with literature data.⁵⁴



Scheme 2.5. Synthesis of $\text{HN}(\text{C}_6\text{F}_5)_2$.⁵⁴

We have obtained and determined the molecular structure of $\text{HN}(\text{C}_6\text{F}_5)_2$ by single-crystal X-ray diffraction studies after recrystallization from a concentrated petroleum ether solution. The NMR characterization has been compared with the reported spectroscopic data in the literature. The ^{19}F NMR spectrum shows the three expected resonances; a doublet for the four fluorine atoms in *ortho* position at $\delta_{19\text{F}} = -154.42$ ppm (d, $J_{\text{FF}} = 20.5$ Hz), a triplet for the *para* fluorine atoms at

$\delta_{19\text{F}} = -163.19$ ppm (t, $J_{\text{FF}} = 21.9$ Hz) and a triplet for the *meta* fluorine atoms at $\delta_{19\text{F}} = -163.48$ ppm (t, $J_{\text{FF}} = 22.5$ Hz). It is completely soluble in common organic solvents.

2.2.2 Synthesis of alkaline-earth fluoroamides

This section aims to present the synthesis and characterization of homoleptic and heteroleptic calcium and barium complexes starting from the fluorinated amine $\text{HN}(\text{C}_6\text{F}_5)_2$. Alkaline earth homoleptic complexes are sometimes applied in homogeneous catalysis, such as for instance $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{thf})_2]$ used in ring-opening polymerization (ROP), $[\text{Ae}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ and $[\text{Ae}\{\text{CH}(\text{SiMe}_3)_2\}_2\cdot(\text{thf})_2]$ (Ae= Ca, Sr) for intermolecular hydroamination,^{55,56} dehydrocoupling⁵⁷ and hydrophosphonylation.⁵⁸ They can also be formed from unwanted redistribution of the ligands from heteroleptic species $[\{\text{L}\}\text{Ae}-\text{R}(\text{solv})_n]$. Thus, in addition to their potential applications, the study of the structural and spectroscopic features of homoleptic complexes such as $[\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2]$, can be very useful in view of using these compounds in catalysis.

2.2.2.1 Synthesis and characterization of calcium and barium homoleptic complexes

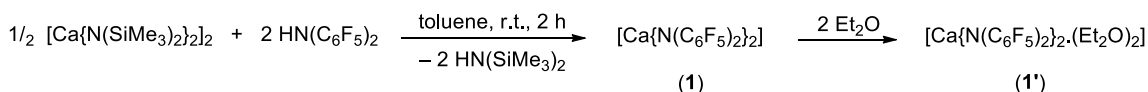
Calcium salts are biocompatible, have a high earth crust abundance (3.4 wt%)⁵⁹ and low prices; organocalcium compounds are also efficient precatalysts for the catalytic conversion of alkenes by polymerization,⁶⁰ hydroamination,^{17,18,20a,61} hydrosilylation,⁶² hydrogenation⁶³ and hydrophosphination⁶⁴. Therefore, the development of calcium-based catalytic systems is attractive.

2.2.2.1.1 Synthesis of $[\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2]$ (**1**) and $[\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2\cdot(\text{Et}_2\text{O})_2]$ (**1'**)

Our investigations started with the preparation of the homoleptic calcium complex $[\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2]$ (**1**) (Scheme 2.6). Two possible pathways could be envisaged: salt metathesis and protonolysis. Salt metathesis that proceeds from generally easily accessible Ae halogenides ($[\text{AeX}]$) and organo-alkaline ($[\text{MR}]$) species sometimes ends-up in the formation of an anionic “ate” complex which is a mixed-metal (Ae/M) product and it is considered as a disadvantage of this method. The separation of this mixture is difficult or impossible. “Ate” complexes of the alkaline-earth metals are mostly known for magnesium and there are fewer cases reported for the heavier congeners because of the reduced metal charge density. Westerhausen and co-workers

have prepared a variety of heavy alkaline-earth metal zincates, aluminates, and cuprates that display alkaline-earth metal–carbon contacts; for instance, they reported the preparation of $[(\text{Me}_3\text{Si})_2\text{N}-\text{Ca}(\mu-\text{CH}_2\text{SiMe}_3)_2\text{Al}(\text{CH}_2\text{SiMe}_3)_2]_2$ from the treatment of calcium bis[bis(trimethylsilyl)amide] with two equivalents of tris(trimethylsilylmethyl).⁶⁵

Therefore, salt metathesis is generally avoided. This is the reason for which we have chosen the protonolysis pathway for the effective synthesis of the Ae fluoride complexes.



Scheme 2.6. Synthesis of fluoroarylamide-containing calcium homoleptic complexes $[\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2]$ (**1**) and $[\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2 \cdot (\text{Et}_2\text{O})_2]$ (**1'**) (solid-state structure for complex **1** unknown).

The homoleptic calcium complex (**1**) was obtained in high yield (82%) by protonolysis between the $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ with a stoichiometric amount of the perfluorinated arylamine $\text{HN}(\text{C}_6\text{F}_5)_2$ in toluene. Several attempts to obtain crystals of **1** free of coordinated solvent (for instance by layering a petroleum ether solution of $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ with a solution of $\text{HN}(\text{C}_6\text{F}_5)_2$ in this solvent) remained unsuccessful; hence the X-ray structure of this solvent-free complex was not established. Yet, the NMR data of the recovered sample agrees with the formulation of the expected homoleptic compound. Colorless crystals of the diethyl ether adduct $[\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2 \cdot (\text{Et}_2\text{O})_2]$ (**1'**) were however successfully isolated from a solution of **1** in diethyl ether.

As expected, the ^1H NMR spectrum of complex **1** in $\text{thf-}d_8$ at room temperature shows no signals. The corresponding ^{19}F NMR spectrum of complex **1** shows three broad resonances at room temperature: $\delta -159.45$ ppm integrating for eight *o*-F atoms, $\delta -168.88$ ppm integrating for eight *m*-F atoms and $\delta -178.23$ ppm integrating approximately for four *p*-F atoms (probably the relaxation time was not sufficient to enable the full relaxation of these F atoms) (Figure 2.12).

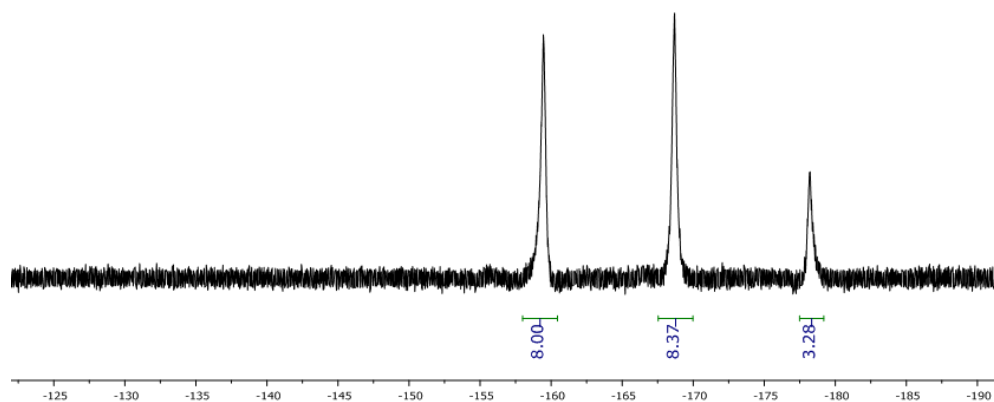


Figure 2.12. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum ($\text{thf-}d_8$, 298 K, 376 MHz) of $[\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2]$ (**1**).

The ^1H NMR spectrum of complex **1'** in benzene- d_6 at room temperature only shows the presence of coordinated diethyl ether (Figure 2.13). The ^{19}F NMR spectrum of complex **1'** in benzene- d_6 shows essentially three resonances at room temperature: a doublet at δ -153.80 ppm for *o*-F atoms, and two overlapping triplets in the region δ -162.60 to -163.00 ppm for *m*- and *p*-F (Figure 2.13).

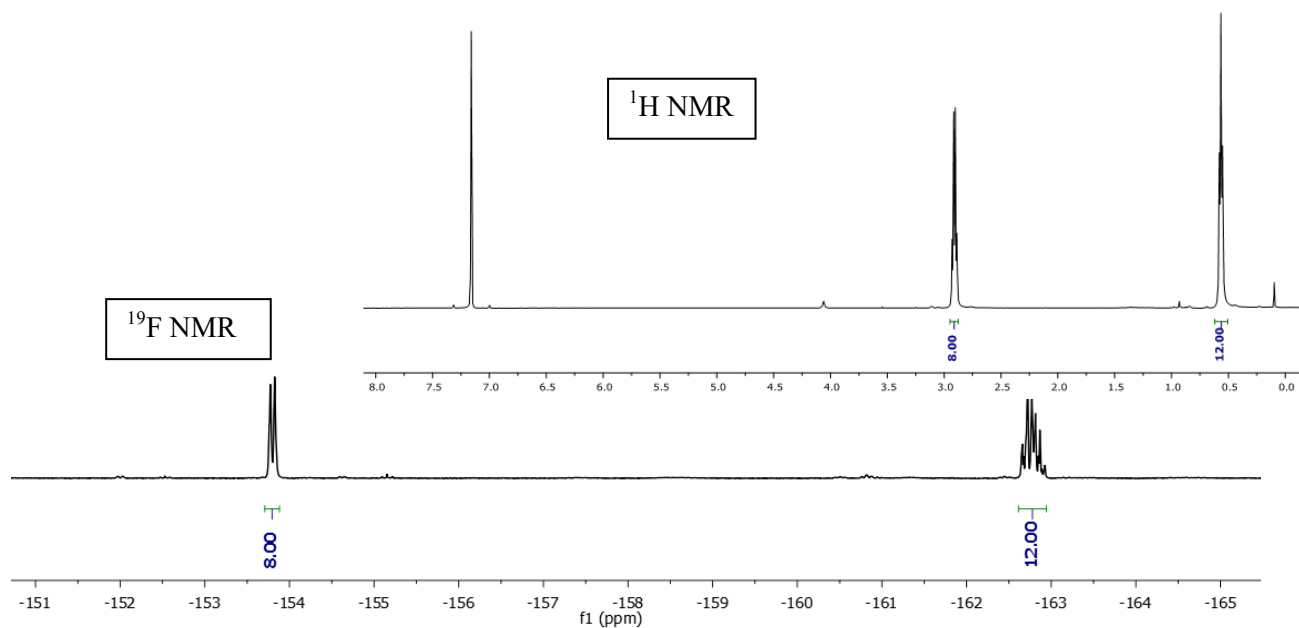


Figure 2.13. ^1H NMR (benzene- d_6 , 298 K, 400 MHz) and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra (benzene- d_6 , 298 K, 376 MHz) of $[\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2\cdot(\text{Et}_2\text{O})_2]$ (**1'**).

The molecular solid-state structure of $[\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2(\text{Et}_2\text{O})_2]$ (**1'**) determined by XRD analysis is depicted in Figure 2.14. It shows a distorted tetrahedral environment for the metal center. The structure features coordination from the two $\text{N}_{\text{C}_6\text{F}_5}$ and two O_{ether} atoms with formerly 4-coordinate calcium atom while the coordination sphere of calcium is further filled by four $\text{Ca}\cdots\text{F}-\text{C}$ intramolecular interactions varying from 2.493(1) to 3.074(1) Å. The weak $\text{Ca}\cdots\text{F}-\text{C}$ secondary interactions are not taken into account as contributing to the coordination. According to the definition of Plenio,³⁶ the accepted limit for $\text{Ca}\cdots\text{F}-\text{C}$ contacts is 3.13 Å (Table 2.1) and thus two of these interactions (at 2.493(1) and 2.523(1)) can be regarded as extremely strong.

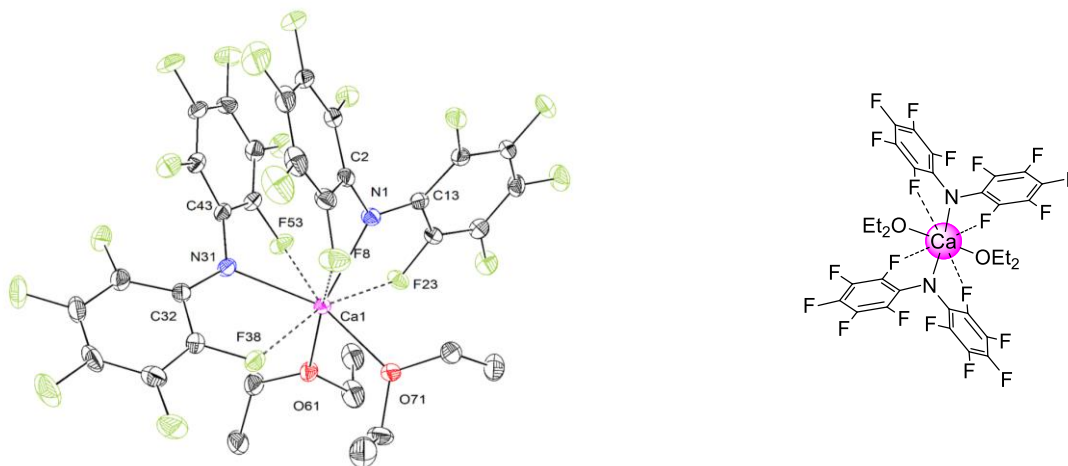


Figure 2.14. ORTEP representation of the molecular solid-state structure of $[\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2(\text{Et}_2\text{O})_2]$ (**1'**). Ellipsoids at the 50% probability level, with only the main component of the disordered Et_2O molecule. H atoms omitted for clarity. $\text{Ca}\cdots\text{F}$ interactions depicted in dashed bonds. Selected bond lengths (Å) and angles (deg): $\text{Ca1}-\text{O61} = 2.3402(12)$, $\text{Ca1}-\text{O71} = 2.3421(12)$, $\text{Ca1}-\text{N31} = 2.3705(14)$, $\text{Ca1}-\text{N1} = 2.3805(14)$, $\text{Ca1}-\text{F23} = 2.4935(10)$, $\text{Ca1}-\text{F38} = 2.5226(10)$, $\text{Ca1}-\text{F53} = 2.7713(11)$, $\text{Ca1}-\text{F8} = 3.0740(12)$; $\text{O61}-\text{Ca1}-\text{O71} = 87.71(4)$, $\text{O61}-\text{Ca1}-\text{N31} = 100.65(5)$, $\text{O71}-\text{Ca1}-\text{N31} = 144.30(5)$, $\text{O61}-\text{Ca1}-\text{N1} = 143.24(5)$, $\text{O71}-\text{Ca1}-\text{N1} = 98.38(5)$, $\text{N31}-\text{Ca1}-\text{N1} = 95.23(5)$.

The two $\text{Ca}\cdots\text{F}-\text{C}$ intramolecular interactions at 2.493(1) and 2.523(1) Å are remarkable considering the distances reported in the literature to date. They are comparable with the contacts found in a homoleptic calcium complex bearing CF_3 substituents in the backbone of the η^1 -bonded ligands, as described by Hill, in the range 2.468(2)-2.489(3) Å (Figure 2.15).⁶⁶ These $\text{Ca}\cdots\text{F}-\text{C}$ interactions may also be a factor contributing to the long $\text{Ca}-\text{NC}_6\text{F}_5$ bond length.

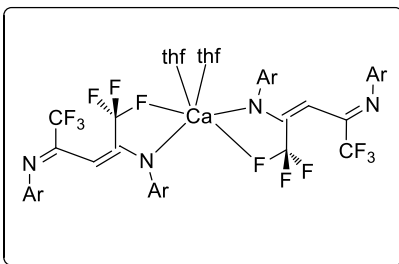


Figure 2.15. Homoleptic calcium complex containing trifluoromethyl interaction with the metal center.⁶⁶

This type of secondary interactions has also been exemplified by work from our group. For the homoleptic complex of $[\{\text{RO}^3\}_2\text{Ca}]$, the $\text{Ca}\cdots\text{F}-\text{C}$ intramolecular interaction shows a greater distance of $\text{Ca}-\text{F69} = 3.002(1) \text{ \AA}$ that is weaker than in **1'** (Figure 2.16).⁴³ However, for the heteroleptic complex $[\{\text{RO}^2\}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$, the $\text{Ca1}-\text{F14}$ distance ($2.832(1) \text{ \AA}$) is comparable to that in complex **1'** ($2.493(1)$ and $2.523(1) \text{ \AA}$).

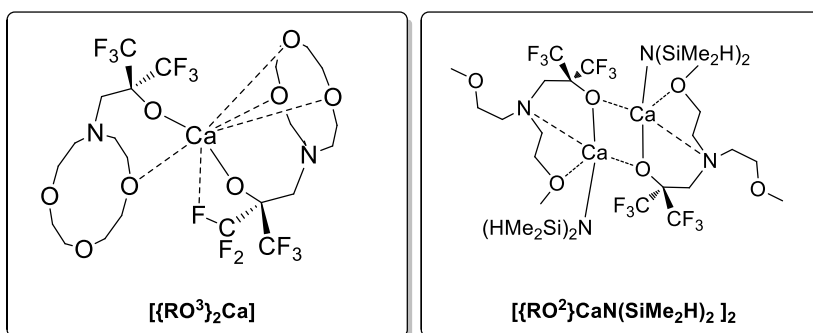


Figure 2.16. Calcium complexes containing trifluoromethyl interaction with metal center: $[\{\text{RO}^3\}_2\text{Ca}]$ ($\text{Ca}-\text{F69} 3.002(1) \text{ \AA}$), $[\{\text{RO}^2\}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$ ($\text{Ca1}-\text{F14} = 2.832(1) \text{ \AA}$).⁴³

The $\text{Ca}-\text{N}_{\text{C}_6\text{F}_5}$ bond lengths in **1'** ($2.370(1)$ and $2.380(1) \text{ \AA}$) are substantially longer than the corresponding ones in $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{thf})_2]_2$ ($2.294(3)$ and $2.309(3) \text{ \AA}$). This reflects the greater electron withdrawing ability of the $\text{N}(\text{C}_6\text{F}_5)_2^-$ moiety and, as a result, the greater ionicity on the $\text{Ca}-\text{N}$ bond in **1'**.⁶⁷ Similar observations have been made in the literature when comparing the magnesium complexes $[\text{Mg}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2\cdot(\text{thf})_2]$ and $[\text{Mg}\{\text{N}(\text{C}_6\text{H}_5)_2\}_2\cdot(\text{thf})_2]$ prepared by Westerhausen and Harder. According to the higher charge delocalization in $\text{N}(\text{C}_6\text{F}_5)_2^-$, the $\text{Mg}-\text{N}_{\text{C}_6\text{F}_5}$ bond ($2.112(2) \text{ \AA}$) is longer than the $\text{Mg}-\text{N}_{\text{C}_6\text{H}_5}$ bond ($2.013(3) \text{ \AA}$).^{68,69} The

$\text{N}_{\text{C}_6\text{F}_5}\text{--Ca--N}_{\text{C}_6\text{F}_5}$ angle in **1'** is narrow ($95.39(6)^\circ$). The distance between the two (C_6F_5) parallel rings is $3.9595(1)$ Å (Figure 2.17).

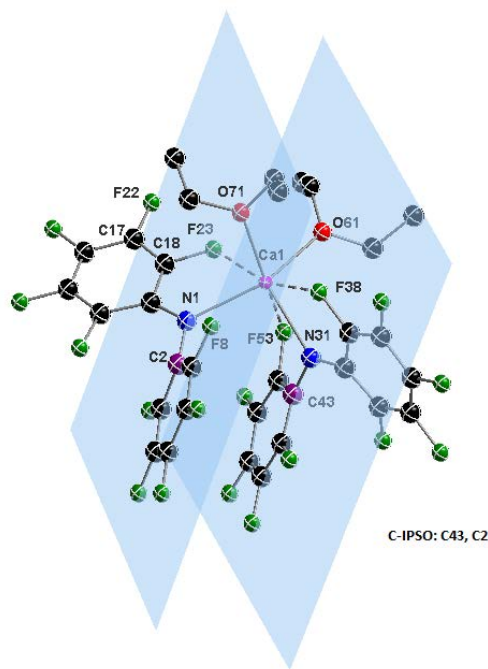


Figure 2.17. The parallel (C_6F_5) rings with the C-*ipso* (C2 and C43) in the structure of **1'**.

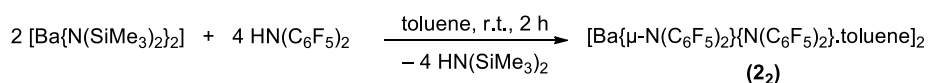
In comparison, Sundermeyer *et al.* have shown that there are three different π -stacking interactions between the neighboring $\text{N}(\text{C}_6\text{F}_5)_2$ moieties in $[\text{Ga}\{\text{N}(\text{C}_6\text{F}_5)_2\}_3]$, with distances of $3.5192(3)$, $3.7848(4)$ and $3.5463(3)$ Å.⁵² Comparison of the data for $[\text{Mg}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2(\text{thf})_2]$ and $[\text{Mg}\{\text{N}(\text{C}_6\text{H}_5)_2\}_2(\text{thf})_2]$ reported by Harder shows the presence of the π -stacking only for the fluorinated analogue which is in agreement with the off-set face-to-face interaction with $\text{ring}_{\text{center}}\cdots\text{ring}_{\text{center}}$ distance of 3.633 Å.⁶⁸ The stabilization of **1'** is also influenced by π -stacking interactions.

It is well-known that the coordination of donating solvent molecules (or other Lewis bases) in Ae complexes provides electron density and hence stabilization to the metal center. In the structure of **1'**, the coordination to O_{ether} indeed provides added stability to complex **1**. The $\text{Ca--O}_{\text{ether}}$ bonds ($2.340(1)$ and $2.342(1)$ Å) are longer than the $\text{Ca--O}_{\text{thf}}$ bonds in $[\text{Ca}\{\text{N}(\text{C}_6\text{H}_5)_2\}_2(\text{thf})_2]$ structure ($2.316(1)$ and $2.377(3)$ Å) reported by Harder. This is explained

by the strong donor ability of thf (compared to Et₂O) which makes the metal less Lewis acidic. In the heteroleptic calcium complex of Hill, ([{BDI^{Dipp}}Ca{N(SiMe₃)₂}.(Et₂O)]), the Ca–O_{ether} bond is 2.3843(15) Å, that is longer than in **1'**.⁴

2.2.2.1.2 Synthesis of [Ba{μ-N(C₆F₅)₂}{N(C₆F₅)₂}.toluene]₂ (**2**₂)

As we descend in group 2 metals from calcium to barium, the ionic radii increase and the bonds between the metal and the ligand become comparably weak and has more ionic nature. This reduces the chance of preparation of the stable complexes with low nuclearity. The fluoroarylamide has been used to study the effect of the Ae···F–C secondary interaction to provide a stable barium complex and gives the opportunity to compare the strength of these interactions with the calcium analogues. The corresponding homoleptic barium complex has been prepared by the reaction of [Ba{N(SiMe₃)₂}]₂ with two equivalents of HN(C₆F₅)₂ in toluene (Scheme 2.7).



Scheme 2.7. Synthesis of the homoleptic Ba-fluoroarylamide [Ba{μ-N(C₆F₅)₂}{N(C₆F₅)₂}.toluene]₂ (**2**₂).

The dinuclear complex [Ba{μ-N(C₆F₅)₂}{N(C₆F₅)₂}.toluene]₂ (**2**₂) was obtained in high yield (82%). Noteworthy, the calcium homoleptic complex **1** did not contain toluene, and calcium was only coordinated to Et₂O when we recrystallized the complex in this solvent to obtain **1'**. In **2**₂, one toluene is coordinated onto each barium center to fill the coordination sphere of the metal. All attempts to remove this toluene *via* heating under dynamic vacuum failed. The presence of the toluene is visible both from X-ray diffraction and NMR spectroscopy analyses. Complex **2**₂ is quite soluble in aromatic hydrocarbons.

For complex **2**₂, the presence of one coordinated toluene molecule per Ba²⁺, as established in the X-ray solid-state structure, is correspondingly observed, yet not quantitatively, in the ¹H NMR spectrum in benzene-*d*₆ (Figure 2.18). Its ¹⁹F NMR spectrum at room temperature shows three broad resonances for *o*-, *m*- and *p*-F atoms centered at δ –157.66, –165.85 and –176.06 ppm

that integrate for 8:8:6 instead of the expected 8:8:4 pattern, possibly arising from a too short relaxation delay (D1) (Figure 2.19).

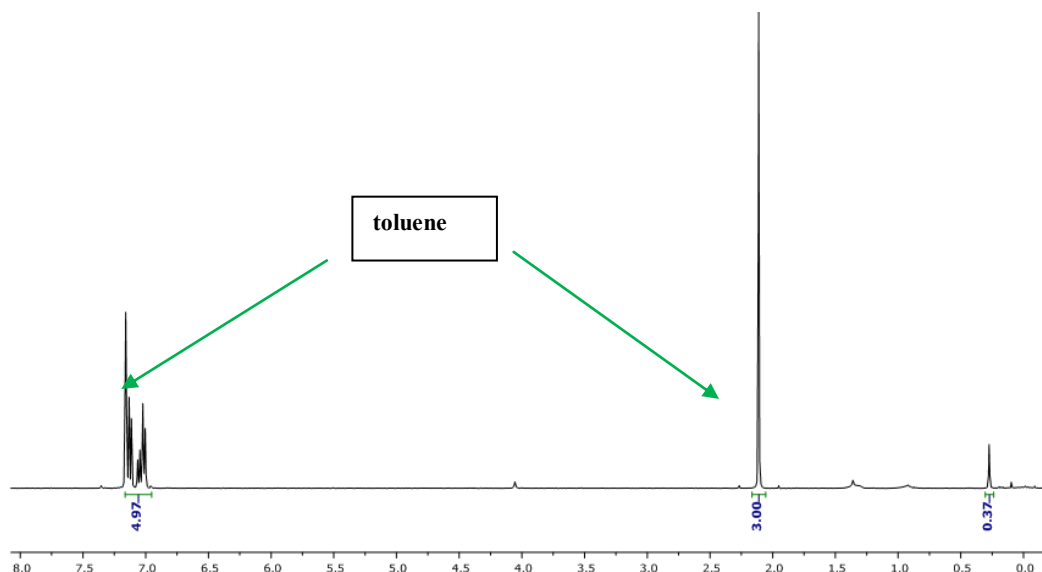


Figure 2.18. ^1H NMR spectrum (benzene- d_6 , 298 K, 400 MHz) of $[\text{Ba}\{\mu\text{-N}(\text{C}_6\text{F}_5)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}.\text{toluene}]_2$ (**2**₂).

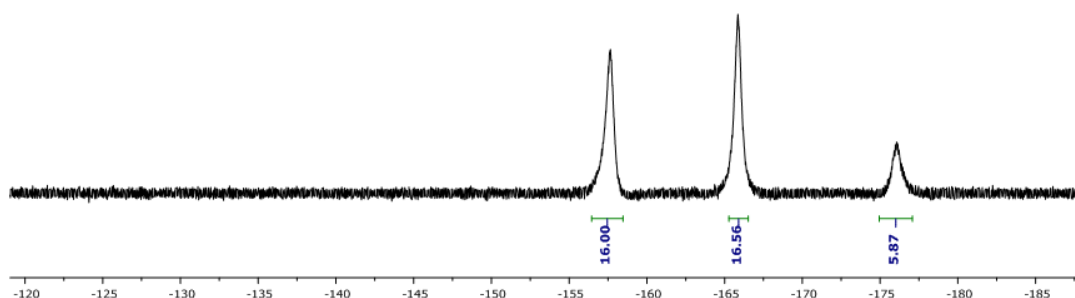


Figure 2.19. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (benzene- d_6 , 298 K, 400 MHz) of $[\text{Ba}\{\mu\text{-N}(\text{C}_6\text{F}_5)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}.\text{toluene}]_2$ (**2**₂).

The complex **2**₂ is centrosymmetric in the molecular solid state (Figure 2.20). Each barium atom is coordinated to one terminal and two bridging *N*-atoms (2.740(3) and 2.871(4)-2.951(3) Å respectively) with bond distances that are longer than the alike ones recorded for $[\text{Ba}\{\mu\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{SiMe}_3)_2\}]_2$ that also contains two bridging and two terminal hexamethyldisilazide

groups (2.576(3) and 2.798(3)-2.846(4) Å).⁷⁰ This is likely due to the greater ionic bonding in **2**₂, as a result of the more pronounced electronegativity of N(C₆F₅)₂[−].

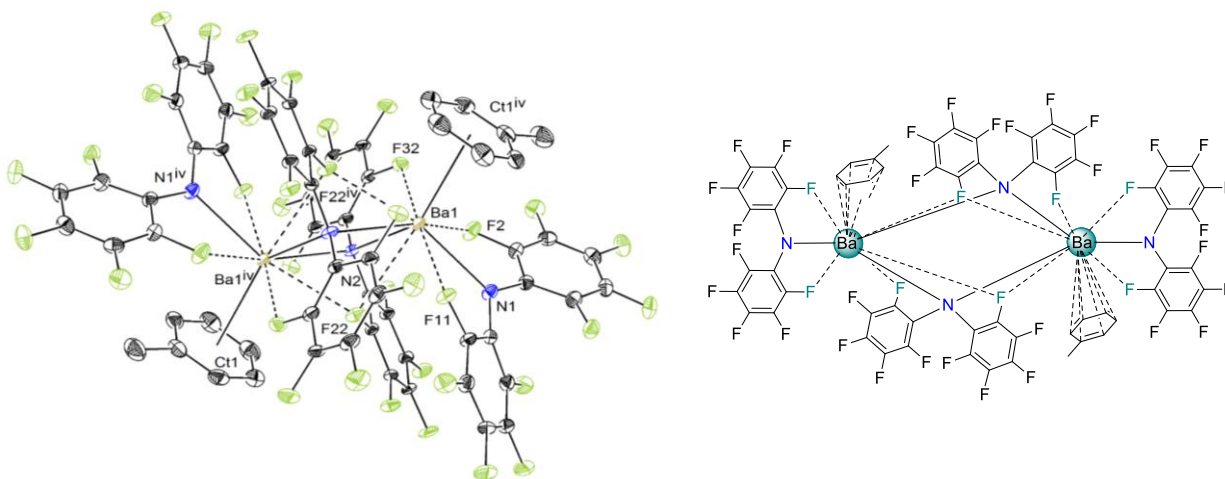


Figure 2.20. ORTEP representation of the molecular solid-state structure of [Ba{μ-N(C₆F₅)₂}{N(C₆F₅)₂}.toluene]₂ (**2**₂). Ellipsoids at the 50% probability level. H atoms omitted for clarity. Ba...F interactions depicted in dashed bonds. Selected bond lengths (Å): Ba1–N1 = 2.740(3), Ba1–F11 = 2.825(2), Ba1–F32 = 2.832(2), Ba1–N2 = 2.871(4), Ba1–F2 = 2.910(3), Ba1–F22^{iv} = 2.923(3), Ba1–N2^{iv} = 2.951(3), Ba–F22 = 3.014(3), Ba1–C44 = 3.287(5), Ba1–C43 = 3.290(5), Ba1–C45 = 3.357(5), Ba1–C21 = 3.383(4).

The coordination sphere of each Ba atom is filled by five close Ba...F–C interactions (2.825(2)-3.014(3) Å). The X-ray structure of **2**₂ shows a dinuclear molecule while in **1'**, the presence of the solvent (Lewis base) and the Ca...F–C secondary interactions, provide a mononuclear structure. In **2**₂, there are also more secondary interactions of the type Ae...F–C than in complex **1'**.

According to Plenio, the known minimal distance for Ba...F–C secondary interaction is 2.99 Å which is the sum of the ionic radius of barium ion (r_{ion}) and the van der Waals radius of fluorine (1.47 Å) (Table 2.1), while the maximum for a tangible barium-fluorine interaction is set at 3.48 Å (the maximum barium-fluorine distance considered in Plenio's study is the sum of the van der Waals radii of fluorine (1.47 Å) and the ionic van der Waals radii of barium calculated by Kollman).³⁶ Other Ba...F–C interactions have been detected in [(thf)₂Ba{N(H)-2,6-F₂-C₆H₃}]_∞ (Ba–F interatomic distances 2.871(2) and 2.901(3) Å)⁵³ (Figure 2.21, **XV**), and in discrete

monocationic complexes bearing multidentate aminoether-fluoroalkoxides (Ba–F interatomic distances in the range of 2.918(2) to 2.992(3) Å, Figure 2.21, **XVI**).^{20d}

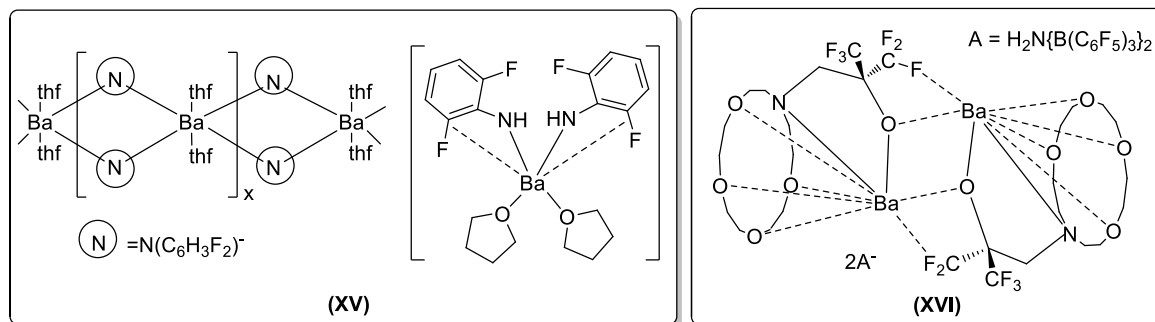


Figure 2.21. **(XV)** Polymeric barium complex $[(\text{thf})_2\text{Ba}\{\text{N}(\text{H})\text{-}2,6\text{-F}_2\text{C}_6\text{H}_3\}_2]_n$ (Ba $\cdots$ F–C contacts of 2.871(2) and 2.901(3) Å),⁵³ and **(XVI)** bimetallic barium dication $[\{\text{RO}^2\}\text{Ba}]_2^+ 2[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ (Ba $\cdots$ F–C = 2.918(2)–2.992(3) Å).^{20d}

Further stabilization is provided to the complex by capping η^6 -coordinated toluene molecule with a Ba–centroid distance of 3.065 Å and corresponding Ba–C_{toluene} distances between 3.287(5)–3.436(6) Å. Such Ba $\cdots$ C $_{\pi}$ interactions are common in complexes of barium, in accordance to the relatively soft nature of barium among the Ae metals and to its interaction with soft arene donors. For instance, in the $[\text{Ba}(\text{AlEt}_4)_2(\text{toluene})]_2$ complex of Anwender, the Ba–C_{toluene} shows an average distance of 3.3107 Å.⁷¹

2.2.2.2 Synthesis and characterization of calcium heteroleptic complexes

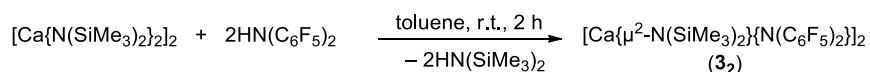
As seen in chapter 1, heteroleptic calcium complexes find many applications in homogeneous catalysis. However, one particular problem that has often plagued the chemistry of Ae metals is that their heteroleptic complexes easily engage side reactions through Schlenk equilibria. However, the use of adequate bulky ancillary ligands usually provides enough stability to the complex to prevent this undesirable phenomenon.

2.2.2.2.1 Synthesis of $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**3₂**)

In order to produce a heteroleptic calcium complex with a bulky ligand (β -diketiminato, iminoanilide, boryloxide) along with the fluorinated arylamide ligand, firstly we have prepared a heteroleptic bisamide including $\text{N}(\text{SiMe}_3)_2^-$ and $\text{N}(\text{C}_6\text{F}_5)_2^-$. The reason for this choice is that

$\text{N}(\text{SiMe}_3)_2^-$ is more basic ($\text{p}K_a$ (thf) 25.8)⁷² than $\text{N}(\text{C}_6\text{F}_5)_2^-$ ($\text{p}K_a$ (MeCN) 23.97),⁷³ so the former amide is better suited to deprotonate bulky protic proligands and, hence, to provide the new heteroleptic complexes.

The synthesis of the simple heteroleptic bis(amido) complex was performed by reacting $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ with an equimolar amount of $\text{HN}(\text{C}_6\text{F}_5)_2$ in toluene. Accordingly, the heteroleptic dinuclear complex $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**3₂**) was isolated in 64% yield (Scheme 2.8). Colorless single crystals were grown by crystallization from a concentrated solution in 1,2-difluorobenzene, and characterized by NMR and FTIR spectroscopies, and X-ray diffraction analysis. In contrast to the homoleptic species **1** and **1'**, it is highly soluble in hydrocarbons, Et_2O and thf. This compound is thermally stable in toluene up to 100 °C.



Scheme 2.8. Synthesis of the heteroleptic calcium fluoroamide $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**3₂**).

The ^1H NMR spectrum of complex **3₂** (benzene- d_6 , 298 K) expectedly features a single resonance, a singlet at δ 0.01 ppm. Furthermore, its ^{19}F NMR spectrum shows a doublet and two triplets at δ -156.14 ppm, and δ -164.58, -172.65 ppm for *o*-, *m*- and *p*-F atoms, respectively (Figure 2.22). In comparison with the parent amine ($\delta_{^{19}\text{F}}$ -154.42, -163.19 and -163.48 ppm for *o*-, *p*- and *m*-F atoms, respectively), the high-field ^{19}F chemical shifts observed in **3₂** evidence the accumulation of negative charge on the N_{amide} atom consistent with the mainly ionic nature of the bonds (therefore shielding the chemical shifts of *o*- and *p*-fluorine atoms). The large shielding of the fluorine atom in the *para* position is due to the substantial charge delocalization from the largely negatively charged $\text{N}_{\text{C}_6\text{F}_5}$ atom. The presence of only three signals in the ^{19}F NMR spectrum indicates the fast rotation around the $\text{Ca}-\text{N}_{\text{C}_6\text{F}_5}$ and $\text{N}-\text{C}_{\text{ipso}}$ bonds.

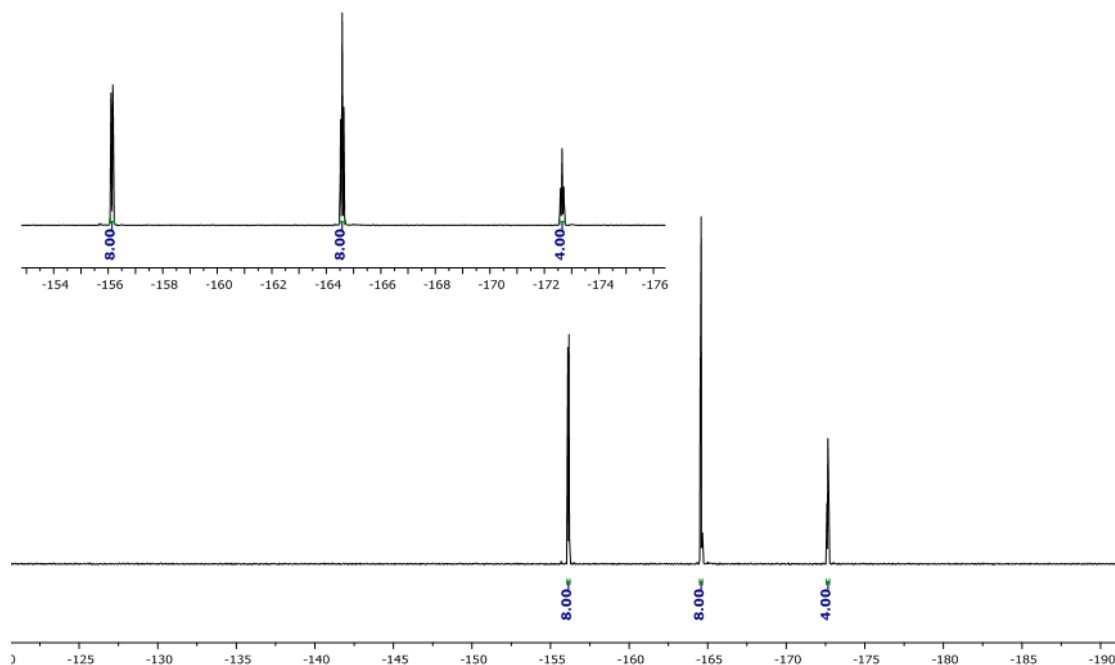


Figure 2.22. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (benzene- d_6 , 298 K, 376 MHz) of $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**32**).

PGSE (the pulsed gradient spin echo) NMR diffusion experiments have been next applied to assess the nuclearity of metal complexes in solution. The hydrodynamic radius of a complex in solution is compared to that in the molecular solid state. This technique has been used for alkaline metal complexes in our research groups as well as in others.^{74,75,76,77,78} This information is highly valuable, since the knowledge of their nuclearity in solution enables to better understand the mechanisms involved in catalyzed reactions promoted by these complexes.

Table 2.2. Hydrodynamic radius in solution ($r_{\text{H,PGSE}}$) and solid-state ($r_{\text{H,Xray}}$) for complex (**32**).^{a,b}

Complex	Solvent	D_t^c ($10^{-9} \text{ m}^2 \text{ s}^{-1}$)	$r_{\text{H,PGSE}}$ [Å]	X-ray		$r_{\text{H,Xray}}$ [Å]
				a [Å]	b [Å]	
$[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (32)	benzene- d_6	0.63	7.13	8.55	4.95	7.50

[a] All NMR spectra were recorded at 298 K using 10.0 mM solutions of complex. [b] $r_{\text{H,PGSE}}$ = hydrodynamic radius of the complex in solution, $r_{\text{H,Xray}}$ = hydrodynamic radius of the complex in the solid state, D_t = diffusion coefficient. [c] Average value of D_t from three or more separate peaks in the ^1H PGSE NMR spectrum of the complex.

The nuclearity of a metal complex can be determined by comparing the hydrodynamic radius in solution ($r_{\text{H,PGSE}}$) to the one obtained in the solid state ($r_{\text{X-Ray}}$). According to the data obtained

for complex **3₂** (Table 2.2), the hydrodynamic radius in solution ($r_{H,PGSE}$) is close to the one in the solid state ($r_{H,X-ray}$), which thus shows that the dinuclearity of the complex is preserved in the solution. In addition, its diffusion-molecular weight analysis by Diffusion-ordered NMR spectroscopy (DOSY) was performed to study the molecular weight of complex **3₂** in the solution state. This technique has been implemented several times according to the low solubility of the complex (**3₂**). Finally the molecular weight of $[Ca\{\mu^2-N(SiMe_3)_2\}\{N(C_6F_5)_2\}]_2$ (**3₂**) in solution at its finest result, was estimated to 2874.03 g mol⁻¹ using benzene (78 g mol⁻¹), naphthalene (128 g mol⁻¹), pyrene (202 g mol⁻¹) and TTMSS (320 g mol⁻¹) as known calibration standards (Figure 2.23). The DOSY analysis suggests that this complex retains its dinuclearity in hydrocarbons. Considering the DOSY analysis and the solubility problems of complex **3₂**, we could not rely completely on the estimated results of the DOSY analysis.

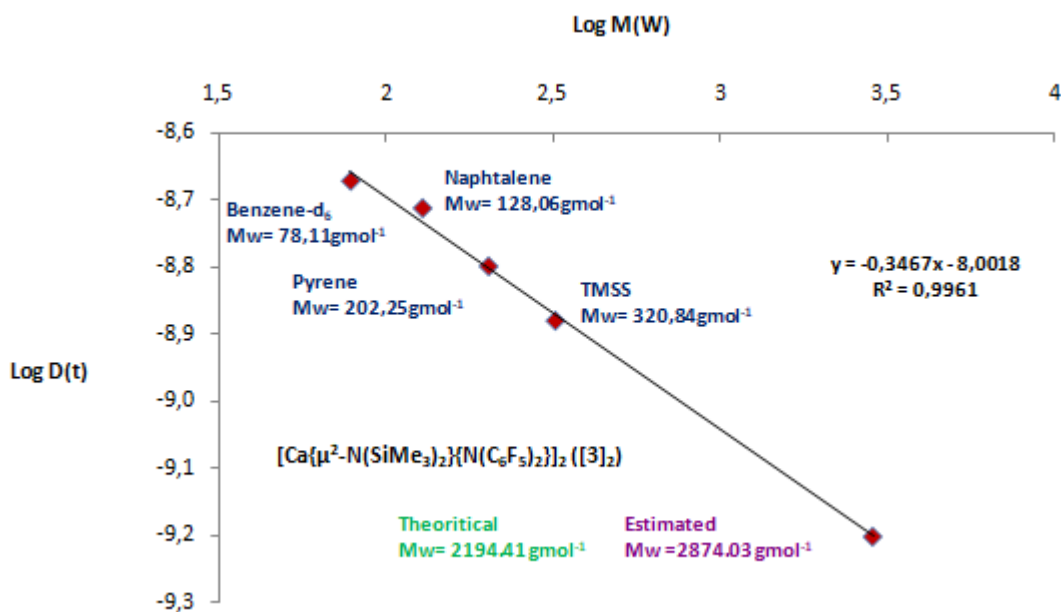


Figure 2.23. Diffusion time–molecular weight analysis for $[Ca\{\mu^2-N(SiMe_3)_2\}\{N(C_6F_5)_2\}]_2$ (**3₂**). All NMR spectra recorded in benzene-*d*₆ at 298 K. TTMSS = Si(SiMe₃)₄. Molecular weight for **3₂**: theoretical, 2194.41 mol⁻¹; estimated, 2874.03 g mol⁻¹.

Single-crystal X-ray diffraction studies performed on $[Ca\{\mu^2-N(SiMe_3)_2\}\{N(C_6F_5)_2\}]_2$ (**3₂**) indicate a dinuclear arrangement with a *C*₁ symmetry (Figure 2.24). Each calcium center is connected to three *N* atoms with a perfect trigonal planar geometry ($\Sigma_\theta(Ca1) = 359.95^\circ$ and $\Sigma_\theta(Ca2) = 359.90^\circ$).

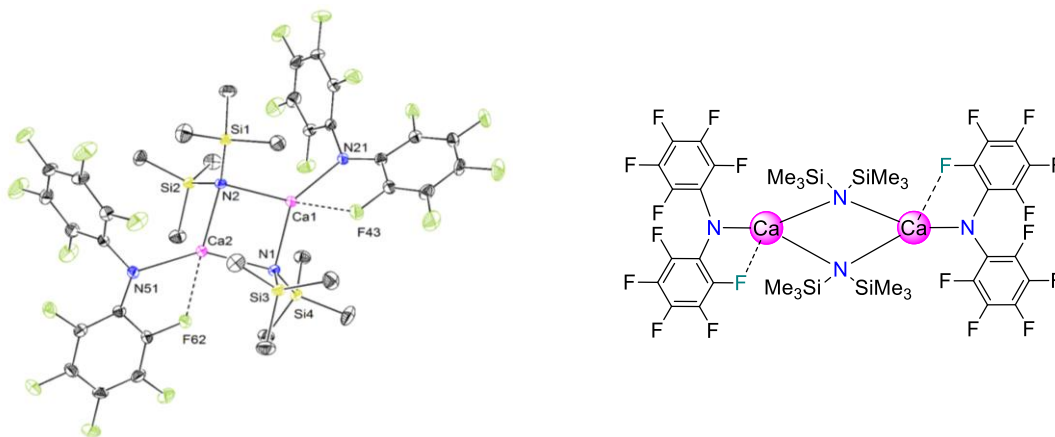


Figure 2.24. ORTEP representation of the molecular solid-state structure of $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**3₂**). Only one of the two independent but similar molecules in the asymmetric unit represented. Ellipsoids at the 50% probability level. H atoms omitted for clarity. $\text{Ca}\cdots\text{F}$ interactions depicted in dashed bonds. Selected bond lengths (Å) and angles (deg): $\text{Ca1-N21} = 2.385(2)$, $\text{Ca1-N2} = 2.404(2)$, $\text{Ca1-F43} = 2.4227(18)$, $\text{Ca1-N1} = 2.433(2)$, $\text{Ca2-N51} = 2.383(2)$, $\text{Ca2-N2} = 2.411(2)$, $\text{Ca2-N1} = 2.439(2)$, $\text{Ca2-F62} = 2.4560(18)$; $\text{N21-Ca1-N2} = 125.47(8)$, $\text{N21-Ca1-N1} = 145.63(8)$, $\text{N2-Ca1-N1} = 88.85(8)$, $\text{F43-Ca1-N1} = 85.00(7)$, $\text{N51-Ca2-N2} = 125.06(8)$, $\text{N51-Ca2-N1} = 145.99(8)$, $\text{N2-Ca2-N1} = 88.55(8)$.

The *N*-atoms of the two hexamethyldisilazide groups $\text{N}(\text{SiMe}_3)_2^-$ are more electron-rich than their counterparts in $\text{N}(\text{C}_6\text{F}_5)_2^-$; therefore, they occupy the bridging position between the two metal centers, while the $\text{N}(\text{C}_6\text{F}_5)_2^-$ ligands take up the terminal positions. The bridging $\text{Ca-N}_{\text{HMDS}}$ bond lengths (2.404(2)-2.439(2) Å) are shorter than their homologues in $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{SiMe}_3)_2\}]_2$ (2.431(7) and 2.521(7) Å),⁷⁹ and this could be due to the exchange of the terminal amide with $\text{N}(\text{C}_6\text{F}_5)_2^-$ that increases the Lewis acidity of the metal center. The $\text{Ca-N}_{\text{C}_6\text{F}_5}$ bond lengths are similar to those in **1'** (2.385(2) vs 2.383(2)) and they are longer than the terminal $\text{Ca-N}_{\text{HMDS}}$ bonds in the corresponding homoleptic complex of calcium $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{SiMe}_3)_2\}]_2$ (2.282(6) and 2.267(7) Å) due to the charge delocalization in the fluorinated ligand ($\text{N}(\text{C}_6\text{F}_5)_2^-$).

Usually, the use of a multidentate bulky ancillary ligand is required to kinetically stabilize heteroleptic complexes against Schlenk equilibria. However, in the case of **3₂**, the formation of the heteroleptic complex is favored on the basis of electronic factors. The mixture of the electron rich ($\text{N}(\text{SiMe}_3)_2^-$) and electron poor ($\text{N}(\text{C}_6\text{F}_5)_2^-$) amides encourage the formation of the final

heteroleptic complex **3₂**.⁶⁷ The terminal $\text{N}(\text{C}_6\text{F}_5)_2^-$ ligands stabilize these mixed dimers with $\text{Ca}\cdots\text{F}-\text{C}$ interactions. The coordination sphere of calcium is filled by very strong $\text{Ca}\cdots\text{F}-\text{C}$ interactions of $\text{Ca}_1-\text{F}_{43}$ and $\text{Ca}_2-\text{F}_{62}$ short distances (2.423(2) and 2.456(2) Å) that are even shorter than the homoleptic ether adduct **1'**. This is a remarkable result for $\text{Ca}\cdots\text{F}-\text{C}$ secondary interactions which still ought to be supported by DFT calculations.

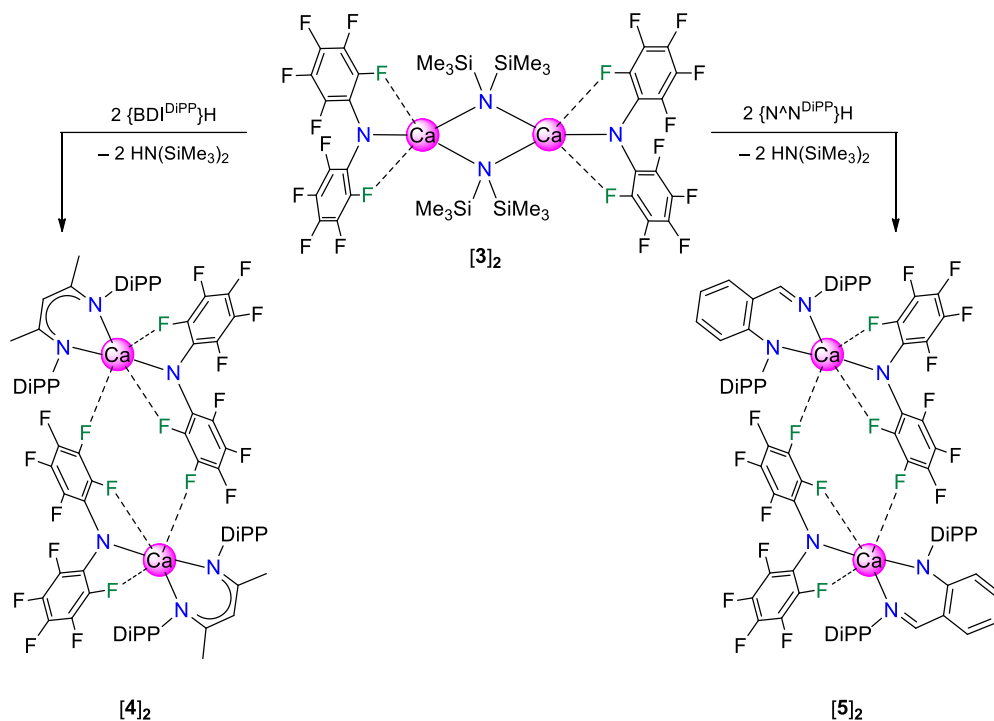
In the X-ray structure of the calcium fluoroalkoxide ($[\{\text{RO}^1\}\text{CaN}(\text{SiMe}_3)_2]_2$), the shortest distance for the interaction between calcium and fluorine atom in α position to the alkoxide is 2.712(5) Å (see Scheme 2. 4).⁴³ The formal coordination number of both metals in the solvent-free complex **3₂** is just three, without taking the $\text{Ca}\cdots\text{F}-\text{C}$ secondary interactions into account. Some other examples of 3-coordinate complexes include $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$,⁸⁰ $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2]$ (**II**),^{4,5,78,81} $[\text{Ca}(\text{O}-i\text{Bu}_2-2,6-\text{C}_6\text{H}_3)_2]_2$,⁸² *N*-heterocyclic carbene adducts $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2.\text{NHC}^{\text{aryl}}]$ (aryl = mesityl or 2,6-*i*Pr₂C₆H₃),⁸³ and the imine adduct $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2.\text{PhCH}=\text{N}^t\text{Bu}]$.⁸⁴

2.2.2.2.2 Application of bidentate, *N*-based and bulky ancillary ligands to the preparation of heteroleptic complexes $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**4₂**) and $[\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**5₂**)

Our target was to provide new calcium complexes bearing *N*-based ligands akin to β -diketiminato and iminoanilide (see Scheme 2.9) *without* the presence of the solvent and therefore having a lower coordination number, with the hope to eventually obtain catalysts that are more efficient. Two heteroleptic complexes were here synthesized by using **3₂** as a starting reagent. This is a convenient precursor, as it contains the $\text{N}(\text{SiMe}_3)_2^-$ moiety as a relatively strong base ($pK_a = 25.8$ in thf).⁸⁵ Since β -diketiminato $\{\text{BDI}^{\text{DiPP}}\}\text{H}$ has proved a very convenient ancillary ligand for the preparation of stable calcium complexes, we have selected it for our first attempt on an NMR scale reaction in toluene-*d*₈ to produce a new heteroleptic calcium complex, namely $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**4₂**) (Scheme 2.9). The release of $\text{HN}(\text{SiMe}_3)_2$ is clearly established by ¹H NMR spectroscopy. The reaction was then performed on large scale in a Schlenk vessel, and afforded the three-coordinate **4₂** as a colorless solid in reproducible 80–90% yield.

The iminoanilide $\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}^-$ has a backbone related to that of the β -diketiminato $\{\text{BDI}^{\text{DiPP}}\}^-$ and provides kinetically stable complexes in solution,^{13,14,15} and Ae complexes supported by this

ligand do resist Schlenk equilibria. $[\{N^{\wedge}N^{\text{DiPP}}\}CaN(SiMe_3)_2(thf)]$ is for instance one of the heteroleptic calcium compounds prepared with this prolignand. Our group has prepared several other stable heteroleptic complexes of calcium, strontium and barium with $\{N^{\wedge}N^{\text{DiPP}}\}^-$ bearing different nucleophilic ligands as $N(SiMe_3)_2^-$, $N(SiMe_2H)_2^-$ and $CH(SiMe_3)_2^-$.^{13,14,15,20a,20b} Applying the diarylamine $HN(C_6F_5)_2$ facilitates the formation of kinetically stable complexes by extra stabilization *via* the $Ca \cdots F-C$ secondary interaction. The heteroleptic complex $[\{N^{\wedge}N^{\text{DiPP}}\}CaN(C_6F_5)_2]_2$ (**5**₂) was next obtained (90% yield) in a similar procedure to that used for **4**₂, upon reacting one equivalent of the iminoaniline $\{N^{\wedge}N^{\text{DiPP}}\}H$ with **3**₂. Both of complexes **4**₂ and **5**₂ are just moderately soluble in petroleum ethers and toluene.



Scheme 2.9. Synthesis of fluoroarylamide-containing $[\{BDI^{\text{DiPP}}\}CaN(C_6F_5)_2]_2$ (**4**₂) and $[\{N^{\wedge}N^{\text{DiPP}}\}CaN(C_6F_5)_2]_2$ (**5**₂) with representation of their molecular solid-state structures.

The ^1H NMR spectrum recorded for complex **4**₂ in toluene-*d*₈ showed a singlet at δ 4.77 ppm diagnostic of the $\{BDI^{\text{DiPP}}\}^-$ backbone methine *CH* hydrogen atom, and there is no sign of the hexamethyldisilazide present in the starting material **3**₂ (Figure 2.25). A doublet at δ -158.11 and two triplets at δ -164.85 and -175.62 ppm for *o*-, *m*- and *p*-F atoms, respectively, are detected in the ^{19}F NMR spectrum (Figure 2.26). Complex **4**₂ can be regarded as the derivative of Hill's

$[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2]$ (**II**),⁴ although the fluoroarylamide is not as basic and reactive as the $\text{N}(\text{SiMe}_3)_2^-$ residue in (**II**).

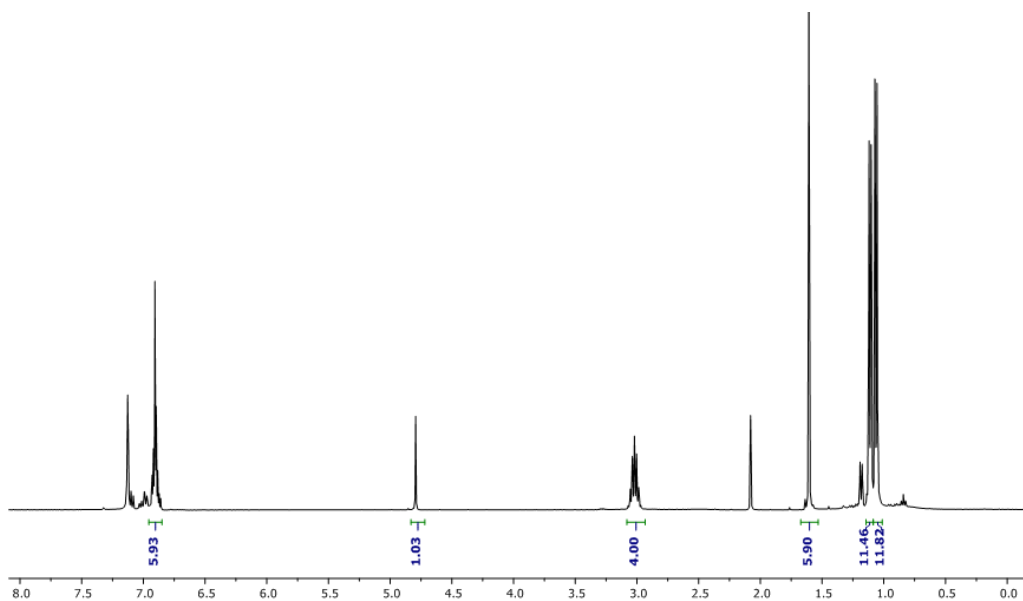


Figure 2.25. ^1H NMR spectrum (toluene- d_8 , 298 K, 400 MHz) of $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**42**).

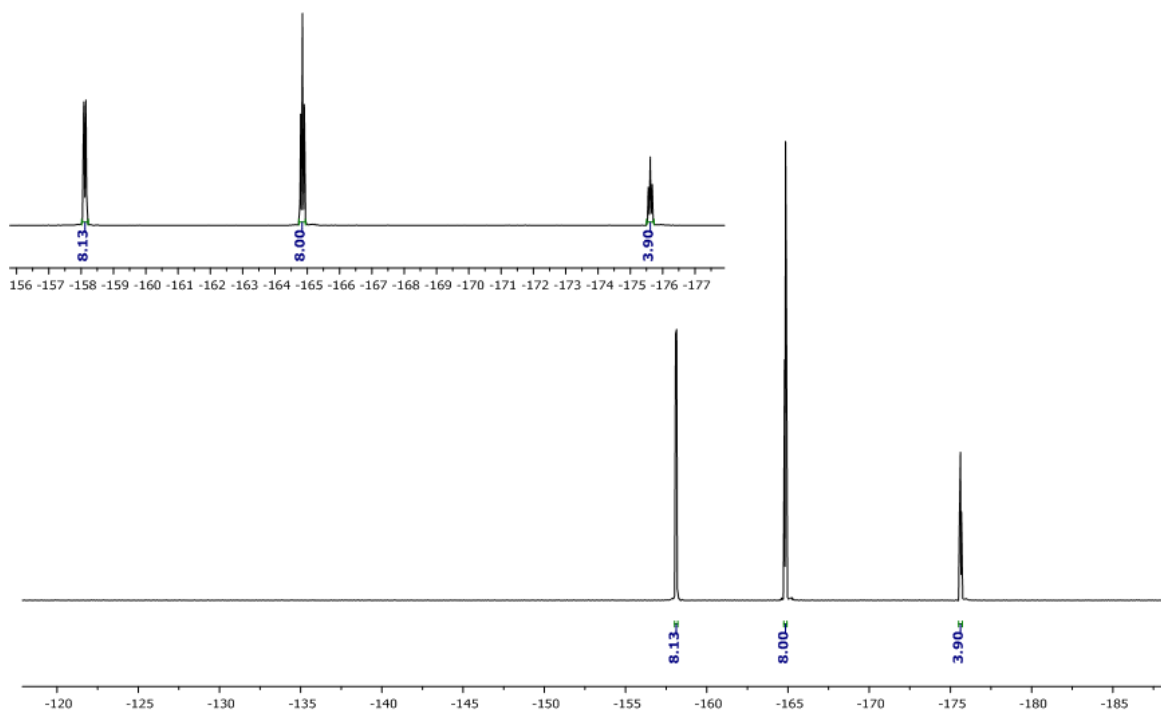


Figure 2.26. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (toluene- d_8 , 298 K, 376 MHz) of $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**42**).

The ^1H spectrum of **5₂** recorded at 25 °C in toluene-*d*₈ (Figure 2.27) features a typical resonance at δ 7.92 ppm assigned to the $\text{CH}=\text{N}$ hydrogen atom. The resonances for *o*-, *m*- and *p*-F atoms are located at δ -158.11, -164.78 and -175.95 ppm, respectively, in the ^{19}F NMR spectrum (Figure 2.28).

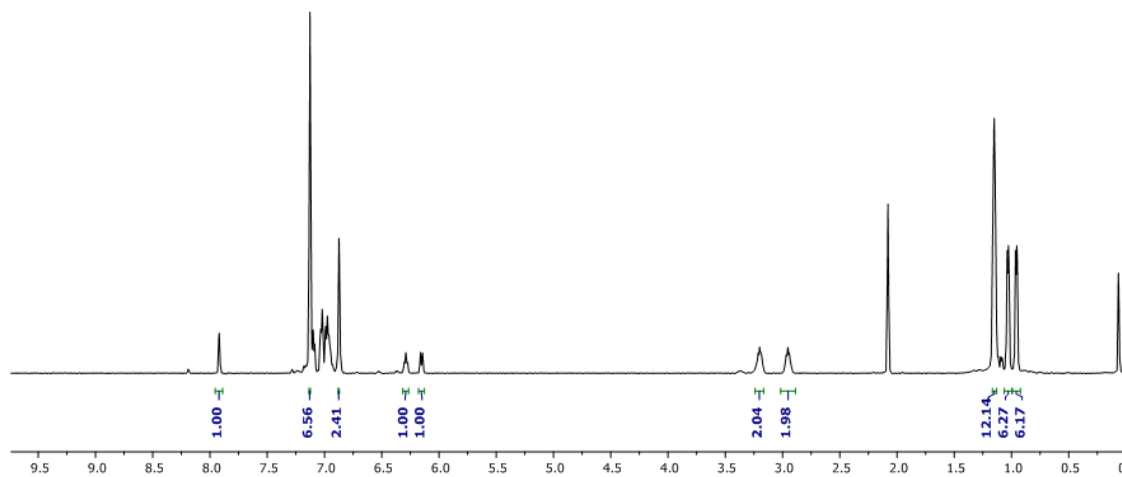


Figure 2.27. ^1H NMR spectrum (toluene-*d*₈, 298 K, 400 MHz) of [$\text{N}^{\text{DiPP}}\text{N}$] $\text{CaN}(\text{C}_6\text{F}_5)_2$ (**5₂**).

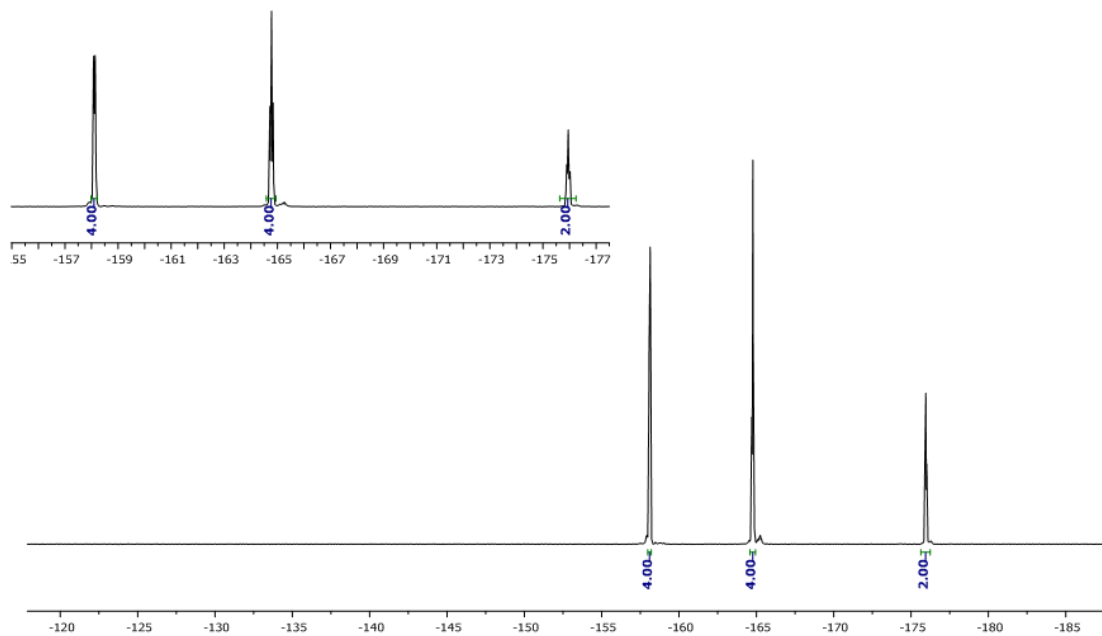


Figure 2.28. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (toluene-*d*₈, 298 K, 376 MHz) of [$\text{N}^{\text{DiPP}}\text{N}$] $\text{CaN}(\text{C}_6\text{F}_5)_2$ (**5₂**).

The molecular structure of $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**4₂**) was obtained by heating a concentrated benzene solution to 60 °C and then slowly cooling it down to room temperature. As depicted in Figure 2.29, it forms a dimer with crystallographic C_2 symmetry axis that goes through the two calcium atoms.

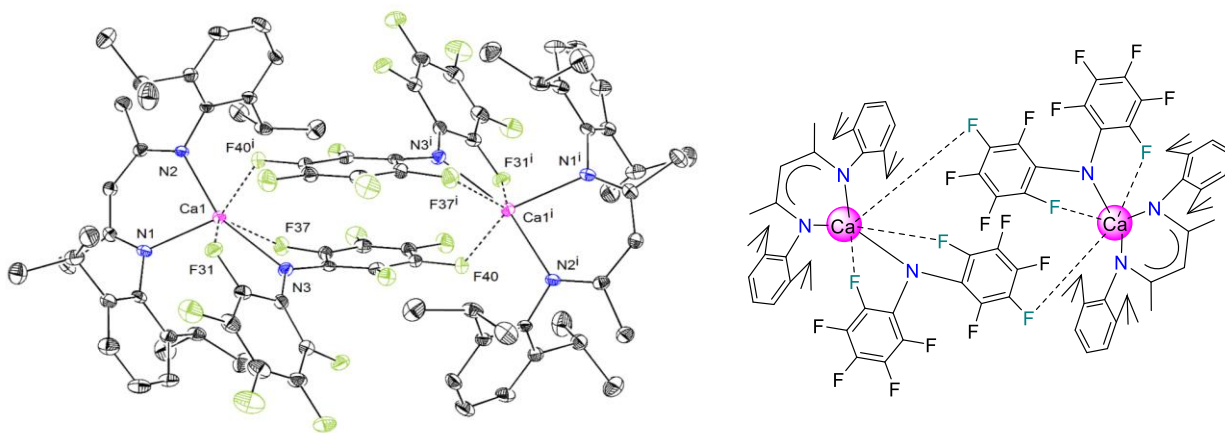


Figure 2.29. ORTEP representation of the molecular solid-state structure of $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**4₂**). Ellipsoids at the 50% probability level. H atoms and non-interacting benzene molecule omitted for clarity. $\text{Ca}\cdots\text{F}$ interactions depicted in dashed bonds. Selected bond lengths (Å): $\text{Ca1}-\text{N1} = 2.3066(19)$, $\text{Ca1}-\text{N2} = 2.3465(18)$, $\text{Ca1}-\text{N3} = 2.3880(19)$, $\text{Ca1}-\text{F40}^i = 2.5325(15)$, $\text{Ca1}-\text{F31} = 2.5559(15)$, $\text{Ca1}-\text{F37} = 2.7120(17)$.

The calcium centers are formally three-coordinated (2 $\text{Ca}-\text{N}_{\text{BDI}}$ and 1 $\text{Ca}-\text{N}_{\text{C}_6\text{F}_5}$). In addition, the coordination sphere of each calcium center is filled by three $\text{Ca}\cdots\text{F}-\text{C}$ secondary interactions; two from its $\text{N}(\text{C}_6\text{F}_5)_2^-$ ligand (intramolecular) and one with the neighboring fluorinated ligand (intermolecular). The secondary interactions have not been counted in the formal number of metal coordinations. This uncommon type of intermolecular bridging by $\text{Ca}\cdots\text{F}-\text{C}$ secondary interactions is noteworthy. The dinuclear system forms contacts from the neighboring $\text{N}(\text{C}_6\text{F}_5)_2^-$ ligand *via* intermolecular $\text{Ca}\cdots\text{F}-\text{C}$ interactions. The two C_6F_5 moieties between the metal centers are in parallel positions due to the symmetry in **4₂**, but there is no substantial π -stacking interaction as they are in offset positions. The distance between the two parallel rings is 4.4490(5) Å. The $\text{Ca}\cdots\text{F}-\text{C}$ secondary interactions in **4₂** (intramolecular, 2.556(1), 2.712(2) Å and intermolecular, 2.532(1) Å), are weaker than in **1'** and **6₂**, while they are shorter compared with complexes like $[\{\text{RO}^2\}\text{CaN}(\text{SiMe}_3)_2]_2$ ($\text{Ca}-\text{F} = 2.920(1)$ and 3.113(1) Å) and

$[\{\text{RO}^1\}\text{CaN}(\text{SiMe}_3)_2]_2$ ($\text{Ca}-\text{F} = 2.712(5) \text{ \AA}$, $3.084(6) \text{ \AA}$, and $3.056(6) \text{ \AA}$) (see Scheme 2.4).⁴³ The $\text{Ca}-\text{N}_{\text{BDI}}$ distances in **4**₂ ($2.306(2)$ and $2.346(2) \text{ \AA}$) match those in the tetrameric complex $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2]$ (**II**) ($2.323(3)$ and $2.331(3) \text{ \AA}$). However, the weaker $\text{Ca}-\text{N}_{\text{C}_6\text{F}_5}$ bond length in **4**₂ ($2.3880 \text{ \AA}$) is as expected longer than ($2.299(3) \text{ \AA}$) bridging $\text{Ca}-\text{N}$ in complex (**II**). As in **4**₂, the calcium centers are three-coordinate in $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2]$ (**II**).

The X-ray crystallographic data for $[\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**5**₂) indicate structural features similar to those **4**₂ (Figure 2.30). The dinuclear system is connected *via* intermolecular $\text{Ca}\cdots\text{F}-\text{C}$ contacts. Each calcium is coordinated to three N donors including with $\text{Ca}-\text{N}_{\text{BDI}} = 2.253(2)$, and $2.389(3) \text{ \AA}$, and $\text{Ca}-\text{N}_{\text{C}_6\text{F}_5} = 2.388(3) \text{ \AA}$. Three $\text{Ca}\cdots\text{F}-\text{C}$ secondary interactions fill the coordination sphere of the metal center in **5**₂ with two intramolecular $\text{Ca}-\text{F}$ contacts at $2.558(2)$ and $2.559(2) \text{ \AA}$, and an intermolecular one with $\text{Ca}-\text{F} 2.530(1) \text{ \AA}$.

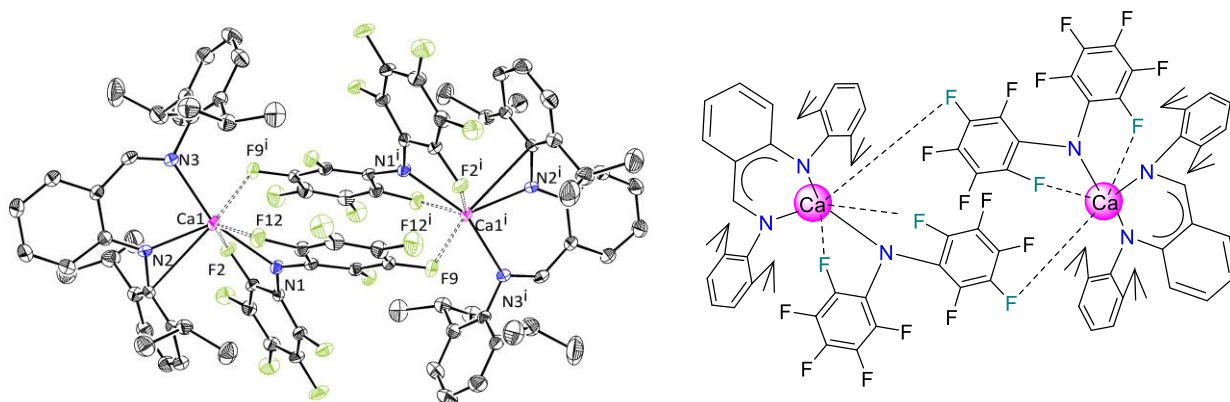
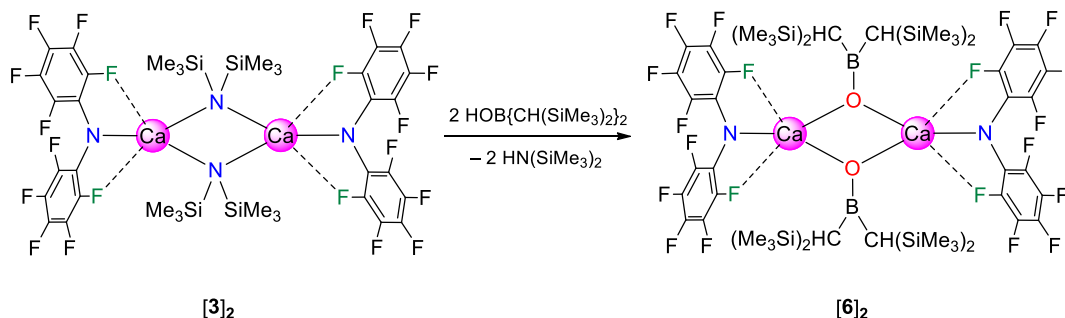


Figure 2.30. ORTEP representation of the molecular solid-state structure of $[\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**5**₂). Ellipsoids at the 50% probability level. H atoms and non-interacting benzene molecule omitted for clarity. $\text{Ca}\cdots\text{F}$ interactions depicted in dashed bonds. Selected bond lengths ($\text{\AA}$): $\text{Ca1}-\text{N1} = 2.388(3)$, $\text{Ca1}-\text{N2} = 2.253(2)$, $\text{Ca1}-\text{N3} = 2.389(3)$, $\text{Ca1}-\text{F9}^i = 2.530(1)$, $\text{Ca1}-\text{F2} = 2.558(2)$, $\text{Ca1}-\text{F12} = 2.559(2)$.

2.2.2.2.3. Application of monodentate, *O*-based and bulky ancillary ligands to the preparation of heteroleptic complex $[\text{Ca}\{\mu\text{-OB}(\text{CH}(\text{SiMe}_3)_2\}_2\{\text{N}(\text{C}_6\text{F}_5)_2\}_2]_2$ (**6**₂)

In order to investigate the effect of the oxophilicity and of the natural π -donating ability of oxygen atoms along with the impact of the presence of fluoroarylamides in the chemistry of calcium as an Ae oxophilic metal, the stoichiometric reaction of borinic acid $\text{HOB}\{\text{CH}(\text{SiMe}_3)_2\}_2$ with $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2]_2$ (**3**₂) was studied. The reaction led to $[\text{Ca}\{\mu\text{-OB}(\text{CH}(\text{SiMe}_3)_2\}_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2]_2$ (**6**₂), the first reported example of calcium boryloxide,⁸⁶ as the colorless complex isolated in 76% yield (Scheme 2.10). It is only moderately soluble in hydrocarbons, but dissolves upon heating. In **6**₂, the boryloxides bridge the two metal atoms, presumably as the more electron-poor $\text{N}(\text{C}_6\text{F}_5)_2^-$ amides must take the terminal positions.



Scheme 2.10. Synthesis of fluoroarylamide-containing $[\text{Ca}\{\mu\text{-OB}(\text{CH}(\text{SiMe}_3)_2\}_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2]_2$ (**6**₂), with representation of their molecular solid-state structures.

The ^1H NMR spectrum (recorded in benzene-*d*₆) of the calcium boryloxide **6**₂ is in agreement with the expected intensities for $\text{CH}(\text{SiMe}_3)_2$ (δ 0.21 and 0.20 ppm) and CH_3 hydrogens (δ 0.15 and 0.05 ppm) in non-equivalent boryloxides (Figure 2.31). The ^{19}F NMR spectrum also features two sets of approximately matching intensities for *o*-, *m*- and *p*-F atoms at δ -155.79 (d, 8F), -163.59 (t, 8F) and -173.47 (t, 4F) ppm for one, and at δ -158.73 (d, 8F), -164.74 (t, 8F) and -174.45 (t, 4F) ppm for the other (Figure 2.32). The 47:53 relative integration of the signals in the ^{19}F NMR spectrum suggests the presence of two types of products in solution. The recording of the ^{19}F NMR in variable temperatures (low or higher temperatures) should have been carried out to assess the possible presence of an equilibrium between two species; however, the lack of complete solubility of the complex has been the major drawback for further investigations.

The ^{11}B NMR spectrum shows a single resonance at δ 53.71 ppm (Figure 2.33).

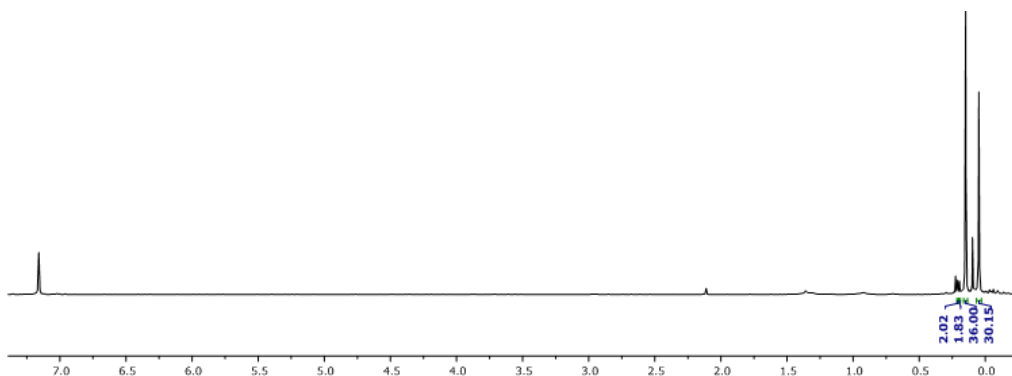


Figure 2.31. ^1H NMR spectrum (benzene- d_6 , 298 K, 400 MHz) of $[\text{Ca}\{\mu\text{-OB}(\text{CH}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**62**).

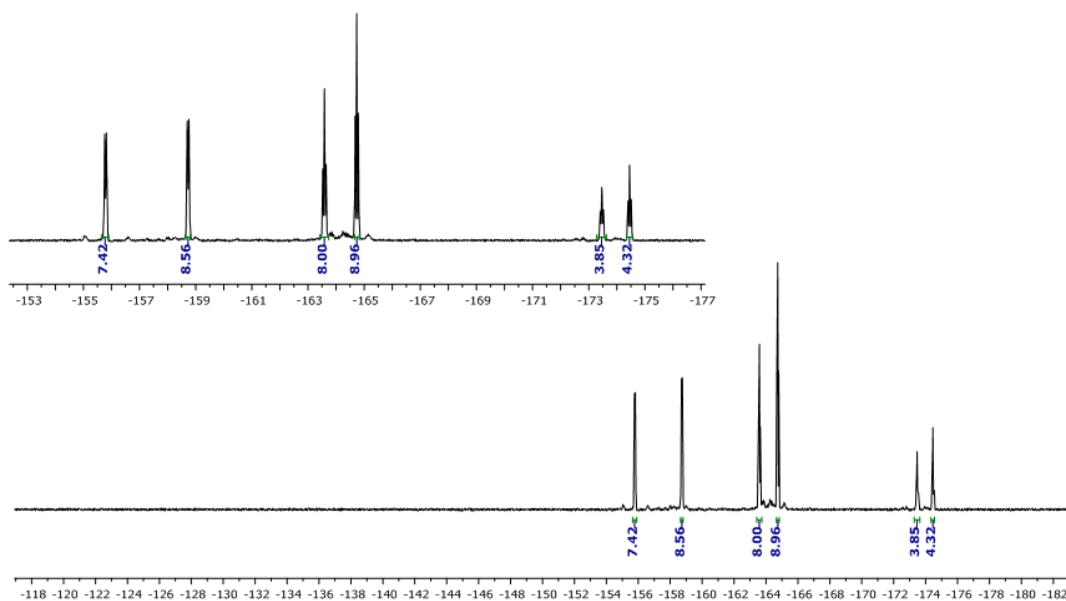


Figure 2.32. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (benzene- d_6 , 298 K, 376 MHz) of $[\text{Ca}\{\mu\text{-OB}(\text{CH}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**62**).

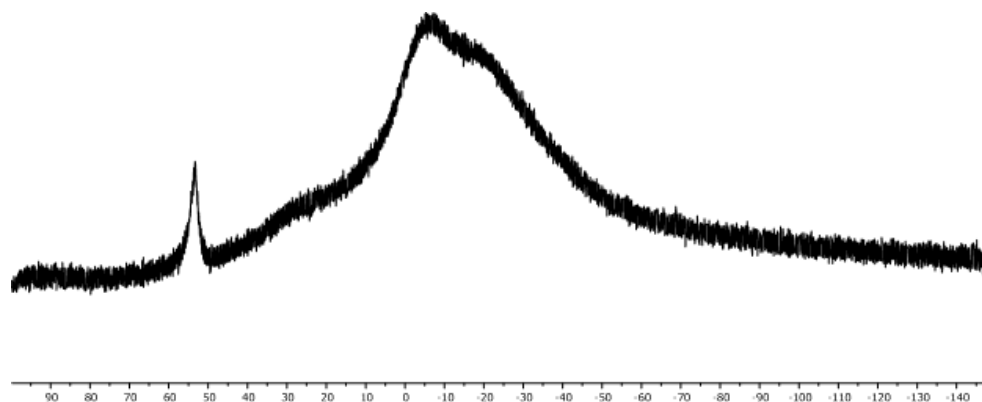


Figure 2.33. ^{11}B NMR spectrum (benzene- d_6 , 298 K, 128 MHz) of $[\text{Ca}\{\mu\text{-OB}(\text{CH}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2]$ (**6**₂). The very broad signal at δ 0 to -60 ppm is due to the borosilicates present in the NMR tube.

Complex **6**₂ is a heteroleptic boryloxide/fluoroarylamide showing a dinuclear structure in the solid state (Figure 2.34). It contains three-coordinate calcium centers connected to boryloxides in bridging and amides in terminal positions. The arrangement around Ca1 and Ca2 in **6**₂ is irregular ($\Sigma_\theta(\text{Ca1}) = 345.35^\circ$ and $\Sigma_\theta(\text{Ca2}) = 353.37^\circ$, taking *N* and *O* atoms into account), while in **3**₂ each three-coordinated Ca^{2+} is in a trigonal planar geometry. This could be the result of steric hindrance around the metal center or of the presence of two $\text{Ca}\cdots\text{F}\cdots\text{C}$ secondary interactions for each metal which is more than in **3**₂. However the distances of $\text{Ca}\cdots\text{F}\cdots\text{C}$ interactions in **6**₂ (for Ca1: 2.544(2) and 2.597(2) Å and for Ca2: 2.498(2) and 2.553(2) Å) are longer than **3**₂. The geometry around the boron, oxygen and nitrogen atoms approaches the perfect trigonal planarity in all cases ($\Sigma_\theta(\text{B1}) = 359.90^\circ$ and $\Sigma_\theta(\text{B2}) = 359.90^\circ$; $\Sigma_\theta(\text{O1}) = 359.96^\circ$ and $\Sigma_\theta(\text{O2}) = 359.96^\circ$; $\Sigma_\theta(\text{N1}) = 359.80^\circ$ and $\Sigma_\theta(\text{N2}) = 359.90^\circ$).

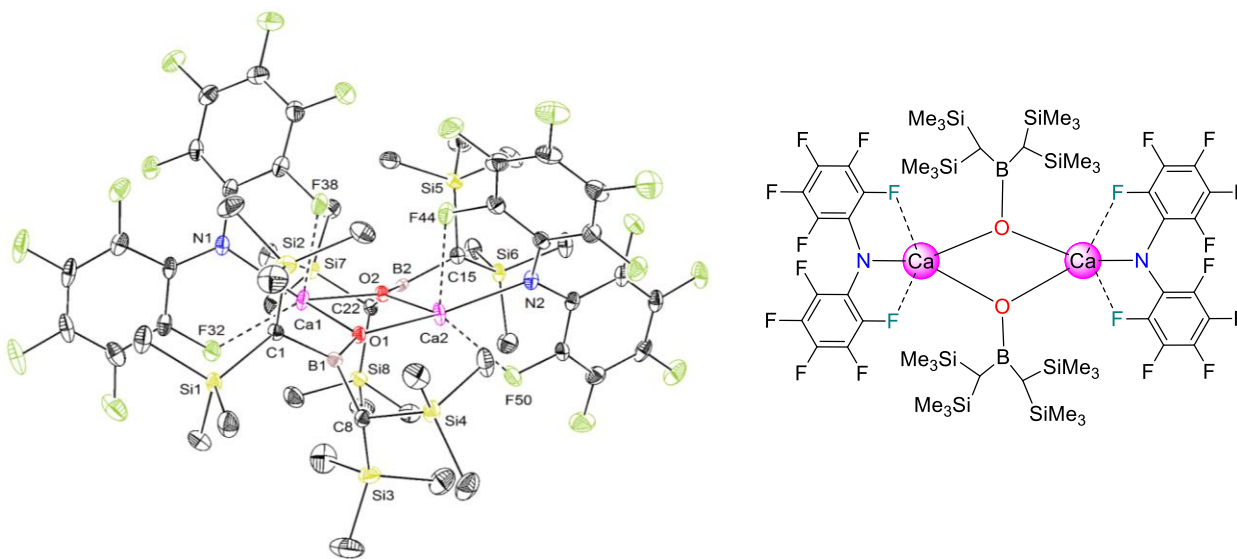


Figure 2.34. ORTEP representation of the molecular solid-state structure of $[\text{Ca}\{\mu\text{-OB}(\text{CH}(\text{SiMe}_3)_2\}_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2]$ (**62**). Ellipsoids at the 50% probability level. H atoms omitted for clarity. $\text{Ca}\cdots\text{F}$ interactions depicted in dashed bonds. Selected bond lengths (Å): $\text{Ca1-O2} = 2.269(2)$, $\text{Ca1-O1} = 2.271(2)$, $\text{Ca1-N1} = 2.370(3)$, $\text{Ca1-F32} = 2.544(2)$, $\text{Ca1-F38} = 2.597(2)$, $\text{Ca2-O1} = 2.243(2)$, $\text{Ca2-O2} = 2.259(2)$, $\text{Ca2-N2} = 2.356(3)$, $\text{Ca2-F50} = 2.498(2)$, $\text{Ca2-F44} = 2.553(2)$; $\text{O2-Ca1-O1} = 82.58(8)$, $\text{O2-Ca1-N1} = 138.45(9)$, $\text{O1-Ca1-N1} = 124.32(10)$, $\text{O1-Ca2-O2} = 83.40(8)$, $\text{O1-Ca2-N2} = 143.23(10)$, $\text{O2-Ca2-N2} = 126.74(9)$.

In cases of the amido/alkoxo barium dimers reported in the literature, the metal centers are bridged through $\text{O}_{\text{alkoxide}}$ atoms. On the contrary, in the dinuclear barium complex $[\text{Ba}\{\mu\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2$, the $\text{N}(\text{SiMe}_3)_2^-$ ligand takes the bridging position between the metal centers. This structure highlights the considerable steric bulkiness of $\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2^-$ and the limited electron density of the oxygen in the boryloxide (according to the π -back donating toward the empty $2p_z$ orbital of boron). But upon examination of complexes **32** and **62**, in the presence of the fluoroarylamide, both boryloxide and hexamethyldisilazide are bridging between the calcium centers as a result of the less electron density on $\text{N}(\text{C}_6\text{F}_5)_2^-$ ligand. Therefore, it can be concluded that the electron availability and bridging (donating) properties follow the trend of $\text{N}(\text{C}_6\text{F}_5)_2^- < \text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2^- < \text{N}(\text{SiMe}_3)_2^-$ in these monoanionic ligands (Figure 2.35). Such a tendency is useful to the future design of Ae (and other metal) complexes based on these monoanionic, monodentate ligands.

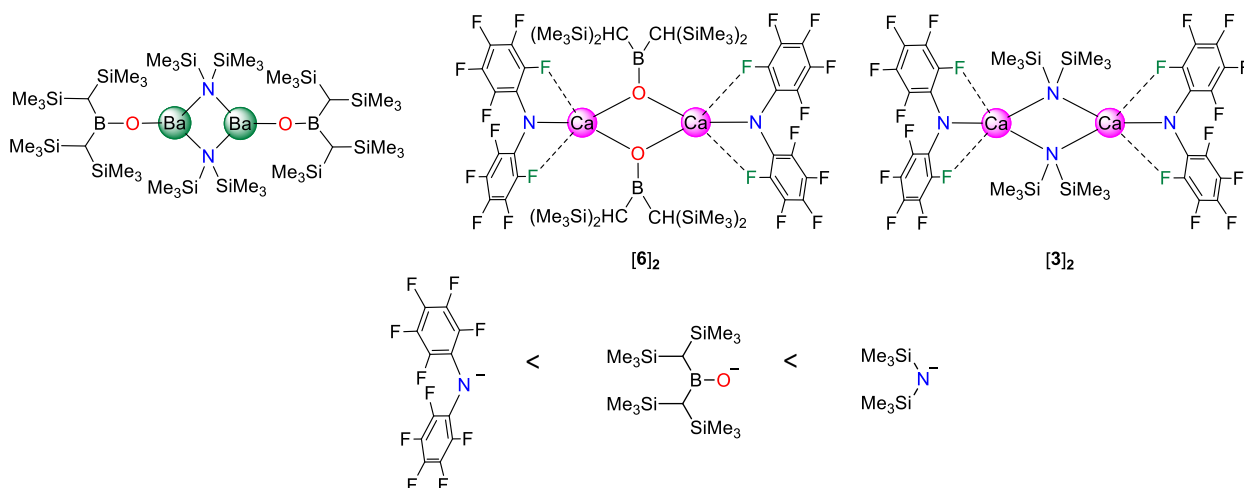
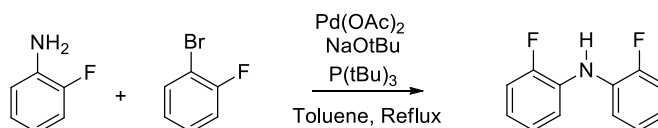


Figure 2.35. Molecular solid-state structure of complexes **3**₂, **4**₂, and **6**₂ in the molecular solid-state.

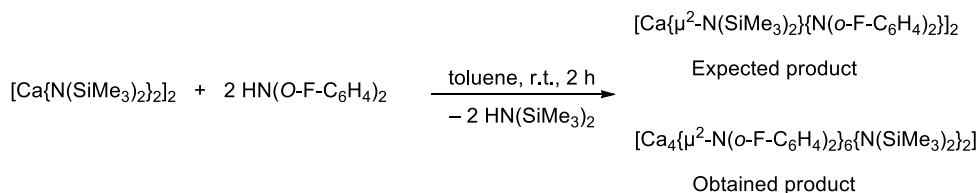
2.2.2.2.4 Synthesis of bis(2-fluorophenyl)amido proligand $\text{N}(o\text{-F-C}_6\text{H}_4)_2^-$ and corresponding calcium complexes $[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}\{\text{N}(o\text{-F-C}_6\text{H}_4)_2\}]$ (**8**) and $[\{\text{BDI}^{\text{Dipp}}\}\text{CaN}(o\text{-F-C}_6\text{H}_4)_2\cdot(\text{thf})]$ (**9**)

Bis(2-fluorophenyl)amine $\text{HN}(o\text{-F-C}_6\text{H}_4)_2$ has not been previously used as a proligand. It has two aromatic groups, having each one fluorine atom in the *ortho* position which would give the possibility of creating $\text{Ca}\cdots\text{F}\cdots\text{C}$ interactions with the metal center in an electrophilic complex. Furthermore, compared to the amide $\text{N}(\text{C}_6\text{F}_5)_2^-$, removing the fluorine atoms from the *meta* and *para* positions provides a more accessible and less sterically hindered complex. $\text{HN}(o\text{-F-C}_6\text{H}_4)_2$ was prepared in 65% yield following the Buchwald–Hartwig coupling of 2-fluoroaniline with 1-bromo-2-fluorobenzene (Scheme 2.11).⁸⁷ This amine is fully soluble in common organic solvents and has been characterized by multinuclear NMR spectroscopy.



Scheme 2.11. Synthesis of $\text{HN}(o\text{-F-C}_6\text{H}_4)_2$.⁸⁷

For the attempted preparation of the heteroleptic bis(amido) calcium complex $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{o-F-C}_6\text{H}_4)_2\}]_2$ using the amine $\text{HN}(\text{o-F-C}_6\text{H}_4)_2$, the same procedure as that for $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**32**) was followed, i.e. protonolysis between the $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ with an equimolar amount of $\text{HN}(\text{o-F-C}_6\text{H}_4)_2$ in toluene (Scheme 2.12).



Scheme 2.12. Attempted synthesis of the heteroleptic calcium fluoroamide $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{O-F-C}_6\text{H}_4)_2\}]_2$.

However, the result was not as expected. A small amount of single crystals of a tetranuclear calcium complex, $[\text{Ca}_4\{\mu_2\text{-N}(\text{o-F-C}_6\text{H}_4)_2\}_6\{\text{N}(\text{SiMe}_3)_2\}_2]$ (**74**), was the only isolable product (Figure 2.36). The number of the $\text{N}(\text{o-F-C}_6\text{H}_4)_2^-$ in the **74** complex is not in accordance with the 1:1 stoichiometry of the starting materials ($[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ and $\text{HN}(\text{o-F-C}_6\text{H}_4)_2$) (Scheme 2.12). This compound is most probably a by-product of the reaction. Although this reaction was repeated several times with different reaction conditions and upon adjusting the stoichiometry of the starting reagents according to the observed crystal structure, all attempts only resulted in the formation of very small amounts of **74**. Besides, the quality of the crystal structure was not satisfactory to enable a reliable discussion of relevant metric parameters; yet, the connectivity was established without ambiguity. Unfortunately, we could not isolate sufficient amounts of the complex to perform a complete NMR analysis.

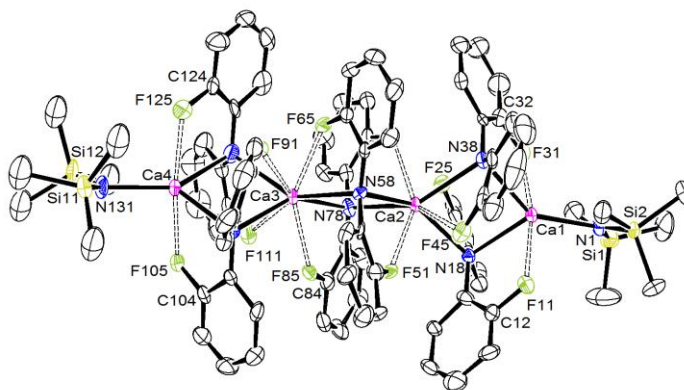
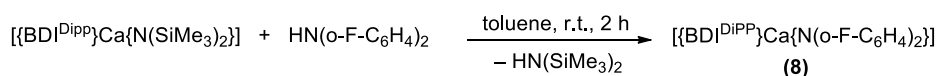


Figure 2.36. ORTEP representation of the molecular structure of $[\text{Ca}_4\{\mu^2\text{-N}(\text{o-F-C}_6\text{H}_4)_2\}_6\{\text{N}(\text{SiMe}_3)_2\}_2]$ (**74**). Ellipsoids at the 50% probability level. Hydrogen atoms omitted for clarity. Poor data set ($R_{\text{int}} = 16.76\%$) and refinement ($R_1 = 13.86\%$) preclude accurate measurement of interatomic distances.

The preparation of the calcium heteroleptic complex $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(\text{o-F-C}_6\text{H}_4)_2\}]$ (**8**) was carried out by using the solvent-free β -diketiminate supported calcium complex of $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}]$ which was prepared by Hill and co-workers in 2010.^{3,4} The final product $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(\text{o-F-C}_6\text{H}_4)_2\}]$ (**8**) is presumably obtained *via* transamination between an equimolar amount of $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}]$ and $\text{HN}(\text{o-F-C}_6\text{H}_4)_2$ (32% yield; Scheme 2.13).



Scheme 2.13. Synthesis of the calcium heteroleptic complex $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(\text{o-F-C}_6\text{H}_4)_2\}]$ (**8**).

The ^1H NMR spectrum of **8** recorded in benzene- d_6 at room temperature exhibits a diagnostic singlet at δ 4.91 ppm for the $\{\text{BDI}^{\text{DiPP}}\}^-$ backbone methine CH hydrogen atom (Figure 2.37). The ^{19}F NMR spectrum consists of a multiplet at δ -130.66 ppm for both fluorine atoms in the *ortho* position of the fluoroarylamide (Figure 2.38). This complex is highly soluble in hydrocarbons. Despite several attempts, single crystals of this complex could not be obtained.

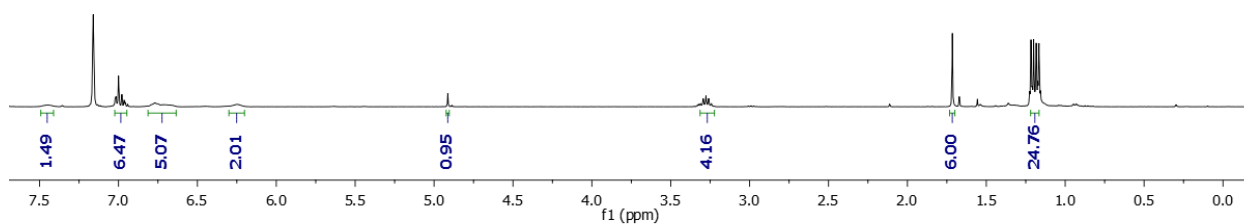


Figure 2.37. ^1H NMR spectrum (benzene- d_6 , 298 K, 400 MHz) of $[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}\{\text{N}(\text{C}_6\text{FH}_4)_2\}]$ (**8**).

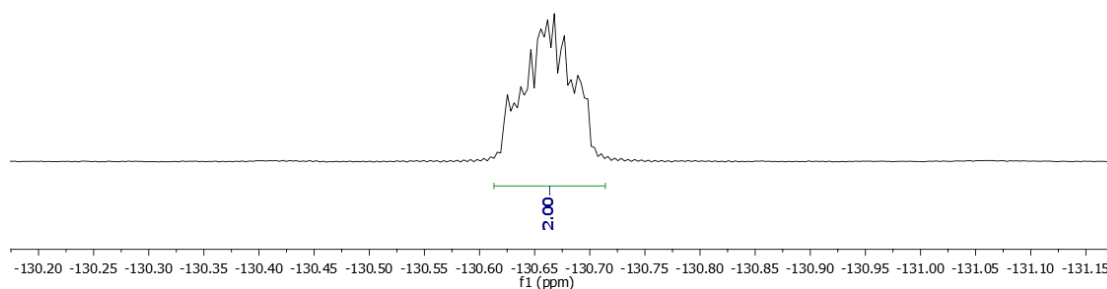
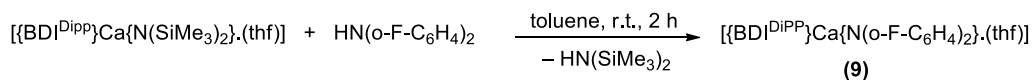


Figure 2.38. ^{19}F NMR spectrum (benzene- d_6 , 298 K, 376 MHz) of $[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}\{\text{N}(\text{C}_6\text{FH}_4)_2\}]$ (**8**).

Since all efforts for getting the crystal structure of **8** failed, we attempted to prepare a similar complex by reacting $\text{HN}(o\text{-F-C}_6\text{H}_4)_2$ with the thf-adduct $[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}\{\text{N}(\text{SiMe}_3)_2\} \cdot (\text{thf})]^{19\text{a}}$. The transamination between this complex and the proligand $\text{HN}(o\text{-F-C}_6\text{H}_4)_2$ afforded the mononuclear thf adduct $[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}\{\text{N}(o\text{-F-C}_6\text{H}_4)_2\} \cdot (\text{thf})]$ (**9**) in 30% yield (Scheme 2.14).



Scheme 2.14. Synthesis of fluoroarylamide-containing calcium heteroleptic complex $[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}\{\text{N}(o\text{-F-C}_6\text{H}_4)_2\} \cdot (\text{thf})]$ (**9**).

The ^1H NMR (recorded in benzene- d_6 at room temperature, Figure 2.39) spectrum confirms the identity of complex **9**, with in particular a singlet at δ 4.97 ppm for the methine CH hydrogen

atom. The presence one thf molecule is also observed, with the related resonances at δ 3.05 and 0.89 ppm. A single broad resonance at δ -130.67 ppm is detected in the ^{19}F NMR spectrum of complex **9** (Figure 2.40).

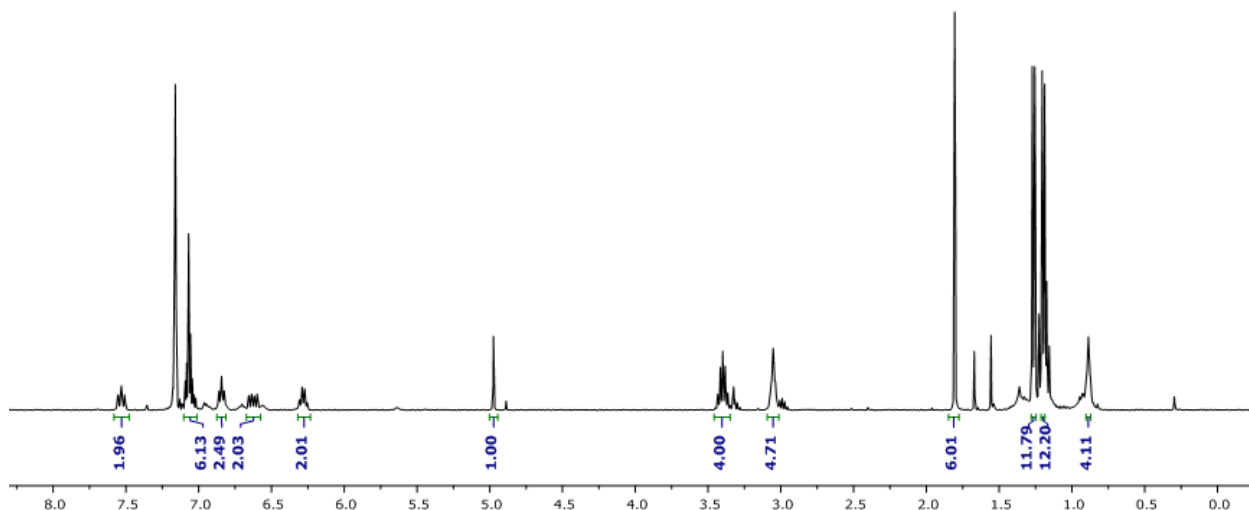


Figure 2.39. ^1H NMR spectrum (benzene- d_6 , 298 K, 400 MHz) of $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(o\text{-F-C}_6\text{H}_4)_2\cdot(\text{thf})]$ (**9**).

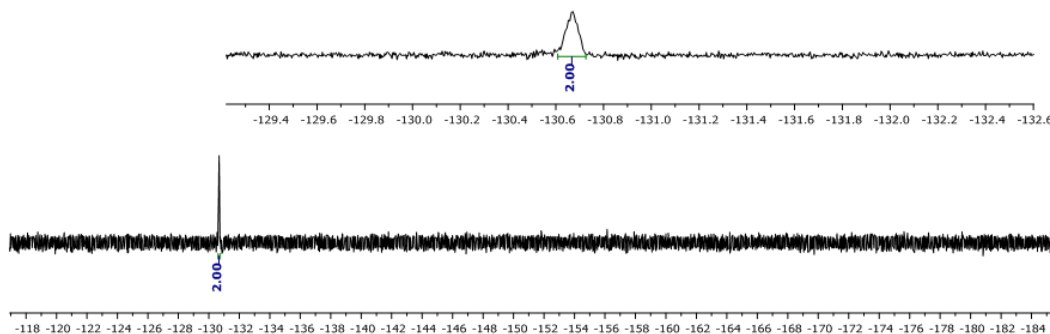


Figure 2.40. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (benzene- d_6 , 298 K, 376 MHz) of $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(o\text{-F-C}_6\text{H}_4)_2\cdot(\text{thf})]$ (**9**).

$[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(o\text{-F-C}_6\text{H}_4)_2\}\cdot(\text{thf})]$ (**9**) was recrystallized as a monomer from a concentrated pentane solution at room temperature. The X-ray diffraction reveals a four-coordinate calcium complex (Figure 2.41), in which the bidentate β -diketiminato $\{\text{BDI}^{\text{DiPP}}\}^-$ provides two Ca–N bonds around the metal (Ca–N_{BDI}: 2.367(4) and 2.316(4) Å). As previously mentioned, the fluorinated $\text{N}(o\text{-F-C}_6\text{H}_4)_2^-$ ligand has the potential to provide properties including a larger C–F

bond dipole, a stronger $\text{Ae} \cdots \text{F}-\text{C}$ interaction, more accessible and less sterically hindered metal center and more basic character proper for catalytic objectives. $\text{N}(\text{o}-\text{F}-\text{C}_6\text{H}_4)_2^-$ is relatively more electron rich than $\text{N}(\text{C}_6\text{F}_5)_2^-$ and supposed to provide stronger $\text{M} \cdots \text{F}-\text{C}$ interaction; it is thus not surprising to observe that the $\text{Ca}-\text{N}_{\text{C}_6\text{FH}_4}$ bond is also strong in **9** (2.337(4) Å). In $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ **42**, the $\text{Ca}-\text{N}_{\text{C}_6\text{F}_5}$ distance (2.3880(19) Å) is longer because of the low electron density on the nitrogen ($\text{N}_{\text{C}_6\text{F}_5}$).



Figure 2.41. ORTEP representation of the molecular solid-state structure of $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(\text{o}-\text{F}-\text{C}_6\text{H}_4)_2\} \cdot (\text{thf})]$ (**9**). Ellipsoids at the 50% probability level. H atoms omitted for clarity. $\text{Ca} \cdots \text{F}$ interactions depicted in dashed bonds. Selected bond lengths (Å): $\text{Ca}(1)-\text{N}(1) = 2.367(4)$, $\text{Ca}(1)-\text{N}(19) = 2.316(4)$, $\text{Ca}(1)-\text{N}(41) = 2.337(4)$, $\text{Ca}(1)-\text{F}(48) = 2.486(3)$, $\text{Ca}(1)-\text{F}(55) = 2.549(3)$, $\text{Ca}(1)-\text{O}(61) = 2.348(3)$.

Another distinctive feature of the molecular structure of **9** is the presence of the solvent (thf) in the solid structure ($\text{Ca}-\text{O} = 2.348(3)$ Å) which fills the coordination sphere and warrants the formation of this mononuclear complex; this is in agreement with the NMR data of the complex. The presence of the solvent affects the length and strength of all $\text{Ca}-\text{N}$ and $\text{Ca} \cdots \text{F}-\text{C}$ interactions in the complex, therefore it is not possible to rely completely on the structure of this complex for comparison with the strength of similar bonds in complex **42**. The $\text{Ca}-\text{N}_{\text{BDI}}$ bond distances (2.367(4) and 2.316(4) Å) and $\text{Ca}-\text{O}_{\text{thf}}$ bond distance (2.348(3) Å) in **9** are shorter than the

similar contacts in [$\{\text{BDI}^{\text{Dipp}}\}\text{CaN}(\text{SiMe}_3)_2\cdot(\text{thf})$] ($\text{Ca}-\text{N}_{\text{BDI}} = 2.352(1)$ and $2.370(1)$ Å, $\text{Ca}-\text{O}_{\text{thf}} = 2.359(1)$ Å),^{19b} while $\text{Ca}-\text{N}_{\text{C}_6\text{FH}_4}$ bond in **9** ($2.337(4)$ Å) is longer than the $\text{Ca}-\text{N}_{\text{HMDS}}$ bond ($2.313(1)$ Å) in [$\{\text{BDI}^{\text{Dipp}}\}\text{CaN}(\text{SiMe}_3)_2\cdot(\text{thf})$]. All these differences are related to the fact that $\text{N}(\text{SiMe}_3)_2^-$ is more electron-rich than $\text{N}(\text{C}_6\text{F}_5)_2^-$ ligand; hence it leads to stronger contacts between the metal center and $\{\text{BDI}^{\text{Dipp}}\}^-$ and also the shorter metal-solvent contact in **9**.

2.2.3 Bond valence sum analysis

Bond valence sum analysis (BVSA) is applicable for XRD structures of molecular compounds in the solid-state. It is estimated according to the contribution of donating atoms toward the coordination sphere of the metal center. This method is originally based on Pauling's rules that lead to predicting and rationalizing the crystal structure of the compounds. Accordingly, the valence of the M-X bond is defined as the ratio between the charge and coordination number of M (central atom). Pauling also realized the shortening of the relative ionic radii of the cation and its neighboring anion in the case of increased electronic density between them. This shows the relation of the bond length to its strength. Later, Donnay and Allmann deduced the correlation of valence and bond length. Finally, in 1985, Brown and Altermatt proposed an equation to predict the valence through the sum of all the bond lengths.

$$V_i = \sum S_{ij} \equiv \sum \exp \left[\frac{(R_0 - r_{ij})}{b} \right] \quad (\text{eqn. 2-1})$$

V_i is the oxidation state of atom i ; S_{ij} and r_{ij} are the valence and the length of the bond between atom i and atom j respectively. The b parameter does not vary a lot from one pair of atoms to the other pair. Brown and Altermatt described that the value of 0.37 for b was consistent for most cases. The value of R_0 is calculated for each cation environment and it is the experimental value for the distance of a given cation-anion pair. The required parameters for calculation of the valences from bond lengths have been determined through the studies on the atom pairs in the Inorganic Crystal Structure Database (ICSD).

Pauling's concept has been previously used to study the bond strength or bond valence of mineral structures for many years.⁸⁸ Brown and Altermatt determined the essential parameters for calculating the bond valences according to the bond lengths for 750 atoms,⁸⁹ and this method was

further developed by O'Keefe and Brese.⁹⁰ The descriptive study about the developments of this method has been reported by Brown recently.⁹¹ This empirical treatment makes use of interatomic distances measured by single-crystal X-ray diffraction to evaluate the relative contributions of each neighboring atom towards the coordination sphere of a given metallic center. This technique has been used recently to assess the nature of the bonding pattern around the metals and, relevantly to our case, gauge the role of non-covalent interactions in complexes of oxophilic elements.^{31,43,92}

The contribution of $\text{Ca}\cdots\text{F}-\text{C}$ secondary interactions in the global coordination sphere of the metal center was qualitatively evaluated for complexes **1'**, **3₂**, **4₂**, **6₂**, **9** applying BVSA. Having established the molecular structure of the complex, the valence of calcium has been calculated for elements interacting with the metal (O, N, F). The BVSA calculations are collected in Table 2.3. Apart from the $\text{Ca}\cdots\text{F}-\text{C}$ secondary interaction, the remaining coordination sphere is filled by the $\text{Ca}-\text{O}$ or $\text{Ca}-\text{N}$ bonds. In the case of the dinuclear aminoetherfluoroalkoxide $[\{\text{RO}^1\}\text{CaN}(\text{SiMe}_3)_2]_2$ which has been studied by our group (see Scheme 2.3),⁴³ $\text{Ca}\cdots\text{F}-\text{C}$ interactions contribute to *ca.* 4.5% of the overall coordination sphere around the metal center. This is much less than the estimated influence of $\text{Ca}\cdots\text{F}-\text{C}$ contacts in **1'** (20%). We believe the effect of the additional metal-bound heteroatoms with the aminoether-fluoroalkoxide $\{\text{RO}^{\text{F}}\}^-$ and the resulting greater coordination number (= 5) in $[\{\text{RO}^1\}\text{CaN}(\text{SiMe}_3)_2]_2$ may reduce the strength of the pertaining $\text{Ca}\cdots\text{F}-\text{C}$ contacts. By contrast, in complex **1'**, there is a much greater importance of these interactions owing to the low coordination number (CN of complex **1'** = 4) of the metal.

The data in Table 2.3 indicate that for **3₂** complex, $\text{Ca}\cdots\text{F}-\text{C}$ interactions contribute *ca.* 12% to the overall coordination sphere of calcium centers which is lower than for complex **1'**. This is due to the $\text{N}(\text{SiMe}_3)_2^-$ ligand which is relatively electron rich compared to $\text{N}(\text{C}_6\text{F}_5)_2^-$. The presence of the bulky $\text{N}(\text{SiMe}_3)_2^-$ ligand in the bridging position should also provide steric hindrance; therefore there is only one $\text{Ca}\cdots\text{F}-\text{C}$ interaction per metal center. According to the calculations for **4₂** and **5₂**, the $\text{Ca}\cdots\text{F}-\text{C}$ contact contributes quite similarly to **1'** with quite 20% of participation in the whole coordination sphere of Ca^{+2} cation, and the remaining of the coordination sphere is filled out by $\text{Ca}-\text{N}$ bonds. It is noteworthy that in the solid state structures of **4₂** and **5₂**, there are relatively more contributions of the $\text{Ca}\cdots\text{F}-\text{C}$ secondary interactions to the

whole bonding pattern than in **3₂** and **6₂**. The intermolecular Ca $\cdots$ F–C interactions in complexes **4₂** and **5₂** give stability and also have the bridging role between the two molecules (Ca $\cdots$ F40–C and Ca $\cdots$ F9–C in **4₂** and **5₂** respectively). On the basis of X-ray and BVSA, one can conclude that the complexes featuring the N(C₆F₅)₂[–] ligand in the bridging position receive more electron density from the Ca $\cdots$ F–C secondary interactions (**4₂** and **5₂**). The calculations according to the derived X-ray structure of **9** indicate a lower contribution of the Ca $\cdots$ F–C contacts in the total coordination sphere of the calcium cation (13%) compared to **4₂** (19%). Several items contribute to this fact; there are only two Ca $\cdots$ F–C secondary interactions in **9** resulting from the two fluorine atoms in the *ortho* position to the nitrogen in N(*o*-F-C₆H₄)₂[–] ligand; N(*o*-F-C₆H₄)₂[–] contains less electron withdrawing groups compared to N(C₆F₅)₂[–], and there is a coordinated thf molecule in **9** that provides stability and electron density to the metal center.

In general, BVSA showed that, to a large extent, the metal centers were actively supported by Ae $\cdots$ F–C secondary interactions which contributed 17% to 20% of the total coordination sphere except for **3₂** and **9**.

Table 2.3. Bond valence sum analysis (BVSA) for the calcium complexes **1'**, **3₂**, **4₂**, **5₂**, **6₂**, **9**.

Complex	M	$d(\text{Ca-N})^a$	$d(\text{Ca-F})^a$	$d(\text{Ca-O})^a$	$v(\text{Ca-N})^b$	$v(\text{Ca-F})^b$	$v(\text{Ca-O})^b$	$\Sigma(v_{\text{Ca1-X}})$
[Ca{N(C ₆ F ₅) ₂ } ₂ .(Et ₂ O) ₂] (1') One 4-coordinate Ca atom	Ca(1)	2.380	2.493	2.340	0.52	0.17	0.36	
		2.370	2.523	2.342	0.54	0.16	0.36	
		-	2.771	-	-	0.08	-	
		-	3.074	-	-	0.04	-	
	$\Sigma(v_{\text{Ca1-X}})$				1.06	0.45	0.73	2.24
	%($v_{\text{Ca1-X}}$)				47	20	33	100%
[Ca{ μ^2 -N(SiMe ₃) ₂ } {N(C ₆ F ₅) ₂ }] ₂ (3₂) Two distinct 3-coordinate Ca atoms	Ca(1)	2.433	2.423	-	0.45	0.21	-	
		2.404	-	-	0.49	-	-	
		2.385	-	-	0.52	-	-	
	$\Sigma(v_{\text{Ca1-X}})$				1.46	0.21	-	1.67
	%($v_{\text{Ca1-X}}$)				87	13	-	100
	Ca(2)	2.439	2.456	-	0.45	0.19	-	
		2.411	-	-	0.48	-	-	
		2.383	-	-	0.52	-	-	
$\Sigma(v_{\text{Ca1-X}})$				1.44	0.19	-	1.63	
%($v_{\text{Ca1-X}}$)				88	12	-	100	
[{BDI ^{DiPP} }CaN(C ₆ F ₅) ₂] ₂ (4₂) Two identical 3-coordinate Ca atoms	Ca(1)	2.307	2.532	-	0.64	0.15	-	
		2.346	2.556	-	0.57	0.14	-	
		2.388	2.712	-	0.51	0.09	-	
	$\Sigma(v_{\text{Ca1-X}})$				1.72	0.39	-	2.11
	%($v_{\text{Ca1-X}}$)				81	19	-	100
[{N ^{DiPP} }CaN(C ₆ F ₅) ₂] ₂ (5₂) Two identical 3-coordinate Ca atoms	Ca(1)	2.388	2.558		0.511	0.144		
		2.253	2.559		0.737	0.144		
		2.389	2.530		0.510	0.155		
	$\Sigma(v_{\text{Ca1-X}})$				1.758	0.443		2.201
	%($v_{\text{Ca1-X}}$)				80	20		
[Ca{ μ -OB(CH(SiMe ₃) ₂) ₂ } {N(C ₆ F ₅) ₂ }] ₂ (6₂) Two distinct 3-coordinate Ca atoms	Ca(1)	2.370	2.544	2.271	0.54	0.15	0.44	
		-	2.597	2.269	-	0.13	0.44	
	$\Sigma(v_{\text{Ca1-X}})$				0.54	0.28	0.88	1.70
	%($v_{\text{Ca1-X}}$)				32	16	52	100
	Ca(2)	2.356	2.498	2.243	0.56	0.17	0.47	
		-	2.553	2.259	-	0.15	0.45	
	$\Sigma(v_{\text{Ca1-X}})$				0.56	0.32	0.93	1.81
%($v_{\text{Ca1-X}}$)				31	18	51	100	

Table 2.3. Bond valence sum analysis (BVSA) for the calcium complexes **1'**, **3₂**, **4₂**, **5₂**, **6₂**, **9**.

Complex	M	$d(\text{Ca-N})^a$	$d(\text{Ca-F})^a$	$d(\text{Ca-O})^a$	$v(\text{Ca-N})^b$	$v(\text{Ca-F})^b$	$v(\text{Ca-O})^b$	$\Sigma(v_{\text{CaI-X}})$
	%($v_{\text{CaI-X}}$)				31	18	51	100
[$\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(\text{o-F-C}_6\text{H}_4)_2\} \cdot (\text{thf})$] (9) One 4-coordinate Ca atom	Ca(1)	2.367	2.486	2.348	0.541	0.175	0.357	
		2.316	2.549		0.621	0.148		
		2.337			0.587			
	$\Sigma(v_{\text{CaI-X}})$				1.749	0.323	0.357	2.429
	%($v_{\text{CaI-X}}$)				72	13	15	

[a] Data from the X-ray structure of (**1'**, **3₂**, **4₂**, **5₂**, **6₂**, **9**). [b] Calculated using Equation 2-1 of BVSA. $R_{\text{Ca-O}} = 1.967 \text{ \AA}$, $R_{\text{Ca-F}} = 1.842 \text{ \AA}$, $R_{\text{Ca-N}} = 2.14 \text{ \AA}$; $B = 0.37$.

2.3 Bonding analysis by DFT calculations

In order to get an insight according to the nature and strength of the $\text{Ae}\cdots\text{F}-\text{C}$ interactions, we have performed DFT calculations. The computations in this section have been obtained through collaboration with Dr. Jean-Yves Saillard and Dr. Samia Kahlal. The calculations have been provided by means of model systems at the PBE0/Def2-TZVP and PBE0/Def2-TZVP-D3 levels.

Since, in these compounds, both Ae and F belong to the same molecule, one might have to consider the potential role of the pinch intramolecular effect that could force the two atoms to get close to each other. In a first approach, we ruled out this possibility by investigating bimolecular systems, i.e. the interaction between one F-containing molecule or ion, namely $\text{C}_6\text{H}_5\text{F}$, CH_3F and F^- , and a simplified calcium complex. Since most of the molecular structures described above exhibit an Ae^{2+} ion in a trigonal planar coordination mode (not considering the $\text{Ae}\cdots\text{F}-\text{C}$ interactions), the model complex chosen for this initial study was the simple $[\{\text{NH}(\text{CH})_3\text{NH}\}\text{Ca}(\text{NH}_2)]$ (**A**). The optimized geometries of the three $\text{A}(\text{C}_6\text{H}_5\text{F})$, $\text{A}(\text{CH}_3\text{F})$ and AF^- bimolecular systems are shown in Figure 2.42. Optimizations were performed with and without considering the 3-parameter Grimme's empirical corrections (D3)⁹³ for dispersion forces. Such corrections are expected to take satisfyingly into account the van der Waals component of the $\text{Ca}\cdots\text{F}$ bonding. The Ca–F distances obtained with and without D3 corrections are reported at the top of Figure 2.42 in black and blue colors, respectively. A weak shortening of the Ca–F distances (lower than 1%) occurs when introducing dispersion forces, indicating that van der Waals bonding does not play a crucial role in the interaction. The Ca–F distance is only slightly shortened when going from $\text{A}(\text{C}_6\text{H}_5\text{F})$ to $\text{A}(\text{CH}_3\text{F})$, and Ca remains in an approximate planar CaN_3 coordination. The AF^- structure is different, with a very short Ca–F distance (2.09 Å) and a pyramidalized (sp^3) Ca atom. Clearly, AF^- exhibits strong $\text{Ca}\cdots\text{F}$ bonding.

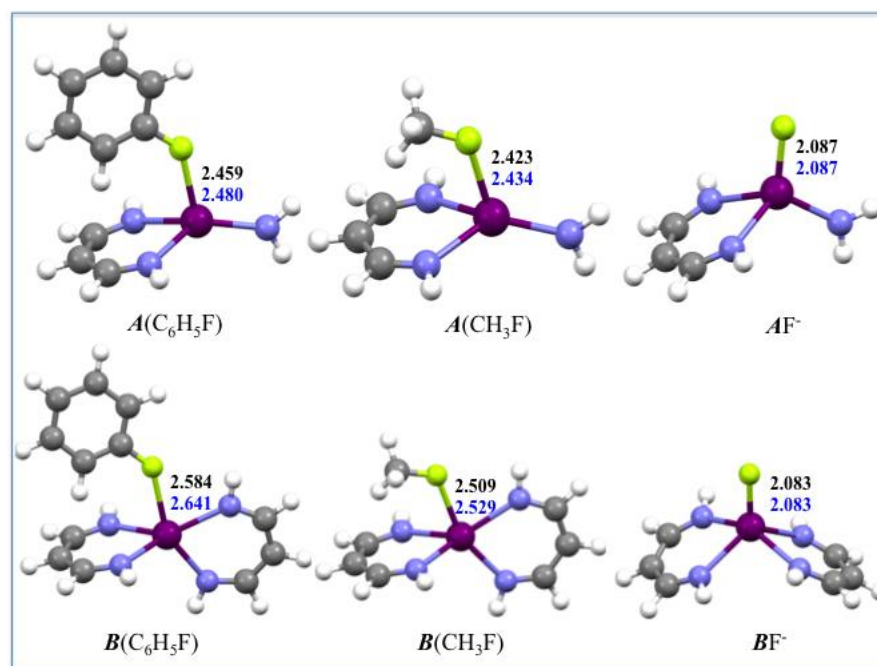


Figure 2.42. Optimized geometries of the $A(C_6H_5F)$, $A(CH_3F)$, AF^- , $B(C_6H_5F)$, $B(CH_3F)$ and BF^- models. Interatomic distances are given in Å; in black, with D₃ corrections; in blue, without D₃ corrections.

A more detailed understanding of the nature of the $Ca \cdots F(-C)$ bonding in the above series is obtained by an energy decomposition analysis (EDA) of the interaction between two fragments, according to the Morokuma-Ziegler procedure.⁹⁴ The decomposition of the total bonding energy (TBE) between A and the C_6H_5F , CH_3F and F^- fragments in the three optimized systems of Figure 2.42 is provided in Table 2.4 (D3 corrections considered). TBE is expressed as the sum of four components, the Pauli repulsion (E_{Pauli}), the electrostatic interaction energy (E_{elstat}), the orbital interaction energy (E_{orb}) and the component associated with the dispersion forces (E_{disp}). Unsurprisingly, E_{Pauli} increases with a decrease of the $Ca \cdots F-C$ separation. It is overbalanced by the three other stabilizing components, of which E_{elstat} prevails, indicating predominance of ionic bonding. In $A(C_6H_5F)$, the E_{orb} component is about half of E_{elstat} , indicating weak, although non-negligible, covalent interactions. Consistently with the above discussion on bond distances, the E_{disp} contribution is minor, corroborating weak van der Waal interactions. While the EDA analysis of $A(CH_3F)$ provides rather similar values and conclusions as those for $A(C_6H_5F)$, different results were obtained for AF^- . Clearly, this other model contains a real and strong Ca–F

single bond of ionocovalent nature, whereas in the two other models, the $\text{Ca}\cdots\text{F}-\text{C}$ interaction is about six-fold weaker.

Table 2.4. Morokuma-Ziegler energy decomposition analysis in the model compounds $\mathbf{4}'_2$ and those derived from $[\{\text{NH}(\text{CH})_3\text{NH}\}\text{Ca}(\text{NH}_2)]$ ($=\mathbf{A}$) and $[\{\text{NH}(\text{CH})_3\text{NH}\}_2\text{Ca}]$ ($=\mathbf{B}$).^a

	$A(\text{C}_6\text{H}_5\text{F})$	$A(\text{CH}_3\text{F})$	AF^-	$\mathbf{4}_2$	$A(\text{CH}_4)$	$A(\text{C}_6\text{H}_6)$	$A(\text{C}_2\text{H}_4)$	$B(\text{C}_6\text{H}_5\text{F})$	$B(\text{CH}_3\text{F})$	BF^-
E_{Pauli}	0.42	0.50	2.14	0.98	0.29	0.48	0.52	0.39	0.47	2.16
E_{elstat}	-0.53	-0.71	-4.46	-0.95	-0.24	-0.53	-0.54	-0.44	-0.61	-4.22
E_{orb}	-0.28	-0.28	-1.31	-0.62	-0.19	-0.41	-0.27	-0.21	-0.22	-1.43
E_{disp}	-0.15	-0.11	-0.02	-0.80	-0.09	-0.21	-0.11	-0.17	-0.11	-0.02
TBE	-0.55	-0.60	-3.65	-1.39	-0.24	-0.66	-0.43	-0.43	-0.48	-3.51

^a all values in eV. ^b Total bonding energy = $E_{\text{Pauli}} + E_{\text{elstat}} + E_{\text{orb}} + E_{\text{disp}}$.

The weak $\text{Ca}\cdots\text{F}-\text{C}$ covalent contribution in $A(\text{C}_6\text{H}_5\text{F})$ and $A(\text{CH}_3\text{F})$ is in line with the natural atomic orbital (NAO) population analysis. In the two models, the computed $\text{F}\rightarrow\text{Ca}$ charge transfer is virtually nil (lower than 10^{-2}), whereas it is 0.07 in AF^- . Surprisingly, the fluorine charge in $A(\text{C}_6\text{H}_5\text{F})$ and $A(\text{CH}_3\text{F})$ (-0.36 and -0.40, respectively) is more negative than in the free $\text{C}_6\text{H}_5\text{F}$ and CH_3F ligands (-0.31 and -0.35, respectively). This is diagnostic of strong electrostatic interaction with Ca, which attracts electron density towards the fluorine, but without any significant $\text{F}\rightarrow\text{Ca}$ electron transfer due to the poor bond covalence.

Since in the solid state, compounds $\mathbf{4}_2$ and $\mathbf{5}_2$ are dimers of mononuclear three-coordinate Ca complexes paired through intermolecular $\text{Ca}\cdots\text{F}-\text{C}$ contacts, an EDA analysis of the interaction between the two monomers was also carried out. Compound $\mathbf{4}_2$ was slightly simplified by replacing its Dipp and methyl substituents by hydrogen atoms. The geometry of this model ($\mathbf{4}'_2$) was fully optimized at the PBE0/Def2-TZVP-D3 level. It showed the presence of $\text{Ca}\cdots\text{F}-\text{C}$ intermolecular contacts with interatomic distances of 2.584 and 2.612 Å, whereas the intramolecular contact was 2.581 Å. The EDA data obtained for $\mathbf{4}'_2$ on the basis of two monomeric fragments are given in Table 2.4. Considering that there are four inter-monomer $\text{Ca}\cdots\text{F}-\text{C}$ contacts (but somewhat longer than in $A(\text{C}_5\text{H}_5\text{F})$, see below and Table 2.5), and that

other van de Waals contacts are also present (see the structure of **4**₂ in Figure 2.29), the interaction energy component of **4**₂ are fully consistent with that of the simple *A*(C₅H₅F) model.

In the above-computed models, the calcium atom lies in an approximate trigonal planar geometry (except for *AF*[−]), thus having its accepting 3p_z orbital essentially pointing in the direction of the electron-rich fluorine atom. A point of interest is the importance of the (weak) covalent interaction when calcium is tetravalent, being in a distorted sp³ hybridization. To probe this aspect, three other models, namely *B*(C₆H₅F), *B*(CH₃F) and *BF*[−] in which *B* is [{NH(CH)₃NH }₂Ca], were investigated. Their optimized geometries are shown in Figure 2.42 (bottom). On going from *A* to *B* systems, only a small lengthening of the Ca–F distances is noticed. Consistently, the EDA components of the various *B* models do not differ much from that of their *A* homologues. Thus, on switching from a sp² to a sp³ calcium, its (moderate) accepting properties do not vary significantly, owing to its propensity for hypervalence. In the weakly bonded *B*(C₆H₅F) and *B*(CH₃F), the Ca-centered CaN₄ polyhedron maintains its distorted tetrahedral configuration. On the other hand, *BF*[−] is structurally different from the two other *B* systems. With a real Ca–F single bond, Ca is in a hypercoordinated square-pyramidal environment in *BF*[−].

The real intramolecular Ca⋯F–C interactions detected in the molecular structures of compounds **1**[′], **3**₂, **4**₂ and **6**₂ are also suitably reproduced in the structure of the fully optimized molecules (dispersion forces included, Table 2.5). There is however one noticeable exception, namely the long Ca⋯F–C contact (3.074(12) Å) observed in the X-ray structure of **1**[′], which is found to be much shorter (2.769 Å) in the nearly C₂-symmetric optimized structure. This discrepancy is attributed to the packing interactions in the solid state, which distort the molecule away from ideal C₂ symmetry. It is noteworthy that the DFT calculations are carried out in gas phase, while the X-ray structure shows the molecule in the solid state in which the molecules are sometimes distorted to fit together in the crystal layers.

The smaller deviation of ca. 0.10 Å found for the inter-monomer contact in **4**₂ is likely the result of the simplification made on going from **4**₂ to the less crowded **4**₂[′] model. As a whole, these data are fully consistent with those obtained in our simple intermolecular models, providing full confidence on the validity of our analysis of the bonding scenario. The above-

observed electro-attracting effect of calcium onto the fluorine without any noticeable F→Ca electron transfer is also present in these compounds. With a NAO charge comprised between –0.30 and –0.38, all fluorine atoms involved in Ca···F–C bonding are more negatively polarized than the other fluorine atoms, the NAO charge of which being comprised between –0.27 and –0.29. The major ionic character of the interaction is also consistent with the large positive charge computed for calcium in these compounds (between +1.81 and +1.84).

Table 2.5. Comparison of experimental and computed Ca···F–C interatomic distances for the calcium complexes **1'**, **3₂**, **4₂** and **6₂**.

Complex		$d_{\text{Ca-F}}(\text{XRD})^a$	$d_{\text{Ca-F}}(\text{DFT})^b$
[Ca{N(C ₆ F ₅) ₂ } ₂ ·(Et ₂ O) ₂] (1') One 4-coordinate Ca atom	Ca1	2.4935	2.553
		2.5226	2.552
		2.7713	2.761
		3.0740	2.769
[Ca{μ ² -N(SiMe ₃) ₂ }{N(C ₆ F ₅) ₂ }] ₂ (3₂) Two distinct 3-coordinate Ca atoms	Ca1	2.4227	2.477
		-	-
	Ca2	2.4560	2.477
		-	-
[{BDI ^{DiPP} }CaN(C ₆ F ₅) ₂] ₂ (4₂) Two identical 3-coordinate Ca atoms	Ca1	2.5325	2.581 ^c
		2.5559	2.584 ^c
		2.7120	2.612 ^c
[Ca{μ-OB(CH(SiMe ₃) ₂) ₂ }{N(C ₆ F ₅) ₂ }] ₂ (6₂) Two distinct 3-coordinate Ca atoms	Ca1	2.544	2.549
		2.597	2.637
	Ca2	2.498	2.551
		2.553	2.583

^a Measured interatomic distances to X = N, F or O atoms, given in Å; see Figure. 2.14, 2.24, 2.29, 2.34 for detail.

^b PBE0/Def2-TZVP-D3-optimised distances.

^c Values calculated on the simplified **4₂** model (see above).

Owing to the dominant electrostatic nature of the $\text{Ca}\cdots\text{F}-\text{C}$ interactions, the propensity for Ca to also trigger $\text{Ca}\cdots\text{H}-\text{C}$ non-ionic bonds raises the question of the nature of these interactions. Therefore, for the sake of comparison of the strength of $\text{Ca}\cdots\text{F}-\text{C}$ interactions with $\text{Ca}\cdots\text{C}(\pi)$ and $\text{Ca}\cdots\text{H}-\text{C}$ interactions, the non-fluorinated equivalent of $A(\text{CH}_3\text{F})$, i.e. $A(\text{CH}_4)$, was also investigated. Its optimized structure (Figure 2.43) exhibits a η^3 -coordinated methane, with one shorter (2.621 Å) and two longer (2.817 Å) contacts. These values are commensurate with experimentally determined anagostic $\text{Ca}\cdots\text{H}-\text{C}$ distances, e.g. 2.8933(6) Å in $[\text{Ca}\{\text{N}(\text{SiMe}_3)(\text{mesityl})\}(\text{thf})_2]$ and 2.7741(15) Å in $[\text{Ca}\{\text{N}(\text{SiMe}_3)(\text{mesityl})\}.\text{tmeda}]$.⁹⁵

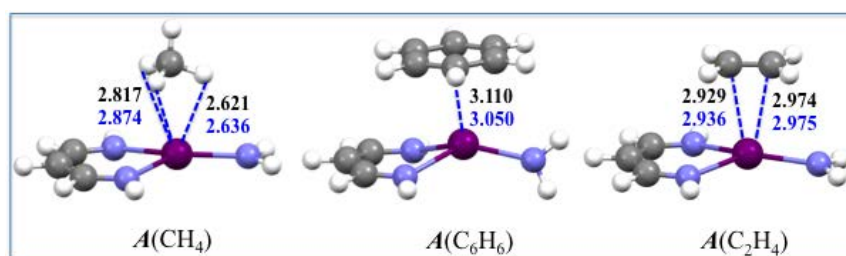


Figure 2.43. Optimized geometries of the $A(\text{CH}_4)$, $A(\text{C}_6\text{H}_6)$ and $A(\text{C}_2\text{H}_4)$ models. Interatomic distances are given in Å; in black, with D_3 corrections; in blue, without D_3 corrections.

The EDA data (Table 2.4) indicate substantially weaker bonding in the $A(\text{CH}_4)$ case (by more than 50%), but still with the same energy component order. Thus, the $\text{Ca}\cdots\text{H}-\text{C}$ interaction also has a major electrostatic and a weaker van der Waals character. Interestingly, the optimized structure of the $A(\text{C}_6\text{H}_6)$ model (Figure 2.43) does not exhibit any $\text{Ca}\cdots\text{H}-\text{C}$ contact, but rather features a weakly η^6 -coordinated benzene ligand ($\text{Ca}-\text{C} = 3.054\text{--}3.165$ Å). This indicates prevailing $\text{Ca}\cdots\text{C}(\pi)$ over $\text{Ca}\cdots\text{H}-\text{C}$ interactions, due to stronger covalent and van der Waals bonding (see Table 2.3). The interaction of calcium with a single unsaturated $\text{C}=\text{C}$ bond is exemplified in the $A(\text{C}_2\text{H}_4)$ model (Figure 2.43). The $\text{Ca}-\text{C}$ distances (2.929 and 2.974 Å) are shorter than in $A(\text{C}_6\text{H}_6)$. Its EDA values (Table 2.4) are very close to those of $A(\text{CH}_3\text{F})$, except for E_{elstat} which indicates, as anticipated, weaker ionic bonding. Thus, amongst the various weak $\text{Ca}\cdots\text{X}$ ($\text{X} = \text{F}, \text{H}, \text{C}(\pi)$) interactions reported in the literature, our computations suggest that the $\text{Ca}\cdots\text{F}-\text{C}$ one appears to be the strongest, due to the high positive charge of Ca^{2+} which in any case favours electrostatic interactions. This is in agreement with our earlier experimental

findings, using structurally characterized alkyl-substituted complexes that display a range of $\text{Ca}\cdots\text{F}-\text{C}$ and $\text{Ca}\cdots\text{C}(\pi)$ interactions (as well as $\text{Ca}\cdots\text{H}-\text{Si}$ anagostic contacts).^{42,45,96} The electrostatic nature of the $\text{Ca}\cdots\text{F}-\text{C}$ interactions is consistent with the computation results from the previous experiments of our group on the heteroleptic calcium π -adducted fluoroaminoalkoxides such as $[\{\text{RO}^{12}\}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$ and $[\{\text{RO}^{11}\}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$ (Figure 2.44).^{42,45,96}

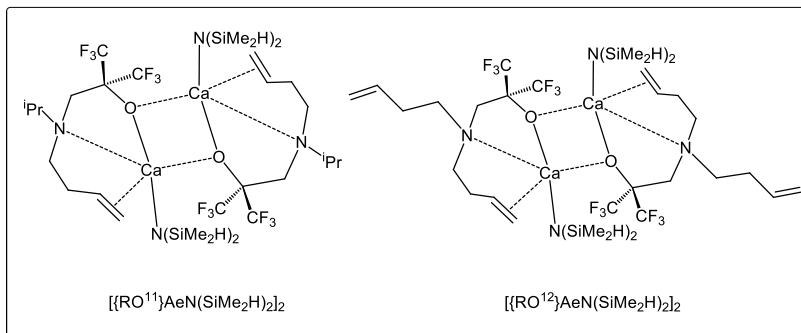


Figure 2.44. The structure of heteroleptic calcium fluoroaminoalkoxides $[\{\text{RO}^{12}\}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$ and $[\{\text{RO}^{11}\}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$.^{42,45,96}

2.4 Hydrophosphination catalysis by $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (4₂) and $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(\text{o-F-C}_6\text{H}_4)_2\} \cdot (\text{thf})]$ (9)

As described in chapter 1, the catalysis of hydroelementation reactions such as hydroamination, hydrophosphination and hydrosilylation are some of the useful applications of Ae complexes. The β -diketiminato-stabilized calcium amide $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2 \cdot (\text{thf})]$ (**I**) has been reported to be very efficient for intramolecular hydroamination of aminoalkenes by Hill and co-workers.¹⁵ Our group has made several contributions in catalyzed intermolecular hydroamination reactions utilizing the $[\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{AeN}(\text{SiMe}_3)_2 \cdot (\text{thf})]$ (especially for Ae = Ba) complexes.^{13,14} Recently, Okuda *et al.* have catalyzed hydrosilylation reactions with a cationic calcium hydride (Figure 2.45).⁹⁷

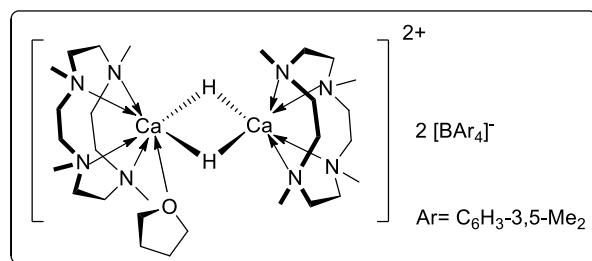
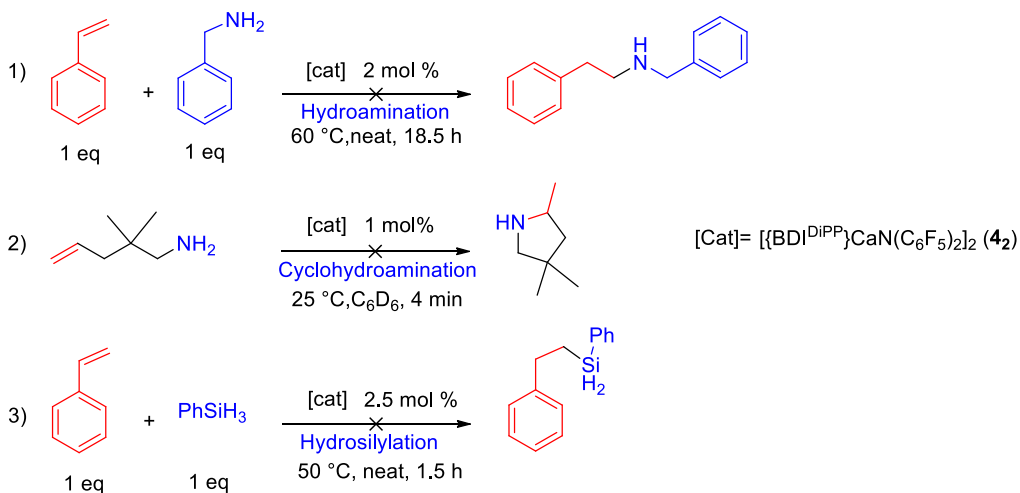


Figure 2.45. Cationic calcium hydride stabilized by an N[^]N[^]N[^]N macrocycle applied in hydrosilylation.⁹⁷

In this section, the behavior of [$\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2\}_2$ (**4₂**) and [$\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(o\text{-F-C}_6\text{H}_4)_2\}(\text{thf})$] (**9**) in hydroelementation catalysis is detailed. Both complexes **4₂** and **9** bear the ancillary $\{\text{BDI}^{\text{DiPP}}\}^-$ ligand and are hence related to [$\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2(\text{thf})$] (**I**). The hydroamination of styrene with benzylamine, cyclohydroamination of 2,2-dimethylpent-4-en-1-amine and hydrosilylation of styrene with phenylsilane, have been investigated using **4₂** under standard reaction conditions as described in the literature (Scheme 2.15).^{13,15,62a} The resulting data show that this complex is inactive in all attempted reactions. This could be due to its low basicity. In a catalytic cycle, the catalyst formation from the precatalyst ([$\{\text{L}\}\text{AeR}$]) happens usually with displacement of the reactive group (R^-) with the substrate molecule HX (e.g. amine, phosphine, silane). This step takes place according to the difference in the basicity of R^- and that of X^- .



Scheme 2.15. Attempted intermolecular hydroamination, cyclohydroamination and intermolecular hydrosilylation reactions by precatalyst **4₂**.

We therefore sought to use these complexes in hydrophosphination catalysis, making use of more acidic phosphine substrates. There are some examples of calcium precatalysts with β -diketiminate, iminoanilide, iminoamidinate and multidentate phenolate ligands that have been applied for hydrophosphination reactions (Figure 2.46).^{13,14,64,98,99} In particular, the efficiency of [$\{\text{BDI}^{\text{Dipp}}\}\text{CaN}(\text{SiMe}_3)_2(\text{thf})$] (**I**) as a catalyst, has been established by Hill *et al.*² Recently, there has been a growing number of alkene hydrophosphination reactions catalyzed by Ae complexes.

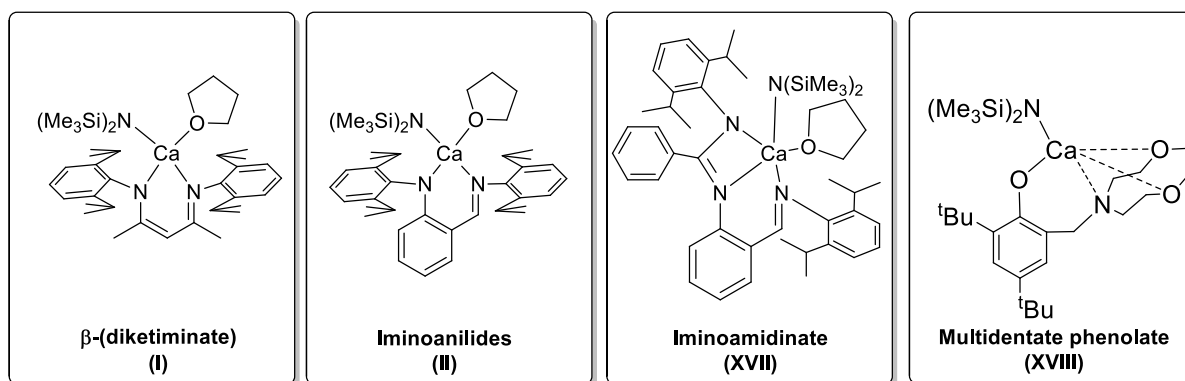
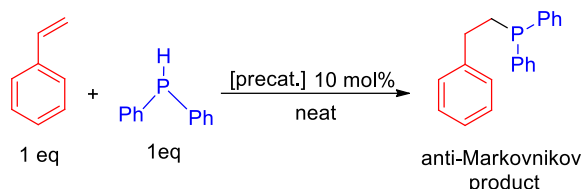


Figure 2.46. Heteroleptic calcium precatalysts reported for the hydrophosphination of styrene with Ph_2PH .^{13,14,64,98,99}

Complexes **4₂** and **9** proved potent precatalysts in the benchmark intermolecular hydrophosphination of styrene with diphenylphosphine (Ph_2PH) (Table 2.6). The basicity of the reactive residue, $\text{N}(\text{C}_6\text{F}_5)_2^-$ ($\text{p}K_{\text{a}} = 23.97$ in MeCN), is a key feature; it is sufficiently basic to deprotonate the HPPH_2 substrate ($\text{p}K_{\text{a}} = 22.9$) and, therefore, suitable to generate substantial amounts of catalytically active species.

Table 2.6. Hydrophosphination of styrene with Ph₂PH promoted by [{BDI^{DiPP}}CaN(C₆F₅)₂]₂ (**4**₂), [{BDI^{DiPP}}Ca{N(*o*-F-C₆H₄)₂}.(thf)] (**9**) or [{BDI^{DiPP}}CaN(SiMe₃)₂}.(thf)] (**I**).



Entry ^a	Precatalyst	[Styrene] ₀ /[Ph ₂ PH] ₀ /[precat] ₀	T (°C)	t (h)	Conv. (%) ^b	TOF (h ⁻¹)
1	[{BDI ^{DiPP} }CaN(C ₆ F ₅) ₂] ₂ (4 ₂)	10/10/1	60	12	88	0.7
2	[{BDI ^{DiPP} }Ca{N(<i>o</i> -F-C ₆ H ₄) ₂ }.(thf)] (9)	10/10/1	60	12	95	0.8
3	[{BDI ^{DiPP} }CaN(SiMe ₃) ₂ }.(thf)] (I) ^c	10/10/1	75	20	95	0.5

^aReaction conditions: Ph₂PH (11.6 μL, 0.06 mmol), Styrene (7.6 μL, 0.06 mmol), [precat] = 0.006 mmol. ^bConversion of styrene as determined by ¹H NMR spectroscopy. ^cThe reaction is carried out in neat condition.

The catalytic tests were performed at 60 °C directly in an NMR tube. The reaction with complexes **4**₂ and **9** took place in neat substrates over 12 h and with 10 mol% of the precatalyst. Complex **9** could readily convert 95 equiv of styrene and Ph₂PH to the product. After 12 h, the reaction was quenched by addition of wet benzene-*d*₆ and the ¹H NMR spectrum was then recorded. Gratifyingly, the observed catalytic activity for complexes **4**₂ and **9** is improved compared to that achieved under identical conditions with the archetypal [{BDI^{DiPP}}CaN(SiMe₃)₂}.(thf)] (**I**).⁶⁴ 2,1-Anti-Markovnikov regioselectivity was observed in the intermolecular hydrophosphination reaction of styrene with HPPH₂.

Overall, both precatalysts **4**₂ and **9** hence show satisfactory efficiency in the standard hydrophosphination reaction. The fluoroarylamide group N(*o*-F-C₆H₄)₂⁻ in **9** is more basic than N(C₆F₅)₂⁻ in **4**₂, and it is hence somewhat more effective. In order to clarify which ligand between N(*o*-F-C₆H₄)₂⁻ or {BDI^{DiPP}}⁻ is responsible for the deprotonation of the PhPH₂, the hydrophosphination reaction has been carried out with the “BDI^{DiPP}-free” complex [Ca{N(C₆F₅)₂}₂.(Et₂O)₂] (**1'**). The reaction under otherwise identical conditions gives a lower conversion (80%), thus confirming that the N(*o*-F-C₆H₄)₂⁻ ligand is mostly responsible for the observed catalytic activity. The addition of the P–H bond to an unsaturated C–C bond, is an atom-efficient route for the preparation of organophosphines.

Schelter *et. al.* have reported that the $\text{HN}(o\text{-F-C}_6\text{H}_4)(\text{SiMe}_3)$ ligand engages in stronger $\text{M}\cdots\text{F-C}$ secondary interactions than $\text{HN}(\text{C}_6\text{F}_5)(\text{SiMe}_3)$. $\text{HN}(o\text{-F-C}_6\text{H}_4)(\text{SiMe}_3)$ has less electron withdrawing groups, and the application of the highly electrophilic $-\text{SiMe}_3$ group in $\text{N}(o\text{-F-C}_6\text{H}_4)(\text{SiMe}_3)^-$ could increase the reactivity of the amine in catalytic cycles.^{47c,47f} The preparation of new Ae complexes using $\text{HN}(o\text{-F-C}_6\text{H}_4)(\text{SiMe}_3)$ as a synthetic precursor should be studied. Further investigations to this end are in progress in our group.

2.5 Conclusion

This chapter introduced the application of fluorinated aryl amides for the synthesis of stable, low coordinate and solvent-free Ae species. Complexes **1-6**₂ were prepared from the perfluorinated arylamine HN(C₆F₅)₂. All complexes were characterized by multinuclear NMR spectroscopy. Moreover, crystals suitable for X-Ray diffraction studies were obtained for the series of Ca complexes **1'**, **3**₂, **4**₂, **5**₂, **6**₂ and for the Ba compound **2**₂. Noteworthy, it was found that the observed distances between the metal center and the fluorine atoms are amongst the shortest ones known to date (typically Ca–F = 2.423 Å for **3**₂). Moreover, DOSY NMR experiments suggest that **3**₂ remains dinuclear in a hydrocarbon solvent; for the other dinuclear complexes **4**₂, **5**₂, **6**₂, this analysis has so far been impeded by their poor solubility in common deuterated solvents used for PGSE NMR studies, together with reproducibility issues. The heteroleptic calcium complexes **4**₂ and **5**₂ bearing the β-diketiminato {BDI^{DiPP}}[–] and iminoanilido ligands, and complex **6**₂ made of the *O*-donor boryloxide ligand, constitute formally three-coordinate calcium complexes.

The use of the difluorinated HN(*o*-F-C₆H₄)₂ proligand led to three novel compounds. The reaction of [Ca{N(SiMe₃)₂}₂]₃ with HN(*o*-F-C₆H₄)₂, afforded a small crop of crystals of the tetranuclear [Ca₄{μ²-N(*o*-F-C₆H₄)₂}₆{N(SiMe₃)₂}₂] (**7**₄) that reminds the trinuclear structure of [Ca{N(SiMe₂H)₂}₂]₃, reported by our group.¹⁰⁰ However, the quality of the crystal structure was not satisfactory. Despite the several crystallization attempts, we did not succeed to crystallize the solvent-free heteroleptic complex ([{BDI^{DiPP}}Ca{N(*o*-F-C₆H₄)₂}]) (**8**). However, the X-ray structure of the thf-adduct of this complex (**9**) reveals a mononuclear complex including strong intramolecular Ca···F–C interactions. The {BDI}[–] ligand has proven to be effective for the stabilization of the calcium heteroleptic complexes [{BDI^{DiPP}}CaN(SiMe₃)₂.(thf)] (**I**) and its solvent-free analogue [{BDI^{DiPP}}CaN(SiMe₃)₂] (**II**). However, it has been less effective for strontium and barium alike complexes. In the case of barium, it results in an unreactive homoleptic complex of [Ba{BDI^{DiPP}}₂].^{4,6} Noteworthy, the new fluorinated complexes **4**₂ and **9** that we have synthesized are stabilized by {BDI}[–] and have the advantage of further stabilization through Ca···F–C secondary interactions.

Bond-Valence Sum Analysis showed that to a large extent, the calcium was actively supported by the $\text{Ca}\cdots\text{F}-\text{C}$ interactions which mostly contribute to 17% to 20% of the whole coordination sphere of the metal center. DFT studies highlighted that the total bonding energy for $\text{Ca}\cdots\text{F}-\text{C}$ interactions has electrostatic characteristics which take the major role, and the covalent bond is weaker, and finally the dispersion forces are very low. There is no real charge transfer from the fluorine atoms to the calcium cation. Computations also indicate that the observed $\text{Ca}\cdots\text{F}(-\text{C})$ interaction is the strongest one among the three type of secondary interactions in calcium complexes including $\text{Ca}\cdots\text{F}(-\text{C})$, $\text{Ca}\cdots\text{H}(-\text{C})$ and $\text{Ca}\cdots\text{C}(\pi)$. DFT calculations support the molecular structures that are observed experimentally.

Since Hill's complex $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2(\text{thf})]$ (**1**) has proved to be efficient in hydroelementation reactions, we decided to test out the catalytic activity of complexes **4**₂ and **9** in such reactions. It was found that the benchmark hydrophosphination reaction of styrene with HPPH_2 catalyzed by complexes **4**₂ and **9**, affords the *anti*-Markovnikov product. Therefore, these original compounds represent new additions to a limited list of complexes that catalyze such intermolecular hydrophosphination reactions in a controlled fashion. Kinetic experiments need to be performed to propose a mechanism for these reactions.

Overall, the combination of structural data, BVS analysis, computational and spectroscopic data provide strong evidence of the importance of $\text{Ae}\cdots\text{F}-\text{C}$ secondary interactions in the stabilization and coordination chemistry of electrophilic Ae metals ($\text{Ae} = \text{Ca}, \text{Ba}$) as a useful tool to design original molecular structures. We have concentrated our work on calcium complexes stabilized by secondary interactions. Further investigations will focus on other alkaline earth metals (Sr and Ba) that would be valuable to draw better conclusions on the role and the nature of this type of interactions in the whole characteristics of the Ae complexes.

2.6 Experimental section

2.6.1 General procedures

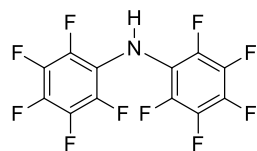
All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glove-box (Jacomex; $O_2 < 1$ ppm, $H_2O < 5$ ppm). CaI_2 and BaI_2 (Aldrich, 99.999% anhydrous beads) were used as received. $HN(SiMe_3)_2$ (Acros) and $HN(SiMe_2H)_2$ (ABCR) were dried over CaH_2 and distilled prior to use. $[Ca\{N(SiMe_3)_2\}_2]_2$ and $HOB\{CH(SiMe_3)_2\}_2$ were prepared following the literature procedure.^{26,101}

Solvents (thf, Et_2O , pentane and toluene) were purified and dried (water contents all in the range 1–5 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-vacuum-thaw 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 probe head. All ^1H and ^{13}C chemical shifts were determined using residual signals of the deuterated solvents and were calibrated vs. $SiMe_4$ (δ 0 ppm). $^{29}Si\{^1H\}$ chemical shifts were determined against $Si(CH_3)_4$. $^{19}F\{^1H\}$ chemical shifts were determined by external reference to an aqueous solution of $NaBF_4$. ^{11}B chemical shifts were determined against $BF_3 \cdot Et_2O$. Coupling constants are given in Hertz. Assignment of the signals was carried out using 1D (^1H , $^{13}C\{^1H\}$) and 2D (COSY, edited HSQC and HMBC) NMR experiments. DOSY 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 $G \cdot cm^{-2}$ over 16 or 32 increments with 4 dummy scans and 8 scans per increment.

FTIR spectra were recorded between 400 and 4000 cm^{-1} as nujol mulls in KBr plates on a Shimadzu IRAffinity-1 spectrometer.

2.6.2 Synthesis and characterization of proligands and related complexes

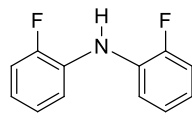


HN(C₆F₅)₂

By adaptation of a known literature procedure,⁵⁴ hexafluorobenzene (6.0 mL, 52 mmol) was added to a suspension of LiNH₂ (1.44 g, 58 mmol) in THF (50 mL) at 15 °C. The reaction mixture was refluxed for 2 h. The heating was stopped and diethyl ether (50 mL) was added at 0 °C. The mixture was then hydrolyzed with aqueous HCl 5%. The organic layer was separated and the aqueous phase was extracted with diethyl ether (2 × 30 mL). The combined organic layers were dried over MgSO₄ and volatiles were then evaporated under vacuum. The title compound was obtained as colorless crystals by crystallization from petroleum ether. Yield 3.75 g (42%).

¹H NMR (benzene-*d*₆, 400 MHz, 298 K): δ = 4.10 (s, 1H, NH) ppm.

¹⁹F{¹H} NMR (benzene-*d*₆, 376 MHz, 298 K): δ = -154.42 (d, 4F, ³J_{F-F} = 20.5 Hz, *o*-F), -163.19 (t, 2F, ³J_{F-F} = 21.9 Hz, *p*-F), -163.48 (t, 4F, ³J_{F-F} = 22.5 Hz, *m*-F) ppm.

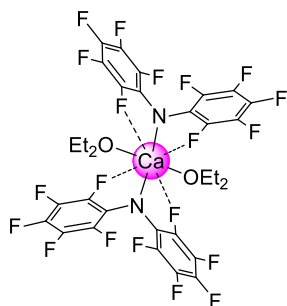


HN(*o*-F-C₆H₄)₂

Under dry argon atmosphere, a mixture of 1-bromo-2-fluorobenzene (5.6 mL, 51.2 mmol), 2-fluoroaniline (5.0 mL, 51.2 mmol), Pd(OAc)₂ (0.29 g, 1.2 mmol, 2.5 mol %), P(^{*t*}Bu)₃ (2.5 mL, 2.5 mmol, 5 mol %), and NaO^{*t*}Bu (0.61 g, 6.1 mmol) in toluene (50 mL) was heated at 90 °C for 16 hours.⁸⁷ After cooling to room temperature, saturated ammonium chloride solution was added to quench the reaction. The solution was extracted with ethyl acetate. After drying the organic fraction with MgSO₄, it was concentrated under reduced pressure. The purification of the residue was fulfilled by flash column chromatography on silica gel (ethyl acetate-hexanes 1:20). A colorless liquid was obtained. Yield 6.8 g (65%).

¹H NMR (CDCl₃, 400 MHz, 298 K): δ (ppm) 7.31 (t, 2H, *J* = 8.2 Hz, arom-CH), 7.13 (t, 2H, *J* = 9.7 Hz, arom-CH), 7.07 (t, 2H, *J* = 7.8 Hz, arom-CH), 6.87-6.97 (m, 2H, arom-CH), 5.90 (s, 1H, NH).

¹⁹F{¹H} NMR (CDCl₃, 376 MHz, 298 K): δ -131.24 (s, 2F, CF) ppm.



[Ca{N(C₆F₅)₂}₂] (1) and [Ca{N(C₆F₅)₂}₂.(Et₂O)₂] (1')

A solution of HN(C₆F₅)₂ (0.70 g, 2.00 mmol) in toluene (25 mL) was added dropwise to a solution of [Ca{N(SiMe₃)₂}₂]₂ (0.36 g, 0.50 mmol) in toluene (25 mL). The mixture was stirred at room temperature for 3 h. The solvent was pumped off under vacuum and the resulting solid was washed with pentane (3 × 3 mL) and dried off to constant weight to afford **1** as a colorless solid (0.60 g, 82%). Attempts to obtain crystals of **1** free of coordinated solvent and suitable for XRD studies were unsuccessful. It crystallized as the diethyl ether adduct [Ca{N(C₆F₅)₂}₂.(Et₂O)₂] (**1'**) from an Et₂O solution stored at −30 °C overnight.

[Ca{N(C₆F₅)₂}₂] (1)

¹⁹F{¹H} NMR (benzene-*d*₆, 376 MHz, 298 K): δ = −159.45 (br s, 8F, *o*-F), −168.88 (br s, 8F, *m*-F), −178.23 (br s, 4F, *p*-F) ppm.

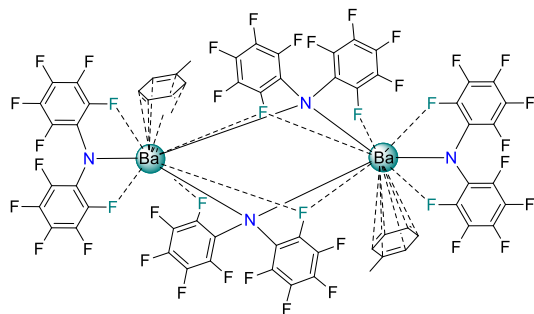
FTIR (nujol in KBr plates): $\tilde{\nu}_{\text{C-F}} = 779$ (s), 826 (s), 897 (s), 972 (s), 997 (s), 1020 (s), 1088 (s), 1150 (s), 1200 (s), 1271 (s), 1306 (s), 1391 (s), 1474 (s), 1501 (s), 1645 (s) cm^{−1}.

[Ca{N(C₆F₅)₂}₂.(Et₂O)₂] (1')

¹H NMR (benzene-*d*₆, 400 MHz, 298 K): δ = 2.90 (q, 8H, ³J_{H-H} = 7.1 Hz, OCH₂), 0.56 (t, 12H, ³J_{H-H} = 7.0 Hz, OCH₂CH₃) ppm.

¹³C{¹H} NMR (benzene-*d*₆, 125 MHz, 298 K): δ = 142.04, 140.27, 139.63, 137.62, 133.56, 131.59 (arom-C₆F₅), 65.15 (OCH₂), 13.30 (CH₃CH₂O) ppm.

¹⁹F{¹H} NMR (benzene-*d*₆, 376 MHz, 298 K): δ = −153.80 (d, 8F, ³J_{F-F} = 19.0 Hz, *o*-F), −162.60 to −163.00 (overlapping m, 12F, *m*- and *p*-F) ppm.



[Ba{μ-N(C₆F₅)₂}{N(C₆F₅)₂}.toluene]₂ (2)

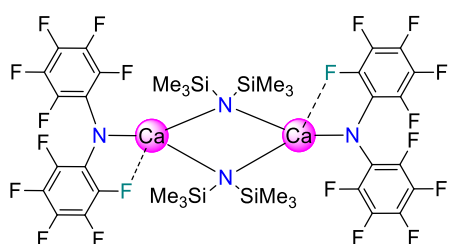
A solution of HN(C₆F₅)₂ (0.20 g, 0.57 mmol) in toluene (3 mL) was added dropwise to a solution of [Ba{N(SiMe₃)₂}₂]₂ (0.13 g, 0.14 mmol) in toluene (5 mL). The mixture was stirred at room temperature for 2 h. The solvent was pumped off under vacuum and

to afford a solid which was washed with pentane (3×3 mL). The resulting solid was dried off to give the title compound as a colorless solid (0.19 g, 82%). X-ray quality crystals were grown from a concentrated toluene solution at -30 °C.

^1H NMR (benzene- d_6 , 400 MHz, 298 K): δ = 7.15-6.98 (m, 5H, arom-CH), 2.11 (s, 3H, CH_3) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 125 MHz, 298 K): δ = 141.88, 140.08, 137.90 (arom- C_6F_5), 159.04, 129.34, 128.57, 127.52 (arom- C_6H_5), 21.43 (CH_3) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (benzene- d_6 , 376 MHz, 298 K): δ = -157.66 (br s, 16F, *o*-F), -165.85 (br s, 16F, *m*-F), -176.06 (br s, 8F, *p*-F) ppm.



[Ca $\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2$ (3₂**)**

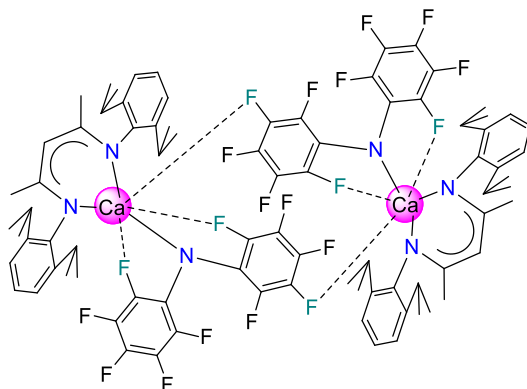
A solution of $\text{HN}(\text{C}_6\text{F}_5)_2$ (0.30 g, 0.86 mmol) in toluene (3 mL) was added dropwise at -78 °C to a solution of $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (0.41 g, 0.57 mmol, 1.33 eq) in toluene (5 mL). The cold bath was removed after the addition was complete to let the mixture warm up to room temperature. Stirring was ensured for 2 h at room temperature. The solvent was then pumped off under vacuum, and the resulting solid was washed with petroleum ether (3×3 mL) and was dried off to constant weight. The title complex was isolated as a colorless solid (0.30 g, 64%). X-ray quality crystals were grown from a concentrated solution in 1,2-difluorobenzene at -30 °C.

^1H NMR (benzene- d_6 , 400 MHz, 298 K): δ = 0.01 (s, 18H, SiCH_3), ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 125 MHz, 298 K): δ = 142.78, 141.01, 139.78, 137.77, 134.56, 132.67 (arom- C_6F_5), 4.55 (s, SiCH_3) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (benzene- d_6 , 376 MHz, 298 K): δ = -156.14 (d, 8F, $^3J_{\text{F-F}} = 21.2$, *o*-F), -164.58 (t, 8F, $^3J_{\text{F-F}} = 21.8$ Hz, *m*-F), -172.65 (t, 4F, $^3J_{\text{F-F}} = 22.6$, *p*-F) ppm.

FTIR (nujol in KBr plates): $\tilde{\nu}_{\text{C-F}} = 760$ (s), 808 (s), 831 (s), 862 (s), 945 (s), 972 (s), 1001 (s), 1026 (s), 1101 (s), 1194 (s), 1256 (s), 1271 (s), 1306 (s), 1342 (s), 1427 (s), 1472 (s), 1508 (s), 1597 (s), 1647 (s), 1659 (s) cm^{-1} .



$[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**4₂**)

A solution of **3₂** (0.27 g, 0.25 mmol) and $\{\text{BDI}^{\text{DiPP}}\}\text{H}$ (0.20 g, 0.47 mmol) in toluene (5 mL) was heated at 95 °C for 2 days. The solvent was pumped off under vacuum and the residue was washed with pentane (3 × 3 mL) and dried to constant weight to afford **7₂** as a colorless solid (0.23 g, 86%). Single crystals were

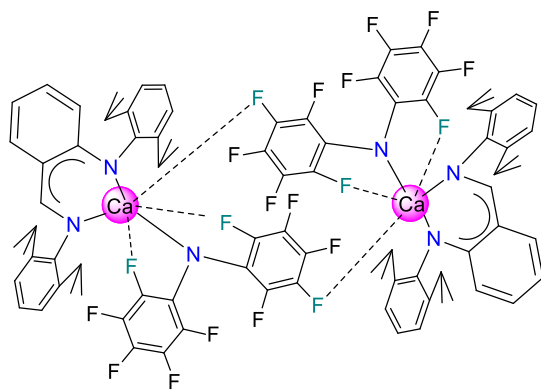
grown at room temperature from a benzene solution.

^1H NMR (toluene-*d*₈, 400 MHz, 298 K): δ = 6.94-6.89 (m, 6H, arom-CH), 4.77 (s, 1H, C(Me)CHC(Me)), 3.03 (hept, 4H, $^3J_{\text{H-H}}$ = 6.8 Hz, CH(CH₃)₂), 1.62 (s, 6H, C(CH₃)CHC(CH₃)), 1.11 (d, 12H, $^3J_{\text{H-H}}$ = 7.0 Hz, CH(CH₃)₂), 1.06 (d, 12H, $^3J_{\text{H-H}}$ = 7.0 Hz, CH(CH₃)₂) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (toluene-*d*₈, 125 MHz, 298 K): δ = 166.74 (C(Me)=N), 144.06 (*o*-C₆F₅), 142.72 (*i*-NC₆H₃), 141.62 (*m*-C₆F₅), 129.18 (*o*-NC₆H₃), 128.26 (*p*-C₆F₅), 125.41 (*p*-NC₆H₃), 124.36 (*m*-NC₆H₃), 123.52 (*i*-C₆F₅), 94.39 (C(Me)CHC(Me)), 28.82 (CH(CH₃)₂), 24.58 (CH(CH₃)₂), 24.15 (CH₃CCHCCH₃) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (toluene-*d*₈, 376 MHz, 298 K): δ = -158.11 (d, 8F, $^3J_{\text{F-F}}$ = 23.2 Hz, *o*-F), -164.85 (t, 8F, $^3J_{\text{F-F}}$ = 22.1 Hz, *m*-F), -175.62 (t, 4F, $^3J_{\text{F-F}}$ = 22.8 Hz, *p*-F) ppm.

FTIR (nujol in KBr plates): $\tilde{\nu}_{\text{C-F}}$ = 708 (s), 731 (s), 754 (s), 789 (s), 926 (s), 964 (s), 1005 (s), 1020 (s), 1096 (s), 1165 (s), 1198 (s), 1265 (s), 1298 (s), 1381 (s), 1402 (s), 1470 (s), 1504 (s), 1645 (s), 1651 (s) cm⁻¹.



$[\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**5₂**)

A solution of **3₂** (0.30 g, 0.27 mmol) and $\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{H}$ (0.18 g, 0.41 mmol) in toluene (5 mL) was heated at 95 °C for 2 h. The solution was then filtered to eliminate residual insoluble impurities, and volatiles were evaporated. Drying under vacuum to constant weight afforded the title compound as a

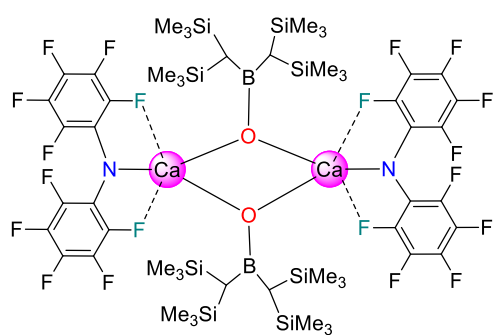
yellow solid (0.31 g, 90%). X-ray quality crystals of **5₂** were obtained upon slow cooling of a hot, concentrated toluene solution.

¹H NMR (toluene-*d*₈, 400 MHz, 298 K): δ = 7.92 (s, 1H, N=CH), 7.13 (br s, 6H, arom-CH), 6.87 (s, 2H, arom-CH), 6.29 (t, 1H, ³*J*_{H-H} = 7.7 Hz, arom-CH), 6.15 (d, 1H, ³*J*_{H-H} = 9.3 Hz, arom-CH), 3.20 (m, 2H, CH(CH₃)₂), 2.95 (m, 2H, CH(CH₃)₂), 1.15 (s, 12H, CH(CH₃)₂), 1.03 (d, 6H, ³*J*_{H-H} = 6.7 Hz, CH(CH₃)₂), 0.96 (d, 6H, ³*J*_{H-H} = 6.7 Hz, CH(CH₃)₂) ppm.

¹³C{¹H} NMR (toluene-*d*₈, 125 MHz, 298 K): δ = 170.38 (CH=N), 157.37 (*i*-NC₆H₄), 145.58 (*i*-NC₆H₃), 143.51, 142.25, 139.61, 137.97, 136.89, 133.70, 128.33, 127.56, 125.50, 124.69, 124.64, 124.19, 123.26, 116.67, 116.09, 111.73, 28.40 (CH(CH₃)₂), 27.78 (CH(CH₃)₂), 24.86 (CH(CH₃)₂), 24.70 (CH(CH₃)₂), 22.83 (CH(CH₃)₂), 21.33 (CH(CH₃)₂) ppm.

¹⁹F{¹H} NMR (toluene-*d*₈, 376 MHz, 298 K): δ = -158.11 (d, 4F, ³*J*_{F-F} = 21.9 Hz, *o*-F), -164.78 (t, 4F, ³*J*_{F-F} = 21.9 Hz, *m*-F), -175.95 (m, 2F, ³*J*_{F-F} = 23.5 Hz, *p*-F) ppm.

FTIR (nujol in KBr plates): $\tilde{\nu}_{\text{C-F}}$ = 731 (s), 785 (s), 880 (s), 959 (s), 1020 (s), 1057 (s), 1113 (s), 1182 (s), 1219 (s), 1271 (s), 1381 (s), 1470 (s), 1736 (s), 2297 (s), 2388 (s) cm⁻¹.



[Ca{μ-OB(CH(SiMe₃)₂)₂}{N(C₆F₅)₂}]₂ (**62**)

A solution of HOB{CH(SiMe₃)₂}₂ (0.14 g, 0.41 mmol) and **3₂** (0.30 g, 0.27 mmol, 1.33 eq) in toluene (5 mL) was heated to 95 °C for 2 h. Residual insoluble impurities were then removed by filtration, and volatiles were evaporated. Drying under vacuum to constant

weight afforded the title compound as a colorless solid (0.23 g, 76%). Single crystals were obtained by slow cooling down to room temperature of a hot toluene solution.

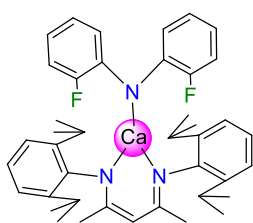
¹H NMR (benzene-*d*₆, 400 MHz, 298 K): δ = 0.21 (s, 2H, CH(SiMe₃)₂), 0.20 (s, 2H, CH(SiMe₃)₂), 0.15 (s, 36H, Si(CH₃)₃), 0.05 (s, 36H, Si(CH₃)₃) ppm.

¹³C{¹H} NMR (benzene-*d*₆, 125 MHz, 298 K): δ = 129.34, 128.57, 128.35, 125.70 (arom-C₆F₅), 23.27 (CH(SiMe₃)₂), 2.77 (Si(CH₃)₃) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (benzene- d_6 , 376 MHz, 298 K): $\delta = -155.79$ (d, 8F, $^3J_{\text{F-F}} = 22.4$ Hz, *o*-F), -158.73 (d, 8F, $^3J_{\text{F-F}} = 22.3$ Hz, *o*-F), -163.59 (t, 8F, $^3J_{\text{F-F}} = 22.4$ Hz, *m*-F), -164.74 (t, 8F, $^3J_{\text{F-F}} = 22.0$ Hz, *m*-F), -173.47 (t, 4F, $^3J_{\text{F-F}} = 22.7$ Hz, *p*-F), -174.45 (t, 4F, $^3J_{\text{F-F}} = 22.5$ Hz, *p*-F) ppm.

$^{11}\text{B}\{^1\text{H}\}$ NMR (benzene- d_6 , 128 MHz, 298 K): $\delta = 53.71$ (br s) ppm.

FTIR (nujol in KBr plates): $\tilde{\nu}_{\text{C-F}} = 683$ (s), 833 (s), 851 (s), 968 (s), 999 (s), 1024 (s), 1126 (s), 1221 (s), 1248 (s), 1302 (s), 1425 (s), 1476 (s), 1506 (s), 1647 (s) cm^{-1} .



Synthesis of $[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}\{\text{N}(\text{C}_6\text{FH}_4)_2\}]$ (**8**)

A solution of $[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}]$ (0.36 g, 0.58 mmol) in toluene (5 mL) was cooled to -78°C and the solution of $\text{HN}(\text{C}_6\text{FH}_4)_2$ (0.12 g, 0.58 mmol) in toluene (3 mL) was added dropwise overtime. The cold bath was removed after addition to let the mixture warm up to room temperature. The mixture was stirred for 2 h. The solvent was pumped off under vacuum and the solid was washed with pentane (3×3 mL). The resulting solid was dried off (0.12 g, 32%).

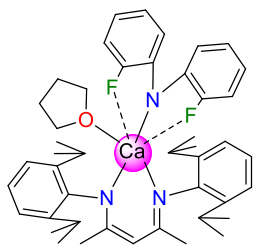
Complex (**8**) shows a high solubility in hydrocarbons (pentane and toluene) but it is not completely soluble in benzene. Despite several attemptst for crystallization, the crystal structure has not been provided.

^1H NMR (benzene- d_6 , 400 MHz, 298 K): δ 7.45 (s, 1H, arom-CH), 7.04-6.93 (m, 6H, arom-CH), 6.74 (m, 5H, arom-CH), 6.25 (s, 2H, arom-CH), 4.91 (s, 1H, $\text{C}(\text{Me})\text{CHC}(\text{Me})$), 3.28 (s, 4H, $\text{CH}(\text{CH}_3)_2$), 1.72 (s, 6H, $(\text{CH}_3)\text{CCH}(\text{CH}_3)$), 1.19 (dd, 24H, $^3J_{\text{H-H}}=13.4$, 6.8 Hz, $\text{CH}(\text{CH}_3)_2$) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 125 MHz, 298 K): 167.62 ($\text{C}(\text{Me})=\text{N}$), 166.63 (*o*- $\text{C}_6\text{H}_4\text{F}$, CF), 161.54 (arom-CH), 146.88, 142.82 (*o*- NC_6H_3), 141.85 (*p*- NC_6H_3), 141.30 (*i*- $\text{C}_6\text{H}_4\text{F}$), 136.44 (*m*- NC_6H_3), 125.88 (*m*- $\text{C}_6\text{H}_4\text{F}$), 125.13 (*m*- NC_6H_3), 124.07 (*p*- $\text{C}_6\text{H}_4\text{F}$), 123.62 (*o*- $\text{C}_6\text{H}_4\text{F}$), 114.25 (d, $^2J_{\text{C-F}} = 11.2$ Hz, *m*- $\text{C}_6\text{H}_4\text{F}$), 113.90 (d, $^2J_{\text{C-F}} = 23.9$ Hz, *m*- $\text{C}_6\text{H}_4\text{F}$), 94.32 ($\text{N}-\text{C}=\text{CH}$), 28.68, 28.40 ($\text{CH}-\text{CH}_3$), 24.88, 24.48, 23.47, 23.15 ($\text{CH}-\text{CH}_3$), 20.81, 20.54 ($\text{CH}-\text{C}-\text{CH}_3$) ppm.

$^{19}\text{F}\{^1\text{H}\}$ NMR (benzene- d_6 , 376 MHz, 298 K): $\delta -130.66$ (m, 2F, CF) ppm.

FTIR (nujol in KBr plates): $\tilde{\nu}_{\text{C-F}} = 737$ (s), 789 (s), 802 (s), 895 (s), 928 (s), 1028 (s), 1088 (s), 1142 (s), 1169 (s), 1221 (s), 1242 (s), 1288 (s), 1312 (s), 1354 (s), 1404 (s), 1431 (s), 1487 (s), 1520 (s), 1547 (s), 1601 (s), 1618 (s) cm^{-1} .



[{BDI^{Dipp}}CaN(*o*-F-C₆H₄)₂.(thf)] (9)

A solution of [{BDI^{Dipp}}Ca{N(SiMe₃)₂}.(thf)] (0.27 g, 0.39 mmol) in toluene (5 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and a solution of HN(C₆FH₄)₂ (0.080 g, 0.39 mmol) in toluene (3 mL) was added dropwise. Upon complete addition, the mixture was stirred for 2 h at room temperature. Volatiles were then pumped off under vacuum to give a solid which was washed with pentane ($3 \times 3\text{ mL}$). Drying off under vacuum afforded the title compound as a colorless solid (0.080 g, 30%). Single-crystals were obtained from a solution in petroleum ether stored at room temperature overnight. CCDC 1900852.

¹H NMR (benzene-*d*₆, 400 MHz, 298 K): δ = 7.53 (t, 2H, ³*J*_{H-H} = 9.4 Hz, arom-CH), 7.09-7.02 (m, 6H, arom-CH), 6.84 (t, 2H, ³*J*_{H-H} = 8.1 Hz, arom-CH), 6.63 (m, 2H, arom-CH), 6.28 (m, 2H, arom-CH), 4.97 (s, 1H, C(Me)CHC(Me)), 3.40 (m, 4H, CH(CH₃)₂), 3.05 (t, 4H, ³*J*_{H-H} = 6.3 Hz, CH₂O), 1.81 (s, 6H, (CH₃)CCH(CH₃)), 1.26 (d, 12H, ³*J*_{H-H} = 7.8 Hz, CH(CH₃)₂), 1.20 (d, 12H, ³*J*_{H-H} = 7.8 Hz, CH(CH₃)₂), 0.89 (t, 4H, ³*J*_{H-H} = 6.3 Hz, CH₂CH₂O) ppm.

¹⁹F{¹H} NMR (benzene-*d*₆, 376 MHz, 298 K): δ = -130.67 (m, 2F, CF) ppm.

FTIR (nujol in KBr plates): $\tilde{\nu}_{\text{C-F}}$ = 735 (s), 802 (s), 895 (s), 918 (s), 1028 (s), 1092 (s), 1161 (s), 1219 (s), 1242 (s), 1288 (s), 1310 (s), 1346 (s), 1408 (s), 1447 (s), 1485 (s), 1603 (s), 1618 (s) cm⁻¹.

2.6.3 Typical procedure for hydrophosphination reactions

The precatalyst was loaded in an NMR tube in the glove-box. All subsequent operations were carried out on a vacuum manifold using Schlenk techniques. The required amount of styrene and HPPPh₂ were added with a syringe to the precatalyst. 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-*d*₆ to the reaction mixture. The conversion was determined by ¹H NMR spectroscopy.

2.6.4 X-ray diffraction crystallography

X-ray diffraction data were collected at 150 K using a Bruker APEX CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The crystal structures for all complexes (CCDC numbers 1895996-1896001 and 1900852-1900853) were solved by direct methods, and remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares based on F₂ (programs SIR97 and SHELXL-97).¹⁰² 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.

2.6.5 Computational details

Geometry optimisations at the density functional theory (DFT) level were performed with the Gaussian 09 package.¹⁰³ The PBE0 functional¹⁰⁴ was used together with the general triple- ξ polarised Def2-TZVP basis set from EMSL basis set exchange library.¹⁰⁵ Unless specified in the text, Grimme's 3-parameter empirical dispersion correction (DFT-D3) were applied. Analytical calculations of the vibrational frequencies were performed on all the optimised geometries to verify that these structures are local minima on the potential energy surface. Natural orbital populations were computed with the NBO 5.0 program,¹⁰⁶ In to get a more detailed analysis of the bonding between the two components of our simple bimolecular models, a Morokuma-Ziegler energy decomposition analysis (EDA) was carried out, with the help of the ADF2016 program.¹⁰⁷ The ADF calculations were carried out as single-points on the Gaussian-optimized structures, using the standard STO TZVP basis set,¹⁰⁸ with the same PBE0 functional⁵⁶ and with (and without) Grimme's D3 dispersion corrections.⁹³

2.7 References

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Chapter 3

Barium heteroleptic complexes supported by crown-ether functionalized N-based ligands and their application for the hydrophosphination of vinylarenes

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Chapter 3: Barium heteroleptic complexes supported by crown-ether functionalized N-based ligands and their application for the hydrophosphination of vinylarenes

3.1 Introduction

The present chapter focuses on the synthesis and characterization of original barium heteroleptic complexes that feature new *N*-donor, bidentate ancillary ligands with an aza-crown-ether side-arm encapsulating the metal center. The complementary intramolecular β -Si-H anagostic interactions give further stabilization beyond that provided by the macrocyclic tether, without any extra Lewis base (solvent) being required. The catalytic activity of the resulting heteroleptic barium complexes has been illustrated in the intermolecular hydrophosphination of vinylarenes.

3.1.1 Designing suitable stabilizing ancillary ligands for alkaline-earth heteroleptic complexes

The important factors that need to be considered for the preparation of heteroleptic alkaline earth (Ae) complexes are the nature of the metal (in particular its size, electropositivity, Lewis acidity) and the stabilizing bulky ligand (in particular its chelating and electron donating ability). A common way to solve the stability problem of a complex is to design a new ligand or modify an existing ligand by introducing new functionalities. The ancillary ligand should stabilize the complex, yet without impeding its reactivity.

The ionic nature of the bonding in Ae complexes increases with the ionic radius and electropositivity of the cationic metal, and the tendency for ligand scrambling among Ae metals is hence the highest with barium ($\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$). Therefore, the preparation of stable heteroleptic complexes of barium [$\{\text{L}\}\text{Ba-R}$] (where $\{\text{L}\}$ is a monoanionic ancillary ligand and R is the reactive co-ligand) is very challenging. Indeed, side reactions that result in the formation of aggregates and of poorly soluble species often occur (Schlenk equilibrium).

3.1.2 Stabilization of Ae heteroleptic complexes by β -Si-H anagostic interactions

Anwander has investigated the contribution of Si-H agostic stabilizing interactions in complexes of the rare-earth metals.¹ Inspired by this work, our group and others^{2,3} have focused on the use of the $\text{N}(\text{SiMe}_2\text{H})_2^-$ amido group to prepare $[\text{Ae}\{\text{N}(\text{SiMe}_2\text{H})_2\}_2(\text{thf})_n]$ ($\text{Ae} = \text{Ca}$, $n=1$; Sr , $n = 2/3$; Ba , $n = 0$) by salt metathesis involving the Ae metal iodides and $[\text{K}\{\text{N}(\text{SiMe}_2\text{H})_2\}]$, or by transamination between $[\text{Ae}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{thf})_2]$ and $\text{HN}(\text{SiMe}_2\text{H})_2$.⁴ These precursors have thus enabled the synthesis of Ae heteroleptic complexes which contain internal β -anagostic interactions between the metal center and the Si-H moieties ($\text{Ae}\cdots\text{H-Si}$ β -anagostic interactions : $[\{\text{LO}^3\}\text{AeN}(\text{SiMe}_2\text{H})_2]$; $\text{Ae} = \text{Ca}, \text{Sr}, \text{Ba}$; $\{\text{LO}^3\}\text{H} = (2-\{(1,4,7,10\text{-tetraoxa-13-azacyclopentadecan-13-yl)-methyl}\}-4,6\text{-di-}i\text{-tert-butylphenol})$)^{3d,4} similarly to the calcium complex $[\text{Ca}\{\text{C}(\text{SiMe}_2\text{H})_3\}_2]$ reported by Sadow.⁵ The $\text{N}(\text{SiMe}_2\text{H})_2^-$ amido group thereby demonstrated the ability to stabilize heteroleptic complexes against ligand redistribution and Schlenk equilibrium in solution.

The anagostic distortions in $[\{\text{L}\}\text{Ae-R}]$ complexes are being supported by X-ray diffraction crystallography. The narrow angle of Ae-N-Si ($100\text{--}115^\circ$) is seen in the case of $\text{Ae}\cdots\text{H-Si}$ interactions, whereas in the absence of this interaction, the Ae-N-Si angle is more obtuse (130° or thereabout). In most of the cases, XRD data show only one of the SiH moieties in the $\text{N}(\text{SiMe}_2\text{H})_2^-$ amide interacting with the metal center (eg. $[\{\text{LO}^3\}\text{CaN}(\text{SiMe}_2\text{H})_2]$: Ca1-N32-Si33 and much more acute Ca1-N32-Si36 angles ($130.65(13)$ and $99.17(11)^\circ$, respectively), corresponding to a much shorter Ca1-Si36 distance ($3.13(2)$) with respect to Ca1-Si33 ($3.72(2)$).^{3d,4} These $\text{Ae}\cdots\text{H-Si}$ anagostic interactions are weak interactions ($1\text{--}10 \text{ kcal mol}^{-1}$) and essentially have an electrostatic characteristic. The secondary non-covalent interaction ($\text{Ae}\cdots\text{H-Si}$) is also evidenced by spectroscopic methods. ^1H or 2D $^1\text{H}\text{-}^{29}\text{Si}$ HMQC NMR spectra in solution enable to access the $^1J_{\text{Si-H}}$ coupling constant; (eg. Etienne *et. al.* reported the evidence for $\text{Ae}\cdots\text{H-Si}$ β -anagostic interactions in $[\text{Ca}\{\text{N}(\text{SiMe}_2\text{H})_2\}_2]$ came from a $^1\text{H}\text{-}^{29}\text{Si}$ HMQC 2D NMR experiment at 183 K with the correlations between five different ^{29}Si signals at $\delta = -23.7, -15.3, -14.0, -13.9$, and -11.8 ppm and the $\text{H}_\text{A}, \text{H}_\text{C}, \text{H}_\text{B}, \text{H}_\text{D}$, and H_E protons, respectively ($^1J_{\text{Si-H}} = 152, 146, 143, 147$, and 122 Hz , respectively)⁶, where $^1J_{\text{Si-H}}$ of ca. $165\text{--}170 \text{ Hz}$ hints for no anagostic interaction. FTIR spectroscopy also enables to probe the intensity of the metal- β -Si-H anagostic interaction. The stretching wavenumber $\nu_{\text{Si-H}}$ for a

Ae $\cdots$ H–Si interaction is expected to be in the range of 1900–1990 cm⁻¹. In the case of a regular Si–H moiety, $\nu_{\text{Si-H}}$ is above 2000 cm⁻¹ (See Chapter 1, Figure 1.9).^{2,3,4,5,7,8,9}

3.1.3 Stabilization of Ae heteroleptic complexes by a multidentate ancillary ligand

During the 2000–2015 period, the ancillary ligands reported to successfully stabilize the Ae heteroleptic complexes [$\{L\}\text{Ae-R}$] (L = ancillary ligand; R = reactive ligand such as amide, alkyl, alkoxide, hydride) were, mostly, N-based β -diketiminates,¹⁰ iminoanilides,^{11,12} tris(pyrazolyl)borates,¹³ aminotrope(imi)nates,¹⁴ bis- or tris-(imidazolin-2-ylidene-1-yl)borates¹⁵ imino-amidates¹⁶, fluoroalkoxides^{3c} (Figure 3.1) and phenolates (Chapter 1, Figure 1.8)^{3d,4,8,12,44}

As explained in the previous chapter, the β -diketimate ligand $\{\text{BDI}^{\text{Dipp}}\}^-$ (where $\text{BDI}^{\text{Dipp}} = \text{CH}[\text{C}(\text{CH}_3)\text{N}^{\text{Dipp}}]_2$, Dipp = 2,6-diisopropylphenyl) is one of the most successful ancillary ligands in Ae chemistry. It was initially applied for lactide polymerization by Chisholm, and later used for hydroelementation reactions such as hydroamination (intramolecular¹⁷ and intermolecular^{11,18}) and (alkene^{3c,19} and alkyne²⁰) hydrophosphination reactions.^{3a,10a,12,21}

Similarly to the $\{\text{BDI}^{\text{Dipp}}\}^-$ ligand, the iminoanilide ligand $\{\text{N}^{\wedge}\text{N}^{\text{Dipp}}\}^-$ ($\{\text{N}^{\wedge}\text{N}\} = [\text{DippN}(\text{o-C}_6\text{H}_4)\text{C}(\text{H})=\text{N}^{\text{Dipp}}]$), afforded the heteroleptic Ae complexes $[\{\text{N}^{\wedge}\text{N}^{\text{Dipp}}\}\text{AeN}(\text{SiMe}_3)_2(\text{thf})_n]$ (Ae = Ca, n = 1; Sr, n = 2; Ba, n = 2). These complexes are not contaminated by homoleptic species and they are stable against ligand redistribution. These new precatalysts have been compared in hydroelementation reactions to the amido $[\{\text{BDI}^{\text{Dipp}}\}\text{AeN}(\text{SiMe}_3)_2(\text{thf})_n]$ (Ae = Ca, n = 1; Sr, n = 2; Ba, n = 2) and phenolate complexes $[\{\text{LO}^4\}\text{AeN}(\text{SiMe}_3)_2(\text{thf})_n]$ (Ae = Ca, n = 0; Sr, n = 1; Ba, n = 0; $\{\text{LO}^4\} = 2\text{-}\{[\text{bis}(2\text{-methoxyethyl})\text{amino}]\text{methyl}\}\text{-4,6-di-tert-butylphenolate}$). In intermolecular hydroamination of styrene with benzylamine and in intermolecular hydrophosphination of styrene with HPCy₂ or HPPH₂ (catalyst loading 2 mol%, 60 C, neat), the iminoanilido complexes $[\{\text{N}^{\wedge}\text{N}^{\text{Dipp}}\}\text{AeN}(\text{SiMe}_3)_2(\text{thf})_n]$ (Ae = Ca, n = 1; Sr, n = 2; Ba, n = 2) show, under identical operating conditions, a substrate conversion that increases with the size of the metal (Ca < Sr < Ba).¹¹ Both types of reaction proceed with perfect anti-Markovnikov regioselectivity. The hydrophosphination reaction ($[\text{styrene}]_0/[\text{phosphine}]_0/[\text{precatalyst}]_0 = 50:50:1$) with HPCy₂ was partially achieved even after 18.5 h, while this same reaction with the less basic phosphine (HPPH₂) was considerably faster and, with $[\{\text{N}^{\wedge}\text{N}^{\text{Dipp}}\}\text{BaN}(\text{SiMe}_3)_2(\text{thf})_2]$

(2 mol%), resulted in 96% conversion after 15 min. This was the first barium complex showing impressive catalytic efficiency in these types of reactions.¹²

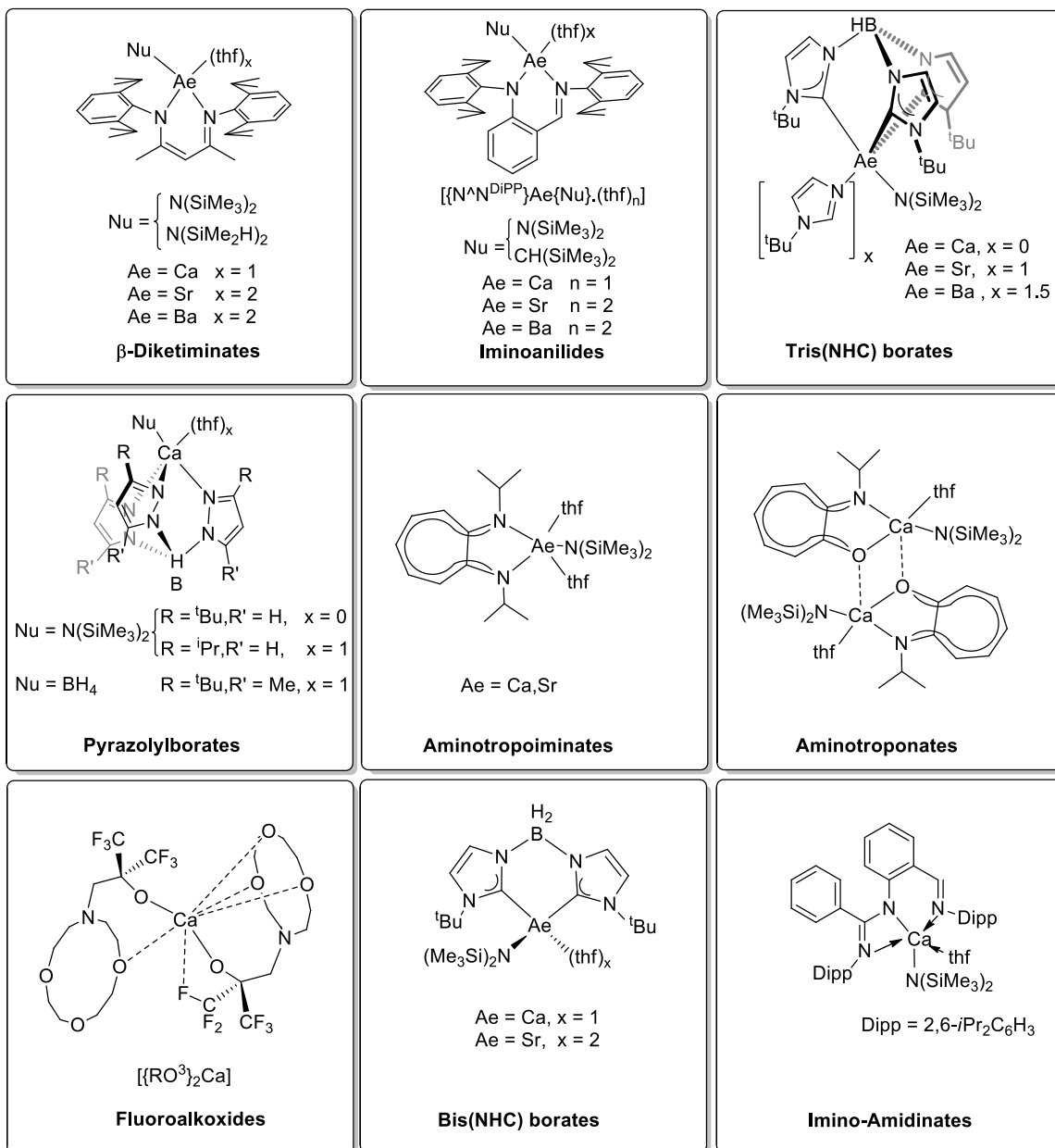


Figure 3.1. Heteroleptic Ae complexes stabilized by multidentate ancillary ligands.¹⁰⁻¹⁶

The anti-Markovnikov regioselectivity of these intermolecular hydrophosphination reactions catalyzed by Ae metals, depends on the rate-determining step, i.e. the 2,1-insertion of the highly polarized C=C double bond in the metal-phosphide bond, Figure 3.2. The substitution at the

para position of the styrene, has also an influence on the transition state leading to the formation of the C–P bond, since it affects the developing negative charge on the benzylic (α) carbon atom. Indeed, the electron-withdrawing groups (CF_3 , Cl) increase the reactivity and the electron-donating *para* substituents (Me, $t\text{Bu}$, OMe) decrease the reaction rates ($\text{CF}_3 > \text{Cl} > \text{H} > \text{Me} > t\text{Bu} > \text{OMe}$). The stabilization effect of the electron-withdrawing groups cannot occur in 1,2-insertion.

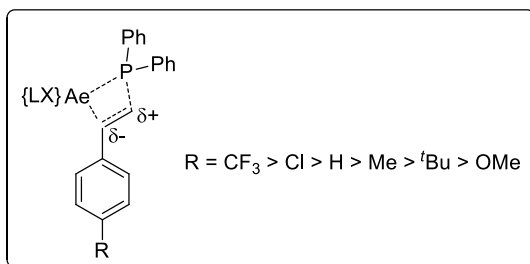


Figure 3.2. Proposed transition state in the intermolecular hydrophosphination of *p*-substituted styrene.

The second order kinetic rate law with this latter barium complex obeys $r = k[\text{HPPPh}_2]^0[\text{styrene}]^1[\text{precatalyst}]^1$. These experiments revealed similar results as the hydrophosphination reactions with $[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}\{\text{N}(\text{SiMe}_3)_2\} \cdot (\text{thf})]$ described by Hill's and suggest a stepwise σ insertion mechanism where the insertion of the polarized C=C bond into the Ae–P bond is considered as the rate-determining step.^{11,12}

Ae metals often have high coordination numbers, usually 6–8 and potentially greater. In many cases, a Lewis base (solvent) is present in the structure to complete the coordination sphere and it is detected by X-ray diffraction and NMR spectroscopy analyses. In order to avoid saturation of the metal coordination sphere by such Lewis bases and to still enable catalysis, the use of a coordinating solvent should be avoided. Also, the substituents on the N,N-bidentate amidinate ligands can be advantageously tuned to allow the efficient encapsulation of metal cations of different sizes such as oxophilic metals K^+ , Ba^{2+} and Yb^{2+} .²² In comparison to β -diketimines, these amidinates have a narrow bite angle due to the decrease of the six- to four-membered metallacycle with oxophilic metals, while offering several coordination modes (Figure 3.3).²³ For Ae metals, the coordination mode (a) is mostly observed in the organometallic amidinate structures. Bidentate ligands of the type $\{(\text{R}'\text{N})_2\text{C}=\text{R}\}^-$ are widely used. The large R' substituents (like 2,6-diisopropylphenyl = Dipp) provide effective shielding groups that allow stabilization of reactive metals. The negative charges are localized within 1,3-diazaallyl moieties

that reduce the nucleophilicity and the tendency to attack the solvent. This provides kinetic stabilization and less sensitivity toward moisture.²⁴

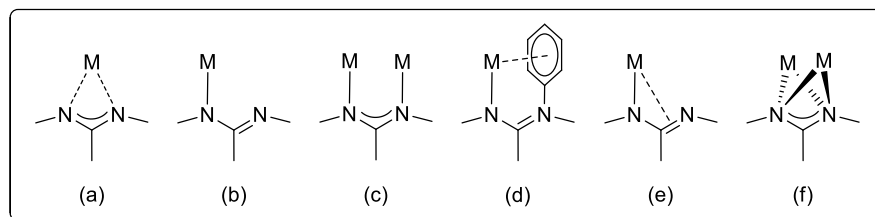
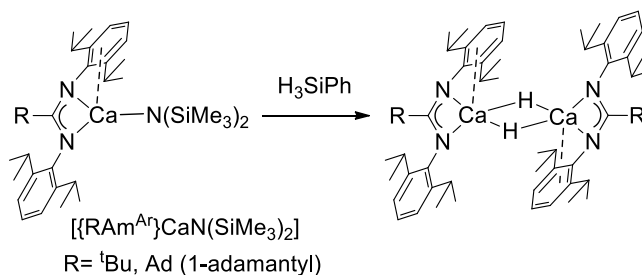


Figure 3.3. Representative coordination modes of amidinate ligand.²⁴

Recently Harder *et.al.* have prepared a new amidinate that provides stable Ae heteroleptic complexes such as $[\{\text{RAm}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2]$ (Am = amidinate, R = ^tBu, Ad)²⁴ and $[(^t\text{BuAm}^{\text{DiPP}})_2\text{Sr}]$ and $[p\text{TolAm}^{\text{Ar}^\dagger}\text{SrN}(\text{SiHMe}_2)_2]$ ($\text{Ar}^\dagger$ = 2,6-Ph₂CH-4-*i*Pr-phenyl) as $p\text{TolAm}^{\text{Ar}^\dagger}$).²⁵

The bulky Dipp group in this ligand prevents the ligand exchange and Schlenk equilibria. The large backbone substituent of 1-adamantyl (Ad) provides a solvent-free monomer. The complexes with the large backbone substituent (^tBu and Ad) give the stable calcium hydrides through reaction of amidinate amido complex ($[\{\text{RAm}^{\text{Ar}}\}\text{CaN}(\text{SiMe}_3)_2]$) with H₃SiPh (Scheme 3.1). Their ability for Ca...aryl interaction makes these ligands more sterically sheltering.



Scheme 3.1. Synthesis of heteroleptic calcium hydrides from the amidinate amido complexes $[\{\text{RAm}^{\text{Ar}}\}\text{CaN}(\text{SiMe}_3)_2]$.²⁴

Also, Jones and co-workers have recently developed two extremely bulky amidinates $[\text{RC}\{\text{N}(\text{Dip})\}\{\text{N}(\text{Ar}^\dagger)\}]^-$ (Dip = 2,6-diisopropylphenyl; $\text{Ar}^\dagger$ = C₆H₂{C(H)Ph₂}₂ⁱPr-2,6,4; R = 1-

adamantyl (L^{Ad}), *tert*-butyl (L^{tBu})) in order to provide kinetic stabilization to strontium and magnesium hydrides $[L^{\text{Ad}}\text{Sr}(\mu\text{-H})]_2$ and $[L^{\text{R}}\text{Mg}(\mu\text{-H})]_2$ ($R = \text{Ad}$ or tBu) (Figure 3.4).²⁶

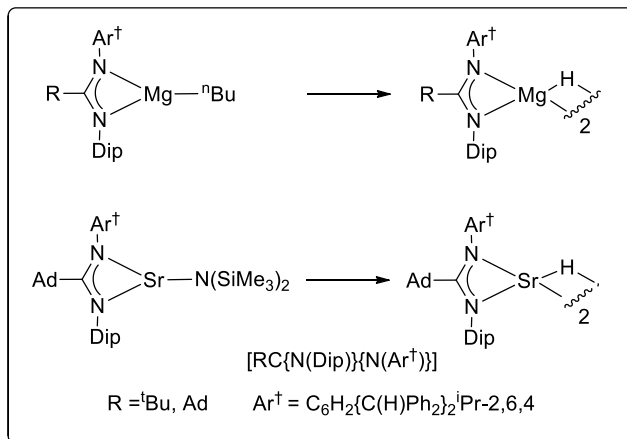
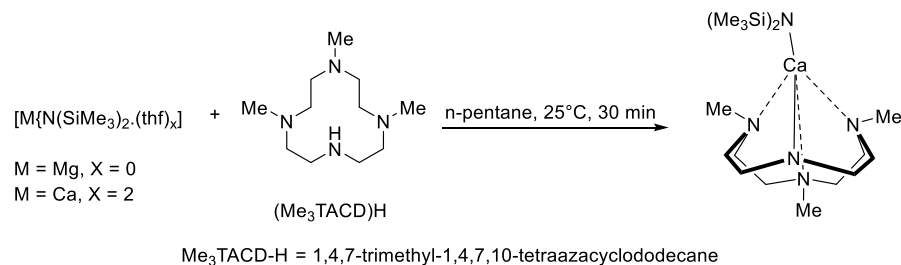


Figure 3.4. Synthesis of strontium and magnesium hydrides from their heteroleptic amidinates.²⁶

Generally, the Lewis base (solvent) coordinated to the metal center is a drawback in homogeneous catalysis. The intramolecular coordination of the metal center to heteroatoms of the ligand provides enough electronic density to the metal and decrease its tendency to attack the solvent. Macrocycles such as polyamines and crown ethers are available in different sizes. Okuda used a tetradentate macrocyclic ligand ($N^{\wedge}N^{\wedge}N^{\wedge}N$) suitable for the stabilization of cationic magnesium and calcium hydrides. The resulting complexes were next used for the polymerization of *meso*-lactide as the first example of Ae metal complexes applied for this type of catalyzed polymerization (Scheme 3.2).^{27,28,29}



Scheme 3.2. Synthesis of $[\{Me_3TACD\}M\{N(SiMe_3)_2\}]$ complexes with $M = \text{Mg}$ and $M = \text{Ca}$.^{27,28,29}

This type of tetraamine ligand has been applied by Okuda and co-workers to give the heteroleptic calcium dihydride complex $[\{Me_3TACD\}Ca\{SiPh_3\}]$ ($Me_3TACD-H = 1,4,7$ -trimethyl-1,4,7,10-tetraazacyclododecane).³⁰ They have also reported the reactive fragment

$[\text{CaH}]^+$ which has been stabilized by NNNN-type ligand (Me_4TACD = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane) and shows high efficiency in the hydrogenation of non-activated 1-alkenes (Figure 3.5).³¹

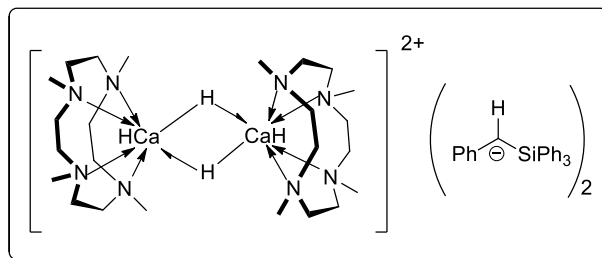


Figure 3.5. Cationic calcium hydride featuring a tetraamine ligand stabilized by silylated benzyl anions.³¹

Okuda and co-workers also prepared the $[\text{Ca}(\text{Me}_4\text{TACD})(\text{SiPh}_3)_2]$ complex starting from the $(\text{Me}_4\text{TACD})\text{H}$ polyamine ligand. During hydrogenolysis under mild conditions (1 bar of H_2), it provided the cationic dicalcium trihydride core $[\text{Ca}_2\text{H}_3(\text{Me}_4\text{TACD})_2](\text{SiPh}_3)_2$, instead of the neutral calcium dihydride $[\text{CaH}_2\{\text{Me}_4\text{TACD}\}]$.³²

Ruhlandt-Senge *et al.* used the 18-crown-6 ligand to stabilize the monocationic $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}\{18\text{-crown-6}\}]^+[\text{CHPh}_2]^-$ complex, and also characterized the barium complex of $\text{Ba}(18\text{-crown-6})(\text{CHPh}_2)_2$.³³

With magnesium, calcium and strontium, Okuda *et al.* synthesized heteroleptic complexes $([\{\text{O}^-\text{O}^-\text{O}^-\text{O}^-\}\text{AeNu}])$ using a tetradentate polyether ligand which was highly active in the polymerization of lactide (Figure 3.6).³⁴ This “half-crown ether” moiety is sufficiently flexible to coordinate the three Ae metals with different sizes; however, it is rigid enough to control the stereoselectivity in ring-opening polymerization (ROP) of *meso*-, *rac*- and L-lactide; polymerization resulted in the formations of syndiotactic, heterotactic and isotactic polylactides, respectively.

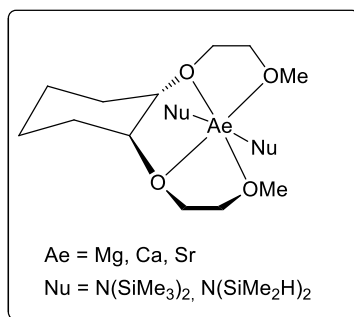


Figure 3.6. Alkaline earth metal complexes with neutral polyether ligand.³⁴

In 1967, Pedersen used the crown ethers to prepare, for the first time, stabilized alkali and alkaline earth complexes.³⁵ Later on, increasing attention was given to the study of the binding properties of crown ethers toward Ae metals.³⁶ One of the most important features inherent to the crown ethers is the “size fit” of the metal that is the match of the ionic diameter of the metallic ion with the size (diameter) of the crown ether cavity. This idea has been incorporated in the design of multidentate ligands. Itoh *et al.* originally prepared the Ae complexes (Mg, Ca, Sr) by application of aza-crown ethers (1-aza-15-crown-5-ether and 1-aza-18-crown-6-ether group).

The amine mono(phenolate) ligand with two donor side-arms {LO⁴}H was designed by Kol *et al.* for the synthesis of group IV catalysts.³⁷ {LO³}H (2-((1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)-methyl)-4,6-di-*tert*-butylphenol) is flexible and has more chelating ability compared to the number of heteroatoms in {LO⁴}H (Figure 3.7).³⁸ More recently, our group has prepared several heteroleptic Ae complexes from the phenolate ligands with chelating ability ({LO¹}[−] = 4-(*tert*-butyl)-2,6-bis(morpholinomethyl)phenolate, {LO³}[−], {LO⁴}[−]) (Figure 3.7).^{3d,4,8,12,39} These aminoether-phenolate complexes have shown high efficiency in ROP of lactide (LA). The catalytic activity of the complex increased with the metal size (Ca < Sr < Ba).^{3d} These aminophenolate Ae catalysts also showed an appreciable efficiency for intermolecular and intramolecular hydroamination reactions.

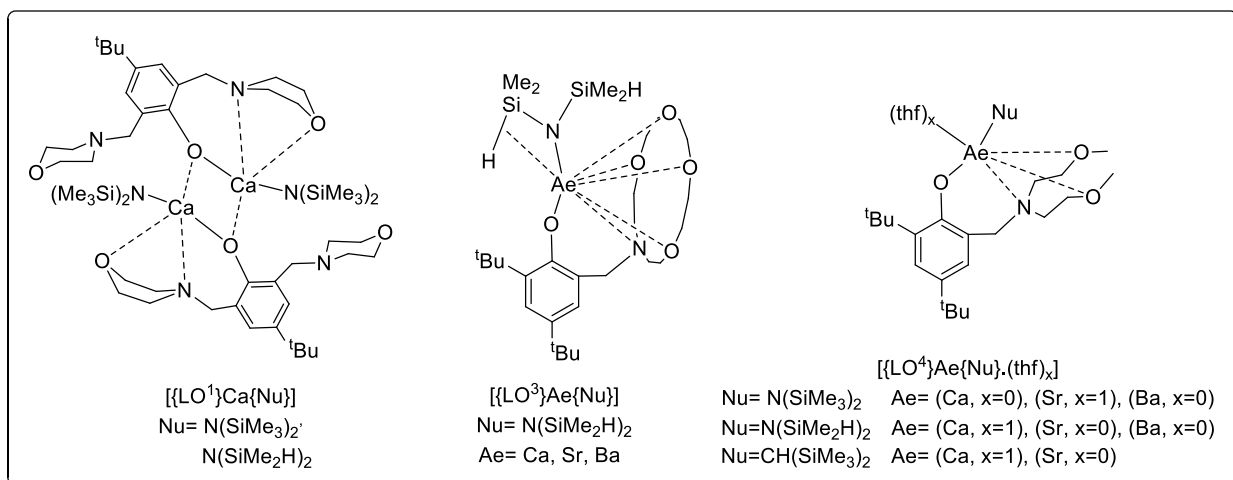


Figure 3.7. Multidentate phenolate ligands for heavy Ae metal complexes.^{3d,4,8,12,39}

3.1.4 Objective

Designing a bulky, monoanionic ligand that is able to shelter the Ae ions, has been a key in Ae-mediated catalysis. The implementation of an ancillary ligand such as nitrogen-based iminoanilide {N[^]N^{DiPP}}⁻, was a breakthrough in this field. The amidinates have also shown suitable characteristics for synthesis of the heteroleptic Ae complexes. In this chapter, we will then explore new pathways to stabilize neutral alkaline earth heteroleptic complexes featuring factors to serve several purposes: optimize the steric hindrance of the ligand to impart kinetic stability, prevent the aggregation of the resulting complexes, increase the lifetime of the complex in solution, and most importantly stop the ligand exchange and Schlenk equilibria. In order to achieve these goals all together, we have combined three specific ideas in one complex. First, to use the N-donor, bidentate and bulky ancillary ligands (based on iminoaniline, amidinate and β-diketiminato skeleton) to shelter the polarizable Ae⁺² ion; second, to use a crown ether macrocycle side-arm with chelating ability and flexibility known to efficiently stabilize through metal-heteroatoms bonds and finally, to introduce Ae⋯Si–H β-anagostic interactions through which we could encapsulate the metal center (Figure 3.8).

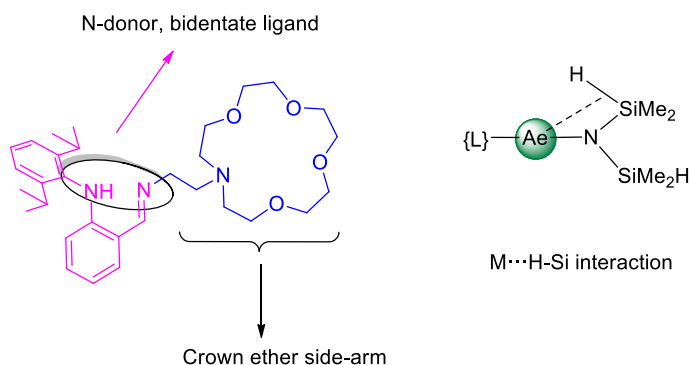
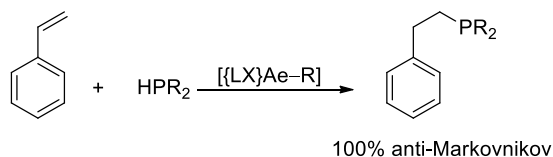


Figure 3.8. The proligand $\{I^A^{crown}\}H$ and its two main components

Hill *et al.* showed that the hydrophosphination reaction catalyzed by $[\{BDI^{Dipp}\}Ca\{N(SiMe_3)_2\} \cdot (thf)]$ is possible at high temperature (catalyst loading 10 mol%, 75°C, in C_6D_6 , Scheme 3.3).^{19a} The experiments have evidenced an anti-Markovnikov regioselectivity along with the kinetic dependence on the size of the metal center of the precatalyst. According to investigations of our group, the barium-based iminoanilido complex ($[\{N^A^{DiPP}\}BaN(SiMe_3)_2 \cdot (thf)_2]$) showed high activity in the hydrophosphination catalytic cycle.¹²



Scheme 3.3. Hydrophosphination of styrene promoted by Ae complexes.

Given the reported increase of the hydrophosphination reaction rate upon going down group 2 metals, our investigations are based on the preparation of barium-amido heteroleptic complexes. As explained, according to the experiments by our group, the reaction rate in intermolecular hydroamination and hydrophosphination reaction increases with the size of the metal center. Therefore, the new reported iminoaniline and amidine proligands have been applied for the preparation of heteroleptic barium amido complexes. These two types of ligands have shown their ability to kinetically stabilize Ae complexes against ligand scrambling, paired with a tethered macrocycle known for its ability to stabilize otherwise electronically unsaturated Ae species. The present chapter focuses on the synthesis, structural characterization and catalytic

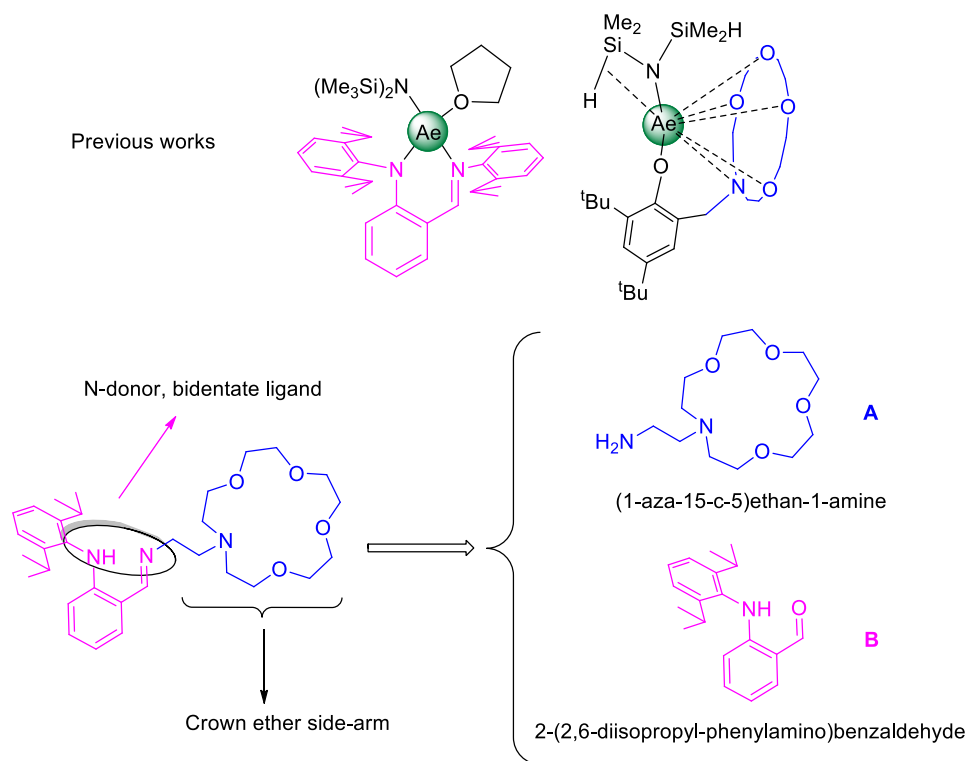
study of new barium precatalysts for hydrophosphination reactions. This work was produced in our group in collaboration with E. Le Coz who synthesized the proligand $\{\text{AdAm}^{\text{crown}}\}\text{H}$ and the complex $[\{\text{AdAm}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ as well as assessed its catalytic activity.

3.2 Synthesis of barium heteroleptic complexes $[\{\text{I}^{\wedge}\text{A}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (10) and $[\{\text{AdAm}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (11)

3.2.1 Synthesis and characterization of the iminoaniline $\{\text{I}^{\wedge}\text{A}^{\text{crown}}\}\text{H}$ and amidine $\{\text{AdAm}^{\text{crown}}\}\text{H}$ proligands

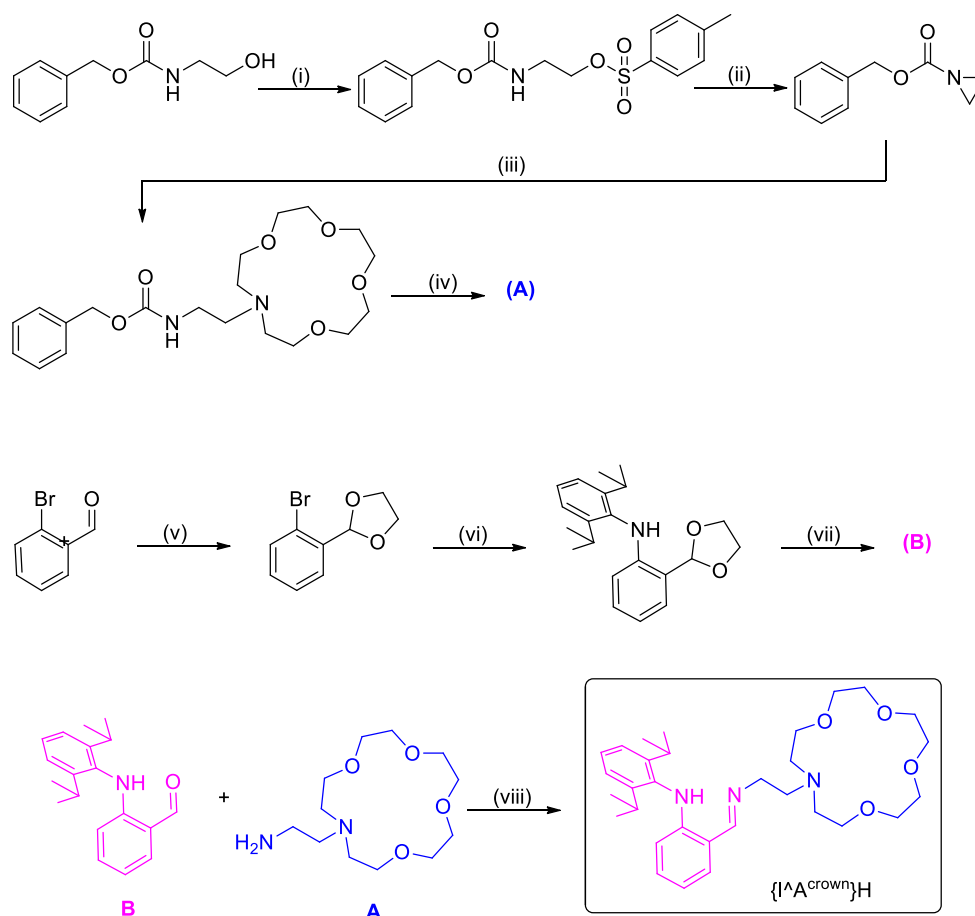
In our search of nitrogen-based and multidentate ligands, the objective was to synthesize a ligand that will be able to encapsulate the metal center in order to limit the kinetic lability and provide electronic stability. To achieve our goal, we modified the original iminoanilide proligand ($\{\text{N}^{\wedge}\text{N}^{\text{Dipp}}\}^-$) by adding a different side arm providing the extra bonding, stability and also flexibility to the proligand. Thus, the 2-(1-aza-15-c-5)ethan-1-amine (**A**) was prepared to provide sufficient flexibility.^{3d,4,40}

This chosen functionalized iminoaniline proligand, $\{\text{I}^{\wedge}\text{A}^{\text{crown}}\}\text{H}$, contains a tethered 15-member macrocycle ($\{\text{I}^{\wedge}\text{A}^{\text{crown}}\} = [\text{DippN}(o\text{-C}_6\text{H}_4)\text{C}(\text{H})=\text{N}(\text{crown ether})]$) with Dipp = 2,6-*i*Pr₂-C₆H₃, crown ether = 2-[(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)methyl] (Scheme 3.4). The ligand was prepared from the condensation of **A** with the Dipp-*N*-substituted benzaldehyde **B** which have been first prepared independently, and combined to afford $\{\text{I}^{\wedge}\text{A}^{\text{crown}}\}\text{H}$ (Scheme 3.4).



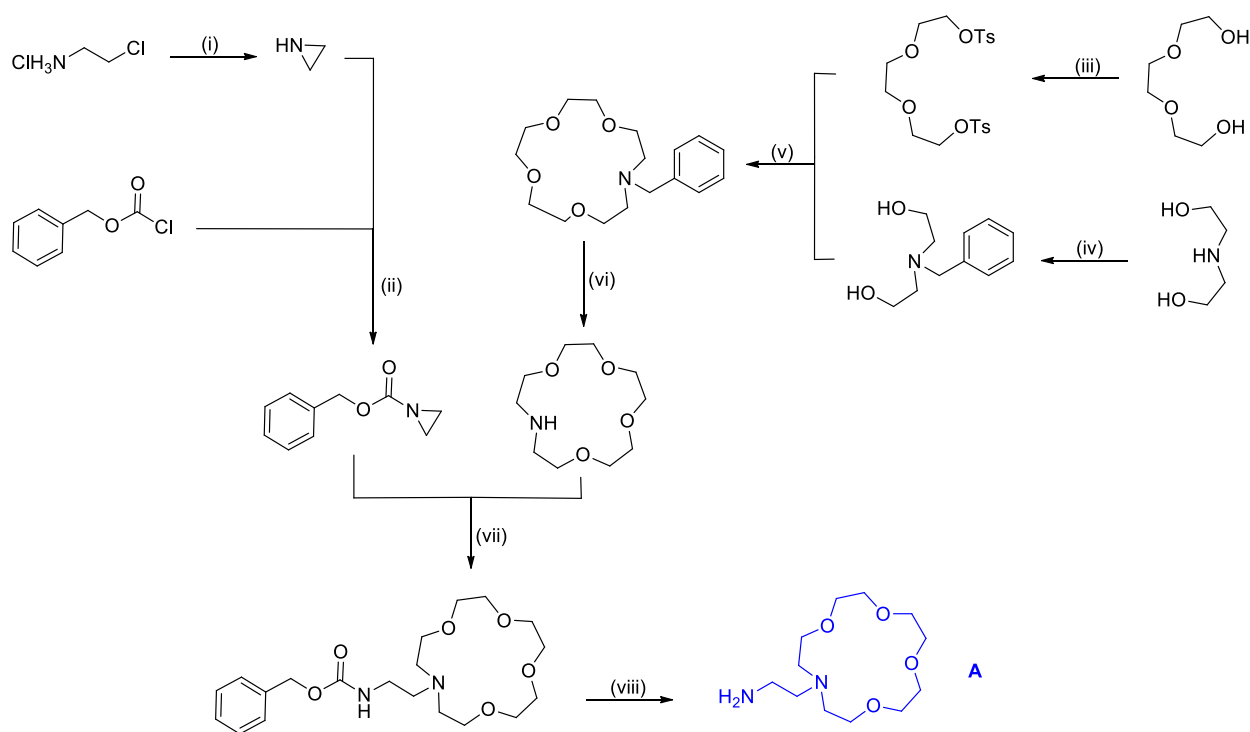
Scheme 3.4. The proligand $\{I^{\wedge}A^{\text{crown}}\}H$ and its two main components.^{8,11,12}

The two fractions of the proligand (**A** and **B**) were prepared over several steps as depicted in Scheme 3.5. The diamine **A** was synthesized through a process that involved four consecutive steps: (1) Synthesis of (*N*-benzyloxycarbonyl)-2-aminoethyl *p*-toluenesulfonate starting from (*N*-benzyloxycarbonyl)-2-aminoethanol;⁴¹ (2) Synthesis of *N*-benzyloxycarbonyl-aziridine;⁴² (3) Synthesis of *N*-benzyloxycarbonyl-protected (1-aza-15-c-5)ethan-1-amine; (4) Synthesis of (1-aza-15-c-5)ethan-1-amine (**A**). Each step contains several procedures including column chromatography to purify the target product.



Scheme 3.5. Synthesis of the proligand $\{I^A{}^{\text{crown}}\}H$. Reaction conditions: (i) TsCl, DMAP, NEt_3 , CH_2Cl_2 , RT, 48 h, 61%; (ii) thf, 45 °C, 48 h, 71%; (iii) CH_3CN /toluene (1:1 v/v), 1-aza-15-crown-5, reflux, 48 h, 47%; (iv) H_2 , Pd/C, MeOH, 20 °C, 15 h, 97%; (v) $\text{HOCH}_2\text{CH}_2\text{OH}$, PTSA, toluene, reflux, 48 h, 61%; (vi) 2,6-*i*Pr₂C₆H₃NH₂, Pd(OAc)₂, *t*BuOK, *Pt*Bu₃, thf, reflux, 16 h; (vii) CF₃COOH, MeOH, 1 h, 20 °C, 38%; (viii) petroleum ether, reflux, 10 d, 90%.

In another, more efficient protocol, the preparation of 2-(1-aza-15-crown-5)-ethan-1-amine (A) fraction of the proligand described in Scheme 3.5 was scaled-up and as the procedure presented Scheme 3.6.



Scheme 3.6. Optimized synthesis of the first step towards $\{I^A{}^{\text{crown}}\}H$. Reaction conditions: (i) NaOH, H_2O , 50 °C, 4 h, 75%; (ii) Et_2O , NEt_3 , 0 to 20 °C, 12 h, 51%; (iii) TsCl, DMAP, NEt_3 , CH_2Cl_2 , 0 to 20 °C, 12 h, 85%; (iv) BnBr, Na_2CO_3 , acetone, reflux, 4 h, 80%; (v) NaOH, nBu_4NBr , toluene, 70 °C, 10 h, 82%; (vi) H_2 , Pd/C, MeOH, 20 °C, 12 h, 80%; (vii) CH_3CN /toluene (1:1 v/v), reflux, 24 h, 70%; (viii) H_2 , Pd/C, MeOH, 20 °C, 15 h, 97%.

Ultimately, the $\{I^A{}^{\text{crown}}\}H$ proligand was prepared through condensation of the two fractions **A** and **B** with global yield of 66% (Scheme 3.5). This last step is not trivial since several days of reaction and addition of the amine (**A**) in several portions are required. Finally, the optimized conditions resulted in high yield (3.66 g, 97%) of an off-white oil that solidified slowly upon standing at room temperature. It is completely soluble in common organic solvents, including aliphatic hydrocarbons. The proligand was fully characterized by NMR spectroscopy, mass spectrometry and combustion analyses.

The ^1H NMR spectrum of the final proligand $\{I^A{}^{\text{crown}}\}H$ in chloroform-*d* at room temperature (Figure 3.9) shows a characteristic signal for the NH hydrogen atom at δ 10.50 ppm, expected to disappear in the NMR spectrum of the related Ae complex due to the bonding of this nitrogen to the metal center. There is also another characteristic signal for CH=N hydrogen atom at δ 8.46 ppm.

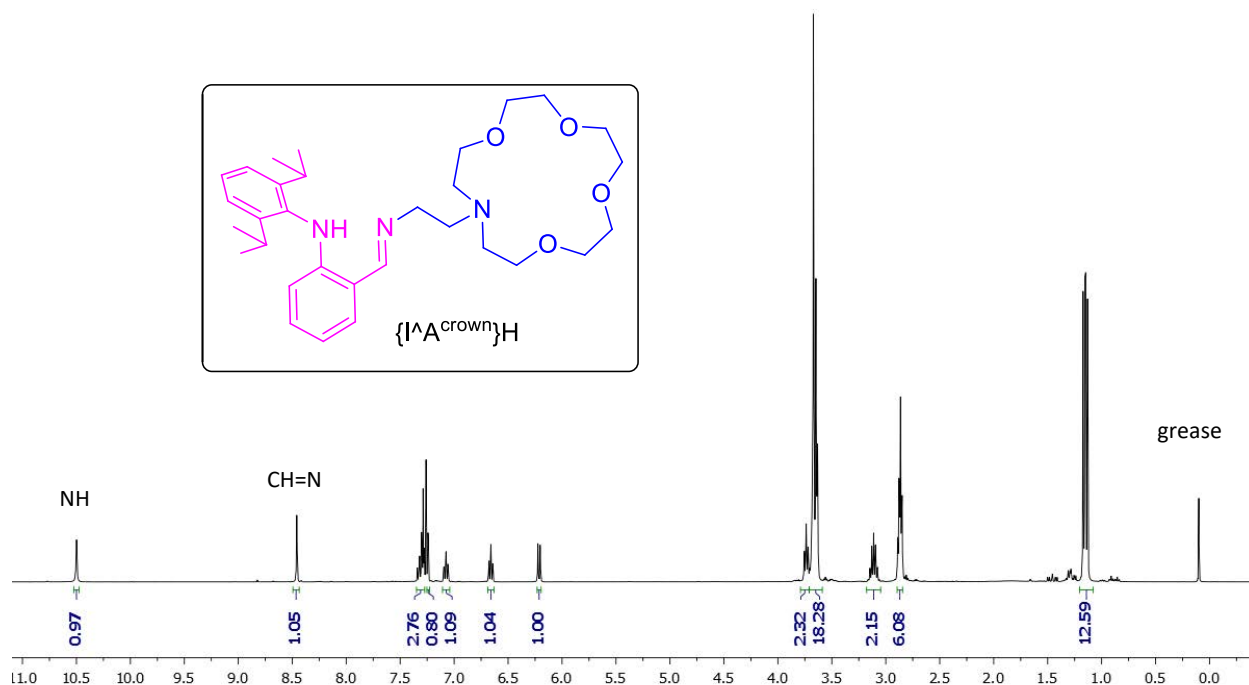


Figure 3.9. ^1H NMR spectrum (CDCl_3 , 298 K, 400 MHz) of $\{\text{I}^{\text{A}^{\text{crown}}}\}\text{H}$.

The single-crystal X-ray diffraction studies of crystals of **A** grown from the first oily material upon standing at room temperature revealed its molecular solid-state structure (Figure 3.10).

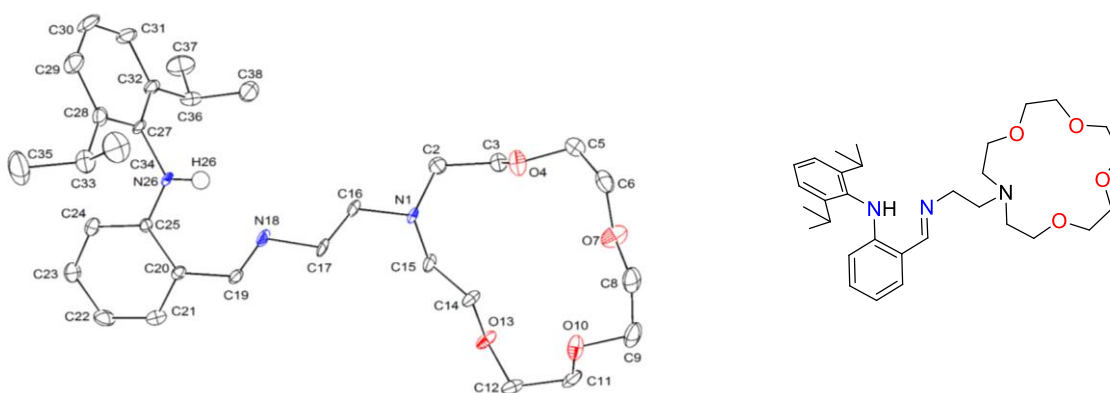
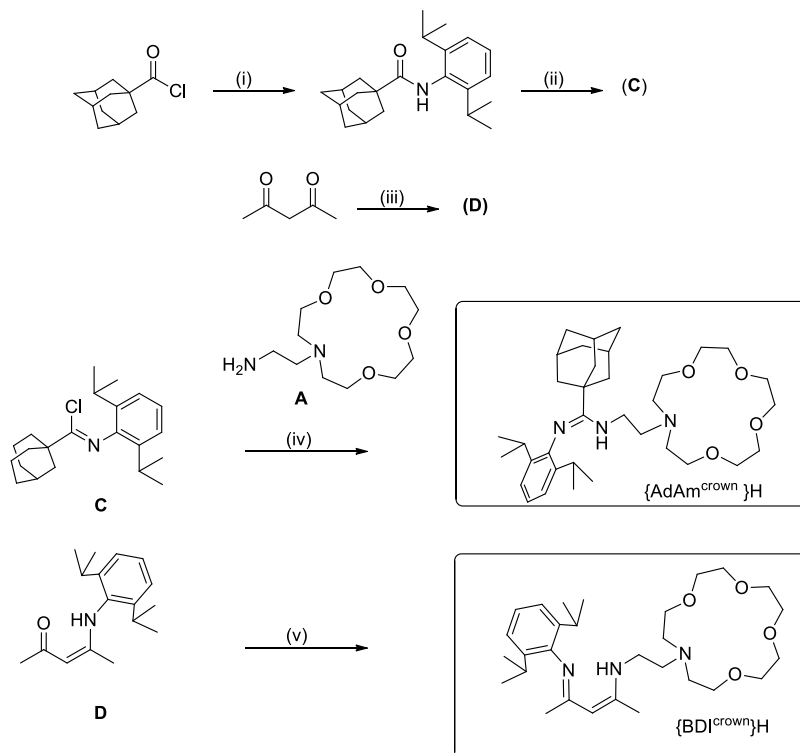


Figure 3.10. ORTEP representation of the molecular solid-state structure of $\{\text{I}^{\text{A}^{\text{crown}}}\}\text{H}$. Ellipsoids at the 50% probability level. Only one of the two identical molecules in the asymmetric unit is depicted. H atoms omitted for clarity. Selected bond lengths ($\text{\AA}$): C17–N18 = 1.461(4), N18–C19 = 1.268(4), N1–C16 = 1.458(3), N1–C15 = 1.469(4), N1–C2 = 1.470(4), C25–N26 = 1.369(4), N26–C27 = 1.428(4).

Following the same concepts implemented for the iminoaniline ligand $\{I^A^{crown}\}H$, the amidine $\{R\text{Am}\}H$ ($R = t\text{Bu}$, $\text{Ad} = 1\text{-adamantyl}$, $\text{Am} = \text{amidinate}$) ligand (**C**) and the archetypal $\{\text{BDI}^{\text{Dipp}}\}H$ (**D**), have been also modified to prepare $\{\text{AdAm}^{crown}\}H$ and $\{\text{BDI}^{crown}\}H$ proligands, respectively (Scheme 3.7).

The sterically congested amidine $\{\text{AdAm}^{crown}\}H$ was synthesized straightforwardly as analytically pure pale yellow crystals (ca. 30%, non-optimized) from the reaction of **A** with **C** under mild operating conditions. It is highly soluble in hydrocarbons. X-ray structure of this compound showed a high disorder in the crown ether area and the final refinement of the structure remained poor ($R_w > 20\%$). The X-ray structure of $\{\text{BDI}^{crown}\}H$ proligand has been suggested, but repeated purification attempts were unsuccessful.



Scheme 3.7. Synthesis of the proligands $\{\text{AdAm}^{crown}\}H$ and $\{\text{BDI}^{crown}\}H$. Reaction conditions: (i) 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}_2$, toluene, NEt_3 , 70°C , 3 h, 98%; (ii) SOCl_2 , reflux, 3 h, 90%; (iii) 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}_2$, toluene, PTSA, reflux, 12 h, 78%; (iv) NEt_3 , CH_2Cl_2 , 20°C , 72 h, 32%; (v) $\text{Et}_3\text{O}.\text{BF}_4$, NEt_3 , CH_2Cl_2 , 25°C .

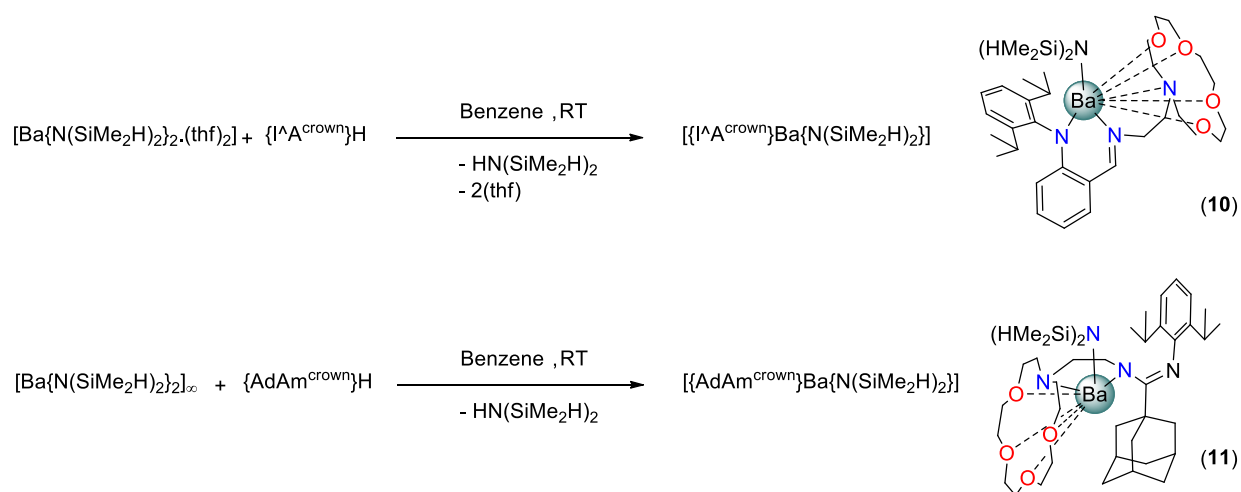
3.2.2 Synthesis and characterization of barium heteroleptic complexes $[\{I^A{}^{\text{crown}}\}BaN(SiMe_2H)_2]$ (**10**) and $[\{AdAm^{\text{crown}}\}BaN(SiMe_2H)_2]$ (**11**)

This section aims to present the synthesis and characterization of heteroleptic barium complexes starting from the barium amide $[Ba\{N(SiMe_2H)_2\}_2 \cdot (thf)_n]$ ($n = 0, 2$) and the abovementioned side-functionalised iminoaniline $\{I^A{}^{\text{crown}}\}H$ and amidine ($\{AdAm^{\text{crown}}\}H$) proligands.

Following our main strategy for the preparation new stabilized barium heteroleptic complexes, we have obtained barium heteroleptic complexes by protonolysis of barium amides ($[Ba\{N(SiMe_2H)_2\}_2 \cdot (thf)_2]$ or $[Ba\{N(SiMe_2H)_2\}_2]_{\infty}$ with the corresponding proligands $\{I^A{}^{\text{crown}}\}H$ and $\{AdAm^{\text{crown}}\}H$), respectively. This is indeed an easy and generally straightforward method.

According to the work reported by our group on alkaline earth metal heteroleptic complex using the $\{LO^3\}H$ (Figure 3.7) proligand, the investigations showed that $N(SiMe_3)_2^-$ was not able to stabilize the complex. Reacting $\{LO^3\}H$ with $[Ca\{N(SiMe_3)_2\}_2 \cdot (thf)_2]$ complex yielded intractable mixtures of $[Ca\{N(SiMe_3)_2\}_2 \cdot (thf)_2]$, $[\{LO^3\}_2Ca]$, $[\{LO^3\}Ca\{N(SiMe_3)_2\}_2]$, and some unidentified species, in the case of the Sr and Ba congeners the resulted compounds were not identifiable.^{4,40} The amido group $N(SiMe_2H)_2^-$ has been applied for preparation of the barium complexes offering the possibility of extra stabilization through $Ba \cdots H-Si$ anagostic interactions (eg. in monometallic aminoether-phenolato complex $[\{LO^3\}BaN(SiMe_2H)_2]^4$ or in the trinuclear cluster $[\{OSi(OtBu)_3\}_3Ba_3\{N(SiHMe_2)_2\}_3])^{43}$

The reaction of an equimolar amount of the iminoaniline proligand $\{I^A{}^{\text{crown}}\}H$ with barium amide $[Ba\{N(SiMe_2H)_2\}_2 \cdot (thf)_2]$, at room temperature in benzene, returned the heteroleptic complex $[\{I^A{}^{\text{crown}}\}Ba\{N(SiMe_2H)_2\}]$ (**10**) as an orange solid in 86% yield (Scheme 3.8). Similarly, the stoichiometric reaction of the barium amide $[Ba\{N(SiMe_2H)_2\}_2]_{\infty}$ and amidinate $\{AdAm^{\text{crown}}\}H$ proligand, led to the formation of colorless microcrystals of $[\{AdAm^{\text{crown}}\}BaN(SiMe_2H)_2]$ (**11**) in 85% yield. Both reactions released one equivalent of $HN(SiMe_2H)_2$ and afforded the targeted compounds **10** and **11**. Complexes **10** and **11** are sparingly to moderately soluble in hydrocarbons (petroleum ether, benzene and toluene), and dissolve well in ethers.



Scheme 3.8. Synthesis of $[\{\text{I}^{\wedge}\text{A}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**) and $[\{\text{AdAm}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**11**).

The ^1H NMR spectrum of **10** in $\text{thf-}d_8$ at room temperature shows a singlet and a multiplet at δ 8.04 ppm and δ 4.57 ppm that are characteristic of the $\text{CH}=\text{N}$ imine hydrogen and the SiH hydrogen, respectively (Figure 3.11). The resonances for OCH_2 , $\text{CH}(\text{CH}_3)_2$ and $\text{Si}(\text{CH}_3)_2$ moieties are broad at room temperature, as the result of some substantial level of fluxionality in the complex. The corresponding $^1J_{\text{Si-H}}$ coupling constant was estimated at ca. 162 Hz,^{3a} and testifies of mild $\text{Ae}\cdots\text{H-Si}$ β -anagostic interaction. Such interactions are known to contribute to the stability of electron deficient alkaline earth architectures (Table 3.1).⁴⁴

The ^1H NMR spectrum of **11** recorded in $\text{thf-}d_8$ at room temperature shows, besides the typical signals of the $\{\text{AdAm}^{\text{crown}}\}^-$ ligand, the characteristic SiH moiety at δ 4.64 ppm ($^1J_{\text{Si-H}} = 160$ Hz) (Figure 3.12, Table 3.1).

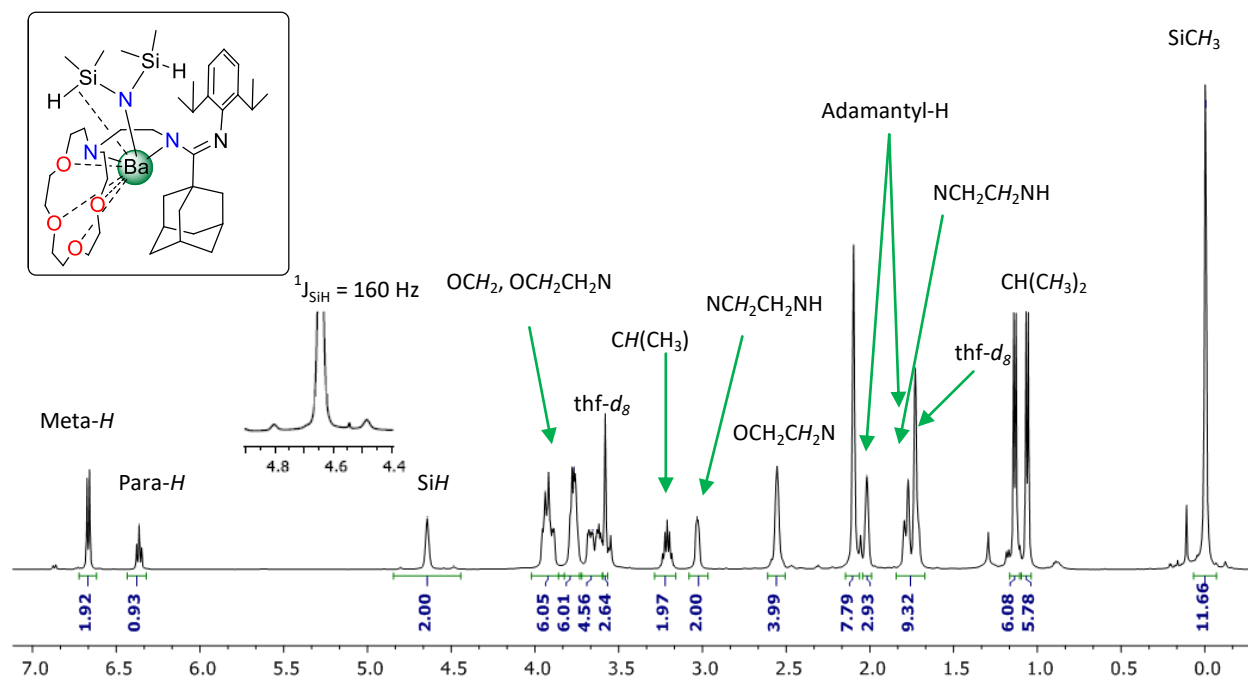
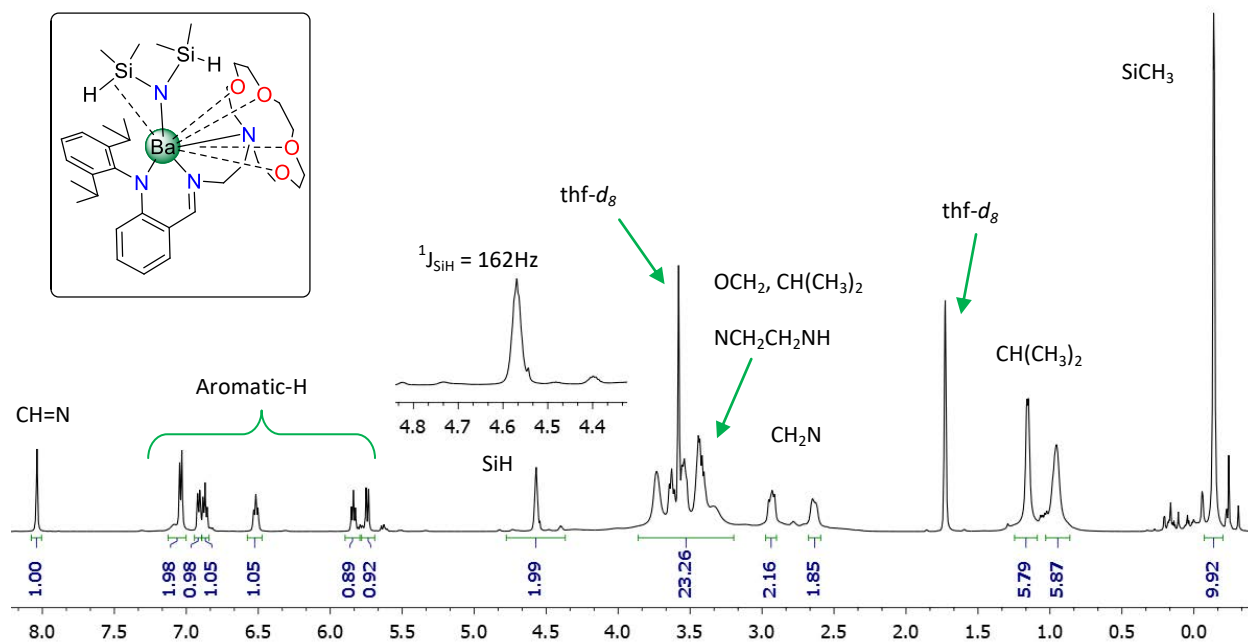


Table 3.1. NMR and FTIR spectroscopic data for complexes [$\{I^A^{crown}\}BaN(SiMe_2H)_2$] (**10**), [$\{AdAm^{crown}\}BaN(SiMe_2H)_2$] (**11**)⁴ and $HN(SiMe_2H)_2$.

Compound	FTIR ^a ν_{Si-H} (cm ⁻¹)	¹ H NMR δ_{SiH} (ppm)	J_{Si-H} (Hz)	⁹ Si NMR (ppm)
$HN(SiMe_2H)_2$	2122	4.70 ^b	194	-11.5 ^b
$[\{I^A^{crown}\}BaN(SiMe_2H)_2]$ (10)	$\tilde{\nu}_{Si-H}$	4.57 ^c	162 ^c	-30.09 ^c
$[\{AdAm^{crown}\}BaN(SiMe_2H)_2]$ (11)	2014, 1975	5.64 ^c	160 ^c	-30.92 ^c

^a Recorded at room temperature as Nujol mulls in KBr plates (cm⁻¹).

^b Recorded in benzene-*d*₆.

^c Recorded in thf-*d*₈.

The FTIR spectra of complexes **10** and **11** were recorded as Nujol mulls. They show two stretching bands for Si–H bonds at 2052 and 1990 cm⁻¹ for **10** and two bands for **11** at 2014 and 1975 cm⁻¹ that are in agreement with the data derived from the solid state structure related to Ba···H–Si anagostic interactions. These wavenumbers are much lower than that of the free amine $HN(SiMe_2H)_2$ (2122 cm⁻¹), due to the Ba···H–Si interactions in the solid state structures of the complexes that weakens the Si–H bond (Table 3.1). This confirms the ¹H NMR spectrum of **11** recorded in thf-*d*₈, where the ¹ J_{SiH} coupling constant of 160 Hz suggests mild Ba···H–Si interactions in solution.

The molecular solid-state structure of [$\{I^A^{crown}\}Ba\{N(SiMe_2H)_2\}$] (**10**) determined by XRD analysis of orange monocrystals formed at room temperature in a C₆D₆ solution, is displayed in Figure 3.13. It shows an eight-coordinate metal center surrounded by the Ba–N_{amine} coordination of the ancillary ligand. The structure features coordination from all the oxygen atoms of the ancillary ligand onto the barium center. Along with the Ba–O and Ba–N_{amine} bonds, the coordination sphere around the metal is further filled by the N_{silazide} atom from the tetramethyldisilazide nucleophilic ligand.

In comparison with the phenolato complex [$\{LO^3\}BaN(SiMe_2H)_2$]⁴ which has been mentioned formerly, the Ba–O and Ba–N_{amine} interatomic distances to the heteroatoms in the aza-crown-ether fragment are similar. The Ba–N_{silazide} bond length in **10** (2.704(3) Å) is also almost identical to the one in [$\{LO\}BaN(SiMe_2H)_2$] (2.688(2) Å). Following coordination of the N_{imine}

atom onto barium, there is no real difference between the complex and the proligand in the stretching of the C=N bond (1.287(5) Å in **10** and 1.268(4) Å in the proligand). The barium center stands out of the mean plane formed by the atoms N2, C13, C14, C19 and N3 to a great extent (1.76 Å). The iminoanilido core including the six carbon atoms along with C13, N2 and N3 also diverges from the plane observed in the proligand. The Ba²⁺ ion is too large to fit inside the crown ether; therefore, it stays above the mean plane that is defined by the five heteroatoms in the side-arm macrocycle (Figure 3.14).

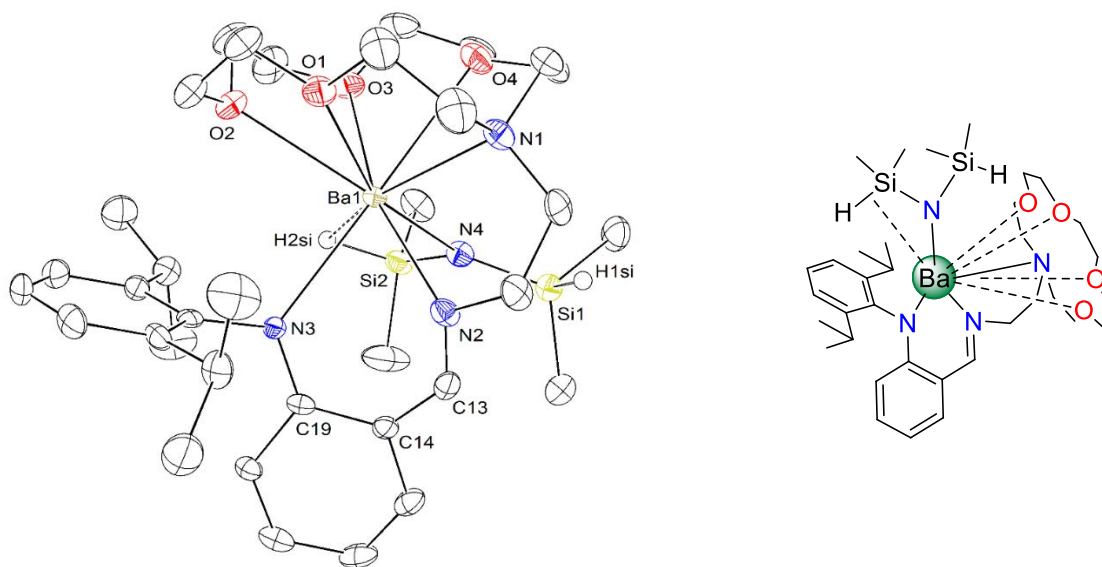


Figure 3.13. ORTEP representation of the molecular solid-state structure of [I^{crown}] $BaN(SiMe_2H)_2$ (**10**); Ellipsoids at the 50% probability level. H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ba1–N1 = 3.025(3), Ba1–N2 = 2.746(3), Ba1–N3 = 2.756(3), Ba1–N4 = 2.704(3), Ba1–O1 = 2.934(3), Ba1–O2 = 2.849(3), Ba1–O3 = 2.906(3), Ba1–O4 = 2.928(3), N2–C13 = 1.287(5), N2–C12 = 1.461(5); Si1–N4–Ba1 = 126.02(16), Si2–N4–Ba1 = 104.90(14).

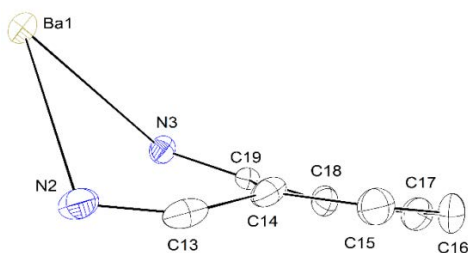


Figure. 3.14. Representation of the non-planar iminoanilide core in the molecular solid-state structure of **10**.

The molecular structure of **10** further shows the presence of a β -Si-H $\cdots$ Ba anagostic interaction. This effect is illustrated by the short and Ba(1) $\cdots$ Si(2) (3.525(1) Å) distances, and the Ba(1)–N(4)–Si(2) angle which is also very narrow (104.90(14)°). A comparison with the other Si(1)–H(1) bond shows that Ba(1) $\cdots$ H(1) (3.84(4) Å) and Ba(1) $\cdots$ Si(1) (3.919(1) Å) distances are longer, and the Ba(1)–N(4)–Si(1) angle is also bigger than the former one (126.02(16)°). Therefore, a β -Si-H $\cdots$ Ba anagostic interaction is present for one of the Si–H bonds in the solid state (Si(2)–H(2)).

The molecular structure of complex **11**, which has been obtained from colorless monocrystals formed at room temperature from a C₆D₆ solution, is given in Figure 3.15. It shows the presence of one molecule of complex **11** along with one benzene molecule in the asymmetric unit. However, the final refinement for the structure ($R_1 = 14.9\%$) is insufficient to enable a thorough discussion of the metric parameters, but the connectivity in the solid state could still be unambiguously established. The barium atom is seven-coordinate, with the binding of all five heteroatoms of the aza-crown-ether fragment completed by one nitrogen atom of tetramethylsilazide (N1) and, remarkably, by only one of the N atoms (N28) in the hence η^1 -coordinated amidinate; the other N atom (N30) points away from the metal center.

The η^1 -coordination mode observed for the amidinate in **11** is unusual, yet not unknown. While a similar coordination mode was previously reported in calcium-hydride amidinates by Harder, these latter complexes yet featured an additional stabilization from Ca $\cdots$ C(π) interactions involving the 2,6-*i*Pr₂C₆H₃ substituents; such interactions are not present in complex **11**.²³ On the other hand, the geometrical features of the tetramethyldisilazide group in **11**, and especially the largely different Ba1–N1–Si2 (105.76(51)°) and Ba1–N1–Si1 (122.39(56)°) angles, strongly suggest the presence of a Ba1 $\cdots$ Hi2 β -Si–H anagostic interactions with Hi₂ with an interatomic distance of 3.112(9) Å.^{4,3d,12,18,44b,44e,45}

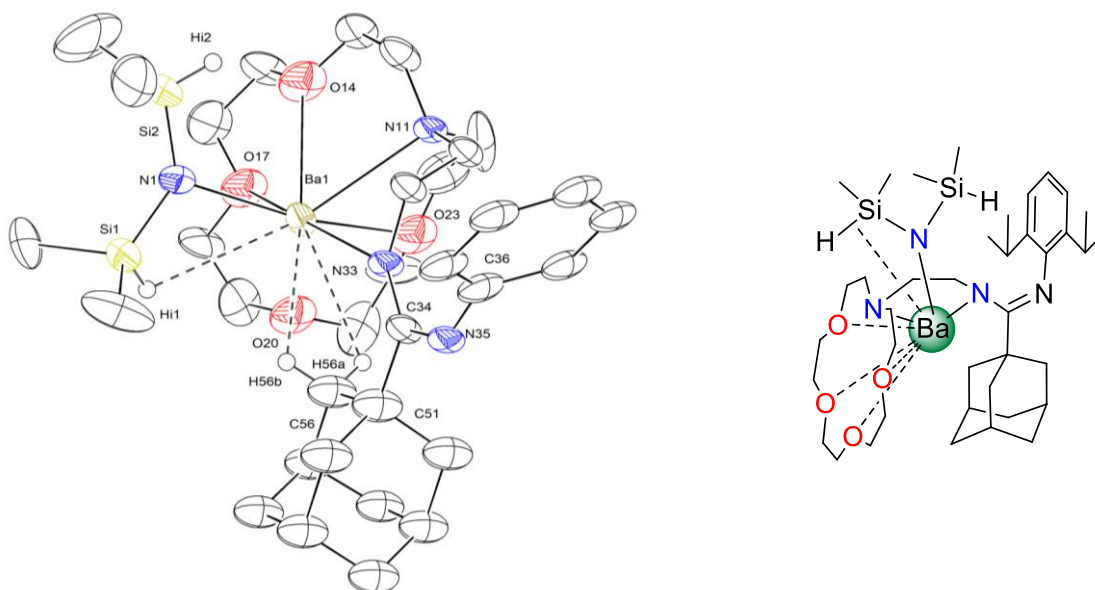
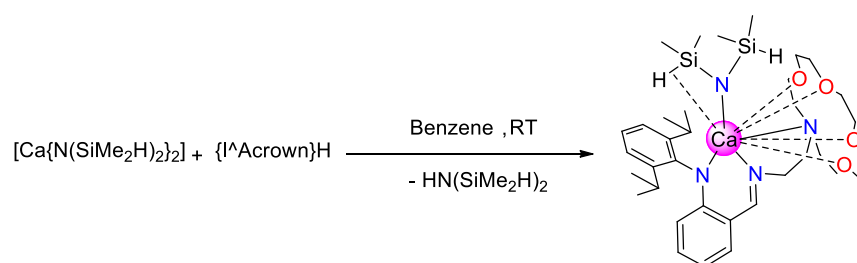


Figure 3.15. ORTEP representation of the molecular solid-state structure of $[\{\text{AdAm}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**11**); Ellipsoids at the 50% probability level. Non-interacting benzene molecule, *i*Pr groups and H atoms other than those interactions with barium omitted for clarity. Selected bond lengths (Å) and angles (deg): Ba1–N1 = 2.637(11), Ba1–N11 = 2.879(12), Ba1–N28 = 2.705(7), Ba1–O14 = 2.767(9), Ba1–O17 = 2.892(10), Ba1–O20 = 2.867(14), Ba1–O23 = 2.858(11), Ba1–H2 = 3.112(9), Ba1–H58a = 2.856(8), Ba1–H58b = 2.803(8); Si1–N1–Ba1 = 122.39(56), Si2–N1–Ba1 = 105.76(51).

Finally, the adamantyl substituent of the amidinate is directed towards the metal, and the short distances to the two hydrogen atoms H58a and H58b indicates additional $\text{Ba}\cdots\text{H}-\text{C}$ anagostic bonding (2.856 Å and 2.802 Å, respectively).

3.2.3 Attempted synthesis of the calcium heteroleptic complexes with the $\{\text{I}^{\wedge}\text{A}^{\text{crown}}\}\text{H}$ proligand

The stoichiometric reaction of the $\{\text{I}^{\wedge}\text{A}^{\text{crown}}\}\text{H}$ proligand with calcium bis(amide) $[\text{Ca}\{\text{N}(\text{SiMe}_2\text{H})_2\}_2]$ has been also studied at the NMR-tube scale. ^1H NMR analysis shows the presence of some unreacted iminoaniline $\{\text{I}^{\wedge}\text{A}^{\text{crown}}\}\text{H}$ after the reaction. The reaction of an equimolar amount of $\{\text{I}^{\wedge}\text{A}^{\text{crown}}\}\text{H}$ and $[\text{Ca}\{\text{N}(\text{SiMe}_2\text{H})_2\}_2]$ showed 88% conversion of the ligand (Scheme 3.9). The spectrum of the reaction mixture shows the diagnostic signal of $\text{CH}=\text{N}$ imine hydrogen for the new heteroleptic complex which appears in the same range (δ 0.8 ppm) as in the barium heteroleptic complex **10** (Figure 3.16).



Scheme 3.9. Attempted NMR-tube scale reaction of $\{\text{I}^{\wedge\text{A}^{\text{crown}}}\text{H}\}$ proligand with $[\text{Ca}\{\text{N}(\text{SiMe}_2\text{H})_2\}_2]$.

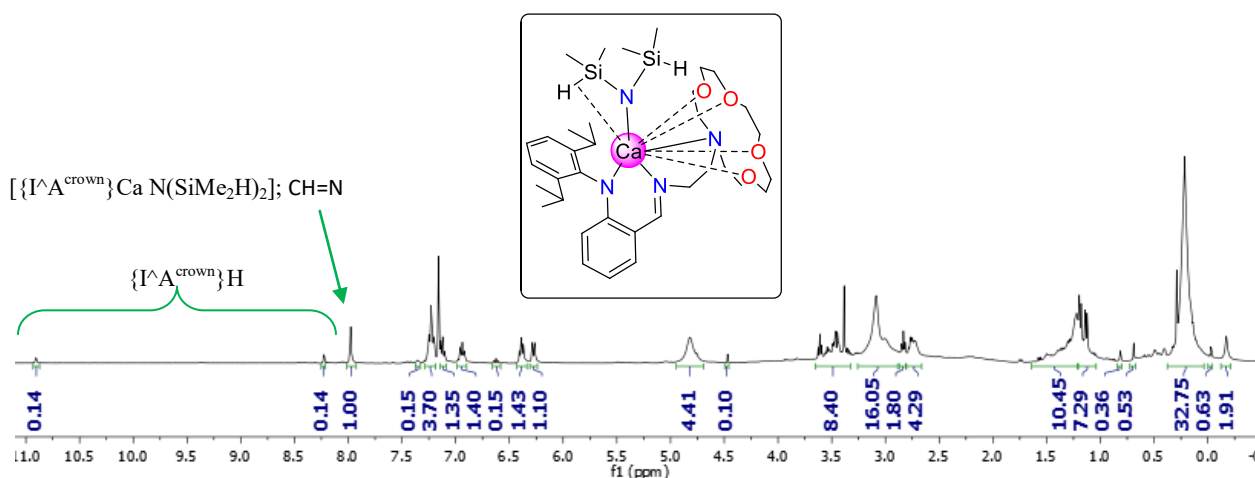
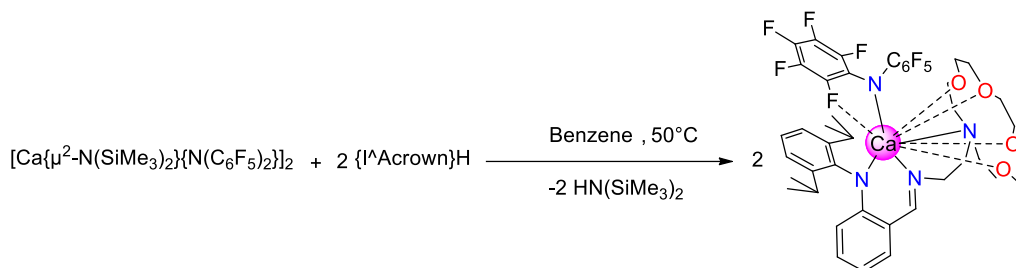


Figure 3.16. ^1H NMR spectrum (benzene- d_6 , 298 K, 400.16 MHz) of the attempted NMR-tube scale reaction of $\{\text{I}^{\wedge\text{A}^{\text{crown}}}\text{H}\}$ proligand with $[\text{Ca}\{\text{N}(\text{SiMe}_2\text{H})_2\}_2]$.

In order to study the bonding of the iminoaniline ($\{\text{I}^{\wedge\text{A}^{\text{crown}}}\text{H}\}$) to calcium and also to benefit from the work presented in chapter 2 describing the isolation of the calcium heteroleptic complex $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**3**₂), the stoichiometric reaction of **3**₂ and the proligand $\{\text{I}^{\wedge\text{A}^{\text{crown}}}\text{H}\}$ was carried out in NMR-tube scale in benzene d_6 at 50 °C. Complex **3**₂ bears the fluorinated arylamide that could provide $\text{Ca}\cdots\text{F}-\text{C}$ secondary interaction to the targeted heteroleptic complex. Furthermore, **3**₂ has the $\text{N}(\text{SiMe}_3)_2^-$ ligand that is more basic than $\text{N}(\text{C}_6\text{F}_5)_2^-$ (as discussed in chapter 2). Therefore, we expected the $\{\text{I}^{\wedge\text{A}^{\text{crown}}}\text{H}\}$ proligand to replace the $\text{N}(\text{SiMe}_3)_2^-$ amide and thus that the related hydrogen of free hexamethyldisilazane would appear in the ^1H NMR spectrum. The ^1H NMR and ^{19}F NMR spectroscopies of this NMR-scale reaction indicates complete consumption of

$\{I^A{}^{\text{crown}}\}H$ and the quantitative release of the hexamethyldisilazade ($\text{HN}(\text{SiMe}_3)_2$) in the reaction medium (Scheme 3.10).



Scheme 3.10. Attempted NMR-tube scale reaction of $\{I^A{}^{\text{crown}}\}H$ proligand with $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**3**₂).

The ^1H NMR spectroscopy is consistent with the expected composition $[\{I^A{}^{\text{crown}}\}\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**12**), including a resonance for the imine proton ($\text{CH}=\text{N}$) at δ 7.79 ppm. (Figure 3.17). Furthermore, the corresponding ^{19}F NMR spectrum indicates three resonances at δ -160.86 , -170.18 , and -185.45 ppm (for *o*-, *m*- and *p*-F atoms, respectively) (Figure 3.18). The large-scale synthesis of this complex still needs to be optimized.

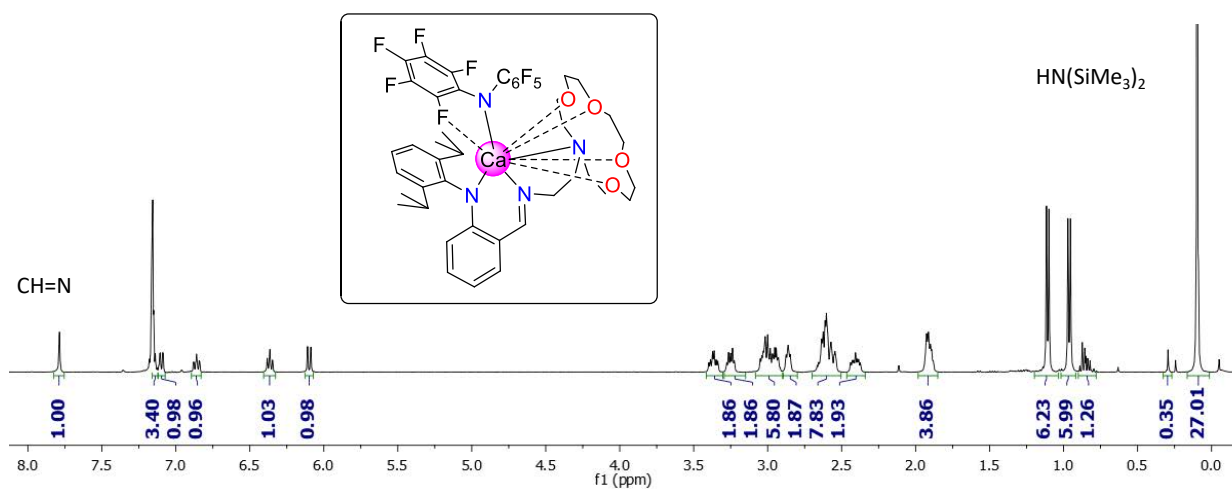


Figure 3.17. ^1H NMR spectrum (benzene- d_6 , 298 K, 400.16 MHz) of the attempted NMR-tube scale reaction of $\{I^A{}^{\text{crown}}\}H$ proligand with $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$.

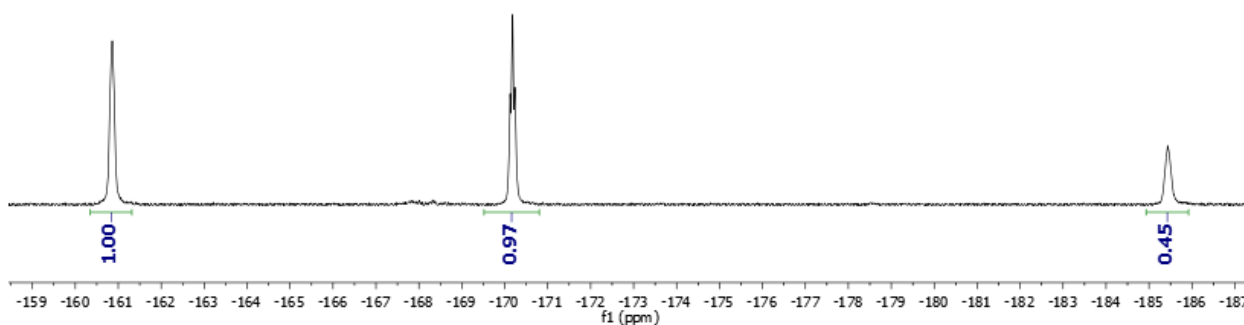


Figure 3.18. ^{19}F NMR spectrum (benzene- d_6 , 298 K, 376.47 MHz) of the attempted NMR scale reaction of $\{\text{I}^{\wedge\text{A}^{\text{crown}}}\}\text{H}$ proligand with $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**32**).

3.3 Application to the intermolecular hydrophosphination of vinylarenes

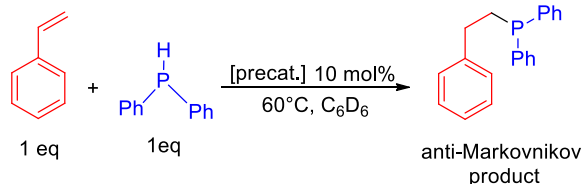
Phosphorus compounds have valuable applications in antibiotics, antitumor agents and organocatalytic transformations.⁴⁶ Pringle and co-workers reported the first example of alkene hydrophosphination catalyzed by a metal complex in 1990.⁴⁷ The construction of a C–P bond by catalyzed intermolecular hydrophosphination has been the subject of many organometallic investigations in recent years, since it could afford phosphine derivatives in a clean atom-efficient way. Ae complexes have been successfully implemented as homogenous precatalysts for intermolecular hydrophosphination of activated alkenes. They enable the efficient formation of C–P bonds and are less prone to interacting with phosphines (*i.e.* to be deactivated due to excessive strong coordination of this substrate).

This section thus presents the tests that were performed in order to determine the catalytic activity of the complex **10** in the benchmark hydrophosphination of styrene and its derivatives in comparison with the previous experiments from our group.^{3c,11,12,19b}

3.3.1. Comparison of the catalytic activity of $[\{\text{I}^{\wedge\text{A}^{\text{crown}}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**) and $[\{\text{AdAm}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**11**) with that of $[\{\text{N}^{\wedge\text{N}^{\text{DiPP}}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}](\text{thf})_2]$

The hydrophosphination reaction of styrene with diphenylphosphine, a monofunctional substrate typically studied for such hydrophosphination reactions, has been previously done with $[\{\text{N}^{\wedge\text{N}^{\text{DiPP}}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}](\text{thf})_2]$ in our group ($[\text{Ph}_2\text{PH}]_0/[\text{styrene}]_0/[\text{precat}]_0 = 50/50/1$), in solvent-free conditions at 60 °C (Scheme 3.11). With this precatalyst (2 mol%), after 15 min,

96% conversion towards the anti-Markovnikov product ($\text{PhCH}_2\text{CH}_2\text{PPh}_2$ $\delta_{31\text{P}} = -16.04$ ppm) was observed through NMR spectroscopy.¹¹ The efficacy of the precatalysts $[\{\text{I}^\wedge\text{A}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**), $[\{\text{AdAm}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**11**) has been studied and compared with the barium heteroleptic complex $[\{\text{N}^\wedge\text{N}^{\text{DiPP}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)_2\} \cdot (\text{thf})_2]$ in intermolecular hydrophosphination reaction of styrene with HPPH_2 (Figure 3.19).



Scheme 3.11. Anti-Markovnikov hydrophosphination reaction of styrene with HPPH_2 .

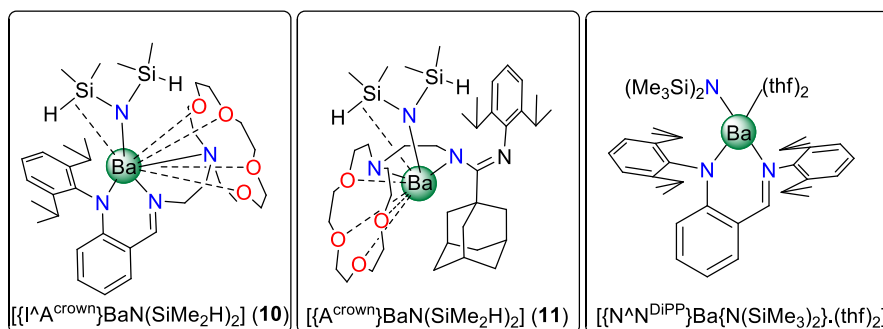


Figure 3.19. Structure of the barium heteroleptic complexes $[\{\text{I}^\wedge\text{A}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**), $[\{\text{AdAm}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**11**) and $[\{\text{N}^\wedge\text{N}^{\text{DiPP}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)_2\} \cdot (\text{thf})_2]$ used as the precatalysts in the hydrophosphination reaction.

A preliminary set of experiments of the equimolar hydrophosphination of styrene with HPPH_2 was performed under identical experimental conditions ($[\text{styrene}]_0/[\text{HPPH}_2]_0/[\text{Ba}]_0 = 10:10:1$, benzene- d_6 , 60 °C, 60 min). The results showed that $[\{\text{I}^\wedge\text{A}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**) and $[\{\text{AdAm}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**11**) are similarly active precatalysts, and slightly better than the iminoanilide precatalyst $[\{\text{N}^\wedge\text{N}^{\text{DiPP}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)_2\} \cdot (\text{thf})_2]$ (Table 3.2).^{11,12}

Table 3.2. Hydrophosphination of styrene with Ph₂PH catalyzed by [$\{I^A^{crown}\}Ba\{N(SiMe_2H)_2\}$] (**10**), [$\{AdAm^{crown}\}BaN(SiMe_2H)_2$] (**11**) and [$\{N^N^{DiPP}\}Ba\{N(SiMe_3)_2\} \cdot (thf)_2$]

Entry ^a	Precatalyst	[Styrene] ₀ /[Ph ₂ PH] ₀ /[precat] ₀	Conv.	TOF
			(%) ^b	(h ⁻¹)
1	[$\{I^A^{crown}\}BaN(SiMe_2H)_2$] (10)	10/10/1	52	5.2
	[$\{AdAm^{crown}\}BaN(SiMe_2H)_2$] (11)	10/10/1	49	4.9
2	[$\{N^N^{DiPP}\}Ba\{N(SiMe_3)_2\} \cdot (thf)_2$] ^{11,12}	10/10/1	32	3.2

^aReaction conditions: Ph₂PH (11.6 μL, 0.06 mmol), styrene (7.6 μL, 0.06 mmol), [precat] = 1.12 10⁻⁷ M, solvent C₆D₆ (0.6 mL), T = 60 °C, t = 60 min. ^bConversion of styrene, determined by ¹H NMR spectroscopy.

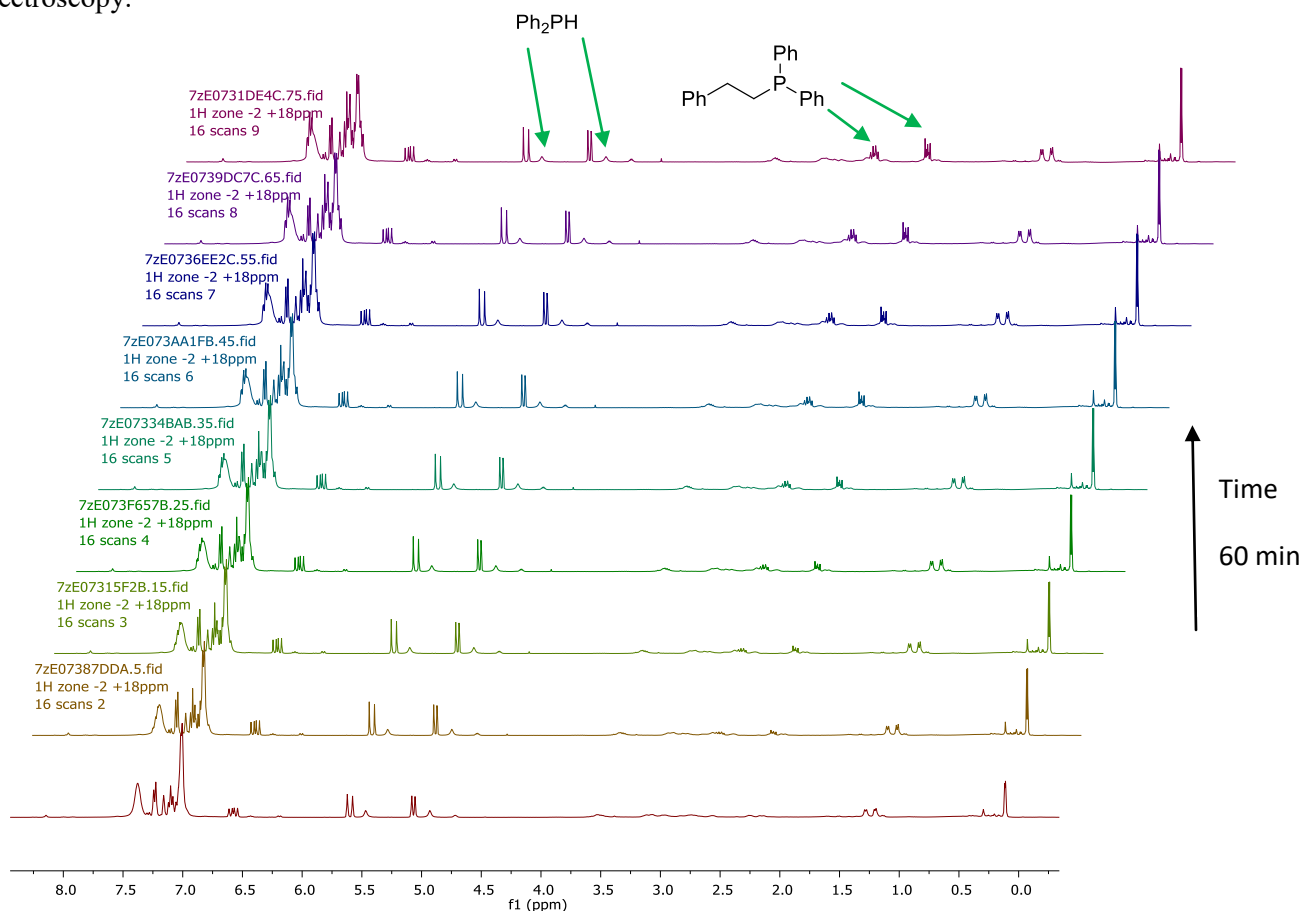


Figure 3.20. Stacked ¹H NMR spectra (400 MHz, benzene-*d*₆, 333 K) of substrate conversion for the hydrophosphination of styrene with diphenylphosphine catalyzed by [$\{I^A^{crown}\}BaN(SiMe_2H)_2$] (**10**). Reaction conditions: Ph₂PH (11.6 μL, 0.06 mmol), styrene (7.6 μL, 0.06 mmol), [precat] = 1.12 10⁻⁷ M, solvent C₆D₆ (0.6 mL), [Ph₂PH]₀/[styrene]₀/[precat]₀ = 10/10/1.

The reactions performed with **10** and **11** were monitored through ¹H NMR spectroscopy (Figure 3.20). The spectra showed the progressive appearance of only the anti-Markovnikov

$\text{PhCH}_2\text{CH}_2\text{PPh}_2$ product identified with its methylene groups at δ_{H} 2.74 and 2.27 ppm (Figure 3.21).

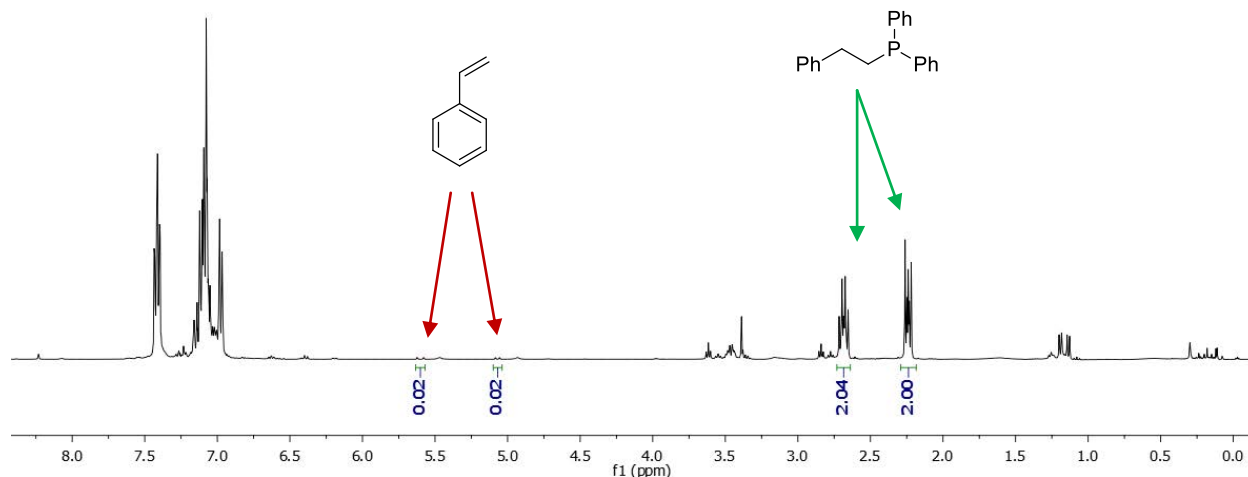


Figure 3.21. ^1H NMR spectrum (400 MHz, benzene- d_6 , 60 °C) of the product of hydrophosphination of styrene with diphenylphosphine catalyzed by $[\{\text{I}^{\text{A crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**) after 12 h. Reaction conditions: Ph_2PH (11.6 μL , 0.06 mmol), styrene (7.6 μL , 0.06 mmol), $[\textbf{10}] = 1.12 \cdot 10^{-7}$ M, solvent C_6D_6 (0.6 mL), $[\text{Ph}_2\text{PH}]_0/[\text{styrene}]_0/[\textbf{10}]_0 = 10/10/1$ (99% conversion to anti-Markovnikov product).^{19a,48}

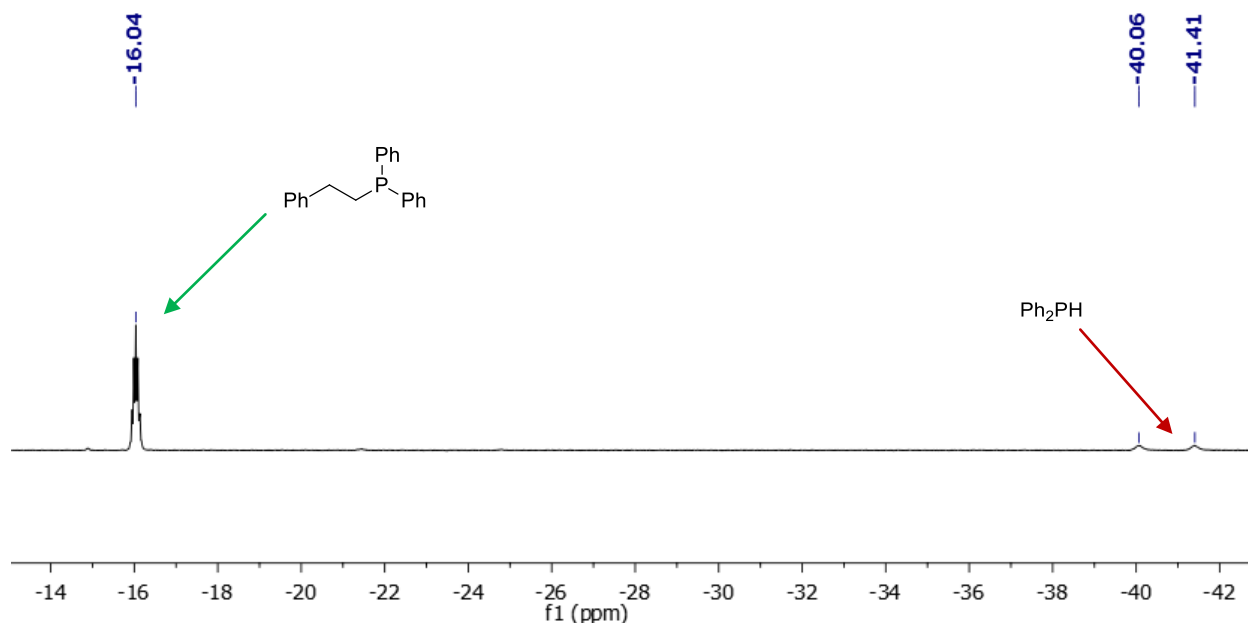


Figure 3.22. ^{31}P NMR spectrum (400 MHz, benzene- d_6 , 60 °C) of the product of hydrophosphination of styrene with diphenylphosphine catalyzed by $[\{\text{I}^{\text{A crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**) after 12 h. Reaction conditions: Ph_2PH (11.6 μL , 0.06 mmol), styrene (7.6 μL , 0.06 mmol), $[\textbf{10}] = 1.12 \cdot 10^{-7}$ M, solvent C_6D_6 (0.6 mL), $[\text{Ph}_2\text{PH}]_0/[\text{styrene}]_0/[\textbf{10}]_0 = 10/10/1$.

The consumption of HPPH_2 during the reaction catalyzed by **10** as monitored by ^1H NMR analysis (see Figure 3.20), showed that it is zeroth-order in the concentration of $[\text{HPPH}_2]$ (Figure 3.23). This is reminiscent of the behavior already reported for $[\{\text{N}^{\text{DiPP}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}(\text{thf})_2]$, for which the kinetic rate law : $\text{rate} = k \cdot [\text{HPPH}_2]^0[\text{styrene}]^1[\text{Ba}]^1$, was established.¹¹

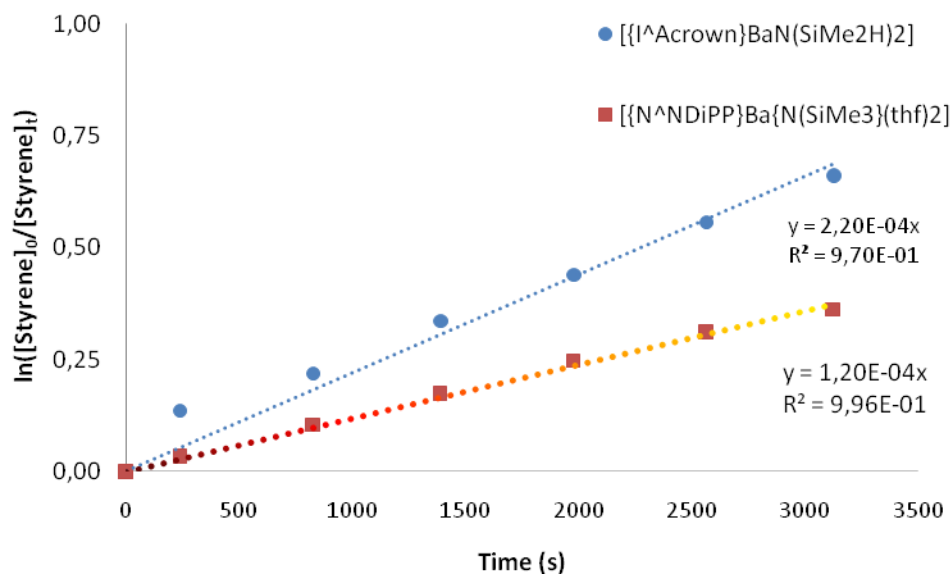


Figure 3.23. $\ln([\text{Styrene}]_0/[\text{Styrene}]_t) = k_{\text{app}}t$ plots as a function of the reaction time for the hydrophosphination of styrene and diphenylphosphine catalyzed by $[\{\text{I}^{\text{Acrown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**) and $[\{\text{N}^{\text{DiPP}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}(\text{thf})_2]$ precatalysts. Reaction conditions: Ph_2PH (11.6 μL , 0.06 mmol), Styrene (7.6 μL , 0.06 mmol), $[\text{precat}] = 1.12 \cdot 10^{-7}$ M, solvent C_6D_6 (0.6 mL), $[\text{Ph}_2\text{PH}]_0/[\text{styrene}]_0/[\text{precat}]_0 = 10/10/1$.

$[\{\text{I}^{\text{Acrown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**) ($k_{\text{app}} = (2.20 \pm 0.10) \cdot 10^{-4} \text{ s}^{-1}$) demonstrated similar reaction rates compared to $[\{\text{N}^{\text{DiPP}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}(\text{thf})_2]$ complex ($k_{\text{app}} = 1.20 \pm 0.02 \cdot 10^{-4} \text{ s}^{-1}$, Figure 3.23). The reaction rate was improved when the reaction was run without any solvent. In neat conditions with **10** as precatalyst, the reaction rate increases compared to the observed result with $[\{\text{N}^{\text{DiPP}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}(\text{thf})_2]$ complex ($[\{\text{N}^{\text{DiPP}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}(\text{thf})_2]$; in 15 min, > 96% conversion, $\text{TOF} = 192 \text{ h}^{-1}$). Thus, with **10**, full conversion of HPPH_2 and styrene ($[\text{Ph}_2\text{PH}]_0/[\text{styrene}]_0/[\text{precat}]_0 = 50/50/1$) was then quantitative at 60 °C within 15 min, which then corresponds to a TOF value $\geq 200 \text{ h}^{-1}$.

During the hydrophosphination of styrene with diphenylphosphine catalyzed by $[\{I^A^{crown}\}BaN(SiMe_2H)_2]$ (**10**) carried out in benzene- d_6 at 60 °C, the complex $[\{I^A^{crown}\}BaPPh_2]$ (**13**) was isolated as a small crop of orange crystals in the NMR tube solution. The structure of this complex was authenticated *via* X-ray diffraction analysis (Figure 3.24).

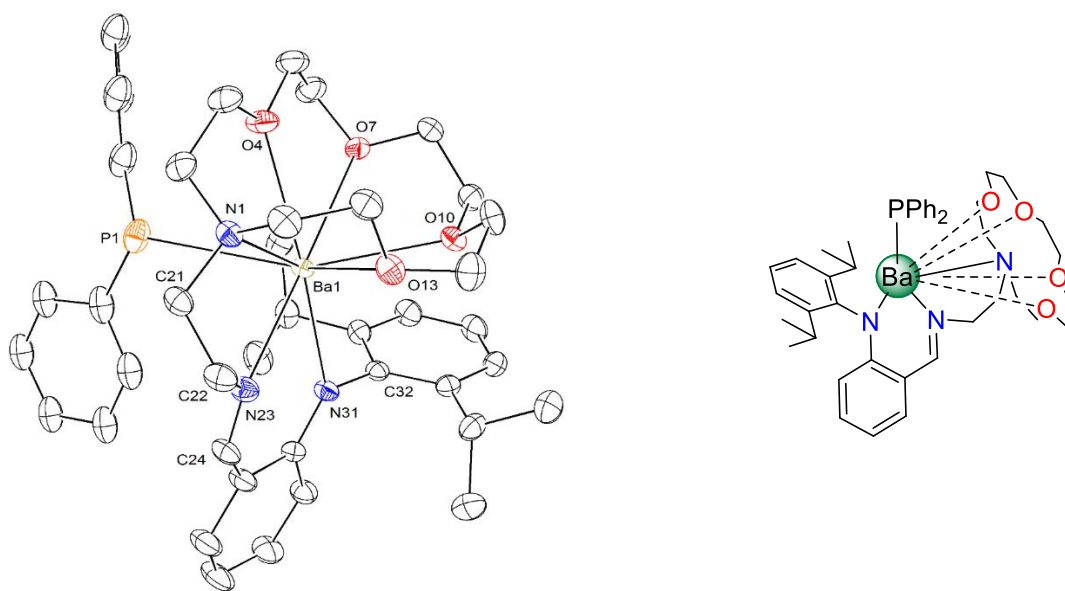
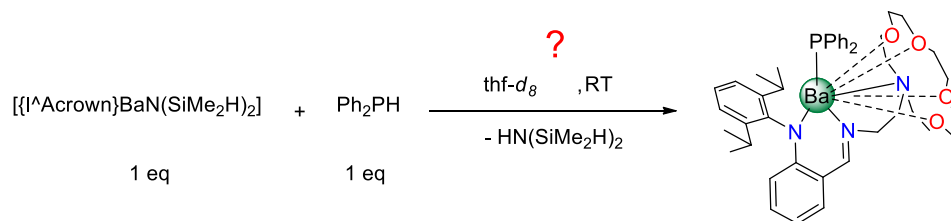


Figure 3.24. ORTEP representation of the molecular solid-state structure of $[\{I^A^{crown}\}BaPPh_2]$ (**13**). Ellipsoids at the 50% probability level. H atoms and non-interacting benzene molecule omitted for clarity. One component of each disordered C_6H_5 moieties is depicted. Selected interatomic distances (Å): Ba1–N31 = 2.691(2), Ba1–N23 = 2.780(2), Ba1–O10 = 2.847(2), Ba1–O4 = 2.869(2), Ba1–O7 = 2.886(2), Ba1–O13 = 2.886(2), Ba1–N1 = 2.972(2), Ba1–C32 = 3.302(3), Ba1–P1 = 3.3686(9).

The Ba–N interatomic distances in **13** correspond to those of the parent amido pre-catalyst **10**. Barium stays eight-coordinated with the heteroatoms of the macrocycle. This is one of the first heteroleptic barium-phosphide complexes structurally characterized. There have been homoleptic barium-phosphide complexes reported in the literature including $[\{([Me_3Si]_2CH)(C_6H_3-2-OMe-3-Me)P\}_2Ba.(thf)_2]$,⁴⁹ $[Ba\{P(SiMe_3)_2\}_2.(thf)_4]$,⁵⁰ $[Ba(PPh_2)_2.(thf)_5]$,⁵¹ and $[Ba(PPh_2)_2.(18-crown-6)]$.⁵² The Ba–P bond length in **13** (3.3686(9) Å) is comparable to those in $[Ba(PPh_2)_2.(thf)_5]$ (3.328(2) and 3.345(2) Å) and $[Ba(PPh_2)_2.(18-crown-6)]$ (3.3484(7) Å).^{53,54} The Ba–N interatomic distances in **13** are commensurate with those

measured in the parent amido complex **10**. Heteroleptic calcium-phosphides already exist in the literature such as the $[\{\text{BDI}^{\text{Dipp}}\}\text{CaPPH}_2]$ complex reported by Hill.^{19a}

The formation of the mononuclear complex **13** occurs under catalytic conditions after deprotonation of diphenylphosphine which is relatively acidic ($\text{p}K_{\text{a}}$ (DMSO) = 21.7),⁵³ and it must be concomitant with the release of $\text{HN}(\text{SiMe}_2\text{H})_2$. The independent reaction of the complex **10** with one equivalent of HPPH_2 was done in a NMR-tube scale in $\text{thf-}d_8$ in an attempt to prepare **13** (Scheme 3.12). Besides the formation of the new complex **13**, the release of $\text{HN}(\text{SiMe}_2\text{H})_2$ and the quantitative consumption of HPPH_2 were clearly obvious according to the NMR spectrum (Figure 3.25).



Scheme 3.12. Attempted synthesis of $[\{1^{\text{A}}\text{crown}\}\text{Ba}\{\text{PPh}_2\}]$ (**13**).

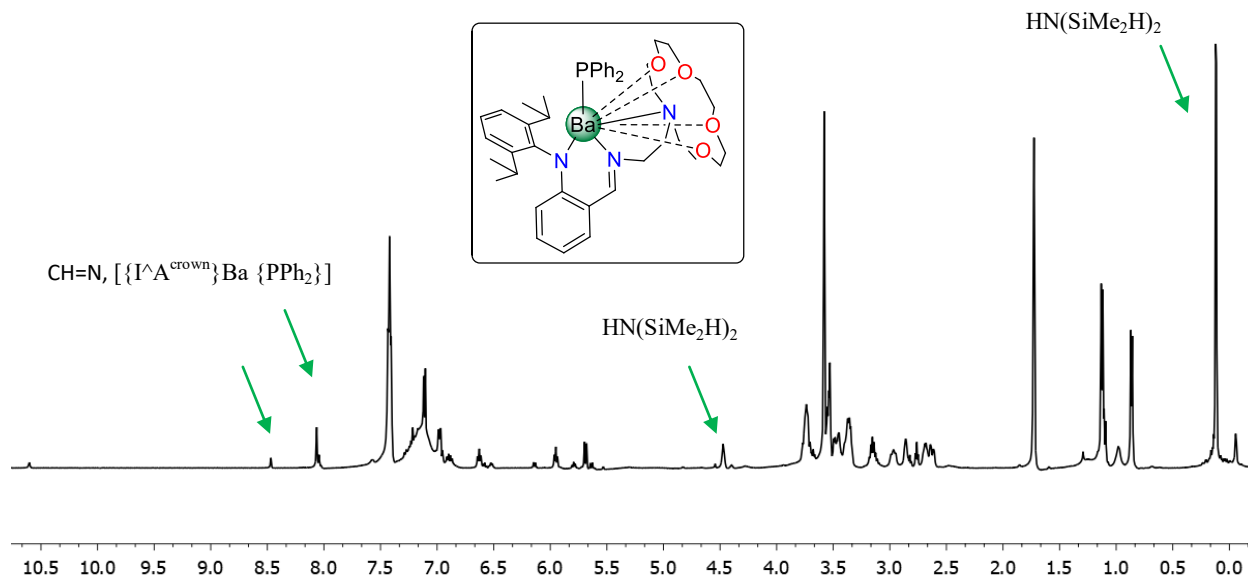


Figure 3.25. ^1H NMR spectrum ($\text{thf-}d_8$, 500.13 MHz, 25°C) of the reaction between **10** and HPPH_2 . Reaction carried out in the J-Young NMR tube for 30 min.

Also, the ^1H NMR analysis shows the formation a small amount of the free ligand $\{\text{I}^{\text{A}^{\text{crown}}}\text{H}\}$ present in the mixture (*ca.* 15%) which is presumably released through hydrolysis during the preparation of the sample or it might be released due to deprotonation of diphenylphosphine. In the ^{31}P NMR spectrum, a new, broad resonance at $\delta_{31\text{P}} +4.37$ ppm assigned to **13** and compatible with a $[\text{Ba}]\text{-PPh}_2$ species (Figure 3.26).^{53,54} The residual HPPH_2 and by-product $\text{Ph}_2\text{P-PPh}_2$ appear respectively at $\delta_{31\text{P}} -38.1$ and -13.8 ppm.. Attempts to prepare and isolate **13** remained unsuccessful.

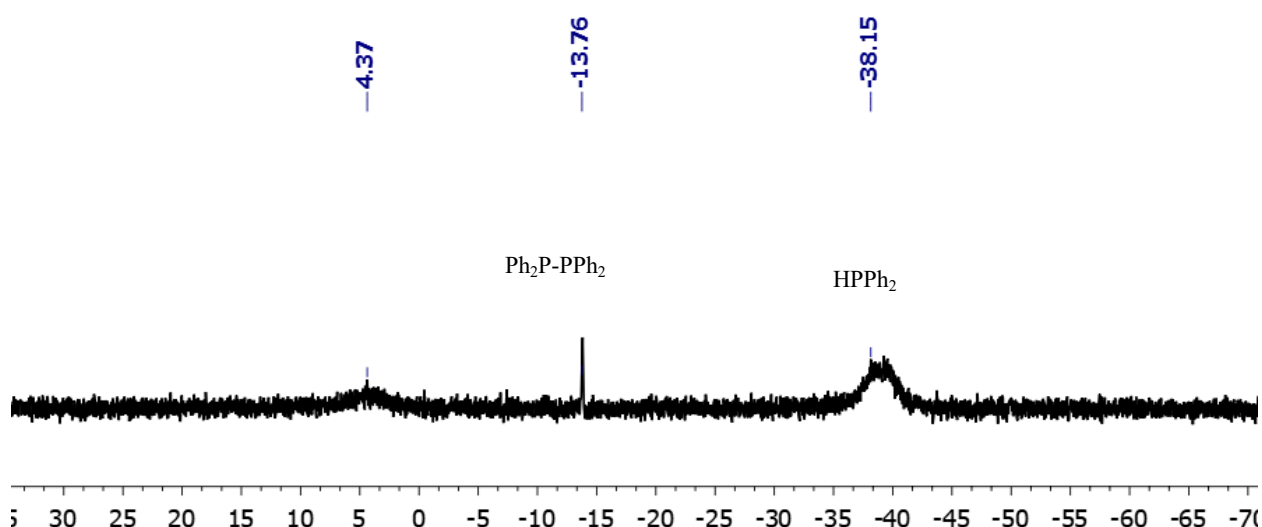
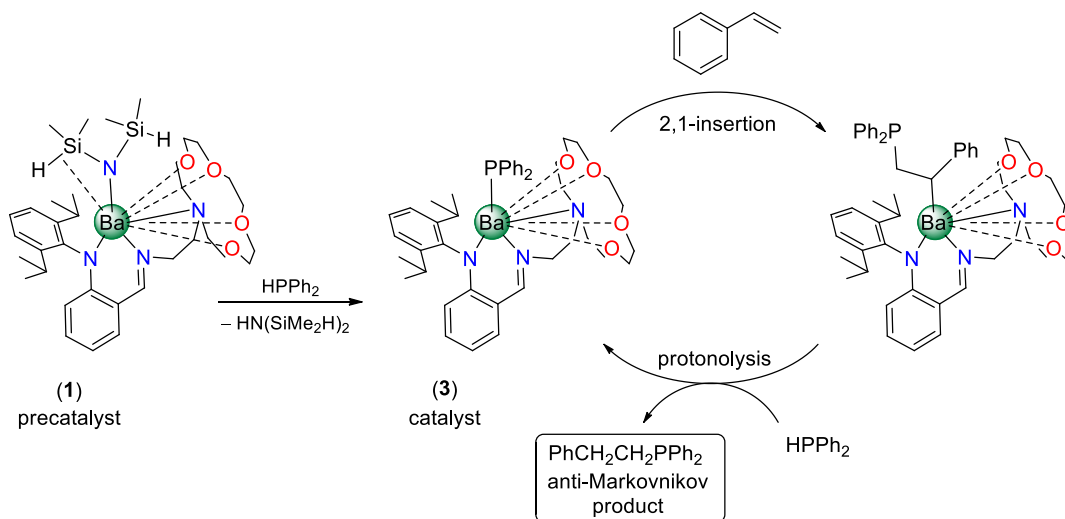


Figure 3.26. ^{31}P NMR spectrum (thf-d_8 , 161.98 MHz, 25°C) of the reaction between **10** and HPPH_2 . Reaction carried out in a J-Young NMR tube at 298 K in thf-d_8 . Reaction time 30 min.

In the hydrophosphination reactions of alkenes performed with the β -diketiminato-calcium ($[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}.\text{(thf)}]$) by Hill *et al.*, the presence of a calcium-phosphide active species during the catalytic cycle was suggested. These authors proposed a mechanism involving σ -bond metathesis, olefin insertion in Ae-P bond and release of the product via σ -bond metathesis.^{19a} In agreement with earlier intermolecular hydrophosphination investigations from our group,^{11,12} the mechanism displayed in Scheme 3.13 is proposed. The complex $[\{\text{I}^{\text{A}^{\text{crown}}}\}\text{BaPPh}_2]$ (**13**) could be the catalytically active species for the hydrophosphination of styrene. Since the reactions only generate the anti-Markovnikov addition products, the mechanism probably involves a 2,1-insertion of the polarized $\text{C}^{(\delta-)}=\text{C}^{(\delta+)}$ double bond into the

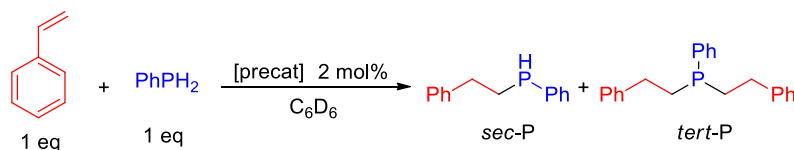
[Ba]–PPh₂ bond of **13**, leading to the rapid protonation of this intermediate by an incoming HPPH₂. This regenerates the active species **13** and releases the final product, PhCH₂CH₂PPh₂. The formation of the crystals of the complex [$\{I^{\wedge}A^{crown}\}BaPPh_2$] (**13**) during catalysis is strongly in favor of this proposed mechanism.



Scheme 3.13. Proposed mechanism for styrene/HPPH₂ hydrophosphination catalyzed by [$\{I^{\wedge}A^{crown}\}BaN(SiMe_2H)_2$] (**10**).

3.3.2 The catalytic activity of [$\{I^{\wedge}A^{crown}\}BaN(SiMe_2H)_2$] (**10**) in hydrophosphination of styrene with phenylphosphine^{19b}

In hydrophosphination reactions, primary phosphines are more reactive than the secondary phosphines,⁵⁴ which is likely related to steric and electronic effects. Creation of phosphines *via* intermolecular hydrophosphination reactions results from addition of the P–H moiety across C=C double bonds and formation of the P–C bonds. It is not an easy task. Some successful experiments by late transition metals have been reported in the literature.⁵⁵ There are few examples of reactions done with the primary phosphines (e.g. phenylphosphine) in the literature (Scheme 3.14).^{19b,56} PhPH₂ is the typical bifunctional substrate allowing to consider consecutive reactions. There are two possible products expected from this reaction. Based on the chemoselectivity and also the ratio of the starting materials (styrene and phenylphosphine), the reaction could result in *secondary* phosphine, *tertiary* phosphine or a mixture of both.



Scheme 3.14. Anti-Markovnikov hydrophosphination of styrene with PhPH_2 giving *sec*- and *tert*-phosphines.

In our group, a range of divalent rare-earth $[\{\text{LO}^3\}\text{LnN}(\text{SiMe}_3)_2]$ ($\text{Ln} = \text{Yb}, \text{Sm}$),^{19b,57c} calcium and strontium $[\{\text{LO}^4\}\text{CaN}(\text{SiMe}_3)_2]$ and $[\{\text{LO}^4\}\text{Ae}\{\text{CH}(\text{SiMe}_3)_2\}_2(\text{thf})_n]$ ($\text{Ae} = \text{Ca}, n = 1; \text{Sr}, n = 0$) heteroleptic complexes with phenolate ancillary ligands (Figure 3.27) were assessed in the intermolecular hydrophosphination of styrene with PhPH_2 (Scheme 3.14).

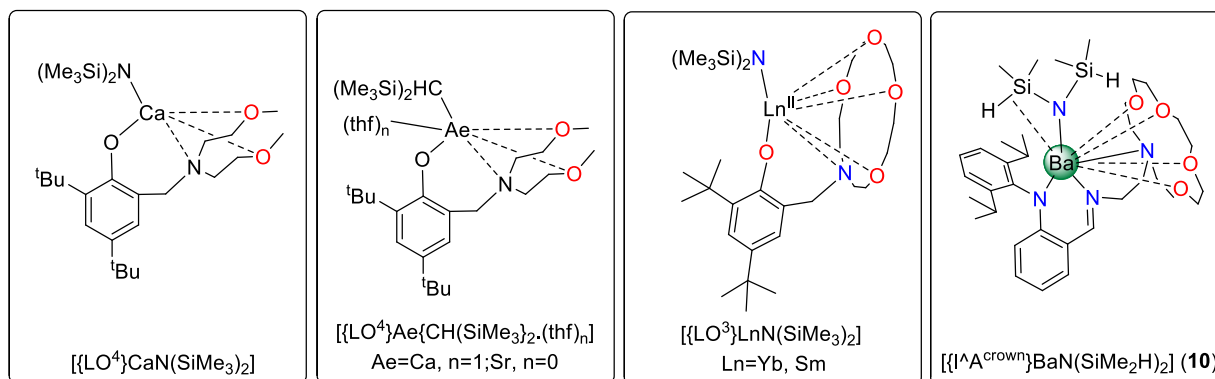


Figure 3.27. Structure of heteroleptic precatalysts used for intermolecular hydrophosphination reaction of styrene with PhPH_2 .^{19bc,57c}

In hydrophosphination reaction of equimolar amounts of styrene and phenylphosphine ($[\text{styrene}]_0/[\text{PhPH}_2]_0/[\text{precat}]_0 = 50/50/1$) (25 °C, 60 min), the best results were obtained with the Yb and Sm complexes which have shown almost full anti-Markovnikov regioselectivity.^{19b} These complexes share some structural similarities with our new barium heteroleptic complex $[\{\text{IA}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**), namely the side arm in the ancillary ligand and its interaction with the metal center. Therefore, we have used **10** to catalyze the hydrophosphination of styrene with PhPH_2 , under identical reaction conditions as those reported previously (Table 3.3).^{19b}

Table 3.3. Hydrophosphination of styrene with PhPH₂ catalyzed by [$\{I^{\wedge A^{crown}}\}BaN(SiMe_2H)_2\}$ (**10**) and [$\{LO^3\}Ln\{N(SiMe_3)_2\}$] (Ln = Yb, Sm).

Entry ^a	Precatalyst	[Styrene] ₀ /[PhPH ₂] ₀ /[precat] ₀	Conv. (%) ^b	TOF (h ⁻¹) ^b	<i>sec</i> -P/ <i>tert</i> -P ^c
1	[$\{I^{\wedge A^{crown}}\}BaN(SiMe_2H)_2\}$ (10)	50/50/1	93	47	94/6
2	[$\{LO^3\}Yb\{N(SiMe_3)_2\}$] ^{19b}	50/50/1	74	37	97/3
3	[$\{LO^3\}Sm\{N(SiMe_3)_2\}$] ^{19b}	50/50/1	63	32	97/3

^aReaction conditions: PhPH₂ (31.6 μL, 0.2 mmol), styrene (33.0 μL, 0.2 mmol), [precat] = 11.5 × 10⁻³ M, solvent C₆D₆ (0.5 mL), T = 25 °C, t = 60 min, [PhPH₂]₀/[styrene]₀/[precat]₀ = 50/50/1. ^bDetermined by ¹H NMR spectroscopy. ^c*sec*-P/*tert*-P product regioselectivity determined by ³¹P NMR spectroscopy.

The heteroleptic [$\{I^{\wedge A^{crown}}\}BaN(SiMe_2H)_2\}$ (**10**) mediates the regiospecific anti-Markovnikov hydrophosphination of styrene with PhPH₂, yielding the monocoupled product with excellent selectivity. The conversion of 50 equivalents of styrene and phosphine ([styrene]₀/[PhPH₂]₀/[**10**]₀ = 50 : 50 : 1) performed at 25 °C in benzene-*d*₆ is nearly quantitative within 60 min (Table 3.3). According to the ¹H and ³¹P NMR spectra, it selectively (typically > 94%) affords the secondary phosphine PhPHCH₂CH₂Ph (*sec*-P; doublet at δ_{31P} = -52.41 ppm in benzene-*d*₆ at 60 °C), with minimal formation of the tertiary phosphine PhP(CH₂CH₂Ph)₂ (*tert*-P; singlet at δ_{31P} = -24.09 ppm) (Figure 3.28 and 3.29). Note that under identical experimental conditions ([styrene]₀/[PhPH₂]₀/[**10**]₀ = 50 : 50 : 1, 25 °C, 60 min, [metal]₀ = 11.5 mM in benzene-*d*₆), the performance of **10** (93% conversion, TOF = 47 h⁻¹) was slightly better than that exhibited by the divalent rare-earth precatalysts [$\{LO^3\}YbN(SiMe_3)_2\}$ and [$\{LO^3\}SmN(SiMe_3)_2\}$] supported by the multidentate aminoetherphenolate $\{LO^3\}^-$.^{19b}

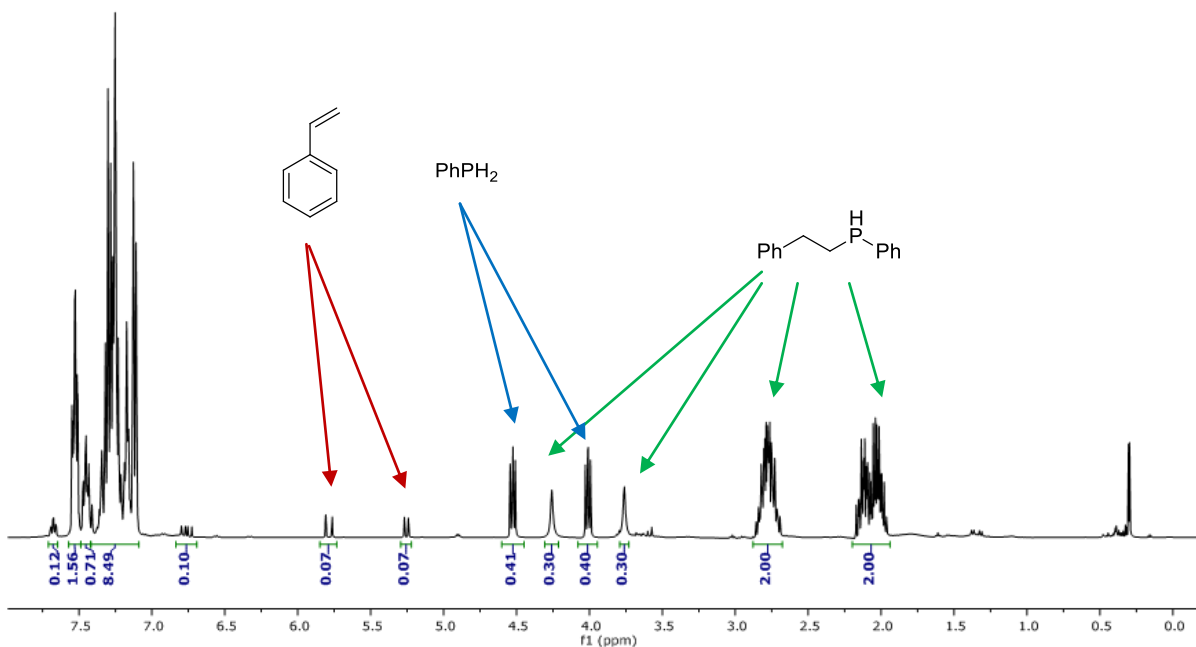


Figure 3.28. ^1H NMR spectrum (400 MHz, benzene- d_6 , 25 °C) of the hydrophosphination of styrene with phenylphosphine catalyzed by $[\{\text{I}^{\text{A}^{\text{crown}}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**) after 1 h. Reaction conditions: PhPH_2 (31.6 μL , 0.2 mmol), styrene (33.0 μL , 0.2 mmol), **[10]** = $11.5 \cdot 10^{-3}$ M, solvent C_6D_6 (0.5 mL), $[\text{PhPH}_2]_0/[\text{styrene}]_0/[\text{precat}]_0 = 50/50/1$.

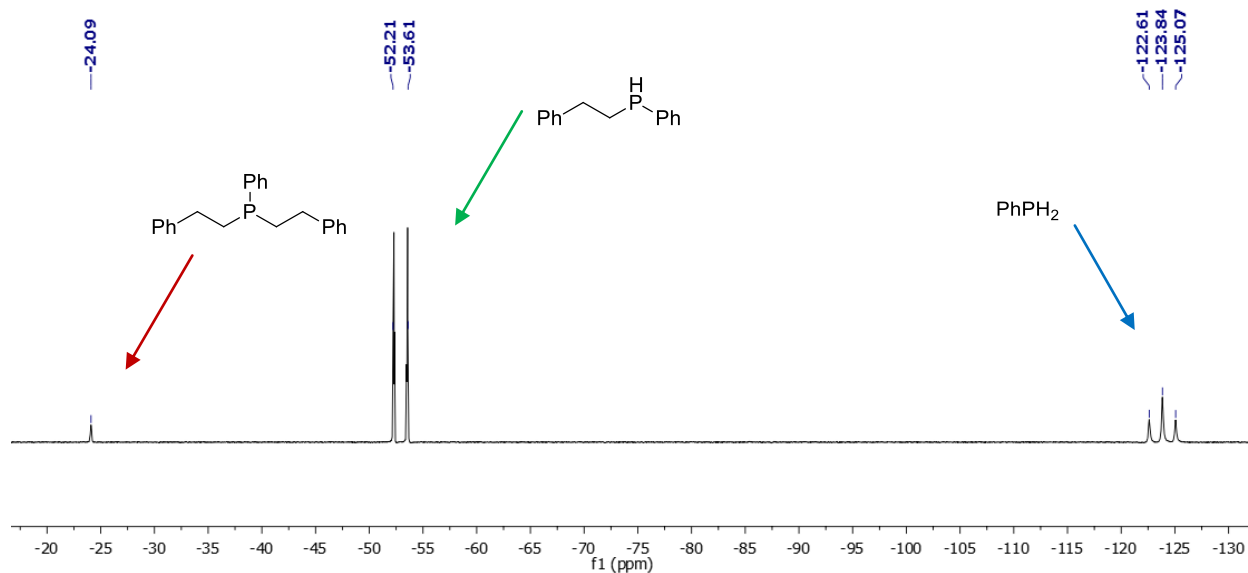
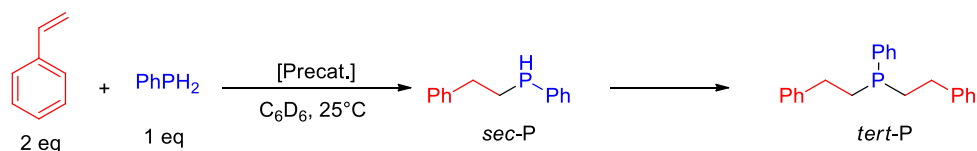


Figure 3.29. ^{31}P NMR spectrum (162 MHz, benzene- d_6 , 25 °C) of the hydrophosphination of styrene with phenylphosphine catalyzed by $[\{\text{I}^{\text{A}^{\text{crown}}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**) after 1 h. Reaction conditions: PhPH_2 (31.6 μL , 0.2 mmol), styrene (33.0 μL , 0.2 mmol), **[10]** = $11.5 \cdot 10^{-3}$ M, solvent C_6D_6 (0.5 mL), $[\text{PhPH}_2]_0/[\text{styrene}]_0/[\text{precat}]_0 = 50/50/1$ (*sec*-P/*tert*-P = 94:6).

3.3.3 One-pot, one-step synthesis of tertiary phosphines $\text{PhP}(\text{CH}_2\text{CH}_2\text{R})_2$ by hydrophosphination

3.3.3.1 Hydrophosphination of styrene with phenylphosphine

Complex **10** was next employed in the hydrophosphination of styrene with PhPH_2 in a 2:1 ratio (as opposed to the 1:1 ratio used in the previous sections 3.3.1 and 3.3.2) in benzene- d_6 at 25°C ($[\text{styrene}]_0/[\text{PhPH}_2]_0/[\mathbf{10}]_0 = 50/25/1$) to prepare the *tert*-phosphine $\text{Ph}(\text{CH}_2\text{CH}_2\text{Ph})_2$ (Scheme 3.15). The kinetics of this reaction was monitored in order to study the chemoselectivity of this process (Figure 3.30).



Scheme 3.15. One-pot, one-step synthesis of tertiary phosphine from hydrophosphination of 2 equivalents of styrene with PhPH_2 catalyzed by $[\{\text{I}^{\text{A}^{\text{crown}}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**).

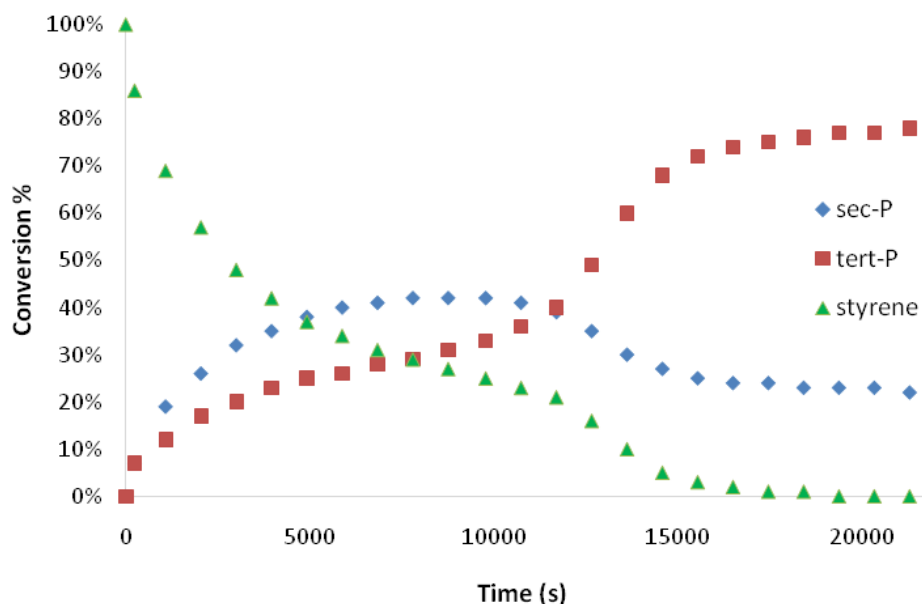


Figure 3.30. Conversion of styrene during the hydrophosphination catalyzed by $[\{\text{I}^{\text{A}^{\text{crown}}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**). PhPH_2 (11 μL , 0.1 mmol), styrene (23 μL , 0.2 mmol), [precat] = 8 mM, $T = 25^\circ\text{C}$, solvent C_6D_6 (0.5 mL). $[\text{styrene}]_0/[\text{PhPH}_2]_0/[\mathbf{10}]_0 = 50/25/1$.

The kinetic of the reaction is not typical of consecutive reactions. In section 3.3.2 we have shown that at the 1:1 molar ratio of substrates, the reactions lead to the formation of secondary phosphine in 94–97 % yield while the yield of tertiary phosphine does not exceed 3–6 %. When the reaction was carried out at molar ratio $[\text{styrene}]_0:[\text{PhPH}_2]_0 = 2:1$ in 6 h at 25 °C, complex **10** enables a double addition of styrene to phenylphosphine, and a quantitative conversion was achieved (*sec*-phosphine / *tert*-phosphine = 7% / 93%). Similarly, Trifonov *et. al.* have recently reported the selective formation of the *tert*-phosphine by increasing the $[\text{styrene}]_0/[\text{PhPH}_2]_0$ ratio with calcium heteroleptic complexes (eg. $[\{2-(\text{Ph}_2\text{P}=\text{NPh})\text{C}_6\text{H}_4\text{NC}(\text{tBu})=\text{N}(2,6\text{-R}_2\text{C}_6\text{H}_3)\}\text{Ca}\{\text{N}(\text{SiMe}_3)_2\} \cdot (\text{thf})\} \{\text{R} = i\text{Pr} \text{ (1)}; \text{R} = \text{Me} \text{ (2)}\}]$.^{19e,57e}

As evidenced by ^1H and ^{31}P NMR analyses (Figures 3.31, 3.32), the reaction proceeds with perfect anti-Markovnikov regioselectivity. Changing the stoichiometric ratio between styrene and phenylphosphine (2:1) changes the chemoselectivity of the reaction towards the *tert*-phosphine.

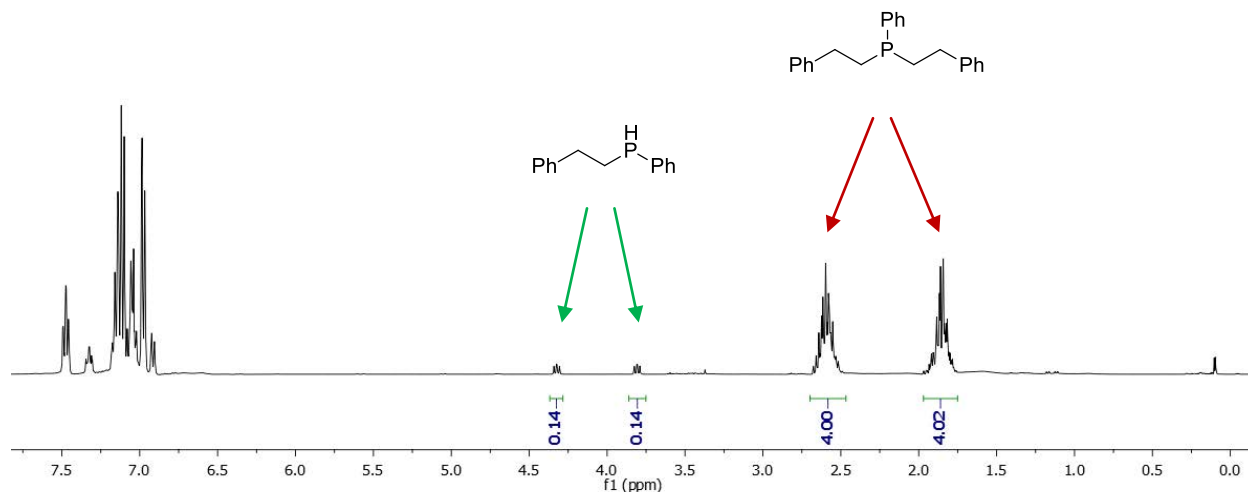


Figure 3.31. ^1H NMR spectrum (400 MHz, benzene- d_6 , 25 °C) of the one-pot, one-step synthesis of tertiary phosphine from hydrophosphination of 2 equivalent of styrene with PhPH_2 catalyzed by $[\{\text{I}^{\text{A crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**) after 6 h. Reaction conditions: PhPH_2 (11 μL , 0.1 mmol), Styrene (23 μL , 0.2 mmol), $[\text{precat}] = 8 \text{ mM}$. $[\text{styrene}]_0/[\text{PhPH}_2]_0/[\textbf{10}]_0 = 50/25/1$.

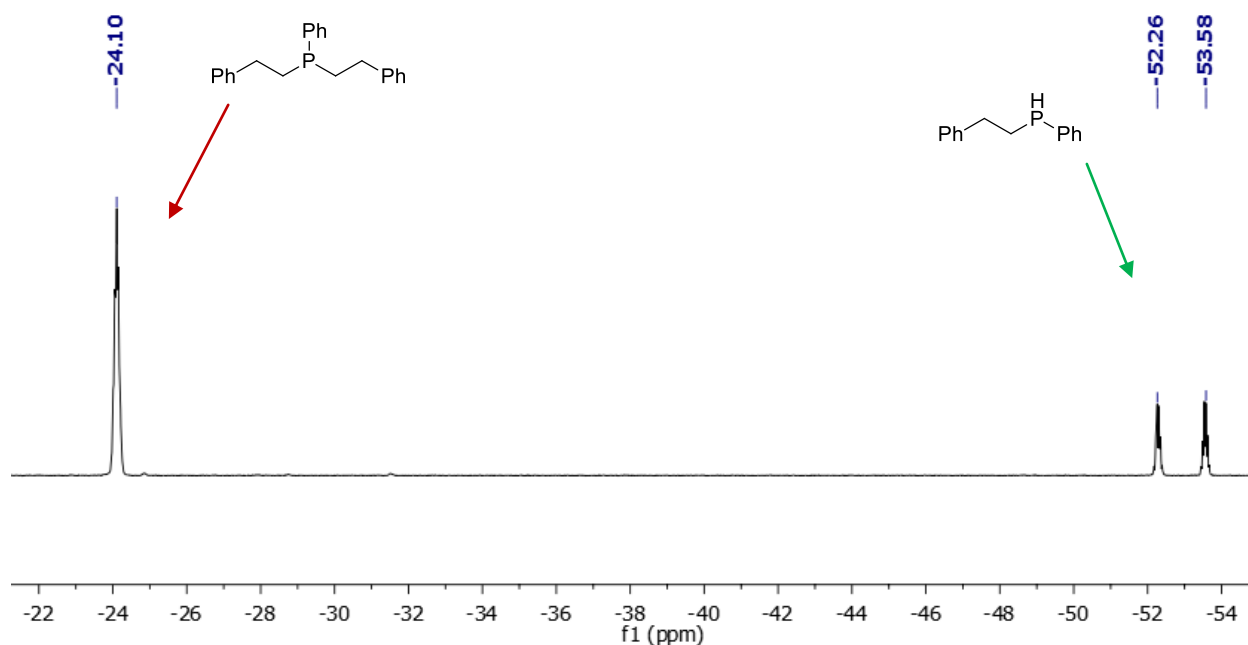
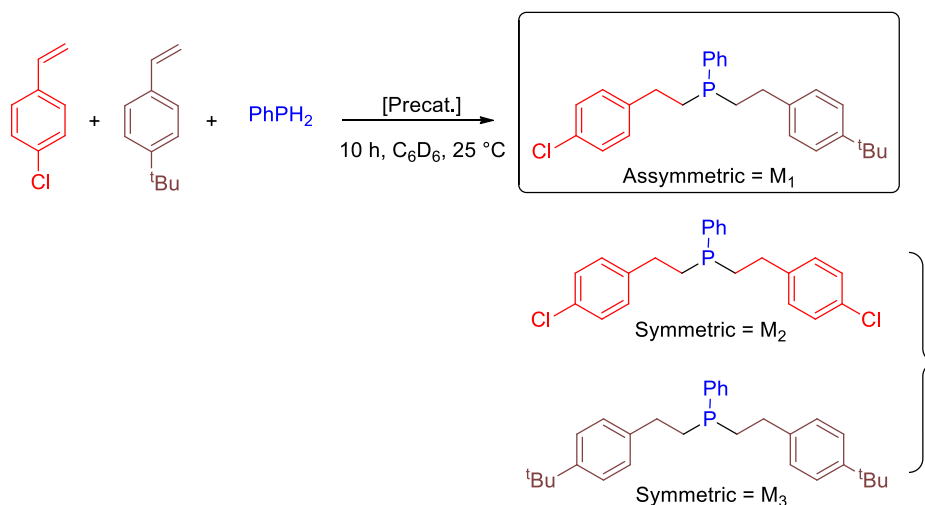


Figure 3.32. ^{31}P NMR spectrum (162 MHz, benzene- d_6 , 25 °C) of the one-pot, one-step synthesis of tertiary phosphine from hydrophosphination of 2 equivalent of styrene with PhPH_2 catalyzed by $[\{\text{I}^{\text{A}^{\text{crown}}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**). Spectrum recorded after 6 h. Reaction conditions: PhPH_2 (11 μL , 0.1 mmol), Styrene (23 μL , 0.2 mmol), $[\text{precat}] = 8 \text{ mM}$. $[\text{styrene}]_0/[\text{PhPH}_2]_0/[\textbf{10}]_0 = 50/25/1$.

3.3.3.2 Hydrophosphination with substituted styrene

To take advantage of the activity of complex **10**, it was employed for the one-pot, one-step synthesis of unsymmetrical tertiary phosphines having three different substituents on the phosphorus atom. The experiments were performed with loading equimolar amounts of two different styrene derivatives at the same time in the presence of PhPH_2 in benzene- d_6 at 25 °C ($[\textit{p}\text{-X-styrene}]_0/[\textit{p}\text{-X}'\text{-styrene}]_0/[\text{PhPH}_2]_0/[\text{precatalyst}]_0 = 25/25/25/1$). A series of such experiments have been conducted with different styrene derivatives with substituents in the *para* position ($\text{X}, \text{X}' = \text{H}, \text{Cl}, \text{tBu}$). Concerning the experiments reported in the literature,^{19b} the rate of the hydrophosphination reaction of *p*-substituted styrene derivatives follows the trend $\textit{p}\text{-Cl} > \textit{p}\text{-H} > \textit{p}\text{-Me} > \textit{p}\text{-tBu}$.¹¹ Therefore, introducing *para*-chloro and *para*-*tert*-butyl-styrene derivatives together in the reaction, could first lead to the reaction of *p*-Cl-styrene with phenylphosphine before the *p*-*tert*-butyl-styrene would react. With this assumption, the experiment was performed in an NMR-tube at 25 °C in benzene- d_6 . The reaction was monitored for 60 min with $[\textit{p}\text{-Cl-styrene}]_0/[\textit{p}\text{-tBu-styrene}]_0/[\text{PhPH}_2]_0/[\textbf{10}]_0 = 25/25/25/1$. *Para*-chloro and *para*-*tert*-

butyl-styrene derivatives were introduced into a J-young NMR tube together at the starting point of the reaction. Hydrophosphination of *para*-chloro-styrene with PhPH₂ occurred with a very high rate, allowing for the complete conversion of the styrene derivative within minutes (Figure 3.33). Longer reaction time was required for the subsequent hydrophosphination with *para*-*tert*-butyl-styrene. The final product has been characterized by ³¹P NMR spectroscopy and mass spectrometry analyses. According to such analyses, there is not only the expected asymmetric *tert*-phosphine PhP(CH₂CH₂-C₆H₄-*p*-Cl)(CH₂CH₂-C₆H₄-*p*-*t*Bu) (aka **M**₁) in the recovered reaction mixture, but the two symmetric phosphines (PhP(CH₂CH₂-C₆H₄-*p*-Cl)₂ = **M**₂) and (PhP(CH₂CH₂-C₆H₄-*p*-*t*Bu)₂ = **M**₃) are also observed. (Scheme 3.16)



Scheme 3.16. One-pot, one-step synthesis of unsymmetrical tertiary phosphines from hydrophosphination of *p*-Cl-Styrene and *p*-*t*Bu-styrene with PhPH₂ catalyzed by [¹A^{crowd}}BaN(SiMe₂H)₂] (**10**).

There are three different signals observed in the ³¹P NMR spectrum of the reaction mixture displayed in Figure 3.34. The peak at δ -24.25 ppm is probably related to the targeted unsymmetrical *tert*-phosphine.⁵⁷ The peaks at δ -24.59 and δ -23.93 ppm are related to two symmetric phosphines PhP(CH₂CH₂-C₆H₄-*p*-Cl)₂ and PhP(CH₂CH₂-C₆H₄-*p*-*t*Bu)₂ respectively.

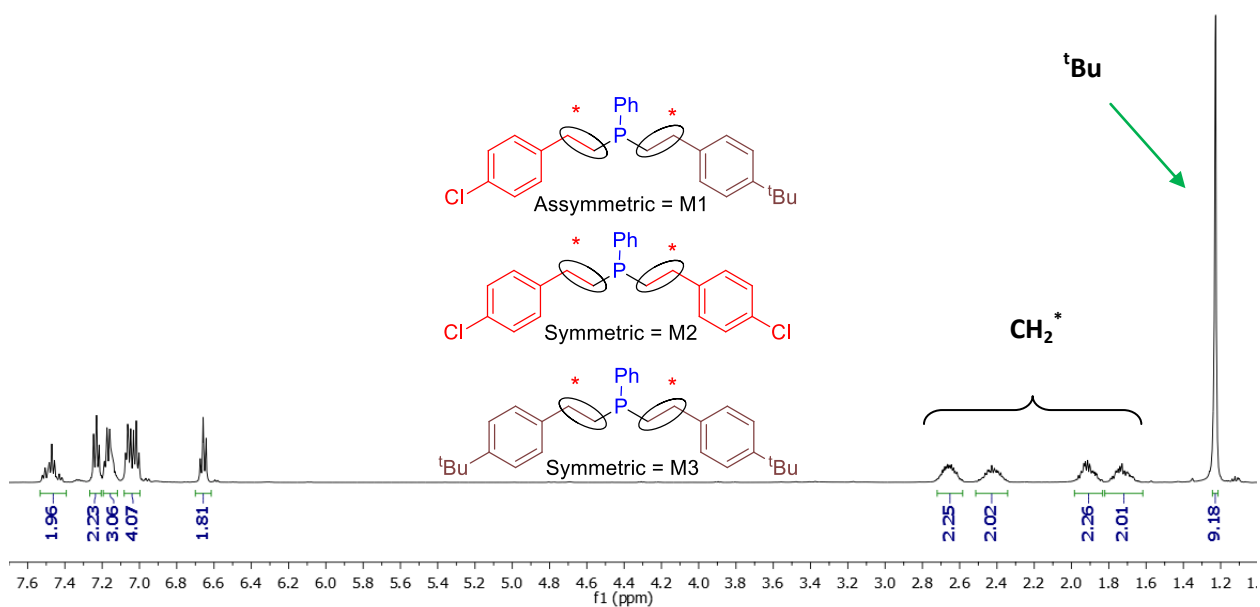


Figure 3.33. ^1H NMR spectrum (400 MHz) of one-pot, one-step reaction of [*p*-Cl styrene] and [*p*-^tBut styrene] with PhPH_2 catalyzed by $[\{\text{I}^\wedge\text{A}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**), recorded in benzene- d_6 at 298 K.

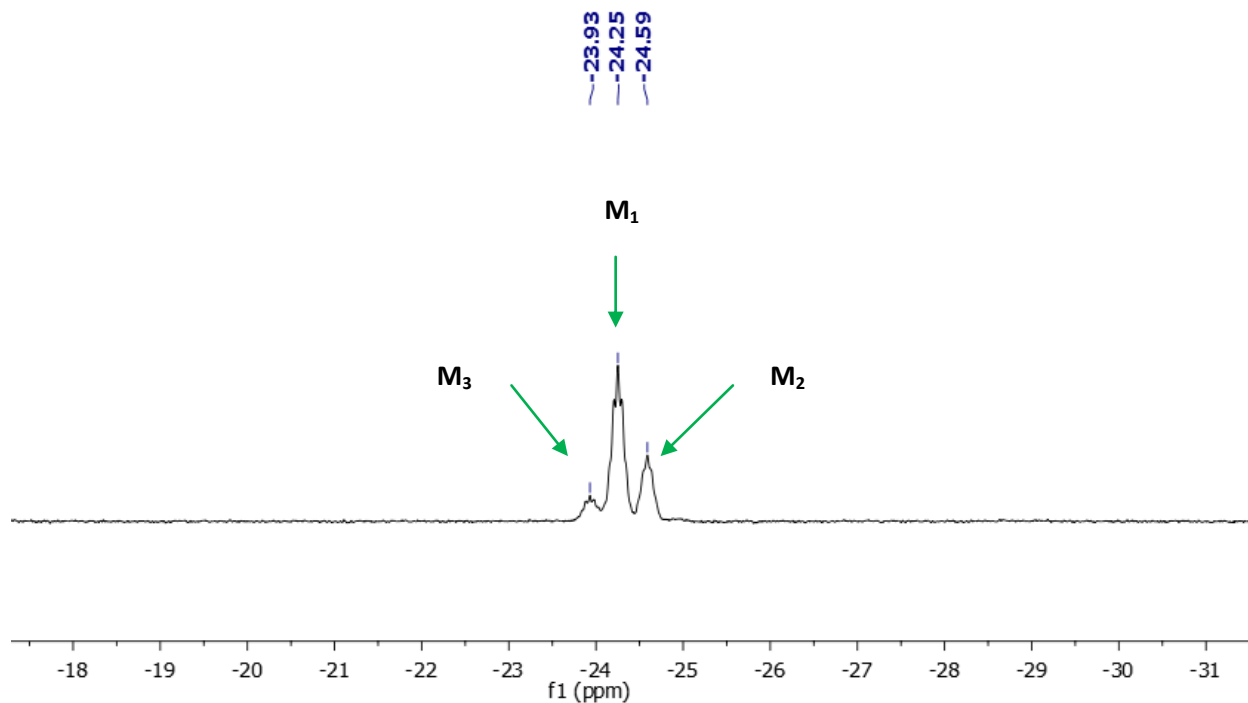


Figure 3.34. ^{31}P NMR spectrum (162 MHz, benzene- d_6 , 298 K) of the one-pot, one-step reaction of [*p*-Cl styrene] and [*p*-^tBut styrene] with PhPH_2 catalyzed by $[\{\text{I}^\wedge\text{A}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**).

According to the analysis of the NMR and ESI-MS data of the reaction mixture, the results are not consistent with the formation of a single species (unsymmetrical *tert*-phosphine, $M_1 = \text{PhP}(\text{CH}_2\text{CH}_2\text{-C}_6\text{H}_4\text{-}p\text{-Cl})(\text{CH}_2\text{CH}_2\text{-C}_6\text{H}_4\text{-}p\text{-tBu})$) but instead indicate a mixture of products (M_1 , M_2 and M_3). The relative intensity of $[\text{M}_1+\text{H}]^+$ (100) is higher comparing to $[\text{M}_2+\text{H}]^+$ (13.11) and $[\text{M}_3+\text{H}]^+$ (76.82) (Figure 3.35).

According to the results derived from this experiment, one must conclude that in order to prepare selectively the unsymmetrical tertiary phosphines such as M_1 sought here, a sequential addition of the styrene derivatives to the reaction vessel must be done.

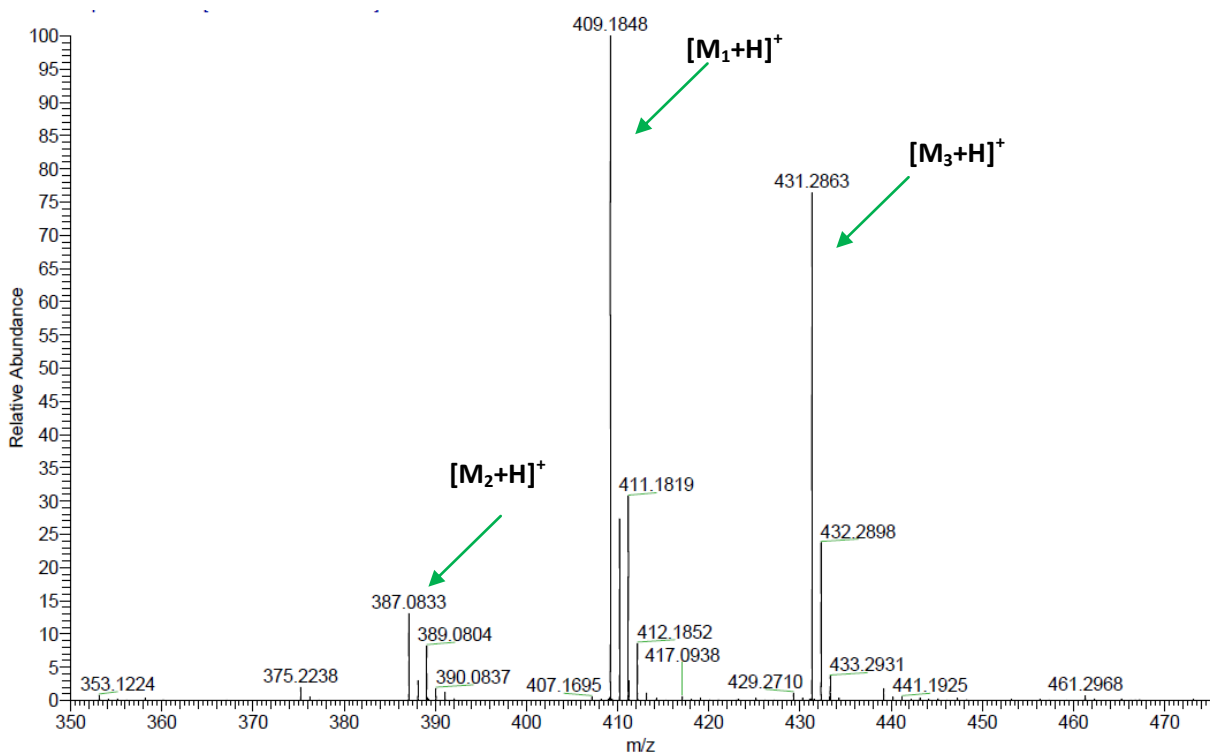


Figure 3.35. ESI-MS analysis (NaI) of the crude product (Zoomed spectrum). Reaction conditions: PhPH_2 (11 μL , 0.1 mmol), *p*-Cl-Styrene (12 μL , 0.1 mmol), *p*-^tBu-styrene (18 μL , 0.1 mmol), $[10] = 8$ mM, $T=25^\circ\text{C}$, solvent C_6D_6 (0.5 mL). $[\text{PhPH}_2]_0/[\text{p-Cl-styrene}]_0/[\text{p-}^t\text{Bu-styrene}]_0/[10]_0 = 25/25/25/1$; $[\text{precat}] = [\{\text{I}^{\wedge}\text{A}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**).

3.4 Conclusion

This chapter described the synthesis of some new proligands of iminoaniline ($\{I^A^{crown}\}H$) and amidine ($\{AdAm^{crown}\}H$), each featuring a coordinating tethered crown-ether side arm. The main objective was to use such ligands to prepare stable heteroleptic Ae complexes by encapsulating the metal center into the crown ether thus avoiding redistribution reactions. These multi-step syntheses required considerable time and accuracy. These new bidentate ancillary ligands thus enabled to prepare new barium heteroleptic complexes. The stoichiometric reaction of the solvent-adduct of barium tetramethyldisilazade $[Ba\{N(SiMe_2H)_2\}_2 \cdot (thf)_2]$ with $\{I^A^{crown}\}H$ and the protonolysis of $\{AdAm^{crown}\}H$ by the solvent-free barium amide $[Ba\{N(SiMe_2H)_2\}_2]_\infty$ led to the formation of barium heteroleptic complexes $[\{I^A^{crown}\}Ba\{N(SiMe_2H)_2\}]$ (**10**) and $[\{AdAm^{crown}\}BaN(SiMe_2H)_2]$ (**11**) respectively. The X-ray structural data and NMR spectroscopic analyses confirm the highly coordinated metal center to the bidentate ancillary ligand including the contacts with the side-arm heteroatoms resulting in encapsulated Ae complexes.

The use of $N(SiMe_2H)_2^-$ instead of more common ligand $N(SiMe_3)_2^-$, provides $Ba \cdots H-Si$ anagostic interactions in the complex that provide some stabilization. This was confirmed by XRD, NMR and FTIR spectroscopies. The iminoanilido complex $[\{I^A^{crown}\}BaN(SiMe_2H)_2]$ (**10**) has been applied for hydrophosphination of styrene with secondary phosphine $HPPH_2$. The precatalyst has shown relatively high reactivity. During the catalytic study, the $[\{I^A^{crown}\}BaPPh_2]$ has been isolated; it probably is the active species in the catalytic cycle. These experiments also reveal an anti-Markovnikov selectivity of the new barium precatalysts. One of the most remarkable properties of our new barium heteroleptic complex of $[\{I^A^{crown}\}BaN(SiMe_2H)_2]$ (**10**) is its chemoselectivity toward the production of secondary and tertiary phosphines.

During the addition of two equivalents of styrene to $PhPH_2$, the kinetic profile reflects the formation of tertiary phosphine with high conversion and chemoselectivity. Therefore, increasing the equivalent of styrene changes the chemoselectivity of the reaction. The attempt for preparation of unsymmetrical *tert*-phosphine by *p*-Cl and *p*-^tBu styrenes, has resulted in a mixture of products that included the sought asymmetric $PhP(CH_2CH_2-C_6H_4-p-Cl)(CH_2CH_2-C_6H_4-p-tBu)$ together with two extra symmetrical *tert*-phosphines of $PhP(CH_2CH_2-C_6H_4-p-Cl)_2$

and $\text{PhP}(\text{CH}_2\text{CH}_2\text{-C}_6\text{H}_4\text{-}i\text{-Bu})_2$ with two identical substituents on the phosphine. In order to prepare unsymmetrical phosphines, we should try the sequential addition of the different styrene derivatives to the reaction mixture, or identify the appropriate pair(s) of styrene substrates that gives the proper reactivity rates to our barium catalyst and finally lead to the target unsymmetrical *tertiary* phosphine. In this aim, the use of different precatalysts, for instance those derived from **10** but based on calcium or strontium, could also provide different reaction rates, selectivity and, hence, outcome.

During these experiments, we have encountered many difficulties including the price of the starting materials and the multiple steps required before achieving the isolation of the final ancillary ligand that were time consuming and synthetically challenging. Our new developed procedure was a success to overcome some of these problems. The outcomes of the application of these new precatalysts in hydrophosphination reactions, is partially encouraging

The new ancillary ligands have a large potential for investigating new possibilities in the chemistry of Ae metals. Knowing the efficiency of the new barium heteroleptic complexes $[\{\text{I}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**) and $[\{\text{AdAm}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**11**), we should now carry out a wide range of kinetic studies in hydrophosphination reactions. We should also evaluate the capability of these complexes in other types of hydroelementation reactions and compare their effectiveness with the previous investigations. This work also opens the opportunity to prepare the complexes of calcium and strontium with these proligands and study the differences in structures and catalytic capability of the resulting compounds.

3.5 Experimental Section

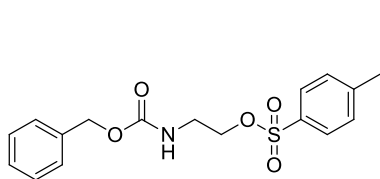
3.5.1 General procedures

All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glove-box (Jacomex; $O_2 < 1$ ppm, $H_2O < 3$ ppm). BaI_2 (Aldrich, 99.995% anhydrous beads) was used as received. $HN(SiMe_2H)_2$ (ABCR) was dried over CaH_2 and distilled prior to use. $[Ba\{N(SiMe_2H)_2\}_2 \cdot (thf)_2]$ and $[Ba\{N(SiMe_2H)_2\}_2]_\infty$ were prepared following the literature procedure.^{4,6}

Solvents (thf, Et_2O , petroleum ether bp 40-60 °C, 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 prior to use.

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 ^{13}C chemical shifts were determined using residual signals of the deuterated solvents and were calibrated vs. $SiMe_4$ ($\delta = 0$ ppm). Assignment of the signals was carried out using 1D (^1H , $^{13}C\{^1H\}$) and 2D (COSY, edited HSQC and HMBC) NMR experiments. Solid-state FTIR spectra were recorded between 400 and 4000 cm^{-1} as Nujol mulls in KBr plates on a Shimadzu IRAffinity-1 spectrometer. Elemental analyses were performed at the “*Centre de Mesures Physiques de l’Ouest*” (CRMPO, Rennes). However, the extreme air-sensitivity of the barium complexes precluded the acquisition of reliable and reproducible data sets. ESI mass spectra were recorded at the CRMPO Scanmat (Rennes, France) on an orbitrap type Thermo Fisher Scientific Q-Exactive instrument, with an ESI source in positive or negative mode by direct introduction at 5-10 $\mu g \cdot mL^{-1}$. Samples were prepared as CH_2Cl_2 solutions with concentrations of 10 $\mu g \cdot mL^{-1}$.

3.5.2 Synthesis and characterization of the proligand and the related complex



Synthesis of (N-benzyloxycarbonyl)-2-aminoethyl *p*-toluenesulfonate⁴¹ (Scheme 3.5, step i)

(N-benzyloxycarbonyl)-2-aminoethanol (5.0 g, 26.1 mmol) and 4-dimethylaminopyridine (DMAP) (0.6 g, 5.4 mmol, 0.2 eq) were dissolved in dry dichloromethane (90 mL) and the mixture was cooled down to 0 °C in an ice-water bath, then tosyl chloride (5.6 g, 28.8 mmol, 1.1 eq) and triethylamine (4.0 mL, 28.8 mmol, 1.1 eq) were added dropwise, respectively (all the process was done under argon). The mixture was warmed up to room temperature gradually and the reaction was stirred overnight. The solvent was removed afterwards and the organic phase was extracted with ethyl acetate (50 mL). The aqueous layer was washed with water (3×50 mL). All the organic fractions were combined and washed with brine (50 mL). After drying the organic fraction with MgSO₄, it was concentrated and solved in a small amount of ethylacetate (10 mL). The solution resulted into crystals in the fridge overnight which was filtered to give the tosylate. Yield 5.57 g (61%).

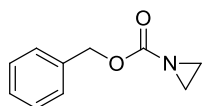
¹H NMR (CDCl₃, 400 MHz, 298 K): δ 7.77 (d, 2H, ³J_{H-H} = 8.2 Hz, C=CH), 7.42–7.27 (m, 7H, C=CH), 5.17 (s, 1H, NH), 5.06 (s, 2H, Ph-CH₂-O), 4.09 (t, 2H, ³J_{H-H} = 5.0 Hz, N-CH₂-CH₂-O), 3.44 (q, 2H, ³J_{H-H} = 5.2 Hz, N-CH₂-CH₂-O), 2.42 (s, 3H, CH₃) ppm.

Synthesis of aziridine (Scheme 3.6, step i)



An aqueous solution of NaOH (77.6 g, 1.94 mol) in deionized water (460 mL) was added to a 1L round-bottom flask containing 2-chloroethylamine hydrochloride (90.0 g, 0.77 mol). The resulting solution was stirred for 2 h at 50 °C. Aziridine was then recovered by distillation at 75 °C under partial static vacuum. It was then dried over NaOH pellets in a round-bottom flask stored at –30 °C overnight (a round-bottom flask must be used as the volume of the mixture will increase substantially during drying). Phase separation occurred, and aziridine was recovered as the upper layer of the biphasic mixture. The drying process was repeated once more, after what analytically pure aziridine was obtained as a colorless oil. Yield 24.9 g (75%).

¹H NMR (CDCl₃, 400.16 MHz, 298 K): δ = 4.61 (br s, 1H, NH), 1.55 (s, 4H, CH₂) ppm.



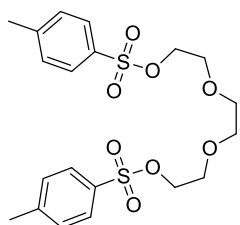
Synthesis of *N*-benzyloxycarbonyl-aziridine:⁴² (Scheme 3.5, step ii)

A suspension of NH (0.3 g, 8.4 mmol, 1.2 eq) in thf (40 mL) was heated at 45 °C under argon. Then a solution of (*N*-benzyloxycarbonyl)-2-aminoethyl *p*-toluenesulfonate (2.5 g, 7.1 mmol) in thf (20 mL) was added dropwise and the mixture was stirred at 45 °C for 20 h. The sodium toluene-*p*-sulfonate was removed. After evaporation of the solvent, the purification of the oily residue was fulfilled by column chromatography on silica gel (diethylether-petroleum ether 1:1) to give the oily product. Yield 0.9 g (71%).

¹H NMR (CDCl₃, 400.13 MHz, 298 K): δ = 7.37 (m, 5H, arom-*H*), 5.14 (s, 2H, CH₂Ph), 2.23 (s, 4H, NCH₂) ppm.

Optimized protocol (Scheme 3.6, step ii)

Dry Et₂O (400 mL), NEt₃ (38.8 mL, 280 mmol) and aziridine (3.6 mL, 70.0 mmol) were mixed in a 1L round-bottom flask under inert atmosphere. This mixture was cooled at 0 °C and benzyl chloroformate (11.9 mL, 80.0 mmol) was then added dropwise. The formation of a white solid was observed during the addition. After complete addition, the reaction mixture was stirred at 0 °C for 1 h and then at room temperature overnight. It was extracted with water (2×200 mL), and the combined aqueous layers were washed with CH₂Cl₂ (3×50 mL). The two organic layers were combined and eluted through a pad of silica gel. The volatiles were then removed under vacuum at a temperature below 40 °C. The resulting oil was purified by thin layer chromatography over silica gel, using first neat petroleum ether, and then 90:10 and 80:20 v/v mixtures of petroleum ether and Et₂O. After evaporation of the volatiles, the title compound was obtained as a colourless oil. Yield 6.3 g (51%).

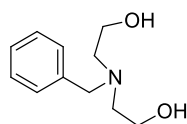


Synthesis of triethylene glycol bis-*p*-toluenesulphonate (Scheme 3.6, step iii)

N,N-Dimethylaminopyridine (0.78 g, 6.40 mmol), triethylene glycol (14.2 mL, 107 mmol) and dry CH₂Cl₂ (50 mL) were mixed in a 500 mL round-bottom flask under inert atmosphere. The mixture was cooled to 0 °C and a solution of tosyl chloride (46.7 g, 245 mmol) in dry CH₂Cl₂ (200 mL) was added. It was followed by the dropwise addition of neat NEt₃ (36.0 mL, 266 mmol). After complete addition, the reaction mixture was

stirred at 0 °C for 1.5 h and then at room temperature overnight. The volatiles were removed under vacuum, and the residue was suspended in ethyl acetate and washed with water (2×100 mL). The aqueous phase was back-extracted with ethyl acetate (50 mL), and the combined organic layers were dried over MgSO₄ and then concentrated under vacuum. Crystallisation from ethyl acetate at –40 °C afforded the title compound as colorless crystals (41.7 g, 85%).

¹H NMR (CDCl₃, 400.13 MHz, 298 K): δ = 7.78 (d, ³J_{HH} = 9.0 Hz, 4H, arom-*H*), 7.34 (d, ³J_{HH} = 9.0 Hz, 4H, arom-*H*), 4.13 (t, ³J_{HH} = 6.0 Hz, 4H, TsOCH₂), 3.65 (t, ³J_{HH} = 6.0 Hz, 4H, TsOCH₂CH₂), 3.52 (s, 4H, CH₂OCH₂), 2.44 (s, 6H, CH₃) ppm.

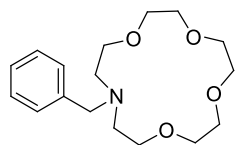


Synthesis of *N*-benzyl diethanolamine (Scheme 3.6, step iv)

A solution of diethanolamine (6.09 g, 57.9 mmol) in acetone (15 mL) was added to a suspension of benzyl bromide (9.00 g, 52.6 mmol) and Na₂CO₃ (6.13 g, 57.9 mmol) in acetone (30 mL). The mixture was refluxed for 4 h. The volatiles were then removed under vacuum. Water (20 mL) was added to the resulting material, and the aqueous solution was extracted with CH₂Cl₂ (30 mL). The organic phase was dried over MgSO₄, and all volatiles were evaporated in vacuo to afford an oil which was washed with hexane (2×15 mL). The title compound was isolated as a colorless oil. Yield 8.22 g (80%).

¹H NMR (CDCl₃, 400.13 MHz, 298 K): δ = 7.32 (m, 5H, arom-*H*), 3.73 (s, 2H, CH₂Ph), 3.63 (t, ³J_{HH} = 6.0 Hz, 4H, CH₂), 2.89 (s, br, 2H, OH), 2.74 (t, ³J_{HH} = 6.0 Hz, 4H, CH₂) ppm.

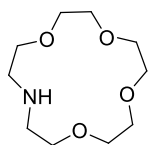
Synthesis of *N*-benzyl-protected 1-aza-15-c-5 (Scheme 3.6, step v)



In a 2 L round-bottom flask, a solution of *N*-benzyl-diethanolamine (9.80 g, 50.0 mmol) in toluene (100 mL) was added under very vigorous stirring to a mixture containing a 50% aqueous solution of NaOH (100 mL) and tetrabutylammonium bromide (4.04 g, 12.5 mmol). This addition was immediately followed by addition of a solution of triethylene glycol bis-*p*-toluenesulphonate (23.0 g, 50.0 mmol) in toluene (500 mL). The mixture was stirred at 70 °C for 10 h and then cooled down to room temperature. The organic layer was extracted and washed with water (3×100 mL). The volatiles

were removed under vacuum, yielding an oil obtained which was then refluxed in hexane (150 mL) for 5 min. The solution was separated from insoluble material by filtration. This extraction process was repeated another three times. The organic layers were combined, and evaporation of the volatiles afforded a yellow oil (12.7 g, 82%) which was used without further purification.

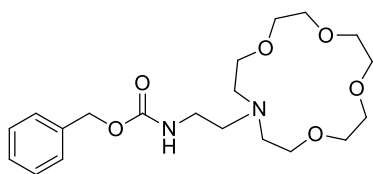
^1H NMR (CDCl_3 , 400.13 MHz, 298 K): δ = 7.32 (m, 5H, arom-*H*), 3.65 (m, 18H, CH_2), 2.83 (br m, 4H, CH_2) ppm.



1-aza-15-crown-5 (Scheme 3.6, step vi)

A solution of *N*-benzyl-protected 1-aza-15-c-5 (6.50 g, 21.0 mmol) and two drops of acetic acid in dry methanol (35 mL) were added under inert atmosphere to a 50 mL autoclave charged with Pd/C (400 mg). The reaction mixture was stirred for 12 h under a 10 bar pressure of H_2 . The solution was then filtered over celite to dispose of solid materials, and volatiles were removed under vacuum. The resulting yellowish oil was trap-to-trap transferred at 100 °C to give the title compound as a colorless oil (3.68 g, 80%). The final compound contain residual acetic acid that could not be removed.

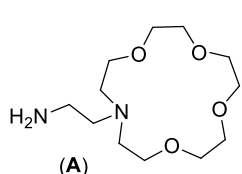
^1H NMR (CDCl_3 , 400.13 MHz, 298 K): δ = 5.52 (br s, 1H, *NH*), 3.69 (m, 4H, CH_2), 3.66 (br s, 4H, CH_2), 3.63 (br s, 8H, CH_2), 2.87 (m, 4H, CH_2) ppm.



Synthesis of *N*-benzyloxycarbonyl-protected (1-aza-15-c-5)ethan-1-amine (Scheme 3.5, step iii)

In a 500 mL round-bottom flask, a solution of *N*-benzyloxycarbonyl-aziridine (3.72 g, 21.0 mmol) in a mixture 1:1 *v/v* of dry toluene and dry acetonitrile (250 mL) was added under argon to 1-aza-15-crown-5 (4.58 g, 21.0 mmol). The reaction mixture was then refluxed for 24 h, after what volatiles were removed in vacuo. The resulting yellow oil was purified by column chromatography (silica), using a 99:1 *v/v* mixture of CH_2Cl_2 and MeOH as the eluent. The title compound was isolated as a yellowish oil (5.85 g, 70%).

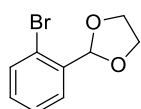
^1H NMR (CDCl_3 , 400.13 MHz, 298 K): δ = 7.34 (m, 5H, arom-*H*), 6.06 (br s, 1H, *NH*), 5.09 (s, 2H, CH_2Ph), 3.60-3.54 (m, 16H, CH_2), 3.28 (br s, 2H, CH_2), 2.72-2.65 (br m, 6H, CH_2) ppm.



Synthesis of (1-aza-15-c-5)ethan-1-amine (A) (Scheme 3.5, step iv, Scheme 3.6, step viii)

A solution of *N*-benzyloxycarbonyl-(1-aza-15-c-5)ethan-1-amine (5.70 g, 14.4 mmol) in dry methanol (110 mL) was added under argon to a 250 mL round-bottom flask a charged with Pd/C (0.40 g). H_2 was bubbled in the reaction mixture for 3 h. The bubbling of H_2 was then stopped, the reaction vessel was closed, and the mixture was stirred overnight. Solid materials were then removed by filtration over filter paper, and the volatiles were removed under vacuum. The title compound was obtained as a yellowish oil (3.66 g, 97%).

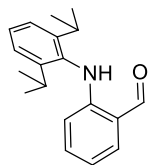
^1H NMR (CDCl_3 , 400.13 MHz, 298 K): δ = 3.65 (m, 12H, OCH_2), 3.60 (t, $^3J_{\text{HH}}$ = 6.0 Hz, 4H, $\text{NCH}_2\text{CH}_2\text{O}$), 2.74 (m, 6H, $\text{H}_2\text{NCH}_2\text{CH}_2\text{N}$ and $\text{NCH}_2\text{CH}_2\text{O}$), 2.60 (t, $^3J_{\text{HH}}$ = 5.9 Hz, 2H, CH_2NH_2), 2.32 (br s, 2H, NH_2) ppm.



Synthesis of 2-(2-bromophenyl)-1,3-dioxolane (Scheme 3.5, step v)

In a Dean-Stark apparatus, a mixture of 2-bromobenzaldehyde (3.0 mL, 25.7 mmol), ethylene glycol (1.9 mL, 33.4 mmol) and *p*-toluenesulphonic acid (45.0 mg, 0.25 mmol) in toluene (40 mL) was refluxed until no more water was collected (ca. 2 d). The mixture then was cooled and washed with 10% aqueous sodium hydroxide (2×30 mL), then deionized water (2×30 mL) and finally with brine (30 mL). The organic layer was dried over MgSO_4 , and removal of the volatiles under reduced pressure afforded the title compound as a yellow viscous oil. Yield 3.60 g (61%).

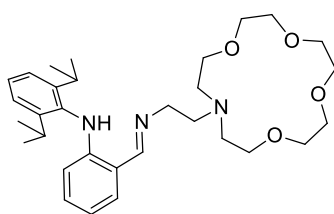
^1H NMR (CDCl_3 , 400.13 MHz, 298 K): δ 7.61-7.56 (m, 2H, arom-*H*), 7.33 (m, 1H, arom-*H*), 7.24-7.22 (m, 1H, arom-*H*), 6.11 (s, 1H, *o*-Br- C_6H_4 -CH), 4.19-4.05 (m, 4H, OCH_2) ppm.



Synthesis of 2-(2,6-diisopropyl-phenylamino)benzaldehyde (B) (Scheme 3.5, steps vi and vii)

2-(2-Bromophenyl)-1,3-dioxolane (3.60 g, 15.7 mmol) and then PtBu_3 (0.31 mL, 0.31 mmol) and 2,6-diisopropylaniline (3.2 mL, 17.1 mmol) were added to a suspension of $\text{Pd}(\text{OAc})_2$ (0.03 g, 0.15 mmol) and NaOtBu (3.01 g, 31.4 mmol) in thf (50 mL). The mixture was refluxed for 16 h, cooled down to room temperature and filtered. The organic layer was extracted with ethyl acetate and washed with deionized water. It was then dried over MgSO_4 and the volatiles were removed under vacuum. The resulting solid was mixed with trifluoroacetic acid (1.10 g, 9.6 mmol) in methanol (30 mL) and stirred for 1 h at room temperature. The solvent was then removed under reduced pressure. The residue was extracted with ethyl acetate and washed twice with deionized water. The organic layer was then dried over MgSO_4 , and after filtration the solvent was evaporated. The product was purified by column chromatography (diethyl ether - petroleum ether 5:95 v/v) to afford the title compound as a yellow solid. Yield 1.60 g (38%).

^1H NMR (CDCl_3 , 400.13 MHz, 298 K): δ = 9.97 (s, 1H, $\text{C}_6\text{H}_3\text{NH}$), 9.56 (s, 1H, $\text{C}_6\text{H}_4\text{CHO}$), 7.55 (d, 1H, $^3J_{\text{HH}}$ = 7.7 Hz, arom-*H*), 7.39–7.27 (m, 4H, arom-*H*), 6.73 (t, 1H, $^3J_{\text{HH}}$ = 7.4 Hz, arom-*H*), 6.22 (d, 1H, $^3J_{\text{HH}}$ = 8.6 Hz, arom-*H*), 3.05 (hept, 2H, $^3J_{\text{HH}}$ = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$), 1.15 (d, 6H, $^3J_{\text{HH}}$ = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$), 1.11 (d, 6H, $^3J_{\text{HH}}$ = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$) ppm.



Synthesis of $\{\text{I}^{\text{A}^{\text{crown}}}\}\text{H}$ (Scheme 3.5, step viii)

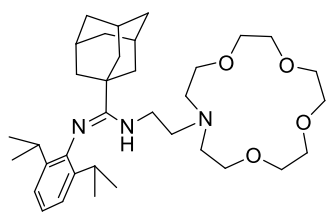
A mixture of **B** (1.00 g, 3.50 mmol) and a first fraction of **A** (0.46 g, 1.75 mmol) in petroleum ether (20 mL) was refluxed in a Dean-Stark apparatus overnight. The solvent was then evaporated to monitor conversion (aliquot for ^1H NMR spectroscopy). The remaining of **A** (0.54 g, 2.06 mmol) was introduced over the course of 8 days as four identical fractions dissolved in petroleum ether (135 mg each in 20 mL of solvent), and reflux of the reaction mixture was maintained for a total of 8 days. Complete conversion of **B** was observed. The mixture was then filtered to eliminate insoluble materials and the volatiles were removed under vacuum. The title compound was obtained as an analytically pure colorless oil (1.60 g, 90%) which afforded X-ray quality crystals upon extended drying under dynamic vacuum at room temperature.

^1H NMR (CDCl_3 , 400.13 MHz, 298 K): δ = 10.50 (s, 1H, *NH*), 8.46 (s, 1H, *CH=N*), 7.35-7.24 (m, 4H, *arom-H*), 7.08 (m, 1H, *arom-H*), 6.67 (m, 1H, *arom-H*), 6.21 (d, 1H, $^3J_{\text{HH}}$ = 8.3 Hz, *arom-H*), 3.74 (t, 2H, $^3J_{\text{HH}}$ = 7.0 Hz, CH_2), 3.67-3.63 (m, 16H, OCH_2), 3.11 (hept, $^3J_{\text{HH}}$ = 6.9 Hz, 2H, *CH*), 2.86 (m, 6H, NCH_2), 1.16 (d, 6H, $^3J_{\text{HH}}$ = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$), 1.14 (d, 6H, $^3J_{\text{HH}}$ = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.62 MHz, 298 K): δ = 165.21 (*CH=N*), 149.41 (*arom-C*), 147.45 (*arom-C*), 135.17 (*arom-C*), 133.50 (*arom-C*), 130.95 (*arom-C*), 127.16 (*arom-C*), 123.67 (*arom-C*), 116.68 (*arom-C*), 114.94 (*arom-C*), 111.63 (*arom-C*), 71.04 (CH_2O), 70.47 (CH_2O), 70.27 (CH_2O), 70.21 (CH_2O), 59.77 ($\text{NCH}_2\text{CH}_2\text{N=CH}$), 57.93 ($\text{NCH}_2\text{CH}_2\text{O}$), 55.17 ($\text{NCH}_2\text{CH}_2\text{N=CH}$), 28.43 ($\text{CH}(\text{CH}_3)_2$), 24.92 ($\text{CH}(\text{CH}_3)_2$), 22.93 ($\text{CH}(\text{CH}_3)_2$) ppm.

Anal. Calcd for $\text{C}_{31}\text{H}_{47}\text{N}_3\text{O}_4$ (525.72 $\text{g}\cdot\text{mol}^{-1}$): theoretical, C 70.82%, H 9.01%, N 7.99%; found C 69.65%, H 8.90 %, N 7.83 %.

Mass spectrometry ESI [$\text{M} + \text{Na}^+$] ($\text{C}_{31}\text{H}_{47}\text{N}_3\text{O}_4\text{Na}$) m/z theoretical: 548.3459; found 548.3457.



Synthesis of $\{\text{AdAm}^{\text{crown}}\}\text{H}$ (Scheme 3.7, step iv)

A solution of **A** (1.80 g, 6.9 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a solution of **C** (3.68 g, 10.3 mmol) and dry NEt_3 (28.7 mL, 205.8 mmol) in CH_2Cl_2 (25 mL). The mixture was stirred at room temperature for 36 h, during which the precipitation of ammonium chloride was observed. After addition of water (25 mL), the organic layer was recovered and washed with distilled water (25 mL), and the volatiles were removed in vacuo. The resulting oily residue was suspended in petroleum ether (20 mL), and the suspension was filtered over sintered glass to remove insoluble impurities. The filtrate was then concentrated to the third of the initial volume and stored in the freezer at -43°C . Colorless crystals of $\{\text{AdAm}^{\text{crown}}\}\text{H}$ were obtained after 4 days (1.54 mg, 39%).

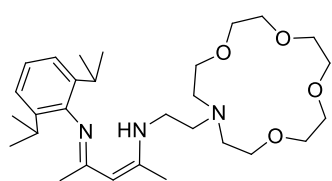
^1H NMR (CDCl_3 , 500.13 MHz, 298 K): δ = 6.94 (d, $^3J_{\text{HH}}$ = 8.0 Hz, 2H, *meta-H*), 6.84 (t, $^3J_{\text{HH}}$ = 8.0 Hz, *para-H*), 5.46 (br s, 1H, *NH*), 3.66-3.62 (m, 12H, OCH_2CH_2), 3.57 (t, $^3J_{\text{HH}}$ = 6.0 Hz, 4H, $\text{OCH}_2\text{CH}_2\text{N}$), 3.01 (hept, $^3J_{\text{HH}}$ = 7.0 Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.62 (t, $^3J_{\text{HH}}$ = 6.0 Hz, 4H,

OCH₂CH₂N), 2.43 (m, 2H, NCH₂CH₂NH), 2.34 (m, 2H, NCH₂CH₂NH), 2.08 (br s, 3H, adamantyl-*H*), 2.00 (br s, 6H, adamantyl-*H*), 1.76 (br s, 6H, adamantyl-*H*), 1.16 (d, ³*J*_{HH} = 7.0 Hz, 12H, CH₃) ppm.

¹³C{¹H} NMR (CDCl₃, 125.77 MHz, 298 K): δ = 157.18 (CH=N), 147.43 (arom-C), 137.83 (arom-C), 121.73 (arom-C), 120.63 (arom-C), 71.26 (OCH₂), 70.60 (OCH₂), 70.35 (OCH₂), 70.26 (OCH₂CH₂N), 55.72 (NCH₂CH₂NH), 54.65 (OCH₂CH₂N), 40.95 (adamantyl-C), 40.56 (adamantyl-C), 39.71 (adamantyl-C), 37.01 (adamantyl-C), 28.98 (adamantyl-C), 28.37 (CH(CH₃)₂), 23.33 (CH(CH₃)₂), 22.62 (CH(CH₃)₂) ppm.

Anal. Calcd for C₃₅H₅₇N₃O₄ (583.86 g·mol⁻¹): C, 72.00; H, 9.84; N, 7.20; O, 10.96. Found: C, 72.12; H, 9.82; N, 7.00.

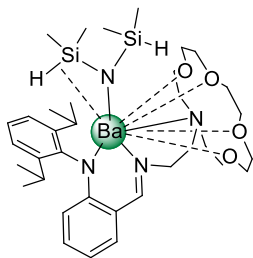
Mass spectrometry: [M-H]⁺, m/z theoretical 584.4422, found 584.4420 (0 ppm).



Synthesis of {BDI^{crown}}H (Scheme 3.7, step v)

A solution of **D** (0.80 g, 3.08 mmol) in 5 mL of CH₂Cl₂ is added dropwise to a solution of Et₃O·BF₄ (0.59 g, 3.08 mmol) in 5 mL of CH₂Cl₂. The mixture is then stirred for 3 h at room temperature. After 3 h, triethylamine (0.43 mL, 3.08 mmol) is added dropwise to the solution and the mixture is stirred for 15 min. A solution of triethylamine (3.0 mL, 21.5 mmol) and **A** (0.81 g, 3.08 mmol) in 6 mL of CH₂Cl₂ is added to the solution before the leave stirring for 12 h at room temperature. All volatiles are then removed in vacuo and the resulting orange residue is then extracted with petroleum ether (3 × 15 mL) and concentrated in vacuo. The product is obtained as an orange oil containing **D** which has not been possible to separate.

¹H NMR (CDCl₃, 400.16 MHz, 298 K): δ = 10.70 (br, 1H, NH), 7.09 (m, 2H, meta-*H*), 6.99 (m, 1H, para-*H*), 4.62 (br, 1H, CH), 3.63-3.52 (m, 16H, OCH₂CH₂ and OCH₂CH₂N), 3.29 (m, 2H, NCH₂CH₂NH), 2.86 (hept, ³*J*_{HH} = 6.9 Hz, 2H, CH(CH₃)₂), 2.75 (t, ³*J*_{HH} = 6.0 Hz, 4H, OCH₂CH₂N), 2.64 (m, 2H, NCH₂CH₂NH), 2.00 (s, 3H, CH₃), 1.61 (s, 3H, CH₃), 1.15 (d, ³*J*_{HH} = 6.8 Hz, 6H, CH₃), 1.12 (d, ³*J*_{HH} = 6.8 Hz, 6H, CH₃) ppm.



Synthesis of $[I^A^{crown}\{BaN(SiMe_2H)_2\}_2]$ (**10**)

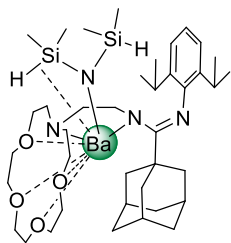
A solution of $\{I^A^{crown}\}H$ (0.11 g, 0.21 mmol) and $[Ba\{N(SiMe_2H)_2\}_2 \cdot (thf)_2]$ (0.11 g, 0.20 mmol) in benzene (4.0 mL) was stirred for 2 h. The volatiles were then removed under vacuum to yield **5** as an orange solid which was washed with petroleum ether (5 mL). Yield 0.13 g (86%). X-ray quality crystals were grown from a saturated benzene solution. NMR characterisation was performed in $thf-d_8$ due to the insufficient solubility of **5** in aromatic solvents.

^1H NMR ($thf-d_8$, 500.13 MHz, 298 K): δ = 8.04 (s, 1H, $CH=N$), 7.04 (d, $^3J_{HH}$ = 7.5 Hz, 2H, arom- H), 6.92 (d, $^3J_{HH}$ = 8.0 Hz, 1H, arom- H), 6.87 (t, $^3J_{HH}$ = 7.5 Hz, 1H, arom- H), 6.52 (m, 1H, arom- H), 5.84 (t, $^3J_{HH}$ = 7.0 Hz, 1H, arom- H), 5.74 (d, $^3J_{HH}$ = 9.0 Hz, arom- H), 4.57 (m, 2H, SiH), 3.80-3.23 (overlapping br m, 22H, OCH_2 and $CH(CH_3)_2$), 2.94 (m, 2H, NCH_2), 2.65 (m, 2H, NCH_2), 1.15 (m, 6H, $CH(CH_3)_2$), 0.96 (br s, 6H, $CH(CH_3)_2$), -0.14 ppm (br s, 12H, $Si(CH_3)_2$) ppm.

$^{13}C\{^1H\}$ ($thf-d_8$, 125.77 MHz, 298 K): δ = 168.19 ($CH=N$), 158.66 (arom-C), 145.19 (arom-C), 139.42 (arom-C), 130.71 (arom-C), 124.15 (arom-C), 122.12 (arom-C), 118.87 (arom-C), 118.56 (arom-C), 108.17 (arom-C), 70.16 (OCH_2), 69.47 (OCH_2), 69.26 (OCH_2), 68.74 (OCH_2), 68.10 (OCH_2), 60.24 (NCH_2), 59.20 (NCH_2), 55.24 (NCH_2), 28.54 ($CH(CH_3)_2$), 26.40 ($CH(CH_3)_2$), 25.99 ($CH(CH_3)_2$), 5.64 ($SiCH_3$) ppm. Traces of free $\{I^A^{crown}\}H$ due to minimal hydrolysis during sample analysis are also visible.

$^{29}Si\{^1H\}$ NMR ($thf-d_8$, 79.49 MHz, 298 K): δ = -30.09 (SiH) ppm.

FTIR (Nujol mull in KBr): $\tilde{\nu}_{Si-H}$ = 2052.3 (s), 1990.5 (s), 1728.2 (w), 1604.8 (s), 1512.2 (s), 1458.2 (s), 1357.9 (s), 1303.9 (m), 1234.4 (s), 1103.28 (s), 1072.4 (s), 941.3 (s), 895.0 (s), 825.5 (s), 771.5 (m), 740.7 (s), 663.5 (m), 624.9 (m), 532.3 (w), 424.3 (s). Bands above 2300 cm^{-1} are only for Nujol.



Synthesis of $[\{\text{AdAm}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**11**)

$\{\text{AdAm}^{\text{crown}}\}\text{H}$ (90.0 mg, 0.15 mmol) and $\text{Ba}[\text{N}(\text{SiMe}_2\text{H})_2]_2$ (60.0 mg, 0.15 mmol) were mixed and stirred in benzene (2.0 ml) at room temperature for 5 min, and the solution was kept at room temperature without stirring for 24 h.

After 15-20 min, the formation of colourless crystals was observed. After 24 h the solution was removed with a cannula and the crystals were dried under vacuum (114 mg, 85%). Single crystals suitable for XRD analysis were obtained from C_6D_6 .

^1H NMR ($\text{thf-}d_8$, 500.13 MHz, 298 K): δ = 6.67 (d, $^3J_{\text{HH}}$ = 7.0 Hz, 2H, meta-*H*), 6.36 (t, $^3J_{\text{HH}}$ = 7.0 Hz, 1H, para-*H*), 5.64 (s, 2H, $^1J_{29\text{Si-1H}}$ = 160.2 Hz, Si*H*), 3.92 (m, 6H, OCH_2), 3.77 (m, 6H, OCH_2), 3.65-3.55 (m, 4H, $\text{OCH}_2\text{CH}_2\text{N}$), 3.21 (hept, $^3J_{\text{HH}}$ = 7.0 Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 3.02 (m, 2H, $\text{NCH}_2\text{CH}_2\text{NH}$), 2.55 (m, 4H, $\text{OCH}_2\text{CH}_2\text{N}$), 2.10 (br s, 8H, adamantyl-*H*), 2.02 (br s, 3H, adamantyl-*H*), 1.77 (m, 2H, $\text{NCH}_2\text{CH}_2\text{NH}$), 1.73 (br s, 4H, adamantyl-*H*), 1.14 (d, $^3J_{\text{HH}}$ = 7.0 Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 1.07 (d, $^3J_{\text{HH}}$ = 7.0 Hz, 6H, $\text{CH}(\text{CH}_3)_2$), -0.01 (s, 12H, SiCH_3) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{thf-}d_8$, 125.77 MHz, 298 K): δ = 164.61 (NCN), 153.93 (arom-C), 137.31 (arom-C), 121.36 (arom-C), 116.18 (arom-C), 70.50 (OCH_2), 69.71 (OCH_2), 69.60 (OCH_2), 68.98 ($\text{OCH}_2\text{CH}_2\text{N}$), 62.37 ($\text{NCH}_2\text{CH}_2\text{NH}$), 55.69 ($\text{OCH}_2\text{CH}_2\text{N}$), 44.68 (adamantyl-C), 44.33 (adamantyl-C), 44.15 (adamantyl-C), 38.75 (adamantyl-C), 30.87 (adamantyl-C), 29.18 ($\text{CH}(\text{CH}_3)_2$), 24.64 ($\text{CH}(\text{CH}_3)_2$), 23.03 ($\text{CH}(\text{CH}_3)_2$), 5.24 (SiCH_3) ppm.

$^{29}\text{Si}\{^1\text{H}\}$ NMR ($\text{thf-}d_8$, 79.49 MHz, 298 K): δ = -30.92 (Si*H*) ppm.

FTIR (Nujol mull in KBr): $\tilde{\nu}_{\text{Si-H}}$ = 2276.0 (m), 2013.7 (s), 1975.1 (s), 1782.2 (w), 1658.8 (w), 1535.3 (s), 1458.2 ((s), 1373.3 (s), 1303.9 (m), 1234.4 (s), 1111.0 (s), 1080.1 (s), 895.0 (m), 817.8 (m), 748.4 (s), 378.9 (w), 632.6 (w), 493.8 (s). Bands above 2300 cm^{-1} are only for Nujol.

The attempts to synthesize and isolate complex $[\{\text{I}^{\text{A crown}}\}\text{BaPPh}_2]$ (**13**) were unsuccessful and we just obtained small amounts of its crystals from the hydrophosphination reaction.

3.5.3 Typical procedure for hydrophosphination reactions

3.5.3.1 Regular hydrophosphination reactions in neat condition

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. Styrene was added with a syringe to the precatalyst, followed by addition of phosphine. The NMR tube was immersed in an oil bath set at the desired temperature. The reaction time was measured from this point. The reaction was terminated by addition of “wet” benzene- d_6 to the reaction mixture. The conversion was determined by ^1H NMR spectroscopy.

3.5.3.2 Kinetic study of the 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 solvent was added with a syringe to the precatalyst, followed by addition of styrene and phosphine. The NMR tube was quickly closed and introduced to the NMR machine to record the ^1H NMR spectroscopy in order to study the kinetic of the reaction.

3.5.3.3 Preparation the unsymmetrical phosphines

In a typical reaction to prepare unsymmetrical phosphines, the precatalyst was loaded in an NMR tube in the glovebox. All subsequent operations were carried out on a vacuum manifold using Schlenk techniques. The two styrene derivatives were introduced to the NMR tube, then phenylphosphine and benzene- d_6 were added and the NMR tube was quickly closed and introduced to the NMR machine to record the ^1H NMR spectroscopy in order to study the kinetic of the reaction.

3.5.4 X-ray diffraction crystallography

X-ray diffraction data for all compounds (CCDC 1896037-1896039 and 1897231) were collected at 150 K using a Bruker APEX CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). A combination ω and Φ scans was carried out to obtain at least a unique data set. The structures were solved by dual-space algorithm using the SHELXT program, and then refined with full-matrix least-squares methods based on F^2 (SHELXL).⁵⁸ The

SiH hydrogen atoms could be found from the Fourier difference analysis. Other hydrogen atom contributions were calculated, but not refined. Carbon-, oxygen-, and nitrogen- bound hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. 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.

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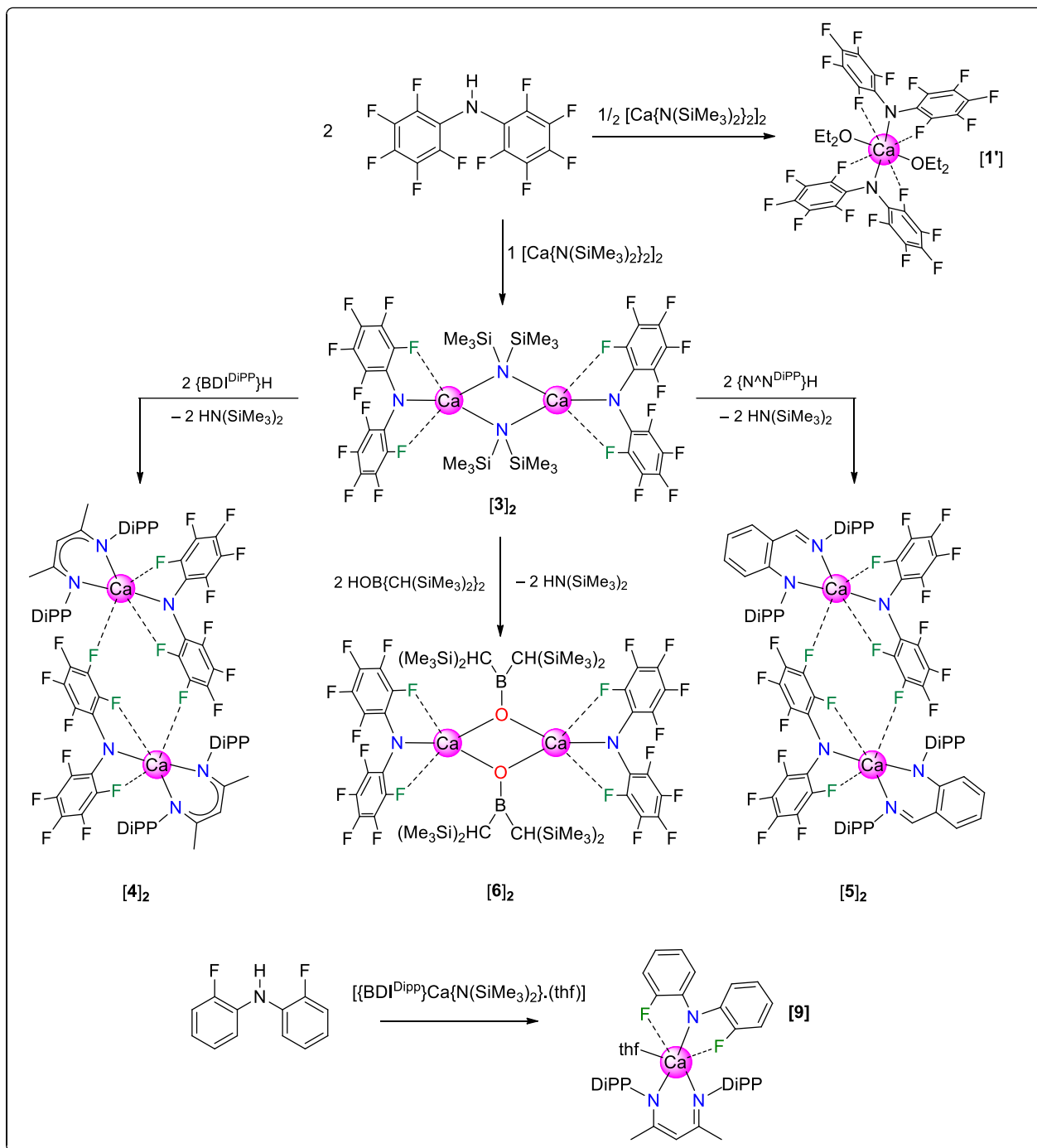
General Conclusion and Perspectives

General Conclusion and Perspectives

The main objective of this PhD thesis was the synthesis of new classes of alkaline-earth complexes stabilized by ancillary ligands and/or secondary interactions, and the evaluation of their applicability in challenging homogeneously-catalyzed processes, notably in hydrophosphination reactions.

In the first part of this manuscript, we have presented the synthesis and characterization of several Ae homoleptic and heteroleptic complexes containing fluorinated arylamide ligands: $\text{N}(\text{C}_6\text{F}_5)_2^-$ and $\text{N}(o\text{-F-C}_6\text{H}_4)_2^-$. The complexes that were obtained, namely $[\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2\cdot(\text{Et}_2\text{O})_2]$ (**1'**), $[\text{Ba}\{\mu\text{-N}(\text{C}_6\text{F}_5)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}\cdot\text{toluene}]_2$ (**2**), $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**3**), $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**4**), $[\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**5**), $[\text{Ca}\{\mu\text{-OB}(\text{CH}(\text{SiMe}_3)_2)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**6**) and $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(o\text{-F-C}_6\text{H}_4)_2\}\cdot(\text{thf})]$ (**9**) (Scheme A), have proved to be stable against ligand redistribution in solution. In line with our initial hypotheses, the crystallographic data indicated that not only the coordination of the N and O heteroatoms from the ligands are responsible for the stabilization of the complexes, but also the inter- and intramolecular $\text{Ae}\cdots\text{F-C}$ secondary interactions provide additional stabilizing effect.

A first group of complexes was prepared using the highly fluorinated arylamine $\text{HN}(\text{C}_6\text{F}_5)_2$. We first isolated the solvent-adduct of the homoleptic calcium complex $[\text{Ca}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2\cdot(\text{Et}_2\text{O})_2]$ (**1'**) with two $\text{Ca}\cdots\text{F-C}$ intramolecular interactions (2.493(1) and 2.523(1) Å). The $\text{Ca-N}_{\text{C}_6\text{F}_5}$ bond lengths in **1'** (2.370(1) and 2.380(1) Å) are substantially longer than the corresponding ones in $[\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2\cdot(\text{thf})_2]_2$ (2.294(3) and 2.309(3) Å). This reflects the greater electron withdrawing ability of the $\text{N}(\text{C}_6\text{F}_5)_2^-$ moiety combined with the steric effect of the (C_6F_5) groups compared to (SiMe_3) . The heteroleptic solvent-free calcium complex $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**3**) was also obtained. Considering the maximum accepted limit for $\text{Ca}\cdots\text{F-C}$ contacts (3.13 Å),¹ the resulted bond distances between the metal center and the fluorine atoms were remarkably short (e.g. complex **3**, with Ca-F distances of (2.423(2) and 2.456(2) Å, Table A) and were comparable to Hill's previously reported homoleptic bis(amido) calcium complex with CF_3 substituents in the backbone (Ca-F distances = 2.489(3) and 2.468(2) Å).²



Scheme A. Homoleptic and heteroleptic calcium complexes synthesized in this work, featuring $\text{Ca} \cdots \text{F} \cdots \text{C}$ secondary interactions ($\text{DiPP} = 2,6\text{-iPr}_2\text{-C}_6\text{H}_3$).

The related heteroleptic complexes $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**4**₂) and $[\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**5**₂) were next obtained from the reaction of $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**3**₂) with two *N*-donor proligands, ($\{\text{BDI}^{\text{DiPP}}\}\text{H}$ and $\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{H}$) (see Scheme A). These proligands have previously proved to be very convenient for the preparation of stable calcium complexes. These two heteroleptic complexes are both dimers in the molecular solid-state, with the $\text{N}(\text{C}_6\text{F}_5)_2^-$ bridging the metal centers through intermolecular $\text{Ca}\cdots\text{F}-\text{C}$ secondary interactions. This is a more straightforward method to obtain stable solvent-free heteroleptic complexes of calcium, unlike the more challenging synthetic routes for other solvent-free low-coordinate compounds, such as the well-known $[\{\text{BDI}\}\text{CaN}(\text{SiMe}_3)_2]$.

Recently in our group, we have isolated new homoleptic and heteroleptic barium complexes using the *O*-donor borinic acid $\text{HOB}\{\text{CH}(\text{SiMe}_3)_2\}_2$.^{3,4} The X-ray structure of the barium heteroleptic dimer $[\text{Ba}\{\mu\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2$ shows the $\text{N}(\text{SiMe}_3)_2^-$ in the bridging position which admits our expectations. The partial delocalization of *O*-electrons into the empty p_z orbital at boron in the boryloxide reduces the electron density on oxygen and decreases its propensity to act as a bridging atom. We explored the effect of the steric bulk and delocalization of the oxygen lone pairs in the vacant $2p_z$ orbital at boron in $\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2^-$ ligand combined with the potential $\text{Ae}\cdots\text{F}-\text{C}$ secondary interactions of fluoroarylamides. The borinic acid $\text{HOB}\{\text{CH}(\text{SiMe}_3)_2\}_2$ was used here as a proligand to prepare the first example of calcium boryloxide, namely $[\text{Ca}\{\mu\text{-OB}(\text{CH}(\text{SiMe}_3)_2)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**6**₂) (Figure A, Scheme A).⁵ The solid-state structure of this compound shows the $(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)^-$ in the bridging position, which is different from the above-mentioned observations on $([\text{Ba}\{\mu\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2)$.

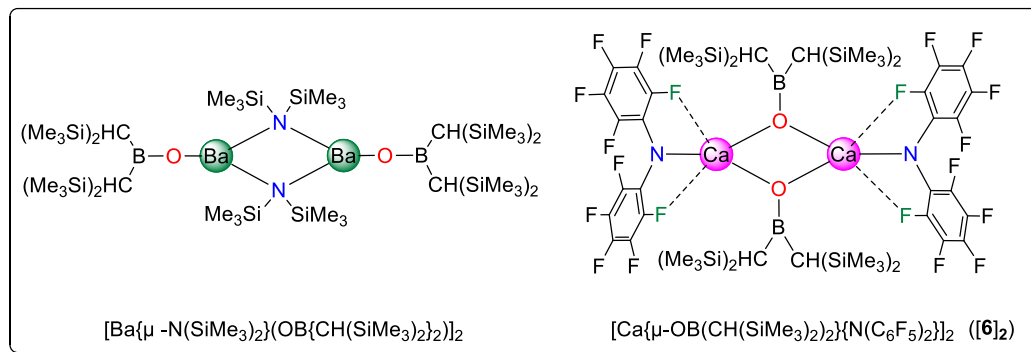


Figure A. Calcium and barium heteroleptic complexes featuring the $\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2^-$ ligand: $[\text{Ca}\{\mu\text{-OB}(\text{CH}(\text{SiMe}_3)_2)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**6**₂) and $[\text{Ba}\{\mu\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2$.

Comparison of the solid-state molecular structures of binuclear complexes **3**₂ and **4**₂ shows the following trend in bridging (donating) properties of the related monoanionic ligands: $\text{N}(\text{C}_6\text{F}_5)_2^- < \text{N}(\text{SiMe}_3)_2^-$ (Figure B). This could be based on the available electron density on nitrogen atoms of these ligands that enable the bridging of the metal center. The comparison of complexes **3**₂ and **6**₂ reveals the $\text{N}(\text{C}_6\text{F}_5)_2^- < \text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2^-$ trend in donating properties of both ligands (Figure B). Previous DFT calculations revealed the bridging ability of $\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2^- < \text{N}(\text{SiMe}_3)_2^-$.⁴ Therefore, considering all the results leads to the following trend $\text{N}(\text{C}_6\text{F}_5)_2^- < \text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2^- < \text{N}(\text{SiMe}_3)_2^-$ among these three ligands. The presence of the electron-withdrawing fluorine atoms on the aromatic rings in the $\text{N}(\text{C}_6\text{F}_5)_2^-$ ligand reduces drastically the ability of the fluoroarylamide to bridge the calcium centers (Figure B). These results will be useful for the future design of Ae metal complexes based on these monoanionic, monodentate ligands.

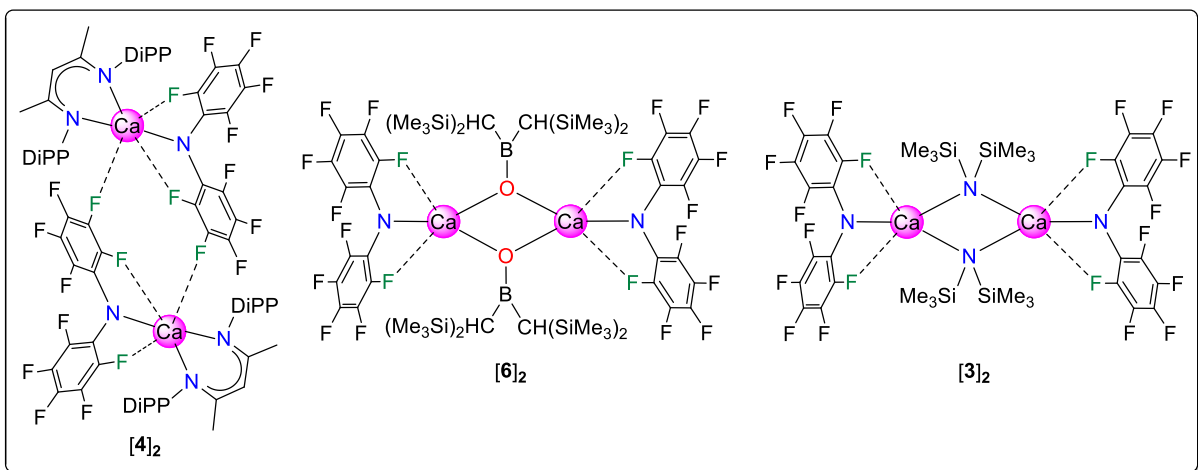


Figure B. Molecular solid-state structure of complexes **3**₂, **4**₂, and **6**₂.

In order to study the influence of the number of electron-withdrawing atoms on the coordination properties of fluoroarylamides, the monofluorinated arylamine $\text{HN}(o\text{-F-C}_6\text{H}_4)_2$ was used instead of the perfluorinated one ($\text{HN}(\text{C}_6\text{F}_5)_2$). With only two *ortho* fluorine atoms, $\text{HN}(o\text{-F-C}_6\text{H}_4)_2$ is less sterically hindered than $\text{HN}(\text{C}_6\text{F}_5)_2$, and has also less electron-withdrawing fluorine atoms which increases the comparative basicity of the amine. The unsuccessful crystallization of the solvent-free complex $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(o\text{-F-C}_6\text{H}_4)_2\}]$ (**8**) requires further investigation; it would be much helpful so as to study the sole influence of the $\text{Ca}\cdots\text{F}-\text{C}$ secondary interaction. We then successfully synthesized and characterized the solvated complex

$[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(\text{o-F-C}_6\text{H}_4)_2\}.\text{(thf)}]$ (**9**). The X-ray diffraction analysis shows a calcium complex with two intramolecular $\text{Ca}\cdots\text{F}-\text{C}$ interactions from the $\text{N}(\text{o-F-C}_6\text{H}_4)_2^-$ ligand.

The calcium heteroleptic complex $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2.\text{(thf)}]$ (**I**) has been proved by Hill to be an effective precatalyst for hydroelementation reactions such as hydrophosphination of styrene with diphenylphosphine.⁶ Due to the close similarity of our new charged-neutral fluorinated complexes $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**4**₂) and $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(\text{o-F-C}_6\text{H}_4)_2\}.\text{(thf)}]$ (**9**) with this complex, their activities were evaluated in the benchmark hydrophosphination reaction ($[\text{styrene}]_0/[\text{Ph}_2\text{PH}]_0/[\text{precat}]_0 = 10:10:1$, 60 °C, 12 h, 10 mol-% precatalyst). Full anti-Markovnikov regioselectivity was observed, yielding exclusively the linear *tertiary* phosphine $(\text{PhCH}_2\text{CH}_2)\text{PPh}_2$. These precatalysts showed better activities ($\text{TOF} = 0.7 \text{ h}^{-1}$ for **4**₂ and 0.8 h^{-1} for **9**) compared to Hill's benchmark complex $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2.\text{(thf)}]$ (**I**) ($\text{TOF h}^{-1} = 0.5 \text{ h}^{-1}$), under milder reaction conditions including lower temperature and shorter reaction time (60 °C vs 75 °C and 12 h vs 20 h). Therefore, these original fluorinated compounds represent valuable additions to a limited list of complexes that efficiently catalyze such intermolecular hydrophosphination reactions.

DFT computations conducted on the fluorinated complexes, specifically **1'**, **3**₂, **4**₂, **6**₂, **9** and suggested molecular structures in agreement with the experimental observations and indicated that due to the high positive charge of Ca^{2+} , the nature of $\text{Ae}\cdots\text{F}-\text{C}$ interactions is mostly made of electrostatic contributions with only a weak covalent character. The comparison of fluorinated and non-fluorinated equivalents through energy decomposition analysis (EDA) indicated the $\text{Ca}\cdots\text{F}-\text{C}$ interaction prevails over the other two types of secondary interactions ($\text{Ca}\cdots\text{H}-\text{C}$ and $\text{Ca}\cdots\text{C}(\pi)$). The $\text{Ca}\cdots\text{F}-\text{C}$ distances of the resulting fluorinated structures are gathered in Table A.

These metric parameters indicate short distances between the metal center and fluorine atoms translating into strong interactions (e.g. $2.423(2) \text{ \AA}$ in **3**₂) compared to the strongest ones reported in the literature. $\text{Ae}\cdots\text{F}-\text{C}$ interactions have been previously applied together with other secondary interactions (like $\text{Ae}\cdots\text{C}(\pi)$ and $\text{Ae}\cdots \text{H}-\text{Si}$ β -anagostic interactions; e.g. $[\{\text{RO}^{12}\}\text{CaN}(\text{SiMe}_2\text{H})_2]_2$) or extra contacts (e.g. contacts with ligand macrocyclic donating heteroatoms $[\{\text{RO}^3\}\text{Ae}]_2^+ \cdot 2[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$) to provide a stable structure (Figure C).⁷

Table A. Summary of Ca $\cdots$ F–C secondary interactions for complexes **1'**, **3₂**, **4₂**, **5₂**, **6₂**, **9**.

Complex	Nuclearity	Ca $\cdots$ F			
[Ca{N(C ₆ F ₅) ₂ } ₂ ·(Et ₂ O) ₂] (1')	Monomeric	2.4935(10) ^a	2.5226(10) ^a	2.7713(11) ^a	3.0740(12) ^a
[Ca{μ ² -N(SiMe ₃) ₂ }{N(C ₆ F ₅) ₂ }] ₂ (3₂)	Dimeric	2.4227(18) ^a	2.4560(18) ^a	-	-
[{BDI ^{DiPP} }CaN(C ₆ F ₅) ₂] (4₂)	Dimeric	2.5559(15) ^a	2.7120(17) ^a	-	-
		2.5325(15) ^b	-	-	-
[{N ^{DiPP} }CaN(C ₆ F ₅) ₂] (5₂)	Dimeric	2.558(2) ^a	2.559(2) ^a	-	-
		2.530(1) ^b	-	-	-
[Ca{μ-OB(CH(SiMe ₃) ₂) ₂ }{N(C ₆ F ₅) ₂ }] ₂ (6₂)	Dimeric	2.544(2) ^a	2.597(2) ^a	2.498(2) ^a	2.553(2) ^a
[{BDI ^{DiPP} }Ca{N(<i>o</i> -F-C ₆ H ₄) ₂ }·(thf)] (9)	Monomeric	2.486(3) ^a	2.549(3) ^a	-	-

[a] Intramolecular secondary interaction. [b] Intermolecular secondary interaction.

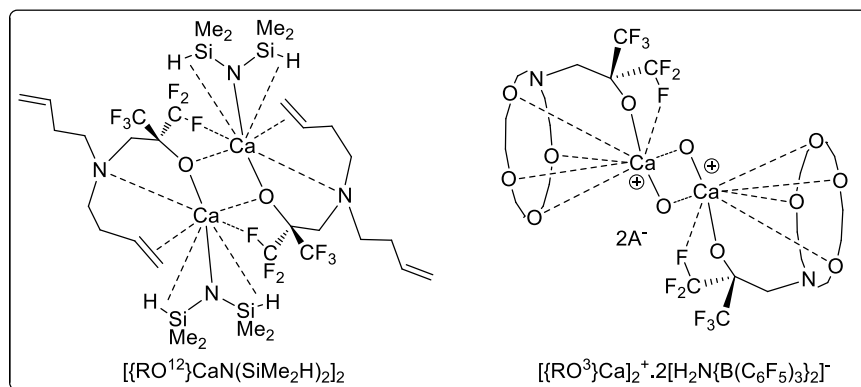


Figure C. The structure of heteroleptic calcium fluoroaminoalkoxide [$\{RO^{12}\}CaN(SiMe_2H)_2$]₂ and [$\{RO^3\}Ae$]₂⁺·2[$H_2N\{B(C_6F_5)_3\}_2$][−].

During my investigations, the Ca $\cdots$ F–C interactions revealed decisive to achieve the preparation of stable, low-coordinate and solvent-free Ae compounds. In order to exclude the effect of fluorine atoms beside the presence of the other noncovalent interactions such as Ae $\cdots$ Si–H β-anagostic interactions in one complex, the design of new ligands would be helpful. For instance, fluorinated aryl amines with tetramethyldisilazade have the potential to provide combined Ae $\cdots$ F–C and Ae $\cdots$ Si–H β-anagostic interactions (Figure D).

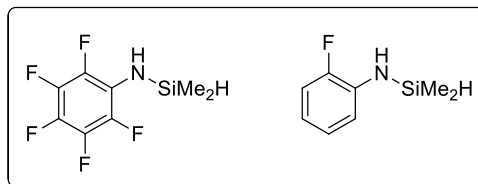
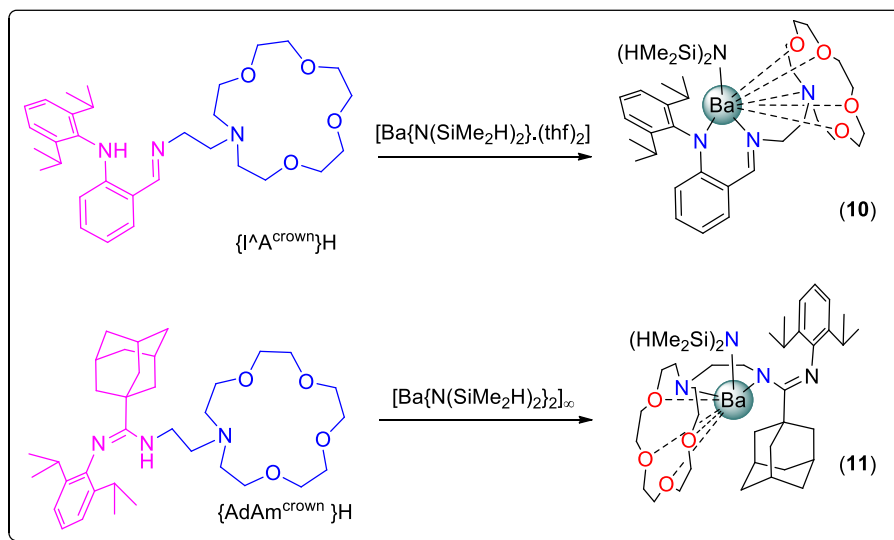


Figure D. Example of amine proligands with potential for combined $\text{Ae} \cdots \text{Si-H}$ and $\text{Ae} \cdots \text{F-C}$ secondary interactions.

The new isolated calcium compounds showed high reactivity in hydrophosphination reactions that is one of the challenging hydroelementation reactions. Thus, the analogous heavy Ae complexes could be prepared. The arrangements of the $\text{Ae} \cdots \text{F-C}$ secondary interactions could differ between the Ae analogues according to the size of the metal, including the presence of inter- and intramolecular interactions and the nuclearity of the complexes. For instance, barium requires more contacts with the ligand and there may be more intramolecular interactions for the barium analogue of complexes **4**₂ and **5**₂. Furthermore, obtaining stable strontium and barium analogues of the calcium complexes **4**₂ and **9** (with BDI backbone) could be very interesting, since $[\{\text{BDI}\}\text{AeN}(\text{SiMe}_3)_2(\text{thf})]$ complexes are not stable in solution for Sr and Ba. We could also proceed with further catalytic investigations. Barium complexes have revealed excellent results in hydrophosphination reactions, therefore the preparation of barium analogues of complexes like **4**₂ and **9** could be followed by interesting catalytic experiments in this area such as hydrosilylation and alkene transfer hydrogenation⁸.

As the ionic nature of the bonding in Ae complexes increases descending group 2 metals, the tendency for ligand scrambling is intensified with the ionic radius ($\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$), hence, the preparation of stable heteroleptic complexes of barium $[\{\text{L}\}\text{Ba-R}]$ (where $\{\text{L}\}$ is a monoanionic ancillary ligand and R is the reactive co-ligand) is challenging. On the other hand, the reaction rate in intermolecular hydroamination and hydrophosphination reaction increases with the size of the metal center. Therefore, in the second part of my PhD research, the possibility of stabilizing a barium heteroleptic complex using multidentate ancillary ligands paired with $\text{Ae} \cdots \text{Si-H}$ β -anagostic interactions was explored. In regard to heavy Ae chemistry, the nitrogen-based iminoanilide ($[\{\text{N}^{\text{DiPP}}\}\text{AeN}(\text{SiMe}_3)_2(\text{thf})_n]$ (Ae = Ca, $n = 1$; Sr, $n = 2$; Ba, $n = 2$)⁹ and the amidinate-type ligands (such as $[\{\text{RAm}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2]$ (Am = amidinate, R = ^tBu, Ad)¹⁰ and $[\{p\text{-TolAm}^{\text{Ar}^\ddagger}\}\text{SrN}(\text{SiHMe}_2)_2]$ ($\text{Ar}^\ddagger = 2,6\text{-Ph}_2\text{CH-4-}i\text{Pr-phenyl}$)¹¹) provided stable

heteroleptic structures. In order to explore new possibilities in creating kinetically stable and catalytically effective barium complexes, we have designed new *N*-donor and bulky ancillary ligands including a macrocyclic crown ether side arm with chelating ability and flexibility. Once obtained following multi-step protocols, the new proligands $\{I^A\}H$ and $\{AdAm\}H$ were applied to the synthesis of the corresponding heteroleptic barium complexes. The ancillary ligands were combined with the $Ae\cdots Si-H$ β -anagostic interactions provided by the $N(SiMe_2H)_2^-$ amido group; this led to the eventual stabilization of the unsolvated barium heteroleptic complexes $[\{I^A\}BaN(SiMe_2H)_2]$ (**10**) and $[\{AdAm\}BaN(SiMe_2H)_2]$ (**11**, Scheme B).



Scheme B. New bidentate proligands and their related heteroleptic barium complexes.

The molecular structures of these complexes were characterized by spectroscopic and X-ray diffraction analyses. The analytic data and the molecular solid-state structure of the complexes, indicate the contribution of β - $Si-H\cdots Ba$ anagostic interactions towards the coordinative saturation of the metal. ^1H NMR spectroscopy showed that these anagostic interactions also persist in solution ($^1J_{Si-H}$ coupling constant = 162 Hz (**10**), 160 Hz (**11**)). The solid-state FTIR spectra showed two stretching bands for $Si-H$ bonds for **10** (2052 and 1990 cm^{-1}) and **11** (2014 and 1975 cm^{-1}) that are in agreement with the data derived from the solid state structure related to $Ba\cdots H-Si$ anagostic interactions. Considering the oxophilic nature of barium, the absence of thf in the structure of complex $[\{I^A\}BaN(SiMe_2H)_2]$ (**10**) is remarkable, because it has

been prepared from the thf-containing barium precursor ($[\text{Ba}\{\text{N}(\text{SiMe}_2\text{H})_2\}_2(\text{thf})_2]$). The aza-crown-ether provides four Ba–O contacts and takes the role instead of the solvent.

The performances of complexes **10** and **11** in the benchmark hydrophosphination of styrene and HPPH_2 were evaluated. Both precatalysts demonstrated slightly higher activities ($\text{TOF} = 5.2 \text{ h}^{-1}$ for **10** and 4.9 h^{-1} for **11**) compared to the previous reported results of the solvent-adduct barium complex $[\{\text{N}^{\text{DiPP}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)\}(\text{thf})_2]$ ($\text{TOF} = 3.2 \text{ h}^{-1}$), along with complete anti-Markovnikov regioselectivity. While the synthesis of complexes **10** and **11** is challenging due to the multistep preparation of the ligand, they are more effective (better conversion and reaction rate) in hydrophosphination catalysis compared to the previously reported barium complex $[\{\text{N}^{\text{DiPP}}\}\text{Ba}\{\text{N}(\text{SiMe}_3)\}(\text{thf})_2]$.⁹ The phosphide $[\{\text{I}^{\text{Acrown}}\}\text{BaPPh}_2]$ (**13**) has been isolated as a small crop of crystals and characterized by X-ray analysis during these studies; it represents the first heteroleptic barium-phosphide complex reported in the literature (Figure E).

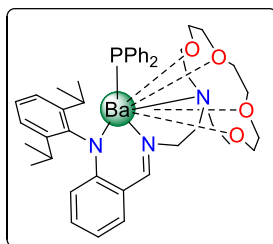


Figure E. Structure of heteroleptic barium-phosphide complex $[\{\text{I}^{\text{Acrown}}\}\text{BaPPh}_2]$ (**13**).

The formation of the mononuclear complex **13** occurs under catalytic conditions after deprotonation of diphenylphosphine which is relatively acidic ($\text{p}K_{\text{a}}(\text{DMSO}) = 21.7$),¹² concomitantly to the release of $\text{HN}(\text{SiMe}_2\text{H})_2$. This shows that the $\{\text{I}^{\text{Acrown}}\}^-$ ligand could give enough stability to the barium phosphide **13**. According to the formation of crystals of complex **13** during catalysis, it could be surmised that this complex constitutes the in-cycle active catalytic species. Furthermore, based on the generation of the anti-Markovnikov product in the catalytic reaction, it involves the 2,1-insertion of the polarized $\text{C}^{(\delta-)}=\text{C}^{(\delta+)}$ double bond into the $[\text{Ba}]\text{--PPh}_2$ bond of **13**.

In hydrophosphination reaction of equimolar amounts of styrene and phenylphosphine ($[\text{styrene}]_0/[\text{PhPH}_2]_0/[\textbf{10}]_0 = 50:50:1$), complex **10** also proved to be chemoselective toward the *secondary* phosphine. According to the ^1H and ^{31}P NMR spectra, it affords selectively the

secondary phosphine PhPHCH₂CH₂Ph with minimal formation of the tertiary phosphine PhP(CH₂CH₂Ph)₂ (*sec*-P/*tert*-P > 94:6%). Under identical experimental conditions, the performance of **10** (93% conversion, TOF = 47 h⁻¹) was even better than the previous activities reported by our group from the divalent rare-earth precatalysts [$\{\text{LO}^3\}\text{YbN}(\text{SiMe}_3)_2$] (TOF = 37 h⁻¹, *sec*-P/*tert*-P = 97:3 %, 74% conversion) and [$\{\text{LO}^3\}\text{SmN}(\text{SiMe}_3)_2$] (TOF = 32 h⁻¹, *sec*-P/*tert*-P = 97:3%, 63% conversion) supported by the multidentate aminoetherphenolate $\{\text{LO}^3\}^-$ ($\{\text{LO}^3\}\text{H} = (2-\{(1,4,7,10\text{-tetraoxa-13-azacyclopentadecan-13-yl)-methyl}\}-4,6\text{-di-}i\text{-tert-butylphenol})$).¹³ The results obtained with barium complex **10** show higher conversion and TOF value compared to the ones achieved with Yb and Sm complexes, albeit with a slight less chemoselectivity toward the production of the *secondary* phosphine.

We investigated the preparation of the unsymmetrical *tert*-phosphine using *p*-Cl and *p*-^tBu-substituted styrenes ([PhPH₂]₀/[*p*-Cl-styrene]₀/[*p*-^tBu-styrene]₀/[**10**]₀ = 25:25:25:1). According to the literature, these substrates showed the best and the poorest reactivity in hydrophosphination reactions, respectively. Unfortunately, these attempts remained unsuccessful and resulted in the formation of the unsymmetrical product (PhP(CH₂CH₂-C₆H₄-*p*-Cl)(CH₂CH₂-C₆H₄-*p*-tBu) = M₁) together with the two symmetrical *tert*-phosphines of (PhP(CH₂CH₂-C₆H₄-*p*-Cl)₂ = M₂) and (PhP(CH₂CH₂-C₆H₄-*p*-^tBu)₂ = M₃) in a 6:2.5:1 ratio, as observed by ³¹P NMR spectroscopy. There is a competition between the formation of M₁ and M₂ but the rate of the reaction is higher toward M₁. The formation of M₃ is not favored. In order to prepare selectively unsymmetrical *tertiary* phosphines, two strategies can be envisioned: (i) the sequential addition of the distinct styrene derivatives to the reaction mixture (starting from addition of *p*-^tBu-substituted styrene), or (ii) identification of the appropriate pair(s) of substrates that give(s) the proper reactivity rates to our barium catalyst. Based on the study with [$\{\text{LO}^3\}\text{YbN}(\text{SiMe}_3)_2$] complex¹⁴ (yet considering the higher activity of our Ba complex), a suitable pair could be *p*-bromostyrene (less reactive than *p*-Cl-styrene derivative) and *p*-^tBu-styrene.

Our new barium complexes **10** and **11** showed rewarding results in hydrophosphination reactions. The preparation of heavy Ae analogues (Ca, Sr) could be informative. There are still many items to explore such as hydroamination reactions. Previously barium and calcium complexes have shown the highest catalytic activity for intermolecular and intramolecular hydroamination respectively. Beside the catalyst stability and reactivity, the most important issue

of hydroamination and hydrophosphination reactions is the stabilization of the transition state. Considering the required application to activated olefins substrates, catalysts which are active also in the reactions involving non-activated substrates are highly desirable. Ae-mediated hydroamination and cross-dehydrocoupling are very important reactions from the catalytic point of view and they have been separately performed with remarkable results. The combination of these two types of catalytic reactions in a one-pot condition, in order to catalyze the bond formation (namely C–N and Si–N), could represent applications of the new barium heteroleptic complexes.

From a general point of view, the collective results gathered in this PhD thesis demonstrate that secondary interactions ($\text{Ae} \cdots \text{F}-\text{C}$ and $\text{Ae} \cdots \text{Si}-\text{H}$ β -anagostic interactions) can be effective in providing low coordinate and/or reactive Ae complexes. Less crowded and non-aggregated complexes are not easy to access and the investigations based on both families of proligands (including the fluoroarylamides and crown-ether functionalized *N*-based ligands) have been performed bearing this idea in mind. The fluorinated arylamido complexes revealed an easy and efficient method for preparation of the stable, solvent-free calcium complexes with low nuclearity.

The balance between stability and reactivity of the catalyst during the catalytic cycle are of great importance and challenging. The new iminoanilide and amidinate proligands ($\{\text{I}^{\text{crown}}\}\text{H}$ and $\{\text{AdAm}^{\text{crown}}\}\text{H}$) are capable of realizing this important characteristic to the related barium complexes. The newly designed *N*-based ancillary ligands **10** and **11** open a large area of possibilities. They could be used for anionic alkene polymerization.¹⁵ The challenging synthetic target of Ae hydrides could also be considered. However, this would require some modifications to the ligand (Figure F). In fact, the imine function ($\text{CH}=\text{N}$) of complexes **10** and **11** would be sensitive to nucleophilic attack from the generated Ba–H and lead to self-decomposition. The introduction of a bulky group at the imine carbon or the use of analogue but more robust groups ($\text{R}_2\text{P}=\text{N}$) could potentially lead to stable hydride species. (Figure F).

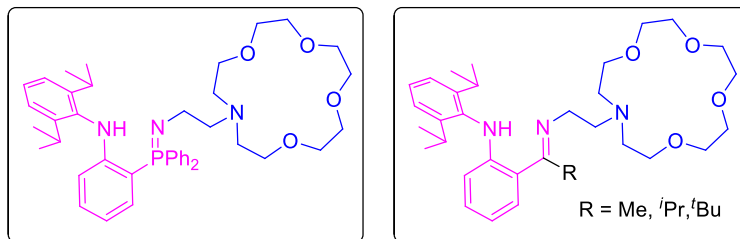


Figure F. Potential modifications to protect the imine function in the ligand structure.

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**Métaux alcalino-terreux: Chimie de coordination
et applications catalytiques**

Chimie de coordination des métaux alcalino-terreux: Synthèse et application en catalyse

L'objectif principal de cette thèse était la synthèse de nouvelles classes de complexes alcalino-terreux stabilisés par des ligands ancillaires et / ou des interactions secondaires, ainsi que l'évaluation de leur performance dans des processus de catalyse homogène, notamment dans les réactions d'hydrophosphination.

1. Introduction

La chimie organométallique des métaux alcalino-terreux lourds s'est principalement inspirée des travaux de Victor Grignard sur la chimie du magnésium en 1900. La chimie des métaux alcalino-terreux (Ae = Ca, Sr, Ba) est intéressante car ces métaux sont relativement moins nocifs pour l'homme, respectueux de l'environnement et présentent des avantages économiques (relativement peu coûteux et facilement accessibles) par rapport aux métaux de transition de la droite. Généralement, la haute réactivité des complexes Ae est liée à leur électropositivité élevée, leur grands rayons ioniques et à leurs facultés de former des liaisons ioniques (Figure A).^{1,2,3}

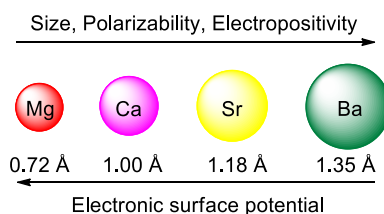


Figure A. Variation des rayons ioniques des ions du groupe 2, Ae^{2+} .

Au cours des deux dernières décennies, la chimie organométallique des métaux Ae s'est développée rapidement, principalement en raison de leur énorme potentiel en catalyse homogène de réactions de polymérisation (par exemple des esters cycliques⁴ et des styrènes⁵), de réactions d'hydroélémentation (hydroamination,⁶ hydrophosphination,⁷ hydrosilylation,⁸ hydroboration⁹ et hydrogénation¹⁰) et de réactions de couplage déshydrogénant¹¹. Les complexes hétéroleptiques Ae du type $[\{Ln\} AeR]$ (Ln = ligand monoanionique ancillaire, R = groupe réactif nucléophile monoanionique et / ou réactif basique) sont non seulement très sensibles à l'air et à l'humidité (réaction du métal avec l'oxygène ou l'eau donnant des oxydes ou hydroxydes), mais ils peuvent

également être désactivés en solution par des réactions de redistribution des ligands, nommées équilibre de Schlenk. L'équilibre de Schlenk conduit à la formation du mélange thermodynamiquement plus stable correspondant les espèces homoleptiques $[\{Ln\}_2Ae]$ et $[AeR_2]$ (Schéma A). La propension des complexes Ae à s'engager dans les équilibres de Schlenk augmente en descendant dans le groupe 2 ($Mg < Ca < Sr < Ba$) du fait de la taille et de l'électropositivité du centre métallique. En effet, à mesure que la taille du métal augmente, la force de liaison Ae-ligand diminue et l'échange de ligands devient plus difficile à contrôler. D'autres paramètres affectent la probabilité de cette redistribution, notamment la température, la concentration, la nature du solvant et du ligand.

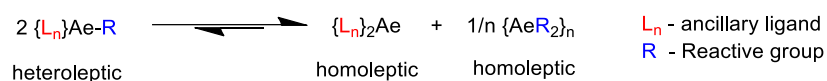


Schéma A. Redistribution des ligands des complexes Ae hétéroleptiques cinétiquement labiles, connus sous le nom d'équilibre de Schlenk

Afin de surmonter les problèmes d'échange de ligands des complexes hétéroleptiques Ae en solution, différentes stratégies ont été proposées. Dans les complexes hétéroleptiques Ae du type $[\{Ln\}AeR]$, le coligand (R) est généralement un groupe $N(SiMe_3)_2^-$, $N(SiMe_2H)_2^-$ ou $CH(SiMe_3)_2^-$ volumineux qui assure une protection stérique, stabilise la charge négative, affaiblie la nucléophilie et améliore la solubilité du complexe dans les solvants hydrocarbonés. Ce coligand correspond également à la partie réactive du précatalyseur initial dans les cycles catalytiques. Selon le caractère ionique des métaux Ae, les approches synthétiques mises en œuvre pour surmonter l'équilibre de Schlenk reposent sur des effets stériques (stabilité cinétique) en utilisant des ligands volumineux et / ou une stabilisation électronique (effet thermodynamique) via la coordination intramoléculaire des hétéroatomes liés.

En raison de leur faible rapport charge / taille et d'une carence en électrons, les métaux Ae lourds ont une forte tendance à former des structures oligonucléaires agrégées. Un remède courant est l'utilisation de ligands qui pourraient fournir des interactions secondaires / non covalentes (y compris les interactions (a) $M \cdots C\pi$,¹² (b) $M \cdots H-R$ ($R = Si, C$),¹³ et (c) $M \cdots F-C$ ¹⁴) pour saturer la sphère de coordination du centre métallique et donc réduire la nucléarité de la structure finale. Cependant, les interactions secondaires sont plus faibles que les interactions primaires covalentes car elles n'impliquent aucun partage d'électrons.

2. Fluoroarylamides alcalino-terreux de faible coordination contenant des interactions secondaires $Ae \cdots F-C$

Dans la première partie de ce manuscrit, nous avons présenté la synthèse et la caractérisation de plusieurs complexes Ae homoleptiques et hétéroleptiques contenant des ligands arylamides fluorés: $N(C_6F_5)_2^-$ et $N(o-F-C_6H_4)_2^-$. Les complexes obtenus, à savoir $[Ca\{N(C_6F_5)_2\}_2.(Et_2O)_2]$ (**1'**), $[Ba\{\mu-N(C_6F_5)_2\}\{N(C_6F_5)_2\}.toluene]_2$ (**2**), $[Ca\{\mu^2-N(SiMe_3)_2\}\{N(C_6F_5)_2\}]_2$ (**3**), $[\{BDI^{DiPP}\}CaN(C_6F_5)_2]_2$ (**4**), $[\{N^{\wedge}N^{DiPP}\}CaN(C_6F_5)_2]_2$ (**5**), $[Ca\{\mu-OB(CH(SiMe_3)_2)_2\}\{N(C_6F_5)_2\}]_2$ (**6**), et $[\{BDI^{DiPP}\}Ca\{N(o-F-C_6H_4)_2\}.(thf)]$ (**9**) (Schéma B), se sont révélés stables vis-à-vis de la redistribution des ligands en solution. Conformément à nos hypothèses initiales, les données cristallographiques ont indiqué que non seulement la coordination des hétéroatomes N et O des ligands est responsable de la stabilisation des complexes, mais qu'également les interactions secondaires inter- et intramoléculaires $Ae \cdots F-C$ contribuent à un effet stabilisant supplémentaire.

Une première série de complexes a été préparée en utilisant l'arylamine hautement fluorée $HN(C_6F_5)_2$. Nous avons d'abord isolé l'adduit solvaté du complexe de calcium homoleptique $[Ca\{N(C_6F_5)_2\}_2.(Et_2O)_2]$ (**1'**) qui présente deux interactions intramoléculaires $Ca \cdots F-C$ (2.493(1) et 2.523(1) Å). Les longueurs des liaisons $Ca-N_{C_6F_5}$ de **1'** (2.370(1) et 2.380(1) Å) sont sensiblement plus longues que celles correspondantes en $[Ca\{N(SiMe_3)_2\}_2.(thf)_2]_2$ (2.294(3) et 2.309(3) Å). Cela reflète la plus grande électro-attractivité du groupement $N(C_6F_5)_2^-$ combinée à l'effet stérique des groupes (C_6F_5) par rapport à $(SiMe_3)$. Un complexe de calcium hétéroleptique non solvaté $[Ca\{\mu^2-N(SiMe_3)_2\}\{N(C_6F_5)_2\}]_2$ (**3**) a également été obtenu. Au total, en tenant compte de la limite maximale acceptée pour les contacts $Ca \cdots F-C$ (3.13 Å),¹⁵ les distances de liaison entre le centre métallique et les atomes de fluor sont remarquablement courtes (par exemple pour le complexe **3**: distances $Ca-F$ de 2.423(2) et 2.456(2) Å, Tableau A) et sont comparables aux valeurs obtenues par le groupe de Hill dans une précédente étude pour le complexe homoleptique bis(amido) de calcium avec des substituants CF_3 dans le squelette (distances $Ca-F$ = 2.489(3) et 2.46 8(2) Å).^{14a}

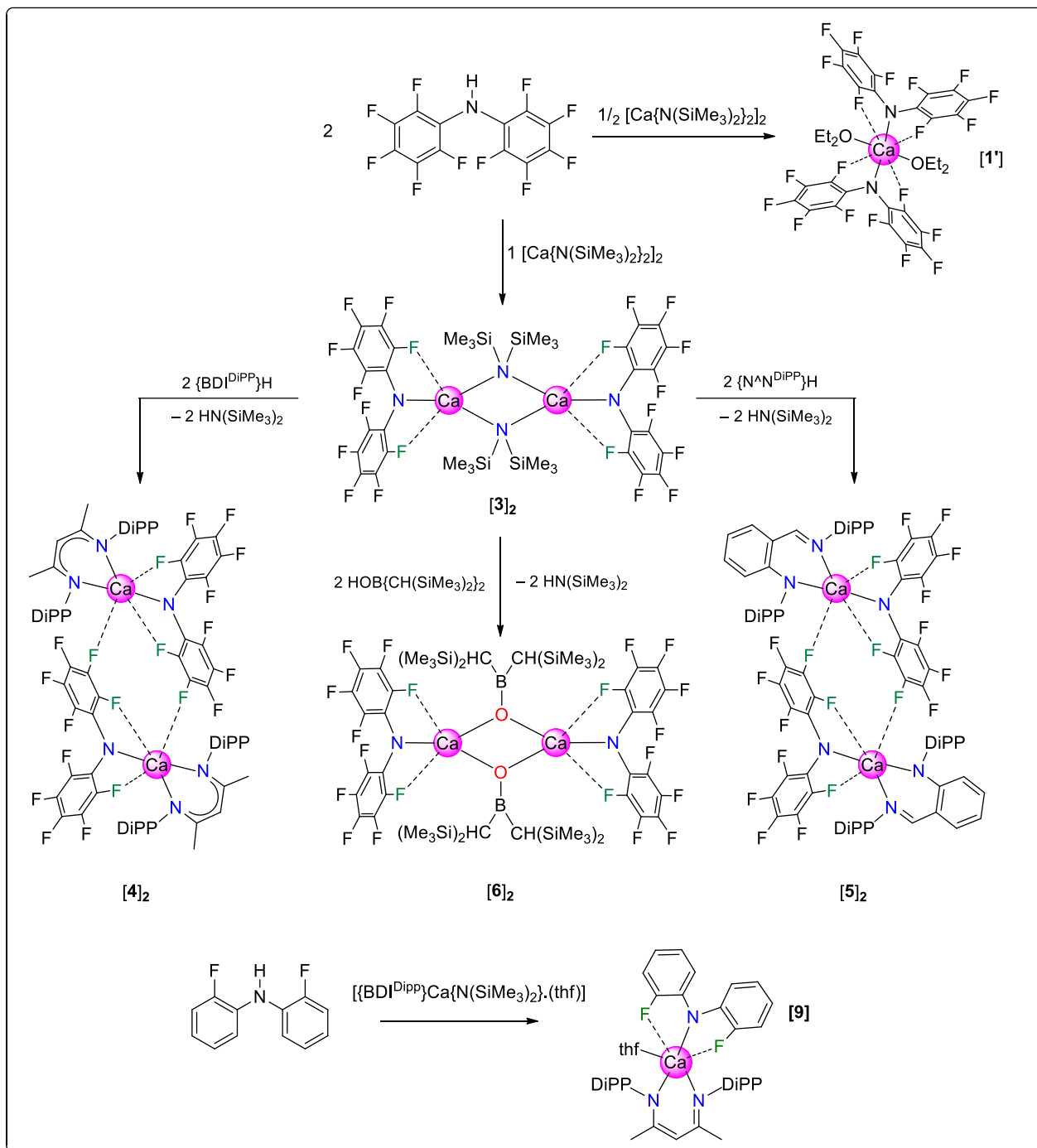


Schéma B. Complexes de calcium homoleptiques et hétéroleptiques synthétisés dans ce travail, présentant des interactions secondaires $\text{Ca} \cdots \text{F}-\text{C}$ ($\text{DiPP} = 2,6\text{-}i\text{Pr}_2\text{-C}_6\text{H}_3$).

Les complexes hétéroleptiques apparentés $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**4**₂) et $[\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**5**₂) ont ensuite été obtenus à partir de la réaction de $[\text{Ca}\{\mu^2\text{-N}(\text{SiMe}_3)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**3**₂) avec deux proligands *N*-donneurs, ($\{\text{BDI}^{\text{DiPP}}\}\text{H}$ et $\{\text{N}^{\wedge}\text{N}^{\text{DiPP}}\}\text{H}$) (Schéma B). Dans une étude précédente, ces proligands se sont révélés très utiles pour la préparation de complexes de calcium stables. Ces deux complexes hétéroleptiques sont tous deux des dimères à l'état solide moléculaire, le $\text{N}(\text{C}_6\text{F}_5)_2^-$ reliant les centres métalliques par des interactions secondaires intermoléculaires $\text{Ca}\cdots\text{F}-\text{C}$. Il s'agit d'une méthode plus simple pour obtenir des complexes de calcium hétéroleptiques stables et sans solvant, contrairement aux voies de synthèse plus difficiles pour d'autres composés de faible coordinance exempts de solvant, tels que le composé bien connu $[\{\text{BDI}\}\text{CaN}(\text{SiMe}_3)_2]$.

Récemment, dans notre groupe, nous avons isolé de nouveaux complexes de baryum homoleptiques et hétéroleptiques en utilisant l'acide borinique *O*-donneur $\text{HOB}\{\text{CH}(\text{SiMe}_3)_2\}_2$.^{16,17} La structure du dimère hétéroleptique de baryum $[\text{Ba}\{\mu\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2$, déterminée par diffraction des rayons X, montre le $\text{N}(\text{SiMe}_3)_2^-$ pontant, ce qui est en accord avec nos attentes. La délocalisation partielle des électrons de l'oxygène dans l'orbitale p_z vide du bore dans le boryloxyde réduit la densité électronique sur l'oxygène et diminue sa propension à agir comme un atome pontant. Nous avons exploré l'effet de l'encombrement stérique et de la délocalisation des paires isolées d'oxygène dans l'orbitale $2p_z$ vacante du bore dans le ligand $\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2^-$ combinée avec les interactions secondaires potentielles $\text{Ae}\cdots\text{F}-\text{C}$ des fluoroarylamides. L'acide borinique $\text{HOB}\{\text{CH}(\text{SiMe}_3)_2\}_2$ a été utilisé ici comme proligand pour préparer le premier exemple de boryloxyde de calcium, à savoir $[\text{Ca}\{\mu\text{-OB}(\text{CH}(\text{SiMe}_3)_2)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}]_2$ (**6**₂) (Figure B, Schéma B).¹⁸ La structure à l'état solide de ce composé montre le $(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)^-$ en position de pontage, ce qui est différent des observations mentionnées ci-dessus sur le composé $([\text{Ba}\{\mu\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)]_2)$.

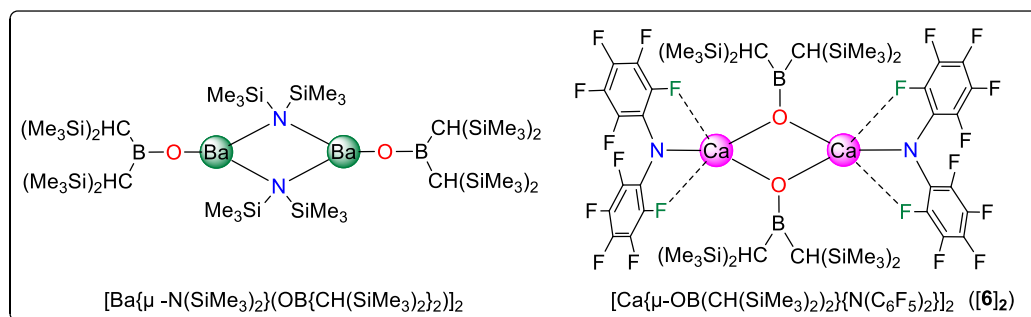


Figure B. Complexes hétéroleptiques de calcium et de baryum contenant le ligand $\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2^-$: $[\text{Ca}\{\mu\text{-OB}(\text{CH}(\text{SiMe}_3)_2)_2\}\{\text{N}(\text{C}_6\text{F}_5)_2\}_2]_2$ (**6**₂) and $[\text{Ba}\{\mu\text{-N}(\text{SiMe}_3)_2\}(\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2)_2]$.

La comparaison des structures moléculaires à l'état solide des complexes binucléaires **3**₂ et **4**₂ montre la tendance suivante dans la formation de ponts (donneur d'électrons) des ligands monoanioniques apparentés: $\text{N}(\text{C}_6\text{F}_5)_2^- < \text{N}(\text{SiMe}_3)_2^-$ (Figure C). Cela pourrait être basé sur la densité électronique disponible sur les atomes d'azote de ces ligands qui permettent le pontage du centre métallique. La comparaison des complexes **3**₂ et **6**₂ révèle la tendance $\text{N}(\text{C}_6\text{F}_5)_2^- < \text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2^-$ dans les propriétés électrodonneuse des deux ligands (Figure C).

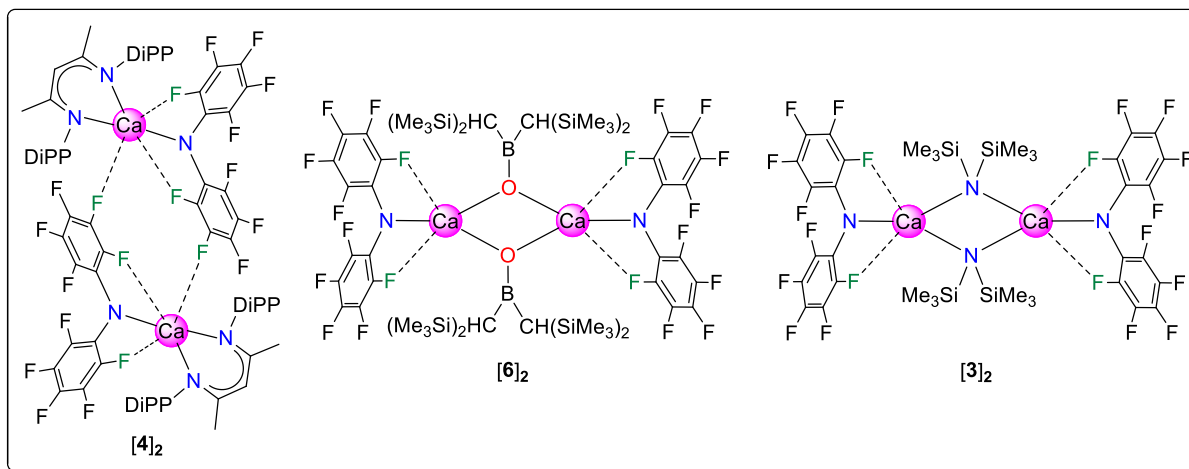


Figure C. Structure moléculaire à l'état solide des complexes **3**₂, **4**₂, and **6**₂.

Les calculs DFT précédents ont révélé la capacité de pontage de $\text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2^- < \text{N}(\text{SiMe}_3)_2^-$. Par conséquent, la considération de tous les résultats conduit à la tendance suivante $\text{N}(\text{C}_6\text{F}_5)_2^- < \text{OB}\{\text{CH}(\text{SiMe}_3)_2\}_2^- < \text{N}(\text{SiMe}_3)_2^-$ parmi ces trois ligands. La présence des atomes de fluor attracteurs d'électrons sur les cycles aromatiques du ligand $\text{N}(\text{C}_6\text{F}_5)_2^-$ réduit

considérablement la capacité du fluoroarylamide à ponter les centres calciques (Figure C). Ces résultats seront utiles pour la conception future de complexes métalliques Ae basés sur ces ligands monoanioniques monodentés.

Afin d'étudier l'influence du nombre d'atomes électro-attracteurs sur les propriétés de coordination des fluoroarylamides, l'arylamine monofluorée $\text{HN}(o\text{-F-C}_6\text{H}_4)_2$ a été utilisée à la place de celle perfluorée ($\text{HN}(\text{C}_6\text{F}_5)_2$). Avec seulement deux atomes de fluor en position *ortho*, $\text{HN}(o\text{-F-C}_6\text{H}_4)_2$ est moins encombré stériquement que $\text{HN}(\text{C}_6\text{F}_5)_2$, et a également moins d'atomes de fluor électro-attracteurs, ce qui augmente la basicité comparative de l'amine. La cristallisation infructueuse du complexe non solvate $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(o\text{-F-C}_6\text{H}_4)_2\}]$ (**8**) nécessite un examen plus approfondi; il serait très utile d'étudier la seule influence de l'interaction secondaire $\text{Ca}\cdots\text{F}-\text{C}$. Nous avons ensuite réussi à synthétiser et à caractériser le complexe solvate $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(o\text{-F-C}_6\text{H}_4)_2\}.\text{(thf)}]$ (**9**). L'analyse par diffraction des rayons X montre un complexe de calcium avec deux interactions intramoléculaires $\text{Ca}\cdots\text{F}-\text{C}$ provenant du ligand $\text{N}(o\text{-F-C}_6\text{H}_4)_2^-$.

Le complexe hétéroleptique de calcium $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2.\text{(thf)}]$ (**I**) a été étudié par Hill en tant que précatalyseur efficace pour les réactions d'hydroélémentation telles que l'hydrophosphination du styrène avec la diphenylphosphine.⁷ En raison de l'étroite similitude de nos nouveaux complexes fluorés neutres $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**4**₂) et $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(o\text{-F-C}_6\text{H}_4)_2\}.\text{(thf)}]$ (**9**) avec ce complexe, leurs activités ont été évaluées dans la réaction d'hydrophosphination de référence ($[\text{styrène}]_0/[\text{Ph}_2\text{PH}]_0/[\text{precat}]_0 = 10:10:1$, 60 °C, 12 h, 10% molaire de précatalyseur (Schéma C).

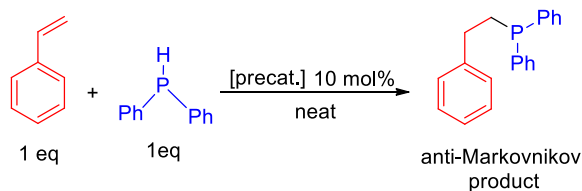


Schéma C. Hydrophosphination du styrène avec Ph_2PH favorisée par $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{C}_6\text{F}_5)_2]_2$ (**4**₂), $[\{\text{BDI}^{\text{DiPP}}\}\text{Ca}\{\text{N}(o\text{-F-C}_6\text{H}_4)_2\}.\text{(thf)}]$ (**9**) ou $[\{\text{BDI}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2.\text{(thf)}]$ (**I**).

Une régiospécificité anti-Markovnikov complète a été observée, produisant exclusivement de la phosphine tertiaire linéaire (PhCH₂CH₂)PPh₂. Ces précatalyseurs ont montré de meilleures activités (TOF = 0.7 h⁻¹ pour **4₂** et 0.8 h⁻¹ pour **9**) par rapport au complexe de référence de Hill [{BDI^{DiPP}}CaN(SiMe₃)₂.(thf)] (**I**) (TOF = 0.5 h⁻¹), dans des conditions de réaction plus douces, notamment une température plus basse et un temps de réaction plus court (60 °C vs 75 °C et 12 h vs 20 h). Par conséquent, ces composés fluorés originaux représentent des ajouts précieux à une liste limitée de complexes qui catalysent efficacement ces réactions d'hydrophosphination intermoléculaires.

Les calculs DFT effectués sur les complexes fluorés, en particulier **1'**, **3₂**, **4₂**, **6₂**, **9** ont suggéré des structures moléculaires en accord avec les observations expérimentales et ont indiqué qu'en raison de la charge positive élevée de Ca²⁺, la nature des interactions Ae···F–C est principalement constituée de contributions électrostatiques avec seulement un faible caractère covalent. La comparaison des équivalents fluorés et non fluorés par analyse de décomposition énergétique (EDA) a indiqué que l'interaction Ca···F–C prévaut sur les deux autres types d'interactions secondaires (Ca···H–C et Ca···C(π)). Les distances Ca···F–C des structures fluorées résultantes sont rassemblées dans le Tableau A.

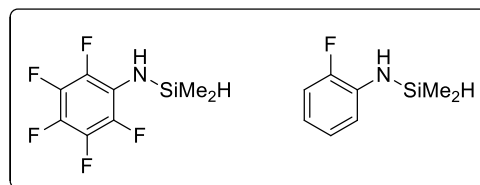
Ces paramètres métriques indiquent de courtes distances entre le centre métallique et les atomes de fluor se traduisant par de fortes interactions (par exemple 2.423(2) Å en **3₂**) par rapport à celles plus fortes rapportées dans la littérature. Les interactions Ae···F–C ont déjà été appliquées en combinaison avec d'autres interactions secondaires (comme les interactions β-anagostiques Ae···C(π) et Ae···H–Si; e.g. [{RO¹²}CaN(SiMe₂H)₂]₂)¹² ou des contacts supplémentaires (par exemple, contacts avec un ligand macrocyclique donnant des hétéroatomes [{RO³}Ae]₂⁺.2[H₂N{B(C₆F₅)₃]₂]⁻) pour fournir une structure stable.¹⁹

Table A. Résumé des interactions secondaires Ca $\cdots$ F–C pour les complexes **1'**, **3₂**, **4₂**, **5₂**, **6₂**, **9**.

Complexe	Nucléarité	Ca $\cdots$ F			
[Ca{N(C ₆ F ₅) ₂ } ₂ .(Et ₂ O) ₂] (1')	Monomeric	2.4935(10) ^a	2.5226(10) ^a	2.7713(11) ^a	3.0740(12) ^a
[Ca{μ ² -N(SiMe ₃) ₂ }{N(C ₆ F ₅) ₂ }] ₂ (3₂)	Dimeric	2.4227(18) ^a	2.4560(18) ^a	-	-
[{BDI ^{DiPP} }CaN(C ₆ F ₅) ₂] (4₂)	Dimeric	2.5559(15) ^a	2.7120(17) ^a	-	-
		2.5325(15) ^b	-	-	-
[{N ^{DiPP} }CaN(C ₆ F ₅) ₂] (5₂)	Dimeric	2.558(2) ^a	2.559(2) ^a	-	-
		2.530(1) ^b	-	-	-
[Ca{μ-OB(CH(SiMe ₃) ₂) ₂ }{N(C ₆ F ₅) ₂ }] ₂ (6₂)	Dimeric	2.544(2) ^a	2.597(2) ^a	2.498(2) ^a	2.553(2) ^a
[{BDI ^{DiPP} }Ca{N(<i>o</i> -F-C ₆ H ₄) ₂ }.(thf)] (9)	Monomeric	2.486(3) ^a	2.549(3) ^a	-	-

[a] Interaction secondaire intramoléculaire. [b] Interaction secondaire intermoléculaire.

Au cours de mes investigations, les interactions Ca $\cdots$ F–C se sont révélées décisives pour aboutir à la préparation de composés Ae stables, faiblement coordonnés et non solvatés. Afin d'exclure l'effet des atomes de fluor en présence d'autres interactions non covalentes telles que les interactions anagostiques Ae $\cdots$ Si–H β dans un complexe, la conception de nouveaux ligands serait utile. Par exemple, les arylamines fluorées avec la tétraméthylsilazade ont le potentiel de fournir des interactions combinées Ae $\cdots$ F–C et Ae $\cdots$ Si–H β-anagostiques (Figure D).

**Figure D.** Exemple de prolégands d'amine ayant un potentiel d'interactions secondaires combinées Ae $\cdots$ Si–H et Ae $\cdots$ F–C.

Les nouveaux composés de calcium isolés ont montré une réactivité élevée dans les réactions d'hydrophosphination qui est l'une des réactions d'hydroélémentation les plus difficiles. Ainsi, les complexes analogues lourds d'Ae pourraient être préparés, du fait de l'augmentation de la réaction avec la taille du centre métallique. Les arrangements des interactions secondaires Ae $\cdots$ F–C pourraient différer entre les analogues Ae selon la taille du métal, y compris la

présence d'interactions inter- et intramoléculaires et la nucléarité des complexes. Par exemple, le baryum nécessite plus de contacts avec le ligand, et il peut y avoir plus d'interactions intramoléculaires dans l'analogue de baryum des complexes **4**₂ et **5**₂. En outre, l'obtention de complexes stables de strontium et de baryum analogues des complexes de calcium **4**₂ et **9** (avec squelette BDI) pourrait être très intéressant, car les complexes [$\{\text{BDI}\}\text{AeN}(\text{SiMe}_3)_2(\text{thf})$] ne sont pas stables en solution pour Sr et Ba. Nous pourrions également poursuivre les investigations catalytiques. Les complexes de baryum ont révélé d'excellents résultats dans les réactions d'hydrophosphination. Par conséquent, la préparation d'analogues de baryum de complexes tels que **4**₂ et **9** pourrait être suivie d'intéressantes expériences catalytiques dans ce domaine telles que l'hydrosilylation et l'hydrogénation par transfert d'alcène.^{10d}

3. Complexes hétéroleptiques de baryum supportés par des ligands à base N fonctionnalisés par une éther couronne et leur application pour l'hydrophosphination des vinylarènes

Comme la nature ionique de la liaison dans les complexes Ae augmente avec les métaux descendants du groupe 2, la tendance à l'échange des ligands augmente avec le rayon ionique ($\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$), ce qui implique que la préparation de complexes hétéroleptiques stables de baryum [$\{\text{L}\}\text{Ba}-\text{R}$] (où $\{\text{L}\}$ est un ligand ancillaire monoanionique et R est le co-ligand réactif) est difficile. D'autre part, la vitesse de réaction dans la réaction d'hydroamination et d'hydrophosphination intermoléculaire augmente avec la taille du centre métallique. Par conséquent, dans la deuxième partie de mes recherches, la possibilité de stabiliser un complexe hétéroleptique de baryum en utilisant des ligands ancillaires multidentates couplés avec des interactions anagostiques $\text{Ae}\cdots\text{Si}-\text{H}$ β -anagostiques, a été explorée. En ce qui concerne la chimie des Ae lourds, l'iminoanilide à base d'azote ($[\{\text{N}^{\text{DiPP}}\}\text{AeN}(\text{SiMe}_3)_2(\text{thf})_n]$ (Ae = Ca, $n = 1$; Sr, $n = 2$; Ba, $n = 2$)⁶ et les ligands de type amidinate (tels que $[\{\text{RAm}^{\text{DiPP}}\}\text{CaN}(\text{SiMe}_3)_2]$ (Am = amidinate, R = ^tBu, Ad)²⁰ et $[\{p\text{-TolAm}^{\text{Ar}^\ddagger}\}\text{SrN}(\text{SiHMe}_2)_2]$ ($\text{Ar}^\ddagger = 2,6\text{-Ph}_2\text{CH-4-}i\text{Pr-phenyl}$)²¹) ont fourni des structures hétéroleptiques stables. Afin d'explorer de nouvelles possibilités dans la création de complexes de baryum cinétiquement stables et catalytiquement efficaces, nous avons conçu de nouveaux ligands auxiliaires N-donneurs volumineux, comprenant un bras latéral macrocyclique en éther couronne combinant une forte capacité de chélation avec une haute flexibilité. Une fois obtenus par synthèse multi-étapes, les nouveaux prolégands $\{\text{I}^{\text{A}^{\text{crown}}}\}\text{H}$ et

$\{\text{AdAm}^{\text{crown}}\}\text{H}$ ont été utilisés pour la synthèse des complexes de baryum hétéroleptiques correspondants. Les ligands auxiliaires ont été combinés avec les interactions $\text{Ae}\cdots\text{Si-H}$ β -anagostiques fournies par le groupe amidure $\text{N}(\text{SiMe}_2\text{H})_2^-$; cela a conduit à la stabilisation des complexes hétéroleptiques de baryum non solvatés $[\{\text{I}^{\text{A}^{\text{crown}}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**) et $[\{\text{AdAm}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**11**, Schéma D).

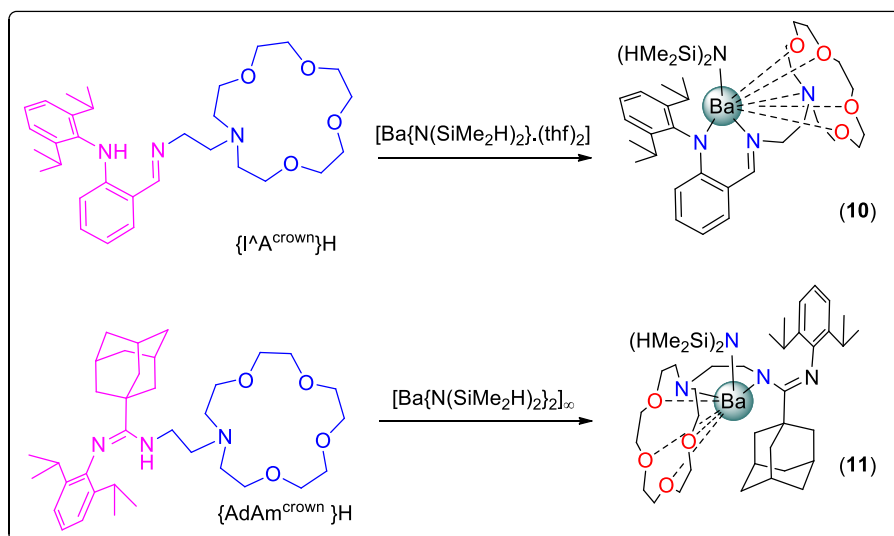


Schéma D. Nouveaux prolégands bidentés et leurs complexes de baryum hétéroleptiques apparentés.

Les structures moléculaires de ces complexes ont été caractérisées par des analyses spectroscopiques et de diffraction des rayons X. Les données analytiques et la structure moléculaire à l'état solide des complexes indiquent une contribution des interactions anagostiques $\beta\text{-Si-H}\cdots\text{Ba}$ à la saturation coordonnée du métal. La spectroscopie RMN ^1H a montré que ces interactions anagostiques persistent également en solution (constante de couplage $^1J_{\text{Si-H}} = 162 \text{ Hz}$ (**10**), 160 Hz (**11**)). Les spectres FTIR à l'état solide ont montré deux bandes d'élongation pour les liaisons Si-H pour **10** (2052 et 1990 cm^{-1}) et **11** (2014 et 1975 cm^{-1}) qui sont en accord avec les données dérivées de la structure à l'état solide liées aux interactions anagostiques $\text{Ba}\cdots\text{H-Si}$. Compte tenu de la nature oxophile du baryum, l'absence de thf dans la structure du complexe $[\{\text{I}^{\text{A}^{\text{crown}}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**) est remarquable, car il a été préparé à partir du précurseur de baryum solvaté au thf ($[\text{Ba}\{\text{N}(\text{SiMe}_2\text{H})_2\}_2 \cdot (\text{thf})_2]$). L'éther aza-couronne fournit quatre contacts Ba-O et joue le rôle du solvant.

Les performances des complexes **10** et **11** dans l'hydrophosphination de référence du styrène et du HPPH₂ ont été évaluées. Les deux précatalyseurs ont montré des activités légèrement plus élevées (TOF = 5.2 h⁻¹ pour **10** et 4.9 h⁻¹ pour **11**) par rapport aux résultats précédemment rapportés pour le complexe de baryum solvate [{N^{^N}DiPP} Ba {N(SiMe₃)(thf)₂ }] (TOF = 3.2 h⁻¹), ainsi qu'une régiospécificité anti-Markovnikov complète. Bien que la synthèse des complexes **10** et **11** soit difficile en raison de la préparation en plusieurs étapes du ligand, ils sont plus efficaces (meilleure conversion et vitesse de réaction) en catalyse d'hydrophosphination par rapport au complexe de baryum précédemment mentionné [{N^{^N}DiPP} Ba {N(SiMe₃)(thf)₂ }].⁶ Le phosphore [{I^{^A}crown} BaPPh₂] (**13**) a été isolé sous forme de quelques cristaux et caractérisé par analyse aux rayons X au cours de mes études; il représente le premier complexe hétéroleptique de phosphore de baryum rapporté dans la littérature (Figure E).

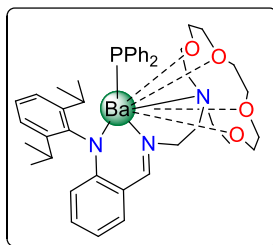


Figure E. Structure du complexe hétéroleptique de phosphore de [{I^{^A}crown} BaPPh₂] (**13**).

La formation du complexe mononucléaire **13** est produite dans des conditions catalytiques après déprotonation de la diphenylphosphine qui est relativement acide (pK_a (DMSO) = 21.7),²² provoquant simultanément la libération de HN(SiMe₂H)₂. Cela montre que le ligand {I^{^A}crown}⁻ pourrait apporter suffisamment de stabilité au phosphore de baryum **13**. Du fait de la formation de cristaux du complexe **13** pendant la réaction de catalyse, on pourrait supposer que ce complexe constitue l'espèce catalytique active en cours de cycle. De plus, basé sur la génération du produit anti-Markovnikov dans la réaction catalytique, il implique l'insertion 2,1 de la double liaison polarisée C^{(δ-)=C^(δ+)} dans la liaison [Ba]–PPh₂ de **13** (Schéma E).

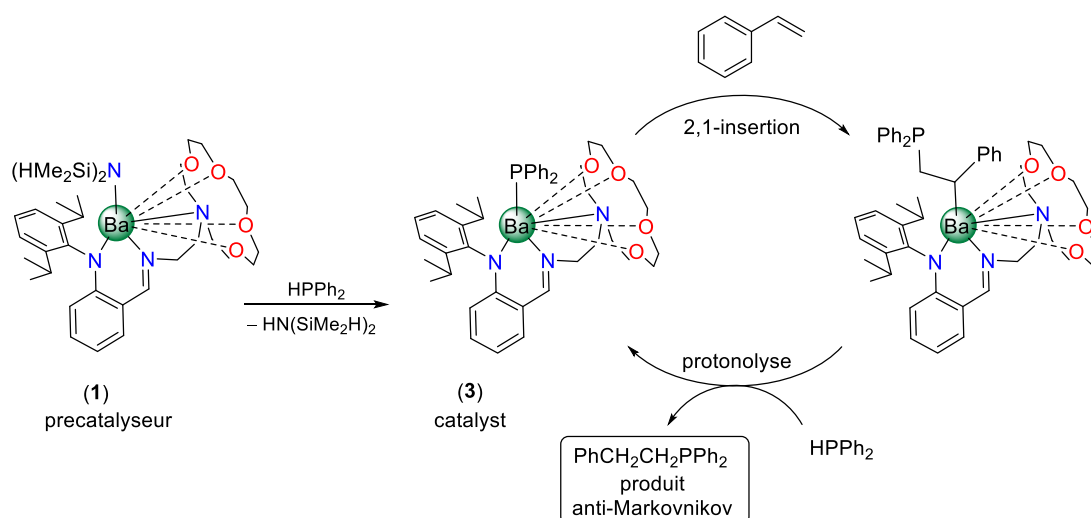


Schéma E. Mécanisme proposé pour l'hydrophosphination du styrène/ HPPh_2 catalysée par le complexe $[\{\text{I}^{\text{crown}}\}\text{BaN}(\text{SiMe}_2\text{H})_2]$ (**10**).

Dans la réaction d'hydrophosphination de quantités équimolaires de styrène et de phénylphosphine ($[\text{styrène}]_0/[\text{PhPH}_2]_0/[\textbf{10}]_0 = 50:50:1$), le complexe **10** s'est également révélé chimiosélectif envers la phosphine secondaire (Schéma F). Selon les spectres RMN ^1H et ^{31}P , il fournit sélectivement la phosphine secondaire $\text{PhPHCH}_2\text{CH}_2\text{Ph}$ avec une formation minimale de la phosphine tertiaire $\text{PhP}(\text{CH}_2\text{CH}_2\text{Ph})_2$ ($\text{sec-P}/\text{tert-P} > 94:6\%$). Dans des conditions expérimentales identiques, la performance de **10** (conversion de 93%, $\text{TOF} = 47 \text{ h}^{-1}$) était encore meilleure que les activités précédemment rapportées par notre groupe à partir de pré-catalyseurs de terres rares divalents $[\{\text{LO}^3\}\text{YbN}(\text{SiMe}_3)_2]$ ($\text{TOF} = 37 \text{ h}^{-1}$, $\text{sec-P}/\text{tert-P} = 97:3\%$, 74% de conversion) et $[\{\text{LO}^3\}\text{SmN}(\text{SiMe}_3)_2]$ ($\text{TOF} = 32 \text{ h}^{-1}$, $\text{sec-P}/\text{tert-P} = 97:3\%$, 63% de conversion) supporté par multidentate l'aminoétherphénolate $\{\text{LO}^3\}^-$ ($\{\text{LO}^3\}\text{H} = (2 - \{(1,4,7,10\text{-tétraoxa-13-azacyclopentadécane-13-yl)-méthyl}\}-4,6\text{-di-}t\text{-butylphénol})$).²³ Les résultats obtenus avec le complexe de baryum **10** montrent une conversion et une valeur TOF plus élevées que celles obtenues avec les complexes Yb et Sm, mais avec une chimiosélectivité légèrement inférieure vers la production de la phosphine secondaire.

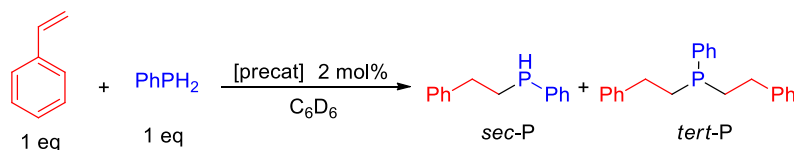


Schéma F. Hydrophosphination anti-Markovnikov de styène avec PhPH₂ donnant des phosphines secondaires et tertiaires.

Nous avons étudié la préparation de la *tert*-phosphine asymétrique en utilisant des styrènes *p*-Cl et *p*-^tBu substitués ([PhPH₂]₀/[*p*-Cl-styrène]₀/[*p*-^tBu-styrène]₀/[10]₀ = 25:25:25:1, Schéma G). Selon la littérature, ces substrats ont montré respectivement la meilleure et la plus faible réactivité dans les réactions d'hydrophosphination. Malheureusement, ces tentatives sont restées infructueuses et ont abouti à la formation du produit asymétrique (PhP(CH₂CH₂-C₆H₄-*p*-Cl)(CH₂CH₂-C₆H₄-*p*-^tBu) = M₁) avec les deux *tert*-phosphines symétriques de (PhP(CH₂CH₂-C₆H₄-*p*-Cl)₂ = M₂) et (PhP(CH₂CH₂-C₆H₄-*p*-^tBu)₂ = M₃) dans un rapport 6:2,5:1, comme observé par spectroscopie RMN ³¹P.

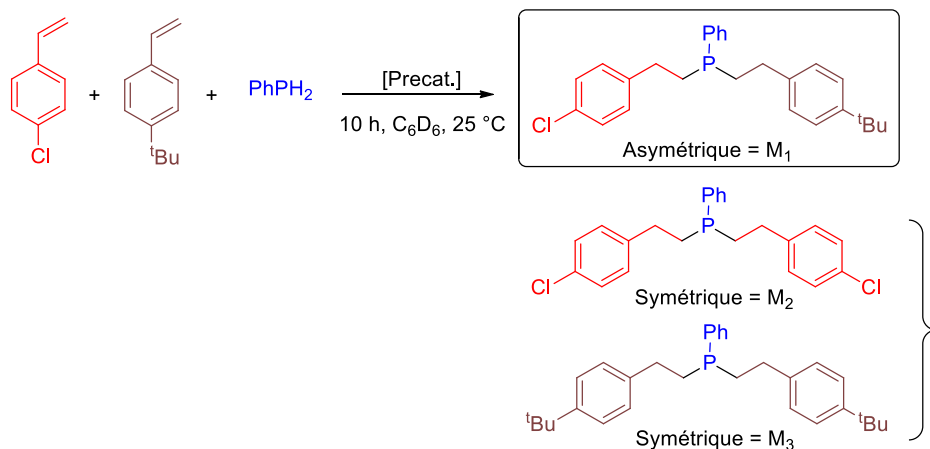


Schéma G. Synthèse monophasée en une étape de phosphines tertiaires asymétriques issues de l'hydrophosphination du *p*-Cl-styrène et du *p*-^tBu-styrène avec PhPH₂ catalysé par [I^{Acrown} BaN(SiMe₂H)₂] (**10**).

Il existe une compétition entre la formation de M₁ et M₂ mais la vitesse de la réaction est plus élevée vers M₁. La formation de M₃ n'est pas favorisée. Afin de préparer sélectivement des phosphines tertiaires asymétriques, deux stratégies peuvent être envisagées: (i) l'addition séquentielle des dérivés de styrène distincts au mélange réactionnel (à partir de l'addition de

styrène substitué par *p*-^tBu), ou (ii) l'identification des paire(s) appropriée(s) de substrats qui donnent les taux de réactivité appropriés à notre catalyseur au baryum. Sur la base de l'étude avec le complexe $[\{LO^3\}YbN(SiMe_3)_2]^{23a}$ (tout en considérant l'activité plus élevée de notre complexe Ba), une paire appropriée pourrait être le *p*-bromostyrène (moins réactif que le dérivé de *p*-Cl-styrène) et le *p*-^tBu-styrène.

Nos nouveaux complexes de baryum **10** et **11** ont montré des résultats intéressants et prometteurs dans les réactions d'hydrophosphination. La préparation d'analogues Ae lourds (Ca, Sr) permettrait de mieux comprendre ce processus de catalyse. De plus, il y a encore de nombreux domaines à explorer tels que les réactions d'hydroamination. Auparavant, les complexes de baryum et de calcium ont montré l'activité catalytique la plus élevée respectivement pour l'hydroamination intermoléculaire et intramoléculaire. Outre la stabilité et la réactivité du catalyseur, le problème le plus important des réactions d'hydroamination et d'hydrophosphination est la stabilisation de l'état de transition. Compte tenu de l'application requise aux substrats d'oléfines activés, des catalyseurs qui sont également actifs dans les réactions impliquant des substrats non activés sont hautement souhaitables. L'hydroamination et le couplage déshydrogénéant catalysé par des complexes Ae sont des réactions très importantes du point de vue catalytique et elles ont été étudiées séparément avec des résultats remarquables. La combinaison de ces deux types de réactions catalytiques en un seul milieu réactionnel, afin de catalyser la formation de liaisons (à savoir C–N et Si–N), pourrait représenter des applications des nouveaux complexes hétéroleptiques au baryum.

D'un point de vue général, l'ensemble des résultats collectés au cours de mes travaux de doctorat démontrent que les interactions secondaires (β -anagostiques Ae $\cdots$ F–C et Ae $\cdots$ Si–H) peuvent être efficaces pour former des complexes Ae réactifs et / ou faiblement coordonnés. Les complexes moins encombrés et non agrégés ne sont pas faciles d'accès et les investigations basées sur les deux familles de prolégands (y compris les fluoroarylamides et les ligands à base de *N*-ligands fonctionnalisés à l'éther couronne) ont été réalisées d'après cette problématique. Les complexes arylamido fluorés ont révélé une méthode simple et efficace pour la préparation de complexes de calcium stables, sans solvant et à faible nucléarité.

L'équilibre entre la stabilité et la réactivité du catalyseur pendant le cycle catalytique est d'une grande importance et reste difficile. Les nouveaux prolégands iminoanilide et amidinate

($\{I^{\wedge A}{}^{\text{crown}}\}H$ et $\{AdAm^{\text{crown}}\}H$) sont capables de d'apporter ces caractéristiques importantes aux complexes de baryum apparentés. Les ligands auxiliaires à base d'azote nouvellement conçus **10** et **11** ouvrent un large éventail de possibilités. Ils pourraient être utilisés pour la polymérisation d'alcène anionique.²⁴ La cible synthétique difficile des complexes hydrures d'Ae extrêmement réactif pourrait également être considérée. Cependant, cela nécessiterait quelques modifications du ligand (Figure F). En effet, la fonction imine ($CH=N$) des complexes **10** et **11** est potentiellement sensible à l'attaque nucléophile du Ba-H généré et conduirait à une auto-décomposition. L'introduction d'un groupe volumineux au niveau du carbone imine ou l'utilisation de groupes analogues mais plus robustes ($R_2P=N$) pourraient potentiellement conduire à des espèces d'hydrures stables (Figure F).

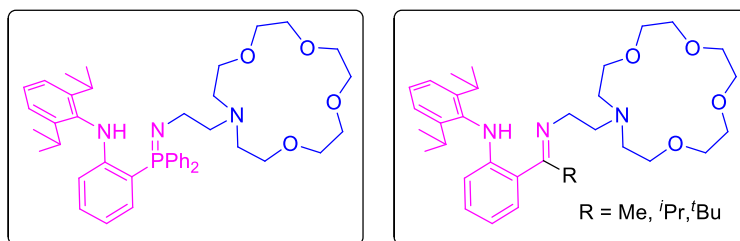


Figure F. Modifications potentielles pour protéger la fonction imine dans la structure du ligand.

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Titre : Métaux alcalino-terreux: Chimie de coordination et applications catalytiques

Mots clés : Métaux alcalino-terreux, Interaction secondaire, Hydrophosphination, Catalyse homogène

Résumé : La chimie organométallique des métaux alcalino-terreux (Ae) lourds (Ca, Sr, Ba) est plus difficile que celle de leur analogue plus léger (Mg). Cela est dû à leurs grands rayons ioniques, leur forte électropositivité et leur liaison ionique qui les rendent également très réactifs, sensibles à l'hydrolyse et au brouillage des ligands (c'est-à-dire à l'équilibre de Schlenk).

Cette thèse de doctorat décrit la synthèse et la caractérisation de nouvelles familles de complexes Ae stabilisés par des ligands ancillaires et des interactions secondaires, ainsi que l'évaluation de leurs performances dans certaines réactions organiques difficiles catalysées de manière homogène.

Une série de complexes homoleptiques et hétéroleptiques Ae supportés par des arylamides fluorés est d'abord présentée. Les études de diffraction des rayons X montrent qu'en plus de la coordination des hétéroatomes, les interactions secondaires inter- et intramoléculaires $Ae \cdots F-C$ remarquablement courtes fournissent une stabilisation cinétique supplémentaire.

Des études informatiques complémentaires (DFT) ont révélé que les interactions $Ae \cdots F-C$ sont principalement de nature électrostatique. L'évaluation de certains de ces nouveaux complexes hétéroleptiques de calcium dans la réaction d'hydrophosphination de référence du styrène et de la diphenylphosphine a mis en évidence des activités élevées et une régiospécificité anti-Markovnikov complète dans des conditions douces.

La deuxième partie du travail décrit l'étude de nouveaux prolégands comportant un bras latéral coordinant éther couronne pour stabiliser les complexes hétéroleptiques de baryum exempts de solvant. Les données structurales aux rayons X et les analyses spectroscopiques RMN montrent un centre métallique hautement coordonné au ligand ancillaire bidenté, en plus des contacts avec les hétéroatomes du bras latéral, ce qui conduit à des complexes Ba encapsulés combinés avec des interactions secondaires $\beta-Si-H \cdots Ae$. Ces complexes originaux ont montré des résultats gratifiants dans les réactions d'hydrophosphination.

Title : Alkaline-earth metals: Coordination chemistry and catalytic applications

Keywords : Alkaline-earth metals, Secondary interaction, Hydrophosphination, Homogeneous catalysis

Abstract : The organometallic chemistry of heavy alkaline-earth metals (Ae = Ca, Sr, Ba) is more challenging than that of their lighter analogue (Mg). This is due to their large ionic radii, strong electropositivity and ionic bonding which also make them highly reactive, sensitive to hydrolysis and to ligand scrambling (i.e. to Schlenk equilibrium).

This PhD thesis describes the synthesis and characterization of new families of Ae complexes stabilized by ancillary ligands and secondary interactions, along with the evaluation of their performances in some challenging homogeneously-catalyzed organic reactions.

A series of homoleptic and heteroleptic Ae complexes supported by fluorinated arylamides is first presented. X-ray diffraction studies show that beside the coordination of the heteroatoms, remarkably short inter- and intramolecular $Ae \cdots F-C$ secondary interactions provide additional kinetic stabilization.

Complementing computational (DFT) studies revealed that $Ae \cdots F-C$ interactions are mostly electrostatic in nature. Evaluation of some of these new calcium heteroleptic complexes in the benchmark hydrophosphination reaction of styrene and diphenylphosphine evidenced high activities and full anti-Markovnikov regioselectivity under mild conditions.

The second part of the work describes the study of new prolégands featuring a coordinating tethered crown-ether side arm to stabilize solvent-free barium heteroleptic complexes. X-ray structural data and NMR spectroscopic analyses support the highly coordinated metal center to the bidentate ancillary ligand including contacts with the side-arm heteroatoms resulting in encapsulated Ba complexes combined with $\beta-Si-H \cdots Ae$ secondary interactions. These original complexes showed rewarding results in hydrophosphination reactions.