Cyclopentadienyl Free Compounds of p, d, and f Elements

Dissertation

zur Erlangung des Doktorgrades

der Mathematisch-Naturwissenschaftlichen Fakultäten

der Georg-August-Universität zu Göttingen

vorgelegt von

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(Rumänien)

Göttingen 2003

D 7

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Tag der mündlichen Prüfung: 08.05.2003

Aknoledgement

The work described in this thesis has been carried out under the supervision of Professor Dr. Dr. h.c. mult. Herbert W. Roesky at the Institut für Anorganische Chemie der Georg-August-Universität Göttingen between June 2000 and April 2003.

My sincere thanks and gratitude are due to

Prof. Dr. Dr. h.c. mult. Herbert W. Roesky

for his constant guidance, motivation, suggestions, and discussions throughout this work.

I am grateful to Prof. Dr. Jorg Magull, Dr. Regine Herbst-Irmer, Gabor Buncoczi, Christine Schlicker, Priv. Doz. Isabel Uson, Prof. Dr. George Sheldrick, Dr. Bernhard Walfort and Prof. Dr. Dietmar Stalke for their help in the X-ray crystal structure investigations. I thank Mr. W. Zolke, Mr. R. Schöne and Dr. G. Elter (NMR division), Mr. T. Schuchard and Mrs. A. Rehbein (Mass spectral measurements), Mr. M. Hesse and Mr. H.-J. Feine (IR measurements), and the staff of the Analytical Laboratories, Mr. J. Schimkowiak and Mr. M. Schlote for their full collaboration during my research work.

I thank to Priv. Doz. Uwe Ritter, Dr. C. Ackerhans, Dr. S. Kiel, Dr. A. Mohamed, Dr. N. Mösch-Zanetti, G. Anantaraman, Y. Ding, V. Jancik, S. Kumar, K. Most, Y. Peng and many others for an excellent work atmosphere, their friendship and support.

I would like to express gratitude to Prof. Dr. Marius Andruh for his tolerance and for his trust. The help rendered by Dr. M. Witt and Priv. Doz. I. Uson during writing this thesis is gratefully acknowledged.

I am grateful to all of my family members, in particular to my brother Jianu Nicolae who taught me the early lessons in chemistry. But, more than ever I am thankfull to my laboratory partner and wife Mirela, for her love, understanding, and the rest that made my work possible.

Abbreviations

av.	average
br	broad
bp	boiling point
Cp	cyclopentadienyl
D	generic neutral donor group
d	doublet, day
depe	1,2-bis-diethylphosphanyl-ethane
DFT	density functional theory
δ	chemical shift
C	Celsius
EI	electron impact ionization
Eq.	equation
Et	ethyl
HOMO	the highest occupied molecular orbital
HSAB	hard and soft acids and bases
J	coupling constant
K	Kelvin
η	hapto
L	[N,N''-(1,3-dimethyl-1,3-propanediylidene)bis[N',N'-diethyl-1,2-ethanediamine]]
L'	[N,N'-(1,3-dimethyl-1,3-propanediylidene)bis[2-diphenylphosphanyl-ethylamine]]
LUMO	the lowest unoccupied molecular orbital
Ln	4f metals
λ	wavelength
m	multiplet, meta
M^+	molecular ion
m/z	mass/charge
Me	methyl

Mes	mesityl
Mp	melting point
MS	mass spectrometry
μ	bridge
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million
Py	pyridine
^{i}Pr	isopropyl
R	organic substituent
r.t.	room temperature
s	singlet
t	triplet
^{t}Bu	*tert* butyl
tacn	1,4,7-triazacyclononane
THF	tetrahydrofuran
TMS	tetramethylsilane
Z	number of molecules in the unit cell

1. Introduction

The organometallic chemistry has developed along with the nowadays-ubiquitous cyclopentadienyl ligand, a milestone being the discovery of ferrocene by Kealy and Pauson, and Wilkinson *et al*.[1] A cornucopia of Cp derivatives has been synthesized and structurally characterized since[2] and numerous compounds have found applications in many aspects of our life, predominantly in industry as catalysts for various organic processes.[3] Using Cp as ligand, unforeseen compounds, in the light of previously accepted principles, like metallocenes,[4] have been isolated and hence the prior concepts have been affected and the results constitute the basis of modern inorganic chemistry.[5] Over the years the organometallic chemistry has grown from a pure curiosity to an independent area of inorganic chemistry. As a reconnaissance of this fact periodical journals emerged, among others, such as *Journal of Organometallic Chemistry* or *Organometallics*. While the Cp ligand and its congeners constitute the broad basis of organometallic chemistry,[6] many other systems, mostly known from coordination chemistry such as alkoxides,[7] amides,[8] polypyrazolylborates[9] and many others, were employed successfully to enlarge the organometallic chemistry horizon. Such a system is represented by the nitrogen-based monoanionic *β*-diketiminato ligand (see Figure 1) as well.[10]

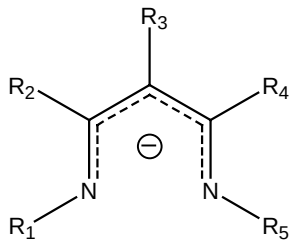
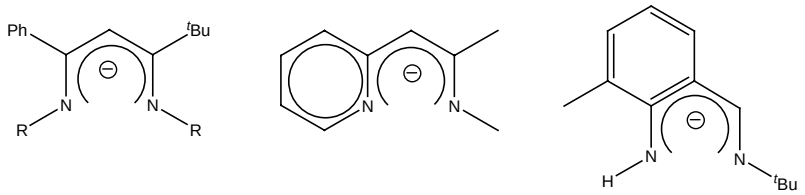


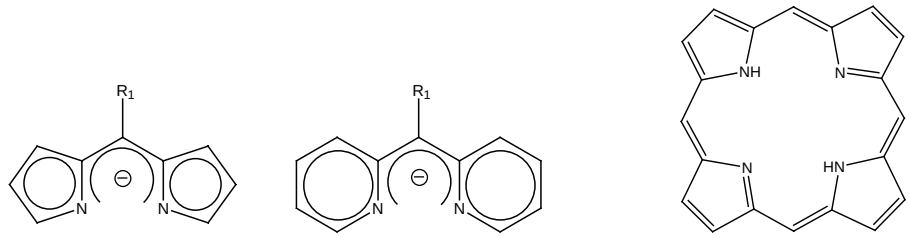
Figure 1. *Schematic representation of β-diketiminato ligand.*

Originating in the late 1960s,[11] *β*-diketiminato ligands came into play in the last decade; once this system has been accepted as a *spectator ligand* (a term that characterizes a ligand of a portion of a ligand sphere wich is not directly involved in the fundamental reactivity of the complexes, *e.g.* ligand exchange or insertion reactions),[12] like Cp, and it is increasingly applied ever since. What makes them distinctive is the fine-tuning

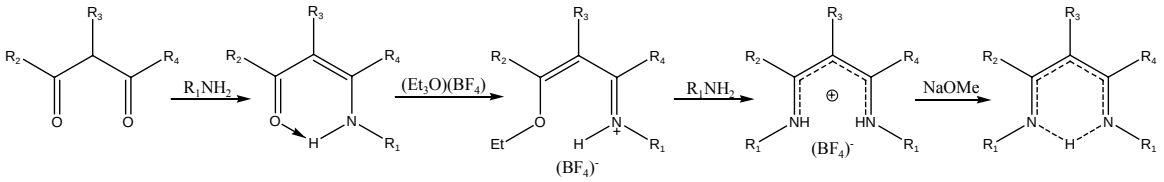
opportunity, given by the nature of the diverse R groups. In spite of this potential diversity the β-diketiminates have been seldom employed in organometallic chemistry.[10] The number of unsymmetrical ligands in which either/both $R_1 \neq R_5$ or/and $R_2 \neq R_4$ is small,[13] mainly ligands with $R_1 = R_5$ and $R_2 = R_4$ are under investigation due to the reasonable ease of preparing them.



When R_1 is linked to R_2 and R_4 is to R_5, two particular ligands can be conceived.[14] Noteworthy is the resemblance of the β-diketiminato ligands with very well known macrocycles, namely porphyrin.[15]



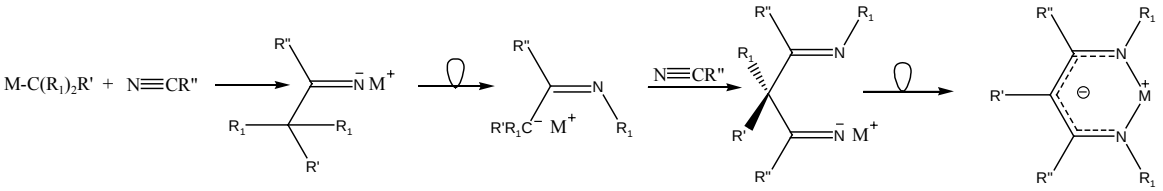
From the point of view of the preparative methods, there are various routes to the β-diketiminates, either as its conjugate acid or as a metal complex. The two most important methods are described as follows. The key route implies the condensation reaction of a primary amine with either β-diketones (Scheme 1),[11a] ketoketals,[16] or β-diacetals[17] such as 1,1,3,3-tetraethoxypropane.



Scheme 1: *The common route to the conjugated acid of β-diketiminato ligands.*

The other path implies the reaction of α-hydrogen-free nitriles[12a] or isonitriles[18] with a metal alkyl. The mechanism involves two C-C couplings and two 1,3 migrations

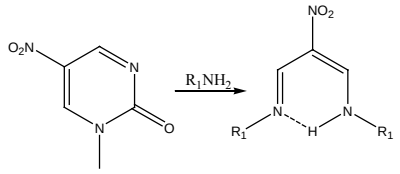
of the group R_1 from carbon to nitrogen. Such shifts are by far easier achieved for groups like $SiMe_3$ than with H.



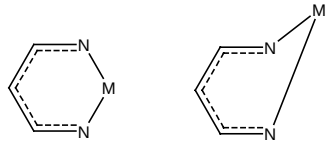
Scheme 2: *The nitrile route to β-diketiminato complexes.*

The reactions involving isonitriles followed principally the same mechanism, with 1,2-groups migration instead.

There are some other different special routes,[13, 19] probably the most interesting is the conversion of a 5-nitropyrimidin-2(1H)-one into a nitro-*β*-diketimine:[20]



With regard to the bonding mode of these chelating ligands there is an extensive variety. Although the resemblance with Cp has been claimed,[12b] it has been demonstrated by Tolman, Solomon *et al.*[21] that this is not the case. Mostly, the majority of the bonding modes occurs through the in plane N-M σ-bonds, implying the ligand acts as a $4e^-$ donor (**I**). Several complexes, however, have the ligand in $2\sigma+\pi$ arrangement, $6e^-$ donor (**II**), the metal is strongly bent away from the NC_3N plane.[19b, 22] Moreover, they can also act as electron sinks through the out of plane LUMO.[23]



I **II**

Scheme 3: *The general η^2 coordinating modes of a β-diketiminato moiety.*

Taking advantage of such ligands, many unique complexes were synthesized and characterized (see for instance Figure 2).

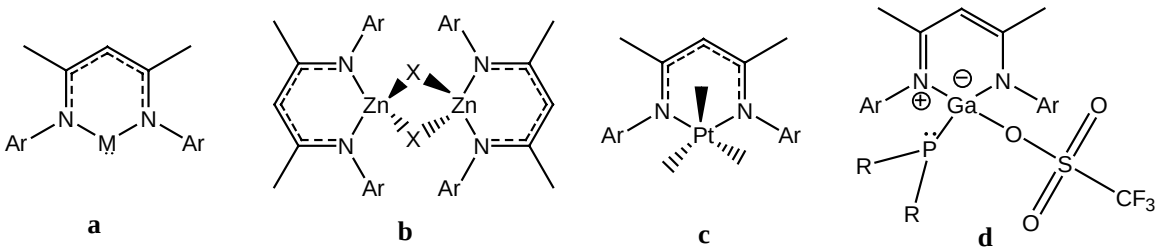


Figure 2. *Significant developments: a) for M = Al the first stable monomeric Al(I) compound,*[24] *for M = Ga a Ga(I) carbene analogue*[25] *(Ar = 2,6-diisopropylphenyl); b) for X = O*^{i}*Pr,*[26] *a catalyst for living polymerization of lactide (Ar = 2,6-diethylphenyl), and for X = OMe*[27] *an active catalyst for copolymerization of* CO_2 *and cyclohexene oxide; for X = F, H,*[28] *first Zn compounds with bridging F or H atoms, (Ar = 2,6-diisopropylphenyl); c) the first stable, coordinatively unsaturated Pt(IV) five-coordinated complex (Ar = 2,6-diisopropylphenyl);*[29] *d) a gallane ligand on phosphine Lewis acceptor.*[30]

Although, β-diiminato complexes have been reported for almost 2/3 of the 63 natural metals and gained an important role in the organometallic ligands gallery by virtue of their strong binding and their tunable steric demands, along with the diversity of bonding modes, it has to be underlined that more has to come. For instance as far as the β-diiminatolanthanide complexes are concerned, very little is known (about 40 complexes have been published up to now).[10] This represents a challenging area considering the growing role of lanthanides in modern catalysis which is attributable to their high Lewis acidity, which might promote important organic processes.[31]

Nevertheless, the interest in such a system is not singular. As already mentioned, the progress seen recently in the field of β-diketiminates is a part of a general tendency encountered in organometallic chemistry towards a Cp free chemistry. Specifically, there is an increasing interest in development of complex and sophisticated ligand systems, "ligand design", which are required for very specific functions.[8c, 32] Typical functions of such tailor-made ligands are to create metal complexes of specific nuclearity, coordination number, geometry and reactivity.[31c] Two complementary approaches have been used, one that takes advantage of the steric hindrance by using bulky substituents, thus stabilizing the resulting complex kinetically, the other trying to stabilize the resulting complex thermodynamically by modulation of the electronic environment. Both methodologies imply a proper choice of the functional groups as well as the structure of the ligand framework, "ligand topology", depending on the desired objective.

The above-mentioned principles may be followed considering the *m*-terphenyl and DCD-pincer type of ligands.

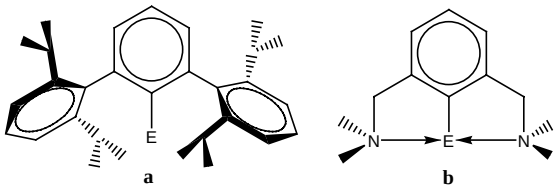


Figure 3. *Two schematic examples of: a) sterically hindered m-terphenyl complex, b) DCD-pincer complex.*

The sterically encumbered ligands like *m*-terphenyls[33] or 2,4,6-tris[bis(trimethylsilyl)methyl], Tbt,[34] were used mostly with elements of groups 13 - 15, where the C-E bonds are reasonably strong, and many interesting complexes were obtained.[35]

The DCD-pincer type of ligands have been developed by van Koten *et al.*, and used mainly with late transition metals. They have found extensive use in catalysis, catalyst immobilization, supramolecular assembly, and sensor materials.[36]

At a first glance these systems are somewhat different from the *β*-diketiminates, however a parallel might be drawn. Their topologies and ultimate goal are actually the same. By comparison, the *β*-diketiminates to date have taken advantage of the bulkiness of the substituents on the ligand core as *m*-terphenyl ligands did. On the other hand, there is no correspondent of the DCD-pincer type of ligands as far as the *β*-diketiminato ligands are concerned.

1.1. *Aims and Objectives of this Dissertation.*

Based on the aforementioned introductory concepts, using of the word 'pivotal' concerning the role of the ligand in the organometallic chemistry it is not too much. In the attempts to replace the cyclopentadienyl paradigm with ligands of similar electronic and steric demands or even more, it can be said that β-diketiminato ligand chemistries are a very open source of promising prospects in scientific and industrial research.

1. Design and synthesis of ligands containing the β-diketiminato framework capable of stabilizing the resulting complexes thermodynamically.

2. Synthesis of Cp-free bis-hydrocarbyl lanthanide complexes, $LLnR_2$.

3. Synthesis of new complexes thereafter.

2. Results and discussion

Although significant progress has been achieved in the past decade vis-à-vis the *β*-diketiminato ligands[10] the continuous row of surprises offered along the periodical table makes us believe that this system is still in its infancy. To date their general skeleton may be included in that of McConville systems in which two trigonal nitrogen donors are held in a chelating arrangement and the metal center around the metal is sculpted by bulky aryl or alkyl groups on the nitrogen atoms.[37] Such an arrangement was used recently by Gibson *et al.*[31b, 38] and Brookhart *et al.*[39] in order to develop novel olefin polymerization catalysts of late transition metals as an attempt to avoid the growing patent minefield in Group 4 cyclopentadienyl systems. The benefit of such arrangements is that neutral, monoanionic and dianionic forms can be prepared and applied, determined by the available oxidation states of the subjected metal.[40]

While the steric bulk has been a key issue for the *β*-diketiminato ligands previously used to gain kinetic stability of the complexes, there has been no published attempt to increase the thermodynamic stability by changing the sterically demanding groups on the nitrogen atoms with pendant arms having donors incorporated instead.[10] Taking into account that the *β*-diketiminates are ideal ligands for metals in the oxidation state +3,[41] characteristic for the lanthanides and the early transition metals[5] and the scarcity of complexes of this type,[10] the design of an ancillary tetradentate *β*-diketiminato ligand, L, conform to the HSAB principle,[42] and its synthesis were carried out:

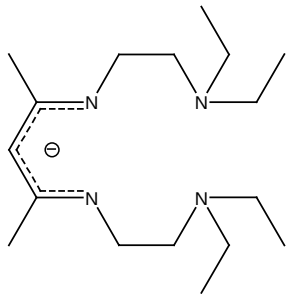
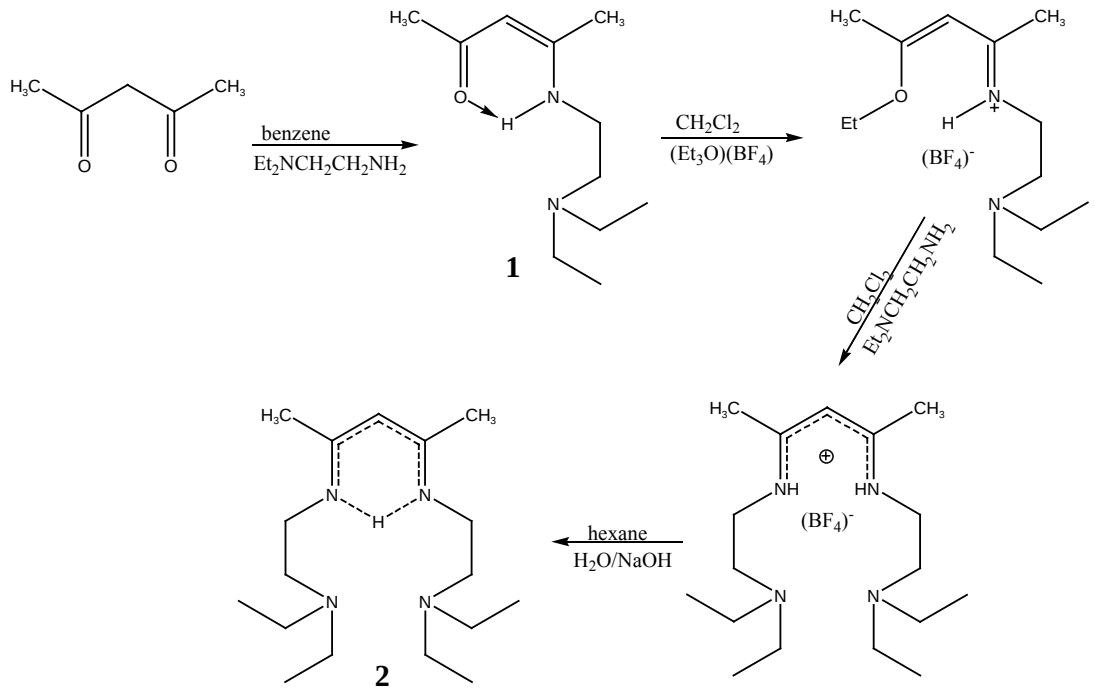


Figure 4. *The anticipated skeleton of the monoanionic ligand, L = [N,N''-(1,3-dimethyl-1,3-propanediylidene)bis[N',N'-diethyl-1,2-ethanediamine]]*

Another important issue is the current interest in the chemistry of neutral bis-hydrocarbyl complexes of the group 3 transition metals and the lanthanides with the general formula LMR_2, which stems from the potentially usefulness of these systems as novel olefin polymerization catalysts and precursors of catalytically active cationic monoalkyl species.[31b, 41, 43] The importance of the cationic monoalkyl species has been previously documented for the d^0 complexes of group 4 transition metals.[44]

2.1. *Synthesis of (2-diethylamino-ethyl)-[3-(2-diethylamino-ethylimino)-1-methyl-but-1-enyl]-amine,* **2**.

The conjugated acid of the ligand L, **2**, was prepared in a two-step synthesis as it is shown in Scheme 4, which represents a slightly modified route of that of McGeachin.[11a]



Scheme 4: *Reagents and solvents for the preparation of the conjugated acid of L,* **2**.

Acetylacetone was reacted with N,N-diethyl(ethylenediamine) in a 1:1 molar ratio giving, 4-(2-diethylaminoethyl)amino-pent-3-en-2-one, **1**, in an excellent yield. Compound **1** is the intermediary step for the preparation of **2**. Treatment of **1** with Meerwein salt, $(Et_3O)(BF_4)$, in dichloromethane followed by N,N-

diethyl(ethylenediamine) and NaOH afforded (2-diethylamino-ethyl)-[3-(2-diethylamino-ethylimino)-1-methyl-but-1-enyl]-amine, **2**, in 52 % yield. Compound **2** is a yellow oil at room temperature and soluble in any common organic solvent.

2.2. *Synthesis of LLi,* **3**.

Compound **2** can be easily transformed into its lithium salt with any alkyl lithium. Reaction of **2** with MeLi in ether at –78 °C, followed by subsequent solvent removal afforded an oily product which soon crystallizes to yield LLi, **3**, almost quantitatively (Eq. (1)). On the other hand, every time when the lithium salt, LLi, was needed it was prepared prior to use, and used without any further purification.

$$\underset{\mathbf{2}}{\mathrm{LH}} + \mathrm{LiMe} \xrightarrow[-\,CH_4]{\text{ether, -78 °C}} \underset{\mathbf{3}}{\mathrm{LLi}} \qquad (1)$$

The complex **3** has been characterized by multinuclear NMR spectrometry, EI-MS, and elemental analysis and shows that no extra molecule of solvent molecule is required to stabilize the product as in the case of the lithium salt of the sterically encumbered *β*-diketiminato ligand, $[Li\{(N(C_6H_3{}^iPr_2\text{-}2,6)CMe)_2CH\}(OEt_2)]$.[13c] A downfield shift of the hydrogen atom of the ligand core was observed for **3** when compared with **2** in the ^1H NMR spectra (C_6D_6, 0.2 ppm).

2.2.1. *Discussion of the crystal structure of* **3**.

The salt crystallizes in the triclinic space group $P\bar{1}$, with two molecules of LLi in the asymmetric unit that are crystallographically independent but chemically equivalent (only one is displayed in Figure 5 for simplicity). The ligand L acts as a tetradentate ligand toward lithium in an almost planar environment. The differences of the bond lengths and angles between the two molecules **3a** and **3b** are small.

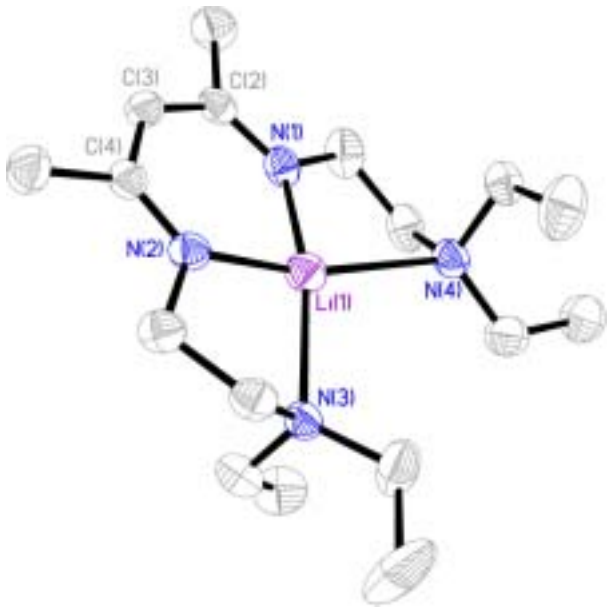
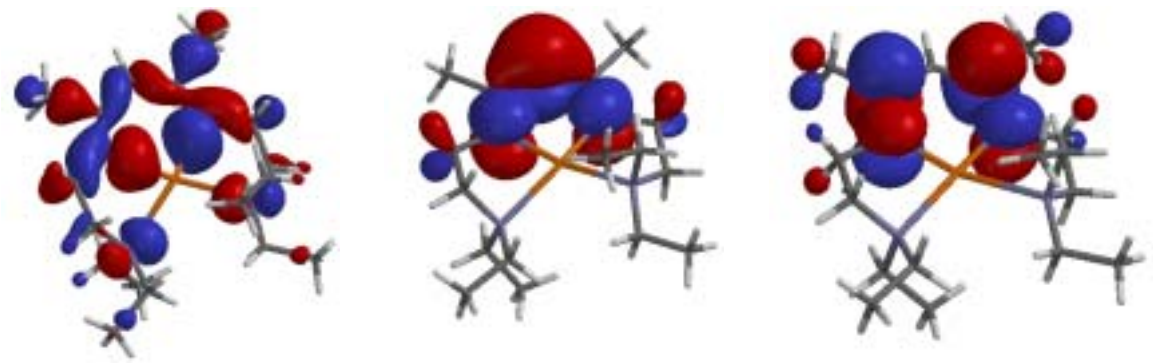


Figure 5. *Molecular structure of* **3** *showing 50 % probability ellipsoids (the hydrogen atoms are omitted for clarity).*

The lithium atom is chelated under formation of *two* five- and *one* six-membered rings. The Li-N bond lengths have two different values corresponding to the two distinct bonding (see Table 1). Albeit, the Li(1)-N(1) and Li(1)-N(2) bonds are somewhat longer than in the case of [Li{(N($C_6H_3{}^iPr_2$-2,6)CMe)$_2$CH}(OEt_2)] (*av.* 1.91 Å),[13c] this does not affect the delocalized π-system which can be deduced from the C-N and C-C bond lengths of the backbone and calculations that were carried out. As far as the Li(1)-N(3) and Li(1)-N(4) distances (dative bonds) are concerned slightly longer bonds are observed by comparison to the Li-N distances found in [(Me_2N)CH_2CH_2)$_2$NLi]$_2$ (*e.g.* 2.08 Å).[45]

A restricted hybrid HF-DFT calculation was performed using the Pulay DIIS extrapolation for **3**a (based on the experimental structure of **3a**) with the Spartan '02 Quantum Mechanics Program,[46] and gave qualitatively the same results, as those obtained by Tolman, Solomon *et al.* for a β-diketiminato Cu(I) complex [Cu{(N(C_6H_3-$^iPr_2$-2,6)CMe)$_2$CH}(SC(C_6H_5)$_3$] (Figure 6).[21] Thus, the HOMO-1, 5b2, is associated with the nitrogen lone pairs oriented toward the lithium atom. The HOMO, 2b1, is characterized by the out of plane p-type orbitals on the two nitrogen atoms and the central carbon atom, the latter being a little bit extended toward the neighboring C-atoms. The LUMO, 2a2, is characterized by the out of the NC_3N plane p-type orbitals.



HOMO - HOMO (-81.17 Kcal/mol) LUMO (24 Kcal/mol)

Figure 6. *Qualitative HOMO-, HOMO and LUMO representations of the molecule* **3***a calculated by means of the RB3LYP level of theory, basis set 6-31G(D).*

Table 1. Selected bond lengths (Å) and angles (°) for LLi, **3**.

Bonds lenghts		Angles	
Molecule **3**a			
Li(1)-N(1)	1.968(3)	N(1)-Li(1)-N(2)	93.55(13)
Li(1)-N(2)	1.974(3)	N(1)-Li(1)-N(4)	79.86(10)
Li(1)-N(3)	2.265(3)	N(2)-Li(1)-N(3)	82.71(10)
Li(1)-N(4)	2.450(3)	N(4)-Li(1)-N(3)	107.02(11)
N(1)-C(2)	1.315(2)	N(1)-C(2)-C(3)	123.79(13)
N(2)-C(4)	1.3143(19)	N(2)-C(4)-C(3)	122.99(14)
C(2)-C(3)	1.409(2)	C(2)-C(3)-C(4)	127.81(14)
C(4)-C(3)	1.414(2)		
Molecule **3**b			
Li(2)-N(6)	1.965(3)	N(6)-Li(2)-N(5)	93.54(12)
Li(2)-N(5)	1.969(3)	N(7)-Li(2)-N(5)	82.03(11)
Li(2)-N(7)	2.275(3)	N(8)-Li(2)-N(6)	82.33(11)
Li(2)-N(8)	2.300(3)	N(8)-Li(2)-N(7)	108.96(12)
N(5)-C(19)	1.317(2)	N(5)-C(19)-C(20)	123.07(15)
N(6)-C(21)	1.319(2)	N(6)-C(21)-C(20)	123.63(15)
C(19)-C(20)	1.409(3)	C(21)-C(20)-C(19)	127.99(15)
C(21)-C(20)	1.405(3)		

2.3. *Synthesis of LLnX$_2$ complexes.*

Generally three major pathways are used to prepare organometallic compounds of the early transition metals and the lanthanides, namely salt, alkane, and amine elimination reactions.[10b] Nevertheless, the method of choice remains the salt elimination due to the

easy handling and starting materials accessibility. A major task prior to the obtaining of any bis-hydrocarbyl complexes of the early transition metals or the lanthanides via the salt elimination route represents the availability of the bifunctional precursors LMX_2 (X = Cl, Br, I), ideally salt (*e.g.* LiCl) and solvent free in order not to dampen further reactions, which constitute the logical starting material for the metathesis reaction.

To date group 3 transition metals and lanthanide β-diketiminato derivatives are known for the following metals: scandium,[23, 41, 47] yttrium,[48] lanthanum,[48] cerium,[22c, 48] praseodymium,[22c, 48, 49] neodymium,[22c] samarium,[22c, 50] gadolinium,[14b, 50] erbium,[51] holmium,[51] thulium,[22c] ytterbium,[22c, 52] and lutetium.[48] Nevertheless, most of these complexes contain two β-diketiminato units, and only three dihalides are known namely $[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Cl_2(THF)]$[41, 47b], $[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C{}^tBu)_2CH\}Cl_2]$[47b] and $[Gd\{(N(Ph)CMe)_2CH\}Br_2(THF)_2]$[50a] that do not incorporate L. The use of the ligand L afforded many of such complexes, which are in the following section described.

2.3.1. *Synthesis of $LPrCl_2$,* **4***, $LPrBr_2$,* **5***, $LSmCl_2$,* **6***, $LSmBr_2$,* **7***, $LTbBr_2$,* **8***, and $LYbBr_2$,* **9**.

Treatment of LLi with equivalent amounts of either anhydrous $LnCl_3$ (Ln = Pr (**4**), Sm (**6**)) or anhydrous $LnBr_3$ (Ln = Pr (**5**), Sm (**7**), Tb (**8**), and Yb (**9**)) in toluene at refluxing temperature afforded $LLnX_2$, (X = Cl, Br) in good yields (Eq. (2)).

$$\underset{\mathbf{3}}{LLi} + LnX_3 \xrightarrow[\text{- 2 LiCl}]{\text{refluxing toluene}} LLnX_2 \qquad (2)$$

All the complexes are well soluble in aromatic solvents, dichloromethane and THF. These compounds are thermally very stable, their melting points are in the range of 164 to 216 ºC, respectively. All the complexes are moisture and moderately air sensitive. Mass spectrometry and elemental analysis showed that compounds **4 - 9** are monomeric, solvent free compounds, and contain no occluded lithium halides. Conspicuously, is that compounds **4 - 9** were prepared using the anhydrous salts and not the THF adducts they are the first non-metallocene, neutral, monomeric and solvent free dihalogeno lanthanide complexes. The monomeric structures of all complexes were confirmed by single crystal

X-ray structural analysis with the exception of **6**. ^{1}H NMR resonances are not observed in all cases due to the paramagnetic nature of the lanthanides.

2.3.1.1. *Discussion of the crystal structures of* **4**, **5**, **7**, **8**, *and* **9**.

Crystals of **4**, **5**, and **7 - 9** suitable for X-ray studies were obtained by slow evaporation followed by refrigeration for several h at –26 ºC. Unfortunately, an X-ray structure of $LSmCl_2$ (**6**) could not be obtained due to a twinning problem. Complexes **4** (Figure 7) and **5** crystallize in the monoclinic space group $P2_1/n$, complex **7** crystallizes in the monoclinic space group $P2_1/c$ while complexes **8** (Figure 8) and **9** crystallize in the orthorhombic space group $Pca2_1$. Selected bond distances and angles for compounds **4**, **5**, and **7 - 9** are listed in Table 2. In all the compounds both pendant arms of the ligand are coordinated to the metal center and all four nitrogen atoms and the metal atom are in the same plane. For the complexes **5**, **7** and **8** a local distortion is observed due to the different orientation of one of the ethyl groups of one of the arms. The coordination number at the metal ion is in every case *six* and the geometry around the metal atom is *pseudooctahedral* (the X-Tb-X angles differ significantly from 180°) which led, as a direct consequence, to unequal Ln-X bond lengths.

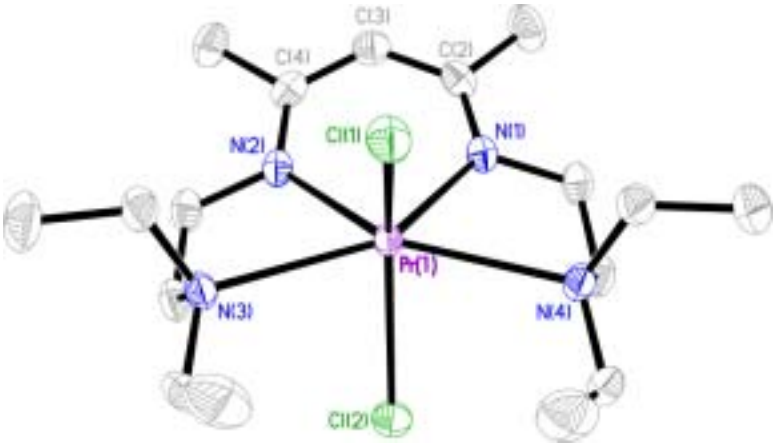


Figure 7. *Molecular structure of* **4** *showing 50 % probability ellipsoids (the hydrogen atoms are omitted for clarity).*

This arrangement can be compared with that of MX_2 (M = heavier group 2 or a divalent group 3 elements and X = halogen or cyclopentadienyl).[53] The Pr-X bond length (X = Cl, 2.896, 2.872 Å),[54] (X = Br, 2.877 Å)[55] are somewhat smaller than similar bonds found in literature as a consequence of both different coordination numbers and steric hindrance surrounding the metal center. The same behavior is observed for the other Ln-Br bonds.[56] The Ln-N bond lengths of the pendant arms are longer than those of the backbone, due to the coordinative and covalent character involved in different bonding modes. The Ln-N (Ln = Pr, Sm, Yb) bond lengths are comparable to those found in the literature (Sm-N[50a] *av*. 2.44 Å, Yb-N[52b] *av*. 2.27 Å).

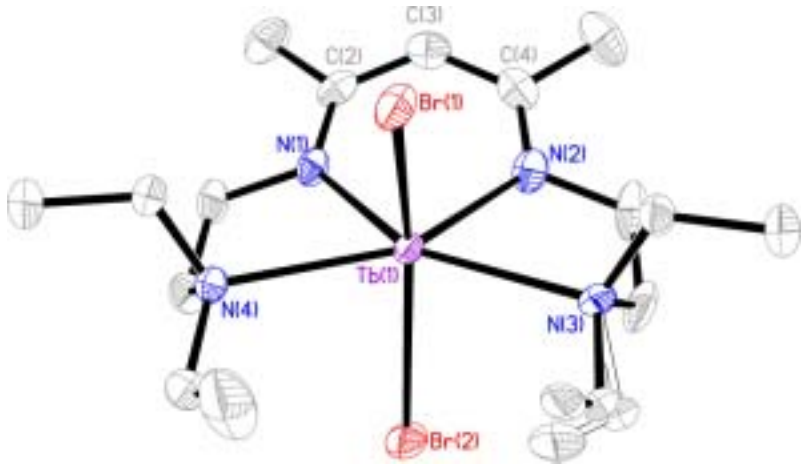


Figure 8. *Molecular structure of* **8** *showing 50 % probability ellipsoids (the hydrogen atoms are omitted for clarity). The disorder of one ethyl group was observed.*

As previously discussed, a β-diketiminato ligand can either act as a donor of 4 electrons, in this case the nature of the bonds is 2σ, or a donor of 6 electrons, in this case the description of the bonds is 2σ-π. Information whether there is predominantly 2σ or 2σ-π bonding between the ligand and metal ion can be deduced from the deviation of the metal ion from the NC_3N ligand backbone plane.

As it can be seen from Table 3 there is a correlation between the electrophilicity of the metal ion and the deviation from the plane for the dibromo complexes (**5**, **7** - **9**). It can be rationalized that the deviation from the plane correlates with the electrophilicity of the cation.

Table 2. Selected bond lengths (Å) and angles (°) for $LPrCl_2$, **4**, $LPrBr_2$, **5**, $LSmBr_2$, **7**, $LTbBr_2$, **8**, and $LYbBr_2$, **9**.

Bond lengths	**4**	**5**	**7**	**8**	**9**
Ln(1)-N(1)	2.442(2)	2.462(2)	2.405(3)	2.353(3)	2.285(3)
Ln(1)-N(2)	2.448(2)	2.455(2)	2.399(3)	2.341(4)	2.282(3)
Ln(1)-N(3)	2.692(2)	2.688(2)	2.643(3)	2.605(4)	2.567(3)
Ln(1)-N(4)	2.694(2)	2.682(2)	2.608(3)	2.610(3)	2.560(4)
Ln(1)-X(1)	2.6836(7)	2.852(1)	2.828(1)	2.743(1)	2.740(1)
Ln(1)-X(2)	2.6903(7)	2.868(1)	2.828(1)	2.801(1)	2.684(1)
N(1)-C(2)	1.332(4)	1.328(3)	1.335(4)	1.333(7)	1.339(6)
N(2)-C(4)	1.338(4)	1.327(3)	1.333(5)	1.338(7)	1.342(6)
C(2)-C(3)	1.398(4)	1.404(4)	1.399(5)	1.407(8)	1.394(7)
C(3)-C(4)	1.393(4)	1.405(4)	1.401(5)	1.398(8)	1.384(7)
Angles					
N(1)-Ln(1)-N(2)	75.79(8)	77.18(7)	78.63(9)	79.28(13)	81.09(13)
N(1)-Ln(1)-N(4)	67.81(7)	69.89(7)	70.74(9)	69.90(12)	151.59(12)
N(4)-Ln(1)-N(3)	126.3(2)	130.45(17)	142.13(9)	141.06(12)	137.72(11)
N(2)-Ln(1)-N(3)	123.9(2)	125.3(2)	70.86(10)	69.74(13)	151.65(12)
Ln(1)-N(1)-C(1)	130.6(3)	131.4(2)	129.9(2)	126.1(3)	125.1(3)
N(1)-C(2)-C(3)	124.5(3)	125.2(2)	124.7(3)	124.5(4)	124.1(4)
C(2)-C(3)-C(4)	125.6(2)	130.32(17)	131.8(3)	129.8(4)	130.4(4)
C(3)-C(4)-N(2)	145.95(7)	144.47(6)	124.6(3)	124.2(4)	123.7(4)
C(4)-N(2)-Ln(1)	69.26(8)	70.31(7)	130.3(2)	125.8(3)	125.0(3)
X(1)-Ln(1)-X(2)	136.42(3)	137.080(12)	142.615(13)	149.611(16)	151.184(16)

Table 3. The mean deviation (Å) from the metal center to the backbone plane (NC_3N plane).

5	**7**	**8**	**9**
0.04	0.07	0.79	0.78

As a consequence, the smallest deviation is found in complex **5** (0.04 Å), which correlates with the size of Pr^{3+} that has the biggest ionic radius of this series (only the bromine derivatives have been considered).[5] Furthermore, the influence on the Ln-Br as well as on Ln-N bond lengths can be observed (see Table 2) and they follow the same tendency as the Ln^{3+} ionic radii.

2.4. *Metathesis reactions*

2.4.1. *Synthesis of LPr(BH$_4$)$_2$,* **10**.

The metathesis reaction of **4** with an excess of $NaBH_4$ (1:3 molar ratio) in toluene under reflux afforded compound **10** (Eq. (3)) in moderate yield.

$$\underset{\mathbf{4}}{LPrCl_2} + 3\ NaBH_4 \xrightarrow[\substack{-2\ NaCl \\ -\ NaBH_4}]{\text{refluxing toluene}} \underset{\mathbf{10}}{LPr(BH_4)_2} \qquad (3)$$

Complex **10** is thermally very stable and as shown by mass spectrometry and elemental analysis contains no halide and coordinated solvent. Complex **10** is air and moisture sensitive. In addition, the monomeric structure of **10** was established by single crystal X-ray structural analysis.

Compound **10** exhibits a ^{11}B NMR spectrum that showed one sharp resonance at room temperature. This suggests that there is either a rapid exchange of the BH_4 groups on the NMR time scale or both BH_4 groups are equivalent. Temperature dependent NMR spectra indicated that both BH_4 groups are equivalent in solution. Moreover, no coupling between ^{11}B and ^{1}H nuclei in the ^{11}B NMR spectrum was observed.

This compound has been obtained for the first time by metathesis reaction from a complex having the general formula, $LLnX_2$, (L = β-diketiminato ligand, Ln = 4f metal; such reactions are known only for scandium β-diketiminato containing complexes, $[Sc\{(N(C_6H_3{}^iPr_2\text{-}2,6)C^tBu)_2CH\}Cl_2])$[41, 47b] thus demonstrating the bifunctionality of them. When **6** was subjected to a similar treatment, only a mixture of $LSm(BH_4)_2$ (82 %) and LSm $(BH_4)Cl$, (18 %), was achieved regardless of the drastic conditions used. The mixture could not be separated neither by fractionated crystallization due to their cocrystallization, nor recrystallization due to similar solubility.

2.4.1.1. *Discussion of the crystal structure of* **10**.

Yellow crystals of **10**, which crystallize in the monoclinic $P2_1/n$ space group, appropriate for X-ray measurement were obtained by slight removal of the solvent *in vacuo* (Figure 9).

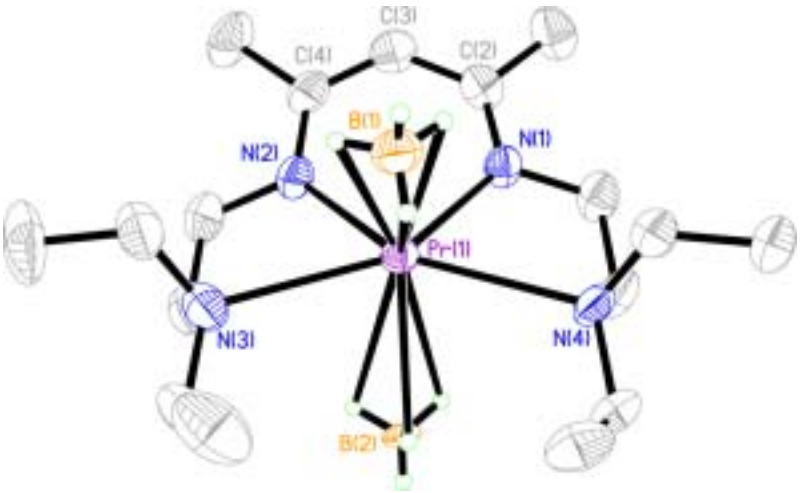


Figure 9. *Molecular structure of* **10** *showing 50 % probability ellipsoids (the hydrogen atoms are omitted for clarity, except those of the BH_4 groups).*

The molecular structure of **10** shows the two BH_4 groups coordinated through 3 H atoms each to the praseodymium atom, thus the coordination number of praseodymium is *ten*.

Table 4. Selected bond lengths (Å) and angles (°) for $LPr(BH_4)_2$, **10**.

Bond lenghts		Angles	
Pr(1)-N(2)	2.421(4)	N(2)-Pr(1)-N(1)	76.66(14)
Pr(1)-N(1)	2.430(4)	N(2)-Pr(1)-N(4)	67.17(15)
Pr(1)-N(3)	2.739(4)	Pr(1)-N(1)-C(1)	124.7(4)
Pr(1)-N(4)	2.749(5)	N(1)-C(1)-C(2)	124.2(5)
Pr(1)-B(1)	2.644(8)	C(1)-C(2)-C(3)	130.8(5)
Pr(1)-B(2)	2.824(5)	C(2)-C(3)-N(2)	124.2(5)
N(2)-C(4)	1.337(7)	C(3)-N(2)-Pr(1)	122.9(4)
N(1)-C(2)	1.329(7)	N(3)-Pr(1)-N(4)	146.08(14)
C(2)-C(3)	1.405(8)	N(1)-Pr(1)-N(3)	68.57(14)
C(4)-C(3)	1.390(8)	B(1)-Pr(1)-B(2)	144.1(2)

The praseodymium atom, which lies in the NC_3N plane, has as in the previous cases like **4** or **5** a *pseudooctahedral* geometry with two different types of Pr-N bonds (Table 4).

By comparison of the Pr-N bond lengths of **4**, **5** and **10**, it can be observed that they vary with the size of X (X = Cl, Br, BH_4). The bulkier X is, the longer are the Pr-N distances. As in the previous complexes, the ligand core shows electron delocalization as

well. The Pr-B distances are to some extent different. However, they are in the range of the previously reported Pr-B distances of related compounds (*av.* 2.757 Å).[57]

2.4.2. *Synthesis of LTb(CH_2SiMe_3)$_2$,* **11**.

Neutral non-cyclopentadienyl dialkyl complexes of the 4*f* elements with the general formula $LLnR_2$, of which very few were reported yet[22b] may be of general interest as catalysts or precursors for further reactions due to the two reactive Ln-C bonds, which would allow greater flexibility in their reactivity, for example toward simple alkenes, as was already shown with similar complexes of early transition metals.[41, 47b, 58] However, to prepare such compounds has proved to be a difficult task.[59] Partly due to the lack of suitable precursors and partly due to the fact that metathesis reactions to achieve the desired $LLnR_2$ compounds are not favored thermodynamically, because Ln-X bonds are stronger than the Ln-C bonds.[5] Additionally, the tendency toward ligands redistribution and elimination reactions of the desired targets makes it difficult to obtain these species in a pure form.[59] Having obtained salt and solvent free derivatives of the general formula $LLnX_2$ (X = Cl, Br), several metathesis reactions using different alkyl lithium or Grignard reagents have been attempted under different conditions. Under optimized conditions a crystalline terbium dialkyl derivative LTb(CH_2SiMe_3)$_2$ has been obtained from $LTbBr_2$, in high yield (Eq. (4)). The reaction was carried out in diethylether (the reaction failed in toluene, THF, benzene, and acetonitrile, respectively at different reaction temperatures) at –78 °C and the mixture was left to reach room temperature overnight. Finally the solvent was removed and the desired compound was extracted with hexane from the crude product and crystallized at –26 °C. Complex **11** is highly air and moisture sensitive.

$$\underset{\mathbf{8}}{LTbBr_2} + 2\ LiCH_2SiMe_3 \xrightarrow[\text{2. hexane, -2 LiBr}]{\text{1. ether, -78 °C}} \underset{\mathbf{11}}{LTb(CH_2SiMe_3)_2} \qquad (4)$$

Apparently, no decomposition was observed for **11** in a deuterated benzene solution at room temperature.

A similar compound of samarium has been also prepared, however no crystalline material was available thus far.

2.4.2.1. *Discussion of the crystal structure of* **11**.

Complex **11** crystallizes in the orthorhombic space group $Pca2_1$ and contains two crystallographically independent but chemically equivalent molecules in the unit cell with only insignificant differences of the bond lengths and angles. These molecules cannot be related by an inversion center. The X-ray structure of **11** is shown in Figure 10 (only one molecule is shown for simplicity).

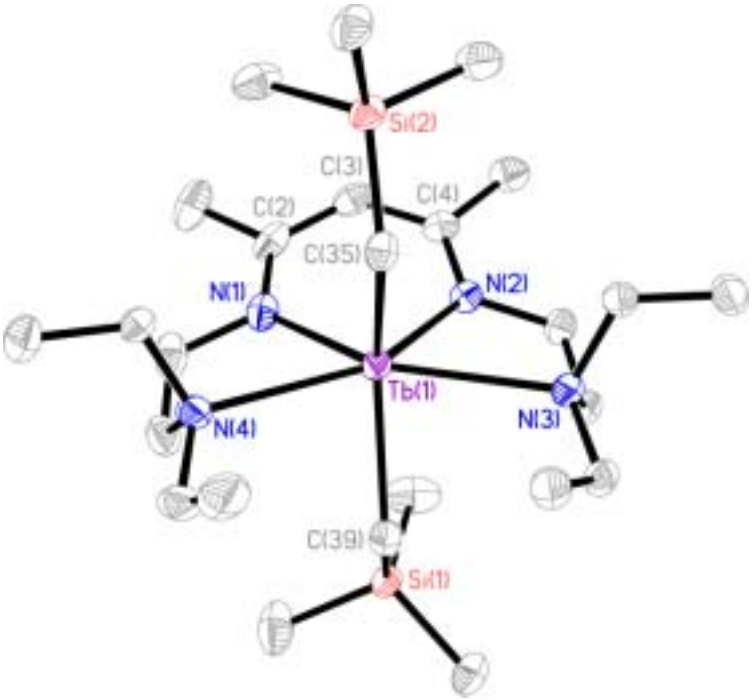


Figure 10. *Molecular structure of* **11** *showing 50 % probability ellipsoids (the hydrogen atoms are omitted for clarity).*

For **11** both pendant arms of the ligand are coordinated to the Tb atom, which was expected due to the electrophilicity of the metal ion. The coordination number at the metal is *six* as in **8** and the geometry around the metal atom is *pseudooctahedral* showing that the ligand is indeed tetradentate. The Tb-C bonds (*av.* 2.507 Å) are shorter than the Tb-Me bonds (2.57 Å) in $[(^tBuC_5H_4)_2Tb(\mu\text{-}Me)]_2$[60] indicating the σ bond character (Table 5). The C-Tb-C angle deviates substantially from 180°. By comparison of the Tb-N bonds of **11** they are little longer than those of **8** regardless of the bonding mode. As expected, the mean deviation of the Tb atom from the NC_3N plane, (0.80 Å for **8**; 0.73 Å

and 0.90 Å for **11)**, are in the same range. The expected delocalization of the electrons on the ligand framework is clearly documented by the C-C and C-N bond lengths.

Table 5. Selected bond lengths (Å) and angles (°) for $LTb(CH_2SiMe_3)_2$, **11**.

Bond lengths		Angles	
Molecule **11**a			
Tb(1)-N(1)	2.383(2)	N(1)-Tb(1)-N(2)	77.91(7)
Tb(1)-N(2)	2.3771(19)	N(1)-Tb(1)-N(4)	68.82(7)
Tb(1)-N(3)	2.6902(19)	N(2)-Tb(1)-N(3)	68.64(6)
Tb(1)-N(4)	2.6954(19)	N(3)-Tb(1)-N(4)	144.32(6)
Tb(1)-C(39)	2.492(2)	N(1)-C(2)-C(3)	124.4(2)
Tb(1)-C(35)	2.508(2)	N(2)-C(4)-C(3)	124.5(2)
N(1)-C(2)	1.329(3)	C(2)-C(3)-C(4)	129.9(2)
C(2)-C(3)	1.403(4)	C(39)-Tb(1)-C(35)	135.47(8)
C(3)-C(4)	1.401(3)		
N(2)-C(4)	1.326(3)		
Molecule **11**b			
Tb(2)-N(5)	2.3867(19)	N(6)-Tb(2)-N(5)	78.93(7)
Tb(2)-N(6)	2.3754(19)	N(7)-Tb(2)-N(8)	141.60(6)
Tb(2)-N(7)	2.694(2)	N(6)-Tb(2)-N(7)	69.74(7)
Tb(2)-N(8)	2.703(2)	N(5)-Tb(2)-N(8)	69.72(6)
Tb(2)-C(43)	2.508(2)	N(5)-C(21)-C(20)	125.0(2)
Tb(2)-C(47)	2.518(3)	N(6)-C(19)-C(20)	125.0(2)
N(6)-C(19)	1.338(3)	C(21)-C(20)-C(19)	130.6(2)
N(5)-C(21)	1.330(3)	C(43)-Tb(2)-C(47)	141.80(8)
C(21)-C(20)	1.396(3)		
C(19)-C(20)	1.400(4)		

2.5. *Synthesis of LMX_2 (M = Al, V).*

Since the ligand L has confirmed to be very useful in lanthanide chemistry, the attraction in expanding its chemistry arose. The chemistry of the early transition metals, especially the chemistry of scandium with L has increased to a great extent, as a result unusual C-H bond activation[47a] and oxidation state being accomplished.[23] Besides, L containing complexes of the following electrophilic metals as titanium,[61] yttrium,[48] lanthanum,[48] cerium,[48] holmium,[48] erbium,[48] and lutetium[48] have been prepared and characterized. New insights about the polydentate behaviour of the ligand L have been

revealed when complexes with aluminum and vanadium were prepared. The literature offers examples of ligands, which are appropriate to form complexes with many kinds of elements,[2] and L is one of them.

2.5.1. *Aluminum Complexes.*

The chemistry of aluminum with *β*-diketiminato ligands has been intensely studied recently.[24, 62] Monomeric aluminum(I) complex, $[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)CMe)_2CH\}]$, reported by Roesky *et al.*[24] or a "triple ion" + free anion, $([Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)CMe)_2CH\}(Me)]_2\text{-}[BMe(C_6F_5)_3])^+[BMe(C_6F_5)_3]^-$, reported by Jordan *et al.*[62a] constitute two of the highlights of the recent years for the *β*-diketiminato containing aluminum complexes. Therefore to obtain new significant complexes has been a great challenge due to the current interest in this field.

2.5.2. *Synthesis of $LAlCl_2$,* **12***, and $LAlMe_2$,* **13**.

First, the ability of the ligand to form complexes with aluminum has been examined by preparing simple starting materials like $LAlCl_2$ (**12**) or $LAlMe_2$ (**13**).

The reaction of **3** and a suspension of Al_2Cl_6 (Eq. (5)) in toluene at 0 °C gave, after filtering off LiCl and removal of the solvent, an oily product which further crystallizes as $LAlCl_2$ (**12**). Unfortunately, all the efforts to obtain a diiodocomplex, which was supposed to be useful for further metathesis reactions, especially reductions, failed. $LAlMe_2$ (**13**) was prepared by the reaction of **2** and $AlMe_3$ (Eq. (6)) at –78 °C in hexane and was isolated as yellow oil at room temperature.

$$\underset{\mathbf{3}}{2\,LLi} + Al_2Cl_6 \xrightarrow[\text{-2 LiCl}]{\text{Toluene, 0 °C}} \underset{\mathbf{12}}{2\,LAlCl_2} \qquad (5)$$

$$\underset{\mathbf{2}}{LH} + Al_2Me_6 \xrightarrow[\text{- CH}_4]{\text{Hexane, -78 °C}} \underset{\mathbf{13}}{LAlMe_2} \qquad (6)$$

Both complexes were characterized by multinuclear NMR spectrometry, EI-MS, and elemental analysis. Additionally, a single crystal X-ray investigation was carried out for **12**.

2.5.2.1. *Discussion of the crystal structure of* **12**.

The X-ray structure of **12** is shown in Figure 11. Complex **12** crystallizes in the triclinic space group $P\bar{1}$.

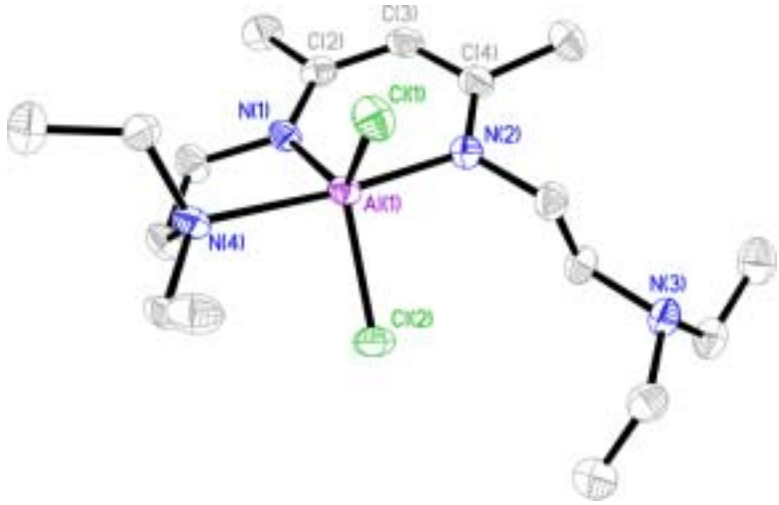
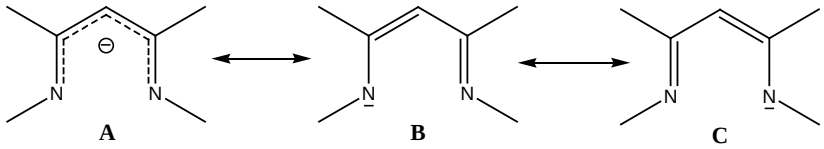


Figure 11. *Molecular structure of* **12** *showing 50 % probability ellipsoids (the hydrogen atoms are omitted for clarity).*

Unlike the preceding complexes in **12** only one arm is coordinated to aluminum. Furthermore, the delocalization of the π-electrons of the backbone that has been previously encountered, does not take place to the same extent as for the former complexes. This aspect is revealed by comparison of the bond lengths from the backbone, such as C(2)-N(1) and C(4)-N(2) or Al(1)-N(1) and Al(1)-N(2) (Table 6).

The explanation is given by considering the resonance forms of the ligand backbone (Scheme 5). Thus it might be assessed that the resonance form **B** (amido-imino) contributes more than **A** and **C** to the bonding mode.



Scheme 5: *The resonance structures of β-diketiminato ligands.*

Somewhat longer Al-Cl bond lengths are observed for **12** by comparison with a similar β-diketiminato derivative as $[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH\}Cl_2]$ (*av.* 2.12 Å).[63] This is caused by different coordination numbers, *five* for **12** and *four* for the latter cpmpound.

Table 6. Selected bond lengths (Å) and angles (°) for $LAlCl_2$, **12**.

Bonds lengths		Angles	
Al(1)-N(1)	1.897(2)	N(1)-Al(1)-N(2)	91.96(8)
Al(1)-N(2)	1.968(2)	N(2)-Al(1)-N(4)	172.27(8)
Al(1)-N(4)	2.220(2)	N(1)-Al(1)-N(4)	80.50(8)
Al(1)-Cl(2)	2.1848(11)	C(2)-N(1)-Al(1)	125.55(15)
Al(1)-Cl(1)	2.1947(10)	C(4)-N(2)-Al(1)	123.96(16)
N(1)-C(2)	1.346(3)	N(1)-C(2)-C(3)	123.1(2)
N(2)-C(4)	1.322(3)	C(2)-C(3)-C(4)	126.4(2)
C(2)-C(3)	1.384(3)	N(2)-C(4)-C(3)	122.3(2)
C(4)-C(3)	1.408(3)	Cl(2)-Al(1)-Cl(1)	114.26(4)

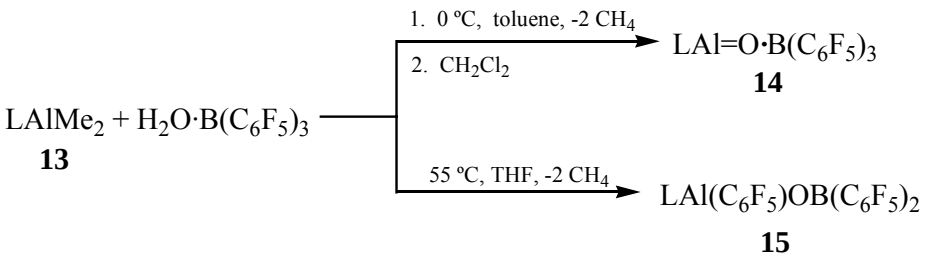
2.5.3. *Synthesis of $LAlO{\cdot}B(C_6F_5)_3$,* **14***, and $LAl(C_6F_5)OB(C_6F_5)_2$,* **15**.

As already mentioned, the β-diketiminatoaluminum chemistry has gained in recent years great interest. Howbeit, there were many attractive goals left and one of them was to synthesize the first monoaluminoxane. Previously, it has been shown that aluminoxanes of the general formula $(RAlO)_n$ for n>1 can be obtained by the controlled reaction of organoaluminum compounds with either water or water contained in hydrated salts or $(Me_2SiO)_3$.[64] Although the simplest member of the series RAlO has been predicted to be obtainable based on the analogy with aluminum imides,[65] its formation and characterization remained a delusive endeavor because it implies an Al-O double bond which is presumably very unstable although π interaction between Al and O atoms has been invoked by several groups.[66] However, compounds with such bonds may be either sterically stabilized (by using bulky ligands bonded to the aluminum) or electronically (by using Lewis acids). The approach for this purpose was to use $H_2O{\cdot}B(C_6F_5)_3$ which was confirmed to act as a strong Brønsted acid,[67] and its ability to protonate M-R bonds has been verified.[68] Furthermore if a monoaluminoxane is formed,

$B(C_6F_5)_3$ may hinder the aggregation due to its strong Lewis acid character,[69] which can stabilize the monoaluminoxane.

Indeed, carrying out the reaction at 0 ºC between **13** and $H_2O{\cdot}B(C_6F_5)_3$ in toluene, $LAlO{\cdot}B(C_6F_5)_3$ (**14**) was formed readily, filtered off at room temperature and crystallized from dichloromethane (–26 ºC), (Eq. (7)).

When the reaction was carried out in THF at 55 ºC for 2 h, after the solvent removal, an oily product is formed which further crystallizes as an isomer of **14**, formulated as $LAl(C_6F_5)OB(C_6F_5)_2$ (**15**), (Eq. (7)).



(7)

Both complexes were characterized by multinuclear NMR, elemental analysis, and X-ray structural analysis and they do support each other. However, by corroborating the ^1H NMR spectra of **14** and **15** with the solid-state structures a rapid interconversion in solution can be conceived in order to account for the equivalency of the dangling arms of the ligand unlike in the solid state where only one arm is coordinated to the Al atom (see Figures 12 and 13).

2.5.3.1. *Comparative discussion of the crystal structures of* **14** *and* **15**.

Both complexes crystallize in the monoclinic space group $P2_1/n$. In both complexes one arm is not coordinated as in the case of **12** (Figure 12).

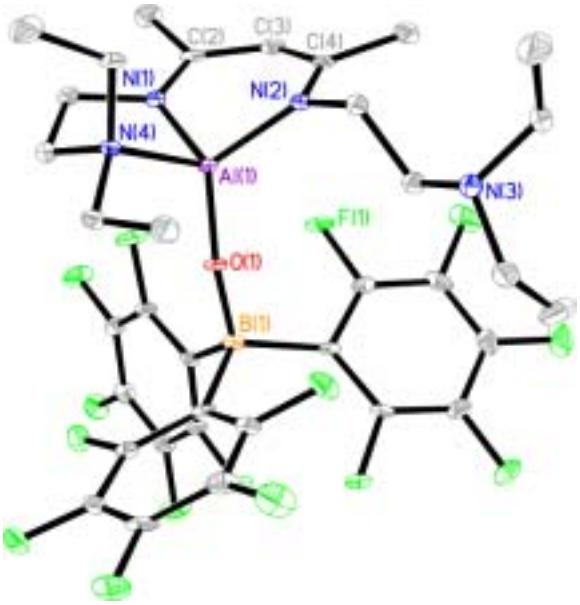
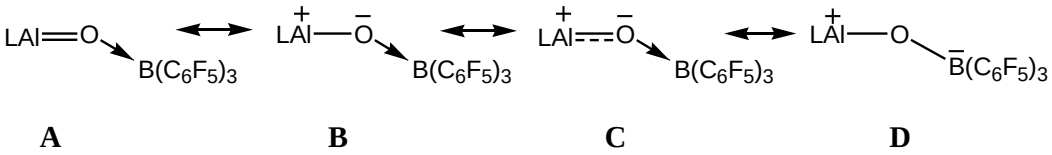


Figure 12. *Molecular structure of* **14** *showing 50 % probability ellipsoids (the hydrogen atoms are omitted for clarity).*

For **14** (Figure 13) the Al-O bond length is 1.659 Å, which is the shortest Al-O bond reported for a tetracoordinated Al atom so far (Table 7), 1.687 Å has been reported for a tricoordinated Al atom.[66a] This can be explained by considering the following resonance structures:



Scheme 6: *Proposed resonance structures for* **14**.

Resonance forms **A** and **C** can be considered to be mainly responsible for the shortness of the Al-O bond length that implies a certain double bond character. These resonance structures can also be taken into account to explain the B-O bond length (1.444 Å) intermediate between a coordinative B-O bond found in $H_2O{\cdot}B(C_6F_5)_3$ (1.597 Å)[67d] and a covalent bond B-O (1.311 Å for **15**). Even so the $B(C_6F_5)_3$ stabilizes the monoalumoxane by dispersing the negative charge from oxygen (**B**, **C**, and **D**) as it can

be seen from Scheme 6, the β-diketiminato ligand must also be taken into consideration because it reduces the positive charge on Al by acting as a Lewis base.[49, 70]

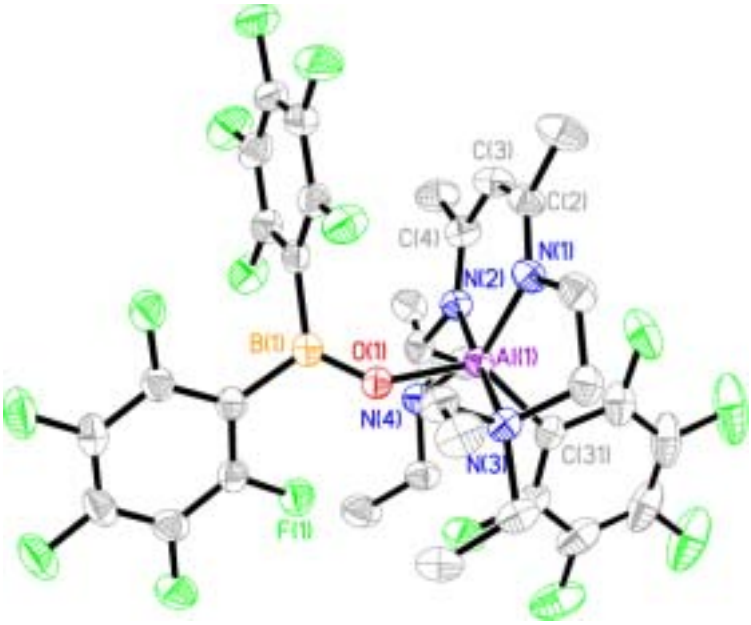


Figure 13. *Molecular structure of* **15** *showing 50 % probability ellipsoids (the hydrogen atoms are omitted for clarity).*

In addition, these resonance structures support the irreversible isomerisation of **14** to **15**. For complex **15** (Figure 13), the Al-O and B-O bond lengths have 1.780 and 1.311 Å, respectively, (Table 8), and they are in the range of those of previously reported compounds.[64, 69c] In both complexes the Al atom is part of two heterocycles (five- and six-membered rings) and none of them is planar. The Al-N bond lengths for **14** (*av.* 1.855 Å) are somewhat shorter than those previously reported for similar compounds (*av.* 1.90 Å).[62] In **15** they have common values (*av.* 1.925 Å).[62, 71] The coordinative Al-N bond lengths follow the same principle as for Al-N bond length. Thus, Al-N(4) in **14** (1.988 Å) is shorter than Al-N(4) in **15** (2.195 Å), still they are in the range of those of previously reported similar compounds.[72] The β-diketiminato C-N and C-C ring distances of both the compounds have values (*av.* 1.34 and 1.40 Å) corresponding to a delocalized π–electron system.[69]

In the light of the alteration of the Al-O bond order for the complexes **14** and **15**, as seen from the different bond distances, a reduction of the Al-O-B angles from 163.76°

(**14**) to 141.69° (**15**) is the expected consequence. As anticipated there are H-F hydrogen like interactions among the discrete molecules in the crystals in both cases (H-F: 2.484 Å for **14** and 2.420 Å for **15**) that are smaller than the sum of the van der Waals radii.[73]

Table 7. Selected bond lengths (Å) and angles (°) for LAlO·B(C_6F_5)$_3$, **14**.

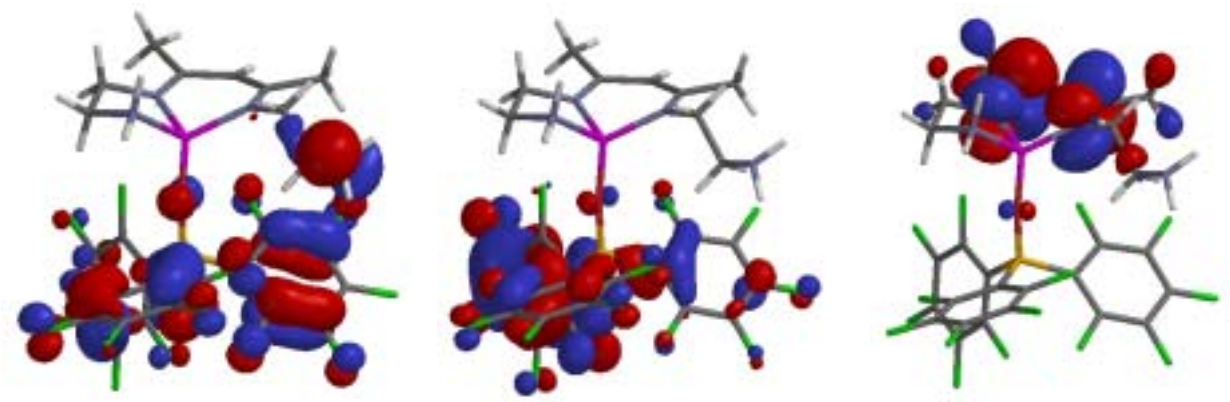
Bond lengths		Angles	
Al(1)-O(1)	1.659(3)	Al(1)-O(1)-B(1)	163.76(2)
B(1)-O(1)	1.444(3)	Al(1)-N(2)-C(4)	118.02(2)
Al(1)-N(1)	1.853(2)	C(2)-N(1)-Al(1)	123.44(2)
Al(1)-N(2)	1.857(4)	N(2)-Al(1)-N(1)	96.69(1)
Al(1)-N(4)	1.988(4)	N(1)-Al(1)-N(4)	86.50(1)
N(2)-C(4)	1.356(3)	N(2)-C(4)-C(3)	123.45(2)
C(3)-C(2)	1.401(3)	C(4)-C(3)-C(2)	126.79(2)
C(4)-C(3)	1.402(0)	C(3)-C(2)-N(1)	119.68(2)
N(1)-C(2)	1.334(4)		

Table 8. Selected bond lengths (Å) and angles (°) for LAl(C_6F_5)OB(C_6F_5)$_2$, **15**.

Bond lengths		Angles	
Al(1)-O(1)	1.780(1)	Al(1)-O(1)-B(1)	141.69(13)
B(1)-O(1)	1.311(2)	Al(1)-N(2)-C(4)	125.62(13)
Al(1)-N(1)	1.964(2)	C(2)-N(1)-Al(1)	125.19(13)
Al(1)-N(2)	1.890(2)	N(2)-Al(1)-N(1)	94.11(7)
Al(1)-N(4)	2.195(2)	N(1)-Al(1)-N(4)	82.48(6)
N(2)-C(4)	1.346(3)	N(2)-C(4)-C(3)	123.68(17)
C(3)-C(2)	1.384(3)	C(4)-C(3)-C(2)	127.43(18)
C(4)-C(3)	1.409(3)	C(3)-C(2)-N(1)	122.50(17)
N(1)-C(2)	1.322(2)	C(31)-Al-O(1)	123.43(7)
Al-C(31)	2.043(2)		

Further insights into the bonding of LAlO·B(C_6F_5)$_3$, **14**, are provided by the electron density surfaces and energies performed by a restricted hybrid HF-DFT SCF calculation performed with Pulay DIIS extrapolation using Spartan '02 Quantum Mechanics Program[46] on the model system L_1AlO·B(C_6F_5)$_3$ with L_1 = $H_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NH_2$. Surprisingly, the HOMO-1 and HOMO do not show any contribution from the π-electron system of the backbone (Figure 14) as in the case of **3**. They are associated with the oxygen lone pairs, the π-orbitals of the C_6F_5

groups, and the lone pair of the uncoordinated nitrogen atom. The existence of only two lone pairs on the oxygen atoms and the non-existence of any electron density on the boron atom tell that the A resonance structure (vide supra) is the most probable one. Consequently, the Al-O bond has a strong double bond character. The LUMO is characterized by the out of plane p-type orbitals of the backbone as in the case of **3**. As expected, the isomer of **14**, the complex **15**, is more stable a fact that can be seen by comparing their calculated frontier molecular orbital energies (Figure 15).



HOMO-1 HOMO LUMO

Figure 14. *Qualitative HOMO-, HOMO and LUMO representations for $L_1AlO{\cdot}B(C_6F_5)_3$ calculated by means of the RB3LYP level of theory, basis set 6-31G(D).*

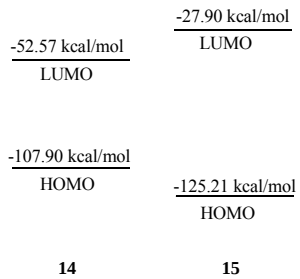
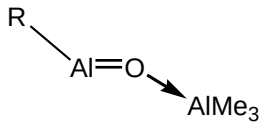


Figure 15. *Calculated energies of the frontier molecular orbitals of the complexes $L_1AlO{\cdot}B(C_6F_5)_3$ and $L_1Al(C_6F_5)OB(C_6F_5)_2$.*

2.5.3.2. *Speculative mechanisms for aging and functioning of the methylaluminoxane, MAO.*

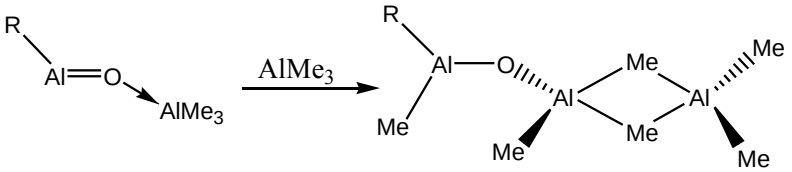
Based on the structures of **14** and **15** a tentative mechanism of the function of MAO can be proposed. The importance of MAO as a cocatalyst in the Ziegler-Natta

polymerization of α-alkenes resulted in a vast amount of research to understand its activity.[74] Due to the complexity of MAO, which is thought to consist of polymers of varying structures $[MeAlO]_n$ with a molecular formula weight ranging from 900 to 1600, the structure and reactivity of MAO remained rather an enigma, although some structural information has been obtained by analogy with complexes obtained by partial hydrolysis of trialkylaluminum (AlR_3, R = Me, ^{t}Bu).[64e, 64f, 74, 75] Worth mentioning is a possible mechanism for the activation of zirconocene-based catalysts like Cp_2ZrMe_2 which has been proposed by Barron *et al.*, that implies an Al-O bond breaking and a methyl anion transfer to aluminum.[75] Nevertheless, such a mechanism does not offer satisfactory explanations to several facts, for instance the high percentage of $AlMe_3$ in MAO[76] and the huge amount of MAO needed in the catalytic process (≥ 1000 eqs.). Another issue would be the deterioration (aging) of MAO to which no clarification has been yet anticipated. An alternative model that might give reasonable solutions to the aforementioned issues can be, by comparison, seen as follows. Taking into account that **14** has been isolated and fully characterized it can be imagined that similar metastable species can be existent as well in MAO ($RAl{=}O{\cdot}AlMe_3$), such a double bond, more reactive than any Al-O-Al bond, is most likely stabilized by coordination of the Lewis acid ($AlMe_3$) to the O atom (Scheme 7).



Scheme 7: *Proposed active catalytic site of MAO.*

An internal thermodynamically favored isomerisation process accounts for the very low concentration of the active sites, and implicitly the huge amount of necessary cocatalyst, and the high amount of $AlMe_3$ present in MAO (Scheme 8).



Scheme 8: *Proposed aging mechanism for MAO.*

The addition of one mol of $AlMe_3$ is needed in order to stabilize the intermediate tricoordinated Al atom. This internal process may be responsible for the deterioration of MAO as well. Another sensitive issue is that only MAO is active but the activity of some other partial hydrolysis derivatives of trialkylaluminum is not comparable with that of MAO.[74, 75] In the light of the proposed formula for the active site, this can be explained by the different Lewis acidity (the highest is for $AlMe_3$) necessary for stabilization of an Al=O double bond as it can be seen in the case of **14** ($B(C_6F_5)_3$ is a very strong Lewis acid).[69]

2.5.4. *Synthesis of $LAl(Me)NH_2{\cdot}B(C_6F_5)_3$,* **16**.

Following the same principle as for the synthesis of the first monoaluminoxane, **14**, the synthesis of an aluminum imide containing an Al-N double bond has been attempted. Albeit the preparation of $[Al\{(N(C_6H_3{}^iPr_2\text{-}2,6)CMe)_2CH\}\text{-}(NC_6H_2{}^iPr_3\text{-}2,4,6)]$ has been published, no crystal structure has been reported so far for an aluminum imide.[65c]

Analogously, in this pursuit the adduct of $B(C_6F_5)_3$ with ammonia, $H_3N{\cdot}B(C_6F_5)_3$, has been used.[77] A similar reaction as for the synthesis of **14** has been performed but unfortunately only $LAl(Me)NH_2{\cdot}B(C_6F_5)_3$, **16,** has been isolated as the major product regardless of the reaction conditions (Eq. (8)).

$$\underset{\mathbf{13}}{LAlMe_2} + H_3N{\cdot}B(C_6F_5)_3 \xrightarrow[-\,CH_4]{\text{toluene, r.t.}} \underset{\mathbf{16}}{LAl(Me)NH_2{\cdot}B(C_6F_5)_3} \qquad (8)$$

The complex **16** was characterized by multinuclear NMR spectrometry, EI-MS, and elemental analysis. In the EI-MS spectrum no molecular peak of **16** has been observed, but the molecular peak of the desired aluminum imide, LAlNH (*m/z* 337), suggesting that it might be obtainable on this route from **16** under more drastic reaction conditions.

2.5.4.1. *Discussion of the crystal structure of* **16**.

Single crystals suitable for X-ray measurements were obtained in CH_2Cl_2 at –26 °C within several days. Complex **16** crystallizes in the triclinic space group $P\bar{1}$ presenting a disorder of one arm over two positions (Figure 16). Selected bond lengths and angles are given in Table 8.

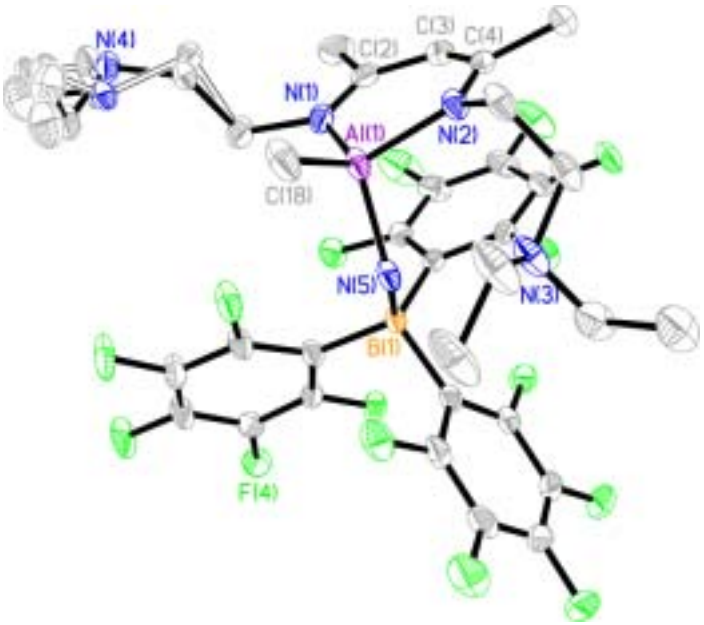


Figure 16. *Molecular structure of* **16** *showing 50 % probability ellipsoids (the hydrogen atoms are omitted for clarity).*

Interestingly, L in this case acts as a bidentate ligand unlike in the previous complexes, thus demonstrating its ability for a multitude of bonding modes. The coordination number of the aluminium atom is *four*. There is a difference between the Al - N belonging to the ligand core and the Al-NH_2 bond lengths due to the different π contributions of the Al-N bonds (Table 8). Howbeit, they are in the range of previously reported similar compounds.[71] The N-B bond length is comparable to those reported for $[Na(OEt_2)_4]^+[H_2N\{B(C_6F_5)_3\}_2]^-$ (1.62 Å).[78] The delocalization of the π-electrons can be derived from the C-N and C-C bond lengths of the backbone. The rather acute B-N-Al angle is normal considering the coordinative nature of the B-N bond. Likewise, there are H-F hydrogen like interactions (2.49 Å) among the discrete molecules of **16** in the crystal as in the case of **14** or **15** (see above).[73]

Table 8. Selected bond lengths (Å) and angles (°) for $LAlCl_2$, **16**.

Bond lengths		Angles	
Al(1)-N(2)	1.8853(17)	N(2)-Al(1)-N(1)	98.87(8)
Al(1)-N(1)	1.869(2)	Al(1)-N(2)-C(4)	122.44(14)
Al(1)-N(5)	1.9466(18)	C(2)-N(1)-Al(1)	122.92(14)
Al(1)-C(18)	1.951(2)	N(2)-C(4)-C(3)	122.91(18)
N(2)-C(4)	1.333(3)	C(4)-C(3)-C(2)	128.4(2)
C(3)-C(2)	1.404(3)	C(3)-C(2)-N(1)	122.5(2)
C(4)-C(3)	1.400(3)	N(5)-Al(1)-C(18)	106.99(10)
N(1)-C(2)	1.340(3)	B(1)-N(5)-Al(1)	129.70(13)
N(5)-B(1)	1.597(3)		

2.5.5. *Vanadium complexes.*

Recently, the groups of Theopold, Gibson, and Budzelaar have exploited the ability of the *β*-diketiminato ligands to prepare various complexes of Cr(III),[79] V(III),[58, 79b] and Ti(III).[58, 79b, 80] Also, it has been shown that such systems might act as paramagnetic homogeneous catalysts for the polymerization of small olefins (ethene, propene, etc).[58, 79] In spite of all of these efforts the *β*-diketiminato chemistry of such metals is not adequate developed. Therefore, useful starting materials have been prepared and subsequent metathesis reactions have been investigated.

2.5.6. *Synthesis of $LVCl_2$,* **17**.

Treatment of **3** with an equivalent amount of $VCl_3{\cdot}3THF$ in toluene at room temperature afforded $LVCl_2$ in good yield (Eq. (9)). $VCl_3{\cdot}3THF$ constitutes the usual common entry for many vanadium complexes in different oxidation states due to the straightforward accessibility and reasonable availability.[81]

$$\underset{\mathbf{3}}{LLi} + VCl_3{\cdot}3THF \xrightarrow[-\,2\,LiCl]{toluene,\ r.t.} \underset{\mathbf{17}}{LVCl_2} \qquad (9)$$

Complex **17** is well soluble in toluene, dichloromethane and THF respectively. It is thermally very stable, but moisture and air sensitive. Mass spectrometry and elemental analysis showed that compound **17** is a monomeric, solvent free compound and contains

no occluded salt. A ^{1}H NMR resonance could not be interpreted because it exhibits strongly broadened resonances due to the paramagnetic nature of the vanadium(III) and a ^{51}V NMR resonance could not be recorded. Unfortunately due to the poor quality of the crystals an X-ray diffraction experiment could not be accomplished. Further proof has been acquired by the following metathesis reaction.

2.5.7. *Synthesis of $LV(OSO_2CF_3)_2$,* **18**.

A straightforward reaction is the metathesis with $AgSO_3CF_3$. Reaction of the dichloro-derivate $LVCl_2$ with $AgSO_3CF_3$ occurred as expected with substitution of both chlorine atoms due to the oxophilic character of vanadium and the thermodynamically favored formation of AgCl (Eq. (10)).

$$\underset{\mathbf{17}}{LVCl_2} + 2\ AgOSO_2CF_3 \xrightarrow[\text{-2 AgCl}]{\text{toluene, r.t.}} \underset{\mathbf{18}}{LV(OSO_2CF_3)_2} \qquad (10)$$

Complex **18** is a green solid very soluble in aromatic solvents and THF, and it has been characterized by ^{19}F NMR spectrometry, EI-MS, elemental analysis and single crystal X-ray diffraction. The ^{19}F NMR spectrum shows as expected only one sharp resonance due to the equivalency of the CF_3 groups. Complex **18** constitutes the first vanadium(III) triflate derivative structurally characterized (two more triflate containing complexes of vanadium(II) were structurally characterized, namely $VPy_4(OSO_2CF_3)_2$[82a] and $V(H_2O)_6(OSO_2CF_3)_2$).[82b] Complex **18** is expected to be a superior starting material than the complex **17** for further metathesis reaction owing to the weak nucleophilicity of the CF_3SO_3 anion, which is a better leaving group than the Cl anion.[82a]

2.5.7.1. *Discussion of the crystal structure of* **18**.

Suitable crystals for an X-ray structural analysis were obtained from toluene at –26 °C within several hours. Compound **18** crystallizes in the monoclinic space group $P2_1/c$ together with two molecules of toluene (the toluene molecules are omitted in Figure 17 for clarity).

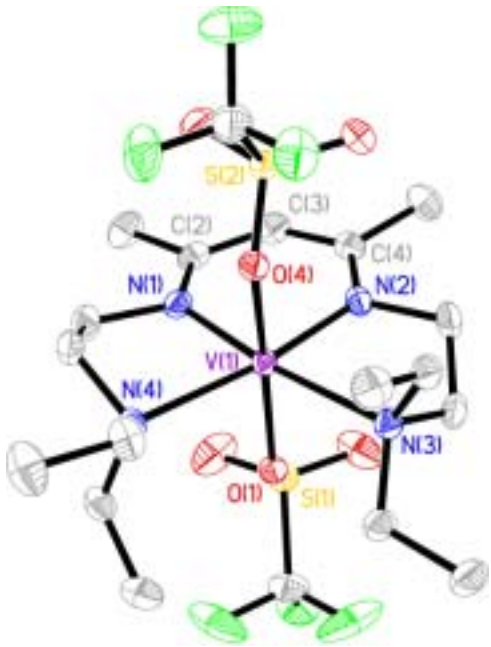


Figure 17. *Molecular structure of* **18** *showing 50 % probability ellipsoids (the hydrogen atoms are omitted for clarity).*

The crystal structure reveals that the vanadium atom in **18** is hexacoordinated (the ligand being tetradentate) with a *pseudooctahedral* geometry and the triflate anions are arranged in the apical positions (O(4)-V-O(1) 167.89°) (Table 9). This distortion might be attributable to the existence of the H-X (X = O, F) hydrogen bond like interaction between the discrete molecules (F-H 2.48 Å, O-H 2.57 Å). From steric and electronic reasons the triflate groups are not coordinated to vanadium in a *chelate* fashion, they bind monodentate through oxygen. The V-O distances of *av.* 2.06 Å in **18** are slightly shorter than those reported for $VPy_4(OSO_2CF_3)_2$ (2.127 Å)[82a] or for $V(H_2O)_6(OSO_2CF_3)_2$ (2.129 Å)[82b] as a consequence of a smaller radius of vanadium(III) compared with that of vanadium(II). The NC_3N atoms of the β-diketiminato backbone as well as the nitrogen atoms of the ligand arms are almost coplanar. The V to the NC_3N plane distance (0.09 Å) clearly indicates a σ bond interaction (η^2) between vanadium and the β-diketiminato ligand. The V-N bond lengths belonging to the backbone are comparable to those found in literature (*e.g.* 1.99 Å).[58, 83]

Table 9. Selected bond lengths (Å) and angles (°) for $LV(OSO_2CF_3)_2$, **18**.

Bond lengths		Angles	
V(1)-N(2)	2.0080(18)	N(2)-V(1)-N(1)	89.13(8)
V(1)-N(1)	2.0090(18)	N(2)-V(1)-N(3)	82.09(7)
V(1)-N(4)	2.3223(18)	N(1)-V(1)-N(4)	81.39(7)
V(1)-N(3)	2.3379(19)	N(2)-V(1)-N(3)	107.40(7)
C(2)-N(1)	1.327(3)	O(1)-V(1)-O(4)	167.89(6)
C(2)-C(3)	1.401(4)	S(2)-O(4)-V(1)	130.27(10)
C(3)-C(4)	1.408(4)	S(1)-O(1)-V(1)	132.67(10)
C(4)-N(2)	1.327(3)	C(2)-N(1)-V(1)	128.80(16)
V(1)-O(1)	2.0606(16)	C(4)-N(2)-V(1)	128.66(16)
V(1)-O(4)	2.0637(16)	N(2)-C(4)-C(3)	122.7(2)
O(1)-S(1)	1.4733(16)	C(2)-C(3)-C(4)	127.3(2)
O(4)-S(2)	1.4788(16)	N(1)-C(2)-C(3)	122.7(2)

2.5.8. *Synthesis of $LVPPh_2$,* **19**.

Although many reactions with alkyl lithium or Grignard reagents were attempted, no definite product was isolated in spite of indications that reactions had taken place (*e.g.* color changes). The reason is probably the electron density, brought about by the alkyl groups and the ligand L itself on the vanadium atom which is too high to be accommodated, giving rise to further decomposition reaction. Therefore, reactions with metal phosphides have been carried out, knowing *a priori* the capacity of the phosphorus atom for π-backbonding, which can stabilize the resulting complexes. On the other hand, the syntheses of some diorganophosphido complexes of vanadium (^{t}BuN=VN^{i}Pr$_2$)[P(SiMe$_3$)$_2$],[84a] ^{t}BuN=V[P(SiMe$_3$)$_2$]$_3$,[84b] [Li(DME)V{(P(C$_6$H$_{11}$)$_2$}$_4$][84c]) have been published, however, none of them has been structurally characterized.

Surprisingly, the reaction of **17** with 2 equivalents of $KPPh_2$ in THF yielded after removal of the THF and extraction in toluene complex **19** as an unexpected product which represents the first neutral heteroleptic terminal diorganophosphido-complex of vanadium(II) (Eq. (11)).

$$\underset{\mathbf{17}}{2\ LVCl_2} + 4\ KPPh_2 \xrightarrow[\text{2. toluene, - 4 KCl}]{\text{1. THF, -78 °C}} \underset{\mathbf{19}}{2\ LVPPh_2} + (Ph_2P)_2 \qquad (11)$$

Complex **19** has been characterized by ^{31}P NMR, EI-MS, elemental analysis, and single crystal X-ray diffraction. Support for the reaction pathway was given by confirmation of $(Ph_2P)_2$ as a byproduct of this reaction by multinuclear NMR spectroscopy. Essentially, such reductions are not unusual when diorganophosphides are involved. Recently similar reactions have been reported for $LnI_3 \cdot 3THF$ (Ln = Sm, Yb) yielding as the major product $Ln(PPh_2)_2 \cdot 4THF$.[85] In the previous scarce examples, ligands of composition PR_2 are mainly acting as bridging units (μ-PR_2).[86] There are only few structurally characterized complexes of transition metals where the bonding pattern is a terminal one.[87] Interestingly, a terminal diorganophosphidoplatinum(II) complex has found application as a catalyst in the asymmetric hydrophosphination of acrylonitrile.[87c]

2.5.8.1. *Discussion of the crystal structure of* **19**.

Complex **19** (Figure 18) has been recrystallized from toluene at –26 °C and crystallizes in the monoclinic space group $P2_1$ with two crystallographically independent but chemically equivalent molecules (Table 10).

Figure 18. *Molecular structure of* **19** *showing 50 % probability ellipsoids (the hydrogen atoms are omitted for clarity).*

The crystal structure analysis reveals that, unlike **18**, the vanadium atom in **19** is pentacoordinated (the ligand is tetradentate) with a square pyramidal geometry. The

vanadium atom lies on the NC_3N β-diketiminato backbone plane (the mean deviation is 0.06 Å). Still, the vanadium atom is lying with about *av.* 0.36 Å above the plane formed by the four nitrogen atoms of the ligand.

Similarly to **18** the V-N bond lengths belonging to the backbone are comparable to those found in the literature (*e.g.* 1.99 Å)[58, 83] although they are slightly longer owing to the increase of the vanadium(II) radius. As expected, the delocalization of the π-electrons can be seen from the C-C and C-N bond lengths of the backbone.

Table 10. Selected bond lengths (Å) and angles (°) for $LVP(C_6H_5)_2$, **19**.

Bond lengths		Angles	
Molecule **19a**			
V(1)-N(2)	2.0498(17)	N(4)-V(1)-N(1)	77.84(6)
V(1)-N(1)	2.0436(17)	N(1)-V(1)-N(2)	89.76(7)
V(1)-N(4)	2.3248(18)	N(2)-V(1)-N(3)	78.16(7)
V(1)-N(3)	2.3057(17)	N(4)-V(1)-N(3)	108.26(6)
V(1)-P(1)	2.5731(10)	N(1)-C(2)-C(3)	123.27(19)
N(1)-C(2)	1.337(3)	N(2)-C(4)-C(3)	123.55(18)
C(2)-C(3)	1.398(3)	C(4)-C(3)-C(2)	128.89(17)
C(3)-C(4)	1.399(3)	C(2)-N(1)-V(1)	127.26(14)
N(2)-C(4)	1.331(3)	C(4)-N(2)-V(1)	127.08(14)
Molecule **19b**			
N(5)-V(2)	2.0380(17)	N(5)-V(2)-N(6)	89.56(9)
V(2)-N(6)	2.0510(17)	N(6)-V(2)-N(8)	79.51(9)
V(2)-N(8)	2.2756(18)	N(5)-V(2)-N(7)	78.93(8)
V(2)-N(7)	2.2878(18)	N(8)-V(2)-N(7)	103.87(8)
V(2)-P(2)	2.5579(9)	N(6)-C(33)-C(32)	122.9(2)
N(5)-C(31)	1.333(3)	N(5)-C(31)-C(32)	122.8(3)
N(6)-C(33)	1.337(3)	C(33)-C(32)-C(31)	129.4(2)
C(33)-C(32)	1.395(3)	C(31)-N(5)-V(2)	127.85(19)
C(31)-C(32)	1.402(3)	C(33)-N(6)-V(2)	127.42(19)
N(5)-V(2)	2.0380(17)	N(5)-V(2)-N(7)	78.93(8)

The phosphido ligands are substantially pyramidalized with bond lengths (2.573 and 2.557 Å respectively) that can be considered remarkably large. These V-P distances are notably longer than those reported for a diphosphene vanadium(II) complex, *trans*-

$[\{V(\eta^5\text{-}C_5H_5)(CO)_3\}_2(PMes)_2]$[88a] (2.397 Å) and a phosphinidene vanadium complex, $[V_2(CO)_4(\eta^5\text{-}C_5H_5)_2\{\mu\text{-}P(2,4,6\text{-}^tBu_3C_3H_2)\}]$[88b] (2.268 Å). Intriguingly, these distances are also longer than the V-P distances found in some complexes containing coordinated phosphines such as $V(N\text{-}2,6\text{-}^iPr_2C_6H_3)Cl_3(depe)$ (*e.g.* 2.52 Å).[88c] This can be attributable to some crystal packing effects, the bigger radius for vanadium(II),[5] and a greater extent of the ionic character of the V-P bond in **19**.

2.6. *Synthesis of the (2-diphenylphosphanyl-ethyl)-[3-(2-diphenylphosphanyl-ethylimino)-1-methyl-but-1-enyl]-amine,* **20**.

It has been shown that the ligand L is tailor made for electrophilic metals in the oxidation state +3. On the other hand, when used for late transition metal chemistry no characterizable compounds were isolable probably due to the high Lewis basicity and the non-existence of the ability for π-backbonding of the ligand L unlike the sterically encumbered β-diketiminato ligands for which quite a number of such complexes have been synthesized.[29, 21, 89] Consequently, another ligand has been designed and prepared bearing P-donor groups attached at the pendant arms (Figure 19). The synthesis of the conjugated acid of L', **20**, follows basically the same route as that for the conjugated acid of L, **2**.

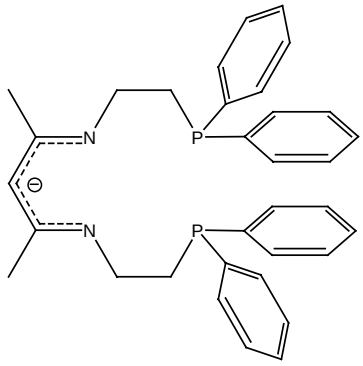
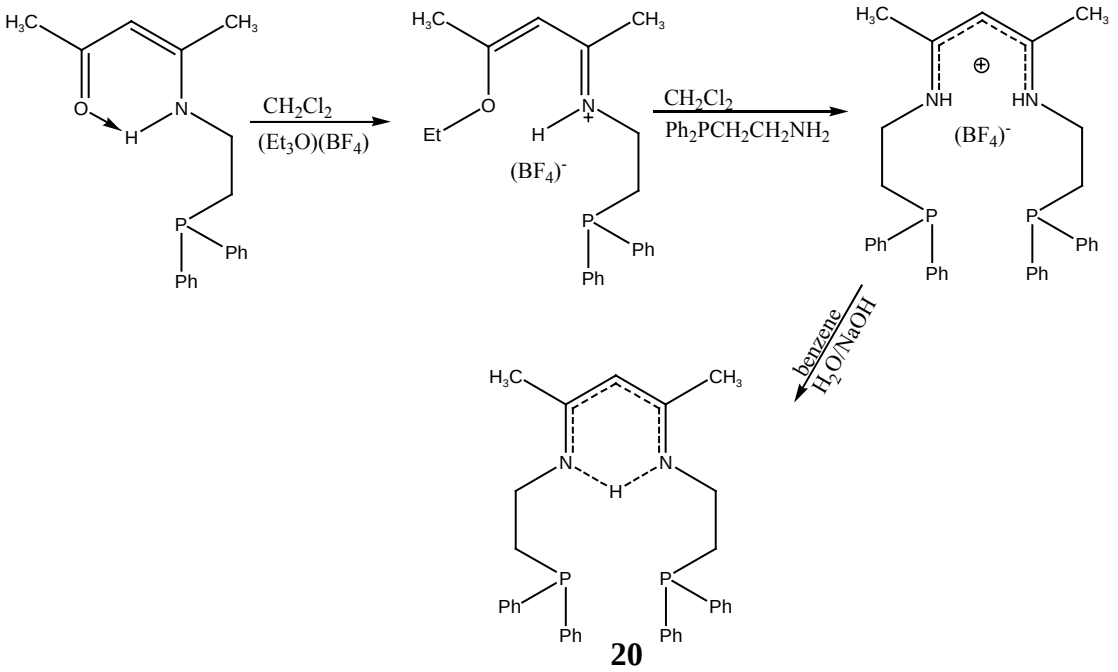


Figure 19. *The projected skeleton of the monoanionic ligand, L' = [N,N'-(1,3-dimethyl-1,3-propanediylidene)bis[2-diphenylphosphanyl-ethylamine]].*

The reaction of 4-(2-diphenylphosphanyl-ethylamino)-pent-3-en-2-one[90] with $(Et_3O)(BF_4)$ in dichloromethane followed by 2-diphenylphosphanyl-ethylamine and NaOH afforded after extraction with benzene and total removal of benzene and washing

with cold ether a white powder, **20**, in 54 % yield (Scheme 9).



Scheme 9: *Reagents and solvents for the preparation of the conjugated acid of L',* **20**.

Compound **20** is soluble in aromatic solvents, CH_2Cl_2, $CHCl_3$, and THF, but only sparingly soluble in aliphatic solvents and diethylether. It was characterized by multinuclear NMR spectrometry, EI-MS, and elemental analysis. ^{31}P NMR spectrum consists of a resonance at δ –21 ppm. An advantage of this ligand L' and its complexes over the fully nitrogen substituted ligand L is the availability of an additional spectroscopic probe from the ^{31}P NMR, while ^{1}H NMR spectra are hard to interpret.

In contrast to the lithiation of **20**, which is an intermediary step, it proved not to be so straightforward as for **2**, LH. Therefore, an alternative pathway was used, and that is to prepare the potassium salt of **20**. When **20** was treated with an excess of KH (refluxing toluene, 1:1.5 molar ratio) the expected potassium salt was obtained.

$$\text{L'H} + 1.5\ \text{KH} \xrightarrow[\substack{-H_2 \\ -\ KH}]{\text{toluene}} \text{L'K} \qquad (13)$$

The completeness of this reaction has been followed by ^{1}H NMR.

2.7. *Synthesis of L'Rh,* **21**.

In order to check the accessibility for L' containing complexes of second or third row transition metals an exemplary experiment has been carried out with the preparation of a rhodium complex with the ligand L'. Some rhodium(I) complexes have been previously prepared using sterically demanding β-diketiminato ligands.[91] Noteworthy is the synthesis of a stable tricoordinated rhodium(I) complex.[91a]

Consequently, the *in situ* prepared potassium salt, L'K, was left to react with [μ-ClRh(CO)$_2$]$_2$ in toluene at –20 °C. Evolution of CO was observed. Subsequent filtration of KCl and concentration of the solution produced after few hours at –26 °C yellow crystals of **21**.

$$2\ \text{L'K} + [\mu\text{–ClRh(CO)}_2]_2 \xrightarrow[\text{-4 CO, -2 KCl}]{\text{toluene}} 2\ \text{L'Rh}\ \mathbf{21} \qquad (14)$$

The complex **21** has been characterized by multinuclear NMR spectrometry, EI-MS, elemental analysis, and single crystal X-ray diffraction. For ^{31}P NMR a downfield shift from δ –21 ppm to 62 ppm has been observed. Although it was not tested with H_2 or simple alkenes, such a complex might be useful for catalytic processes.[92] As revealed by the X-ray crystal structure of the 16 electron complex **21**, the rhodium atom possesses two free coordinating trans positions. Additionally, the potential of interchanging between the coordinated and uncoordinated modes of the ancillary arms, "arms-on arms-off",[93] depending on the reaction condition could prove useful in various catalytic processes.

2.7.1. *Discussion of the crystal structure of* **21**.

A single crystal X-ray diffraction analysis of the yellow crystals obtained from the mother liquor at –26 °C in few hours, shows that the complex **21** crystallizes in the triclinic space group $P\bar{1}$ (Figure 20).

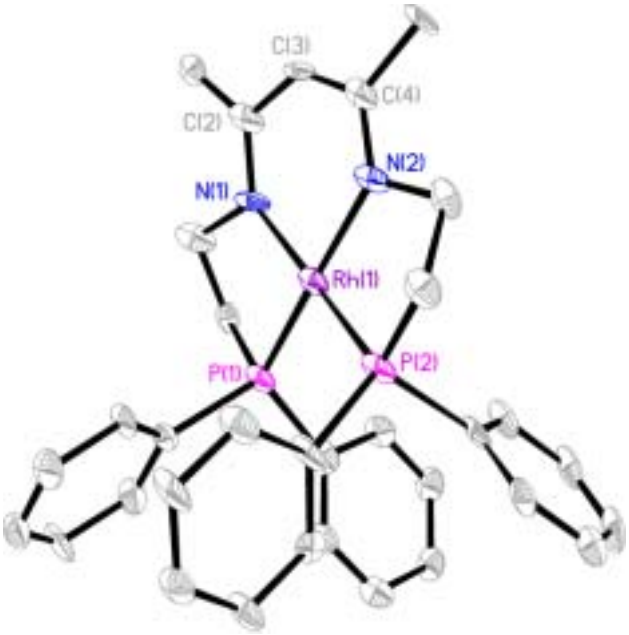


Figure 20. *Molecular structure of* **21** *showing 50 % probability ellipsoids (the hydrogen atoms are omitted for clarity).*

Table 11. Selected bond lengths (Å) and angles (°) for L'Rh, **21**.

Bond lengths		Angles	
Rh(1)-N(2)	2.036(8)	N(2)-Rh(1)-N(1)	92.7(3)
Rh(1)-N(1)	2.060(7)	N(1)-Rh(1)-P(1)	84.5(2)
Rh(1)-P(1)	2.188(3)	N(2)-Rh(1)-P(2)	84.8(2)
Rh(1)-P(2)	2.194(2)	P(1)-Rh(1)-P(2)	98.23(9)
N(1)-C(2)	1.349(12)	C(2)-N(1)-Rh(1)	123.4(6)
C(2)-C(3)	1.397(13)	N(1)-C(2)-C(3)	122.5(8)
C(3)-C(4)	1.412(13)	C(4)-N(2)-Rh(1)	126.7(7)
C(4)-N(2)	1.341(12)	N(2)-C(4)-C(3)	119.1(9)
		C(3)-C(3)-C(4)	133.8(8)

The rhodium atom has the coordination number *four* in a square planar geometry. The ligand L' is tetradentate as expected. The ligand backbone plane is almost coplanar with the plane formed by the two nitrogen atoms and the two phosphorus atoms (the dihedral angle is 174.1°). The Rh-N bond lengths are comparable to those reported for other rhodium β-diketiminato derivatives (*e.g.* 1.95 Å) having a σ bond character (Table 11).[91] The π-electron system of the backbone is delocalised, as proved by the C-C and C-N bond lengths. The Rh-P bond lengths are in the normal range for Rh-P (coordinative

bonds).[94]

2.8. *Synthesis of L'$_2$YCl,* **22**.

As pointed out the synthesis of L' containing complexes seems rather uncomplicated for soft ions like rhodium(I) in the light of Pearson's theory[42] due to the two pendant arms that incorporate P-donors. On the other hand, simple metathesis reactions of the early transition metal or lanthanide halogenides did not follow the same principle as for the previous L ligand system.

In an attempt to obtain difunctional complexes that could be more appropriate, as a result of the π-backbonding feature of the ligand L' capable of the softening of the electron density on the metal ion, the *in situ* prepared potassium salt, L'K, was reacted with YCl_3 in toluene to afford, after solvent removal and extraction in CH_2Cl_2, in complex **22** (Eq. (15)) in low yield.

$$2\ \text{L'K} + \text{YCl}_3 \xrightarrow[-\ 2\ \text{KCl}]{\text{toluene}} \underset{\mathbf{22}}{\text{L'}_2\text{YCl}} \qquad (15)$$

Complex **22** crystallized from CH_2Cl_2 at –26 °C within several days and the elemental analysis is in good agreement with the structure revealed by the single crystal X-ray diffraction. In contrast, EI-MS provides no conclusive information.

2.8.1. *Discussion of the crystal structure of* **22**·*2CH$_2$Cl$_2$.*

The complex **22** crystallizes in the monoclinic space group *C*2/*c* together with two molecules of CH_2Cl_2, one of them being disordered over two positions (Figure 21). The yttrium atom lies on a two-fold axis. The molecule contains two tridentate L' units arranged in an antiperiplanar manner. One arm of every unit is not coordinated, thus the coordination number of yttrium is *seven*. Such an arrangement is not unusual for the early transition metals. The Y-N distances (*av.* 2.375 Å, Table 12) are comparable to those reported for $[\{(Me_3Si)_2NC(N^iPr)_2\}Y(\mu\text{-}Cl)]_2$ [95a] (2.36 Å) and $[^tBuC(N^iPr)_2]Y[CH(SiMe_3)_2]_2(\mu\text{-}Cl)Li(THF)_3$[59] (2.35 Å). The Y-P distance (3.10 Å) is somewhat longer than for instance the Y-P bond length found in a *seven* coordinated

amido complex reported by Fryzuk *et al.* (2.89 Å in $[Y(\eta^3\text{-}C_3H_5)\{N(SiMe_2CH_2PMe_2)_2\}](\mu\text{-}Cl)_2)$),[96a] however comparable to that found in $BrY[C_5H_4(CH_2)_2P(CH_3)_2]_2$ (2.96 Å).[96b]

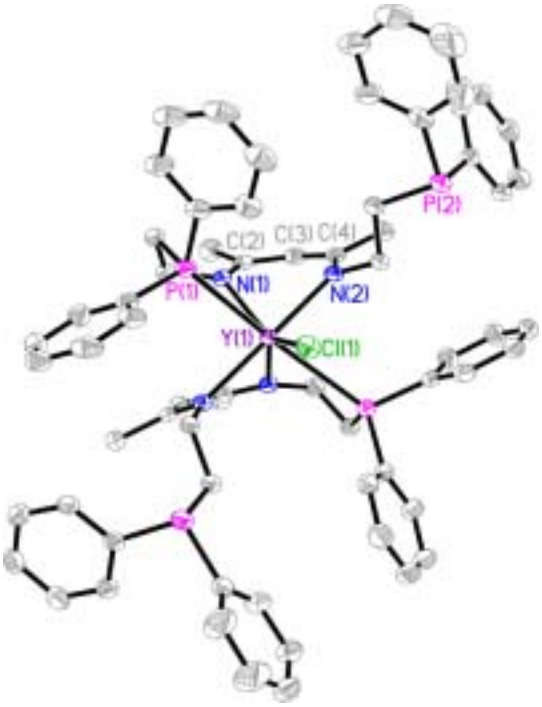


Figure 21. *Molecular structure of* **22** *showing 50 % probability ellipsoids (the hydrogen atoms and the CH_2Cl_2 molecules are omitted for clarity).*

Table 12. Selected bond lengths (Å) and angles (°) for L'_2YCl, **22**.

Bond lengths		Angles	
Y(1)-N(1)	2.3712(15)	N(1)-Y(1)-N(2)	78.12(5)
Y(1)-N(2)	2.3810(15)	N(1)-Y(1)-P(1)	65.44(4)
Y(1)-Cl(1)	2.6652(9)	N(2)-Y(1)-P(1)	100.81(4)
Y(1)-P(1)	3.1019(7)	N(1)-C(2)-C(3)	123.29(17)
N(1)-C(2)	1.329(2)	C(2)-C(3)-C(4)	130.11(18)
N(2)-C(4)	1.336(2)	C(4)-N(2)-Y(1)	120.36(12)
C(2)-C(3)	1.408(3)	N(2)-C(4)-C(3)	124.14(17)
C(3)-C(4)	1.406(3)		

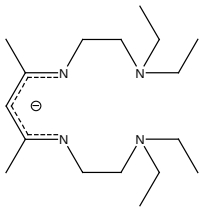
This can be attributable to a better electronic contribution of the β-diketiminato ligand backbone or Cp ligand than in the aforementioned amido complex. As it has been

previously shown, the β-diketiminato framework acts mainly either as a four-electron donor (2σ) or six electron donor (2σ-π). The complex **22** constitutes the first example in this work where the ligand backbone supplies six electrons (the deviation of the yttrium atom from the plane is 1.2 Å).

3. Summary

One of the main objectives of this dissertation was to establish a general route to the Cp-free bis-hydrocarbyl complexes for the 4f metals, $LLnR_2$. By comparison with the early transition metals where, as suggested by Piers and Emsley in their timely review,[10b] the use of bulky amidinate donor ligands,[59, 105] the bis-oxazoline ancillary ligands,[106] the *β*-diketiminato ligands,[10] and the linked amido-tacn ligands[107] could render appropriate environments for obtaining Cp-free bis-hydrocarbyl complexes, for the 4f metals only one *β*-diketiminato ligand proved to date useful. The outcome was a cerium complex as an unique representative for a rather elusive class of compounds with potentially far–reaching functions.[22b]

Taking into account both the Lewis acidic nature of the lanthanide cations and the desired goal, the monoanionic ligand L was designed in order to prevent salt occlusion, dimerization, THF ligation, and ligand redistribution (the ligand must be non-labile). All of these factors had to be carefully considered.

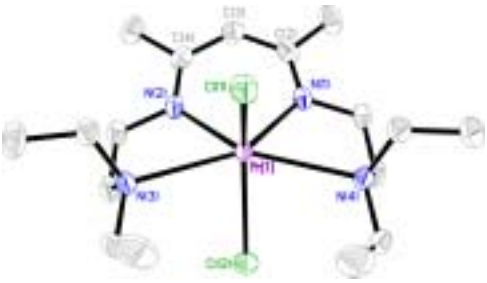


The anticipated skeleton of the monoanionic ligand L: L = [N,N''-(1,3-dimethyl-1,3-propanediylidene) bis[N',N'-diethyl-1,2-ethanediamine]]

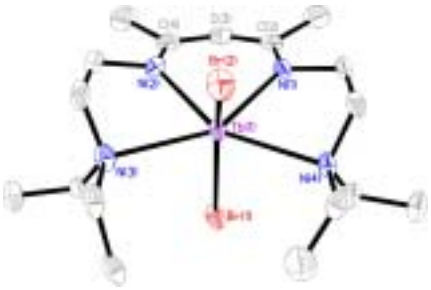
Once the conjugated acid of the ligand L was obtained, its lithiation gave rise to a rich chemistry with main group metals, transition metals, and lanthanides.

Structure of LLi, **3**.

Thus this ligand containing two additional hard donors enabled the synthesis of the first salt and solvent free difunctional lanthanide complexes, such as $LPrCl_2$, **4**, or $LTbBr_2$, **8**.



Structure of $LPrCl_2$, **4**.



Structure of, $LTbBr_2$, **8**.

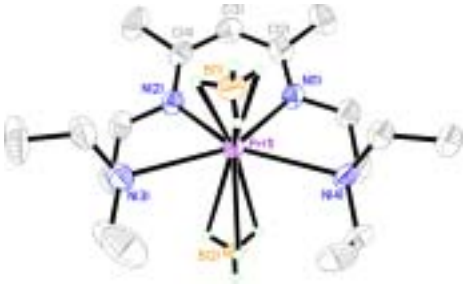
On the other hand the metathesis reactions proved to be difficult depending very much on the reaction conditions. Hence, only $LTb(CH_2SiMe_3)_2$, **11** could be prepared by salt elimination, and it was fully characterized.

Structure of $LTb(CH_2SiMe_3)_2$, **11**.

Despite that, it has been shown that by general reactions the area of Cp-free bis-hydrocarbyl derivatives can be extended and it has been confirmed that incorporating donors onto pendant arms is a valuable strategy for preparing this kind of complexes. For some other type of ligands, for instance amidinates,[59, 108] this possibility has been also validated.

As regard to the use of compounds like **11** in search for potential catalytic activity, it can be assumed that it requires a broader family of similar complexes.

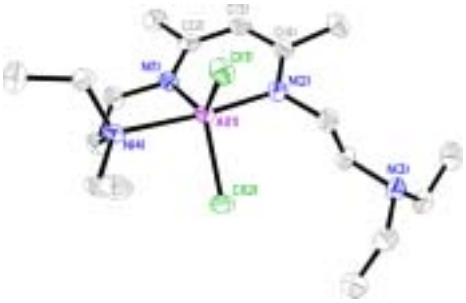
Additionally, it has been revealed that these precursors could undergo further metathesis reactions, for instance with $NaBH_4$, giving rise to interesting complexes such as **10**.



Structure of $LPr(BH_4)_2$, **10**.

In the case of the lanthanide complexes with the ligand L its denticity is *four*, thus the bonding mode of the ligand involves 8-electron donation (2σ and 2 dative bonds) with the metal ion lying in the ligand backbone plane, with small deviations. However this is a reasonable consequence of the nature of the ligand. Additionally, it can be pointed out that the "bite" of a β-diketiminato ligand is big enough to accommodate any metal ion in NC_3N plane.

The versatility of the ligand L has been illustrated by extending of its chemistry with complexes of aluminum and vanadium. For instance, straightforward complexes like $LAlCl_2$, $LAlMe_2$, or $LVCl_2$ have been prepared.

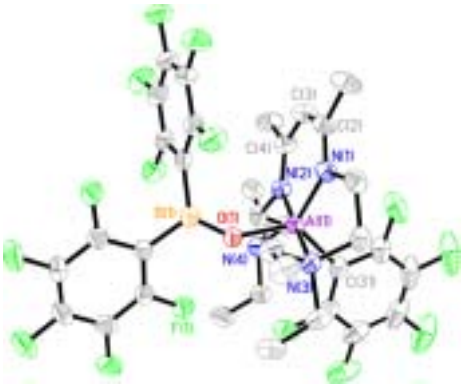


Structure of $LAlCl_2$, **12**.

However, a precursor like $LAlMe_2$ afforded, when reacted with the strong Brønsted acid $H_2O{\cdot}B(C_6F_5)_3$, under different reactions conditions, two isomers **14** and **15**. The rows of surprises offered by combination of a β-diketiminato ligand with aluminium continued with the first monoaluminoxane, compound **14**: its stabilization might be partly

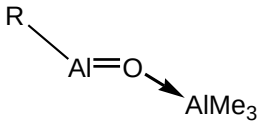
due to interaction with the very strong Lewis acid $B(C_6F_5)_3$, and partly due to the *β*-diketiminato ligand.

Structure of $LAlO{\cdot}B(C_6F_5)_3$, **14**.



Structure of $LAl(C_6F_5)OB(C_6F_5)_2$, **15**.

The most interesting feature of **14** is the shortness of the Al-O bond (1.659 Å, the shortest to date), which characterizes a strong *π*-interaction between Al and O atoms. The existence of both these compounds permits the imagination of a mechanism that might shed some light into the functioning and aging of methylaluminoxane, MAO.



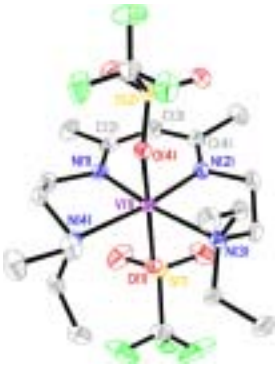
Proposed active catalytic site of MAO.

The attempt to prepare an aluminum imide by the reaction of $LAlMe_2$ and $H_3N{\cdot}B(C_6F_5)_3$ resulted in complex **16** which can be considered as the intermediary step on the way to the desired aluminum imide.

Structure of $LAl(Me)NH_2{\cdot}B(C_6F_5)_3$, **16**.

In the case of the aluminum complexes the potential multitude of the bonding modes of the ligand L take effect, namely the denticity varies from *three* to *two*, unlike in the lanthanide complexes where the ligand is always tetradentate. The reason behind could be the smaller radius of aluminum compared to those of the lanthanides, the lower Lewis acid character, and the presence of additional donor atoms that bind stronger as in the case of **14 - 16**.

Whereas efforts in developing the β-diketiminates of aluminum are considerable, not the same applies to metals like titanium, vanadium, or chromium. Recently, a resurgence of this field has been witnessed since it has been shown that such paramagnetic species could act as catalysts for the polymerization of small olefins.[58, 79] Nonetheless, the β-diketiminato ligand chemistry of these metals is still underdeveloped. Accordingly, some complexes of titanium[61] and vanadium with the L ligand system have been prepared. Even though the structure of the $LVCl_2$, **17**, could not be determined yet, in order to get the final proof about its constitution, the metathesis reaction with $AgOSO_2CF_3$ established the expected difunctionality of **17**. Complex **18** is the first vanadium(III) triflate derivative structurally characterized.



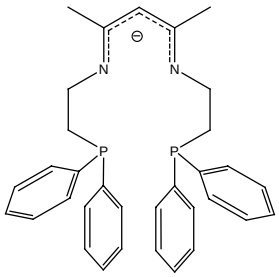
Structure of $LV(OSO_2CF_3)_2$, **18**.

Surprisingly, the reaction of **17** with 2 equivalents of $KPPh_2$ gave complex **19** as an unexpected product representing the first neutral terminal heteroleptic diorganophosphido-complex of vanadium(II) and the first structurally characterized terminal phosphido complex of vanadium.

Structure of $LVPPh_2$, **19**.

The bonding mode of the ligand L in the vanadium complexes is similar to that found in the lanthanide complexes. But in a general survey it has been demonstrated the potential of the interchanging among the coordinated, partially coordinated, and uncoordinated modes of the ancillary arms, "arms-on arms-off",[93] which could prove very valuable in a wide range of catalytic processes.

The quest for a new monoanionic β-diketiminato based ligands, which was a main objective, emerged when the failure of the L ligand system became evident if applied for the second and third row of the late transitional metals. As a result a new ligand L' was designed according to Pearson's theory[42] that incorporate phosphorus donors instead of the previous nitrogen donors and its synthesis was carried out.

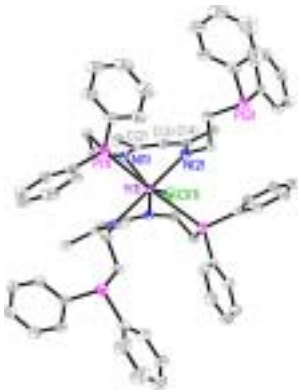


The anticipated skeleton of the monoanionic ligand L':
L' = [N,N'-(1,3-dimethyl-1,3-propanediylidene) bis[2-diphenylphosphanyl-ethylamine]]$^-$

As expected, the *in situ* prepared potassium salt, L'K, from the conjugated acid of L', **20**, and an excess of KH reacted easily with $[\mu\text{-ClRh(CO)}_2]_2$ giving rise to the formation of a very stable rhodium(I) complex **21**.

Structure of L'Rh, **21**.

On the other hand, the reactivity pattern in metathesis reactions of the ligand L' with early transition metals or lanthanide was different of the more basic L. When attempted to obtain difunctional complexes of these metals, the yttrium complex **22** was obtained.



Structure of L'$_2$YCl, **22**.

The same multitude of bonding modes is again observed for the L' as for L ligand system, the denticity varying from *four* to *three*.

3.1. *Outlook*

The main focus of the work presented here has been on the synthesis of new *β*-diketiminato ligands and subsequent employment in order to get bis-hydrocarbyl complexes of the lanthanides. Another issue has been to expand the designed ligand system chemistry. Hence, a logical and very constructive extension of this work would be the preparation of various bis-hydrocarbyl complexes of both ligand systems. A possible route toward bis-hydrocarbyl L' containing complexes of the lanthanides and the early metals would be the alkane or amine elimination. Especially interesting would be screening the resulting complexes as catalysts for various processes.

A further useful expansion is to search for additional evidence with respect to the proposed catalytic active site for MAO and the aging mechanism.

4. Experimental Section

4.1. *General Procedures.*

All manipulations were performed on a high-vacuum line or in a glove box under a purified N_2 atmosphere, using Schlenk techniques with rigorous exclusion of moisture and air. All the necessary glassware was oven-dried at 140 - 150 °C for a minimum period of 12 h, assembled hot and cooled under high vacuum with intermittent flushing of nitrogen. The samples for spectral measurements were prepared inside an MBraun MB 150-GI glove-box where the O_2 and H_2O levels were normally maintained below 1 ppm. Commercial grade solvents were purified and freshly distilled following usual procedures prior to their use.[97]

4.2. *Physical Measurements.*

Melting points of all new compounds were measured in sealed capillaries on a Büchi B 540 instrument.

Elemental analyses were performed at the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.

^{1}H, ^{13}C, ^{11}B, ^{19}F, ^{27}Al, ^{29}Si and ^{31}P NMR *spectra* (C_6D_6, toluene-d_8, THF-d_8, $CDCl_3$) were recorded on AM-250, Avance-500 and Avance-200 instruments. The chemical shifts are reported in ppm with reference to external standards: $SiMe_4$ for ^{1}H, ^{13}C, and ^{29}Si nuclei, $LiCl/D_2O$ for the ^{7}Li nucleus, $BF_3{\cdot}O(C_2H_5)_2$ for the ^{11}B nucleus, $C_6F_6/CFCl_3$ for the ^{19}F nucleus, $AlCl_3/D_2O$ for the ^{27}Al nucleus, and 85 % H_3PO_4 for the ^{31}P nucleus. All heteroatom NMR spectra were measured in the ^{1}H decoupled mode. Downfield shifts from the reference are quoted positive and the upfield shifts are reported as negative values and are reported in ppm. The solvents for NMR measurements were dried over K or CaH_2 and trap-to-trap distilled prior to use.

Mass spectra were obtained on a Finnigan MAT 8230 instrument by EI technique. Only the most abundant peak of any isotope distribution is given.

Crystal structure determination: Suitable crystals were mounted on glass fibers in rapidly cooled perfluoropolyether.[98] Data for crystal structures of **3**, **14**, and **18** were collected on a Bruker Smart Apex CCD diffractometer, for compounds **11**, **19**, **21**, and **22** on a SMART 6000 diffractometer, for compounds **5**, **7**, **8**, and **9** on a Stoe Image Plate IPDS II-System, for compounds **4** and **10** on a Stoe-Siemens four-circle diffractometer, and for compound **16** on a Siemens/Stoe Huber 4-circle diffractometer. The data for all the compounds were collected at low temperatures (the temperatures for individual compounds are mentioned in the tables in Section 6) using graphite Mo-K_α or Cu-K_α radiation. The data reduction and space group determination were carried out using the Bruker SHELXTL or Stoe X-Area families of programs.[99] The structures were solved by direct methods, SHELXS-97,[100] and refined against F^2 using SHELXL-97.[101] R values were defined as $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, $w = [\sigma^2(F_o^2)+(g_1P)^2+ g_2P]^{-1}$, $P = 1/3[\max(F_o^2,0)+2F_c^2]$. Processing of the data for the crystal structures of the non-merohedral twinned crystals of **14** and **21** implicated the determination of the two matrices of the two domains and every domain was integrated on its own. Structure solution was performed by direct methods with the data of the first domain. A new hklf5 file with the reflections of both domains was written in both cases, which was further used for the final refinement. The various advanced features (*e.g.* restraints and constraints) of the SHELXL program were used to treat the disordered groups, lattice solvents such as CH_2Cl_2, and the hydrogen atoms. The crystal data for all the compounds along with structure factors and refinement are given in Section 6.

4.3. *Starting Materials.*

The following substances were purchased from Aldrich and used as received: acetylacetone, $PrCl_3$, $SmCl_3$, $B(C_6F_5)_3$, N,N-diethylenediamine, 1.6 M ether solution of LiMe, 2 M hexane solution of $AlMe_3$, $AgOSO_2CF_3$, 0.5 M THF solution of $KPPh_2$, and 2-diphenylphosphanyl-ethylamine. The following compounds were prepared according to literature protocols: $LiCH_2SiMe_3$,[102] $PrBr_3$,[103] $SmBr_3$,[103] $TbBr_3$,[103] $YbBr_3$,[103] $(Et_3O)(BF_4)$,[103] $H_2O{\cdot}B(C_6F_5)_3$,[67d] $H_3N{\cdot}B(C_6F_5)_3$,[77] and 4-(2-diphenylphosphanyl-ethylamino)-pent-3-en-2-one.[90]

4.3.1. *Preparation of 4-(2-diethylamino-ethylamino)-pent-3-en-2-one,* **1**.

In a 500 mL round bottomed flask equipped with a condenser 29.3 g (0.29 mol) of acetylacetone and 34.0 g (0.29 mol) of N,N-diethylenediamine in 250 mL of benzene were refluxed for 2 d. Subsequently, the solvent was removed and **1** distilled under dynamic vacuum (~ 4.2 mbar) resulting a yellowish oil (bp 90 - 95 °C). Yield 54.7 g (95 %). Anal. Calcd. for $C_{11}H_{22}N_2O$ (198.31, %): C, 66.62; H, 11.18; N, 14.13; Found: C, 66.53; H, 11.21; N, 14.59. ^{1}H NMR (200.13 MHz, C_6D_6): δ 11.1 (s, 1 H), 4.86 (s, 1H), 2.8 (q, 2 H, J = 5.0 Hz), 2.2 (m, 6 H), 1.97 (s, 3 H), 1.51 (s, 3 H), 0.86 (t, 6 H, J = 7.0 Hz); ^{13}C NMR (125.75 MHz, C_6D_6) δ 193.71, 161.54, 95.19, 53.19, 47.55, 41.80, 28.90, 18.70, 12.37. EI-MS: *m/z* (rel. int., %): 198 [M^+, 4], 112 [M^+-$C_5H_{12}N$, 2], 86 [$C_5H_{12}N^+$, 100].

4.3.2. *Preparation of (2-diethylamino-ethyl)-[3-(2-diethylamino-ethylimino)-1-methyl-but-1-enyl]-amine,* **2** *(L-H).*

A 500 mL Schlenk flask topped with a 100 mL addition funnel was charged with 30.0 g (0.15 mol) of **1** in dry dichloromethane (150 mL). A solution of $(Et_3O)(BF_4)$ (54.1 g, 53.2 %) in CH_2Cl_2, was cannula-transferred to the addition funnel and added dropwise to the stirred reaction mixture over a period of 1h. Then, the reaction was allowed to proceed for one additional h at room temperature. Subsequently, 17.58 g of N,N-diethylenediamine in 50 mL dichloromethane were syringed into the reaction mixture over a period of 30 min. Furthermore, stirring was continued overnight to ensure complete reaction. The solvent was removed and 6.1 g (0.15 mol) of NaOH in water (150 mL) and hexane (250 mL) were added. With a separatory funnel, the organic part was separated, washed with water (150 mL), dried over $MgSO_4$, concentrated and distilled under dynamic vacuum (~4.2 mbar) to give **2** as a yellow oil (bp 145 - 150 °C). Yield 23.3 g (52 %). Anal. Calcd. for $C_{17}H_{36}N_4$ (296.49, %): C, 68.87; H, 12.24; N, 18.90; Found: C, 68.82; H, 12.23; N, 19.58. ^{1}H NMR (200.13 MHz, C_6D_6): δ 11.3 (s, 1H, N*H*), 4.55 (s, 1 H, C*H*), 3.28 (t, 4 H, $NCH_2CH_2NEt_2$, J = 6.7 Hz), 2.63 (t, 4 H, $CH_2N(CH_2)_2$, J = 6.0 Hz), 2.45 (q, 8 H, $CH_2N(CH_2CH_3)_2$, J = 7.1 Hz), 1.73 (s, 6 H, CCH_3), 0.97 (t, 12 H, CH_2CH_3, J = 7.1 Hz); ^{13}C NMR (125.75 MHz, C_6D_6): δ 159.78 (*C*CH*C*), 95.04 (*C*H),

55.07 (CN*C*H_2), 47.84 (*C*H_2NEt$_2$), 45.97 (N*C*H_2CH$_3$), 19.44 (CHC*C*H_3), 12.59 (NCH$_2$*C*H_3). EI-MS: *m/z* (rel. int., %): 296 [M^+, 7], 210 [M^+-$C_5H_{12}N$, 36], 114 [$C_6H_{14}N_2$, 100], 86 [$C_5H_{12}N$, 78].

4.3.3. *Preparation of LLi,* **3**.

50 mL of dry diethyl ether were added to 2.85 g (9.6 mmol) of **2** in a 100 mL Schlenk flask. The mixture was cooled to –78 ºC and a solution of 6 mL (1.6 M, 9.6 mmol) LiMe in diethylether was added dropwise. The reaction was stirred for 2 h at –78 °C, and then stirred overnight at room temperature until the methane evolution had ceased. Then the solvent was removed. Yield 2.90 g (>99 %). Anal. Calcd. for **3**. $C_{17}H_{35}LiN_4$ (302.43, %): C, 67.51; H, 11.66; N, 18.53; Found: C, 67.32; H, 11.74; N, 18.43. ^{1}H NMR (200.13 MHz, C_6D_6): δ 4.78 (s, 1 H, C*H*), 3.38 (t, 4 H, NC*H*$_2$CH$_2$NEt$_2$, J = 5.9 Hz), 2.44 (m, 12 H, C*H*$_2$N(C*H*$_2$)$_2$), 2.05 (s, 6 H, CC*H*$_3$), 0.77 (t, 12 H, CH$_2$C*H*$_3$, J = 7.1 Hz); ^{13}C NMR (125.75 MHz, C_6D_6): δ 164.248 (*C*CH*C*), 93.24 (C*H*), 53.89 (CN*C*H_2), 46.84 (*C*H_2NEt$_2$), 45.23 (N*C*H_2CH$_3$), 21.68 (CHC*C*H_3), 10.85 (NCH$_2$*C*H_3); ^{7}Li NMR (116.64 MHz, C_6D_6): δ 1.79. EI-MS: *m/z* (rel. int., %): 302 [M^+, 8], 216 [M^+-$C_5H_{12}N$, 70], 86 [$C_5H_{12}N$, 100].

4.3.4. *Preparation of LPrCl$_2$,* **4**.

A freshly prepared solution of **3** (3.07 g, 10.1 mmol) in toluene (30 mL) was added dropwise to a suspension of 2.50 g (10.1 mmol) $PrCl_3$ in toluene (30 mL) in a 100 mL Schlenk flask and the reaction mixture refluxed overnight. The suspension was filtered, concentrated, until large yellow crystals were formed. Finally, the resulting solution was warmed and it was left undisturbed several h at room temperature. The large yellow crystals that formed were separated by filtration, washed with pentane (50 mL), and dried *in vacuo*. Yield 4.53 g (88.2 %). Mp 164 ºC. Anal. Calcd. for $C_{17}H_{35}Cl_2N_4Pr$ (507.30, %): C, 40.25; H, 6.95; N, 11.04; Found: C, 40.53; H, 6.95; N, 11.04. EI-MS: *m/z* (rel. int., %): 506 [M^+, 12], 471 [M^+-Cl, 7], 420 [M^+-$C_5H_{12}N$, 100].

4.3.5. *Preparation of $LPrBr_2$,* **5***, $LSmCl_2$,* **6***, $LSmBr_2$,* **7***, $LTbBr_2$,* **8***, and $LYbBr_2$,* **9**.

The complexes **5** - **9** were obtained analogously to the protocol delineated for **4** using $PrBr_3$, $SmCl_3$, $SmBr_3$, $TbBr_3$, and $YbBr_3$ respectively.

5. Yield 0.89 g (75.4 %). Mp 188 ºC. Anal. Calcd. for $C_{17}H_{35}Br_2N_4Pr$ (596.20, %): C, 34.25; H, 5.92; N, 9.40; Found: C, 34.25; H, 5.93; N, 8.86. EI-MS: *m/z* (rel. int., %): 596 [M^+, 5], 515 [M^+-Br, 3], 510 [M+-$C_5H_{12}N$, 30], 86 [$C_5H_{12}N$, 100].

6. Yield 0.91 g (81.6 %). Mp 202 ºC. Anal. Calcd. for $C_{17}H_{35}Cl_2N_4Sm$ (516.75, %): C, 39.51; H, 6.83; N, 10.84; Found: C, 39.55; H, 6.78; N, 10.91. EI-MS: *m/z* (rel. int., %): 519 [M^+, 10], 482 [M+-Cl, 5], 433 [M^+-$C_5H_{12}N$, 100]

7. Yield 0.70 g (78.4 %). Mp 205 ºC. Anal. Calcd. for $C_{17}H_{35}Br_2N_4Sm$ (605.65, %): C, 33.71; H, 5.82; N, 9.25; Found: C, 33.51; H, 5.73; N, 8.92. EI-MS: *m/z* (rel. int., %): 607 [M^+, 16], 521 [M^+-$C_5H_{12}N$, 100].

8. Yield 3.85 g (86.0 %). Mp 216 ºC. Anal. Calcd. for $C_{17}H_{35}Br_2N_4Tb$ (612.05, %): C, 33.24; H, 5.74; N, 9.12; Found: C, 33.35; H, 5.75; N, 9.09. EI-MS: *m/z* (rel. int., %): 614 [M^+, 14], 528 [M^+-$C_5H_{12}N$, 66], 86 [$C_5H_{12}N$, 100].

9. Yield 0.97 g (82.4 %). Mp 177 ºC. Anal. Calcd. for $C_{17}H_{35}Br_2N_4Yb$ (628.33, %): C, 32.50; H, 5.61; N, 8.92; Found: C, 32.63; H, 5.65; N, 9.04. EI-MS: *m/z* (rel. int., %): 629 [M^+, 45], 573 [M^+- $C_5H_{12}N$, 100].

4.3.6. *Preparation of $LPr(BH_4)_2$,* **10**.

A mixture of 0.50 g (0.98 mmol) of **4** and 0.11 g (2.96 mmol) $NaBH_4$ in a 50 mL Schlenk flask equipped with a condenser was refluxed in toluene (35 mL) overnight. The suspension was filtered. The resulting clear solution was concentrated under reduced pressure to afford yellow crystals of **5**, which were collected by filtration and washed with pentane (10mL). Yield 0.31 g (68.0 %). Mp 142 ºC. Anal. Calcd. for $C_{17}H_{43}B_2N_4Pr$

(466.08, %): C, 43.81; H, 9.30; N, 12.02; Found: C, 43.56; H, 9.08; N, 11.47. ^{11}B NMR (80.24 MHz, toluene-d_8): δ 67.2. EI-MS: *m/z* (rel. int., %): 466 [M^+, 4], 451 [M^+-BH_4, 76], 366 [M^+-($C_5H_{12}N$+BH_3), 100].

4.3.7. *Preparation of LTb(CH_2SiMe_3)$_2$,* **11**.

To a mixture of $LTbBr_2$ (0.70 g, 1.13 mmol) and $LiCH_2SiMe_3$ (0.21 g, 2.27 mmol) ether (30 mL) were added at –78 °C. The mixture was left to react overnight till it reached room temperature. Removal of the solvent, extraction with hexane (25 mL), and concentration under reduced pressure (10 mL) gave upon cooling to –26 °C 0.88 g (81 %) white crystals of **11**, which were filtered off. Mp 86 ºC. Anal. Calcd. for $C_{25}H_{57}N_4Si_2Tb$ (628.84, %): C, 47.75; H, 9.14; N, 8.91; Found: C, 47.42; H, 9.30; N, 8.81. ^{29}Si NMR (99.36 MHz, C_6D_6): δ -0.09. EI-MS: *m/z* (rel. int., %): 542 [M^+-$C_5H_{12}N$, 4], 86 [$C_5H_{12}N^+$, 100].

4.3.8. *Preparation of LAlCl$_2$,* **12**.

A freshly prepared solution of **3** (3.56 g, 11.8 mmol) in toluene (30 mL) was added dropwise to a suspension of 1.57 g (5.88 mmol) Al_2Cl_6 in toluene (30 mL) in a 100 mL Schlenk flask at 0 °C. The mixture was stirred overnight at room temperature. Next, a precipitate was filtered off and the solvent was removed. The remaining yellowish oil gave upon scratching white crystals washed with pentane (50 mL), and dried *in vacuo*. Yield 3.53 g (76.2 %). Mp 83 - 85 ºC. Anal. Calcd. for $C_{17}H_{35}AlCl_2N_4$ (393.37, %): C, 51.91; H, 8.97; N, 14.84. Found: C, 51.52; H, 8.73; N, 14.97. ^{1}H NMR (200.13 MHz, C_6D_6): δ 4.68 (s, 1 H, C*H*), 3.28 (t, 4 H, NCH_2CH$_2$NEt$_2$, J = 7.0 Hz), 2.63 (m, 12 H, CH_2N(CH_2CH$_3$)$_2$, 1.68 (s, 6 H, CHCCH_3), 0.91 (t, 12 H, CH$_2$CH_3, J = 12.0 Hz); ^{13}C NMR (200.13 MHz, C_6D_6): δ 160.55 (*C*CH*C*), 94.40 (*CH*), 43.61 (CN*C*H$_2$), 43.20 (NCH$_2$*C*H$_2$), 30.67 (N*C*H$_2$CH$_3$), 30.47 (CHC*C*H$_3$), 19.39 (NCH$_2$*C*H$_3$); ^{27}Al NMR (96.29 MHz, C_6D_6): δ 65.0. EI-MS: *m/z* (rel. int., %): 392.1 [M^+, 2], 357.1 [M^+-Cl, 7], 306 [M^+-$C_5H_{12}N$, 15], 86 [$C_5H_{12}N^+$, 100].

4.3.9. *Preparation of LAlMe$_2$,* **13**.

50 mL of dry hexane were added to 1.55 g (5.24 mmol) of **2** in a 100 mL Schlenk flask. The mixture was cooled to –78 ºC and a solution of 7.4 mL (1.42 M, 5.3 mmol) $AlMe_3$ in hexane was added dropwise. The mixture was stirred for 2 h at –78 ºC, and then at room temperature until the methane evolution had ceased. The solvent was removed and the resulting yellowish oil, 1.83 g (> 99 %), has been used without any further purification. Anal. Calcd. for $C_{19}H_{41}AlN_4$ (352.54, %): C 64.73, H 11.72, N 15.89; Found: C 64.50, H 11.80, N 16.30; ^{1}H NMR (200.13 MHz, C_6D_6): δ 4.45 (s, 1 H, C*H*), 3.26 (m, 4 H, NCH_2CH$_2$NEt$_2$), 2.41 (m, 12 H, CH_2N(CH_2CH$_3$)$_2$), 1.72 (s, 6 H, CHCCH_3), 0.91 (t, 12 H, CH$_2$CH_3, J = 7.1 Hz), -0.47 (s, 6 H, Al(CH_3)$_2$); ^{13}C NMR (125.75 MHz, C_6D_6): δ 167.91 (*C*CH*C*), 96.94 (*C*H), 54.20 (CN*C*H$_2$), 47.90 (NCH$_2$*C*H$_2$), 46.70 (N*C*H$_2$CH$_3$), 20.84 (CHC*C*H$_3$), 12.58 (NCH$_2$*C*H$_3$), -8.73 (Al*C*H$_3$); ^{27}Al NMR (65.17 MHz, C_6D_6): δ 150.36.

4.3.10. *Preparation of LAlO·B(C$_6$F$_5$)$_3$,* **14**.

A solution of **13** (0.22 g, 0.61 mmol) in toluene (15 mL) was allowed to react with $H_2O{\cdot}B(C_6F_5)_3$ (0.33 g, 0.61 mmol) in toluene (10 mL) at 0 ºC. The mixture was stirred for 1 h at 0 ºC, and then stirred at room temperature until the methane evolution had ceased. The suspension was filtered and the resulting solid dissolved in CH_2Cl_2 (10 mL). Colorless crystals were obtained by cooling the CH_2Cl_2 solution to –26 ºC. Then the crystals were filtered off. Yield 0.317 g (60.0 %). Mp 156 ºC. Anal. Calcd. for $C_{35}H_{35}AlBF_{15}N_4O$ (850.45, %): C 49.43, H 4.15, N 6.59; Found: C 49.81, H 4.33, N 6.63. ^{1}H NMR (200.13 MHz, C_6D_6/THF-*d*$_8$): δ 4.82 (s, 1 H, C*H*), 3.11 (t, 4 H, NCH_2CH$_2$NEt$_2$, J = 6.9 Hz), 2.41 (m, 12 H, CH_2N(CH_2CH$_3$)$_2$, J = 7.2 Hz), 1.76 (s, 6 H, CHCCH_3), 0.78 (t, 12 H, CH$_2$CH_3, J = 7.1 Hz); ^{13}C NMR (125.75 MHz, C_6D_6): δ 171.82 (*C*CH*C*), 98.32 (*C*H), 54.31 (CN*C*H$_2$), 51.78 (NCH$_2$*C*H$_2$), 45.58 (N*C*H$_2$CH$_3$), 20.95 (CHC*C*H$_3$), 10.17 (NCH$_2$*C*H$_3$); ^{11}B NMR (80.24 MHz, C_6D_6/THF-*d*$_8$): δ - 4.83; ^{19}F NMR (188.28 MHz, C_6D_6/THF-*d*$_8$): δ - 134.5 (m, 6 F, *ortho*), - 163.7 (t, 3 F, *para*), - 166.5 (m, 6 F, *meta*).

4.3.11. *Preparation of LAl(C_6F_5)OB(C_6F_5)$_2$,* **15**.

A solution of **13** (0.25 g, 0.71 mmol) in THF (15 mL) was allowed to react in a THF (10 mL) solution of $H_2O{\cdot}B(C_6F_5)_3$ (0.37 g, 0.71 mmol) at 55 ºC for 2 h. Then the solvent was removed and the oily product was left to crystallize at room temperature. The crystals formed were washed with cold hexane. Yield 0.44 g (73.0 %). Mp 85 - 87 ºC. Anal. Calcd. for $C_{35}H_{35}AlBF_{15}N_4O$ (850.45, %): C 49.43, H 4.15, N 6.59; Found: C 49.75, H 4.27, N 6.46. ^{1}H NMR (200.13 MHz, C_6D_6): δ 4.28 (s, 1 H, C*H*), 3.22 (m, 2 H, NC*H*$_2$CH$_2$N(CH$_2$)$_2$), 2.95 (m, 2 H, NC*H*$_2$CH$_2$NEt$_2$), 2.19 (q, 8 H, C*H*$_2$CH$_3$, *J* = 7.5 Hz), 1.85 (m, 2 H, NCH$_2$C*H*$_2$NEt$_2$), 1.51 (s, 6 H, CHCC*H*$_3$), 0.70 (m, 12 H, CH$_2$C*H*$_3$); ^{13}C NMR (125.75 MHz, C_6D_6): δ 168.61 (*C*CH*C*), 97.29 (*C*H), 50.51 (CN*C*H$_2$), 45.48 (NCH$_2$*C*H$_2$), 45.28 (N*C*H$_2$CH$_3$), 21.57 (CHC*C*H$_3$), 9.62 (NCH$_2$*C*H$_3$); ^{11}B NMR (80.24 MHz, C_6D_6): δ 36.8. ^{19}F NMR (188.28 MHz, C_6D_6) δ - 118.09 (m 2 F, AlC$_6$F$_5$ *ortho*), - 133.2 (m, 4 F, BC$_6$F$_5$ *ortho*), - 152.5 (t, 2 F, BC$_6$F$_5$ *para*), - 155.3 (t, 1 F, AlC$_6$F$_5$ *para*), - 159.7 (m, 2 F, AlC$_6$F$_5$ *meta*), - 161.5 (m, 4 F, AlC$_6$F$_5$ *meta*).

4.3.12. *Preparation of LAl(Me)NH$_2$·B(C_6F_5)$_3$,* **16**.

A solution of **13** (0.50 g, 1.4 mmol) in toluene (20 mL) was allowed to react with $H_3N{\cdot}B(C_6F_5)_3$ (0.75 g, 1.4 mmol) in toluene (15 mL) at 0 ºC. The mixture was stirred for 1 h at 0 ºC and then stirred at room temperature until the methane evolution had ceased. The solvent was removed and the remaining white residue was redissolved in CH_2Cl_2 (10 mL). Colorless crystals of **16** were obtained by cooling the CH_2Cl_2 solution to –26 ºC. Then the crystals were filtered off. Yield 0.82 g (68.0 %). Mp 126 ºC. Anal. Calcd. for $C_{36}H_{40}AlBF_{15}N_5$ (865.52, %): C 49.96, H 4.66, N 8.09; Found: C 49.82, H 4.53, N 8.57. ^{1}H NMR (200.13 MHz, C_6D_6): δ 4.10 (s, 1 H, C*H*), 3.57 (s, 2 H, N*H*$_2$), 3.05 (m, 4 H, NC*H*$_2$CH$_2$NEt$_2$), 2.23 (m, 12 H, C*H*$_2$N(*CH*$_2$CH$_3$)$_2$), 1.52 (s, 6 H, CHCC*H*$_3$), 0.74 (t, 12 H, CH$_2$C*H*$_3$, *J* = 7.1 Hz); ^{13}C NMR (125.75 MHz, C_6D_6): δ 170.54 (*C*CH*C*), 99.77 (*C*H), 54.50 (CN*C*H$_2$), 46.53 (NCH$_2$*C*H$_2$), 45.72 (N*C*H$_2$CH$_3$), 20.95 (CHC*C*H$_3$), 10.98 (NCH$_2$*C*H$_3$), 1.35 (Al*C*H$_3$); ^{11}B NMR (96.29 MHz, C_6D_6): δ - 10.0; ^{19}F NMR (188.28

MHz, C_6D_6): δ -132.9 (m, 6 F, *ortho*), -157.2 (t, 3 F, *para*), - 163.2 (m, 6 F, *meta*); EI-MS: *m/z* (rel. int., %): 522 [$B(C_6F_5)_3$, 20], 337 [M^+- ($B(C_6F_5)_3$+CH_4), 100].

4.3.13. *Preparation of $LVCl_2$,* **17**.

A freshly prepared solution of **3** (2.23 g, 7.37 mmol) in toluene (40 mL) was allowed to react with a toluene (30 mL) suspension of VCl_3·3THF (2.75 g, 7.37 mmol) at room temperature overnight. After removal of the solvent and extraction in CH_2Cl_2, followed by subsequent CH_2Cl_2 removal and washing the remaining green substance with cold hexane 1.80 g of **17** (58.3 %) were obtained. Mp 156 ºC. Anal. Calcd. for $C_{17}H_{35}Cl_2N_4V$ (416.17, %): C, 48.93; H, 8.45; N, 13.42; Found: C, 48.74; H, 8.45; N, 13.55. EI-MS: *m/z* (rel. int., %): 416 [M^+, 5], 381 [M^+-Cl, 2], 86 [$C_5H_{12}N^+$, 100].

4.3.14. *Preparation of $LV(OSO_2CF_3)_2$,* **18**.

A mixture of 0.80 g (1.91 mmol) **17** and 0.985 g (3.83 mmol) of $AgOSO_2CF_3$ in a 100 mL Schlenk flask in toluene (40 mL) was stirred for two d. The suspension was filtered and the resulting clear green solution concentrated under reduced pressure to obtain green crystals of **18**, which were collected by filtration and washed with pentane (10 mL). Yield 0.98 g (81.0 %). Mp 190 - 201 ºC. Anal. Calcd. for $C_{19}H_{35}F_6N_4O_6S_2V$ (644.57, %): C, 35.40; H, 5.47; N, 8.69; Found: C, 35.60; H, 5.91; N, 7.81; ^{19}F NMR (188.28 MHz, C_6D_6): δ - 62.4. EI-MS: *m/z* (rel. int., %): 644 [M^+, 79], 495 [M^+-SO_3CF_3, 100], 558 [M^+- $C_5H_{12}N$, 5].

4.3.15. *Preparation of $LVP(C_6H_5)_2$,* **19**.

30 mL of dry THF were added to 0.46 g (1.1 mmol) of **17** in a 100 mL Schlenk flask. The mixture was cooled to –78 ºC and a solution of 4.4 mL (0.5 M, 2.2 mmol) $KPPh_2$ in THF was added dropwise. The mixture was stirred for 2 h at –78 ºC, and then stirred overnight at room temperature. After the solvent removal and extraction in toluene (25 mL), the resulting solution was concentrated to 15 mL and cooled to –26 °C. The dark red crystals were filtered off. Yield 0.24 g (41.6 %). Mp 160 - 163 ºC. Anal. Calcd. for $C_{29}H_{45}N_4PV$ (531.61, %): C, 65.52; H, 8.53; N, 10.54; Found: C, 65.14; H, 8.31; N,

9.70; ^{31}P NMR (81.01 MHz, C_6D_6): δ - 40.27. EI-MS: *m/z* (rel. int., %): 641 [M^++C_6H_6P, 30], 460 [M^+- $C_5H_{12}N$, 2], 371 [$Ph_4P_2^+$, 100].

4.3.16. *Preparation of (2-diphenylphosphanyl-ethyl)-[3-(2-diphenylphosphanyl-ethylimino)-1-methyl-but-1-enyl]-amine,* **20** *(L'-H).*

A 100 mL Schlenk flask topped with a 100 mL dropping funnel was charged with 5.0 g (16.0 mmol) of 4-(2-diphenylphosphanyl-ethylamino)-pent-3-en-2-one in dry dichloromethane (30 mL). A solution of $(Et_3O)(BF_4)$ (5.73 g, 53.2 %) in CH_2Cl_2, was syringed into the dropping funnel and added dropwise to the stirring reaction mixture over a period of 1h. Afterward, the reaction was allowed to proceed for one additional h at room temperature and 3.66 g of 2-diphenylphosphanyl-ethylamine in 20 mL CH_2Cl_2 were syringed into the reaction mixture over a period of 15 min. Stirring was continued overnight to ensure complete reaction. The solvent was removed and 0.7 g (17.5 mmol) of NaOH in water (20 mL) and benzene (70 mL) were added. With a separatory funnel, the organic part was separated, washed with water (30 mL), concentrated to dryness and washed with cold ether to give **20** as a white solid. Yield 5.02 g (54.0 %). Mp 90 - 94 °C. Anal. Calcd. for $C_{33}H_{36}N_2P_2$ (522.24, %): C, 75.84; H, 6.94; N, 5.36; Found: C, 75.71; H, 6.94; N, 5.26. ^{1}H NMR (200.13 MHz, C_6D_6): δ 11.7 (s, 1H, N*H*), 7.45 (m, 8 H, PC_6H_5-*meta*), 7.00 (m, 12 H, PC_6H_5-*ortho*, *para*), 4.54 (s, 1 H, C*H*), 3.36 (m, 4 H, NCH_2CH_2P), 2.47 (t, 4 H, $CH_2P(C_6H_5)_2$, J = 7.8 Hz), 1.56 (s, 6 H, CCH_3); ^{13}C NMR (75.46 MHz, C_6D_6): δ 160.01 (*C*CH*C*), 95.17 (*C*H), 43.72 ($CNCH_2$), 31.43 (m, CH_2P), 19.27 (CCH_3); ^{31}P NMR (121.49 MHz, ext. H_3PO_4, C_6D_6): δ - 20.2. EI-MS: *m/z* (rel. int., %): 522 [M^+, 10], 337 [M^+-Ph_2P, 90], 185 [Ph_2P^+, 100], 114 [$C_6H_{14}N_2^+$, 100].

4.3.17. *Preparation of L'Rh,* **21**.

A solution of L'K obtained *in situ* by refluxing 0.53 g (1.0 mmol) of L'H, **20**, with 0.05 g (1.2 mmol) KH in toluene (20 mL) followed by filtration from excess KH was added dropwise to a toluene solution of $[\mu\text{-ClRh(CO)}_2]_2$ (0.20 g 0.5 mmol) in toluene (10 mL) at –20 °C. The reaction was allowed then to stir at room temperature overnight. Finally, the precipitate formed was filtered off and the resulting solution concentrated (10

mL). Yellow crystals separated after cooling the solution to -26 °C. Yield 0.46 g (73.0 %). Mp 250 °C. Anal. Calcd. for $C_{33}H_{35}N_2P_2Rh$ (624.50, %): C, 63.47; H, 5.65; N, 4.49; Found: C, 63.60; H, 5.43; N, 4.33. ^{1}H NMR (200.13 MHz, C_6D_6): δ 7.45 (m, 8 H, PC_6H_5-*meta*), 6.92 (m, 12 H, PC_6H_5-*ortho*, *para*), 5.13 (s, 1 H, C*H*), 3.42 (m, 4 H, NCH_2CH_2P), 2.25 (m, 4 H, $CH_2P(C_6H_5)_2$), 2.05 (s, 6 H, CCH_3); ^{13}C NMR (75.46 MHz, C_6D_6): δ 156.74 (*C*CH*C*), 99.32 (d, *C*H, *J* = 2.1 Hz), 52.17 (m, CN*C*H_2), 36.30 (t, *C*H_2P, *J* = 12.9 Hz), 23.65 (m, C*C*H_3); ^{31}P NMR (121.50 MHz, ext. H_3PO_4, C_6D_6): δ 64.93 (d, *J* = 161.8 Hz). EI-MS: *m/z* (rel. int., %): 624 [M^+, 100], 438 [M^+-$C_{12}H_{12}P$, 45].

4.3.18. *Preparation of L'$_2$YCl·2CH$_2$Cl$_2$,* **22**·*2CH$_2$Cl$_2$.*

The solution of L'K that was obtained *in situ* by refluxing 0.75 g (1.40 mmol) of L'H, **20**, with 0.064 g (1.61 mmol) KH in toluene (30 mL) followed by filtration from excess KH was added dropwise to a toluene suspension of 0.27 g (1.4 mmol) YCl_3 in toluene at room temperature. The reaction was heated and refluxed overnight. After solvent removal, extraction with CH_2Cl_2, and subsequent concentration (10 mL) followed by cooling to -26 °C gave 0.46 g·(24.0 %) of **22**·$2CH_2Cl_2$. Mp 99 - 103 °C. Anal. Calcd. for $C_{68}H_{74}Cl_5N_4P_4Y$ (1337.41, %): C, 61.07; H, 5.58; N, 4.19; Found: C, 62.11; H, 6.14; N, 4.45. EI-MS: *m/z* (rel. int., %): 185 [$C_{12}H_{10}P^+$, 100].

5. Handling and Disposal of Solvents and Residual Waste

1. The recovered solvents were condensed into cold-traps under vacuum, and stored for disposal.

2. Used NMR solvents were disposed as heavy metal wastes.

3. The heavy metal residues were dissolved in nitric acid and after neutralization were stored in the containers for heavy metal wastes.

4. Drying agents such as KOH, $CaCl_2$, CaH_2, and P_4O_{10} were hydrolyzed and disposed as acid or base wastes.

5. Na metal used for drying solvents was collected for recycling.[109] The non-reusable sodium metal was hydrolyzed in cold ethanol and used for cleaning glassware in the alkali bath.

6. Ethanol and acetone used for cold baths were subsequently used for cleaning glassware.

7. The residue of the alkali bath used for cleaning glassware was disposed into the container for basic wastes.

8. The residue of the acid bath used for cleaning glassware was neutralized with Na_2CO_3 and washed off in the water drainage system.

Amounts of various types of disposable wastes generated during this work:

Metal containing wastes	14 L,
Solvent wastes	37 L,
Acid wastes	20 L,
Base wastes	30 L.

6. Crystal data and refinement details

Table C1. *Crystal data and structure refinement for* **3**.

Empirical formula	$C_{34}H_{40}Li_2N_8$	
Formula weight	604.86	
Temperature	173(2) K	
λ	0.71073 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.365(9) Å	α = 95.69(2)°
	b = 10.680(11) Å	β = 90.32(2)°
	c = 19.804(2) Å	γ = 101.31(2)°
Volume, Z	1932.3(3) Å^3, 4	
Density (calculated)	1.040 g/cm^3	
Absorption coefficient	0.062 mm^{-1}	
F(000)	672	
Crystal size	0.5 x 0.3 x 0.2 mm^3	
θ range for data collection	1.95 to 28.28°	
Index ranges	$-12 \leq h \leq 12$, $-14 \leq k \leq 14$, $0 \leq l \leq 26$	
Reflections collected	30056	
Independent reflections	8821 [R_{int} = 0.0330]	
Completeness to θ = 28.28°	91.8 %	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8821 / 0 / 409	
Goodness-of-fit on F^2	1.051	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0599, wR_2 = 0.1343	
R indices (all data)	R_1 = 0.0802, wR_2 = 0.1447	
Largest diff. peak and hole	0.236 and -0.248 e.Å^{-3}	

Table C2. *Crystal data and structure refinement for* **4**.

Empirical formula	$C_{17}H_{35}Cl_2N_4Pr$
Formula weight	507.30
Temperature	200(2) K
λ	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 11.865(2) Å
	b = 11.5807(10) Å β = 95.86(2)°
	c = 16.085(3) Å
Volume, Z	2198.6(6) Å^3, 4
Density (calculated)	1.533 g/cm^3
Absorption coefficient	2.466 mm^{-1}
F(000)	1032
Crystal size	0.9 x 0.5 x 0.5 mm^3
θ range for data collection	3.52 to 25.04°
Index ranges	$-14 \leq h \leq 14$, $-12 \leq k \leq 13$, $-17 \leq l \leq 19$
Reflections collected	4804
Independent reflections	3891 [R_{int} = 0.0300]
Completeness to θ = 25.04°	94 %
Absorption correction	psi
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3889 / 0 / 224
Goodness-of-fit on F^2	1.158
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0215, wR_2 = 0.0561
R indices (all data)	R_1 = 0.0215, wR_2 = 0.0561
Largest diff. peak and hole	1.145 and -0.712 e. Å^{-3}

Table C3. *Crystal data and structure refinement for* **5**.

Empirical formula	$C_{17}H_{35}Br_2N_4Pr$
Formula weight	596.22
Temperature	133(2) K
λ	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 10.848(18) Å
	b = 7.952(9) Å β = 90.90(15)°
	c = 25.792(5) Å
Volume, Z	2224.7(6) Å^3,
Density (calculated)	1.780 g/cm^3, 4
Absorption coefficient	5.789 mm^{-1}
F(000)	1176
Crystal size	0.5 x 0.6 x 0.5 mm^3
θ range for data collection	1.88 to 24.80°
Index ranges	$-12 \leq h \leq 12$, $-8 \leq k \leq 9$, $-30 \leq l \leq 30$
Reflections collected	43720
Independent reflections	3806 [R_{int} = 0.0794]
Completeness to θ = 24.80°	99.2 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3806 / 0 / 223
Goodness-of-fit on F^2	1.071
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0182, wR_2 = 0.0451
R indices (all data)	R_1 = 0.0202, wR_2 = 0.0458
Largest diff. peak and hole	0.718 and -1.039 e. Å^{-3}

Table C4. *Crystal data and structure refinement for* **7**.

Empirical formula	$C_{17}H_{35}Br_2N_4Sm$	
Formula weight	605.66	
Temperature	133(2) K	
λ	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.783(9) Å	
	b = 7.874(4) Å	β = 90.28(7) °
	c = 25.925(2) Å	
Volume, Z	2201.3(3) Å^3, 4	
Density (calculated)	1.827 g/cm^3	
Absorption coefficient	6.305 mm^{-1}	
F(000)	1188	
Crystal size	0.6 x 0.4 x 0.5 mm^3	
θ range for data collection	1.89 to 24.76°	
Index ranges	$-12 \leq h \leq 12$, $-9 \leq k \leq 9$, $-30 \leq l \leq 30$	
Reflections collected	26141	
Independent reflections	3761 [R_{int} = 0.0715]	
Completeness to θ = 24.76°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3761 / 0 / 220	
Goodness-of-fit on F^2	1.036	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0215, wR_2 = 0.0546	
R indices (all data)	R_1 = 0.0263, wR_2 = 0.0556	
Largest diff. peak and hole	0.939 and -0.537 e. Å^{-3}	

Table C5. *Crystal data and structure refinement for* **8**.

Empirical formula	$C_{17}H_{35}Br_2N_4Tb$
Formula weight	614.23
Temperature	133(2) K
λ	0.71073 Å
Crystal system	orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	a = 19.891(3)Å
	b = 8.213(2)Å
	c = 13.806(2) Å
Volume, Z	2255.4(7) Å^3, 4
Density (calculated)	1.809 g/cm^3
Absorption coefficient	6.685 mm^{-1}
F(000)	1200
Crystal size	0.5 x 0.4 x 0.4 mm^3
θ range for data collection	2.05 to 24.71°
Index ranges	$-23 \leq h \leq 23$, $-9 \leq k \leq 9$, $-16 \leq l \leq 16$
Reflections collected	30036
Independent reflections	3831 [R_{int} = 0.0774]
Completeness to θ = 24.71°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3831 / 40 / 243
Goodness-of-fit on F^2	1.051
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0206, wR_2 = 0.0546
R indices (all data)	R_1 = 0.0209, wR_2 = 0.0547
Largest diff. peak and hole	1.224 and -0.999 e. Å^{-3}

Table C6. *Crystal data and structure refinement for* **9**.

Empirical formula	$C_{17}H_{35}Br_2N_4Yb$
Formula weight	628.35
Temperature	133(2) K
λ	0.71073 Å
Crystal system	orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	a = 20.083(16) Å
	b = 8.170(5) Å
	c = 13.533(8) Å
Volume, Z	2220.7(3) Å^3, 4
Density (calculated)	1.879 g/cm^3
Absorption coefficient	7.816 mm^{-1}
F(000)	1220
Crystal size	0.3 x 0.2 x 0.3 mm^3
θ range for data collection	2.03 to 24.71°
Index ranges	$-23 \leq h \leq 23$, $-8 \leq k \leq 9$, $-14 \leq l \leq 15$
Reflections collected	19437
Independent reflections	3625 [R_{int} = 0.0462]
Completeness to θ = 24.71°	100.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3625 / 3 / 224
Goodness-of-fit on F^2	1.061
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0164, wR_2 = 0.0385
R indices (all data)	R_1 = 0.0176, wR_2 = 0.0387
Largest diff. peak and hole	0.660 and -0.410 e. Å^{-3}

Table C7. *Crystal data and structure refinement for* **10**.

Empirical formula	$C_{17}H_{43}B_2N_4Pr$
Formula weight	466.08
Temperature	200(2) K
λ	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 11.916(12) Å
	b = 12.461(16) Å β = 96.84(13)°
	c = 15.949(3) Å
Volume, Z	2351.4(6) Å^3, 4
Density (calculated)	1.317 g/cm^3
Absorption coefficient	2.078 mm^{-1}
F(000)	968
Crystal size	0.6 x 0.5 x 0.3 mm^3
θ range for data collection	3.51 to 22.51°
Index ranges	$-12 \leq h \leq 12$, $-11 \leq k \leq 13$, $-15 \leq l \leq 17$
Reflections collected	3680
Independent reflections	3062 [R_{int} = 0.0384]
Completeness to θ = 22.51°	99.4 %
Absorption correction	psi
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3062 / 396 / 247
Goodness-of-fit on F^2	1.059
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0342, wR_2 = 0.0826
R indices (all data)	R_1 = 0.0421, wR_2 = 0.0880
Largest diff. peak and hole	0.859 and -1.029 e. Å^{-3}

Table C8. *Crystal data and structure refinement for* **11**.

Empirical formula	$C_{25}H_{57}N_4Si_2Tb$	
Formula weight	628.85	
Temperature	100(2) K	
λ	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 21.073(3) Å	
	b = 16.359(2) Å	β = 101.06(2)°
	c = 18.641(2) Å	
Volume, Z	6306.8(14) Å^3, 8	
Density (calculated)	1.325 g/cm^3	
Absorption coefficient	11.875 mm^{-1}	
F(000)	2624	
Crystal size	0.2 x 0.1 x 0.1 mm^3	
θ range for data collection	2.14 to 57.95°	
Index ranges	$-23 \leq h \leq 21$, $-17 \leq k \leq 16$, $-20 \leq l \leq 18$	
Reflections collected	26169	
Independent reflections	8602 [R_{int} = 0.0242]	
Completeness to θ = 57.95°	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8602 / 0 / 601	
Goodness-of-fit on F^2	1.034	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0209, wR_2 = 0.0524	
R indices (all data)	R_1 = 0.0232, wR_2 = 0.0536	
Largest diff. peak and hole	0.685 and -0.356 e. Å^{-3}	

Table C9. *Crystal data and structure refinement for* **12**.

Empirical formula	$C_{17}H_{35}AlCl_2N_4$	
Formula weight	393.37	
Temperature	200(2) K	
λ	0.71073 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 9.081(2) Å	α = 73.37(18)°
	b = 10.859(3) Å	β = 81.08(19)°
	c = 11.674(3) Å	γ = 73.44(13)°
Volume, Z	1053.9(5) Å^3, 2	
Density (calculated)	1.240 g/cm^3	
Absorption coefficient	0.357 mm^{-1}	
F(000)	424	
Crystal size	1.2 x 0.3 x 0.1 mm^3	
θ range for data collection	3.62 to 25.10°	
Index ranges	$-10 \leq h \leq 10$, $-12 \leq k \leq 12$, $-5 \leq l \leq 13$	
Reflections collected	3794	
Independent reflections	3716 [R_{int} = 0.1098]	
Completeness to θ = 25.10°	99.3 %	
Absorption correction	psi	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3716 / 0 / 223	
Goodness-of-fit on F^2	1.057	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0408, wR_2 = 0.0962	
R indices (all data)	R_1 = 0.0536, wR_2 = 0.1047	
Largest diff. peak and hole	0.513 and -0.240 e. Å^{-3}	

Table C10. *Crystal data and structure refinement for* **14**.

Empirical formula	$C_{35}H_{35}AlBF_{15}N_4O$	
Formula weight	850.46	
Temperature	133(2) K	
λ	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.618(3) Å	
	b = 17.108(4) Å	β = 100.40(6)°
	c = 20.457(6) Å	
Volume, Z	3655.0(18) Å^3, 4	
Density (calculated)	1.546 g/cm^3	
Absorption coefficient	0.169 mm^{-1}	
F(000)	1736	
Crystal size	0.4 x 0.3 x 0.3 mm^3	
θ range for data collection	1.56 to 28.22°	
Index ranges	$-13 \leq h \leq 13$, $-22 \leq k \leq 20$, $-27 \leq l \leq 26$	
Reflections collected	28476	
Independent reflections	8646 [R_{int} = 0.0646]	
Completeness to θ = 28.22°	90.6 %	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	28476 / 0 / 529	
Goodness-of-fit on F^2	0.977	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0614, wR_2 = 0.1546	
R indices (all data)	R_1 = 0.0823, wR_2 = 0.1663	
Largest diff. peak and hole	0.555 and -0.545 e. Å^{-3}	

Table C11. *Crystal data and structure refinement for* **15**.

Empirical formula	$C_{35}H_{35}AlBF_{15}N_4O$
Formula weight	850.46
Temperature	133(2) K
λ	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 9.899(6) Å
	b = 21.468(17) Å β = 104.31(5)°
	c = 18.114(12) Å
Volume, Z	3730.1(4) Å^3, 4
Density (calculated)	1.514 g/cm^3
Absorption coefficient	0.166 mm^{-1}
F(000)	1736
Crystal size	0.7 x 0.4 x 0.4 mm^3
θ range for data collection	1.90 to 24.78°
Index ranges	$-10 \leq h \leq 11$, $-25 \leq k \leq 25$, $-21 \leq l \leq 19$
Reflections collected	25252
Independent reflections	6368 [R_{int} = 0.0559]
Completeness to θ = 24.78°	99.2 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6368 / 0 / 520
Goodness-of-fit on F^2	1.017
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0387, wR_2 = 0.0874
R indices (all data)	R_1 = 0.0491, wR_2 = 0.0906
Largest diff. peak and hole	0.207 and -0.199 e. Å^{-3}

Table C12. *Crystal data and structure refinement for* **16**.

Empirical formula	$C_{36}H_{40}AlBF_{15}N_5$	
Formula weight	865.52	
Temperature	133(2) K	
λ	0.71073 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.360(6) Å	α = 100.24(3)°
	b = 13.036(7) Å	β = 100.03(3)°
	c = 14.744(8) Å	γ = 93.01(3)°
Volume, Z	1922.61(18) Å^3, 2	
Density (calculated)	1.495 g/cm^3	
Absorption coefficient	0.161 mm^{-1}	
F(000)	888	
Crystal size	0.9 x 0.8 x 0.8 mm^3	
θ range for data collection	2.23 to 27.57°	
Index ranges	$-13 \leq h \leq 8$, $-16 \leq k \leq 16$, $-19 \leq l \leq 19$	
Reflections collected	30634	
Independent reflections	8786 [R_{int} = 0.043]	
Completeness to θ = 27.57°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8786 / 13 / 587	
Goodness-of-fit on F^2	1.047	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0497, wR_2 = 0.1176	
R indices (all data)	R_1 = 0.0698, wR_2 = 0.1277	
Largest diff. peak and hole	0.359 and -0.451 e.Å^3	

Table C13. *Crystal data and structure refinement for* **18**.

Empirical formula	$C_{33}H_{51}F_6N_4O_6S_2V$	
Formula weight	828.84	
Temperature	173(2) K	
λ	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 15.329(2) Å	
	b = 13.388(2) Å	β = 97.77(3)°
	c = 19.652(3) Å	
Volume, Z	3995.8(11) Å^3, 4	
Density (calculated)	1.378 g/cm^3	
Absorption coefficient	0.426 mm^{-1}	
F(000)	1736	
Crystal size	0.4 x 0.3 x 0.1 mm^3	
θ range for data collection	1.34 to 28.22°	
Index ranges	$-20 \leq h \leq 19$, $0 \leq k \leq 17$, $0 \leq l \leq 24$	
Reflections collected	30036	
Independent reflections	9058 [R_{int} = 0.0315]	
Completeness to θ = 28.22°	91.8 %	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9058 / 0 / 477	
Goodness-of-fit on F^2	1.032	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0514, wR_2 = 0.1273	
R indices (all data)	R_1 = 0.0723, wR_2 = 0.1392	
Largest diff. peak and hole	0.613 and -0.428 e. Å^{-3}	

Table C14. *Crystal data and structure refinement for* **19**.

Empirical formula	$C_{29}H_{45}N_4PV$	
Formula weight	531.60	
Temperature	100(2) K	
λ	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 12.740(3) Å	
	b = 14.466(3) Å	β = 93.55(3)°
	c = 15.217(3) Å	
Volume, Z	2799.0(10) Å^3, 4	
Density (calculated)	1.261 g/cm^3	
Absorption coefficient	3.674 mm^{-1}	
F(000)	1140	
Crystal size	0.2 x 0.2 x 0.1 mm^3	
θ range for data collection	3.48 to 59.69°	
Index ranges	$-13 \leq h \leq 14$, $-16 \leq k \leq 16$, $-15 \leq l \leq 16$	
Reflections collected	17902	
Independent reflections	7400 [R_{int} = 0.0197]	
Completeness to θ = 59.69°	95.2 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7400 / 1 / 645	
Goodness-of-fit on F^2	1.152	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0264, wR_2 = 0.0648	
R indices (all data)	R_1 = 0.0264, wR_2 = 0.0648	
Largest diff. peak and hole	0. 352 and -0.361 e. Å^{-3}	

Table C15. *Crystal data and structure refinement for* **21**.

Empirical formula	$C_{33}H_{35}N_2P_2Rh$	
Formula weight	624.48	
Temperature	100(2) K	
λ	1.54178 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.937(2) Å	α = 73.37(2)°
	b = 10.904(2) Å	β = 74.06(2)°
	c = 13.517(3) Å	γ = 69.37(2)°
Volume, Z	1418.1(5) Å^3, 2	
Density (calculated)	1.462 g/cm^3	
Absorption coefficient	6.120 mm^{-1}	
F(000)	644	
Crystal size	0.1 x 0.2 x 0.1 mm^3	
θ range for data collection	3.48 to 59.93°	
Index ranges	$-11 \leq h \leq 12$, $-11 \leq k \leq 12$, $0 \leq l \leq 15$	
Reflections collected	3869	
Independent reflections	3869 [R_{int} = 0.1157]	
Completeness to θ = 59.93°	89.7 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3869 / 315 / 346	
Twin law	Two fold axis, 0 1 0 in the direct space	
BASF	0.45277	
Goodness-of-fit on F^2	1.203	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0693, wR_2 = 0.2034	
R indices (all data)	R_1 = 0.0821, wR_2 = 0.2654	
Largest diff. peak and hole	1.924 and -2.684 e.Å^{-3}	

Table C16. *Crystal data and structure refinement for* **22**·$2CH_2Cl_2$.

Empirical formula	$C_{68}H_{74}Cl_5N_4P_4Y$	
Formula weight	1337.35	
Temperature	100(2) K	
λ	1.54178 Å	
Crystal system	monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	a = 18.365(3) Å	
	b = 14.066(3) Å	β = 100.12(2)°
	c = 25.659(3) Å	
Volume, Z	6525.2(19) $Å^3$, 4	
Density (calculated)	1.361 g/cm^3	
Absorption coefficient	4.406 mm^{-1}	
F(000)	2776	
Crystal size	0.2 x 0.2 x 0.1 mm^3	
θ range for data collection	3.50 to 58.99°	
Index ranges	$-20 \leq h \leq 19$, $0 \leq k \leq 15$, $0 \leq l \leq 28$	
Reflections collected	25640	
Independent reflections	4589 [R_{int} = 0.0267]	
Completeness to θ = 58.99°	97.7 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4589 / 148 / 430	
Goodness-of-fit on F^2	1.069	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0249, wR_2 = 0.0649	
R indices (all data)	R_1 = 0.0260, wR_2 = 0.0656	
Largest diff. peak and hole	0.302 and -0.269 e.$Å^{-3}$	

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