

Non-Cp Metal Complexes Supported by
Nitrogen Donor Ligands:
*Precursors for the Synthesis of New Metal
Fluorides*

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Abbreviations

av	Average
br	Broad
^t Bu	<i>tert</i> -butyl
°C	Celsius degree
ca.	About
Cp	cyclopentadienyl
Cp [*]	pentamethylcyclopentadienyl
Cy	cyclohexyl
d	Doublet
dec.	decomposition
DME	1,2-dimethoxyethane
δ	chemical shift
Δ	difference
EI	electron impact ionization
Et	ethyl
equiv	equivalent(s)
g	gram(s)
h	hour(s)
Hz	hertz
<i>IR</i>	infrared
<i>J</i>	coupling constant
K	Kelvin
λ	wavelength
M	metal
<i>M</i> ⁺	molecular ion
m	multiplet
Me	methyl
mg	milligram(s)
min	minute(s)
mL	milliliter(s)

mmol	millimol(ar)
m/z	mass/charge
MS	mass spectrometry
μ	bridging
$\tilde{\nu}$	wave number
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million
ⁱ Pr	<i>iso</i> -propyl
pz	pyrazolyl
q	quartet
r.t.	room temperature
s	septet
t	triplet
<i>tert</i>	tertiary
THF	tetrahydrofuran
TMS	tetramethylsilane
Tp	tris(pyrazolyl)hydroborato
Z	number of molecules in the unit cell

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1. Introduction

Since the discovery of fluorine by Henri Moissan in 1886,^[1] it had become an indispensable element in a wide range of science. Many advances in solid state chemistry, polymer chemistry, coordination chemistry, main group chemistry, and organometallic chemistry have been reported recently, which rely on the physical and chemical properties of the most electronegative element—fluorine.^[2] However, although some significant progress has been achieved in recent years, organometallic fluorine chemistry is rather scarce compared to heavier congeners.^[3]

1.1. The Preparation of Organometallic Fluorides: Me_3SnF as a Versatile Fluorinating Reagent

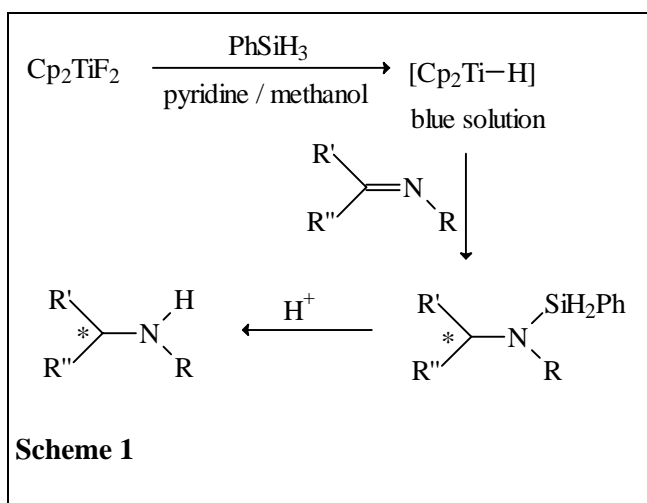
As the most electronegative element fluorine forms very polar, strong chemical bonds between fluorine and non-metals, metalloids and covalent or ionic compounds with metals. Its binary inorganic compounds are either molecular fluorides EF_n or insoluble solids (in which the F^- anions alternate with metal centers to usually form three-dimensional networks), generally unsuitable as starting materials for the preparation of organometallic fluorides. Therefore, most organometallic fluorides have been synthesized from the corresponding organometallic precursors with various fluorinating reagents.^[2] The very polar metal-fluorine bond often results in fluorine bridge formation, and a more covalent rather weak organic ligand-metal bond that is easily cleaved by HF or oxidative fluorinating agents.^[2] Thus, the general scarcity of organometallic fluorides is due to the lack of convenient methods of introducing fluorine into these compounds.

Me_3SnF was first reported as a fluorinating reagent in 1968 by Schmidbaur *et al.*^[4] However, it was Roesky *et al.* that introduced it to transition metals and prepared a series of exciting fluorides, which display distinctive properties compared to the corresponding chlorides.^[2] Me_3SnF is particularly efficient in the conversion of groups 4 – 6 and main group chlorides, as well as transition metal hydride and alkyl derivatives to the corresponding fluorides.^[2]

1.2. The Burgeon of Organometallic Fluorides

Recent years have witnessed the dramatic development of organometallic fluorine chemistry.^[2] Recent reports have shown characteristic properties of organometallic fluorides compared to the analogous chlorides. For instance, out of many specialists' prediction, cyclopentadienylzirconium and titanium fluorides in the presence of methylalumoxane (MAO) as a cocatalyst are highly active in the polymerization of ethylene and styrene, respectively,^[5] increasing up to a factor 30 compared to that of the chlorinated reagent. Noteworthy is that syndiotactic polymer is obtained in the absence of any chiral discriminating reagent with cyclopentadienyltitanium fluoride as the catalyst for the polymerization of styrene.^[2,6] An insight into the mechanism of this homogeneous catalysis for the polymerization of olefins is gained by the studies on the interaction of the alkylalane with the transition-metal center and its ligands. It has been shown that reactions of Cp^*MF_3 ($\text{M} = \text{Zr}, \text{Hf}$) using AlMe_3 in a 1 : 1 molar ratio led to a selective exchange of fluorine atoms for methyl groups and the by-product AlMe_2F acts as a ligand bridging two transition metals to form the dimer *cis*- $[\{\text{Cp}^*\text{M}(\text{Me})(\mu\text{-F})\}\{(\mu\text{-F})_2\text{AlMe}_2\}]_2$.^[7] When Cp^*MF_3 was allowed to react with an excess of AlMe_3 , methane gas evolution and activation of C–H bonds was observed along with the formation of the fluorine free clusters $[(\text{Cp}^*\text{M})_3\text{Al}_6\text{Me}_8(\mu_3\text{-CH})_5(\mu\text{-CH}_2)_2]$, while the oxidation states of zirconium and hafnium remain unchanged.^[7]

Metallocene fluorides are also good catalysts for stereoselective hydrosilylation of imines (scheme 1)^[8] and the chiral addition of allylstannanes to aldehydes.^[9]



Organometallic fluorides of Group 4 metals can also act as complexing agents for inorganic compounds such as LiF, NaF, MgF₂, CaF₂, ZnF₂ and Li₂O, which otherwise are insoluble in organic solvents.^[10] Moreover, they can also form complexes with unstable species like MeZnF (Scheme 2),^[11] resulting in host-guest-type compounds.



Scheme 2

With respect to organometallic main group fluorides, studies have mainly been focused on Group 13 of the element-aluminum and group 14 elements.^[2 b]

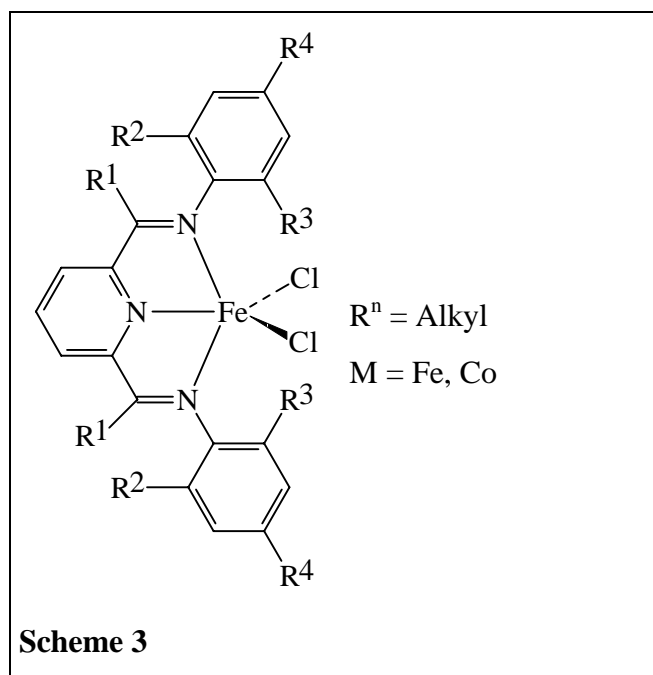
1.3. Prosperity and Perspective of Non-Cp Organometallic Chemistry

Since the discovery of ferrocene, first reported by Kealy and Pauson *et al.* in 1951,^[12] the Cp ligand has been widely used on main group, d-block and f-block metals. The “metallocene revolution” was an ostentatious advance in the catalysis of olefin polymerization. Metallocene-based catalysts are dramatically different from previous generations of catalysts. For example, their homogeneous nature leads to lower polydispersities and more uniform incorporation of α -olefin comonomers than obtained with Ziegler-Natta catalysts. The resulting improvements in the properties of the polymers produced by metallocenes—clarity, strength, and lower hexane-extractables—usually come at a higher price. Market penetration therefore has not been as great as originally predicted.

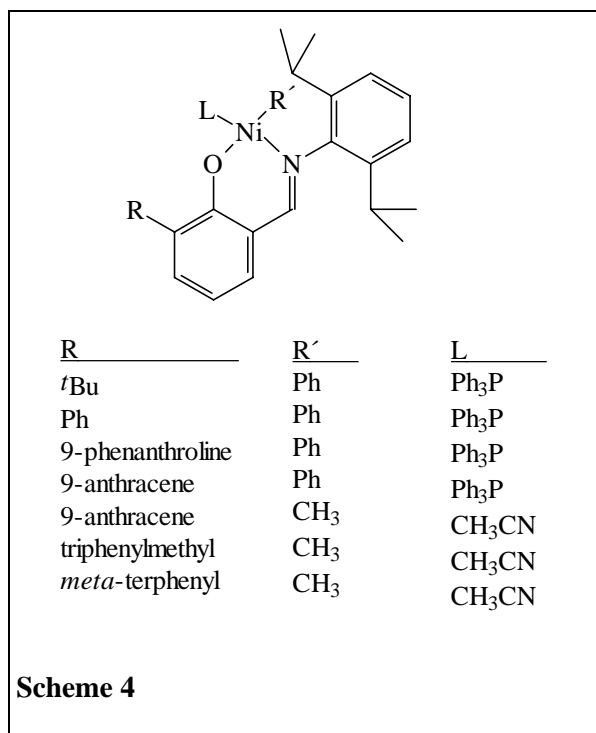
Pursuing the search for less costly polymers with improved properties drives chemists to explore new techniques, catalysts and cocatalysts for olefin polymerization and copolymerization.^[13] The homogeneous catalysts are no longer confined to metallocene complexes. Many non-Cp catalysts have been reported in recent years, which are active for ethylene polymerization.^[14] Amidinato complexes of titanium^[15] have been reported to be active in olefin catalytic polymerization. Many arylimido-containing molybdenum and tungsten complexes are initiators for ring-opening polymerization (ROMP) producing “intelligent” and advanced materials.^[16]

Chelating diamido titanium complexes of the type $[\text{RN}(\text{CH}_2)_3\text{NR}]\text{TiMe}_2$ ($\text{R} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3, 2,6\text{-Me}_2\text{C}_6\text{H}_3$), when activated with $\text{B}(\text{C}_6\text{F}_5)_3$, have been found to catalyze the living polymerization of α -olefins at ambient temperature, thereby producing narrow polydispersity polymers ($M_w/M_n = 1.05 - 1.09$).^[17] Schrock *et al.* have developed the tridentate diamido donor ligand $[(^t\text{Bu-}d_6\text{-N-}o\text{-C}_6\text{H}_4)_2\text{O}]^{2-}$ and prepared its Zr complex, which upon being activated by $\text{B}(\text{C}_6\text{F}_5)_3$, is active for ethylene and living 1-hexene polymerizations.^[18]

Recent findings that a diimine/pyridine ligand system^[19] spectacularly enhances the reactivity of electron-rich late-transition metals toward Ziegler–Natta olefin polymerization have attracted considerable attention. The very high activity of these catalysts and especially of those discovered by Brookhart^[13] and Gibson^[14] (Scheme 3)



opens some fascinating perspectives of nitrogen donor ligand systems. Examples of this kind of catalysts are neutral, single-component nickel(II) polyolefin catalysts that tolerate heteroatoms. Bulky ligand substituted salicylimido complexes of Ni(II) exhibit activities that are comparable to those of the early metallocenes (Scheme 4).^[20] A cationic metal center is not required to achieve high polymerization activity. The catalysts not only tolerate polar monomers such as substituted norbornenes, carbon monoxide, and α - ω functional olefins but can incorporate them into the polymer chain.



1.4. Scope and Aim of the Present Work

Based on the aforementioned background materials, there is clearly a vast potential to be exploited in non-Cp organometallic chemistry, especially in the untapped non-Cp metal fluorine chemistry.

Hence, the objectives of the present work are:

- To synthesize new non-Cp metal complexes supported by N donor ligands with various sizes and hapticities;
- To develop a general methodology for the corresponding fluorides from the new compounds;
- To investigate the reactivity of these new non-Cp metal complexes including the corresponding fluorides and their structurally intrinsic correlation with their reactivity.

2. Results and Discussion

There are numerous alternatives of Cp which have been employed for stabilizing metal complexes. Some of them provide organometallic complexes with properties the Cp congeners do not have. In this thesis, several nitrogen donor ligands have been employed, including a mono-coordinating divalent aryl imido ligand, substituted monoanionic chelating amidinato, guanidinato, 1-aza-allyl, diketiminato, salicylaldiminato, and pyrrolylaldiminato, and tridentate monoanionic tris(pyrazolyl)hydroborato (Tp) ligands (Figure 1). These ligands may exert steric control by variation of the substituents on the backbone and exhibit different hapticities and coordination modes. Metals involved in the present studies are Ti, V, Mo, Zn, Mg, and Al.

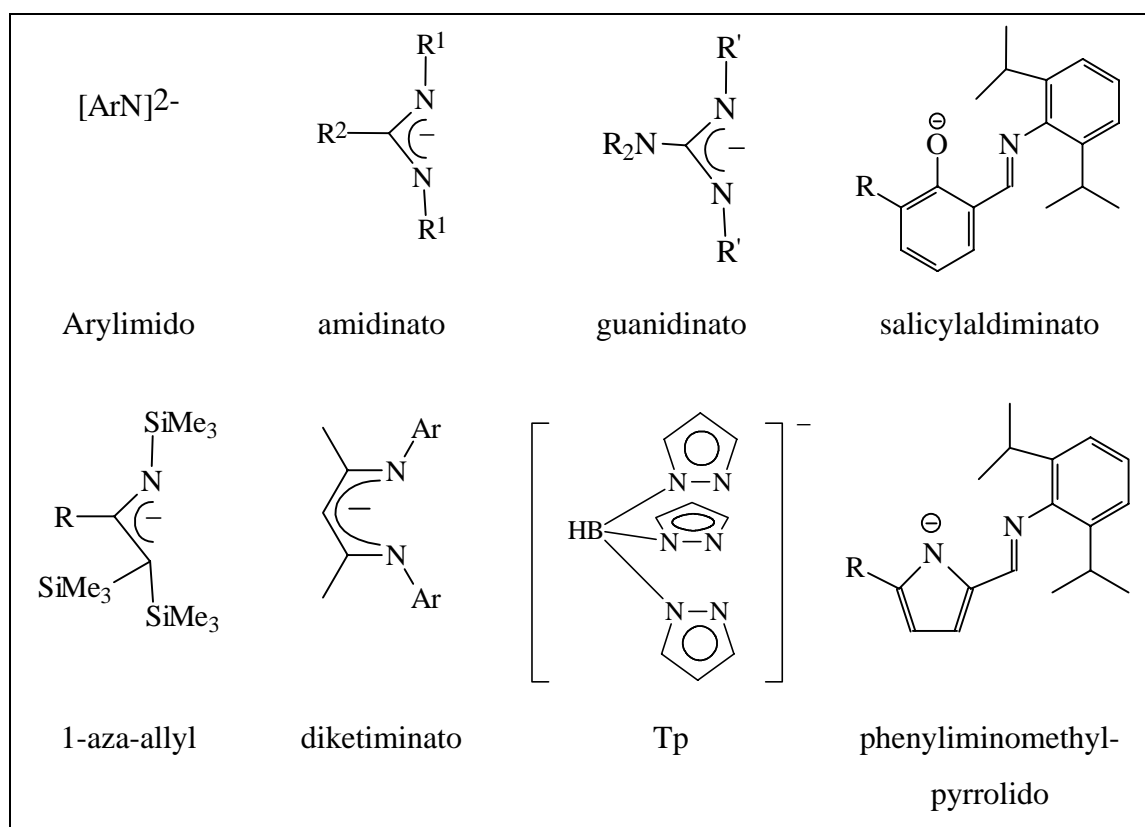


Figure 1. Types of anionic ligands involved in this work

2.1. $[\text{Cp}^*\text{V}(\mu\text{-F})_2]_4$ (1)

Several organometallic niobium and tantalum fluorides have been prepared previously,^[2a] for instance, Cp^*MF_4 ($\text{M} = \text{Nb}, \text{Ta}$).^[21] However, no pure

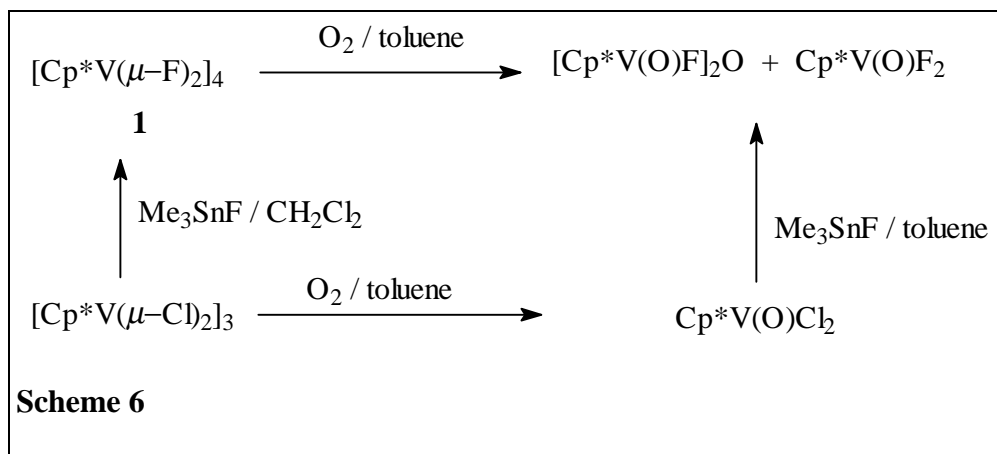
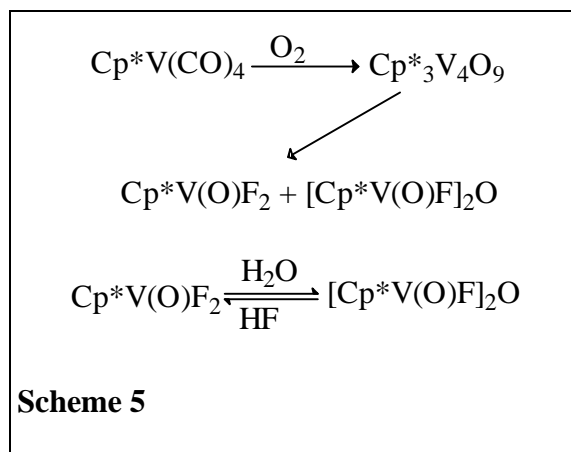
organovanadium fluoride has been separated in pure form before this work due to the lack of suitable starting materials.^[21] Although a few vanadium fluorides had been reported some years ago,^[22] those either contain fluorinating reagents as impurities or are not easily accessible. For example, removal of AsF₅ or SbF₅ from Cp₂V(AsF₆)₂ and Cp₂V(SbF₆)₂ could not be achieved.^[22] Cp*V(O)F₂ and [Cp*V(O)F]₂O have been detected as a mixture in solution,^[22b] although neither of them has yet been isolated in a pure state. Me₃SnF was found ineffective for the fluorination of Cp vanadium chlorides such as Cp₂VCl₂, CpVCl₃ and CpVCl₂(PMe₃)₂, or the dimethylate CpVMe₂(PMe₃)₂.^[23] Recently, three research groups independently reported on the preparation of [Cp*V(μ-Cl)₂]₃,^[24] which was expected to be a suitable precursor for the preparation of an isolable fluoride.

2.1.1. Synthesis, Spectroscopic Studies and Reactivity of [Cp*V(μ-F)₂]₄ (**1**) Towards O₂

Fluorination of [(Cp*V(μ-Cl)₂)₃] with Me₃SnF in CH₂Cl₂ afforded the corresponding fluoride **1** in a 38 % isolated yield. Compound **1** was characterized by mass spectrometry, ¹H NMR spectroscopy, elemental analysis, cryoscopic molecular mass determination in toluene and an X-ray single crystal study.

The ¹H NMR spectrum of **1** shows a broad signal (δ -0.05 ppm) in a C₆D₆ solution, with a line width of 42 Hz, indicating a paramagnetic compound. The result of a molecular mass determination in toluene (M = 212) suggests that it is a monomer in this solvent. The mass spectrum of compound **1** shows the molecular ion peak [M]⁺ (*m/z* 896) and a peak (*m/z* 672) attributed to the [(η⁵-C₅Me₅)V(μ-F)₂]₃⁺ fragment.

Compound **1** is very sensitive towards oxygen and its reaction with O₂ is much faster compared to that of [Cp*V(μ-Cl)₂]₃. In THF solution **1** decomposes into unidentifiable products within a few minutes when exposed to an O₂ atmosphere. The ⁵¹V NMR spectrum reveals that bubbling O₂ through a toluene solution of **1** at room temperature afforded a mixture of [Cp*V(O)F]₂O and Cp*V(O)F₂, characterized by ⁵¹V NMR as a non-separable mixture in solution (Scheme 5).^[22b] The fluorination of Cp*V(O)Cl₂^[24] resulted in the formation of the same products (Scheme 6).



2.1.2. X-Ray Crystal Structure of **1**

The X-ray diffraction analysis shows that **1** has a tetrameric structure in the solid state (Figure 2); selected bond lengths and angles are listed in Table 1.

The four vanadium atoms in this molecule can be regarded as being arranged at vertices of a distorted tetrahedron with four distant edges bridged by one F atom each with a obtuse V–F–V angle (av 129.8°) and the other two close edges bridged by two F atoms with a right angle V–F–V arrangement (av 90.5°). The mean distance between closer V atoms is 2.84 Å out of the range of a V–V bond length,^[24b] while that of the distant edges is 3.63 Å.

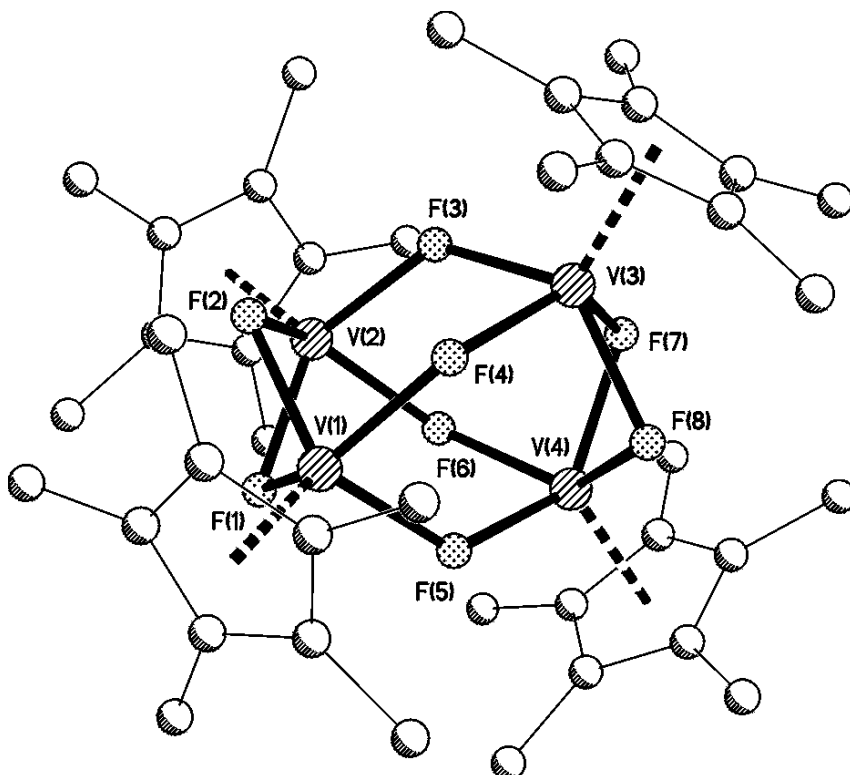


Figure 2. Molecular structure of **1**. Hydrogen atoms are omitted for clarity.

Without structural intimation, we considered the two possible tetrameric structures **1a** and **1b** (Figure 3). The compound **1** crystallized as **1a** rather than **1b**, most likely due to the crystal packing of the molecules. Furthermore, the tetrameric structure completes the nuclearity dependence trend on halides though reasons for which are still unclear.^[24a]

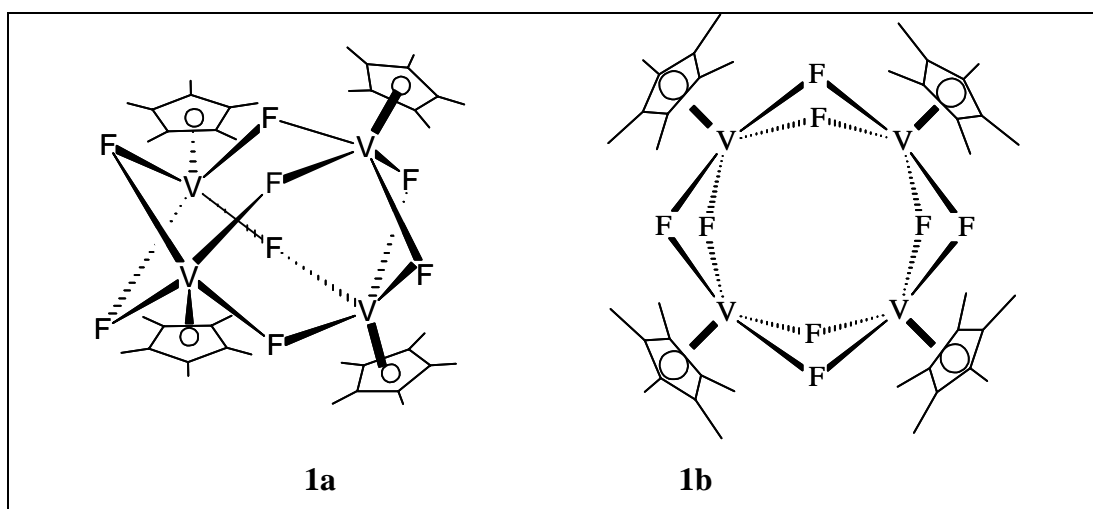


Figure 3. Supposed structural isomers of **1**.

Table 1. Selected bond lengths [Å] and angles [°] for **1**

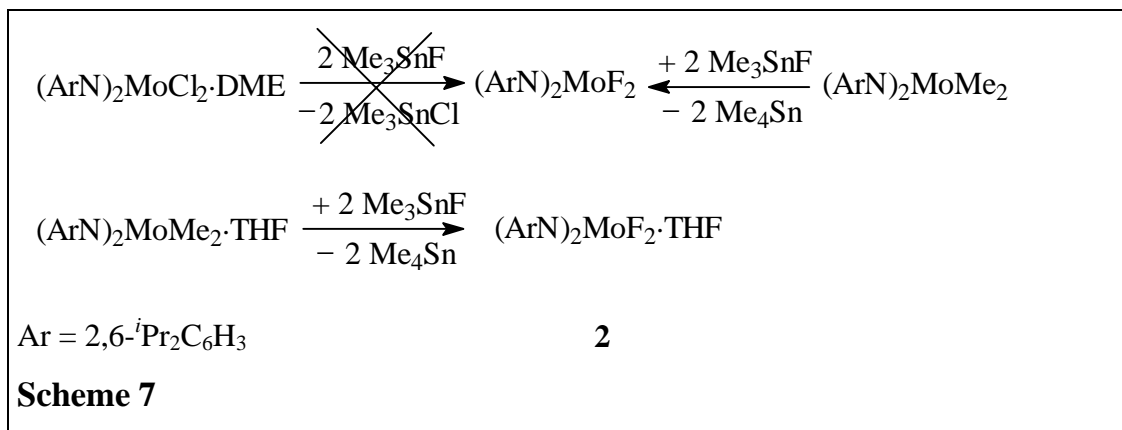
V(1)-F(5)	1.999(3)	F(3)-V(2)-F(1)	128.72(14)
V(1)-F(4)	2.001(3)	F(1)-V(2)-F(6)	80.54(14)
V(1)-F(2)	2.002(3)	F(4)-V(3)-F(7)	129.49(14)
V(1)-F(1)	2.003(3)	F(4)-V(3)-F(8)	81.65(14)
V(1)-V(2)	2.845(2)	F(7)-V(3)-F(8)	73.9(2)
V(2)-F(3)	1.995(3)	F(4)-V(3)-F(3)	81.74(13)
V(2)-F(2)	1.996(3)	F(7)-V(3)-F(3)	80.63(14)
V(2)-F(1)	2.000(3)	F(8)-V(3)-F(3)	129.02(14)
V(2)-F(6)	2.009(3)	F(7)-V(4)-F(8)	74.1(2)
V(3)-F(4)	1.994(3)	F(7)-V(4)-F(5)	129.02(14)
V(3)-F(7)	1.999(4)	F(8)-V(4)-F(5)	80.84(14)
V(3)-F(8)	2.004(4)	F(7)-V(4)-F(6)	80.96(14)
V(3)-F(3)	2.010(3)	F(8)-V(4)-F(6)	129.39(14)
V(3)-V(4)	2.836(2)	F(5)-V(4)-F(6)	82.03(13)
F(3)-V(2)-F(2)	80.83(14)	F(2)-V(2)-F(6)	128.64(14)

2.2. Bis(arylimido) Molybdenum Fluorides

Recent years have witnessed renewed interest in the organometallic chemistry of transition metal complexes of groups 4, 5 and 6 containing imido ligands.^[25] As a dianionic ligand, the imido group RN^{2-} (R = alkyl, aryl group) is able to ligate most transition metals, coordinated in a terminal or bridging fashion. A great variety of imido complexes of group 4 – 6 has been prepared. Imido moieties bestow new properties on complexes.^[16] Bis(imido) molybdenum complexes are of interest due to their ‘isolobal’ relationship to bent metallocenes of the group 4 metals,^[25e] which find widespread application as reagents in organic synthesis^[26] and as polymerisation catalysts.^[27] Imido molybdenum and tungsten complexes are one family of catalysts for ring-opening metathesis polymerization (ROMP).^[16] However, no imido fluorides are known to date.

2.2.1. Synthesis of (2,6-*i*-Pr₂C₆H₃N)₂MoF₂·THF (**2**)

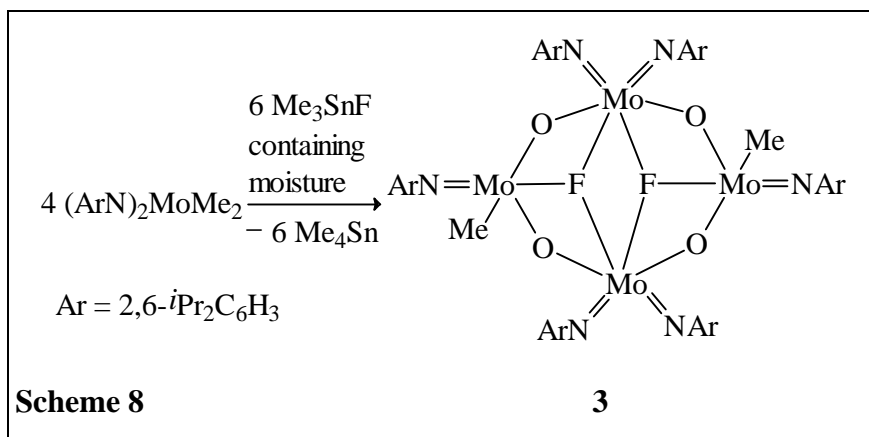
Unlike most transition metal chlorides bearing Cp groups, [(2,6-*i*-Pr₂C₆H₃N)₂MoCl₂·DME]^[25e] does not react with Me₃SnF in common organic solvents CH₂Cl₂ or toluene in fluorine metathesis reactions. Therefore we used the more reactive [(2,6-*i*-Pr₂C₆H₃N)₂MoMe₂] or [(2,6-*i*-Pr₂C₆H₃N)₂MoMe₂]·THF instead,^[25i] which reacted smoothly with Me₃SnF in toluene or THF (Scheme 7). The disappearance of the solid



Me₃SnF indicated the progress of the reaction. After the reaction was complete, the volatiles were removed *in vacuo* and the residue was extracted with *n*-pentane (20 mL). Orange crystals of **2** formed after cooling the extract at -32 °C for 48 h. Well shaped crystals were obtained when the reaction was carried out in THF. The crystals were characterized as [(2,6-*i*-Pr₂C₆H₃N)₂MoF₂]·THF (**2**) by MS, ¹H NMR and elemental analyses.

2.2.2. Formation of [(2,6-*i*-Pr₂C₆H₃N)₆Mo₄(μ₃-F)₂Me₂(μ-O)₄]·(C₅H₁₂) (**3**)

The use of unsublimed Me₃SnF, containing water due to the method of preparation,^[28] led to fine dark-red crystals of [(2,6-*i*-Pr₂C₆H₃N)₆Mo₄(μ₃-F)₂Me₂(μ-O)₄] (**3**) in low yield (4.2 %) after 48 h when toluene was used as a solvent in the reaction and *n*-pentane to extract the crude product (Scheme 8). Once the crystals were formed, they could not be redissolved in *n*-pentane or toluene. The elemental analysis is indicative for a 1 : 1 stoichiometry of *n*-pentane in the tetranuclear complex in the lattice in accordance with the X-ray structural determination (Figure 4).



2.2.3. Single Crystal X-ray Structural Investigation of **3**

The molecular geometry of **3** is centrosymmetric (Figure 4); selected bond lengths and angles are collected in Table 2.

An important structural feature of **3** are the two different geometries about the metal centers (Figure 4). The geometry of the six-coordinated Mo(1) is best described as distorted octahedral, and that of five-coordinated Mo(2) as distorted trigonal bipyramidal. The four Mo atoms lie in a plane defined by the four O atoms. The μ_3 -F atoms F(1) occupy the axial site of Mo(2), which is also the vertex shared by Mo(1) and Mo(1A). Each of the two five-coordinated Mo atoms has one essential linear imido ligand arranged opposite to the μ_3 -F atoms with an angle of $178.1(3)^\circ$ at the nitrogen atom and one methyl group attached in an equatorial position with a Mo–Me bond length of $2.115(5) \text{ \AA}$, slightly longer than that in $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{MoMe}_2]^{[25i]}$ (av 2.109 \AA). It is somehow surprising that the remaining Me groups in **3** are unreactive towards Me_3SnF or water to give a product further fluorinated or hydrolyzed even though an excess amount of Me_3SnF is used. Selective oxygen insertion into the Mo–Me bond has been observed by Gibson *et al.*,^[25i] who reported the reaction of $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{MoMe}_2]$ with O_2 affording the methoxy-bridged complex $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{MoMe}(\mu\text{-OMe})]_2$.

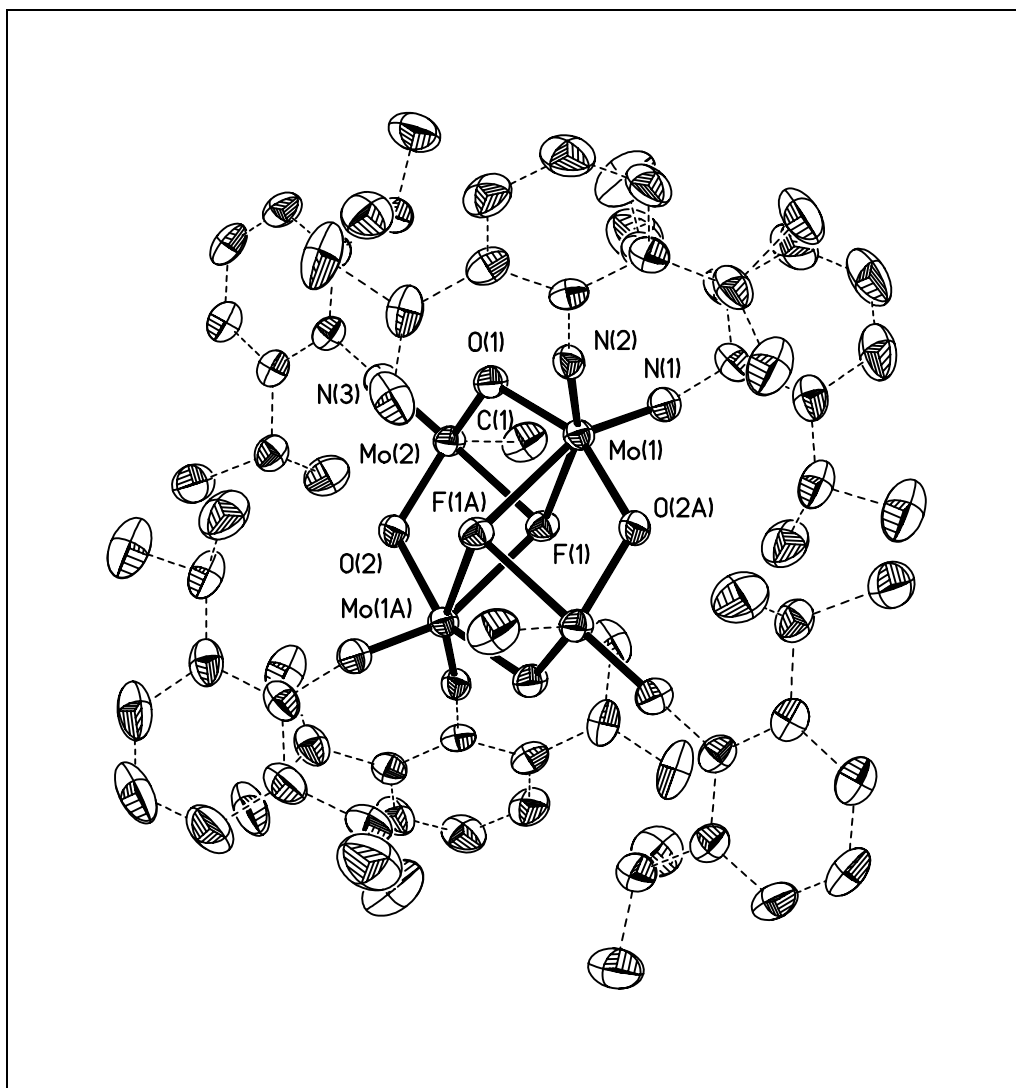


Figure 4. Molecular structure of 3. Hydrogen atoms and lattice solvent are omitted for clarity. (with 50 % probability ellipsoids)

At Mo(1) a nearly linear imido ligand is arranged opposite to F(1) with an angle of $172.2(3)^\circ$ at the nitrogen atom. Compared to that of Mo(2) [$178.1(3)^\circ$], the angle is slightly smaller, whereas the Mo–N bond lengths are nearly the same [$1.739(4) \text{ \AA}$] to [$1.736(4) \text{ \AA}$]. The other imido ligand opposite to F(1A) bent towards the linear imido ligand with a longer Mo–N bond length [$1.751(4) \text{ \AA}$] and a smaller angle $159.5(3)^\circ$ at the nitrogen atom, away from F(1) with ample space for the imido ligand to adopt a linear orientation. This is good evidence that the significant bending at the nitrogen is more likely to be due to electronic rather than crystal packing effects. This has been also observed in trigonal bipyramidal bis(imido) molybdenum compounds.^[25f]

Table 2. Selected bond lengths [Å] and angles [°] for **3**

Mo(1)-N(2)	1.739(4)	O(1)-Mo(1)-F(1)	73.24(10)
Mo(1)-N(1)	1.751(4)	N(2)-Mo(1)-F(1A)	100.40(13)
Mo(1)-O(2A)	2.028(3)	N(1)-Mo(1)-F(1A)	152.30(13)
Mo(1)-O(1)	2.032(3)	O(2A)-Mo(1)-F(1A)	71.25(10)
Mo(1)-F(1)	2.300(2)	O(1)-Mo(1)-F(1A)	86.06(10)
Mo(1)-F(1A)	2.352(2)	N(3)-Mo(2)-O(1)	104.2(2)
Mo(2)-N(3)	1.736(3)	F(1)-Mo(1)-F(1A)	63.64(10)
Mo(2)-O(1)	1.811(3)	N(3)-Mo(2)-O(2)	103.3(2)
Mo(2)-O(2)	1.815(3)	O(1)-Mo(2)-O(2)	121.16(14)
Mo(2)-C(1)	2.115(5)	N(3)-Mo(2)-C(1)	96.0(2)
Mo(2)-F(1)	2.291(2)	O(1)-Mo(2)-C(1)	110.7(2)
F(1)-Mo(1A)	2.352(2)	O(2)-Mo(2)-C(1)	116.8(2)
O(2)-Mo(1A)	2.028(3)	N(3)-Mo(2)-F(1)	178.22(13)
		Mo(2)-O(1)-Mo(1)	117.7(2)
N(1)-Mo(1)-F(1)	91.85(13)	O(2A)-Mo(1)-F(1)	90.52(10)

Although some Mo complexes containing fluorine ligands are known, three-coordinated F atoms are rare.^[25f, 29] In most cases fluorine atoms show a strong bridging tendency connecting Mo atoms to form dimeric complexes and anions, or polynuclear complexes. Recently, Borgmann, Limberg *et al.* reported a dinuclear complex [K(18-crown-6)]⁺ [{Mo(η^3 -C₃H₄Me)(CO)₂]₂(μ -F)₃]⁻,^[30] in which an interaction between μ -F and K⁺ was observed. In spite of the contacts to the cation, the Mo-(μ -F) bond lengths are still within the typical range for Mo-(μ -F) bond lengths (1.98 - 2.22 Å).^[29b, c, 30] The different Mo-(μ_3 -F) bond lengths in **3** (2.291, 2.300 and 2.352 Å) are distinctively longer compared to the Mo-(μ -F) bond lengths.

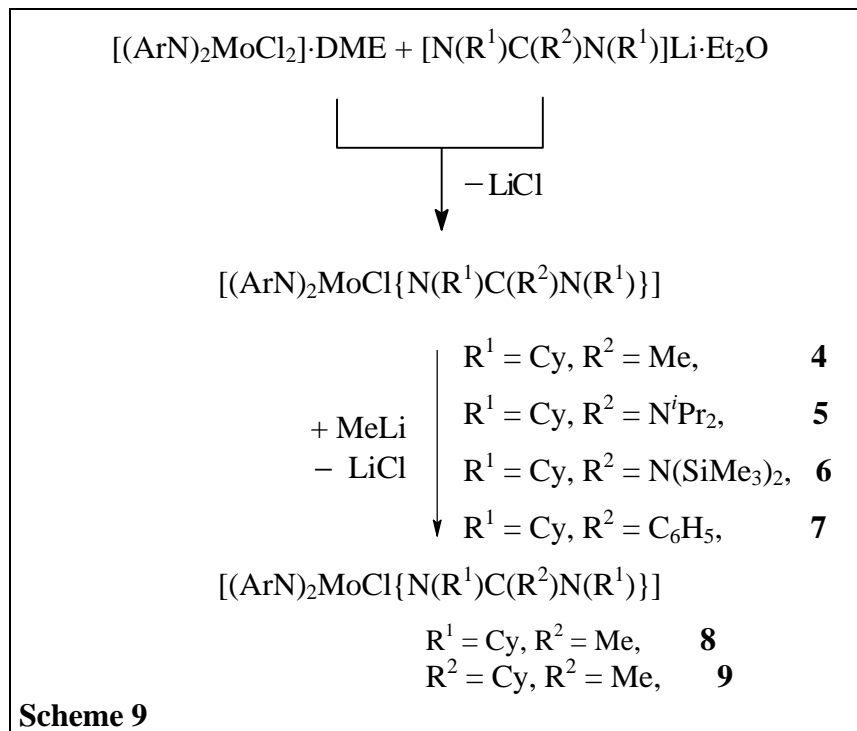
The Mo-(μ -O) bond lengths are 1.813 Å (average) for the five-coordinated Mo atoms and 2.030 Å (average) for the six-coordinated Mo atoms, respectively. This indicates additional π bonding between the five-coordinated Mo atoms and the μ -O atoms. All distances are within the normal range for Mo-(μ -O) bond lengths.^[31]

2.3. Bichelating Amidinato and Guanidinato Ligands

Recently a series of bis(arylimido) molybdenum complexes bearing C,N-^[25k, l] or O,N-bidentate ligands^[32] have been prepared. These five-coordinated bis(arylimido) molybdenum complexes bearing C,N-bidentate ligands have been found active in ring opening metathesis polymerization (ROMP) reactions. It was of interest to investigate this class of compounds having other bidentate ligands. Such studies will give insight into the coordination sphere of Mo and the effect of ligand properties. Bidentate anionic amidinates and guanidates are important ancillary ligands in transition and main group chemistry and have been widely used for Group 13^[33] and 14^[34] metals as well as for Group 4,^[35] 5,^[36] 6^[37] and 7 metals.^[38] Variability of substituents on the backbone of these ligands renders them highly suitable for studying trends. It is also of interest to see whether the fluorinated derivatives of these compounds can be made.

2.3.1. Preparation, Attempted Fluorination and Spectral Characterization of the Bis(arylimido) Molybdenum(VI) Amidinates and Guanidates 4 - 9

The reactions of $[(\text{ArN})_2\text{MoCl}_2]\cdot\text{DME}$ ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) with one equiv of the lithium salts of amidinates and guanidates in THF yielded the compounds $[(\text{ArN})_2\text{MoCl}\{\text{N}(\text{R}^1)\text{C}(\text{R}^2)\text{N}(\text{R}^1)\}]$ ($\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{Me}$ (**4**); $\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{N}^i\text{Pr}_2$ (**5**); $\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{N}(\text{SiMe}_3)_2$ (**6**); $\text{R}^1 = \text{SiMe}_3$, $\text{R}^2 = \text{C}_6\text{H}_5$ (**7**)) with five-coordinated Mo atoms in moderate yields (Scheme 9). Compounds **4** and **5** have low solubility in diethyl ether, but can be recrystallized from toluene to afford orange crystals. In contrast, compounds **6** and **7** are highly soluble in hydrocarbon solvents, even in *n*-pentane, and could not be recrystallized. Nevertheless, removing the volatiles from the *n*-pentane extract afforded the analytically pure brown product. These complexes can be methylated by MeLi, exemplified by the reaction of **4** and **5** with MeLi in THF affording $[(\text{ArN})_2\text{MoMe}\{\text{N}(\text{R}^1)\text{C}(\text{R}^2)\text{N}(\text{R}^1)\}]$ ($\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{Me}$ (**8**); $\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{N}^i\text{Pr}_2$ (**9**)). Attempts to methylate **4** and **5** using MeMgBr instead of MeLi were unsuccessful.



Attempts to fluorinate either chlorides **4** - **7** or methyl derivatives **8** and **9** were unsuccessful. The resistance of **8** and **9** towards the fluorinating reagent Me_3SnF indicates that the two compounds are less reactive compared to $[(\text{ArN})_2\text{MoMe}_2]$ (see section 2.2.1). Compounds **4** - **9** are moisture-sensitive but can be handled in air for a short time without any noticeable change.

The compounds were characterized by elemental analysis, EI mass spectrometry and ^1H NMR spectroscopy. The EI-MS of each compound presents the very clear molecular ion peak and peaks attributable to the $[\text{M} - \text{ArN}]^+$ fragments. The ^1H NMR spectra of **4** - **9** show one septet and two doublet resonances for the ^iPr protons of the ArN ligands, and only one septet and one doublet for the N^iPr_2 protons of **4** and **9** due to the free rotation around the $\text{C}-\text{N}^i\text{Pr}_2$ axis. The Mo-Me resonance single peak of **8** and **9** appears at lower field (δ 1.54 ppm and 1.60 ppm, respectively) compared to those found for the C,N- chelating congeners (δ 1.03 or 1.13 ppm)^[25k, 1] and at slightly higher field than that of a O,N-chelating complex (δ 1.67 ppm).^[32]

2.3.2. X-Ray Crystal Structure of 9

An insight of the molecular geometry of this series of compounds with five-coordinated molybdenum atoms was achieved by X-ray single crystal structure determinations of **8** and **9**. Unfortunately the crystal structural data of **8** were not so good to give credible bond lengths and angles. Nevertheless, good data were obtained for **9**, selected bond lengths and angles are given in Table 3, and the molecular structure is shown in Figure 5.

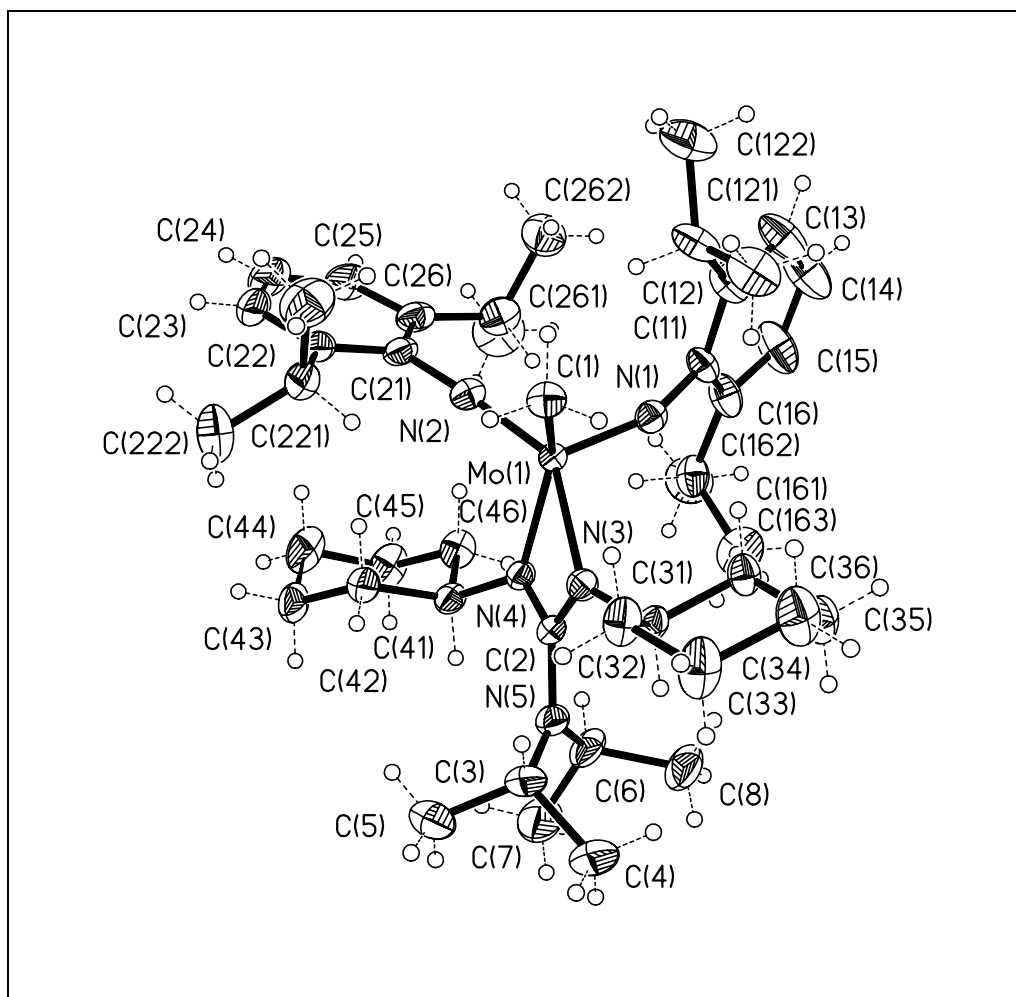


Figure 5. The Molecular structure of **9** in the crystal. Hydrogen atoms are omitted for clarity. (with 50 % probability ellipsoids)

Table 3. Bond lengths [Å] and angles [°] for **9**

Mo(1)-N(1)	1.756(3)	N(1)-Mo(1)-N(3)	107.06(10)
Mo(1)-N(2)	1.757(2)	N(2)-Mo(1)-N(3)	142.45(11)
Mo(1)-N(4)	2.128(2)	N(4)-Mo(1)-N(3)	60.66(9)
Mo(1)-C(1)	2.172(3)	C(1)-Mo(1)-N(3)	84.72(10)
Mo(1)-N(3)	2.211(2)	C(11)-N(1)-Mo(1)	155.6(2)
N(1)-C(11)	1.398(4)	C(21)-N(2)-Mo(1)	175.5(3)
N(2)-C(21)	1.395(3)	C(2)-N(3)-C(31)	121.8(2)
N(3)-C(2)	1.325(3)	C(2)-N(3)-Mo(1)	92.8(2)
N(4)-C(2)	1.344(4)	C(31)-N(3)-Mo(1)	137.4(2)
N(5)-C(2)	1.391(4)	C(2)-N(4)-C(41)	122.1(3)
N(5)-C(6)	1.478(4)	C(2)-N(4)-Mo(1)	96.0(2)
N(5)-C(3)	1.481(5)	C(41)-N(4)-Mo(1)	132.6(2)
N(1)-Mo(1)-N(2)	109.56(13)	C(2)-N(5)-C(6)	116.0(3)
N(1)-Mo(1)-N(4)	110.87(10)	C(2)-N(5)-C(3)	118.6(3)
N(2)-Mo(1)-N(4)	98.06(11)	C(6)-N(5)-C(3)	125.0(3)
N(1)-Mo(1)-C(1)	102.59(11)	N(3)-C(2)-N(4)	110.5(2)
N(2)-Mo(1)-C(1)	95.1(2)	N(3)-C(2)-N(5)	126.7(3)
N(4)-Mo(1)-C(1)	137.13(10)	N(4)-C(2)-N(5)	122.9(3)

Compound **9** has a distorted square pyramidal geometry around the Mo(VI) atom in which the arylimido ligand [ArN(1)] is arranged at the top vertex with an angle at N(1) of 155.6(2)° and a Mo(1)–N(1) bond length of 1.756(3) Å. At the equatorial positions are a bidentate guanidinate ligand, a terminal methyl and an arylimido group with an angle at N(2) of 175.5(3)° and a Mo(1)–N(2) bond length of 1.757(2) Å. The bond lengths of Mo(1)–N(1) and Mo(1)–N(2) are within the range of other arylimido compounds.^[21k,l,32] The Mo(1)–N(3) bond length (2.211(2) Å) is slightly longer than that of Mo(1)–N(4) (2.128(2) Å). The backbone of the guanidinate ligand (N(3)–C(2)–N(4)) together with the Mo atom defines a plane (Mo(1)–N(3)–C(2)–N(4)). The longer Mo–N distances (average 2.1695 Å) compared to those of C–N (average 1.3345 Å) lead

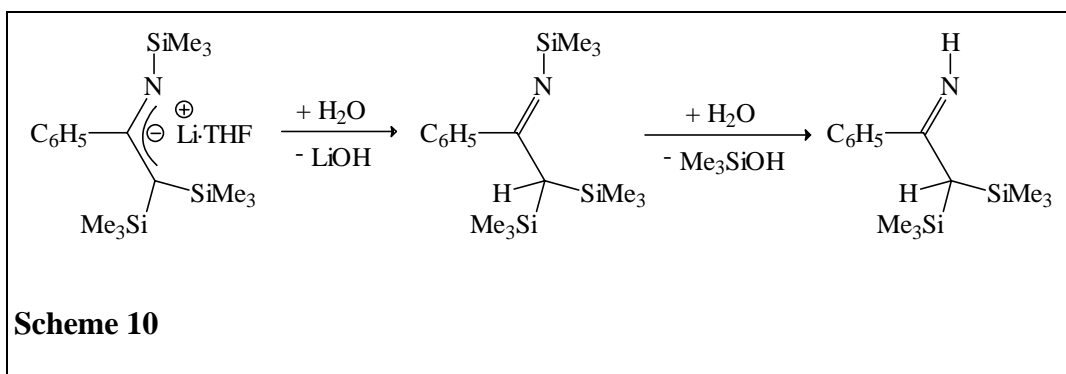
to an acute N(3)–Mo–N(4) angle (60.66(9)°) resulting in a kite-shaped arrangement. The Mo–Me bond length (2.172(3) Å) is similar to those found in the C,N- or O,N-chelating complexes.^[25k,l, 32]

2.4. The 1-Aza-allyl Ligand [N(SiMe₃)C(C₆H₅)C(SiMe₃)₂][−]

The bulky 1-aza-allyl ligand is able to coordinate with main group (K, Li, Pb, Sn) and transition (Cu, Hg, Zr, Sm, Yb, Th) metals.^[39] Cui and Roesky *et al.* have prepared a mono(1-aza-allyl) aluminum difluoride.^[40] However, no other organometallic fluoride containing the 1-aza-allyl moiety is known to date. Therefore we investigated reactions of the lithium salt of the 1-aza-allyl ligand with (2,6-*i*-Pr₂C₆H₃N)₂MoCl₂·DME and TiCl₄, expecting to obtain the corresponding 1-aza-allyl complexes as precursors for fluorides.

2.4.1. Formation and the Structure of [(2,6-*i*-Pr₂C₆H₃N)₂MoCl₂]·[NH=C(C₆H₅)CH(SiMe₃)₂] (10)

Attempts to prepare a molybdenum complex bearing the 1-aza-allyl ligand [N(SiMe₃)C(C₆H₅)C(SiMe₃)₂][−]^[40] which is isoelectronic with amidinate and guanidinate, unexpectedly led to the formation of a Schiff base adduct [(2,6-*i*-Pr₂C₆H₃N)₂MoCl₂]·[NH=C(C₆H₅)CH(SiMe₃)₂] (10) in low yield. Presumably the product arose from unintentional hydrolysis (Scheme 10). The expected compound [(2,6-*i*-Pr₂C₆H₃N)₂MoCl{N(SiMe₃)C(C₆H₅)C(SiMe₃)₂}] was not obtained probably due to the bulkiness of this ligand.



Single crystals of **10** suitable for X-ray diffraction analysis were obtained from diethyl ether solution. The elemental analysis is in agreement with the proposed

structure, and the EI mass spectrum shows the peak of $[M^+ - Cl]$ (m/z 745) and an ion (m/z 570) ascribed to the $[M^+ - Cl - ArN]$ fragment.

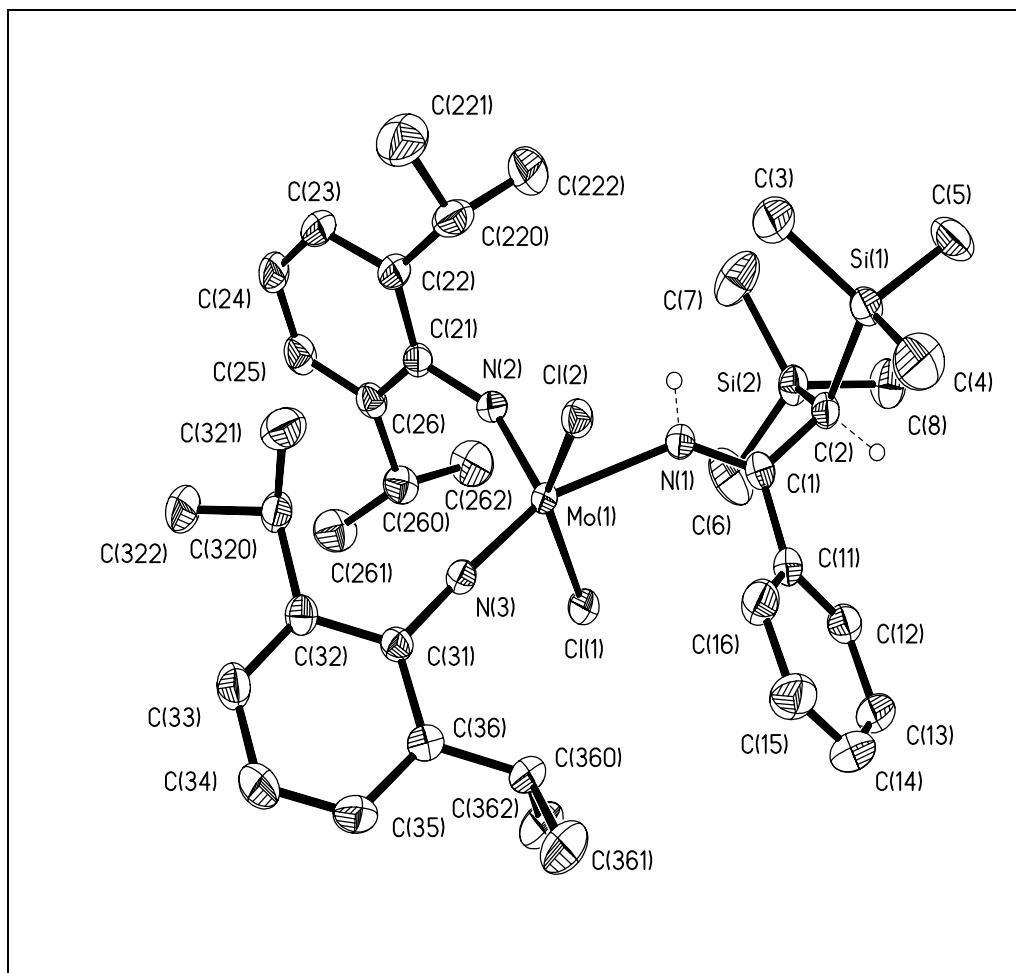


Figure 6. The molecular structure of **10** in the crystal. Hydrogen atoms except those two at N(1) and C(1) are omitted for clarity. (with 50 % probability ellipsoids)

The molecular structure of **10** is best described as a distorted trigonal bipyramid, in which two chlorine atoms and an imido ligand (C(21)-N(2)-Mo(1) 151.1(2)°) occupy the equatorial positions as shown in Figure 6 (selected bond lengths and angles are given in Table 4). Opposite to the apical linear imido ligand (C(31)-N(3)-Mo(1) 176.6(2)°) the Schiff base is coordinated to the Mo atom with a bond length of 2.255(2) Å. The slightly shorter Mo(1)-N(1) bond length compared to that of Mo(1)-N(2) is

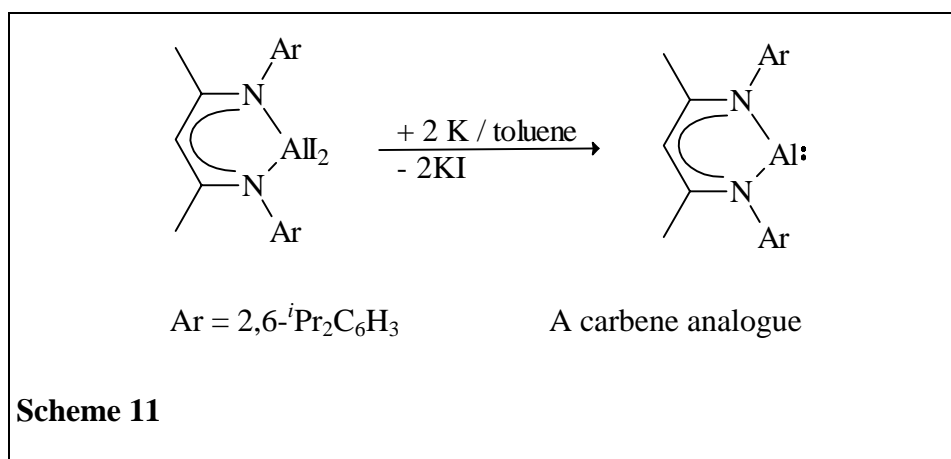
presumably due to the long Mo–N bond of the *trans*-coordinated Schiff base. The average Mo–Cl bond length is 2.418 Å.

Table 4. Selected bond lengths [Å] and angles [°] for **10**

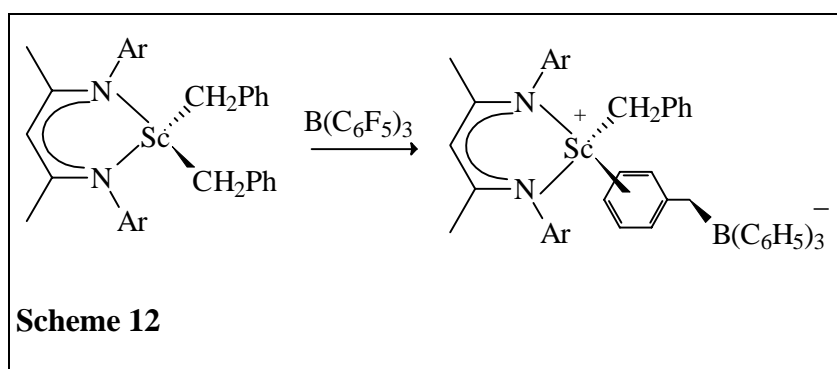
Mo(1)-N(2)	1.749(2)	N(2)-Mo(1)-Cl(1)	104.55(7)
Mo(1)-N(3)	1.752(2)	N(3)-Mo(1)-Cl(1)	93.52(7)
Mo(1)-N(1)	2.255(2)	N(1)-Mo(1)-Cl(1)	81.89(6)
Mo(1)-Cl(1)	2.3940(10)	N(2)-Mo(1)-Cl(2)	102.54(7)
Mo(1)-Cl(2)	2.4415(10)	N(3)-Mo(1)-Cl(2)	92.38(7)
N(1)-C(1)	1.290(3)	N(1)-Mo(1)-Cl(2)	81.04(6)
C(1)-C(11)	1.477(3)	Cl(1)-Mo(1)-Cl(2)	148.89(2)
C(1)-C(2)	1.490(3)	C(1)-N(1)-Mo(1)	140.5(2)
N(2)-C(21)	1.405(3)	N(1)-C(1)-C(11)	119.6(2)
N(3)-C(31)	1.381(3)	N(1)-C(1)-C(2)	121.5(2)
N(2)-Mo(1)-N(3)	108.07(8)	C(11)-C(1)-C(2)	118.8(2)
N(2)-Mo(1)-N(1)	94.46(8)	C(21)-N(2)-Mo(1)	151.1(2)
N(3)-Mo(1)-N(1)	157.43(8)	C(31)-N(3)-Mo(1)	176.6(2)

2.5. The Bischelating β -Diketiminato Ligand [HC(CMeNAr)₂][−] (Ar = Aryl)

One of the most recent advances in aluminum chemistry was the preparation of an unprecedented monomeric aluminum(I) compound [{HC(CMeNAr)₂}Al] (Ar = 2,6-*i*Pr₂C₆H₃, Scheme 11),^[41] a stable aluminum analogue of a carbene. The diketiminato zinc complexes such as [{HC(CMeNAr)₂}ZnN(SiMe₃)₂] have been developed by Coates *et al.* as a new class of single-site catalysts for the copolymerization of CO₂ and cyclohexene oxide.^[42]



Piers *et al.* have reported that dibenzyl scandium complexes bearing a β -diketiminato ligand can be activated rapidly and cleanly with $\text{B}(\text{C}_6\text{F}_5)_3$ to form an ion pair in which the anion is associated with the cation via strong η^6 -bonding (Scheme 12).^[43]



The catalytic activity in olefin polymerization of V, Ti and Zr complexes of this kind of ligands has also been studied.^[44] For their effectiveness in stabilizing low coordination numbers, β -diketiminato ligands have been utilized on Rh and Ir. The Rh complexes have proved to be active in olefin isomerization and hydrogenation. More important, it was found that the shielding properties of the ligand allows direct observation of several species that can be regarded as intermediates in isomerization and hydrogenation cycles, including Rh olefin dihydrogen complexes and an Ir olefin dihydride.^[45]

Therefore, it is of great interest to explore metal fluorides supported by the β -diketiminato ligand.

2.5.1. Preparation and Spectroscopic Characterization of $[\{\text{HC}(\text{CMeNAr})_2\}\text{VF}_2]$ (Ar = 2,6-*i*-Pr₂C₆H₃) (11)

$[\{\text{HC}(\text{CMeNAr})_2\}\text{VCl}_2]$ can be readily prepared from the lithium β -diketiminate salt and vanadium trichloride in toluene.^[44b] It reacts smoothly with Me₃SnF in toluene for 14 h during which time the color changed from dark to red. After removal of all volatiles the residue was extracted with toluene. Cooling the concentrated extract at -32 °C gave red crystalline **11**, which was characterized by elemental analysis, IR and EI-MS.

2.5.2. Preparation and Structural Comparison between Diketiminato Zinc Fluoride $[\{\text{HC}(\text{CMeNAr})_2\}\text{Zn}(\mu\text{-F})]_2$ (18) and Hydride $[\{\text{HC}(\text{CMeNAr})_2\}\text{Zn}(\mu\text{-H})]_2$ (19) (Ar = 2,6-Me₂C₆H₃)

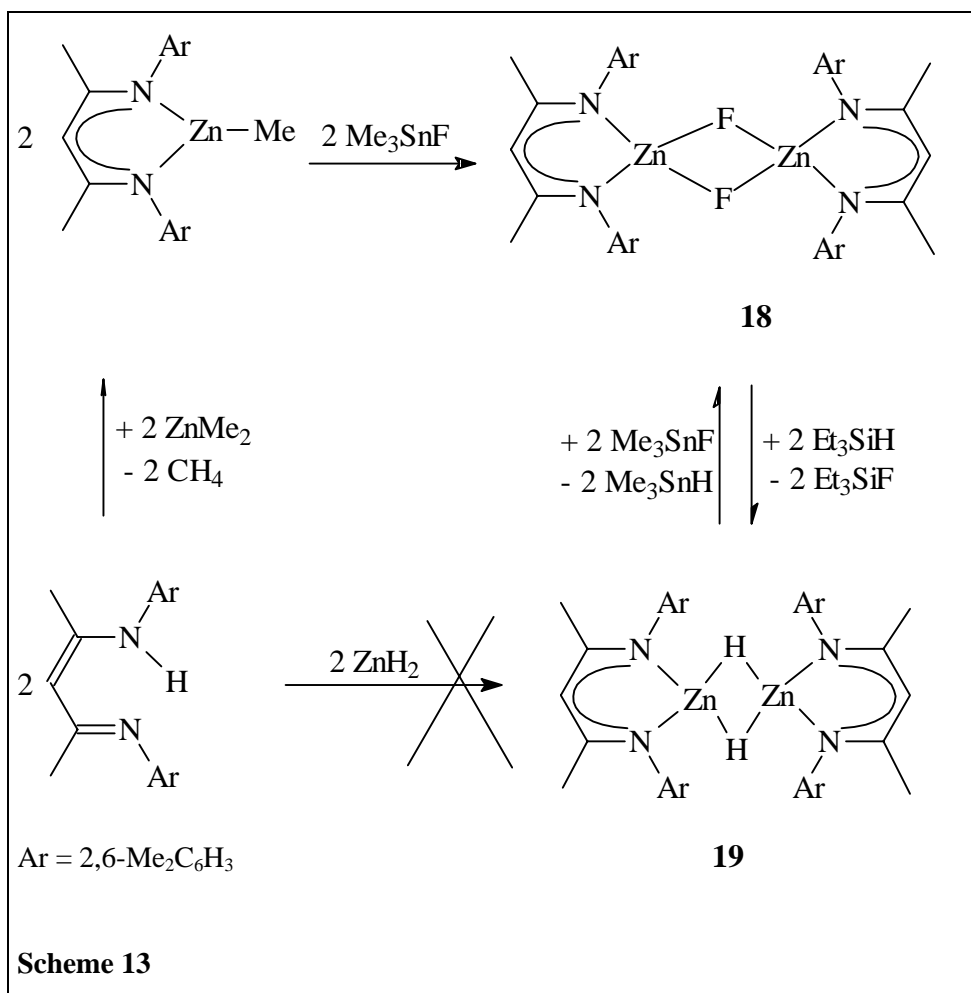
Recent reports have shown increasing interest in the utilization of zinc hydride complexes as reducing reagents^[46] and as precursors for various transformations.^[47] Generally, zinc hydride complexes are synthesized from ZnH₂.^[48] However, the impurity, thermal mobility and the inertness of ZnH₂ compared to its Group 13 analogues often resulted in impure products.^[49] In addition, hydrogen is believed to play a bridging role between two zinc atoms in many zinc hydride complexes as presumed in ZnH₂, resulting in polymeric or oligomeric species that are difficult to crystallize and characterize.^[49] Therefore, zinc hydride complexes are less well known and have been less thoroughly investigated than Group 13 analogues and other zinc reagents. Before this work started only three zinc hydride complexes had been structurally characterized, namely $[\text{Me}_2\text{N}(\text{CH}_2)_2\text{N}(\text{Me})\text{ZnH}]_2$ (**12**),^[50] $[\{\eta^3\text{-HB}(3\text{-R-C}_3\text{N}_2\text{H}_2)_3\}\text{ZnH}]$ (R = *t*Bu) (**13**),^[51] and $[(\text{Me}_3\text{PN})\text{ZnH}]_4 \cdot 4\text{THF}$ (**14**).^[52] In these three compounds, all hydrogen atoms are terminally arranged. The bridging role of hydrogen atoms in zinc hydride complexes remains crystallographically unveiled. Kläui *et al.* had successfully synthesised $[\{\eta^3\text{-HB}(3\text{-R-5-Me-C}_3\text{N}_2\text{H}_2)_3\}\text{ZnH}]$ (R = *p*Tol) from the metathesis reaction of Et₃SiH with the first structurally characterized zinc fluoride compound $[\{\eta^3\text{-HB}(3\text{-R-5-Me-C}_3\text{N}_2\text{H}_2)_3\}\text{ZnF}]$ (R = *p*Tol, **15**).^[53] However, Kläui's fluorination method is not applicable for most of the other zinc precursors due to their moisture sensitivity.

Recently, we trapped ‘molecular’ ZnF_2 and MeZnF by using organotitanium fluorides as matrices to yield $[(\text{Cp}^*\text{TiF}_3)_8(\text{ZnF}_2)_3]$ (**16**) and $[(\text{Cp}^*\text{TiF}_3)_4(\text{MeZnF})_2]$ (**17**), respectively.^[11] Compound **17** is an intermediate for the formation of **16**, the methyl groups in **17** can be easily exchanged by Me_3SnF to afford **16**. This implies that zinc fluorides can be made by fluorination of the corresponding alkyl derivatives with Me_3SnF if suitable supporting ligands are chosen. Herein, we describe the preparation and structural characterisation of $[\{\text{HC}(\text{CMeNAr})_2\}\text{Zn}(\mu\text{-X})_2]$ ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$, $\text{X} = \text{F}$, **18**; $\text{X} = \text{H}$, **19**).

The reaction of $[\{\text{HC}(\text{CMeNAr})_2\}\text{ZnR}]$ ($\text{R} = \text{Me}, \text{Et}$)^[42b] with one equiv of Me_3SnF in toluene at $100\text{ }^\circ\text{C}$ for 8 h resulted in the disappearance of solid Me_3SnF . After removal of all volatiles *in vacuo*, the residue was recrystallized from hot toluene affording **18** as colorless crystals suitable for X-ray single crystal determination in high yield (80%). EI-MS shows the molecular ion peak of the dimeric **18**, in agreement with the structure established by X-ray analysis. Having observed several cases of the same bridging fashion of fluorine and hydrogen,^[40, 54] we inferred that the corresponding hydride should similarly contain bridging hydrogen atoms with a composition of $[\{\text{HC}(\text{CMeNAr})_2\}\text{Zn}(\mu\text{-H})_2]$ (**19**). The electron deficient three-centre two electron intermolecular Zn-H-Zn bonds are more favoured in **19** due to the bulky substituents at N of the diketiminato ligand that prevent the condensation through N atoms as seen in **12** and **14**. Consequently, we treated **18** with an excess amount of Et_3SiH (5-10 fold) in benzene under refluxing condition for 16 h. After the removal of all volatiles, the residue was recrystallized from hot benzene resulting in colorless crystals of **19** in high yield (75 %). The dimeric nature of the compounds is indicated by EI-MS and confirmed by X-ray crystallography. Unlike **12** and **13**, compound **19** cannot be obtained from the reaction of ZnH_2 with $[\text{ArN}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{NHAr}]$. However, upon treatment of **19** with Me_3SnF in benzene under reflux for 6 h, compound **19** can be readily converted back to **18** (Scheme 13). Satisfactory microanalyses of **18** and **19** have been obtained. The ^1H NMR reveals a singlet for the bridging hydrogens of **19** (δ 4.59 ppm), while the ^{19}F NMR of **18** compound shows a singlet for $\mu\text{-F}$ at δ -61.6 ppm.

The structures of **18** and **19** have been determined by X-ray single crystal analysis and are shown in Figure 7 and Figure 8, respectively. Both molecular structures are dimeric

with an inversion centre in the centroid of the four-membered Zn_2X_2 ($X = F, H$) ring. The two zinc atoms in **18** and **19** are bridged by fluorine and hydrogen atoms, respectively, forming the three-centre four electron $Zn-F-Zn$ and the three-centre two electron $Zn-H-Zn$ bonds.



The average Zn–N bond length in **18** (1.955 Å) is quite close to that in **19** (1.967 Å), but the six-membered ring in **19** formed by Zn and the ligand backbone is essentially planar (mean deviation 0.0149 Å). There is a C_2 axis passing through C(2), Zn(1), Zn(1A) and C(2A) atoms in **19**. However, in compound **18**, the ligand backbone is slightly folded. The (μ -F)–Zn bond lengths in **18** [F(1)–Zn(1) 2.0034(11), F(1)–Zn(1A) 1.9473(12), av 1.975 Å] are close to the sum of the covalent radii, and *ca* 0.126 Å longer than the terminal F–Zn bond length found in **16** [1.849(4) Å]. They are also comparable to those in **16** and **17**. The (μ -H)–Zn bond lengths (1.766 Å) from the refinement of X-ray diffraction data are slightly shorter than those in the ionic

MeZnBH₄ (av 1.82 Å).^[55] The distances are longer than the terminal H–Zn bond lengths found in **12** (1.62 Å) and **14** (1.50 Å), respectively.

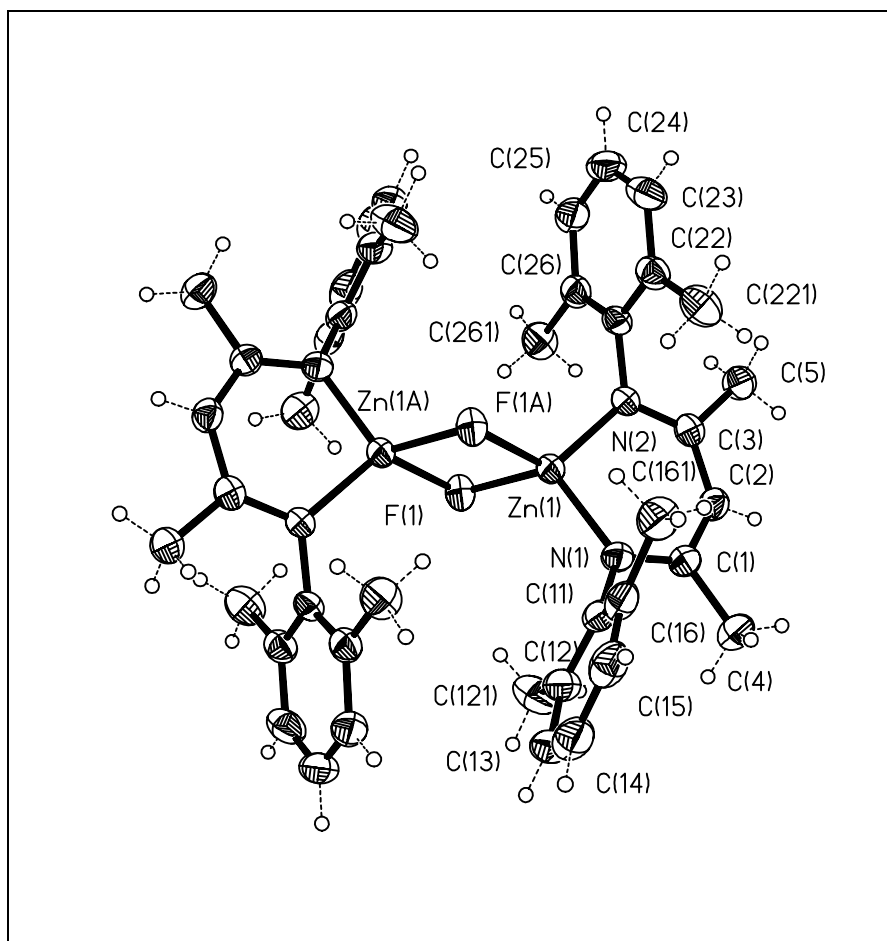


Figure 7. Molecular structure of **18** in the crystal. (with 50 % probability ellipsoids)

Table 5. Selected bond lengths [Å] and angles [°] for **18**

Zn(1)–N(2)	1.951(2)	Zn(1)–N(1)	1.9588(14)
Zn(1)–F(1)	200.34(11)	Zn(1)–Zn(1A)	2.9754(6)
F(1)–Zn(1A)	1.9473(12)	F(1A)–Zn(1)–F(1)	82.28(5)
Zn(1A)–F(1)–Zn(1)	97.72(5)		

The shorter (μ -H)–Zn distance compared to the (μ -F)–Zn bond length correlates well with a smaller Zn(1)–H(1)–Zn(1A) angle (87.9°) and a wider Zn(1)–F(1)–Zn(1A)

angle (97.72°). Consequently, a wider H(1)–Zn(1)–H(1A) angle (92.1°) results compared to the F(1)–Zn(1)–F(1A) angle (82.28°), which leads to a significantly shorter Zn–Zn distance [$2.4513(9)$ Å] in **9** (by 0.522 Å) than that in **8** [$2.9754(6)$ Å]. This short Zn–Zn distance is in the range of the sum of the covalent radii (2.50 Å), but a Zn–Zn interaction is unlikely.

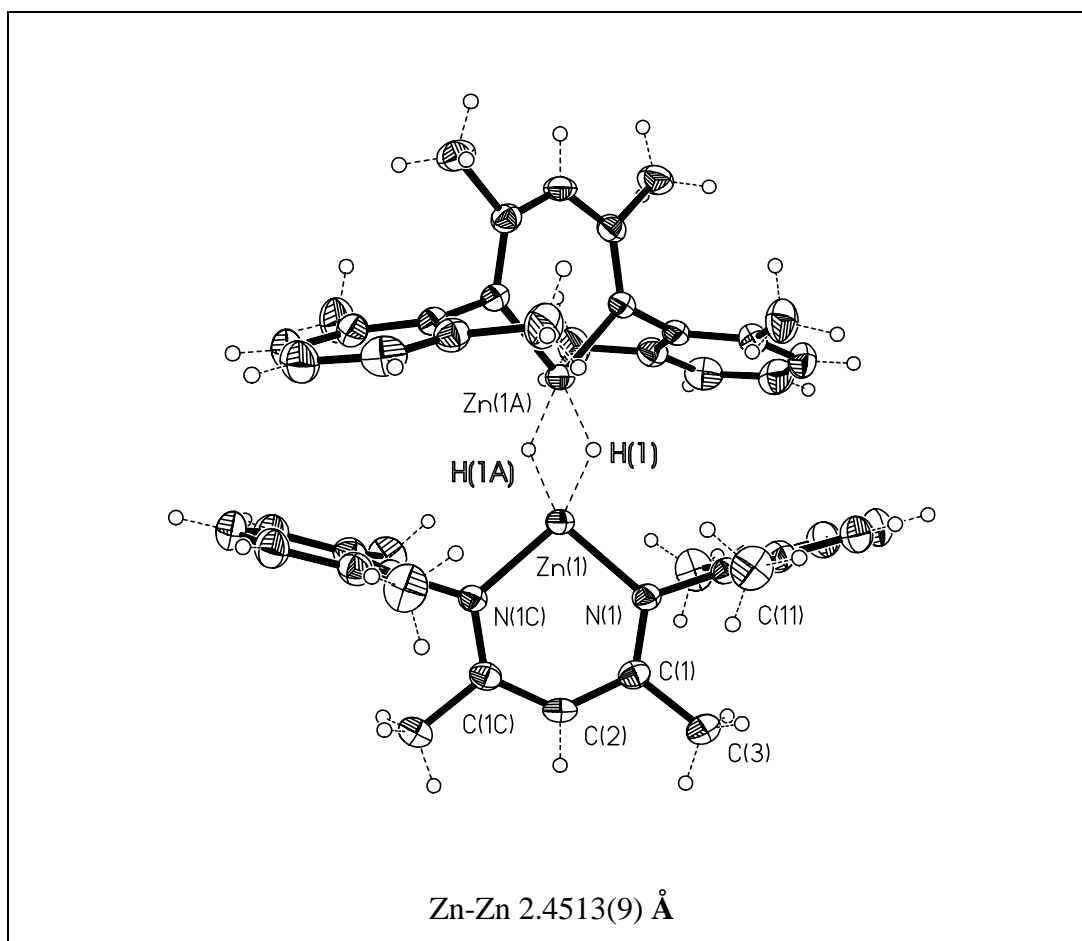


Figure 8. Molecular structure of **19** in the crystal. (with 50 % probability ellipsoids)

Table 6. Selected bond lengths [Å] and angles [$^\circ$] for **19**

Zn(1)–H(1)	1.766	Zn(1)–N(1)	1.9672(17)
Zn(1)–N(1A)	1.9673(17)	Zn(1)–Zn(1A)	2.4513(9)
Zn(1)–H(1)–Zn(1A)	87.9	H(1)–Zn(1)–H(1A)	92.1

2.5.3. β -Diketiminato Magnesium Fluorides

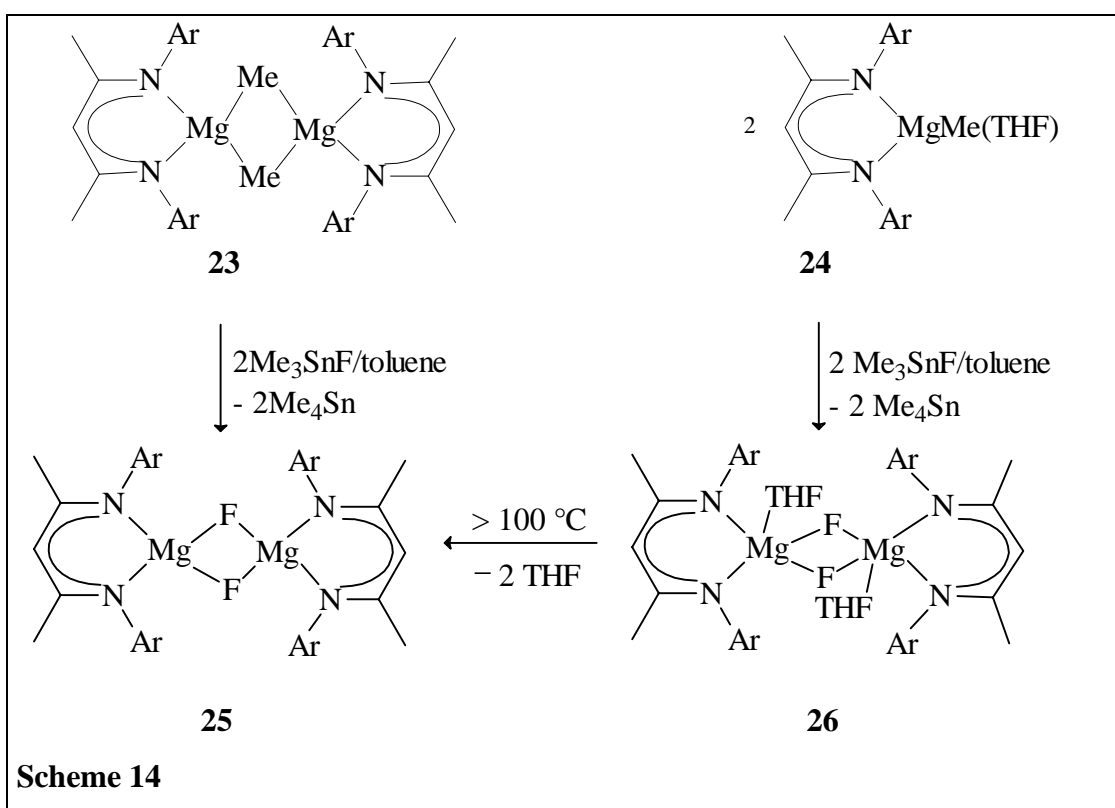
Grignard reagents had become indispensable for synthesis chemistry soon after it was reported in 1900.^[56] Through the past century numerous magnesium halide compounds RMgX (R = various organic substitutes; X = Cl, Br, I) have been synthesized, structurally characterized and applied as active intermediates for diverse transformations. Strikingly, little is known about their fluoride congeners even though Ashby *et al.* had managed to prepare alkyl magnesium fluorides three decades ago.^[57] The mobile Schlenk equilibrium used to describe organomagnesium chlorides, bromides and iodides in the solution does not exist in the case of alkylmagnesium fluorides due to the unusual stability of the Mg-F-Mg bridge bonds.^[58] Therefore, the magnesium fluorides should be more stable than other halide species. Nevertheless, few studies had been followed. Despite of the recent report that the formation of Grignard species MeMgF from the reaction of methyl fluoride with Laser-ablated magnesium atoms has been observed in a matrix infrared study,^[59] in sharp contrast to the well structurally characterized magnesium chloride, bromide and iodide compounds, no structure of the corresponding fluorides had been established by X-ray single crystal determination. Before the start of this work only three bimetallic complexes that contain Mg-F bonds have been structurally characterized, namely $[(\text{MesInF}_2)_{10}\text{MgF}\cdot 5\text{toluene}]$ (Mes = 2,4,6-trimethylphenyl, **20**),^[60] $[\text{Cp}^*_4\text{Ti}_4\text{Mg}_2\text{F}_{12}\cdot 7\text{THF}]$ (Cp^* = C_5Me_5 , **21**)^[10b] and $[\text{Na}_3\text{Mg}(\text{O}_3\text{PCH}_2\text{PO}_3)(\mu\text{-F})\cdot \text{H}_2\text{O}]$ (**22**).^[61] Among them only anionic compound **22** contains F-Mg-F bridge bonds.

2.5.3.1. Preparation of $[\{\text{HC}(\text{CMeNAr})_2\}\text{Mg}(\mu\text{-F})]_2$ (Ar = 2,6-*i*-Pr₂C₆H₃, **25**) and $[\{\text{HC}(\text{CMeNAr})_2\}\text{Mg}(\mu\text{-F})(\text{THF})]_2$ (Ar = 2,6-*i*-Pr₂C₆H₃, **26**)

By taking advantage of the bulkiness of the β -diketiminato ligand provided by the 2,6-*i*-Pr₂C₆H₃ substituent at N, Gibson *et al.* have structurally characterized a coordinatively unsaturated trigonal system of magnesium $[\{\text{HC}(\text{CMeNAr})_2\}\text{Mg}^t\text{Bu}]$ (Ar = 2,6-diisopropylphenyl).^[62] The methyl congener $[\{\text{HC}(\text{CMeNAr})_2\}\text{Mg}(\mu\text{-Me})]_2$ (**23**) is dimeric while its THF adduct $[\{\text{HC}(\text{CMeNAr})_2\}\text{MgMe}(\text{THF})]$ (**24**) is monomeric.^[62, 63] The successful prediction of the feature of bridging hydrogen in **19** by comparison of the similarity of bonding modes

of fluorine and hydrogen, and the fact that several organomagnesium hydrides have been reported,^[64] is encouraging for the preparation of the magnesium fluoride compounds.

The reactions of (or **23**) and **24** with Me_3SnF in toluene at r.t. for 48 h afforded **25** and **26**, respectively. Compound **25** precipitates from toluene as a white powder while **26** formed crystals from toluene. When the temperature was raised above $100\text{ }^\circ\text{C}$, **26** lost its coordinating THF changing from crystallinity to a white powder **25** (Scheme 14). The EI-MS spectrum of **26** shows the peak at 921, which is the molecular ion peak of dimeric **25**. The ^{19}F NMR spectrum shows the fluorine resonance of **26** ($\delta -24.74$ ppm) at slightly lower field compared to that of **25** ($\delta -26.01$ ppm).



2.5.3.2. Molecular Structure of **26**

The crystal structure of **26** is shown in Figure 9. Selected bond lengths and angles are given in Table 7.

The structure of **26** shows the centrosymmetric complex to adopt a distorted square pyramidal geometry around magnesium. Oxygen is arranged at the top vertex with $\text{Mg}(1)\text{--O}(30)$ bond length of $2.073(18)$ Å. The equatorial square is essentially planar formed by N(1), N(2), F(1) and F(1A) atoms, out of which the magnesium center

is displaced by 0.032 Å. The Mg(1)–N(1) (2.144(2) Å) and Mg(1)–N(2) (2.1457(19) Å) bond lengths only differ slightly as do the Mg(1)–F(1) (1.9505(14) Å) and Mg(1)–F(1A) (1.9517(14) Å) bond lengths. The Mg–O bond is nearly perpendicular to the square defined by F(1)-F(1A)-N(1)-N(1A) ($\text{Mg(1A)-Mg(1)-O(30)} = 99^\circ$).

Table 7. Selected bond lengths [Å] and angles [°] for **26**

Mg(1)-F(1)	1.9505(14)	O(30)-Mg(1)-N(1)	99.65(8)
Mg(1)-F(1A)	1.9517(14)	F(1)-Mg(1)-N(2)	95.40(7)
Mg(1)-O(30)	2.0773(18)	F(1A)-Mg(1)-N(2)	162.28(7)
Mg(1)-N(1)	2.144(2)	O(30)-Mg(1)-N(2)	98.99(8)
Mg(1)-N(2)	2.1457(19)	N(1)-Mg(1)-N(2)	87.39(8)
Mg(1)-Mg(1A)	3.0650(14)	Mg(1)-F(1)-Mg(1A)	103.53(6)
F(1)-Mg(1A)	1.9517(14)	C(1)-N(1)-C(11)	115.70(19)
N(1)-C(1)	1.334(3)	C(1)-N(1)-Mg(1)	119.95(15)
N(1)-C(11)	1.449(3)	C(11)-N(1)-Mg(1)	123.55(15)
N(2)-C(3)	1.332(3)	C(3)-N(2)-C(21)	115.49(18)
N(2)-C(21)	1.442(3)	C(3)-N(2)-Mg(1)	120.30(15)
C(1)-C(2)	1.399(3)	C(21)-N(2)-Mg(1)	123.65(14)
C(1)-C(4)	1.518(3)	N(1)-C(1)-C(2)	124.1(2)
C(2)-C(3)	1.394(3)	N(1)-C(1)-C(4)	121.5(2)
C(3)-C(5)	1.525(3)	C(2)-C(1)-C(4)	114.4(2)
F(1)-Mg(1)-F(1A)	76.47(6)	C(3)-C(2)-C(1)	129.5(2)
F(1)-Mg(1)-O(30)	97.67(7)	N(2)-C(3)-C(2)	124.3(2)
F(1A)-Mg(1)-O(30)	97.71(7)	N(2)-C(3)-C(5)	121.2(2)
F(1)-Mg(1)-N(1)	161.79(8)	C(2)-C(3)-C(5)	114.5(2)
F(1A)-Mg(1)-N(1)	95.63(7)		

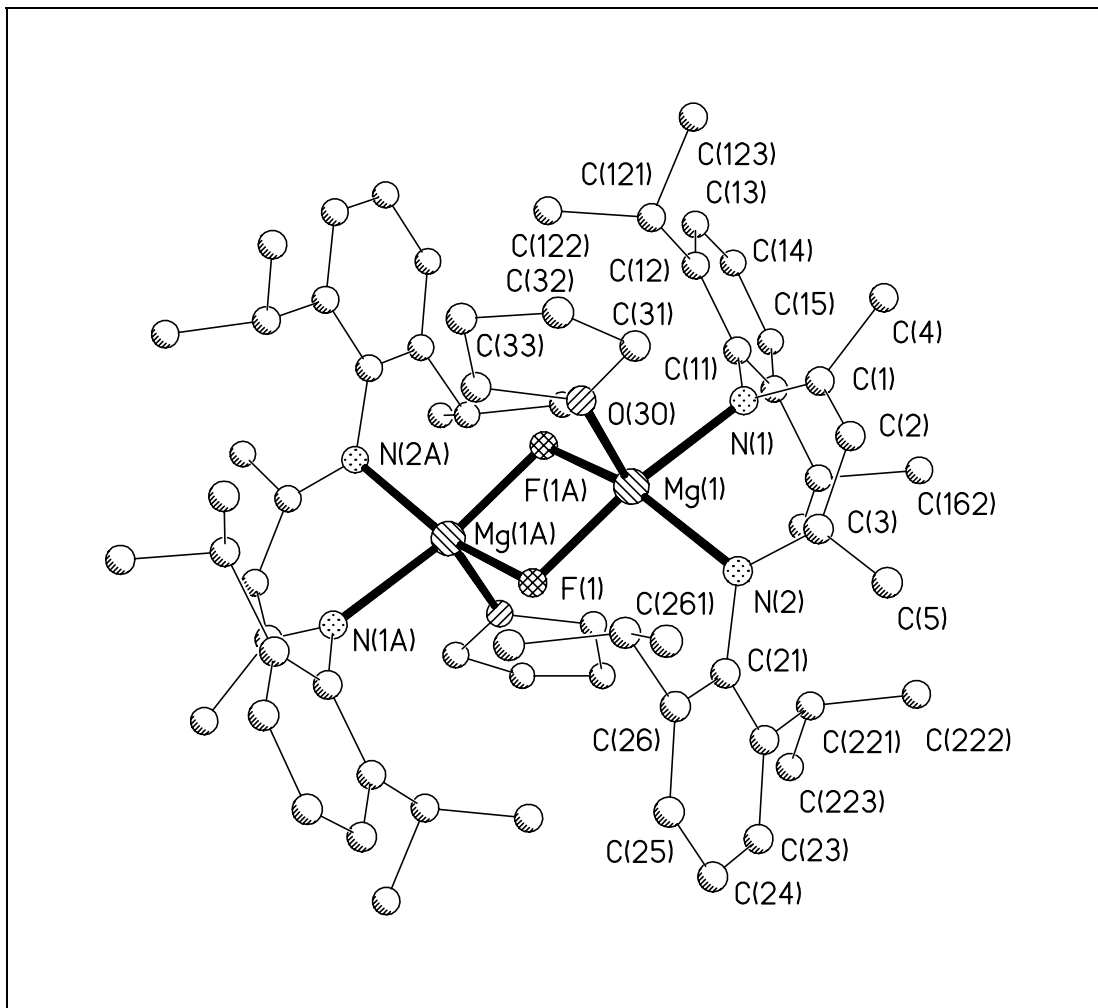


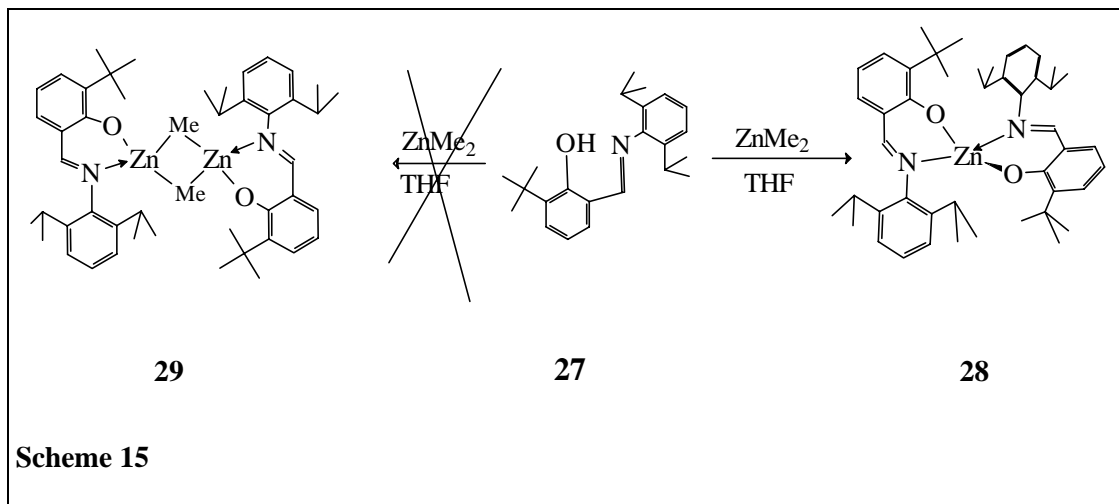
Figure 9. Molecular structure of **26**. Hydrogen atoms are omitted for clarity.

2.6. The Bis-salicylaldiminato Zinc Complex (**28**)

It has been demonstrated that monomeric Zn phenoxides possessing sterically encumbering substituents in the 2- and 6-positions of the phenolate ligands along with two ether donors, typified by $(2,6\text{-}^i\text{Bu}_2\text{C}_6\text{H}_3\text{O})_2\text{Zn}(\text{THF})_2$, are the most active catalysts known for the copolymerization of cyclohexene oxide and carbon dioxide.^[65] It was of interest to see how a substituted salicylaldiminato ligand^[20] affects the Zn center.

$[2\text{-}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{-}6\text{-}^i\text{BuC}_6\text{H}_3\text{OH}]$ (**27**) reacts smoothly with one equiv of ZnMe_2 in THF at $-78\text{ }^\circ\text{C}$, to afford the bis-salicylaldimido zinc complex (**28**) but not the expected mono-salicylaldimido zinc methylate (**29**) (Scheme 15). This is probably due

to the stronger acidity and the lower steric demand of the phenol compared to the β -diketiminato ligand.

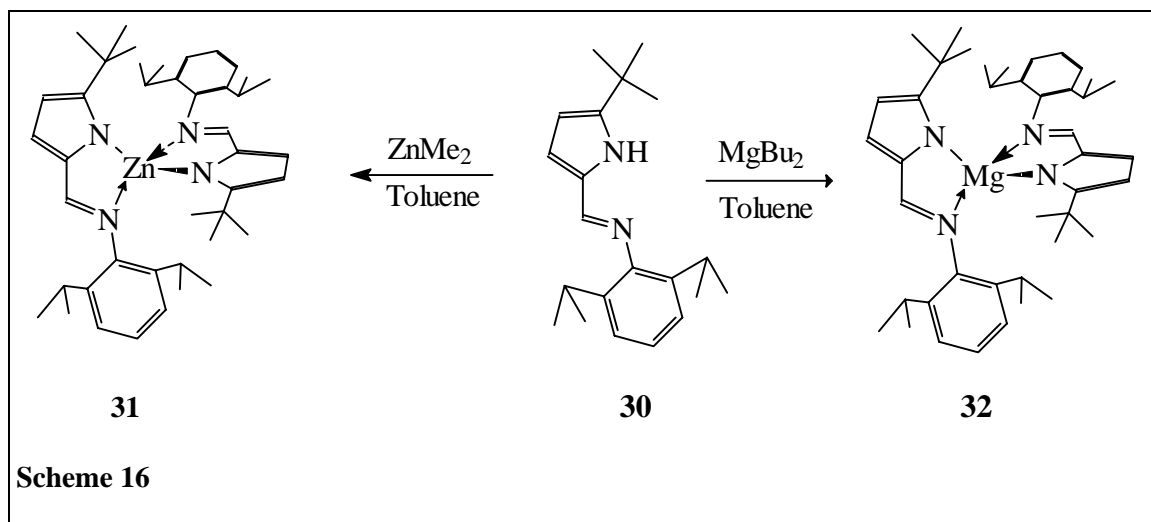


2.7. The Pyrrolylaldiminato Ligand $[2-\{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}-5\text{-RC}_4\text{H}_2\text{N}]^-$ ($\text{R} = \text{}^t\text{Bu}$; $\text{R} = \text{H}$)

2.7.1. Preparation of the Bis-pyrrolylaldiminato Complexes of Zinc (**31**) and Magnesium (**32**)

As shown in section 2.6, the reaction of **27** and ZnMe_2 and MgBu_2 leads to the formation of **28**, but not **29**. Therefore, we chose $[2-\{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}-5\text{-}^t\text{BuC}_4\text{H}_2\text{NH}]$ (**30**),^[66] which is more bulky and less acidic than **27**, to react with ZnMe_2 , with the expectation to get the corresponding methyl zinc compound.

However, the reaction of **30** and ZnMe_2 in toluene followed by recrystallization from *n*-hexane resulted in a colorless crystalline compound characterized as $[2-\{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}-5\text{-}^t\text{BuC}_4\text{H}_2\text{N}]_2\text{Zn}$ (**31**) (Scheme 16). The similar reaction of **30** and MgBu_2 afforded the analogous magnesium compound **32**. Both of **31** and **32** are characterized by IR, elemental analysis, EI-MS, ^1H NMR as well as X-ray single crystal analysis.



2.7.2. The Molecular Structure of [2- $\{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}$ -5- $^t\text{BuC}_4\text{H}_2\text{N}\}_2\text{Zn}$ (**31**)

Single crystals of **31** was grown from a *n*-hexane solution. The molecular structure is shown in Figure 10 (selected bond lengths and angles are given in Table 8).

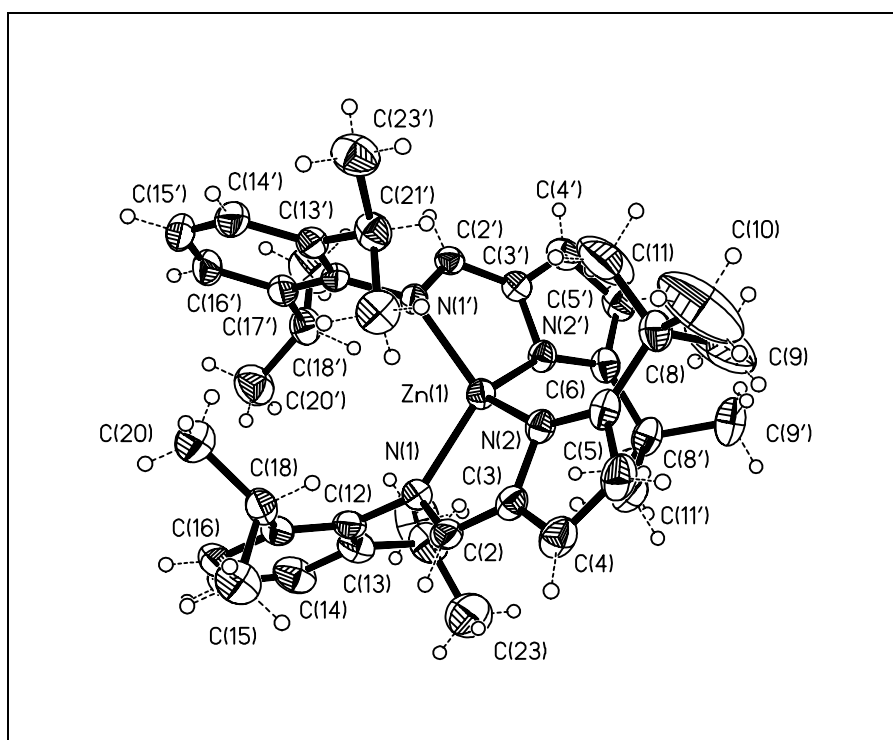


Figure 10. Molecular structure of 31 in the crystal. (with 50 % probability ellipsoids)

The geometry around Zn atoms can be described as a distorted tetredron with four nitrogen atoms located at the vertices. The Zn atom and the backbone N(1)-C(1)-

C(2)-N(2) are coplanar. The imido N–Zn bond length (av 2.06 Å) and pyrrole N–Zn bond length (av 2.00 Å) differ only slightly. The smallest N–Zn–N angle is N1–Zn(1)–N(2) (85.75(8)°). The largest N–Zn–N angle is N(1)–Zn(1)–N(2') (132.73(7)°).

Table 8. Selected bond lengths [Å] and angles [°] for **31**

Zn(1)-N(2)	1.9956(19)	C(12)-N(1)-Zn(1)	135.15(15)
Zn(1)-N(2')	1.9985(19)	C(6')-N(2')-C(3')	106.69(19)
Zn(1)-N(1')	2.0548(19)	C(6')-N(2')-Zn(1)	144.30(16)
Zn(1)-N(1)	2.0683(18)	C(3')-N(2')-Zn(1)	106.91(14)
N(1')-C(2')	1.310(3)	N(1)-C(2)-C(3)	121.3(2)
N(1')-C(12')	1.439(3)	N(1')-C(2')-C(3')	121.0(2)
N(1)-C(2)	1.306(3)	C(6)-N(2)-C(3)	106.70(19)
N(1)-C(12)	1.439(3)	C(6)-N(2)-Zn(1)	146.09(16)
N(2')-C(6')	1.354(3)	C(3)-N(2)-Zn(1)	106.82(14)
N(2')-C(3')	1.386(3)	N(2)-C(6)-C(5)	109.4(2)
C(2)-C(3)	1.407(3)	N(2)-C(6)-C(8)	123.8(2)
C(2')-C(3')	1.407(3)	C(5)-C(6)-C(8)	126.7(2)
N(2)-C(6)	1.354(3)	N(2')-C(6')-C(5')	109.6(2)
N(2)-C(3)	1.388(3)	C(2)-N(1)-C(12)	117.94(19)
C(3)-C(4)	1.390(3)	N(2')-Zn(1)-N(1')	85.36(7)
C(3')-C(4')	1.400(3)	N(2)-Zn(1)-N(1)	85.75(8)
C(2)-N(1)-Zn(1)	106.58(14)	N(2')-Zn(1)-N(1)	132.73(7)
N(2)-Zn(1)-N(2')	116.62(7)	N(1')-Zn(1)-N(1)	113.18(7)
N(2)-Zn(1)-N(1')	129.19(7)	C(12')-N(1')-Zn(1)	134.62(14)

2.7.3. X-Ray Crystal Structure of [2-((2,6-ⁱPr₂C₆H₃)N=CH)-5-^tBuC₄H₂N]₂Mg (**32**)

Good shaped single crystals of **32** crystallized while its hot toluene solution was slowly cooled to ambient temperature. The molecular structure of **32** is shown in Figure 11 (Selected bond lengths and angles are given in Table 9).

Similar to the zinc analogue **31**, the geometry around Mg is tetrahedron with four nitrogen atoms arranged at vertices. The imido N–Mg bond length (av 2.11 Å) is quite close to the pyrrole N–Mg bond length (av 2.05 Å). The smallest N–Mg–N angle is N(2)–Mg(1)–N(3) (84.95(5)°). The largest one is N(1)–Mg(1)–N(3) (134.00(5)°).

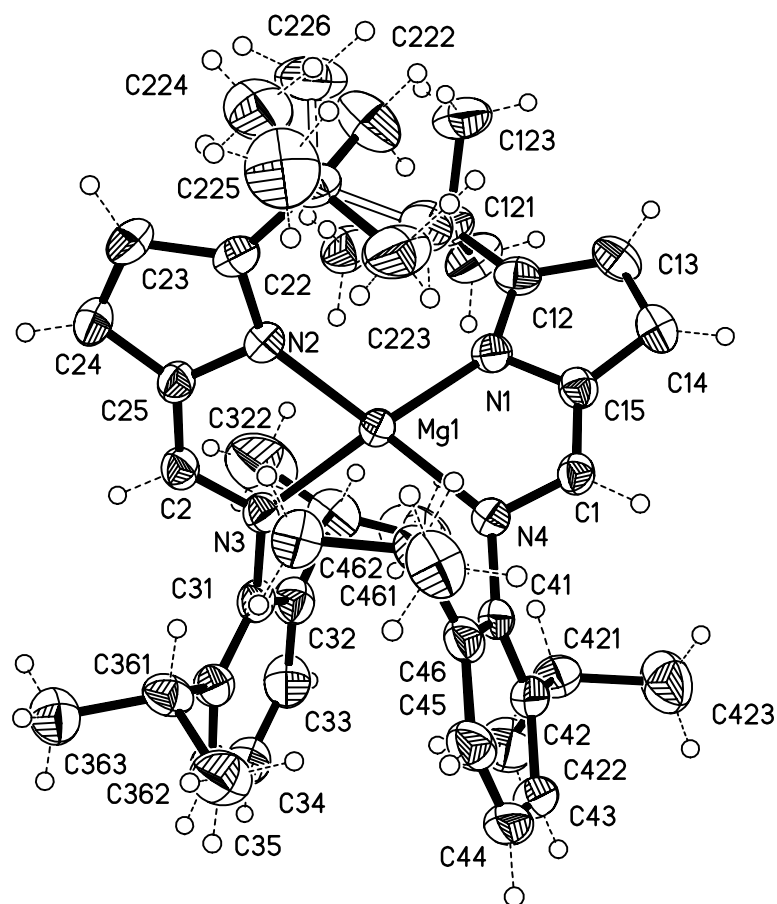


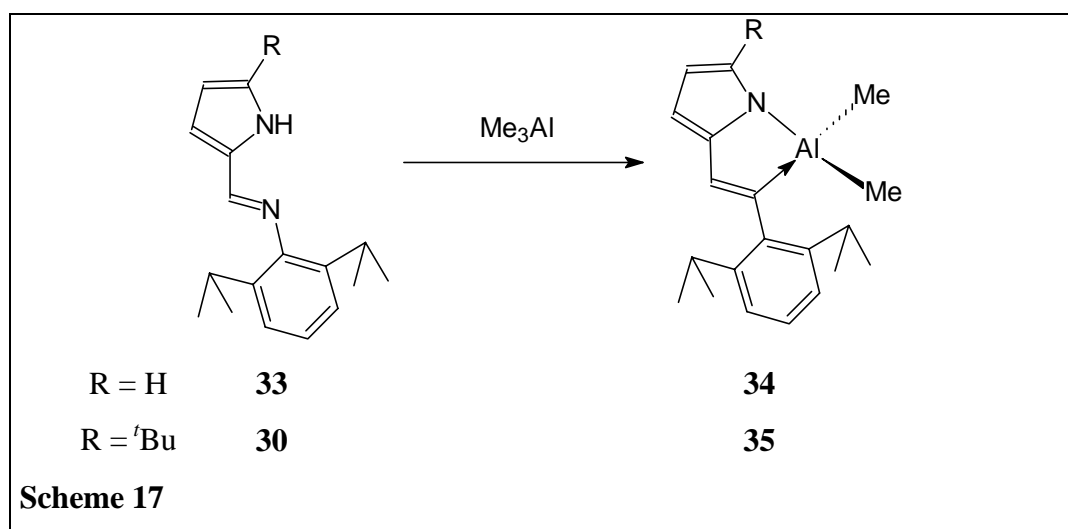
Figure 11. Molecular structure of **32**.

Table 9. Selected bond lengths [\AA] and [$^\circ$] for **32**

Mg(1)-N(2)	2.0476(13)	N(2)-Mg(1)-N(4)	131.06(5)
Mg(1)-N(1)	2.0525(12)	N(1)-Mg(1)-N(4)	84.49(6)
Mg(1)-N(4)	2.1005(13)	N(2)-Mg(1)-N(3)	84.95(5)
Mg(1)-N(3)	2.1154(12)	N(1)-Mg(1)-N(3)	134.00(5)
N(2)-Mg(1)-N(1)	116.87(5)	N(4)-Mg(1)-N(3)	112.14(5)

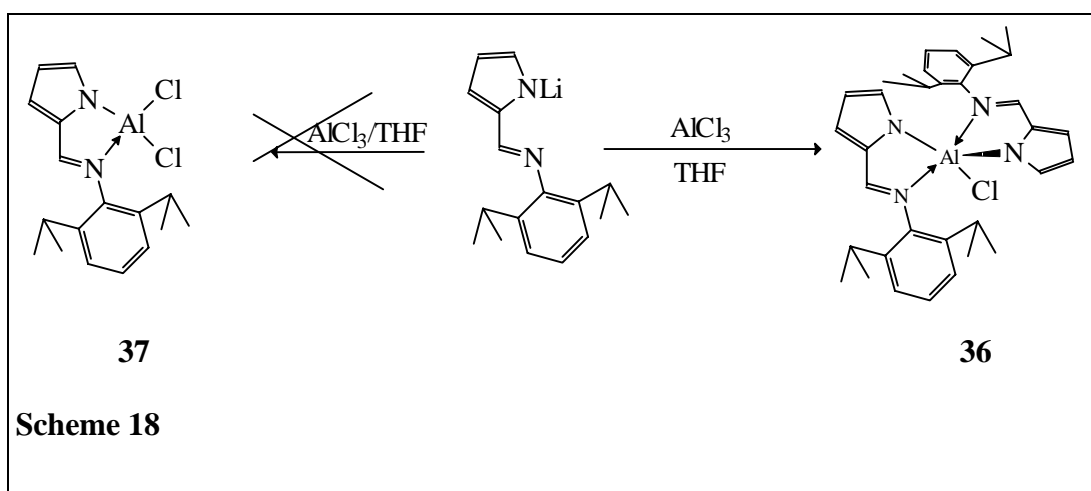
2.7.4. Preparation of Dimethyl Duminum [2-{(2,6-ⁱPr₂C₆H₃)aldiminato}-pyrrolide] (**34**), Dimethyl Aluminum [2-{(2,6-ⁱPr₂C₆H₃)aldiminato}-5-^tBu-pyrrolide] (**35**)

After a slightly excess amount of Me₃Al was added into a solution of [2-{(2,6-ⁱPr₂C₆H₃)aldiminato}-pyrrole] (**33**)^[67] in *n*-hexane, the resulting solution was refluxed for 4 h. After the removal of all volatiles the resulted residue was extracted and recrystallized from *n*-hexane at -30 °C giving the dimethylalane **34**. When the 5-position of pyrrole was substituted by a ^tBu group, the corresponding dimethyl aluminum [2-{(2,6-ⁱPr₂C₆H₃)N=CH}-5-^tBu-pyrrolide] **35** was prepared from the reaction of **30** and Me₃Al in a *n*-hexane at r.t. in high yield (Scheme 17). EI-MS of **34** and **35** show the molecular ion peaks and the peaks of [M⁺-Me] appear to be the base peaks. The interpretation of ¹H NMR are in agreement with the fomular of **34** and **35**.



2.7.5. Bis-[2-{(2,6-ⁱPr₂C₆H₃)aldiminato}pyrrolidyl] Aluminum Chloride (**36**)

The reaction of the lithium salt of **33** with 1 equiv of AlCl₃ in THF resulted in the formation of **36**, but not in [2-{(2,6-ⁱPr₂C₆H₃)aldiminato}pyrrolidyl] aluminum dichloride (**37**) (Scheme 18). Good crystals of **36** were obtained by the recrystallization from toluene, which are suitable for X-ray single crystal analysis. The EI-MS of **36** shows the molecular ion peaks appear to be base peaks. Compound **36** was also characterized by IR, ¹H NMR and X-ray single crystal analysis.



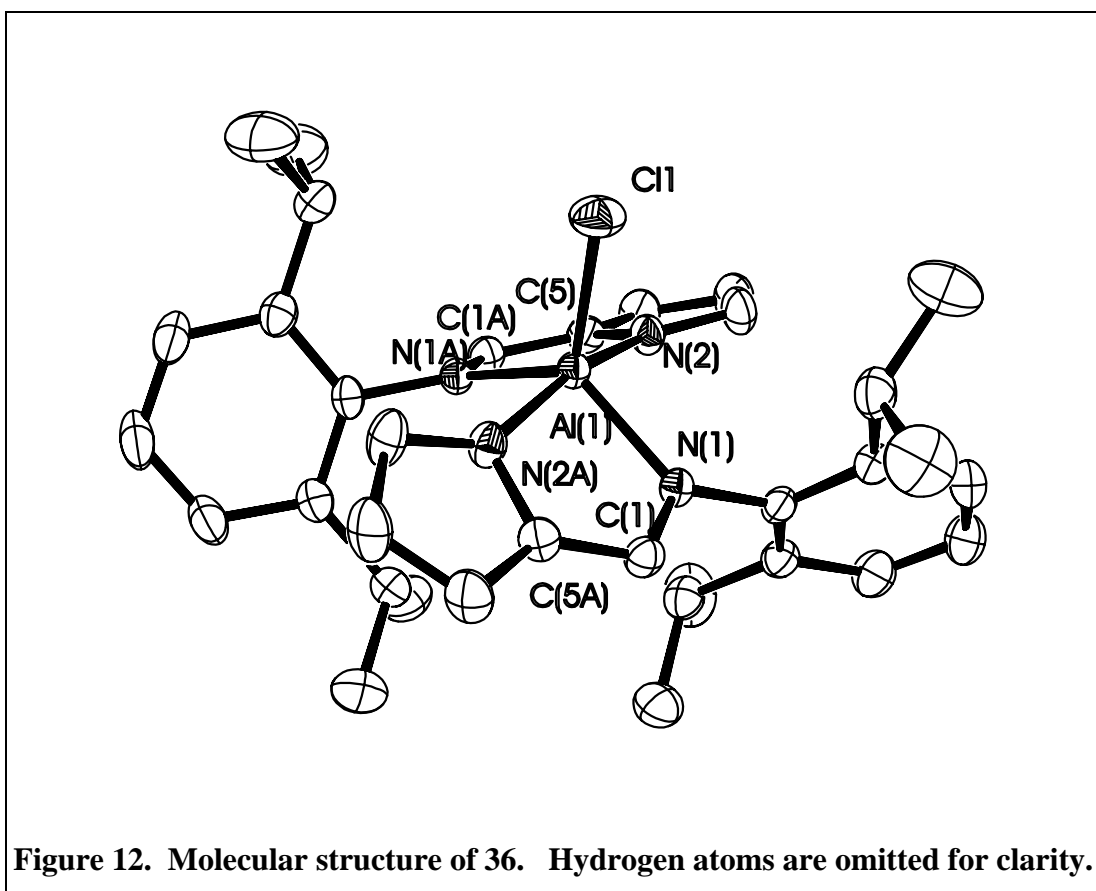
2.7.6. X-ray Crystal Structure of **36**

The molecular structure of **36** is shown in Figure 12 (Selected bond lengths and angles are given in).

Table 10. Selected bond lengths [Å] and angles [°] for **36**

Al(1)-N(2)	1.9615(12)	N(2)-Al(1)-N(1)	91.80(5)
Al(1)-N(2A)	1.9615(12)	N(2A)-Al(1)-N(1)	81.57(5)
Al(1)-N(1A)	1.9931(11)	N(1A)-Al(1)-N(1)	127.01(7)
Al(1)-N(1)	1.9931(11)	N(2)-Al(1)-Cl(1)	97.42(4)
Al(1)-Cl(1)	2.1582(8)	N(2A)-Al(1)-Cl(1)	97.42(4)
N(2)-Al(1)-N(2A)	165.16(8)	N(1A)-Al(1)-Cl(1)	116.50(4)
N(2)-Al(1)-N(1A)	81.57(5)	N(1)-Al(1)-Cl(1)	116.50(4)
N(2A)-Al(1)-N(1A)	91.80(5)		

The aluminum atom has a pyramid geometry with the chlorine atom located in the top vertex and the four nitrogen atoms arranged at the equatorial position. There is a C_2 axis passing through the Al(1)–Cl(1) bond. The Al(1)–Cl(1) bond length is 2.1582(8) Å. The imido N–Al bond length (av 1.99 Å) differs slightly from the pyrrole N–Al bond length (av 1.96 Å). The N(1)–Al(1)–N(1A) angle (127.01(7)°) and a wider N(2)–Al(1)–N(2A) angle (165.16(8)°) is supposed to be resulted from the distortion from ideal plane due to the stereo demanding environment.

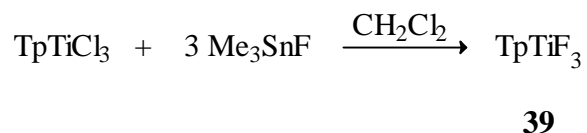


2.8. The Tris(pyrazolyl)hydroborato (Tp) Ligand

Tris(pyrazolyl)hydroborato ligands, so called scorpionates, are famous for their strong binding ability toward metals. This kind of ligands forms complexes with most metals.^[68] Among that vast amount of compounds only three fluorides are known. ^tBuTpFeF and ^tBuTpCoF were prepared by Parkin *et al.* through fluoride abstraction from [BF₄]⁻.^[69] The zinc congener was made by Kläui *et al.*.^[53]

2.8.1. Preparation of TpTiF₃ (**39**)

Fluoride compounds of Group 4 overwhelmingly contain at least one Cp or its derivative ligand. TpTiCl₃ (**38**)^[70] are readily prepared from TiCl₄. Fluorination of **38** with Me₃SnF in CH₂Cl₂ afforded the corresponding fluorides TpTiF₃ (**39**), respectively (Scheme 19). The formation of **39** was confirmed by IR, MS and elemental analysis.

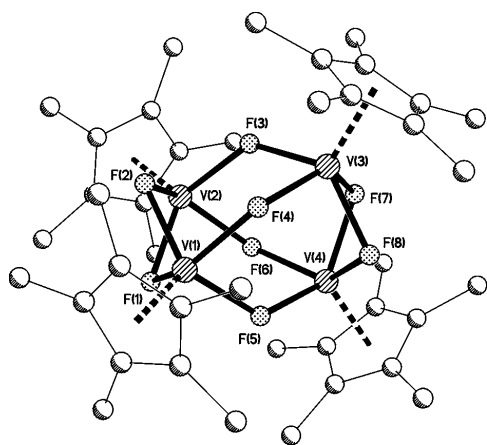


Scheme 19

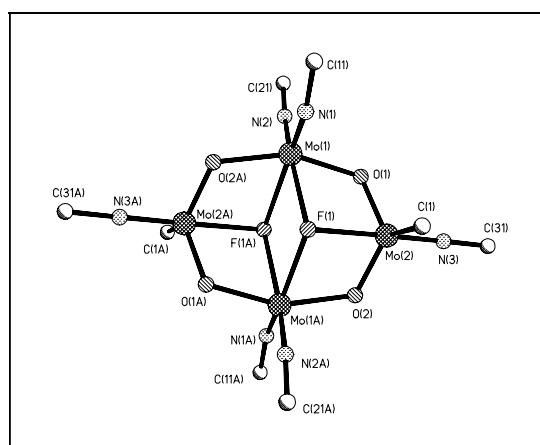
3. Summary and Outlook

3.1. Summary

The first authentic isolated vanadium fluoride $[\text{Cp}^*\text{VF}_2]_4$ (**1**) has been prepared and structurally characterized as the tetranuclear complex. Its reaction with O_2 is much faster than that of the corresponding chloride. Nevertheless, as indicated in section 1.4., the original aim of the present work has been focused on the synthesis of new non-Cp transition and main group compounds of several metals supported by nitrogen donor ligands of varying steric demand and different hapticities, and to synthesize and study the corresponding fluorides.



Structure of **1**

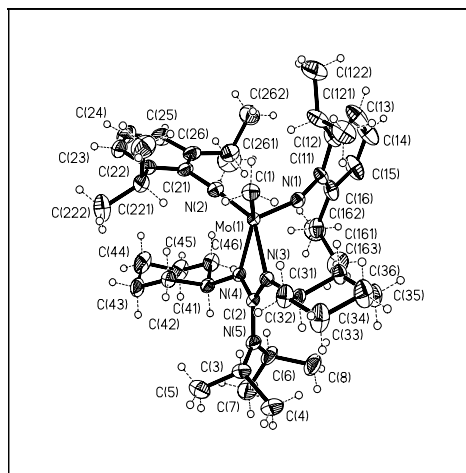


Core structure of **3**

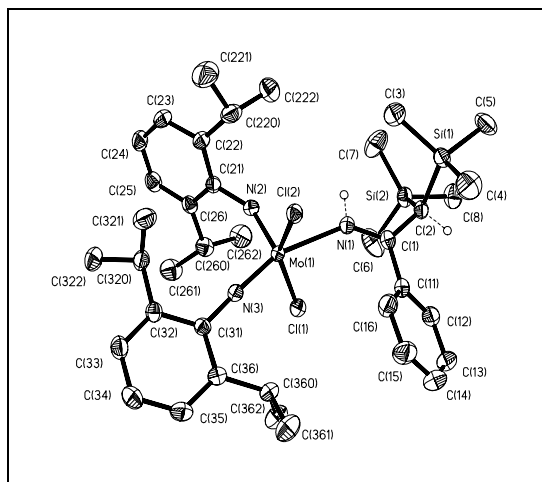
Fluorination of a very reactive bis(arylimido) molybdenum dimethylate $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{MoMe}_2\cdot\text{THF}]$ resulted in the formation of $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{MoF}_2]\cdot\text{THF}$ (**2**). Compound **2** is very sensitive to moisture and oxygen. The moisture contamination in the fluorinating reagent Me_3SnF used is responsible for the formation of compound $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_6\text{Mo}_4(\mu_3\text{-F})_2\text{Me}_2(\mu\text{-O})_4]$ (**3**), which was characterized by elemental analysis and X-ray diffraction analysis. Attempts to fluorinate the chlorides of organoimido, amidinato and guanidinato compounds of Mo, Ti and V were unsuccessful.

A series of bis(arylimido) molybdenum compounds (**4-9**) incorporated by amidinato and guanidinato ligands have been prepared. These compounds have in common five-coordinated molybdenum centers. Arylimido molybdenum complexes are

well-known catalysts for Ring Opening Metathesis Polymerization (ROMP). Nevertheless, neither the chlorides **4-7** nor the methylates **8-9** react with Me_3SnF . The analogous reaction with free 1-aza-allene led to the formation of compound **10**, from the hydrolysis of the 1-aza-allene ligand.



Structure of 9

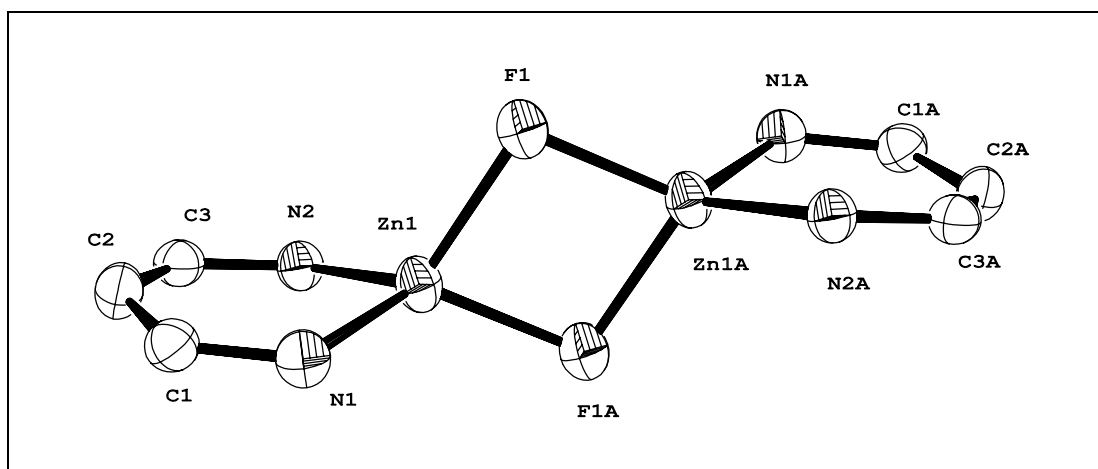


Structure of 10

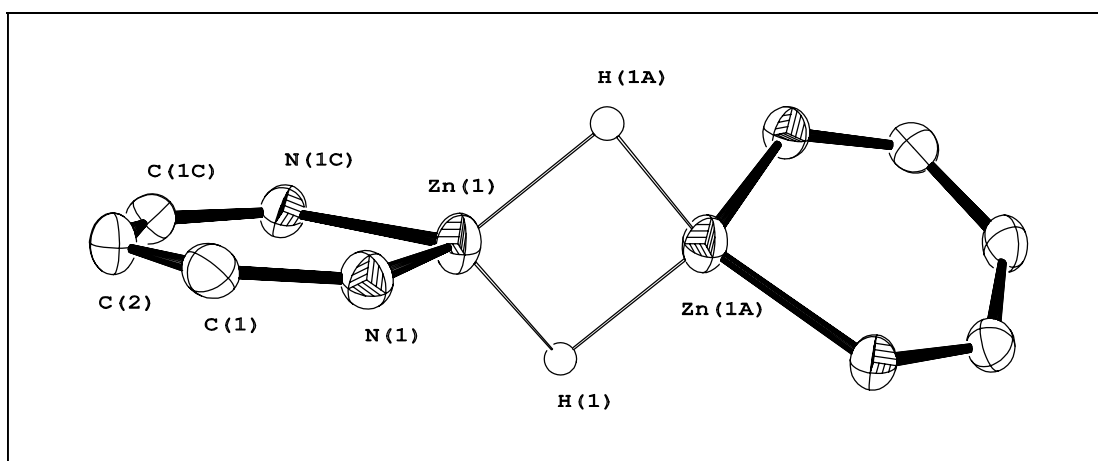
Bulky bischelating β -diketiminato ligands or the tridentate tris(pyrazolyl)hydroborato (Tp) ligand proved to be able to stabilize fluoride compounds of early transition metals. $[\{\text{HC}(\text{CMeNAr})_2\}\text{VF}_2]$ ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) (**11**), TpTiF_3 (**39**) was prepared from the reaction of the corresponding chloride and Me_3SnF , respectively. Compound **11** are crystalline solids, but X-ray diffraction studies were unsuccessful.

Despite the successful preparation of $[\{\eta^3\text{-HB}(3\text{-}^p\text{Tolpz})_3\}\text{ZnF}]$ ($3\text{-}^p\text{Tolpz} = 3\text{-}^p\text{Tol-5-MeC}_3\text{N}_2\text{H}_2$) **15**^[53] and trapping $\text{MeZnF}^{[11]}$ by using Cp^*TiF_3 , no other zinc fluoride complexes had been reported prior to this work. The superbuly Tp ligand prevents **15** from condensation through bridging fluorine atoms that might lead to decomposition. Treating $[\{\text{HC}(\text{CMeNAr})_2\}\text{ZnMe}]$ ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$) with Me_3SnF led to the formation of the fluorine bridged zinc fluoride $[\{\text{HC}(\text{CMeNAr})_2\}\text{Zn}(\mu\text{-F})_2]$ (**18**), its structure was confirmed by X-ray determination. Despite of the common features between fluorine and other halogens or oxygen, fluorine is the element that is most similar to hydrogen (see section 2.5.2.). The first hydrogen bridging zinc compound $[\{\text{HC}(\text{CMeNAr})_2\}\text{Zn}(\mu\text{-H})_2]$ (**19**) was deduced and then consequently prepared from **18** and Et_3SiH . The X-ray structure shows that, similar to **18**, compound **19** has two bridging hydrogen atoms between two zinc atoms. But the Zn–Zn distance

is extremely short, in the range of the sum of covalent radius of Zn, the shortest one that has yet been found in zinc compounds. But the Zn-Zn interaction is unlikely.



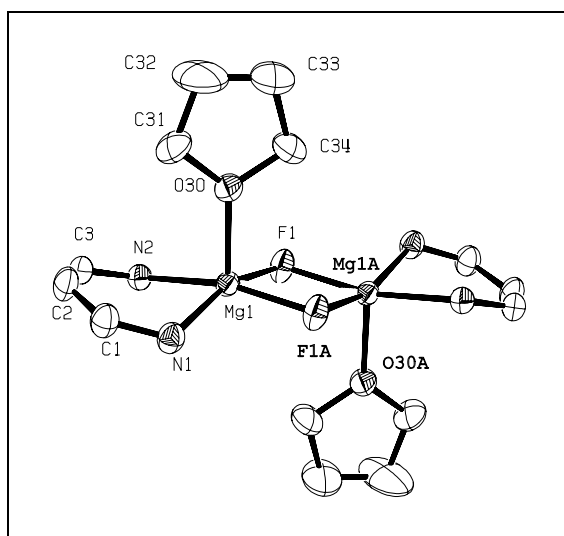
Core structure of 18



Core structure of 19

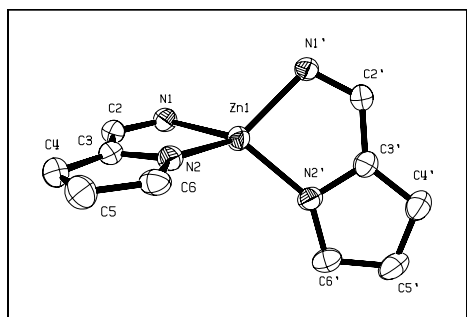
The existence of magnesium hydride complexes poses that the magnesium fluoride complexes may be prepared. Alkyl magnesium β -diketiminates seem convenient precursors for the corresponding fluorides. Consequently, magnesium fluoride complexes $[\{\text{HC}(\text{CMeNAr})_2\}\text{Mg}(\mu\text{-F})_2]$ ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$, **25**) and $[\{\text{HC}(\text{CMeNAr})_2\}\text{Mg}(\mu\text{-F})(\text{THF})_2]$ ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$, **26**) and $[\{\text{HC}(\text{CMeNAr})_2\}\text{MgMe}(\text{THF})]$ ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$, **24**) with Me_3SnF , respectively. X-ray single crystal determination reveals that **26** is a centrosymmetric dimer. The

magnesium atoms are bridged by two fluorine atoms. The geometry around magnesium is a distorted square pyramid with the oxygen at the top vertex.

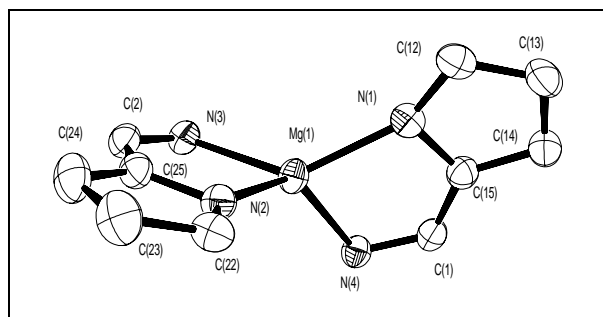


Core structure of 26

Unlike the reaction of $[\text{ArN}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{NHAr}]$ with ZnMe_2 in 1 : 1 molar ratio that leads to the formation of the methylzinc diketiminate, the reaction of $[2-(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})-6\text{-}^t\text{BuC}_6\text{H}_3\text{OH}]$ (**27**) with ZnMe_2 in 1 : 1 molar ratio resulted in the $[2-(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})-6\text{-}^t\text{BuC}_6\text{H}_3\text{O}]_2\text{Zn}$ (**28**) due to the acidity of the phenol proton. The acidity of arylimidomethyl pyrrole $[2-\{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}-5\text{-}^t\text{BuC}_4\text{H}_2\text{NH}]$ (**30**) is in between **27** and $[\text{ArN}=\text{C}(\text{Me})\text{CH}=\text{C}(\text{Me})\text{NHAr}]$. Nevertheless, the reactions of **30** with ZnMe_2 and MgMe_2 in 1 : 1 molar ratio afford $[2-\{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}-5\text{-}^t\text{BuC}_4\text{H}_2\text{N}]_2\text{Zn}$ (**31**) and $[2-\{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}-5\text{-}^t\text{BuC}_4\text{H}_2\text{N}]_2\text{Mg}$ (**32**). The structures of **31** and **32** commonly have a distorted tetrahedron geometry around metal center.

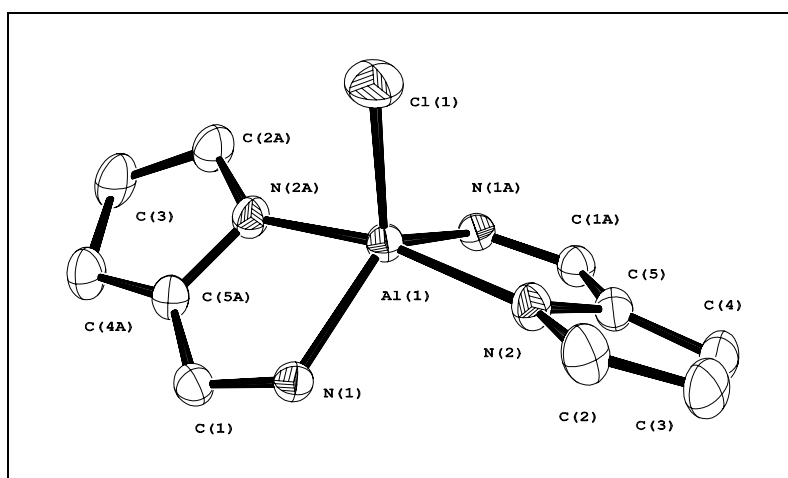


Core Structure of 31



Core Structure of 32

The reaction of arylimidomethyl pyrrole **30** and [2-{(2,6-*i*Pr₂C₆H₃)N=CH}-C₄H₂NH] (**33**) with AlMe₃ readily formed the corresponding dimethyl alane [2-{(2,6-*i*Pr₂C₆H₃)N=CH}-5-*t*Bu-C₄H₂N]AlMe₂ (**35**) and [2-{(2,6-*i*Pr₂C₆H₃)N=CH}-C₄H₂N]AlMe₂ (**34**). [2-{(2,6-*i*Pr₂C₆H₃)N=CH}-C₄H₂NH]Li reacted with one equiv of AlCl₃ in THF affording [2-{(2,6-*i*Pr₂C₆H₃)N=CH}-C₄H₂N]₂AlCl (**36**) instead of [2-{(2,6-*i*Pr₂C₆H₃)N=CH}-C₄H₂N]AlCl₂ (**37**).



Core structure of **36**

3.2. Outlook

The focus of the work reported here has been on the syntheses of new non-Cp organometallic compounds of several different metals supported by nitrogen donor ligands, especially on preliminary exploration of the synthesis, structures and reactivity of their fluorine derivatives. It has been demonstrated that non-Cp organometallic fluorides can be prepared by using Me_3SnF as the fluorinating reagent if suitable nitrogen donors are employed as ligands. Based on the intrinsic structural correlation between fluorine and hydrogen, the first hydrogen bridging organozinc hydride and the first organomagnesium fluoride have been predicted and synthesized.

A continuation of this work would be:

- Synthesizing non-Cp organometallic fluorides of late transition metals;
- Exploring the O, P, S donor ligands of various sizes, substituents and hapticities for organometallics and organometallic fluorides;
- studying their structural features, reactivities and their catalytic activities.

4. Experimental Section

4.1. General procedures

All experimental manipulations, unless otherwise stated, were carried out in an oxygen-free dry dinitrogen atmosphere using Schlenk glassware and techniques.^[71] The handling of solid samples and the preparation of samples for spectral measurements were carried out inside a MBraun MB150-GI glove-box where the O₂ and H₂O levels were normally kept below 2 ppm. The glassware used in all the manipulations was oven-dried at 150 °C for a minimum of 2 h before use, cooled to ambient temperature *in vacuo*, and flushed with nitrogen.

Melting points were determined in sealed capillaries on a Bühler SPA-1 apparatus and were uncalibrated. Elemental analyses were carried out by the Analytical Laboratory of the Institute of Inorganic Chemistry at the University of Göttingen. ¹H, ¹⁹F and ²⁹Si NMR spectra (CDCl₃, C₆D₆, or toluene-d₈ solutions) were recorded on Bruker AS-250 and Bruker AM-200 spectrometers. Heteronuclear NMR spectra were recorded ¹H decoupled. Chemical shifts are reported in ppm with reference to external TMS or CFCl₃, positive values being downfield, and coupling constants *J* in Hz. All NMR grade solvents were dried prior to use and the samples for measurements were freshly prepared in the glove-box. IR spectra were recorded on Bio-Rad FTS-7 spectrometer as nujol mulls between KBr or KCl plates. Intensities are estimated as follows: w (weak), m (medium), s (strong), and vs (very strong). Only very strong, strong, and characteristic absorptions are given. EI-mass spectra were obtained on Finnigan MAT 8230 and Varian MAT CH5 spectrometers. Only the highest peak of the respective isotopic distribution is given. X-ray structure determinations: crystals were mounted on glass fibers in a rapidly cooled perfluoropolyether. Diffraction data of all the crystals were collected on a Siemens/Stoe AED2 four circle diffractometer performing $2\theta/\omega$ scans. The structures were solved by direct methods using the program SHELXS-97^[72] and refined using F^2 on all data by full-matrix-least-squares with SHELXL-97.^[73] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and

refined using a riding model. Crystal data for all the compounds related to the data collection, structure solution, and refinement are listed in Section 6. in tabular form.

4.2. Starting materials

The starting materials $[\text{Cp}^*\text{V}(\mu\text{-Cl})_2]_3$,^[24] $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{MoMe}_2]$, $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{MoMe}_2]\cdot\text{THF}$,^[25i] $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{MoCl}_2]\cdot\text{DME}$,^[25i] TpTiCl_2 ^[74], the lithium salts of amidinate and guanidinate,^[34a,36a] $[\text{N}(\text{TMS})\text{C}(\text{C}_6\text{H}_5)\text{CH}(\text{SiMe}_3)_2]\text{Li}\cdot\text{THF}$,^[39] $[\{\text{HC}(\text{CMeNAr})_2\}\text{VCl}_2]$ (Ar = 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$),^[44] $[\{\text{HC}(\text{CMeNAr})_2\}\text{ZnMe}]$ (Ar = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$),^[42] **27**,^[20] $[2\text{-}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{-}6\text{-}^t\text{BuC}_6\text{H}_3\text{OH}]$,^[20] $[2\text{-}\{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}\text{-}5\text{-}^t\text{Bu}\text{-C}_4\text{H}_2\text{NH}]$ (**30**),^[66] $[2\text{-}\{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}\text{-C}_4\text{H}_2\text{NH}]$ (**33**)^[67] and $[2\text{-}\{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}\text{C}_4\text{H}_3\text{N}]\text{Li}$ ^[67] were prepared by literature methods. Other chemicals used in this work were purchased from Aldrich Chemical Co, ACROS, and Fluka Co and used without further purification.

4.3. Synthesis

4.3.1. $[\text{Cp}^*\text{V}(\mu\text{-F})_2]_4$ (**1**)

$[\text{Cp}^*\text{V}(\mu\text{-Cl})_2]_4$ (0.51 g, 2.0 mmol), Me_3SnF (0.83 g, 4.5 mmol) and CH_2Cl_2 (40 mL) were added to a Schlenk flask. The resulting mixture was stirred for 16 h. After filtration, CH_2Cl_2 was evaporated and the residue was dried *in vacuo* using a warm water bath for 4 h to remove the by-product Me_3SnCl . Recrystallization from toluene / *n*-pentane (1 : 1) at $-30\text{ }^\circ\text{C}$ gave purple red micro crystals. Yield: 0.17g (10 %).

Melting point: $> 220\text{ }^\circ\text{C}$.

Elemental analysis for $\text{C}_{40}\text{H}_{60}\text{F}_8\text{V}_4$ (896.66 g/mol):

	C	H
Calcd.:	53.58	6.74,
Found:	53.3	6.8 %.

^1H NMR (200.13 MHz, C_6D_6): δ -0.05 ($\Delta\nu_{1/2} \approx 42$ Hz) ppm.

MS: m/z (%): 896 ($[M]^+$, 0.1), 672 ($[3/4 M]^+$, 14), 429 ($[1/2 M - F]^+$, 100).

4.3.2. [(2,6-ⁱPr₂C₆H₃N)₂MoF₂] \cdot THF (2)

Me₃SnF (0.46 g, 2.5 mmol) was added to a solution of [(2,6-ⁱPr₂C₆H₃N)₂MoMe₂] \cdot THF (0.59 g, 1.1 mmol) in THF (20 mL). The resulting reaction mixture was stirred at r.t. for 16 h. After removing all volatiles the residue was extracted with *n*-pentane (20 mL). The extract was cooled at -32 °C. Orange crystals were obtained. Yield: 0.29 g (47 %).

Melting point: 171 - 174 °C.

Elemental analysis for C₂₈H₄₂F₂MoN₂O (556.59 g/mol) including one molecule of THF:

	C	H	F	N
Calcd.:	60.42	7.61	5.83	5.03,
Found:	60.2	7.6	6.2	5.2 %.

¹H NMR (200.13 MHz, C₆D₆): δ 7.10 - 6.90 (m, 6 H, C₆H₃), 4.10 (br, 4 H, THF), 3.95 (sept, 4 H, CHMe₂), 1.49 (br t, 4 H, THF), 1.20(d, 24 H, CHMe₂) ppm.

MS: *m/z*: 486.17 ([M - THF]⁺).

4.3.3. [(2,6-ⁱPr₂C₆H₃N)₆Mo₄(μ ₃-F)₂Me₂(μ -O)₄] \cdot (C₅H₁₂) (3)

Me₃SnF (0.20 g, 1.1 mmol) (unsublimed, containing water) was added to a solution of [(2,6-ⁱPr₂C₆H₃N)₂Mo₂Me₂] (0.24 g, 0.50 mmol) in toluene (10 mL) at room temperature, and the reaction mixture stirred overnight. After removing all volatiles and drying the residue *in vacuo* for 2 h, it was extracted with *n*-pentane (10 mL). The extracts were stored at room temperature for 48 h to afford dark-red crystals. Yield: 77 mg (4.2 %).

Melting point: 219 - 222 °C.

Elemental analysis for C₇₉H₁₂₀F₂Mo₄N₆O₄ (1639.61 g/mol) including one molecule of *n*-pentane:

	C	H	N
Calcd.:	57.87	7.38	5.13,
Found:	57.9	7.4	4.9 %.

4.3.4. [(2,6-ⁱPr₂C₆H₃N)₂MoCl{N(Cy)C(Me)N(Cy)}] (4)

[N(C₆H₁₁)C(Me)N(C₆H₁₁)]Li·O(C₂H₅)₂ (1.5 g, 5.0 mmol) was added in several portions to a solution of [(2,6-ⁱPr₂C₆H₃N)₂MoCl₂]·DME (3.0 g, 5.0 mmol) in THF (35 mL) at -78 °C. After warming slowly to ambient temperature (ca. 2 h), the solution was stirred at r.t. for 48 h. After evaporation of all volatiles the residue was extracted with toluene (20 mL). Removing the toluene from the extract, washing the residue with ether (20 mL) and drying it *in vacuo* for 2 h resulted in a yellow powder (1.2 g, 34 %).

Melting point: 218 - 222 °C.

Elemental analysis for C₃₈H₅₉ClMoN₄ (703.30 g/mol):

	C	H	N
Calcd.:	64.90	8.46	7.97,
Found:	64.6	8.5	8.0 %.

¹H NMR (200.13 MHz, C₆D₆): δ 7.10 - 6.90 (m, 6 H, 2,6-ⁱPr₂C₆H₃), 4.00 (m, 4 H, CHMe₂), 3.30 (m, 2 H, Cy), 1.60 (s, 3 H, NC(Me)N), 2.5 - 1.1 (m, 20 H, Cy), 1.24 (d, 12 H, CHMe₂), 1.18 (d, 12 H, CHMe₂) ppm.

MS: *m/z* (%): 704 ([M]⁺, 10), 529 ([M - ArN]⁺, 55), 83 ([Cy]⁺, 100).

4.3.5. [(2,6-ⁱPr₂C₆H₃N)₂MoCl{N(Cy)C(NⁱPr₂)N(Cy)}] (5)

The synthetic procedure is similar to that described for 4. [N(C₆H₁₁)C(N(ⁱPr)₂)N(C₆H₁₁)]Li·O(C₂H₅)₂ (5.9 g, 15.5 mmol) was added in several portions to a solution of [(2,6-ⁱPr₂C₆H₃N)₂MoCl₂]·DME (9.1g, 15.0 mmol) in THF (100 mL) at -78 °C. Yield: 4.5 g (38 %).

Melting point: 218 - 220 °C.

Elemental analysis for C₄₃H₇₀ClMoN₅ (788.45 g/mol):

	C	H	N
Calcd.:	65.50	8.95	8.88,
Found:	65.5	8.9	8.8 %.

¹H NMR (200.13 MHz, C₆D₆): δ 7.10 - 6.90 (m, 6 H, ⁱPr₂C₆H₃), 4.19 (m, 4 H, CHMe₂), 3.65 (m, 2 H, Cy), 3.55 (m, 2 H, NC(N(CHMe₂)₂)N), 1.31 (d, 12 H, CHMe₂), 1.23 (d, 12 H, CHMe₂), 1.20 (d, 12 H, NC(N(CHMe₂)₂)N), 2.70 - 1.10 (m, 22 H, Cy) ppm.

MS: m/z (%) = 789 ($[M]^+$, 100), 614 ($[M - \text{ArN}]^+$, 68).

4.3.6. [(2,6-ⁱPr₂C₆H₃N)₂MoCl{N(Cy)C(N(SiMe₃)₂)N(Cy)}] (6)

A solution of [N(C₆H₁₁)C(N(SiMe₃)₂)N(C₆H₁₁)]Li·O(C₂H₅)₂ (0.75 g, 2.0 mmol) in THF (20 mL) was added dropwise to [(2,6-ⁱPr₂C₆H₃N)₂MoCl₂]·DME (1.20 g, 2.0 mmol) in THF (20 mL) at -70 °C over a period of 10 min. After warming slowly to ambient temperature the resulting solution was stirred at r.t. for 16 h. After evaporation of all volatiles the residue was extracted with *n*-pentane (20 mL). Removal of *n*-pentane from the extract afforded **6** as a brown-yellow powder. Yield: 1.2 g (71 %).

Melting point: 82 - 84 °C.

Elemental analysis for C₄₃H₇₄ClMoN₅Si₂ (848.65 g/mol):

	C	H	N
Calcd.:	60.85	8.78	8.35,
Found:	60.6	9.1	8.9 %.

¹H NMR (200.13 MHz, C₆D₆): δ 7.10 - 6.85 (m, 6 H, ⁱPr₂C₆H₃), 4.08 (m, 4 H, CHMe₂), 3.73 (m, 2 H, Cy), 2.10 - 1.10 (m, 20 H, Cy), 1.28 (d, 12 H, CHMe₂), 1.27 (d, 12 H, CHMe₂), 0.27 (d, 18 H, SiMe₃) ppm.

MS: m/z : 849 $[M]^+$, 674 $[M - \text{ArN}]^+$.

4.3.7. [(2,6-ⁱPr₂C₆H₃N)₂MoCl{C₆H₅C(NSiMe₃)₂}] (7)

The synthetic procedure is similar to that of **6**. [C₆H₅C(NSiMe₃)₂]Li·THF (1.26 g, 3.7 mmol) was dissolved in THF (20 mL) and added dropwise to a solution of [(2,6-ⁱPr₂C₆H₃N)₂MoCl₂]·DME (2.23 g, 3.7 mmol) in THF (20 mL) at -57 °C. Yield: 1.90 g (69 %).

Melting point: 120 - 124 °C.

Elemental analysis for C₃₇H₅₇ClMoN₄Si₂ (745.45 g/mol):

	C	H	N
Calcd.:	59.62	7.31	7.59,
Found:	60.1	8.0	7.4 %.

^1H NMR (200.13 MHz, C_6D_6): δ 7.30 - 6.85 (m, 11 H, 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$ and C_6H_5), 4.08 (m, 4 H, CHMe_2), 1.33 (d, 12 H, CHMe_2), 1.25 (d, 12 H, CHMe_2), 0.26 (s, 9 H, SiMe_3), 0.12 (s, 9 H, SiMe_3) ppm.

MS: m/z (%): 746 ($[\text{M}]^+$, 10), 571 ($[\text{M} - \text{ArN}]^+$, 15), 175 ($[\text{ArN}]^+$, 100).

4.3.8. [(2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}$) $_2\text{MoMe}\{\text{N}(\text{Cy})\text{C}(\text{Me})\text{N}(\text{Cy})\}$] (**8**)

MeLi (0.34 mL, 0.54 mmol, 1.6 M solution in ether) was added dropwise to a solution of **4** (0.37 g, 0.52 mmol) in THF (20 mL) at $-57\text{ }^\circ\text{C}$. After warming slowly to ambient temperature, the solution was stirred at r.t. for 16 h. After removal of all volatiles the residue was extracted with toluene (40 mL). After concentration and cooling to $-32\text{ }^\circ\text{C}$ for several days orange crystals were formed (0.26 g, 73 %).

Melting point: $190 - 195\text{ }^\circ\text{C}$.

Elemental analysis for $\text{C}_{39}\text{H}_{62}\text{MoN}_4$ (682.88 g/mol):

	C	H	N
Calcd.:	68.60	9.15	8.20
Found:	68.1	9.1	7.9 %.

^1H NMR (200.13 MHz, C_6H_6): δ 7.10 - 6.85 (m, 6 H, 2,6- $^i\text{C}_6\text{H}_3$), 4.02 (m, 4 H, CHMe_2), 3.20 (m, 2 H, Cy), 1.57 (s, 3 H, Mo-Me), 1.54 (s, 3 H, $\text{NC}(\text{Me})\text{N}$), 2.10 - 1.10 (m, 20 H, Cy), 1.27 (d, 12 H, CHMe_2), 1.17 (d, 12 H, CHMe_2) ppm.

MS: m/z (%): 684 ($[\text{M}]^+$, 100).

4.3.9. [(2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}$) $_2\text{MoMe}\{\text{N}(\text{Cy})\text{C}(\text{N}^i\text{Pr}_2)\text{N}(\text{Cy})\}$] (**9**)

The synthetic procedure is similar to that for **8**. MeLi (0.63 mL, 1.0 mmol, 1.6 M solution in ether) was added dropwise to a solution of **5** (0.79 g, 1.0 mmol) in THF (20 mL) at $-57\text{ }^\circ\text{C}$. Yield: 0.54 g (70 %).

Melting point: $190 - 195\text{ }^\circ\text{C}$.

Elemental analysis for $\text{C}_{44}\text{H}_{73}\text{MoN}_5$ (768.01 g/mol):

	C	H	N
Calcd.:	68.75	9.58	9.12,
Found:	68.5	9.6	9.0 %.

^1H NMR (200.13 MHz, C_6H_6): δ 7.10-6.85 (m, 6 H, 2,6- $^i\text{C}_6\text{H}_3$), 4.08 (m, 4 H, CHMe_2), 3.65 (m, 2 H, Cy), 3.55 (m, 2 H, $\text{NC}[\text{N}(\text{CHMe}_2)_2]\text{N}$), 1.60 (s, 3 H, Mo-Me), 2.10 - 1.10 (m, 22 H, Cy), 1.31 (d, 12 H, CHMe_2), 1.24 (d, 12 H, CHMe_2), 1.11 (d, 12 H, $\text{NC}[\text{N}(\text{CHMe}_2)_2]\text{N}$) ppm.

MS: m/z (%): 769 ($[M]^+$, 100).

4.3.10. $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{MoCl}_2]\cdot[\text{NH}=\text{C}(\text{C}_6\text{H}_5)\text{CH}(\text{SiMe}_3)_2]$ (10)

A solution of $[\text{N}(\text{SiMe}_3)\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{SiMe}_3)_2]\text{Li}\cdot\text{THF}$ (0.21 g, 0.49 mmol) in ether (15 mL) was added dropwise to a solution of $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{MoCl}_2]\cdot\text{DME}$ (0.30 g, 0.49 mmol) in ether (100 mL) at $-78\text{ }^\circ\text{C}$. After warming slowly to ambient temperature the reaction mixture was stirred for 16 h at r.t.. After removing all volatiles the residue was extracted with *n*-pentane (15 mL). The extract was cooled at $-5\text{ }^\circ\text{C}$ for 18 h to afford yellow crystals. Yield: 34 mg (9 %).

Melting point: $147 - 150\text{ }^\circ\text{C}$.

Elemental analysis for $\text{C}_{38}\text{H}_{59}\text{Cl}_2\text{MoN}_3\text{Si}_2$ (780.90 g/mol):

	C	H	N
Calcd.:	58.45	7.62	5.38,
Found:	58.4	7.6	5.6 %.

^{29}Si NMR(99.36 MHz, C_6D_6): δ 7.47 ppm.

EI-MS: m/z (%): 745($[M - \text{Cl}]^+$, 18), 570 ($[M - \text{Cl} - \text{ArN}]^+$, 18), 175 ($[\text{ArN}]^+$, 100).

4.3.11. $[\{\text{HC}(\text{CMeNAr})_2\}\text{VF}_2]$ (Ar = 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$, 11)

Me_3SnF (0.55 g, 3.0 mmol) was added to a solution of $[\{\text{HC}(\text{CMeNAr})_2\}\text{VCl}_2]$ (0.73 g, 1.35 mmol) in toluene (30 mL). While the resulting reaction mixture was allowed to be stirred at r.t. for 14 h the color of the solution changed from dark green to dark red. After filtration and removal of all the volatiles under reduced pressure the residue was dried *in vacuo* for 4 h. Then it was redissolved in 10 mL of toluene and cooled at $-32\text{ }^\circ\text{C}$ for 16 h. Yield: 0.47 g (69 %).

Melting point: $> 290\text{ }^\circ\text{C}$ (dec.).

IR (Nujol): $\tilde{\nu}$ = 3173 (w), 3001 (m), 2364 (m), 1929 (m), 1862 (m), 1795 (m), 1624 (s), 1554 (s), 1260 (s), 1175 (s), 1100 (s), 1058 (m), 1021 (br vs), 925 (s), 860 (s), 798 (vs), 760 (s), 727 (s), 658 (m), 642 (m) cm^{-1} .

Elemental analysis for $\text{C}_{29}\text{H}_{41}\text{F}_2\text{N}_2\text{V}$ (506.59 g / mol):

	C	H	N
Calcd.:	68.76	8.16	5.53,
Found:	67.7	7.8	5.2 %.

EI-MS: m/z (%): 506 ($[M]^+$, 100).

4.3.12. $[\{\text{HC}(\text{CMeNAr})_2\}\text{Zn}(\mu\text{-F})]_2$ (Ar = 2,6-Me₂C₆H₃, **18**)

A mixture of $[\{\text{HC}(\text{CMeNAr})_2\}\text{ZnMe}]$ (Ar = 2,6-Me₂C₆H₃, 0.38 g, 1.0 mmol) and Me₃SnF (0.18 g, 1.0 mmol) in toluene (20 mL) was stirred at 100 °C for 8 h until all the solid Me₃SnF had disappeared. Cooling the solution to room temperature afforded colorless crystals of **18** (0.31 g, 40 %).

Melting point: 278 - 281 °C.

Elemental analysis for $\text{C}_{42}\text{H}_{50}\text{F}_2\text{N}_4\text{Zn}_2$ (779.64 g/mol):

	C	H	N
Calcd.:	64.70	6.46	7.19
Found:	64.76	6.49	7.16

¹H NMR (200.13 MHz, C₆D₆): δ 6.95 - 6.80 (m, 12 H, Ar-H), 4.68 (s, 2H, $\gamma\text{-CH}$), 1.99 (s, 24 H, Ar-Me), 1.35 (s, 12 H, $\beta\text{-CMe}$) ppm.

¹⁹F NMR (188.28 MHz, C₆D₆): δ -61.62 ppm.

MS: m/z (%): 778 (M^+ , 100).

4.3.13. $[\{\text{HC}(\text{CMeNAr})_2\}\text{Zn}(\mu\text{-H})]_2$ (Ar = 2,6-Me₂C₆H₃) (**19**)

A mixture of compound **18** (0.39 g, 0.5 mmol) and Et₃SiH (1.0 g, 8.6 mmol) in benzene (20 mL) was refluxed for 16 h. Cooling the hot solution to room temperature, colorless crystals were formed (0.28 g, 75 %).

Melting point: 215 - 217 °C.

Elemental analysis for $C_{42}H_{52}N_4Zn_2$ (743.66 g / mol):

	C	H	N
Calcd.:	70.16	7.11	6.82,
Found:	70.0	7.0	7.2 %.

1H NMR (200.13 MHz, C_6D_6): δ 6.92 (s, 12 H, Ar-H), 4.82 (s, 2 H, γ -CH), 4.59 (s, 2 H, Zn(μ -H)), 2.03 (s, 24 H, Ar-Me), 1.44 (s, 12 H, β -CMe) ppm.

EI-MS: m/z (%): 743 ($[M]^+ - H$), 370 ($[1/2 M]^+$, 50), 146 ($[ArNCCH_3]^+$, 100).

4.3.14. $[\{HC(CMeNAr)_2\}Mg(\mu-F)(THF)]_2$ (Ar = 2,6- i -Pr $_2$ C $_6$ H $_3$, **26**)

A mixture of **24** (1.72 g, 3.00 mmol) and Me $_3$ SnF (0.60 g, 3.3 mmol) in toluene (20 mL) was stirred at r.t. for 48 h. Then it was heated to dissolve all of the precipitate. Colorless crystals formed while cooled at 0 °C for 18 h. Yield 0.87 g (27 %).

Melting point: 240 - 245 °C.

IR (Nujol): $\tilde{\nu}$ = 3059 (w), 2461 (w), 2363 (w), 1926 (w), 1851 (w), 1799 (w), 1523 (s), 1409 (s), 1315 (s), 1260 (s), 1173 (s), 1101 (m), 1057 (m), 1031 (s), 725 (m), 884 (m), 842 (m), 791 (s), 761 (s), 740 (m), 727 (s), 694 (m), 637 (m), 521 (m), 442 (s) cm^{-1} .

Elemental analysis for $C_{66}H_{98}F_2Mg_2N_4O_2$ (1066.13 g/mol):

	C	H	N
Calcd.:	74.36	9.27	5.26,
Found:	74.53	9.10	4.91 %.

1H NMR (200.13 MHz, C_6D_6): δ 7.10 - 6.90 (m, 6 H, i Pr $_2$ C $_6$ H $_3$), 4.82 (s, 1 H, γ -H), 3.52 (br, 4 H, THF), 3.05 (sept, 4 H, $^3J(H, H) = 6.8$ Hz, CHMe $_2$), 1.50 (s, 6 H, Me), 1.19 (m, 4 H, THF) 1.10 (d, 12 H, $^3J(H, H) = 6.8$ Hz, CHMe $_2$), 0.96 (d, 12 H, $^3J(H, H) = 6.8$ Hz, CHMe $_2$) ppm.

^{19}F NMR(C_6D_6 , 188.28 MHz): δ -24.742 ppm.

EI-MS : m/z : 921($[M - 2THF]^+$, 75), 503 ($[M - 2THF - \{ArN=CMeCH=CMeNHA r (Ar = 2,6-^iPr_2C_6H_3)\}]^+$, 100).

4.3.15. $[\eta^2\text{-}\{2\text{-}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{-}6\text{-}^t\text{BuC}_6\text{H}_3\text{O}\}]_2\text{Zn}$ (**28**)

A solution of $[2\text{-}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{-}6\text{-}^t\text{BuC}_6\text{H}_3\text{OH}]$ (**27**) (0.70 g, 2.0 mmol) in THF (30 mL) was added dropwise to a solution of ZnMe $_2$ (1.0 mL of a 2.0 M solution in

toluene) in THF (20 mL) at -78 °C. After complete addition the solution was warmed slowly to ambient temperature and stirred at r.t. for 16 h. After removal of all volatiles the residue was extracted with ether (20 mL) and the extract was cooled in a freezer (-32 °C) to afford colorless crystals. Yield 0.58 g (38 % based on **27**).

Melting point: 273 - 275 °C.

IR (Nujol): $\tilde{\nu}$ = 3061 (w), 1931 (w), 1866 (w), 1812 (w), 1759 (w), 1705 (w), 1623 (m), 1598 (s), 1583 (s), 1534 (s), 1421 (s), 1391 (s), 1320 (s), 1233 (s), 1206 (m), 1263 (s), 1098 (m), 1030 (m), 985 (m), 934 (m), 853 (m), 818 (m), 800 (m), 790 (m), 763 (m), 721 (m), 525 (s), 470 (m) cm^{-1} .

Elemental analysis for $\text{C}_{48}\text{H}_{64}\text{N}_2\text{O}_2\text{Zn}$ (766.42 g / mol):

	C	H	N
Calcd.:	75.22	8.42	3.66,
Found:	75.7	8.4	3.6 %.

^1H NMR (200.13 MHz, C_6D_6): δ 7.72 (s, 2 H, N=CH), 7.15 (s, 2 H, C_6H_2), 7.10 - 6.80 (m, 8 H, C_6H_3 and C_6H_2), 3.25 (sept, 4 H, γH), 2.05 (s, 6 H, $\text{C}_6\text{H}_2\text{Me}$), 1.30 (s, 18 H, $\text{C}_6\text{H}_2^t\text{Bu}$), 1.40 - 1.00 (m, 24 H, CHMe_2) ppm.

EI-MS(^{64}Zn): m/z (%): 764 ($[\text{M}]^+$, 85); 350 ($[\text{ligand}]^+$, 100).

4.3.16. $[\eta^2\text{-}\{2\text{-}[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}]\text{-}5\text{-}^t\text{Bu-C}_4\text{H}_2\text{N}\}]_2\text{Zn}$ (**31**)

A solution of $[2\text{-}\{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}\text{-}5\text{-}^t\text{BuC}_4\text{H}_2\text{NH}]$ (**30**) (1.0 g, 3.2 mmol) in toluene (20 mL) was added to a solution of ZnMe_2 (2 mL of a 2.0 M solution in toluene, 4.0 mmol) in toluene (20 mL) at -78 °C with stirring. Then it was warmed slowly to ambient temperature and stirred at r.t. for 16 h. After removal of all volatiles the solid was extracted with 10 mL of hot *n*-hexane. Colorless crystals formed while cooling the hot extract slowly to ambient temperature. Yield 0.73 g (33 % based on **30**).

Melting point: 248 - 250 °C.

IR (Nujol): $\tilde{\nu}$ = 3061 (w), 1661 (br m), 1596 (m), 1566 (vs), 1480 (m), 1361 (s), 1279 (s), 1233 (m), 1184 (m), 1108 (m), 1052 (s), 1012 (s), 987 (m), 894 (m), 802 (m), 788 (m), 769 (m), 751 (m), 719 (m) cm^{-1} .

Elemental analysis for $C_{42}H_{58}N_4Zn$ (684.32 g / mol):

	C	H	N
Calcd.:	73.72	8.54	8.19
Found:	73.76	8.43	8.21

1H NMR (200.13 MHz, C_6D_6): δ 7.47 (s, 2 H, N=CH), 7.18 - 7.00 (m, 8 H, aryl, pyrrole), 6.50 (d, 2 H, $J = 3.77$ Hz, pyrrole), 3.76 (sept, 2 H, $J = 6.84$ Hz, CHMe₂), 2.78 (sept, 2 H, $J = 6.84$ Hz, CHMe₂), 1.33 (s, 18 H, tBu), 1.12 (d, 6 H, $J = 6.82$ Hz, CHMe₂), 1.05 (d, 6H, $J = 5.06$ Hz, CHMe₂), 0.97 (d, 6 H, $J = 5.04$ Hz, CHMe₂), 0.25 (d, 6H, $J = 6.78$ Hz, CHMe₂) ppm.

MS: m/z (%): 682 ($[M]^+$, 100 %).

4.3.17. $[\eta^2\text{-}\{2\text{-}[(2,6\text{-}^iPr_2C_6H_3)N=CH]\text{-}5\text{-}^tBu\text{-}C_4H_2N\}]_2Mg$ (32)

A solution of $[2\text{-}\{(2,6\text{-}^iPr_2C_6H_3)N=CH\}\text{-}5\text{-}^tBuC_4H_2NH]$ (**30**) (0.93 g, 3.0 mmol) in *n*-hexane (30 mL) was added to a solution of Bu_2Mg (3.0 mL of a 1.0 M solution in toluene, 3.0 mmol) in *n*-hexane (20 mL) at -78 °C under stirring. Then the solution was warmed slowly to ambient temperature and stirred at r.t. for 16 h. After filtration and washing the precipitate with *n*-hexane (20 mL), the combined filtrate was concentrated and stored at 0 °C in the refrigerator for 24 h to afford colorless crystals suitable for X-ray single crystal analysis. Yield: 0.58 g (28 % based on **30**).

Melting point: $240 - 242$ °C.

IR (Nujol): $\tilde{\nu} = 2366$ (w), 1927 (w), 1865 (w), 1799 (w), 1722 (w), 704 (w), 1597 (s), 1567 (vs), 1313 (m), 1379 (vs), 1233 (s), 1184 (s), 1144 (m), 1107 (m), 1052 (s), 1012 (s), 933 (m), 894 (s), 802 (m), 788 (m), 768 (m), 751 (s), 719 (m), 687 (m), 562 (m), 427 (m) cm^{-1} .

Elemental analysis for $C_{42}H_{58}N_4Mg$ (684.32 g / mol):

	C	H	N
Calcd.:	78.42	9.09	8.71
Found:	78.34	9.11	8.69

1H NMR (200.13 MHz, C_6D_6): δ 7.53 (s, 2 H, N=CH), 7.00 - 6.90 (m, 8 H, aryl, pyrrole), 6.88 (d, 2 H, $J = 3.6$ Hz, pyrrole), 6.45 (d, 2 H, $J = 3.6$ Hz, pyrrole), 3.57 (sept, 2 H, $J = 6.9$ Hz, CHMe₂), 2.81 (sept, 2 H, $J = 6.8$ Hz, CHMe₂), 1.33 (s, 18 H, tBu),

1.18 (d, 6 H, $J = 6.8$ Hz, CHMe_2), 1.08 (d, 6H, $J = 6.9$ Hz, CHMe_2), 1.01 (d, 6 H, $J = 6.8$ Hz, CHMe_2), 0.28 (d, 6H, $J = 6.8$ Hz, CHMe_2) ppm.

MS: m/z (%): 642 ($[M]^+$, 100 %), 627 ($[M-\text{Me}]^+$, 50 %).

4.3.18. $[\eta^2\text{-}\{2\text{-}[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}]\text{-C}_4\text{H}_2\text{N}\}]\text{AlMe}_2$ (34)

A solution of $[2\text{-}\{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}\text{-C}_4\text{H}_2\text{NH}]$ (**33**) (2.54 g, 10 mmol) and AlMe_3 (5.3g of a 16 % solution in *n*-hexane, 11 mmol) in toluene (40 mL) was refluxed for 4 h. Then the solution was cooled to ambient temperature. Subsequently, all volatiles were removed *in vacuo*. The residue was recrystallized from *n*-hexane at -32 °C resulting in colorless crystals. Yield: 1.77 g (57 %).

Melting point: 83 - 85 °C.

IR (Nujol): $\tilde{\nu} = 3175$ (w), 3119 (w), 3101 (w), 2602 (w), 2571 (w), 2492 (w), 2466 (w), 2439 (w), 2330 (w), 2090 (w), 1937 (w), 1989 (w), 1805 (w), 1767 (m), 1716 (m), 1668 (m), 1571 (br vs), 1500 (s), 1457 (br vs), 1394 (s), 1365 (m), 1326 (s), 1310 (m), 1288 (s), 1262 (s), 1179 (vs), 1099 (s), 1043 (vs), 995 (s), 935 (m), 908 (s), 805 (m), 788 (m), 754 (s), 674 (br vs), 599 (s), 573 (s), 480 (m), 448 (s), 390 (s), 370 (s) cm^{-1} .

^1H NMR (200.13 MHz, C_6D_6): δ 7.76 (d, 1 H, $J = 1.09$ Hz, $\text{N}=\text{CH}$) 7.26 (m, 1 H, pyrrole), 7.20 - 7.05 (m, 4 H, Ar-H), 6.92 (dd, 1 H, $J = 3.64$ Hz, pyrrole), 6.39 (dd, 1 H, $J = 3.64$ Hz, pyrrole), 3.01 (sept, 2 H, $J = 6.8$ Hz, CHMe_2), 1.11 (d, 6 H, $J = 6.8$ Hz, CHMe_2), 1.01 (d, 6 H, $J = 6.8$, CHMe_2), -0.77 (s, 6 H, AlMe_2) ppm.

MS ($\text{C}_{17}\text{H}_{21}\text{N}_2\text{AlMe}_2 = 310$): m/z (%): 310 ($[M]^+$, ~0 %), 295 ($[M-\text{Me}]^+$, 100 %).

4.3.19. $[\eta^2\text{-}\{2\text{-}[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}]\text{-5-}^t\text{BuC}_4\text{H}_2\text{N}\}]\text{AlMe}_2$ (35)

A solution of $[2\text{-}\{(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}=\text{CH}\}\text{-5-}^t\text{BuC}_4\text{H}_2\text{NH}]$ (**30**) (6.2 g, 20 mmol) in *n*-hexane (50 mL) was added dropwise to a solution of AlMe_3 (12 g of a 15 % solution in *n*-hexane, 25 mmol) in *n*-hexane (50 mL). After complete addition the solution was warmed slowly to ambient temperature and stirred at r.t. for 16 h. After removal of all volatiles the residue was extracted with *n*-hexane (20 mL). Cooling the extract at -32 °C for 16 h afforded colorless crystals. Yield: 6.3 g (86 %).

Melting point: 117 - 119 °C.

IR (Nujol): $\tilde{\nu}$ = 3116(w), 3068 (w), 2603 (w), 1938 (w), 1874 (w), 1810 (w), 1720 (w), 1597 (s), 1573 (s), 1495 (s), 1395 (m), 1363 (m), 1307 (s), 1271 (s), 1234 (s), 932 (m), 906 (m), 806 (m), 790 (m), 771 (m), 759 (m), 678 (s), 658 (s), 604 (m), 576 (m), 441 (m), 375 (m), 346 (m) cm^{-1} .

^1H NMR (200.13 MHz, C_6D_6): δ 7.44 (s, 1H, N=CH), 7.18 - 7.00 (m, 4 H, aryl, pyrrole), 6.78 (d, 1 H, $J = 3.77$, pyrrole), 6.34 (d, 1 H, $J = 3.77$, pyrrole), 3.20(sept, 2 H, $J = 6.8$ Hz, CHMe₂), 1.35 (s, 9 H, ^tBu), 1.15 (d, 6H, $J = 6.8$ Hz, CHMe₂), 0.92 (d, 6H, $J = 6.8$ Hz, CHMe₂), -0.23 (s, 6H, AlMe₂) ppm

EI-MS: m/z (%) = 366 (M^+ , 20), 351 ($M^+ - \text{Me}$, 100).

Elemental analysis for $\text{C}_{23}\text{H}_{35}\text{AlN}_2$ (366.52 g / mol):

	C	H	N
Calcd.:	75.37	9.62	7.64,
Found:	75.38	9.67	7.56 %.

4.3.20. [η^2 -{2-[(2,6-ⁱPr₂C₆H₃)N=CH]C₄H₃N}]₂AlCl (36)

A solution of [2-{(2,6-ⁱPr₂C₆H₃)N=CH}C₄H₃N]Li (1.3 g, 5.0 mmol) in THF (20 mL) was added dropwise to a solution of AlCl₃ (0.67 g, 5.0 mmol) in THF (20 mL) at -78 °C. After complete addition the resulting solution was warmed slowly to ambient temperature and stirred at r.t. for 16 h. After removal of all volatiles the residue was extracted with toluene (20 mL). Cooling the extract at -32 °C for 20 h afforded colorless crystals. Yield 2.36 g (83 %).

Melting point: 190 - 213 °C.

^1H NMR (200.13 MHz, C_6D_6): δ 7.53 (d, 2 H, $J = 1.16$ Hz, N=CH), 6.85~7.10 (m, 6 H, pyrrole), 6.57 (dd, 2 H, $J = 3.7$ Hz, pyrrole), 6.16 (m, 2 H, pyrrole), 6.01 (dd, 2 H, $J = 3.7$ Hz, pyrrole), 3.67 (sept, 2 H, $J = 6.82$ Hz, CHMe₂) 2.89 (sept, 2 H, $J = 6.8$ Hz, CHMe₂), 1.42 (d, 6 H, $J = 6.75$ Hz, CHMe₂), 1.01 (d, 6 H, $J = 6.84$ Hz, CHMe₂), 0.96 (d, 6 H, $J = 6.87$ Hz, CHMe₂), 0.72 (d, 6H, $J = 6.86$ Hz, CHMe₂) ppm.

MS: m/z (%): 568 ($[M]^+$, 100 %).

IR (Nujol): $\tilde{\nu}$ = 1919 (w), 1854 (w), 1676 (w), 1603 (s), 1585 (s), 1320 (m), 1253 (m), 1171 (m), 1106 (m), 1091 (m), 1068 (m), 1032 (s), 772 (8m), 935 (m), 914 (m), 889 (m), 784 (m), 742 (s), 621 (m), 561 (m) cm^{-1} .

Elemental analysis for $C_{34}H_{42}AlClN_4$ (569.16 g / mol):

	C	H	N
Calcd.:	71.75	7.74	9.84,
Found:	72.05	7.63	9.90 %.

4.3.21. $TpTiF_3$ (39)

To $TpTiCl_3$ (0.37 g, 1.00 mmol) and Me_3SnF (0.56 g, 3.10 mmol) in a 100 mL Schlenk flask, 20 mL of CH_2Cl_2 was added. The resulting suspension was stirred at r.t. for 72 h. After filtration, all the volatiles were removed from the filtrate. The residue was dried *in vacuo* for 4 h, affording a white solid. Yield 0.30 g (94 %).

Melting point: 256 - 260 °C.

IR (Nujol): $\tilde{\nu}$ = 3143 (w), 3127 (w), 2526 (m), 2494 (w), 1787 (w), 1577 (br m), 1504 (m), 1407 (m), 1309 (s), 1215 (s), 1187 (m), 1102 (s), 1079 (m), 1052 (vs), 990 (s), 818 (m), 782 (s), 763 (s), 714 (s), 667 (s), 638 (s), 602 (s).

Elemental analysis for $C_9H_{10}BF_3TiN_6$ (317.90 g / mol):

	C	H	N
Calcd.:	34.00	3.17	26.44,
Found:	34.1	3.38	25.6 %.

MS: m/z (%): 318 ($[M]^+$, 63), 299 ($[M - F]^+$, 8), 201 ($[Tp - BH]^+$, 100).

5. Handling and Disposal of Solvents and Residual Wastes

- ◆ The recovered solvents were distilled or condensed into cold traps under vacuum, collected in halogen-free or halogen-containing solvent containers, and stored for disposal.
- ◆ Deuterated solvents for NMR were classified into halogen-free and halogen-containing solvents and were disposed as heavy metal wastes and halogen-containing wastes, respectively.
- ◆ The heavy metal residues were dissolved in nitric acid and were stored after neutralization in the containers for heavy metal wastes.
- ◆ Drying agents such as KOH, CaCl₂, and P₄O₁₀ were hydrolyzed and deposited as acid or base wastes.
- ◆ Whenever possible, sodium metal used for drying solvents was collected for recycling.^[75] The non-reusable sodium metal was carefully hydrolyzed in cold ethanol and poured into the base-bath used for cleaning glassware.
- ◆ Ethanol and acetone used for solid CO₂ cold-baths were subsequently used for cleaning glassware.
- ◆ The acid-bath used for cleaning glassware was neutralized with Na₂CO₃ and the resulting NaCl solution was washed-off in the water drainage.
- ◆ The residue of the base bath used for glassware cleaning was poured into the container for base wastes.

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

Metal containing wastes	10 L
Halogen-containing solvent wastes	12 L
Halogen-free solvent wastes	35 L
Acid wastes	12 L
Base wastes	20 L

6. Crystal Data and Refinement Details

Compound	1	
Empirical formula	C ₄₀ H ₆₀ F ₈ V ₄	
Formula weight	896.66	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	<i>P</i> $\bar{1}$	
Unit cell dimensions	<i>a</i> = 11.040(4) Å	α = 85.96(5) ^o
	<i>b</i> = 11.173(5) Å	β = 84.12(3) ^o
	<i>c</i> = 18.775(8) Å	γ = 64.96(2) ^o
Volume, <i>Z</i>	2086(2) Å ³ , 2	
Density (calculated)	1.427 Mg/m ³	
Absorption coefficient	0.931 mm ⁻¹	
<i>F</i> (000)	928	
Crystal size	0.7 x 0.4 x 0.1 mm	
θ range for data collection	3.56 to 25.04 ^o	
Limiting indices	-13 ≤ <i>h</i> ≤ 13, -13 ≤ <i>k</i> ≤ 13, -22 ≤ <i>l</i> ≤ 22	
Reflections collected	10841	
Independent reflections	7347 (<i>R</i> _{int} = 0.1457)	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	7334 / 844 / 460	
Goodness-of-fit on <i>F</i> ²	1.035	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0684, <i>wR</i> 2 = 0.1612	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1078, <i>wR</i> 2 = 0.1964	
Largest diff. peak and hole	1.151 and -0.636 e·Å ⁻³	

Compound	3
Empirical formula	C ₇₉ H ₁₂₀ F ₂ Mo ₄ N ₆ O ₄ incl. One pentane
Formula weight	1639.61
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	$a = 33.363(7)$ Å $b = 11.599(2)$ Å $c = 24.355(5)$ Å $\beta = 115.59(3)^\circ$
Volume, Z	8500(3) Å ³ , 4
Density (calculated)	1.291 Mg/m ³
Absorption coefficient	0.631 mm ⁻¹
$F(000)$	3432
Crystal size	0.6 x 0.6 x 0.6 mm
θ range for data collection	3.51 to 22.52°
Limiting indices	$-35 \leq h \leq 26$, $-12 \leq k \leq 12$, $-26 \leq l \leq 25$
Reflections collected	6318
Independent reflections	5517 ($R_{\text{int}} = 0.0302$)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5506 / 0 / 442
Goodness-of-fit on F^2	1.050
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0376$, $wR2 = 0.0835$
R indices (all data)	$R1 = 0.0502$, $wR2 = 0.0959$
Largest diff. peak and hole	0.354 and -0.622 e·Å ⁻³

Compound	9
Empirical formula	C ₄₄ H ₇₃ MoN ₅
Formula weight	768.01
Temperature	132(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	<i>P na</i> 2 ₁
Unit cell dimensions	<i>a</i> = 20.459 Å <i>b</i> = 12.778(12) Å <i>c</i> = 16.916(2) Å
Volume, <i>Z</i>	4422.4(9) Å ³ , 4
Density (calculated)	1.153 Mg/m ³
Absorption coefficient	0.330 mm ⁻¹
<i>F</i> (000)	1656
Crystal size	0.6 x 0.4 x 0.2 mm
θ range for data collection	3.51 to 25.02°
Limiting indices	-24 ≤ <i>h</i> ≤ 24, -15 ≤ <i>k</i> ≤ 15, -20 ≤ <i>l</i> ≤ 20
Reflections collected	9689
Independent reflections	7782 (<i>R</i> _{int} = 0.0227)
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	7772 / 1 / 464
Goodness-of-fit on <i>F</i> ²	1.068
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0300, <i>wR</i> 2 = 0.058
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0397, <i>wR</i> 2 = 0.0649
Largest diff. peak and hole	0.228 and -0.264 eÅ ⁻³

Compound	10
Empirical formula	$C_{38}H_{59}Cl_2MoN_3Si_2$
Formula weight	780.90
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P \bar{1}$
Unit cell dimensions	$a = 12.832(4) \text{ \AA}$ $\alpha = 74.89(2)^\circ$ $b = 13.493(4) \text{ \AA}$ $\beta = 73.061(15)^\circ$ $c = 14.071(5) \text{ \AA}$ $\gamma = 66.709(11)^\circ$
Volume, Z	$2111.2(12) \text{ \AA}^3$, 4
Density (calculated)	1.228 Mg/m ³
Absorption coefficient	0.522 mm ⁻¹
$F(000)$	824
Crystal size	1.00 x 0.60 x 0.40 mm
θ range for data collection	3.54 - 25.03°
Limiting indices	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-16 \leq l \leq 16$
Reflections collected	14824
Independent reflections	7412 ($R_{\text{int}} = 0.0639$)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7410 / 1 / 433
Goodness-of-fit on F^2	1.058
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0312$, $wR2 = 0.0811$
R indices (all data)	$R1 = 0.0339$, $wR2 = 0.0836$
Largest diff. peak and hole	0.354 and $-0.622 \text{ e} \cdot \text{\AA}^{-3}$

Compound	18
Empirical formula	C ₄₂ H ₅₀ F ₂ N ₄ Zn ₂
Formula weight	779.64
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P2₁/n</i>
Unit cell dimensions	$a = 13.026(2)$ Å, $b = 8.8051(12)$ Å $c = 17.309(2)$ Å $\beta = 105.240(11)^\circ$
Volume	1915.5(4) Å ³
<i>Z</i>	2
Density (calculated)	1.352 Mg/m ³
Absorption coefficient	1.296 mm ⁻¹
<i>F</i> (000)	816
Crystal size	0.6 x 0.5 x 0.5 mm ³
θ range for data collection	3.51 to 25.02°
Index ranges	-15 ≤ <i>h</i> ≤ 15, -10 ≤ <i>k</i> ≤ 10, -20 ≤ <i>l</i> ≤ 20
Reflections collected	6762
Independent reflections	3381 [<i>R</i> (int) = 0.0650]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	3380 / 0 / 232
Goodness-of-fit on <i>F</i> ²	1.113
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0272, <i>wR</i> 2 = 0.0702
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0294, <i>wR</i> 2 = 0.0723
Largest diff. peak and hole	0.380 and -0.233 e·Å ⁻³

Compound	19
Empirical formula	C ₄₈ H ₅₈ N ₄ Zn ₂ incl. benzene
Formula weight	821.77
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Fddd</i>
Unit cell dimensions	$a = 16.941(5)$ Å $b = 20.576(3)$ Å $c = 24.918(4)$ Å
Volume	8686(3) Å ³
Z	8
Density (calculated)	1.257 Mg/m ³
Absorption coefficient	1.141 mm ⁻¹
<i>F</i> (000)	3472
Crystal size	0.8 x 0.6 x 0.5 mm ³
Index ranges	-9 ≤ <i>h</i> ≤ 20, -24 ≤ <i>k</i> ≤ 24, -29 ≤ <i>l</i> ≤ 29
Reflections collected	3065
Independent reflections	1915 [<i>R</i> (int) = 0.0279]
Completeness to $\theta = 25.03^\circ$	99.6 %
Max. and min. transmission	0.5993 and 0.4622
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	1915 / 0 / 129
Goodness-of-fit on <i>F</i> ²	1.102
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0309, <i>wR</i> 2 = 0.0787
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0366, <i>wR</i> 2 = 0.0831
Largest diff. peak and hole	0.286 and -0.579 e.Å ⁻³

Compound	26
Empirical formula	C ₇₃ H ₁₀₆ F ₂ Mg ₂ N ₄ O ₂ incl. one molecule of toluene
Formula weight	579.12
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 12.6483(18) Å <i>a</i> = 90° <i>b</i> = 14.298(3) Å <i>b</i> = 95.493(17)° <i>c</i> = 19.117(3) Å <i>g</i> = 90°
Volume	3441.4(9) Å ³
<i>Z</i>	4
Density (calculated)	1.118 Mg/m ³
Absorption coefficient	0.086 mm ⁻¹
<i>F</i> (000)	1260
Crystal size	0.60 x 0.50 x 0.50 mm ³
θ range for data collection	3.51 to 25.02°.
Index ranges	-15 ≤ <i>h</i> ≤ 15, -17 ≤ <i>k</i> ≤ 17, -2 ≤ <i>l</i> ≤ 22
Reflections collected	10081
Independent reflections	6053 [<i>R</i> (int) = 0.0386]
Completeness to $\theta = 25.02^\circ$	99.7 %
Max. and min. transmission	0.9582 and 0.9501
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	6053 / 0 / 396
Goodness-of-fit on <i>F</i> ²	0.996
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0587, <i>wR</i> 2 = 0.1552
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0838, <i>wR</i> 2 = 0.1777
Largest diff. peak and hole	0.401 and -0.359 e.Å ⁻³

Compound	31
Empirical formula	C ₄₂ H ₅₈ N ₄ Zn
Formula weight	684.29
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P \bar{1}$
Unit cell dimensions	$a = 10.295(3) \text{ \AA}$ $\alpha = 75.56(3)^\circ$. $b = 10.464(3) \text{ \AA}$ $\beta = 6.700(19)^\circ$. $c = 19.861(6) \text{ \AA}$ $\gamma = 8.115(12)^\circ$.
Volume	1921.1(10) Å ³
Z	2
Density (calculated)	1.183 Mg/m ³
Absorption coefficient	0.672 mm ⁻¹
$F(000)$	736
Crystal size	1.00 x 0.50 x 0.40 mm ³
θ range for data collection	3.53 to 25.06°
Index ranges	$-12 \leq h \leq 12, -11 \leq k \leq 12, -22 \leq l \leq 23$
Reflections collected	8855
Independent reflections	6778 [$R(\text{int}) = 0.0530$]
Completeness to $\theta = 25.06^\circ$	99.5 %
Max. and min. transmission	0.7748 and 0.5529
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6778 / 0 / 438
Goodness-of-fit on F^2	1.032
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0391, wR2 = 0.0895$
R indices (all data)	$R1 = 0.0445, wR2 = 0.0939$
Largest diff. peak and hole	0.677 and -0.639 e.Å ⁻³

Compound	32
Empirical formula	C ₄₂ H ₅₈ MgN ₄
Formula weight	643.23
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P \bar{1}$
Unit cell dimensions	$a = 10.335(2) \text{ \AA}$ $\alpha = 75.27(3)^\circ$ $b = 10.455(2) \text{ \AA}$ $\beta = 86.82(3)^\circ$ $c = 20.080(4) \text{ \AA}$ $\gamma = 67.87(3)^\circ$
Volume	1941.9(7) Å ³
Z	2
Density (calculated)	1.100 Mg/m ³
Absorption coefficient	0.079 mm ⁻¹
$F(000)$	700
Crystal size	0.60 x 0.40 x 0.30 mm ³
θ range for data collection	3.53 to 25.01°
Index ranges	$-12 \leq h \leq 12, -12 \leq k \leq 12, -23 \leq l \leq 23$
Reflections collected	11636
Independent reflections	6835 [$R(\text{int}) = 0.0443$]
Completeness to $\theta = 25.01^\circ$	99.6 %
Max. and min. transmission	0.9768 and 0.9544
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6835 / 0 / 478
Goodness-of-fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0397, wR2 = 0.1012$
R indices (all data)	$R1 = 0.0452, wR2 = 0.1059$
Extinction coefficient	0.0063(11)
Largest diff. peak and hole	0.270 and -0.219 e.Å ⁻³

Compound	36
Empirical formula	C ₃₄ H ₄₂ AlClN ₄
Formula weight	569.15
Temperature	203(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 20.284(4) Å <i>b</i> = 9.8282(11) Å <i>c</i> = 16.174(3) Å β = 99.89(2)°
Volume	3176.4(8) Å ³
<i>Z</i>	4
Density (calculated)	1.190 Mg/m ³
Absorption coefficient	0.177 mm ⁻¹
<i>F</i> (000)	1216
Crystal size	0.80 x 0.70 x 0.30 mm ³
θ range for data collection	3.53 to 25.04°
Index ranges	-24 ≤ <i>h</i> ≤ 24, -11 ≤ <i>k</i> ≤ 11, -2 ≤ <i>l</i> ≤ 19
Reflections collected	3179
Independent reflections	2818 [<i>R</i> (int) = 0.0216]
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	2812 / 0 / 187
Goodness-of-fit on <i>F</i> ²	1.041
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0329, <i>wR</i> 2 = 0.0820
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0362, <i>wR</i> 2 = 0.0870
Extinction coefficient	0.0121(6)
Largest diff. peak and hole	0.224 and -0.229 e.Å ⁻³

7. The List of Numbered Compounds

No.	Compounds
1	$[\text{Cp}^*\text{V}(\mu\text{-F})_2]_4$
2	$(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{MoF}_2\cdot\text{THF}$
3	$[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_6\text{Mo}_4(\mu_3\text{-F})_2\text{Me}_2(\mu\text{-O})_4]\cdot(\text{C}_5\text{H}_{12})$
4	$[(\text{ArN})_2\text{MoCl}\{\text{N}(\text{R}^1)\text{C}(\text{R}^2)\text{N}(\text{R}^1)\}]$ ($\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{Me}$)
5	$[(\text{ArN})_2\text{MoCl}\{\text{N}(\text{R}^1)\text{C}(\text{R}^2)\text{N}(\text{R}^1)\}]$ ($\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{N}^i\text{Pr}_2$)
6	$[(\text{ArN})_2\text{MoCl}\{\text{N}(\text{R}^1)\text{C}(\text{R}^2)\text{N}(\text{R}^1)\}]$ ($\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{N}(\text{SiMe}_3)$)
7	$[(\text{ArN})_2\text{MoCl}\{\text{N}(\text{R}^1)\text{C}(\text{R}^2)\text{N}(\text{R}^1)\}]$ ($\text{R}^1 = \text{SiMe}_3$, $\text{R}^2 = \text{C}_6\text{H}_5$)
8	$[(\text{ArN})_2\text{MoCl}\{\text{N}(\text{R}^1)\text{C}(\text{R}^2)\text{N}(\text{R}^1)\}]$ ($\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{Me}$)
9	$[(\text{ArN})_2\text{MoCl}\{\text{N}(\text{R}^1)\text{C}(\text{R}^2)\text{N}(\text{R}^1)\}]$ ($\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{N}^i\text{Pr}_2$)
10	$[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\text{MoCl}_2]\cdot[\text{NH}=\text{C}(\text{C}_6\text{H}_5)\text{CH}(\text{SiMe}_3)_2]$
11	$[\{\text{HC}(\text{CMeNAr})_2\}\text{VF}_2]$ ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$)
12	$[\text{Me}_2\text{N}(\text{CH}_2)_2\text{N}(\text{Me})\text{ZnH}]_2$
13	$[\{\eta^3\text{-HB}(3\text{-R-C}_3\text{N}_2\text{H}_2)_3\}\text{ZnH}]$ ($\text{R} = t\text{Bu}$)
14	$[(\text{Me}_3\text{PN})\text{ZnH}]_4\cdot 4\text{THF}$
15	$[\{\eta^3\text{-HB}(3\text{-R-5-Me-C}_3\text{N}_2\text{H}_2)_3\}\text{ZnF}]$ ($\text{R} = p\text{Tol}$)
16	$[(\text{Cp}^*\text{TiF}_3)_8(\text{ZnF}_2)_3]$
17	$[(\text{Cp}^*\text{TiF}_3)_4(\text{MeZnF})_2]$
18	$[\{\text{HC}(\text{CMeNAr})_2\}\text{Zn}(\mu\text{-F})_2]$
19	$[\{\text{HC}(\text{CMeNAr})_2\}\text{Zn}(\mu\text{-H})_2]$
20	$[(\text{MesInF}_2)_{10}\text{MgF}\cdot 5\text{toluene}]$ ($\text{Mes} = 2,4,6\text{-trimethylphenyl}$)
21	$[\text{Cp}^*_4\text{Ti}_4\text{Mg}_2\text{F}_{12}\cdot 7\text{THF}]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$)
22	$[\text{Na}_3\text{Mg}(\text{O}_3\text{PCH}_2\text{PO}_3)(\mu\text{-F})\cdot\text{H}_2\text{O}]$
23	$[\{\text{HC}(\text{CMeNAr})_2\}\text{Mg}(\mu\text{-Me})_2]$
24	$[\{\text{HC}(\text{CMeNAr})_2\}\text{MgMe}(\text{THF})]$
25	$[\{\text{HC}(\text{CMeNAr})_2\}\text{Mg}(\mu\text{-F})_2]$ ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$)
26	$[\{\text{HC}(\text{CMeNAr})_2\}\text{Mg}(\mu\text{-F})(\text{THF})_2]$ ($\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$)
27	$[2\text{-}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}=\text{CH})\text{-}6\text{-}^t\text{BuC}_6\text{H}_3\text{OH}]$

- 28 [2-(2,6-*i*-Pr₂C₆H₃N=CH)-6-*t*-BuC₆H₃O]₂Zn
- 29 [2-(2,6-*i*-Pr₂C₆H₃N=CH)-6-*t*-BuC₆H₃O]ZnMe
- 30 [2-{(2,6-*i*-Pr₂C₆H₃)N=CH}-5-*t*-BuC₄H₂NH]
- 31 [2-{(2,6-*i*-Pr₂C₆H₃)N=CH}-5-*t*-BuC₄H₂N]₂Zn
- 32 [2-{(2,6-*i*-Pr₂C₆H₃)N=CH}-5-*t*-BuC₄H₂N]₂Mg
- 33 [2-{(2,6-*i*-Pr₂C₆H₃)N=CH}-C₄H₂NH]
- 34 [2-{(2,6-*i*-Pr₂C₆H₃)N=CH}-C₄H₂N]AlMe₂
- 35 [2-{(2,6-*i*-Pr₂C₆H₃)N=CH}-5-*t*-Bu-C₄H₂N]AlMe₂
- 36 [2-{(2,6-*i*-Pr₂C₆H₃)N=CH}-C₄H₂N]₂AlCl
- 37 [2-{(2,6-*i*-Pr₂C₆H₃)N=CH}-C₄H₂N]AlCl₂
- 38 TpTiCl₃
- 39 TpTiF₃

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