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Review

Fluorine functionalized compounds of group 13 elements

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Abstract

The review gives a short survey of some developments in the synthetic chemistry of organoaluminum fluorides. Into the focus is brought the Janus-faced Lewis base–Lewis acid Al compound, group 13 difluorodiorganometalates, fluorine functionalized carbaalane derivatives, fluorination of aluminum imide clusters, diamidoaluminum fluoride, and some group 13 β-diketiminate mono- and difluorides.

Keywords: Group 13 elements; Fluorine; Al–F bonds; Organometallic fluorides; Fluorinating agents

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1. Introduction

Aluminum, the most abundant metal in the earth's crust is valuable as the metal itself or in the form of its various compounds as important chemical substances in modern research. Natural abundance of aluminum is mostly due to its numerous oxide and oxide–hydroxide minerals for example, corundum Al_2O_3, spinel $MgAl_2O_4$, bauxite $AlO_n(OH)_{3-2n}$ ($0 < n < 1$), diaspore α-AlO(OH) and the fluoride containing cryolite Na_3AlF_6 [1]. The naturally occurring compounds of aluminum are essentially inorganic in nature and therefore, the metal itself and many of its minerals can be dissolved in acids and bases forming salts and aluminates, respectively [1]. However, these are either insoluble or sparingly soluble in polar organic solvents. Some of these minerals are beautiful gemstones and the aluminum compounds have useful applications in ceramics and as catalysts or catalysts support in heterogeneous catalysis. In order to meet one of the basic requirements of the new era of organometallic chemistry the metal complexes should have considerable solubility in organic solvents. This can be achieved very easily by incorporating an organic envelop around the metal atom. Good solubility of metal compounds helps to explore new reactions and usage of these compounds especially in homogeneous catalysis [2–6]. In this manner a variety of soluble systems of Al have been developed some of which have very good catalytic activity for olefine polymerization in homogeneous catalysis [7,8].

The aluminum trifluoride $(AlF_3)_x$ has attracted chemists attention for many decades due to its industrial application although it is an involatile and highly insoluble compound [9,10]. Analogous to the preparation of soluble aluminum compounds such as hydroxides [11–14], chlorides [15], and

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alumoxanes [16] it was also a synthetic challenge to synthesize soluble aluminum fluorides. This development gave rise to an important class of organoaluminum fluorides where the aluminum atom is bonded to one or more carbon atoms and other aluminum fluorides where aluminum is also connected to nitrogen atom(s) [17–25]. Replacement of one or two of the fluorine atoms with carbon atoms alters the physical properties of the molecules as the trialkyl and triaryl derivatives of aluminum are volatile liquids or low melting solids, e.g. Al_2Me_6 (mp 15 °C, bp 126 °C) compared to $(AlF_3)_x$ which is involatile (mp 1290 °C). Similarly the solubility of these compounds was also improved with organic groups on aluminum. R_2AlF (R = Me, Et) are soluble compounds whereas AlF_3 is nearly insoluble in spite of the fact that the former compounds are tetrameric [26].

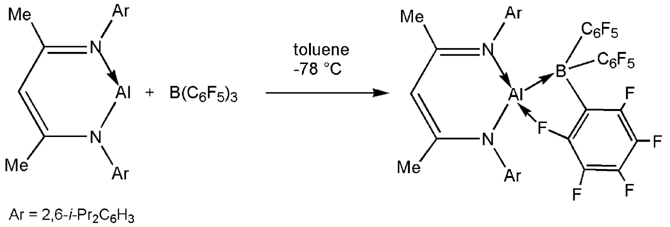
With small or moderately small organic groups on aluminum although the solubility problem was circumvented to some extent the rational syntheses of monomeric organoaluminum fluorides were still desired. We have been interested in this aspect of synthesis of organoaluminum fluorides and our approach has been to utilize carbon based bulky ligands which not only offer better solubility but also the steric bulkiness of the ligand prevents the dimerization or higher aggregation in these systems.

The purpose of this review is to give the reader a short summary of the latest accomplishments by our group in the area of group 13 fluorides especially those of aluminum.

In each of the following sections is given the introductory remark followed by the ^{19}F NMR and necessary X-ray crystal structure description of the respective fluorides.

2. Janus-faced aluminum

Aluminum compounds with Al in the formal oxidation state (+3) are Lewis acids [27] whereas Al in oxidation state (+1) has a dual behaviour and can act as a Lewis base and Lewis acid [28–30]. This property of the latter compound has been postulated based on the results of the ab initio calculations on the [LAl] species [31] [L = HC{(CMe)(2,6-*i*$Pr_2C_6H_3N$)}$_2$]. An orbital with a lone pair of electrons on Al with a quasi-trigonal-planar geometry gives Lewis base character to the molecule and charge depletion close to Al in the semi-planar C_3N_2Al six-membered ring supports the Lewis acidic character [31]. However, there was not a discrete example of such a molecule which shows both the Lewis base and Lewis acid behaviour of the Al atom until we reported the molecule $[LAlB(C_6F_5)_3]$ [32]. This molecule shows a donor Al → B bond and simultaneously also exhibits an acceptor F → Al bond. Therefore, it acts both as a Lewis base and a Lewis acid like the Roman god Janus, who has two faces facing in opposite directions that symbolizes two completely different scenarios. As depicted in Scheme 1, $[LAlB(C_6F_5)_3]$ has been prepared by the reaction of the monomeric Al(I) species [LAl] with $B(C_6F_5)_3$. The ^{19}F NMR of this molecule shows nine partly overlapped resonances (in the range −124.28 to −160.99) indicating distorted $B(C_6F_5)_3$ moiety due to an Al–F interaction, consequently, resulting in magnetically different fluorine atoms on the C_6F_5 rings. No signal was observed in the ^{27}Al NMR of this molecule in solution but solid state measurement of this molecule exhibited a resonance at δ −50 ppm. The ^{11}B NMR spectra shows a resonance at δ −26.52 ppm [32].



Scheme 1. Preparation of the $[LA1B(C_6F_5)_3]$, a compound with Janus-faced aluminum.

Single crystal X-ray analysis of the molecule $[LAlB(C_6F_5)_3]$ shows that it crystallizes in the triclinic space group $P\bar{1}$. One of the *ortho* fluorine atoms of the $B(C_6F_5)_3$ system interacts intramolecularly with the Al atom thus forming a five-membered $AlBC_2F$ ring (Fig. 1). The two nitrogen atoms of the ligand, the boron atom, and the fluorine atom make a distorted tetrahedral arrangement around the Al center. Formation of the donor–acceptor bond results in considerable decrease in the Al–N bond lengths due to the partial transfer of the lone pair of electrons to the aluminum center (av 1.892(6) Å) as compared to the Al–N distances in [LAl] (av 1.957 Å). The change in the electron density on the aluminum center is also due to the relatively close Al–F interaction (2.156(2) Å). The Al → B bond length (2.183(3) Å) in $[LAl \rightarrow B(C_6F_5)_3]$ is slightly longer than that in $[Cp^*Al \rightarrow B(C_6F_5)_3]$ (2.169(2) Å) [29] moreover, the geometry of the $B(C_6F_5)_3$ moiety in the former changed to distorted tetrahedral from trigonal planar. This is also evident in the sum of the C–B–C bond angles around the

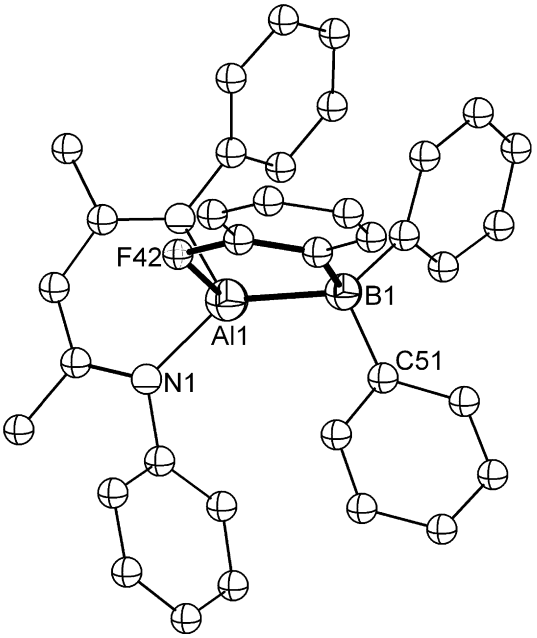


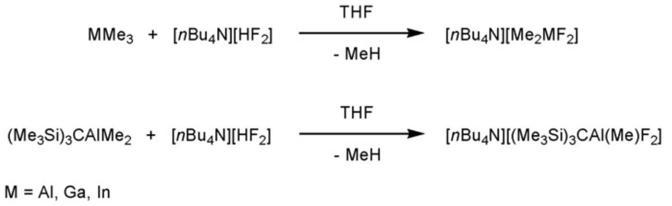
Fig. 1. Single crystal X-ray structure of $[LAlB(C_6F_5)_3]$. Thermal ellipsoids are drawn at 50% probability, hydrogen atoms, *iso*-propyl groups on N-phenyl rings, fluorine atoms on B-phenyl rings except the one interacting with the Al atom have been omitted for clarity.

boron atom (330.3(2)°) which is the smallest of those reported for $B(C_6F_5)_3$ compounds (333.5(2)–342.2(2)°). The Al–F interaction is also supported by the lengthening of the C–F bond (1.414(6) Å) relative to the other 14 C–F bonds (av 1.355 Å).

3. Group 13 difluorodiorganometalates

Group 13 difluorodiorganometalates are relatively rare compounds compared to other group 13 organofluorides, in spite of the fact that they have been known since 1955 [33,34], due to the lack of any straight forward synthesis of these anions. We have reported on the synthesis, X-ray crystal structure, and other spectroscopic properties of some group 13 difluorodiorganometalates $[nBu_4N][R_2MF_2]$ (M = Al, Ga, In). The trialkyl derivatives of group 13 metals when treated with tetra-*n*butylammonium hydrogen difluoride (TBADF) resulted in methane evolution and in the addition of two fluoride anions to the metal center [20] as shown in Scheme 2.

^{19}F NMR spectroscopy is an important tool for the characterization of these molecules and the resonances appear at δ −154.8, −164.8, and −180.9 ppm for the Al, Ga, and In compounds in $[Me_2MF_2]^-$, respectively. This is also consistent with the higher field shift in the Al, Ga, In series. The ^{27}Al NMR value for $[nBu_4N][Me_2AlF_2]$ (δ 123.8 ppm) is typical to that for four coordinated Al compounds. $[Me_2AlF_2]^-$ reacts with water with evolution of gas, whereas $[Me_2GaF_2]^-$ and $[Me_2InF_2]^-$ are stable when exposed to water.



Scheme 2. Preparation of group 13 difluorodiorganometalates.

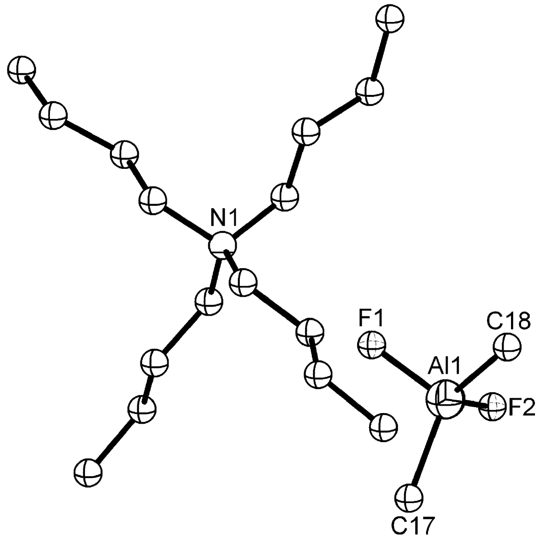


Fig. 2. Molecular structure of tetra-*n*butyl difluorodimethylaluminate. Thermal ellipsoids shown at 50% probability, hydrogen atoms have been omitted for clarity.

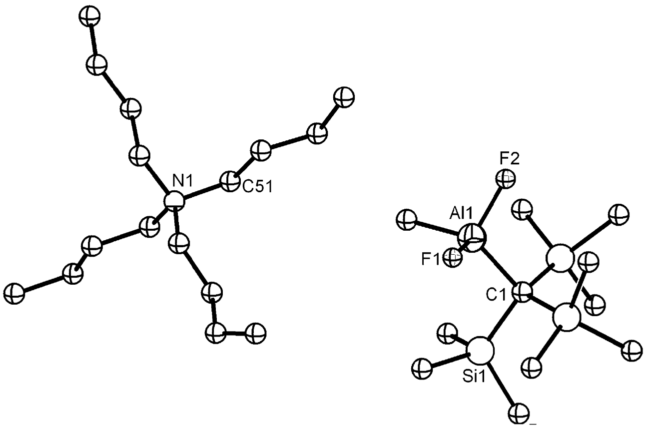


Fig. 3. Molecular structure of tetra-*n*butyl tris(trimethylsilyl)methyldifluoromethylaluminate. Thermal ellipsoids shown at 50% probability, hydrogen atoms have been omitted for clarity.

The compounds $[nBu_4N][Me_2MF_2]$ (M = Al, Ga, In) are isomorphous and crystallize in the monoclinic space group $P2_1/n$ whereas $[nBu_4N][(Me_3Si)_3CAl(Me)F_2]$ crystallizes in the monoclinic space group $P2_1/c$. The metal centers in each of these compounds reside in a distorted tetrahedral environment (Figs. 2 and 3). The Al–F distance (Table 1) is longer than the single bond Al–F distances (1.618–1.657 Å) [21] whereas the Ga–F (1.838 and 1.83 Å) and In–F (2.040 and 2.047 Å) bonds exhibit normal bond distances.

4. Carbaalane fluorine derivatives

Carbaalanes are polyhedral cluster compounds having carbon and aluminum as basic constituents. The first structurally characterized carbaalane $(AlMe)_8(CCH_2Ph)_5H$ was reported by Uhl and co-workers. It had been prepared by the hydroalumination reaction between excess of Me_2AlH and $Me_2AlC{\equiv}CPh$ at 80 °C for 2 days. The reaction steps involve repeated hydroalumination of the aluminum acetylide and the condensation reaction with the concomitant release of Me_3Al [35,36]. Based on the discovery of a facile synthesis of carbaalanes by our group, which involves the hydroalumination reaction on monosubstituted acetylenes with $AlH_3{\cdot}NMe_3$ [37]. We became interested to further explore the reaction chemistry of these carbaalane clusters. We have achieved the carbaalanes via the deprotonation of the acidic acetylenic hydrogen atom followed by the elimination of hydrogen. Subsequent regioselective hydroalumination reaction on this intermediate leads to the formation of $RCH_2C(AlH_2{\cdot}NMe_3)_3$ (R = Ph, Me_3SiCH_2, ferrocenyl), which undergo condensation reaction to yield the carbaalane [37,38]. The hydride functionalities on the carbaalane core can be functionalized in the inner and outer sphere in a step wise manner using appropriate reagents to prepare halogen substituted carbaalanes that also reveals the robust nature of these clusters. Thus, the hydride to fluoride metathesis of $[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ was performed with 6 equiv of

Table 1
Summary of the spectroscopic details and important bond parameters of group 13 organofluorides

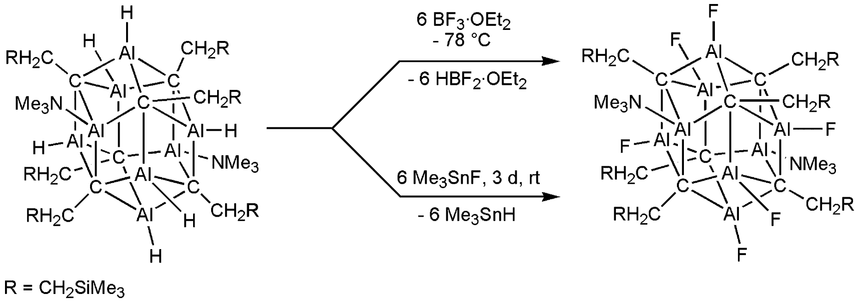
S. No.	Compound	^{19}F NMR	^{27}Al NMR	X-ray crystal structure	M–F (Å)	Ref.
1	$[LAlB(C_6F_5)_3]$	9 signals from −124.28 to −160.99	-50^d	Triclinic, $P\bar{1}$	2.156	[32]
2	$[n\text{Bu}_4\text{N}][\text{Me}_2\text{AlF}_2]$	-154.82^a	123.8^b	Monoclinic, $P2_1/n$	1.711, 1.713	[35]
3	$[n\text{Bu}_4\text{N}][\text{Me}_2\text{GaF}_2]$	-164.76^b	–	Monoclinic, $P2_1/n$	1.838, 1.839	[35]
4	$[n\text{Bu}_4\text{N}][\text{Me}_2\text{InF}_2]$	-180.87^a	–	Monoclinic, $P2_1/n$	2.040, 2.047	[35]
5	$[n\text{Bu}_4\text{N}][(\text{Me}_3\text{Si})_3\text{CAl(Me)F}_2]$	-145.93^c	–	Monoclinic, $P2_1/c$	1.680, 1.702	[35]
6	$[(AlF)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$	-181.5^c	122.3^c		–	[40]
7	$[(AlF)_6(AlNMe_3)_2(CCH_2Ph)_6]$	–	–	Monoclinic, $P2_1/n$	1.667, 1.668, 1.669	[40]
8	$[\{(1\text{-Adamantyl})\text{CH}_2\text{NAl}\}_7\text{H}_{4.74}\text{F}_{2.26}]$	−163.9, −162.8, −162.1	–	Triclinic, $P\bar{1}$	1.506, 1.616, 1.475	[48]
9	$[(t\text{BuNCH}_2\text{AlF})_4]$	-155.7^e	–	Monoclinic, $P2_1/n$	1.666	[48]
10	$[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}]_2(\text{CH}_2)_3\text{AlF(NMe}_3)$	-175.4^c	–	Monoclinic, $P2_1/n$	1.678	[51]
11	$\text{HC}\{(\text{CMe})(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\}_2\text{Al(Me)F}$	8.6^c	–	Monoclinic, $P2_1/c$	1.679	[57]
12	$\text{HC}\{(\text{CMe})(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\}_2\text{AlF}_2$	6.8^c	66.9^c	Monoclinic, $P2_1/n$	1.655, 1.650	[57]
13	$\text{HC}\{(\text{CMe})(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})\}_2\text{GaF}_2$	38.34^c	–	Monoclinic, $P2_1/n$	1.773, 1.755	[57]

^{19}F NMR spectrum for entries 1–6 and 8–10 were measured with respect to $CFCl_3$ and 11–13 were measured with respect to C_6F_6 standard, respectively, in [a]THF–D_8, [b]CD_3CN, [c]C_6D_6, [d]solid sample, [e]$CDCl_3$.

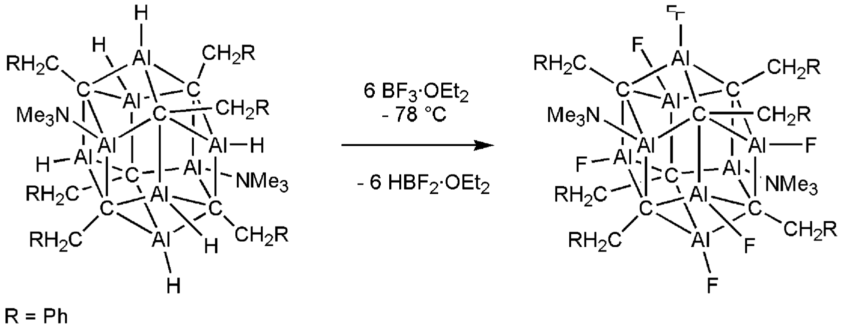
$BF_3\cdot OEt_2$ in toluene at −78 °C under slow warming to room temperature to afford $[(AlF)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ [39]. The same product can also be obtained by using Me_3SnF instead of $BF_3\cdot OEt_2$ [39] as shown in Scheme 3.

The ^{19}F NMR of this molecule shows a broad resonance at δ −181.5 ppm (Table 1) that is consistent with the symmetrical structure and high field region for the terminal Al–F bonds along with a shoulder peak (δ −178) from a small amount of the pentafluorinated species. It can be compared with the tetra coordinated aluminum fluoride $[Me_4N][AlF_4]$ (δ −194.9) [17], which is shifted more upfield than $[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$. The resonance in the ^{27}Al NMR for this compound is strongly shifted upfield to δ 122.3 ppm compared to the parent compound $[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (δ 142.3 ppm).

Fluorination of the carbaalane $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$ with an excess of $BF_3\cdot OEt_2$ in boiling toluene resulted in the substitution of all the hydrides by fluorides to yield $[(AlF)_6(AlNMe_3)_2(CCH_2Ph)_6]$ as shown in Scheme 4. Due to the poor solubility of this compound spectroscopic characterization could not be done. However, single crystal X-ray analysis shows that the compound crystallizes in the monoclinic space group $P2_1/n$ (Fig. 4). The core structure of the molecule consists of a cube of eight aluminum atoms where



Scheme 3. Fluorination of the carbaalane cluster $[(AlH)_6(A1NMe_3)_2(CCH_2CH_2SiMe_3)_6]$.



Scheme 4. Synthesis of the carbaalane cluster $[(AlF)_6(A1NMe_3)_2(CCH_2Ph)_6]$.

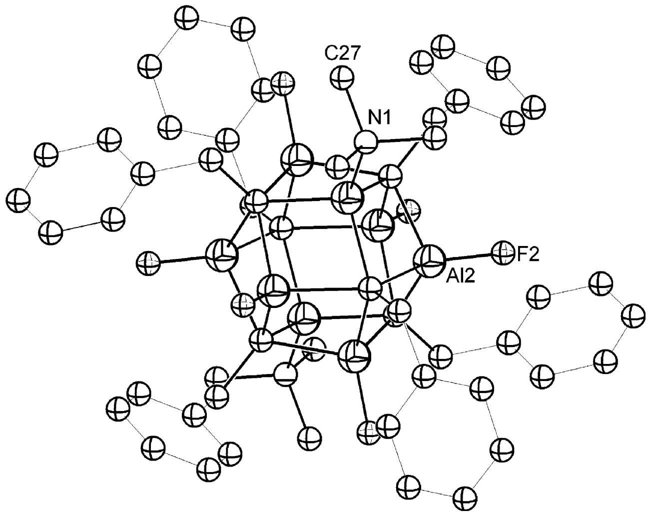


Fig. 4. Molecular structure of the carbaalane fluoro derivative $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$. Thermal ellipsoids shown at 50% probability, hydrogen atoms and toluene molecules have been omitted for clarity.

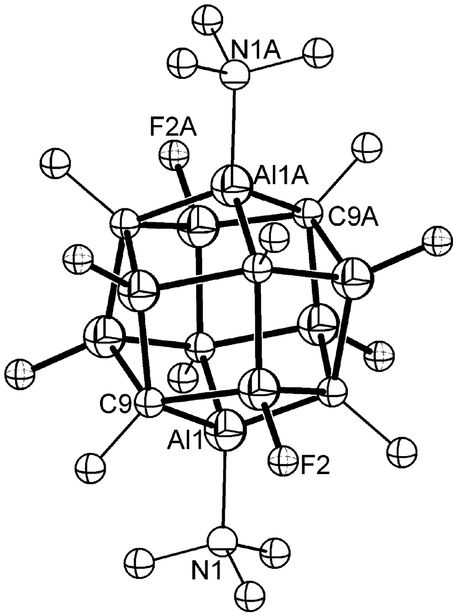


Fig. 5. Molecular structure of the core of the carbaalane fluoro derivative $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$. Thermal ellipsoids shown at 50% probability, hydrogen atoms, toluene molecules, and the phenyl groups on peripheral carbon atoms have been omitted for clarity.

each face is occupied by a carbon atom attached to a CH_2Ph group (Fig. 5). The aluminum atoms on diagonally opposite sides of the cluster are coordinated to a NMe_3 unit. The remaining aluminum atoms are bonded to the fluorine atoms [39]. The Al–F distances in this compound vary from 1.667(2) to 1.669(3) Å (Table 1) and are comparable to those for single bond Al–F distances (1.618–1.657 Å) [21].

5. Surface fluorination of the heptameric aluminum imide clusters

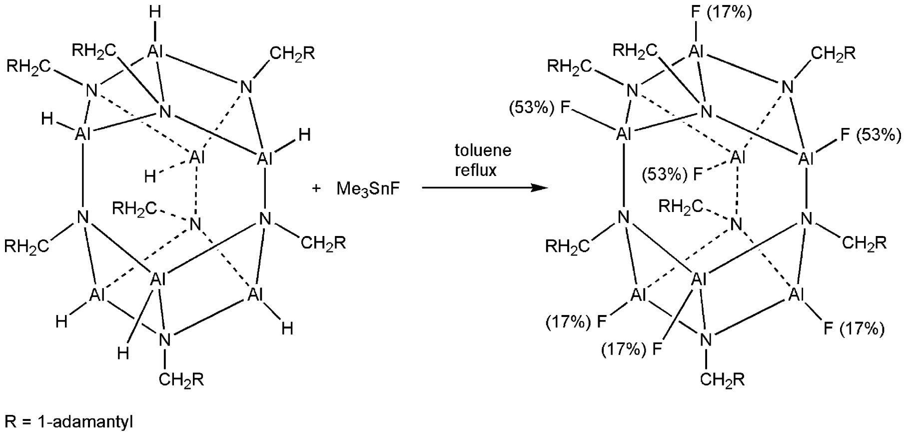
Compounds containing Al–N bonds are important due primarily to their various applications as reducing agents [40], important synthetic intermediates [41,42] and as precursor for chemical vapour deposition of aluminum nitride [43]. This class of compounds containing Al–N bonds also incorporate aluminum imide clusters which are oligomeric in nature and are of the composition $(RNAlH)n$ ($n = 4$, 6, or 8) [44–46]. The rational synthesis of the $n = 7$ derivative $(RCH_2NAlH)_7$ by our group adds an important compound to this series with R = 1-adamantyl [47]. Thus, the reaction of (1-adamantyl)cyanide with an excess of $AlH_3{\cdot}NMe_3$ afforded the heptameric aluminum imide cluster $[(1\text{-adamantyl})CH_2NAlH]_7$. We utilized this molecule to functionalize the hydrides by fluorides in a manner similar to that applied for the carbaalane clusters. This involves the treatment of $[(1\text{-adamantyl})CH_2NAlH]_7$ with Me_3SnF [47]. However, this reaction resulted only in partial fluorination and yields a compound of an average composition $[(1\text{-adamantyl})CH_2NAl]_7F_{2.26}H_{4.74}$ having an asymmetric Al_7N_7 core as shown in Scheme 5. The cage like structure is formed due to the bonding of each nitrogen atom to three aluminum atoms. Higher fluorination of this molecule or use of excess of Me_3SnF leads to the decomposition of the core structure mainly due to the steric demand of the 1-adamantyl group.

In the ^{27}Al NMR spectrum no resonance was detected due to the quadruple moment of the aluminum whereas ^{19}F NMR of this molecule shows three resonances at δ −163.89, −162.77, and −162.15 ppm which is due to the asymmetric structure of the molecule as revealed by the single crystal X-ray structural analysis. This molecule crystallizes in the triclinic space group $P\bar{1}$ with the Al–F distances of 1.506(13), 1.616(3), and 1.475(16) Å. These fluorine atoms have an occupancy factor of 17, 53 and 53%, respectively. The remaining groups are non-replaced hydrides.

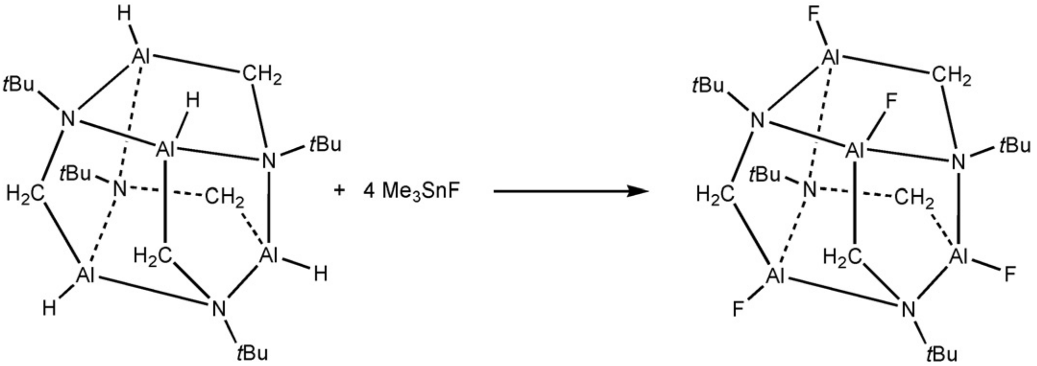
In contrast to the fluorination of $(1\text{-adamantyl})CH_2NAlH)_7$ cluster the fluorination of $(t\text{BuNCH}_2\text{AlH})_4$ proceeds smoothly and integrity of the $Al_4C_4N_4$ core is retained after fluorination [47]. Thus, the tetra fluoro compound $(t\text{BuNCH}_2\text{AlF})_4$ containing terminal Al–F units was obtained by the treatment of the corresponding hydride $(t\text{BuNCH}_2\text{AlH})_4$ with Me_3SnF as depicted in Scheme 6. The ^{19}F NMR of this molecule exhibits a resonance at δ −155.74 ppm. This molecule crystallizes in the monoclinic space group $P2_1/n$. The Al–F distance in this molecule is found to be 1.666(10) Å, which is not very different to the range (1.618–1.657 Å) observed for terminal aluminum fluorides [21].

6. A diamidoaluminum fluoride

Molecular aluminum hydrides have been shown to be very effective in the synthesis of interesting aluminum chalcogenides and compounds such as $LAl(SeH)_2$ [48], $[LAl(SeH)]_2Se$ [48], and $LAl(SH)_2$ [49] could be isolated all starting from $LAlH_2$ and the corresponding chalcogen. In the same way aluminum hydrides are interesting precursor for halide metathesis reactions (see next section), especially for the fluorination reactions. A bulky chelating diamidoaluminum monohydride $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}]_2(\text{CH}_2)_3\text{AlH}(\text{NMe}_3)$ was recently investigated by our group for a metathesis reaction



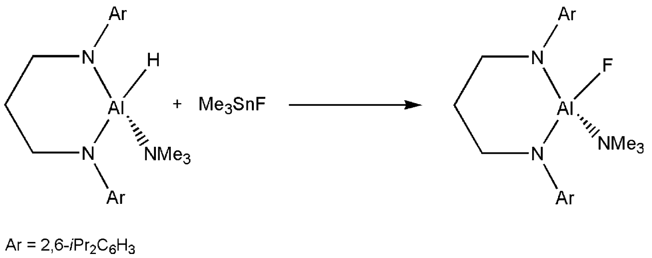
Scheme 5. Fluorination of the aluminum imide cluster [(1-adamantyl)CH_2NA1H]$_7$.



Scheme 6. Synthesis of the tetra fluoro aluminum compound (tBuNCH_2AlF)$_4$.

with Me_3SnF as shown in Scheme 7. The resulting complex $[(2,6\text{-}i\text{Pr}_2C_6H_3)N]_2(CH_2)_3AlF(NMe_3)$ is monomeric where NMe_3 provides the fourth coordination site to the aluminum center [50].

The ^{19}F NMR spectrum of this compound exhibits a singlet at δ −175.4 ppm indicating the terminal nature of the Al–F bond which is consistent with the closely related compounds [ArN{Si(R)Me$_2$}AlF$_2$·THF] (R = Me, δ −178.1 ppm; R = iPr, δ −177.0 ppm; R = tBu, δ −175.1 ppm; Ar = 2,6-iPr$_2$C$_6$H$_3$) [51]. This molecule crystallizes in the monoclinic space group $P2_1/n$. The single crystal X-ray structure of this molecule reveals that the diamide ligand chelates through its nitrogen atoms to the aluminum atom to form a six-membered AlC_3N_2 ring, the third coordination is provided by the fluorine atom and the fourth by the NMe_3 group. The geometry around the Al atom is distorted tetrahedral (Fig. 6). The Al–F distance of 1.678(1) Å is in the range (1.618–1.657 Å) for terminal aluminum fluorides [21].



Scheme 7. Preparation of the diamidoaluminum monofluoride.

7. Group 13 β-diketiminate fluorides

The β-diketiminate ligands incorporate the metal atoms as part of a stable C_3N_2M six-membered ring due to its bidentate

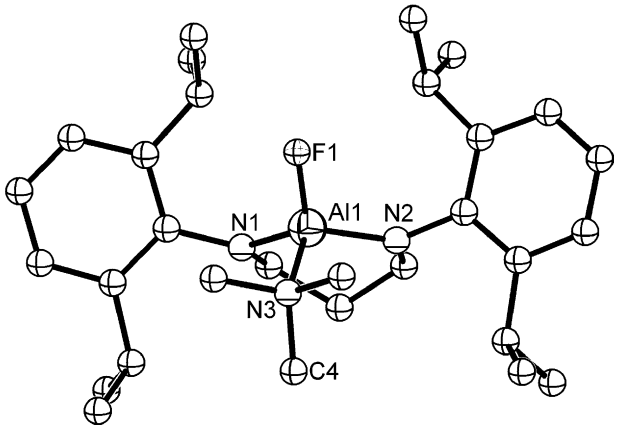
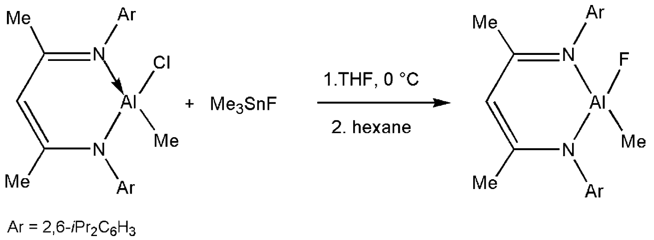
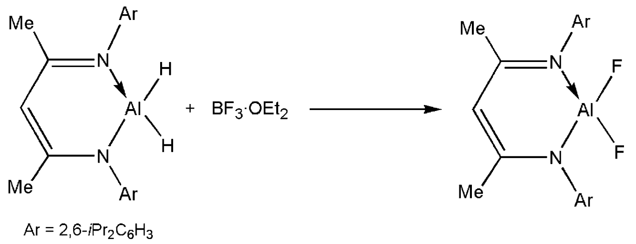


Fig. 6. Single crystal X-ray structure of the diamidoaluminum monofluoride. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms have been omitted for clarity.



Scheme 8. Preparation of the β-diketiminate methylaluminumfluoride.

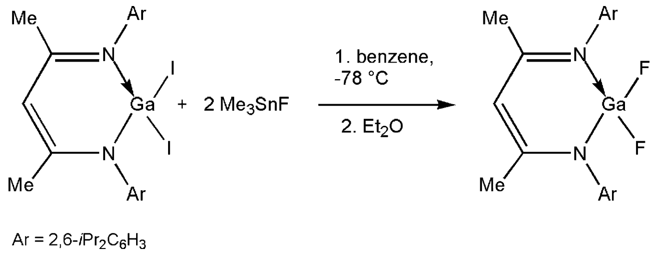


Scheme 9. Preparation of the β-diketiminate aluminum difluoride.

chelating ability through its two nitrogen atoms. Additionally, the steric property of the ligand works synergetically to its electronic factors offering an unique possibility to stabilize the low coordination number at the metal center or low oxidation states [31,52–54]. The mono- and dihalides of Al and Ga synthesized recently by our group are interesting compounds and have been utilized to prepare the corresponding hydroxides [12,14], thiols [49], and amides [55]. Similarly we have also shown that the metathesis reaction of these compounds with suitable fluorinating agents can lead to the formation of the corresponding fluorine derivatives [56]. The reagents Me_3SnF and $BF_3 \cdot OEt_2$ have been very useful in this regard.

The reaction of LAl(Me)Cl with Me_3SnF in THF results in the complete conversion to the corresponding fluorine derivative LAl(Me)F (Scheme 8) which was characterized by its ^{19}F NMR where the Al–F resonates at δ 8.6 ppm. Methyl protons of Al–Me moiety are coupled to the F atom and are observed as a doublet (δ −0.82 ppm).

When $LAlH_2$ was treated with $BF_3 \cdot OEt_2$ at low temperature and allowed to warm to room temperature the difluoride derivative $LAlF_2$ was isolated (Scheme 9). A singlet in the ^{19}F NMR of $LAlF_2$ (δ 6.8 ppm) confirms the formation of Al–F bonds with symmetrically placed F atoms on Al. The corresponding gallium compound $LGaF_2$ was synthesized by the reaction of $LGaI_2$ with Me_3SnF as shown in Scheme 10. The ^{19}F NMR of $LGaF_2$ exhibits the Ga–F to resonate at δ 38.3 ppm.



Scheme 10. Preparation of the β-diketiminate supported gallium difluoride.

The β-diketiminate Al and Ga fluorides have also been investigated by the single crystal X-ray diffraction method. Compound LAl(Me)F crystallizes in the monoclinic space group $P2_1/c$ whereas $LAlF_2$ and $LGaF_2$ are isomorphous and crystallize in the monoclinic space group $P2_1/n$. In all the three compounds the metal atom exhibits a distorted tetrahedral geometry and is part of the nearly planar C_3N_2M six-membered ring (Figs. 7–9). The C–C and C–N distances lie within narrow ranges 1.394–1.410 and 1.325–1.346 Å, respectively, indicating a considerable multiple bond character due to the delocalization in these bonds [56]. The Al–C and Al–F distances in LAl(Me)F are 1.944(2) and 1.679(1) Å, respectively. The Al–F distances in $LAlF_2$ (1.656(1) and 1.650(1) Å) are typical for terminal bonds and are comparable to those in the range from 1.657 to 1.618 Å [21]. The Ga–F distances in $LGaF_2$ (1.755(2) and 1.773(2) Å) are considerably shorter than those found in $[Mes_2Ga(F)(tBuNH_2)]$ (1.838(3) Å) [57] and $(Mes_2GaF)_2$ (1.947(2) Å [58].

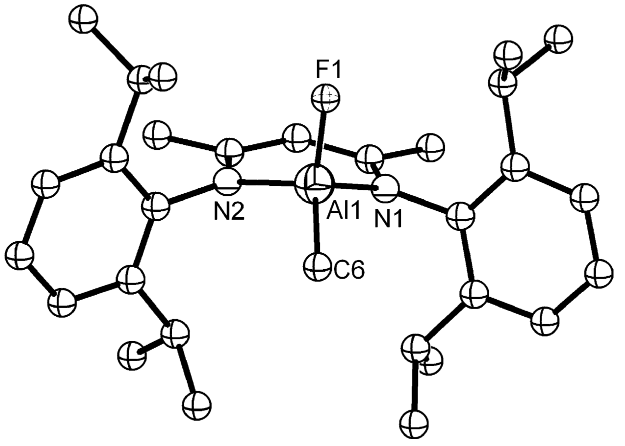


Fig. 7. Molecular Structure of the β-diketiminate aluminum monofluoride. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms have been omitted for clarity.

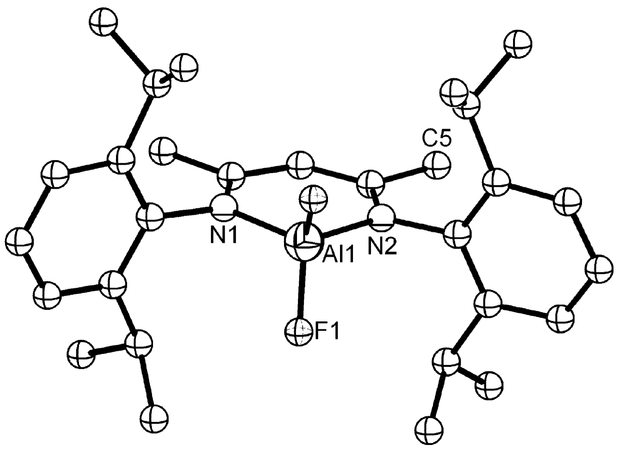


Fig. 8. Molecular Structure of the β-diketiminate aluminum difluoride. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms have been omitted for clarity.

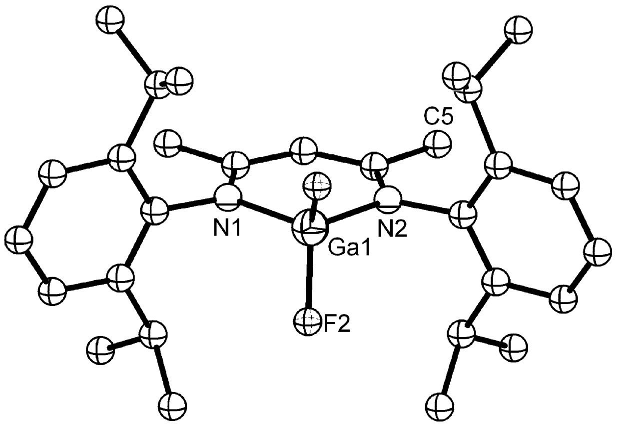


Fig. 9. Molecular Structure of the β-diketiminate gallium difluoride. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms have been omitted for clarity.

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References

[1] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, first ed., Pergamon Press, Oxford, 1984.
[2] E.Y.-X. Chen, M.V. Metz, L. Li, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 120 (1998) 6287–6305.
[3] H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. 34 (1995) 1143–1170.
[4] R.F. Jordan, J. Mol. Catal. 128 (1998) 1–337.
[5] W. Kaminsky (Ed.), Metalorganic Catalysts for Synthesis and Polymerization: Recent Results by Ziegler-Natta and Metallocene Investigations, Springer-Verlag, Berlin, 1999.
[6] R.F. Jordan, Adv. Organomet. Chem. 32 (1991) 325–387.
[7] C.J. Harlan, S.G. Bott, A.R. Barron, J. Am. Chem. Soc. 117 (1995) 6465–6474.
[8] M. Watanabi, N. McMahon, C.J. Harlan, A.R. Barron, Organometallics 20 (2001) 460–467.
[9] J. Lucas, F. Smektala, J.L. Adam, J. Fluorine Chem. 114 (2002) 113–118.
[10] G. Scholz, R. Stösser, J.A. Momand, A. Zehl, J. Klein, Angew. Chem. Int. Ed. 39 (2000) 2516–2519.
[11] H.W. Roesky, S. Singh, V. Jancik, V. Chandrasekhar, Acc. Chem. Res. 37 (2004) 969–981.
[12] G. Bai, Y. Peng, H.W. Roesky, J. Li, H.-G. Schmidt, M. Noltemeyer, Angew. Chem. Int. Ed. 42 (2003) 1132–1135.
[13] H.W. Roesky, G. Bai, V. Jancik, S. Singh, European Patent, PCT/EP, 2005/002741, Int. Pat. Classification, C07F17/00, 2005.
[14] G. Bai, S. Singh, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, J. Am. Chem. Soc. 127 (2005) 3449–3455.
[15] H. Zhu, J. Chai, C. He, G. Bai, H.W. Roesky, V. Jancik, H.-G. Schmidt, M. Noltemeyer, Organometallics 24 (2005) 380–384.
[16] G. Bai, H.W. Roesky, J. Li, M. Noltemeyer, H.-G. Schmidt, Angew. Chem. Int. Ed. 42 (2003) 5502–5506.
[17] J. Pinkas, H.W. Roesky, J. Fluorine Chem. 122 (2003) 125–150.
[18] H. Hatop, H.W. Roesky, T. Labahn, A. Fischer, H.-G. Schmidt, M. Noltemeyer, Organometallics 19 (2000) 937–940.
[19] H. Hatop, H.W. Roesky, T. Labahn, C. Röpken, G.M. Sheldrick, M. Bhattacharjee, Organometallics 17 (1998) 4326–4328.
[20] H.W. Roesky, A. Stasch, H. Hatop, C. Rennekamp, D.H. Hamilton, M. Noltemeyer, H.-G. Schmidt, Angew. Chem. Int. Ed. 39 (2000) 171–173.
[21] C. Schnitter, K. Klimek, H.W. Roesky, T. Albers, H.-G. Schmidt, C. Röpken, E. Parisini, Organometallics 17 (1998) 2249–2257.
[22] D. Chakraborty, S. Horchler, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, Inorg. Chem. 39 (2000) 3995–3998.
[23] H. Hohmeister, H. Wessel, P. Lobinger, H.W. Roesky, P. Müller, I. Usón, H.-G. Schmidt, M. Noltemeyer, J. Magull, J. Fluorine Chem. 120 (2003) 59–64.
[24] P. Yu, P. Müller, M.A. Said, H.W. Roesky, I. Usón, G. Bai, M. Noltemeyer, Organometallics 18 (1999) 1669–1674.
[25] P. Yu, T. Pape, I. Usón, M.A. Said, H.W. Roesky, M.L. Montero, H.-G. Schmidt, A. Demsar, Inorg. Chem. 37 (1998) 5117–5124.
[26] G. Gundersen, T. Haugen, A. Haaland, J. Organomet. Chem. 54 (1973) 77–86.
[27] A.J. Downs (Ed.), Chemistry of Aluminum, Gallium, Indium, Thalium, Chapman and Hall, New York, 1993.
[28] H.W. Roesky, Inorg. Chem. 43 (2004) 7284–7293.
[29] J.D. Gorden, A. Voigt, C.L.B. Macdonald, J.S. Silverman, A.H. Cowley, J. Am. Chem. Soc. 122 (2000) 950–951.
[30] J.D. Gorden, C.L.B. Macdonald, A.H. Cowley, Chem. Commun. (2001) 75–76.
[31] C. Cui, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu, Angew. Chem. Int. Ed. 39 (2000) 4274–4276.
[32] Z. Yang, X. Ma, R.B. Ostwald, H.W. Roesky, H. Zhu, C. Schulzke, K. Starke, M. Baldus, H.-G. Schmidt, M. Noltemeyer, Angew. Chem. Int. Ed. 44 (2005) 7072–7074.
[33] K. Ziegler, E. Holzkamp, R. Köster, H. Lehmkuhl, Angew. Chem. 67 (1955) 213–214.
[34] B.R. Jagirdar, E.F. Murphy, H.W. Roesky, Prog. Inorg. Chem. 48 (1999) 351–455.
[35] W. Uhl, F. Breher, Angew. Chem. Int. Ed. 38 (1999) 1477–1479.
[36] W. Uhl, F. Breher, Eur. J. Inorg. Chem. (2000) 1–11.
[37] A. Stasch, M. Ferbinteanu, J. Prust, W. Zheng, F. Cimpoesu, H.W. Roesky, J. Magull, H.-G. Schmidt, M. Noltemeyer, J. Am. Chem. Soc. 124 (2002) 5441–5448.
[38] S.S. Kumar, J. Rong, S. Singh, H.W. Roesky, D. Vidović, J. Magull, D. Neculai, V. Chandrasekhar, M. Baldus, Organometallics 23 (2004) 3496–3500.
[39] A. Stasch, H.W. Roesky, D. Vidovic, J. Magull, H.-G. Schmidt, M. Noltemeyer, Inorg. Chem. 43 (2004) 3625–3630.
[40] E. Wiberg, E. Amberger, Hydrides of the Elements of Main Groups I–IV, Elsevier, Amsterdam, 1971, pp. 81–461 (Chapters 5 and 6).
[41] H. Nöth, E. Wiberg, Fortschr. Chem. Forsch. 8 (1967) 321–436.
[42] J.E. Park, B.-J. Bae, Y. Kim, J.T. Park, I.I.-H. Suh, Organometallics 18 (1999) 1059–1067.
[43] J.A. Jensen, US Patent, US 5,276,105, 1994 (CAS: 120 (1994) 165 306).
[44] M. Cesari, G. Perego, G. Del Piero, S. Cucinella, E. Cernia, J. Organomet. Chem. 78 (1974) 203–213.
[45] G. Del Piero, M. Cesari, G. Perego, G. Dozzi, A. Mazzei, J. Organomet. Chem. 129 (1977) 281–288.
[46] G. Del Piero, M. Cesari, G. Perego, S. Cucinella, E. Cernia, J. Organomet. Chem. 129 (1977) 289–298.
[47] Y. Peng, J. Rong, D. Vidovic, H.W. Roesky, T. Labahn, J. Magull, M. Noltemeyer, H.-G. Schmidt, J. Fluorine Chem. 125 (2004) 951–957.
[48] C. Cui, H.W. Roesky, H. Hao, H.-G. Schmidt, M. Noltemeyer, Angew. Chem. Int. Ed. 39 (2000) 1815–1817.
[49] V. Jancik, Y. Peng, H.W. Roesky, J. Li, D. Neculai, A.M. Neculai, R. Herbst-Irmer, J. Am. Chem. Soc. 125 (2003) 1452–1453.
[50] H. Zhu, J. Chai, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, D. Vidovic, J. Magull, Eur. J. Inorg. Chem. (2003) 3113–3119.
[51] S.D. Waezsada, F.-Q. Liu, E.F. Murphy, H.W. Roesky, M. Teichert, I. Usón, H.-G. Schmidt, T. Albers, E. Parisini, M. Noltemeyer, Organometallics 16 (1997) 1260–1264.

[52] P.L. Holland, W.B. Tolman, J. Am. Chem. Soc. 121 (1991) 7270–7271.
[53] P.L. Holland, W.B. Tolman, J. Am. Chem. Soc. 122 (2000) 6331–6332.
[54] N.J. Hardman, B.E. Eichler, P.P. Power, Chem. Commun. (2000) 1991–1992.
[55] V. Jancik, L.W. Pineda, J. Pinkas, H.W. Roesky, D. Neculai, A.M. Neculai, R. Herbst-Irmer, Angew. Chem. Int. Ed. 43 (2004) 2142–2145.
[56] S. Singh, H.-J. Ahn, A. Stasch, V. Jancik, H.W. Roesky, A. Pal, M. Biadene, R. Herbst-Irmer, M. Noltemeyer, H.-G. Schmidt, Inorg. Chem. 45 (2006) 1853–1860.
[57] T. Kräuter, B. Neumüller, Z. Anorg. Allg. Chem. 621 (1995) 597–606.
[58] B. Neumüller, F. Gahlmann, Angew. Chem. Int. Ed. Engl. 32 (1993) 1701–1702.