VIP

A Persistent Alkylaluminum Peroxide: Surprising Stability of a Molecule with Strong Reducing and Oxidizing Functions in Close Proximity

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Abstract: The reaction of the β-diketiminato coordinated aluminum dihydride, [{HC[C(Me)N−C$_6$H$_5$]$_2$}AlH$_2$] (**1**) with bis(trimethylsilyl)methyllithium afforded the monoalkylaluminum derivative [{HC[C(Me)N−C$_6$H$_5$]$_2$}Al(H)−CH(SiMe$_3$)$_2$] (**2**) by the precipitation of lithium hydride. Interestingly, treatment of **2** with *tert*-butyl hydrogenperoxide did not result in the formation of the simple oxidation product containing a hydroxo or alkoxo group, instead, elemental hydrogen was released and the hydrido ligand attached to aluminum was replaced by an intact *tert*-butylperoxo group. The Al−C bond, which normally is extremely sensitive towards an attack of oxygen, was not affected. Hence, the product exhibits quite conflicting chemical properties in a close proximity: a strongly reducing Al−C bond beside an oxidizing peroxo group.

Keywords: aluminum · organo-aluminum compounds · peroxide · X-ray diffraction

Introduction

The Al−C bonds of alkylaluminum derivatives are highly sensitive towards attack by elemental oxygen. The formation of peroxides was often claimed as the initiating step of these reactions, but owing to their exceptional reactivity these compounds could never be isolated and characterized.[1] The finally isolated products contained only the expected alkoxo groups attached to aluminum. In very rare cases aluminum peroxides were obtained, which, however, did not possess any intact Al−C bonds.[2,3] For instance, the reaction of di(*tert*-butyl)aluminum methylsalicylate (Mesal) with oxygen afforded the compound [(Me$_3$COO)(Me$_3$CO)Al(μ-OCMe$_3$)Al(Mesal)$_2$], which was the first structurally authenticated aluminum peroxide, had a terminal *tert*-butylperoxo group, and exclusively Al−O bonds. In contrast, the oxidation of tri(*tert*-butyl)element compounds of the heavier Group 13 elements (E) gallium and indium yielded the peroxo compounds [{(Me$_3$C)$_2$E(μ-OOCMe$_3$)}$_2$], which had bridging peroxo groups beside terminal E−C bonds.[4,5] These compounds are, however, highly explosive and decompose spontaneously on mechanical stress. An interesting organodigallium peroxide was isolated in trace quantities by the accidental contact of an alkylgallium derivative with air.[6] It has two gallium atoms terminally attached to the oxygen atoms of a bridging peroxo ligand. Recently, we succeeded in isolating a heterocyclic trigallium trisperoxide in a surprisingly selective reaction. This compound has three alkylgallium groups containing intact Ga−C bonds bridged by three peroxo groups.[7] Al−C bonds are known to be much more reactive and to have stronger reducing properties than Ga−C or In−C bonds which may be caused by the relatively large charge separation between aluminum and carbon. Thus, it was a real preparative challenge to synthesize and characterize such a compound. The first example is reported in this paper.

Results and Discussion

Synthesis and Molecular Structure of the Dihydride [{HC[C(Me)N−C$_6$H$_5$]$_2$}AlH$_2$](1): The strategy for the synthesis of a first alkylaluminum peroxide followed three fundamental ideas. First, coordinative saturation of the aluminum atoms should help to stabilize the Al−C bonds by preventing the intra- or intermolecular approach of a peroxide and the activation of the oxygen transfer by the Lewis-acidity of the metal atoms. Second, owing to our experience Al−C bonds of bis(trimethylsilyl)methyl compounds are particularly stable towards an attack of oxygen. This observation may be strongly related to the electronic properties of

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this substituent, which can act as an electron donor or acceptor by hyperconjugation with its C−Si σ- or σ*-orbitals. Furthermore, we hoped to introduce the peroxo group by hydrogen release and the treatment of an aluminum hydride

$$AlH_3(NMe_2Et) + H_2C[C(Me)=N\text{-}C_6H_5]_2 \longrightarrow \mathbf{1} + H_2 + NMe_2Et \quad (1)$$
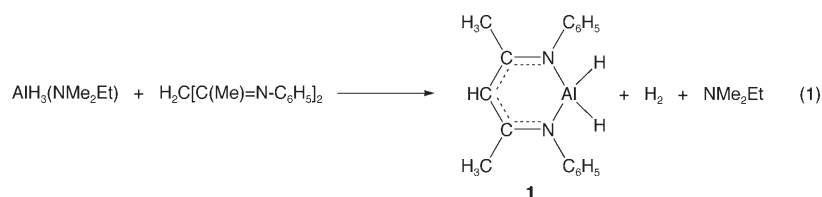
with a soluble hydrogenperoxo species. Thus, first of all we synthesized a dihydridoaluminum compound coordinated by a chelating β-diketiminato ligand (**1**) through the reaction of the alane-amine adduct AlH$_3$·NMe$_2$Et with equimolar quantities of H$_2$C[C(Me)=N−C$_6$H$_5$]$_2$ [Eq. (1)]. Release of hydrogen afforded the product directly in high purity in an almost quantitative yield of 90%. The broad resonance of the hydrogen atoms attached to aluminum has the correct integration ratio compared to the intensities of the phenyl and methyl signals. The occurrence of Al−H bonds is further verified by two absorptions in the IR spectrum at $\tilde{\nu} = 1796$ and 1754 cm^{-1}. The correct molecular mass was detected in the mass spectrum. All attempts to generate a peroxo derivative directly by the treatment of **1** with dihydrogen peroxide or *tert*-butyl hydrogen peroxide failed. Amorphous powders or oily residues were obtained which could not be purified by recrystallization from different solvents. A sterically more shielded β-diketiminatoaluminum dihydride was reported to yield a peroxo compound upon treatment with H-O-O-CMe$_3$.[2c]

The molecular structure of compound **1** is depicted in Figure 1. It has the chelating β-diketiminato ligand attached

to the central aluminum atom through both nitrogen atoms. The distorted tetrahedral coordination sphere of the metal atoms is completed by two terminally arranged hydrogen atoms. The Al−N and Al−H bond lengths (189.3 and 155 pm, respectively) are in the expected ranges, and the C−N and C−C distances in the chelate (133.5 and 139.8 pm) reflect the delocalized π-bonding system. The syntheses and structures of arylaluminum dihydrides and β-diketiminatoaluminum dihydrides similar to **1** bearing alkyl groups or sterically more shielded aromatic rings attached to their nitrogen atoms were published in recent literature.[8]

Synthesis and Molecular Structure of [{HC[C(Me)N−C$_6$H$_5$]$_2$}Al(H)−R] (2) [R = CH(SiMe$_3$)$_2$]: In the next step we treated the dihydride **1** with an equimolar quantity of freshly sublimed and ether-free LiCH(SiMe$_3$)$_2$ in cyclopentane

$$\mathbf{1} + LiCH(SiMe_3)_2 \longrightarrow \mathbf{2} + LiH \quad (2)$$
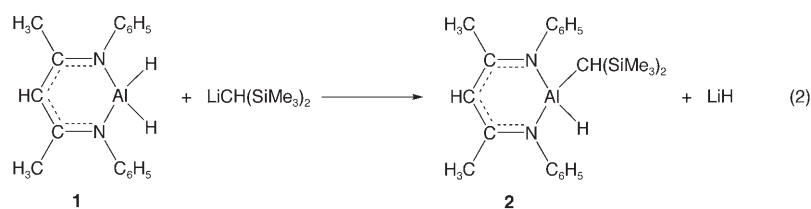
[Eq. (2)]. The brownish compound **2** formed by the precipitation of lithium hydride. It was isolated in 74% yield after recrystallization from *n*-pentane and has one hydrogen atom attached to aluminum replaced by a bulky alkyl group. The integration ratio of the ^{1}H NMR spectrum gave the expected ratio of signal intensities. The resonance of the inner Al−C−H hydrogen atom occurs a relatively high field ($\delta = -1.47$ ppm), which is characteristic of CH(SiMe$_3$)$_2$ groups attached to coordinatively saturated, tetracoordinated aluminum atoms.[9] A broad absorption at $\tilde{\nu} = 1790$ cm^{-1} in the IR spectrum indicated the intact Al−H bond. Complex **2** is more reactive than the dihydrido compound **1**, and fast decomposition occurred on contact with air.

The molecular structure of **2** (Figure 2) exhibits an aluminum atom coordinated to both nitrogen atoms of the chelating ligand, one hydrogen atom and one carbon atom of a CH(SiMe$_3$)$_2$ group in a distorted tetrahedral coordination sphere. The Al−N distances (191.0 pm) are similar to those observed for compound **1**. The same holds for the C−N and C−C bond lengths in the chelate (133.8 and 139.6 pm) and the N−Al−N angles (96.4 versus 95.4°). Thus, the structural parameters are only scarcely influenced by the introduction of the bulky bis(trimethylsilyl)methyl group. The Al−C bond length (199.2 pm) corresponds well to standard values.[9]
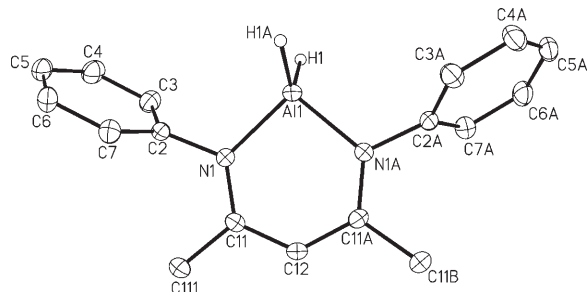

Figure 1. Molecular structure and numbering scheme of compound **1**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms with the exception of those attached to aluminum are omitted for clarity. Selected bond lengths [pm] and angles [°]: Al1−N1 189.3(1), N1−C11 133.5(2), C11−C12 139.8(2), N1−Al1−N1′ 96.40(7); N1′ generated by -x+1, y, -z+0.5.

Figure 2. Molecular structure and numbering scheme of compound **2**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms with exception of the one attached to aluminum, methyl groups attached to the silicon atoms and phenyl groups are omitted for clarity. Selected bond lengths [pm] and angles [°]: Al1−N1 191.1(2), Al1−N2 190.8(2), Al1−C1 199.2(3), N1−C01 134.3(3), C01−C02 139.2(4), C02−C03 140.0(4), C03−N2 133.2(3), N1−Al1−N2 95.38(9), N1−Al1−C1 107.4(1), N2−Al1−C1 120.5(1).
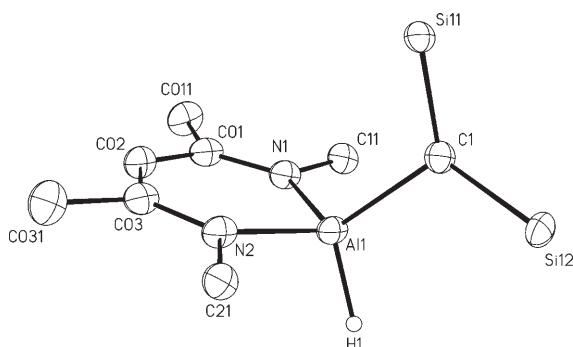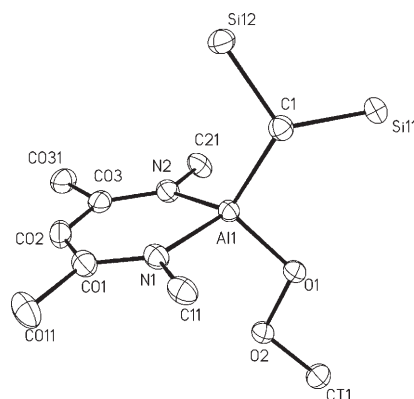

Figure 3. Molecular structure and numbering scheme of compound **3**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms, methyl groups of the SiMe$_3$ and CMe$_3$ substituents and the phenyl groups are omitted for clarity. Selected bond lengths [pm] and angles [°]: Al1−N1 189.3(2), Al1−N2 189.6(2), Al1−C1 197.0(2), Al1−O1 176.1(1), O1−O2 148.2(2), N1−C01 133.8(2) C01−C02 139.5(3), C02−C03 138.8(3), C03−N2 134.3(2), N1−Al1−N2 96.27(7), Al1−O1−O2 112.16(8), O1−O2−CT1 107.5(1).

Synthesis and Molecular Structure of the Peroxide [{HC[C(Me)N−C$_6$H$_5$]$_2$}Al(R)-O-O-CMe$_3$] (3) [R = CH-(SiMe$_3$)$_2$]: Treatment of the alkylhydrido compound **2** with an equimolar quantity of *tert*-butyl hydrogen peroxide in *n*-hexane afforded colorless crystals of the corresponding peroxide **3** in 61% yield [Eq. (3)]. Gas evolution indicated
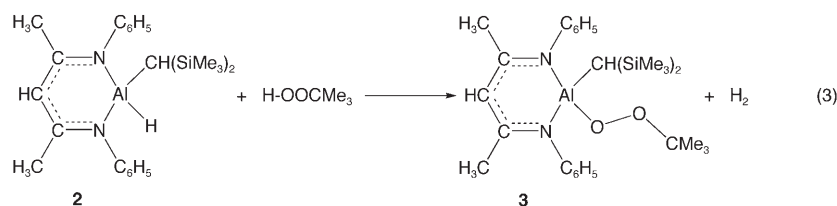
the expected formation of elemental hydrogen. The occurrence of a peroxo group beside an intact Al−C bond was verified by crystal structure determination. Furthermore, we determined the peroxide content analytically by hydrolysis and subsequent oxidation of iodide. NMR characterization gave the correct integration ratio of all resonances. Crystals of compound **3** are stable at room temperature. The decomposition point is 69°C. However, as monitored by NMR spectroscopy, relatively fast decomposition with the formation of a mixture of unknown products was observed in benzene at room temperature. Solutions in *n*-hexane showed a higher stability, and the NMR spectra were recorded in [D$_{14}$]hexane. These solutions could be stored without any sign of secondary processes at −15°C over several weeks. Owing to its high solubility in hydrocarbon solvents and its relatively high stability compound **3** may find some application in particular oxygen transfer processes.

Crystal structure determination (Figure 3) verified the unusual bonding situation of compound **3** with an unaffected Al−C bond beside an intact *tert*-butylperoxo group. Hence,

this molecule contains a strongly reducing group beside an effective oxidant. Such an unusual structure has often been claimed as the first step of the oxidation of alkylaluminum compounds with oxygen, which usually gave the alkoxy derivatives in a very fast secondary process. These possible intermediates could never be isolated or characterized unambiguously with alkylaluminum compounds, but were detected with three explosive *tert*-butyl-gallium and -indium compounds.[4,5] Thus, the strange molecular structure of **3** may reflect the first step of the oxidation of an alkylaluminum compound by the insertion of an oxygen molecule into an Al−C bond. Clearly, the particular stability of this spectacular arrangement in **3** is not a consequence of the steric shielding by the bulky substituents, because the reactive groups are already in close proximity geminally attached to the same aluminum atom. The stability may be caused by the particular electronic properties of the bis(trimethylsilyl)methyl group, which is able to act as an electron donor or acceptor by hyperconjugation with its C−Si bonds. In organoaluminum compounds hyperconjugation may help to diminish the negative charge at the α-carbon atom, which results from the relatively large electronegativity difference between aluminum and carbon. By this partial electron transfer and diminution of the negative charge the intramolecular autooxidative attack at this carbon atom may become slightly less favorable compared to *tert*-butyl groups attached to aluminum, for instance. The O−O bond length in **3** (148.2 pm) is in the expected range of alkylperoxo groups.[4–6,10] Longer distances were observed for dianionic peroxides, which may be caused by electrostat-

ic repulsion.[11] The torsion angle across the O−O bond (Al-O-O-C; 177.7°) is in accordance with an almost ideally planar arrangement and deviates considerably from the conformation observed for hydrogen peroxide.[12] The angles Al−O−O (112.2°) and O−O−C (107.5°) correspond to values obtained for other alkylperoxo species.[4–5,10]

Experimental Section

General: All procedures were carried out under purified argon. Cyclopentane, *n*-pentane and *n*-hexane were dried over LiAlH$_4$. The alane dimethylethylamine adduct AlH$_3$·NMe$_2$Et, the starting ketenimine H$_2$C[C(Me)=N−C$_6$H$_5$]$_2$ and LiCH(SiMe$_3$)$_2$ were obtained according to literature procedures.[13–15] Commercially available solutions of *tert*-butyl hydrogenperoxide (5.5 M in nonane, Aldrich) were stored over molecular sieves prior to use.

Synthesis of the dihydride 1: A solution of H$_2$C[C(Me)=N−C$_6$H$_5$]$_2$ (2.22 g, 8.88 mmol) in 20 mL of *n*-pentane was added dropwise to a cooled solution (−78°C) of AlH$_3$·NMe$_2$Et (0.915 g, 8.88 mmol) in 40 mL of the same solvent. The mixture was slowly warmed to room temperature. Gas evolution started at about −30°C. The solution was stirred at room temperature for 12 h. The solvent was removed in vacuum to yield a colorless solid of compound **1** directly in a high purity. Yield: 2.23 g (90%). M.p. (argon, sealed capillary): 127°C; ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ = 7.07 (*pseudo*-d, 4H; *ortho*-H of phenyl), 7.05 (m, 4H; *meta*-H of phenyl), 6.91 (m, 2H; *para*-H of phenyl), 4.86 (s, very broad, 2H; AlH$_2$), 4.73 (s, 1H; HC of the chelate ligand), 1.54 ppm (s, 6H; CH$_3$); ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ = 168.9 (C=N), 145.5 (*ipso*-C of phenyl), 129.8 (*meta*-C of phenyl), 126.3 (*para*-C of phenyl), 125.9 (*ortho*-C of phenyl), 98.0 (HC of the chelate ligand), 22.6 ppm (CH$_3$); IR (CsBr plates, paraffin): $\tilde{v}$ = 1850 (w, phenyl), 1796 (w), 1754 (m-br, AlH$_2$), 1578 (vs), 1558 (vs, CN, phenyl), 1460 (vs, paraffin), 1402 (s, CH$_3$), 1375 (s, paraffin), 1352 (sh), 1339 (m), 1321 (m), 1304 (m), 1265 (m, CH$_3$), 1111 (vs-br, CN, CC), 931 (w), 921 (w), 814 (m), 785 (m), 775 (m), 763 (m), 719 (s, paraffin), 700 (m), 671 (w), 658 (w), 645 (w), 611 (vw), 592 (w), 561 (m), 515 (m), 474 cm^{-1} (s, AlN, phenyl, CC, CN); MS (EI, 20 eV): *m/z* (%): 277 (100) (M^+−H); elemental analysis calcd (%) for C$_{17}$H$_{19}$AlN$_2$ (278.3): C 73.4, H 6.9, N 10.1, Al 9.7; found: C 72.4, H 6.9, N 9.9, Al 9.6.

Synthesis of the bis(trimethylsilyl)methyl compound 2: A cooled solution (−40°C) of compound **1** (0.453 g, 1.63 mmol) in 20 mL of cyclopentane was treated with freshly sublimed, solid bis(trimethylsilyl)methyllithium (0.27 g, 1.63 mmol) in small portions. The resulting suspension was vigorously stirred and slowly warmed to room temperature. An almost clear solution was obtained upon stirring at room temperature over a period of 16 h. The solvent was removed in vacuum, and the residue was treated with *n*-pentane. After filtration and cooling to −15°C brownish crystals of the product **2** precipitated. Yield: 0.53 g (74%). M.p. (argon, sealed capillary): 118°C; ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ = 7.17 (*pseudo*-d, 4H; *ortho*-H of phenyl), 7.11 (*pseudo*-t, 4H; *meta*-H of phenyl), 6.94 (*pseudo*-t, 2H; *para*-H of phenyl), 5.05 (s, br., 1H; AlH), 4.70 (s, 1H; HC of the chelate ligand), 1.52 (s, 6H; CH$_3$ of the chelate ring), 0.15 (s, 18H; SiMe$_3$), −1.47 ppm (s, 1H; AlCH); ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ = 168.7 (C=N), 145.5 (*ipso*-C of phenyl), 129.6 (*meta*-C of phenyl), 126.7 (*ortho*-C of phenyl), 126.5 (*para*-C of phenyl), 98.0 (HC of the chelate ligand), 23.1 (CH$_3$), 3.7 (SiMe$_3$), 0.7 ppm (AlC); ^{29}Si NMR (C$_6$D$_6$, 79.5 MHz): δ = −1.6 ppm; IR (CsBr plates, paraffin): $\tilde{v}$ = 1946 (vw), 1884 (vw, phenyl), 1790 (m-br, AlH), 1578 (vs), 1558 (vs, phenyl, CN), 1460 (vs, paraffin), 1402 (s, CH$_3$), 1377 (vs, paraffin), 1352 (sh), 1339 (m), 1321 (m), 1304 (m, CH$_3$), 1111 (vs-br, CN, CC), 931 (vw), 918 (vw), 845 (m), 814 (s), 785 (m, CH$_3$(Si)), 719 (s, paraffin), 594 (w), 559 (m), 513 (m), 482 cm^{-1} (s, AlN, phenyl, CC, CN); MS (EI, 20 eV): *m/z* (%) = 435 (43), 436 (64), 437 (19) (M^+); 277 (100) [M^+−CH(SiMe$_3$)$_2$]; elemental analysis calcd (%) for C$_{24}$H$_{37}$AlN$_2$Si$_2$ (436.7): C 66.0 H 8.5, N 6.4, Al 6.2; found: C 66.8, H 8.8, N 6.5, Al 6.0.

Synthesis of the peroxo compound 3: A cooled solution (−40°C) of compound **2** (0.288 g, 0.659 mmol) in 20 mL of *n*-hexane was treated with a solution of *tert*-butyl hydrogenperoxide, HOOCMe$_3$, in nonane (0.12 mL, 5.5 M, 0.659 mmol). The mixture was slowly warmed to −10°C and stirred at that temperature for 1 h. The solution was concentrated to about 5 mL and cooled to −15°C to afford colorless crystals of the product **3**. Yield: 0.21 g (61%). M.p. (argon, sealed capillary): 69°C (dec., color change

Table 1. Crystal data for the compounds **1**, **2**, and **3**.

	1	2	3
formula	C$_{17}$H$_{19}$AlN$_2$	C$_{24}$H$_{37}$AlN$_2$Si$_2$	C$_{28}$H$_{45}$AlN$_2$O$_2$Si$_2$
M_r	278.32	436.72	524.82
size [mm]	0.14×0.12×0.10	0.12×0.07×0.04	0.12×0.10×0.05
crystal system	monoclinic	triclinic	monoclinic
space group	C2/c	P$\bar{1}$	P2$_1$/n
a [pm]	1970.7(3)	905.16(3)	1049.96(4)
b [pm]	732.4(1)	989.86(4)	1843.40(9)
c [pm]	1202.2(2)	1514.27(5)	1604.29(7)
α [°]	90	97.174(3)	90
β [°]	118.347(2)	98.011(2)	92.013(3)
γ [°]	90	97.473(2)	90
V [10^{-30} m^3]	1527.0(4)	1317.90(8)	3103.2(2)
Z	4	2	4
ρ [g cm^{-3}]	1.211	1.101	1.123
μ(Mo$_{K\alpha}$) [mm^{-1}]	0.125	0.180	0.168
T [°C]	−120	−120	−120
θ_{max} [°]	29.97	26.02	26.03
total reflns	8509	7374	17745
unique reflns	2219	4336	5895
R_{int}	0.0344	0.0437	0.0450
obsvd reflns [$I > 2\sigma(I)$]	1841	3689	4663
parameters	97	279	327
R_1 [$I > 2\sigma(I)$]	0.0469	0.0606	0.0406
wR_2 [all data]	0.1290	0.1786	0.1111
GOF	1.073	1.315	1.030
max./min. resd [10^{30} *e* m^{-3}]	0.344/−0.213	0.594/−0.437	0.378/−0.195

from colorless to yellow). The peroxide content was determined by hydrolysis of **3** with acetic or nitric acid (1 M), treatment of the mixture with sodium iodide and titration of the formed elemental iodine with thiosulfate. By this relatively simple procedure 91% of the calculated peroxide content was reproducibly determined; ^{1}H NMR ([D$_{14}$]hexane, 500 MHz): $\delta = 7.33$ (*pseudo*-t, 8H; *meta*-H), 7.19 (*pseudo*-t, 2H; *para*-H of phenyl), 5.06 (s, 1H; HC of the chelate ligand), 1.91 (s, 6H; CH$_3$ of the chelate ring), 1.34 (s, 9H; OOCMe$_3$), 0.19 (s, 18H; SiMe$_3$), −1.79 ppm (s, 1H; AlCH), a very broad resonance resulted for the *ortho*-hydrogen atoms ($\delta \approx 7.4$ ppm), upon cooling to −20°C two broad resonances occurred instead ($\delta \approx 7.0$ and 7.6 ppm), which may indicate a hindered rotation around the C−N bond, all other resonances remained almost unchanged; ^{13}C NMR ([D$_{14}$]hexane, 125 MHz): $\delta = 169.7$ (C=N), 146.7 (*ipso*-C of phenyl), 128.4 and 129.9 (*ortho*-C of phenyl), 127.22 (*para*-C of phenyl), 127.15 (*meta*-C of phenyl), 99.1 (HC of the chelate ligand), 79.1 (CMe$_3$), 27.9 (C*Me$_3$*), 24.1 (CH$_3$ of the chelate), 4.2 (SiMe$_3$), −2.1 ppm (br., AlC); ^{29}Si NMR (C$_6$D$_{14}$, 79.5 MHz): $\delta = -1.8$ ppm; IR (CsBr plates, paraffin): $\tilde{\nu} = 1581$ (vs), 1551 (vs, phenyl, CN), 1447 (vs, paraffin), 1404 (s, CH$_3$), 1375 (vs, paraffin), 1330 (w), 1304 (m), 1254 (w), 1242 (m, CH$_3$), 1193 (m), 1113 (m-br), 1072 (m), 1034 (m, CN, CC), 927 (w), 845 (m), 814 (m), 785 (w, CH$_3$(Si)), 719 (s, paraffin), 704 (m), 669 (w), 592 (w), 559 (w), 521 (w), 467 m cm^{-1} (AlN, phenyl, CC, CN).

Crystal Structure Determinations of 1, 2 and 3: Single crystals were obtained upon recrystallization from *n*-hexane (**1**: 20/−45°C) or *n*-pentane (**2**: 20/0°C; **3**: 10/−15°C). Crystal data, data collection parameters, and structure refinement details are given in Table 1. The crystallographic data were collected with a BRUKER apex diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97[16] by a full-matrix least-squares method based on F^2. The molecules of **1** reside on crystallographic twofold rotation axes. The inner carbon atom of the CH(SiMe$_3$)$_2$ group in **2** is disordered over two positions; it was refined on split positions and occupation factors of 0.82 and 0.18, respectively. The positions of the hydrogen atoms attached to aluminum were taken from electron density maps and refined isotropically. CCDC 668009 (**1**), 668010 (**2**), and 668011 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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