



Reactions of β -diketiminatoaluminum hydrides with *tert*-butyl hydrogenperoxide – Facile formation of dialuminumoxanes containing Al–O–Al groups

Werner Uhl*, Barun Jana

Institut für Anorganische und Analytische Chemie, Universität Münster, D-48149 Münster, Germany

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ABSTRACT

Treatment of diphenyl- β -diketiminatoaluminum dihydride, LAlH_2 [**1**, $\text{L} = \{\text{H}_5\text{C}_6\text{-N}=\text{C}(\text{Me})_2\text{CH}\}$] with neopentyl- or trimethylsilylmethyl lithium afforded the corresponding alkyl derivatives $\text{LAlH}(\text{R})$ [$\text{R} = \text{CH}_2\text{-SiMe}_3$ (**2**), $\text{CH}_2\text{-CMe}_3$ (**3**)] by the precipitation of lithium hydride. Deprotonation of a methyl group instead of salt elimination occurred by the similar reaction of the more basic alkyl lithium compound $\text{LiC}(\text{SiMe}_3)_3$. The reactions of the hydrides **1–3** with *tert*-butyl hydrogenperoxide did not yield the expected peroxy derivatives, instead the dialuminumoxanes $\text{LAl}(\text{R})\text{-O-Al}(\text{R})\text{L}$ [$\text{R} = \text{OCMe}_3$ (**5**), CH_2SiMe_3 (**6**), CH_2CMe_3 (**7**)] were isolated in high yields. Their Al–O–Al bridges deviated from linearity and had Al–O–Al bond angles of about 155° on average.

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1. Introduction

Persistent organoelement peroxides of the heavier elements of the third main-group are extremely rare because the conflicting properties of oxidizing peroxy groups in close proximity to reducing E–C bonds result in very fast quenching reactions and the formation of alkoxy derivatives [1]. Nevertheless, those compounds were postulated to occur as intermediates and were employed in secondary reactions as oxygen transfer reagents at low temperature [2]. Structurally characterized organoelement peroxides, $[(\text{Me}_3\text{C})_2\text{E}(\mu\text{-OOCMe}_3)_2\text{E}(\text{CMe}_3)_2]$, $\text{E} = \text{Ga, In}$, were first reported by the group of Barron [3]. However, they proved to be explosive in the solid state. We isolated trace quantities of an organoelement peroxide, in which a peroxy ligand was terminally coordinated by two alkylgallium groups [4,5]. Despite their inherent instability, such compounds are of particular interest because they may find broader application as oxygen transfer reagents soluble in non-coordinating solvents. Furthermore, they may show unique coordination behaviour similar to transition metal compounds. In recent investigations we found an easy access to those peroxides by the treatment of the corresponding organoelement hydrides with different hydrogenperoxides and by the release of elemental hydrogen [6–8]. One compound possessed $\text{Ga}_3(\text{O}_2)_3$ heterocycles (Scheme 1) in which three gallium atoms

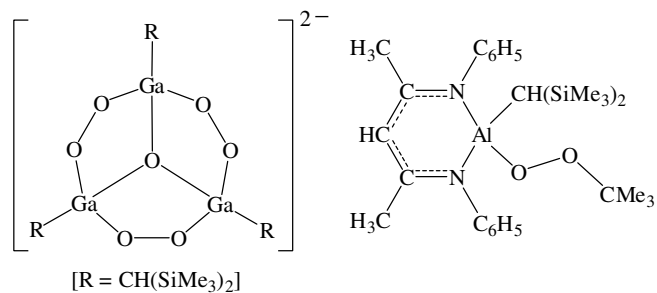
were bridged by three peroxy groups [6,7]. Furthermore, we were able to isolate even an organoaluminum peroxide (Scheme 1) which had a *tert*-butylperoxy ligand beside a strongly reducing and generally very oxygen sensitive Al–C bond [8]. All compounds had $\text{CH}(\text{SiMe}_3)_2$ groups attached to their aluminum or gallium atoms. That particular alkyl group may contribute to the stability of these peroxides by the reduction of the negative charge at the α -carbon atoms through hyperconjugation and, hence, a diminution of the reducing power of the E–C bonds. We report here on some systematic investigations into the generation of further compounds of that type.

2. Results and discussion

2.1. Syntheses of alkyl(β -diketiminato)aluminum hydrides

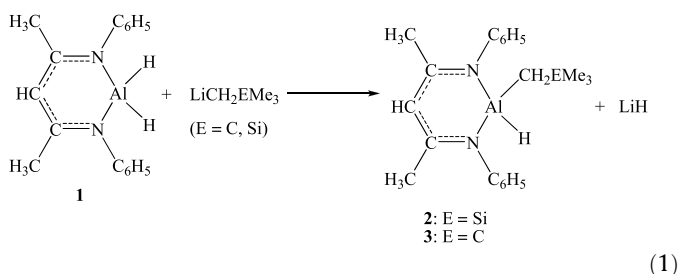
The particular stability of the organoelement *tert*-butylperoxyaluminum compound described before [8] may be due to (i) the coordinative saturation of the aluminum atom by the coordination to a chelating β -diketiminato ligand and (ii) by the diminution of the negative charge at the α -carbon atom by hyperconjugation with σ -orbitals of C–Si bonds. We hoped to apply this strategy for a more systematic approach to this new class of compounds. The β -diketiminato coordinated aluminum dihydride, $\{\text{HC}[\text{C}(\text{Me})\text{N}-\text{C}_6\text{H}_5]_2\}\text{AlH}_2$ (**1**), represents a suitable starting compound for the generation of alkylaluminum interme-

* Corresponding author. Tel.: +49 251 8336610; fax: +49 251 8336660.
E-mail address: uhlw@uni-muenster.de (W. Uhl).

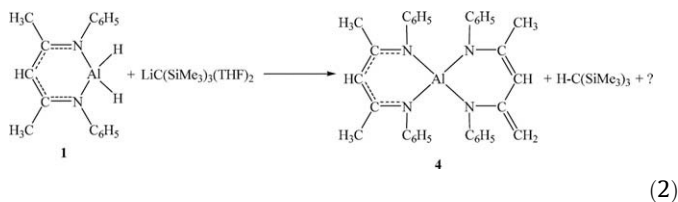


Scheme 1.

diates. It is easily available by the reaction of the free, protonated ligand with aluminum trihydride by hydrogen release [8]. Its reaction with equimolar quantities of trimethylsilylmethyl- and neopentylolithium afforded the alkylhydrido derivatives **2** and **3** by LiH elimination in 80–90% yield, Eq. (1). The NMR spectroscopic parameters of these compounds (integration ratio, chemical shifts) are in accordance to the molecular structures and do not require a detailed discussion. The Al–H stretching vibrations were detected in the IR spectra as broad absorptions at 1791 and 1782 cm⁻¹.



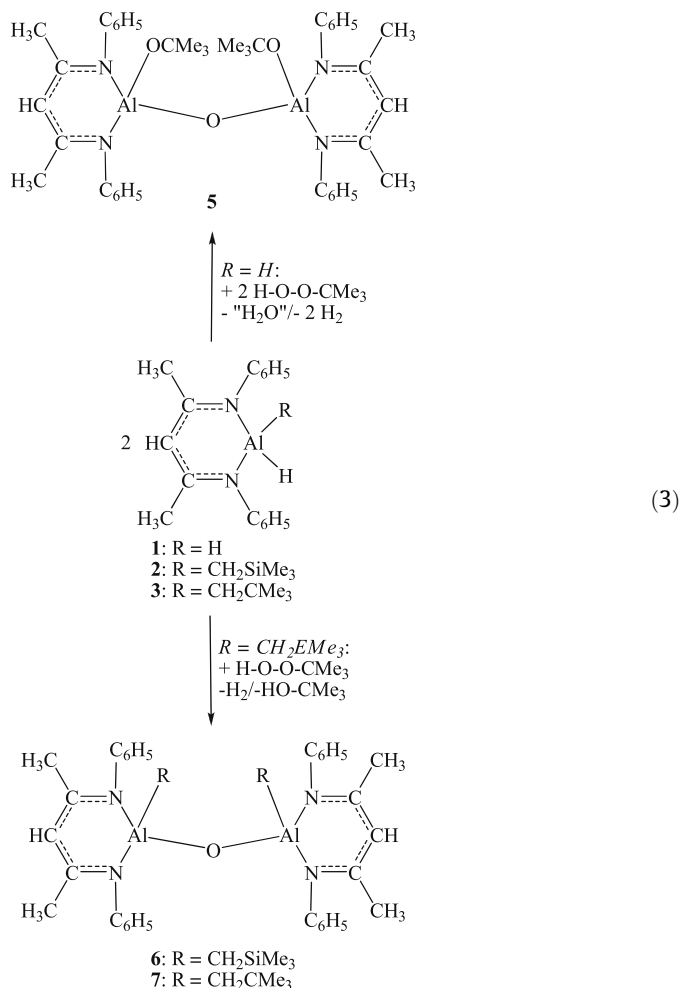
The corresponding reaction of the dihydride **1** with the sterically shielded alkylolithium compound [Li(THF)₂][C(SiMe₃)₃] gave a mixture of products from which few crystals of an orange compound (**4**) could be isolated by recrystallization. Crystal structure determination revealed that a methyl group of the β -ketiminato ligand was deprotonated by the strongly basic tris(trimethylsilyl)methyl anion. Ligand exchange afforded compound **4**, Eq. (2), in which an intact, monoanionic ligand and its dianionic form are coordinated to the central aluminum atom. H-C(SiMe₃)₃ was detected as a major by-product by NMR spectroscopy. In accordance with the schematic formula given in Eq. (2) the ¹H NMR spectrum of **4** is relatively complicated. Beside the resonances characteristic of the intact β -diketiminato ligand the ¹H NMR spectrum showed resonances of the deprotonated form with two resonances for the chemically different hydrogen atoms attached to the exocyclic C=C double bond



2.2. Synthesis of the dialuminoxanes 5–7

The aluminum hydrides **1–3** were subsequently treated with *tert*-butyl hydrogenperoxide at low temperature. In the case of the bis(trimethylsilyl)methyl derivative a similar reaction gave

selectively the corresponding aluminum *tert*-butylperoxide by hydrogen release [8]. However, the reactions described here proceeded on a completely different route, Eq. (3). Crystalline products (**5** to **7**) were isolated in up to 83% yield, which were identified by NMR spectroscopy, mass spectrometry and crystal structure determination as dialuminoxanes having bent Al–O–Al bridges. While the Al–C bonds of **2** and **3** were not affected, the second Al–H bond of **1** was replaced by a *tert*-butoxy group. Thus, in these cases the peroxo starting compound did not yield a peroxoaluminum compound by replacement of a hydrogen atom, but reacted as an oxidant and inserted an oxygen atom into the strongly reducing Al–H bond. The resulting Al–OH group may be deprotonated in a secondary step by the reaction with an intact Al–H species to afford the dialuminoxane by hydrogen release. *tert*-Butanol may be formed as a by-product, which gave the Al–OCMe₃ moiety of **5** by the reaction with the second Al–H bond. Thus, only the bulky CH(SiMe₃)₂ substituent gave a relatively persistent alkylaluminum peroxide, AlAl(R)–O–O–CMe₃. Owing to the close proximity of peroxo and bis(trimethylsilyl)methyl groups in geminal positions we do not believe that steric shielding plays an important role for the stabilization of this singular peroxide. However, the reaction pathway may be influenced. The bulky bis(trimethylsilyl)methyl group may force the hydrogenperoxo group to approach the Al–H bond via its protic hydrogen atom and may, thus, favour the hydrogen release, while an approach via the oxygen atoms may be facilitated by the smaller alkyl groups and may allow the insertion of oxygen atoms



2.3. Crystal structure determinations

The molecular structure of compound **2** is depicted in Fig. 1. A chelating β -diketiminato ligand is coordinated to the central aluminum atom via its both nitrogen atoms. The metal atom is further bonded to a hydrogen atom and a trimethylsilylmethyl group. The aluminum atom is slightly above the plane spanned by the five atoms of the N_2C_3 chelate (11 pm; 72 pm for the minor component of the disordered molecule). All C–C (140.0 pm) and C–N distances (132.9 pm) of the C_3N_2 moiety are consistent with a delocalized π -bonding. Al–N (190.7 pm) and Al–C distances (196.9 pm) are in the expected range. Although β -diketiminatoaluminum compounds are known in the literature in a great number [5c,8,9], similar compounds having an alkyl group and a hydrogen atom attached to their aluminum atoms are rare [8,10]. The molecular structure of **4** (Fig. 2) comprises an unchanged and a deprotonated, dianionic β -diketiminato ligand coordinated to the central metal atom. The unchanged one has structural parameters quite similar to those of compound **2** which verify electronic delocalization. The second one has a negative charge at each nitrogen atom. Accordingly, the Al–N bonds are shortened to 182.2 pm on average. Both C–N bond lengths in the heterocycle (140.7 pm) may be interpreted in terms of localized single bonds, while the alternating C–C distances in that part of the molecule (C04–C05 134.2; C05–C06 145.6; C06–C061 of the exocyclic C=C double bond 135.5 pm) correspond quite well to the situation of butadiene [11]. The C–C bond length to the terminal methyl group is 150.2 pm. The Al atoms are 16 and 43 pm above the planes of the respective ligands.

The aluminum atoms of the dialuminoxanes **5–7** (Fig. 3–5) are coordinated to both nitrogen atoms of the chelating β -diketiminato ligands with quite normal Al–N distances (188.8 to 192.2 pm). Each metal atom is further attached to terminal alkyl (**6** and **7**) or alkoxy groups (**5**) and to the bridging oxygen atom. The Al–O–Al angles are 159.2/154.3° (**5**), 155.9° (**6**) and 155.8° (**7**). A strictly linear arrangement of those dialuminoxanes was observed only for a singular tetraalkyldialuminoxane possessing tricoordinated, coordinatively unsaturated aluminum atoms shielded by very bulky substituents [12]. The Al–O distances to the bridging oxygen atoms are close to the average value of 169.9 pm for the compounds **6** and **7**, while slightly shorter distances (167.9 pm on aver-

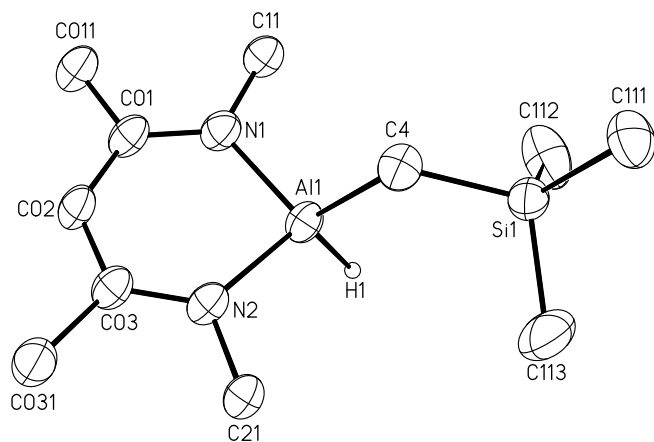


Fig. 1. Molecular structure of **2**. The thermal ellipsoids are drawn at the 40% probability level. CH_3 and CH_2 hydrogen atoms are omitted. Only the *ipso*-carbon atoms of the phenyl rings are shown. Important bond lengths (pm) and angles ($^\circ$): Al1–N1 189.6(2), Al1–N2 191.8(2), Al1–C4 196.9(3), C4–Si1 183.7(3), N1–C01 133.4(3), N2–C03 132.4(3), C01–C02 139.5(3), C02–C03 140.5(3), N1–Al1–N2 95.56(8), Al1–C4–Si1 116.0(1), C01–C02–C03 127.7(2).

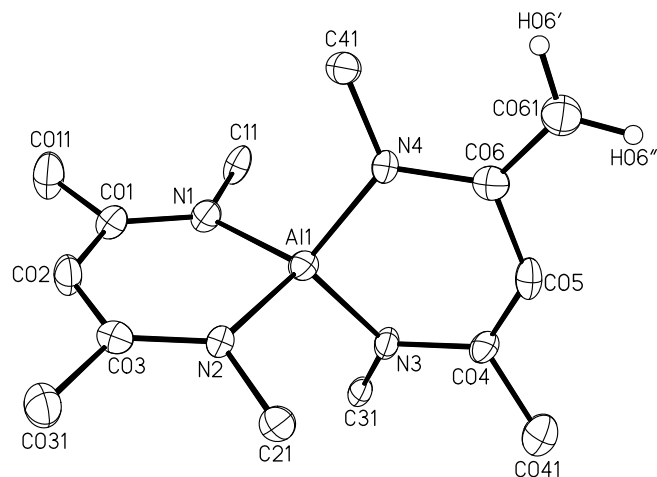


Fig. 2. Molecular structure of **4**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Only the *ipso*-carbon atoms of the phenyl rings are shown. Important bond lengths (pm) and angles ($^\circ$): Al1–N1 185.8(3), Al1–N2 187.5(3), Al1–N3 181.7(3), Al1–N4 182.6(3), N1–C01 134.1(5), C01–C02 138.5(5), C02–C03 139.1(5), C03–N2 134.0(5), N3–C04 140.8(5), C04–C05 134.2(5), C05–C06 145.6(5), C06–N4 140.6(5), C04–C041 150.2(5), C06–C061 135.5(6), N1–Al1–N2 97.1(2), N3–Al1–N4 103.3(2), C01–C02–C03 128.6(4), C04–C05–C06 132.0(4).

age) resulted for the *tert*-butoxy derivative **5**. The last ones correspond to the bond lengths observed for the linear dialuminoxane cited before [12]. An approximate *syn*-arrangement across the Al–O–Al axes resulted for the alkyl groups or the β -diketiminato ligands of all compounds. Few similar dialuminoxanes have been reported in the literature [12,13], but they were generated on different routes which do not involve an oxygen transfer from a peroxy starting compound and the insertion of oxygen atoms into Al–H bonds. A recent report described the application of those compounds as catalysts in ring-opening polymerization reactions [14].

3. Experimental

All procedures were carried out under purified argon. *n*-Pentane, *n*-hexane and cyclopentane were dried over $LiAlH_4$, toluene over Na/benzophenone. The aluminum dihydride **1** [8], neopentyl lithium [15], trimethylsilylmethyl lithium [16] and $LiC(SiMe_3)_3 \cdot 2THF$ [17] were obtained according to literature procedures. Commercially available solutions of *tert*-butyl hydrogenperoxide (5.5 M in nonane, Aldrich) were stored over molecular sieves prior to use.

3.1. Synthesis of $LAl(H)-CH_2SiMe_3$ [**2**, $L = \{H_5C_6-N=C(Me)\}_2CH$]

A cooled solution ($-78^\circ C$) of the dihydride **1** (1.99 g, 7.16 mmol) in 50 ml of *n*-hexane was treated with solid trimethylsilylmethyl lithium (0.674 g, 7.16 mmol) in small portions. The resulting suspension was vigorously stirred and slowly warmed to room temperature. An almost clear solution was obtained after 6 h. The solvent was removed in vacuum, and the residue was treated with 10 ml of toluene. After filtration yellow crystals of compound **2** precipitated at room temperature. Yield: 2.11 g (81%). Mp (argon, sealed capillary): $93^\circ C$. 1H NMR (C_6D_6 , 400 MHz, 298 K): δ = 7.09 (4 H, pseudo-*t*, *m*-H of phenyl), 7.06 (4 H, pseudo-*d*, *o*-H of phenyl), 6.94 (2 H, pseudo-*t*, *p*-H of phenyl), 4.92 (1 H, s, br., AlH), 4.72 (1 H, s, CH of the chelate), 1.54 (6 H, s, CH_3 of the chelate), 0.00 (9 H, s, $SiMe_3$), -0.75 (2 H, s, $AlCH_2$). ^{13}C NMR (C_6D_6 , 100 MHz, 298 K): δ = 168.5 (C=N), 145.6 (*i*-C of phenyl), 129.6 (*m*-C of phenyl), 126.4 (*o*-C of phenyl), 126.2 (*p*-C

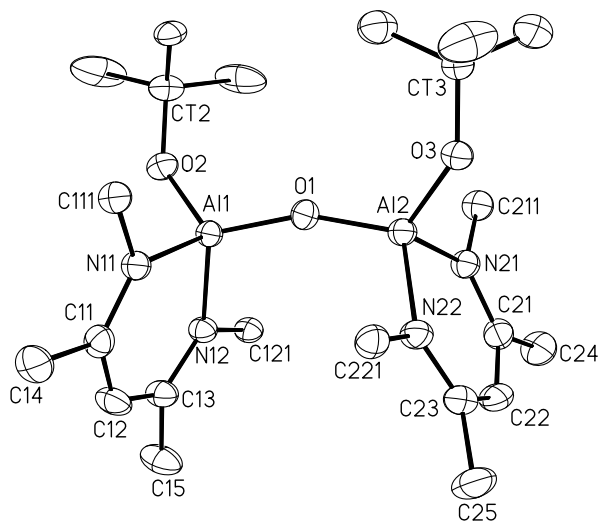


Fig. 3. Molecular structure of **5**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Only the *ipso*-carbon atoms of the phenyl rings are shown. Important bond lengths (pm) and angles ($^{\circ}$) (data of the second molecule in square brackets): Al1–O1 167.8(2) [168.2(2)], Al1–O2 170.5(2) [170.3(2)], Al1–N1 189.4(2) [189.1(2)], Al1–N2 189.0(2) [188.9(2)], Al2–O1 167.7(2) [168.0(2)], Al2–O3 169.7(2) [170.5(2)], Al2–N2 189.2(2) [188.5(2)], Al2–N22 189.5(2) [188.8(2)], Al1–O1–Al2 159.2(1) [154.3(1)], N11–Al1–N12 95.43(9) [95.56(8)], N21–Al2–N22 95.96(9) [95.75(9)].

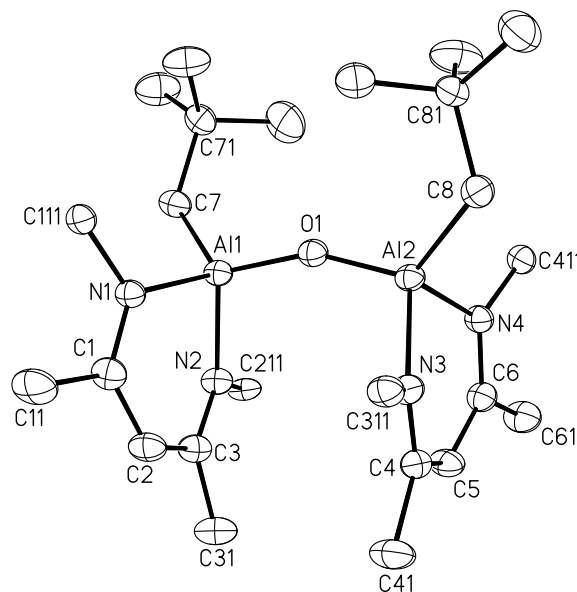


Fig. 5. Molecular structure of **7**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Only the *ipso*-carbon atoms of the phenyl rings are shown. Important bond lengths (pm) and angles ($^{\circ}$): Al1–O1 170.1(2), Al1–C7 193.4(3), Al1–N1 191.3(2), Al1–N2 191.7(2), Al2–O1 169.7(2), Al2–C8 195.6(2), Al2–N3 191.6(2), Al2–N4 191.7(2), Al1–O1–Al2 155.8(1), N1–Al1–N2 94.09(9), N3–Al2–N4 93.39(9).

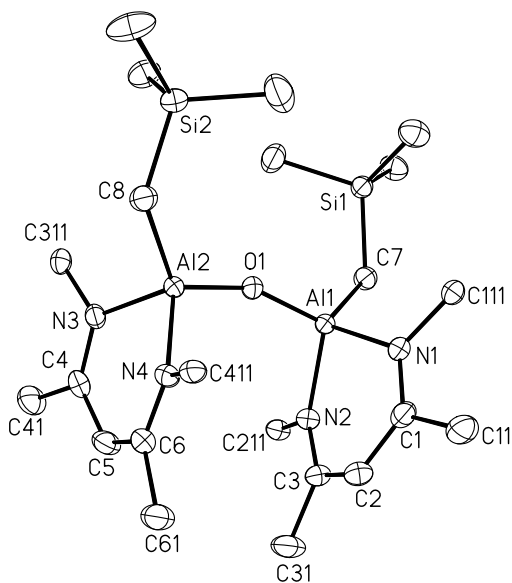


Fig. 4. Molecular structure of **6**. The thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted. Only the *ipso*-carbon atoms of the phenyl rings are shown. Important bond lengths (pm) and angles ($^{\circ}$): Al1–O1 170.0(2), Al1–C7 196.1(2), Al1–N1 192.2(2), Al1–N2 192.2(2), Al2–O1 169.9(2), Al2–C8 195.4(2), Al2–N3 192.1(2), Al2–N4 192.2(2), Al1–O1–Al2 155.9(1), N1–Al1–N2 93.43(8), N3–Al2–N4 93.38(8).

of phenyl), 97.7 (CH of the chelate), 22.8 (CH₃ of the chelate), 2.1 (SiMe₃), –3.3 (br., AlC). ²⁹Si NMR (C₆D₆, 400 MHz, 298 K): = 0.2. IR (cm⁻¹; paraffin; CsBr): 1946 vw; 1791 m, br. νAlH; 1683 w, 1556 vs νCN, (phenyl); 1452 vs (paraffin); 1402 s δCH₃; 1377 s (paraffin); 1352 sh, 1339 m, 1304 w δCH₃; 1070 s, br. δCH₃, νCC, νNC; 970 vw, 930 vw, 889 vw, 851 m, 814 w ρCH₃(Si); 719 s (paraffin); 667 w ν_{as}SiC; 592 w, 559 m, 513 w, 467 s, br. νAlC, νAlN, (phenyl). MS (EI, 20 eV): *m/z* (%) = 364 (17) M⁺; 363 (45) M⁺ – H; 277 (100) M⁺ – CH₂SiMe₃. Anal. Calc. for C₂₁H₂₉N₂AlSi (364.5): C, 69.2; H, 8.0; N, 7.7. Found: C, 68.9; H, 7.9; N, 7.5%.

3.2. Synthesis of *L*Al(H)-CH₂CMe₃ [**3**, L = {H₅C₆-N=C(Me)}₂CH]

A cooled solution (–40 °C) of the dihydride **1** (0.900 g, 3.24 mmol) in 20 ml of cyclopentane was treated with solid neopentyllithium (0.253 g, 3.24 mmol) in small portions. The mixture was slowly warmed to room temperature and stirred over night. The solvent was removed in vacuum, and the residue was treated with *n*-pentane. Colorless crystals of compound **3** were obtained after filtration and cooling of the filtrate to –30 °C. Yield: 1.02 g (90%). Mp (argon, sealed capillary): 79 °C. ¹H NMR (C₆D₆, 400 MHz, 298 K): = 7.09 (4 H, pseudo-*t*, *m*-H of phenyl), 7.07 (4 H, pseudo-*d*, *o*-H of phenyl), 6.94 (2 H, pseudo-*t*, *p*-H of phenyl), AlH not detected, 4.71 (1 H, s, CH of the chelate), 1.55 (6 H, s, CH₃ of the chelate), 0.93 (9 H, s, CMe₃), 0.36 (2 H, s, AlCH₂). ¹³C NMR (C₆D₆, 100 MHz, 298 K): δ = 168.5 (C=N), 145.7 (*i*-C of phenyl), 129.5 (*m*-C of phenyl), 126.5 (*o*-C of phenyl), 126.2 (*p*-C of phenyl), 97.6 (CH of the chelate), 34.1 (CMe₃), 30.8 (CMe₃), 29.6 (br., AlC), 22.8 (CH₃ of the chelate). IR (cm⁻¹; paraffin; CsBr): 1942 vw; 1782 w, br. νAlH; 1653 w, 1597 w, 1558 m, 1530 w νCN, (phenyl); 1458 s (paraffin); 1396 s δCH₃; 1377 s (paraffin); 1300 vw, 1256 w δCH₃; 1227 vw, 1196 vw, 1153 vw, 1123 vw, 1070 vw, 1024 w, 982 m δCH₃, νCC, νNC; 860 vw, 814 vw, 754 m; 721 m (paraffin); 698 m; 592 vw, 559 w, 525 w, 473 m, br. νAlC, νAlN, (phenyl). MS (EI, 20 eV): *m/z* (%) = 348 (2) M⁺; 277 (100) M⁺ – CH₂CMe₃. Anal. Calc. for C₂₂H₂₉N₂Al (348.5): C, 75.8; H, 8.4; N, 8.0. Found: C, 75.3; H, 8.2; N, 7.8%.

3.3. Synthesis of the compound *L*Al[N(C₆H₅)-C(Me)=C(H)-C(=CH₂)-N(C₆H₅)] [**4**, L = {H₅C₆-N=C(Me)}₂CH]

A cooled solution (–78 °C) of the dihydride **1** (0.720 g, 2.59 mmol) in 20 ml of *n*-hexane was treated with solid LiC(SiMe₃)₃ · 2THF (0.990 g, 2.59 mmol) in small portions. The suspension was vigorously stirred and slowly warmed to room temperature. After 1 h at room temperature a clear red solution was obtained, which was stirred for further 12 h. The mixture was filtered. The filtrate was stored at –45 °C. A colorless solid precipitated which was separated. The solution was concentrated to about

Table 1Crystal data and structure refinement for **2**, **4**, **5**, **6**, and **7**^a

	2	4	5	6	7
Formula	C ₂₁ H ₂₉ N ₂ AlSi	C ₃₄ H ₃₃ AlN ₄	C ₄₂ H ₅₂ N ₄ O ₃ Al ₂	C ₄₂ H ₅₆ N ₄ OAl ₂ Si ₂	C ₄₄ H ₅₆ N ₄ OAl ₂
Temperature (K)	153(2)	153(2)	153(2)	153(2)	153(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group [19]	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> 1̄ (no. 2)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>a</i> (pm)	998.42(3)	1330.1(1)	2102.7(4)	1181.93(2)	1146.86(6)
<i>b</i> (pm)	2127.79(6)	1609.3(1)	1903.8(3)	1184.66(2)	1977.5(1)
<i>c</i> (pm)	1080.93(3)	1362.1(1)	2125.9(4)	1801.51(4)	1863.1(1)
α (°)	90	90	90	95.945(1)	90
β (°)	106.836(2)	100.119(2)	112.193(3)	105.519(1)	90.503(1)
γ (°)	90	90	90	115.200(1)	90
<i>V</i> (10 ⁻³⁰ m ³)	2197.9(1)	2870.1(4)	7880(10)	2129.64(7)	4225.2(4)
<i>Z</i>	4	4	8	2	4
<i>D</i> _{calc} (g cm ⁻³)	1.102	1.214	1.205	1.159	1.118
μ (mm ⁻¹)	1.355	0.100	0.117	1.426	0.105
Crystal size (mm)	0.40 × 0.28 × 0.14	0.10 × 0.06 × 0.05	0.23 × 0.11 × 0.06	0.20 × 0.15 × 0.06	0.22 × 0.18 × 0.12
Radiation	Cu Kα	Mo Kα	Mo Kα	Cu Kα	Mo Kα
Theta range (°)	4.16 ≤ θ ≤ 72.28	1.97 ≤ θ ≤ 19.68	1.16 ≤ θ ≤ 30.13	1.21 ≤ θ ≤ 26.07	1.50 ≤ θ ≤ 24.08
Index ranges	-12 ≤ <i>h</i> ≤ 12 -26 ≤ <i>k</i> ≤ 24 -10 ≤ <i>l</i> ≤ 12	-12 ≤ <i>h</i> ≤ 12 -15 ≤ <i>k</i> ≤ 15 -12 ≤ <i>l</i> ≤ 12	-29 ≤ <i>h</i> ≤ 29 -26 ≤ <i>k</i> ≤ 26 -29 ≤ <i>l</i> ≤ 29	-13 ≤ <i>h</i> ≤ 14 -13 ≤ <i>k</i> ≤ 13 -22 ≤ <i>l</i> ≤ 20	-13 ≤ <i>h</i> ≤ 13 -22 ≤ <i>k</i> ≤ 22 -21 ≤ <i>l</i> ≤ 21
Independent reflections	4079 [R _{int} = 0.0370]	2554 [R _{int} = 0.0867]	22997 [R _{int} = 0.1082]	7260 [R _{int} = 0.0268]	6682 [R _{int} = 0.0760]
Reflections observed	3043	1799	11 098	5849	4473
Parameters	258	363	1001	470	470
<i>R</i> = Σ <i>F</i> _o - <i>F</i> _c /Σ <i>F</i> _o [<i>I</i> > 2σ(<i>I</i>)]	0.0505	0.0415	0.0679	0.0463	0.0487
<i>wR</i> ₂ = {Σ <i>w</i> (<i>F</i> _o ² - <i>F</i> _c ²)/Σ <i>F</i> _o ² } ^{1/2} (all data)	0.1435	0.1041	0.1820	0.1318	0.1213
Max./min. residual (10 ³⁰ e ⁻³)	0.395/-0.213	0.181/-0.200	0.398/-0.365	0.402/-0.256	0.269/-0.262

^a Programme SHELXL-97 [18]; solutions by direct methods, full-matrix refinement with all independent structure factors.

5 ml and cooled to -45 °C to obtain an orange solid. Repeated recrystallization yielded few crystals of **4**. Mp (argon, sealed capillary): 143 °C. ¹H NMR (C₆D₆, 400 MHz, 298 K): = 7.44 to 6.66 (several multiplets of phenyl hydrogen atoms), 5.13 and 4.81 (each 1 H, s, CH of the chelates), 4.31 and 4.05 (each 1 H, s, br., C=CH₂), 1.68 (3 H, s, CH₃ of the chelate having the exocyclic C=C double bond), 1.46 (6 H, s, Me of the intact chelate ligand). MS (EI, 20 eV): *m/z* (%) = 524 (58) M⁺, 523 (100) M⁺ - H, 250 (38) LH⁺.

3.4. Synthesis of {LAl(OCMe₃)₂O} [5, L = {H₅C₆-N=C(Me)₂CH}]

A solution of Me₃C-O-O-H in nonane (5.5 M, 0.23 ml, 1.26 mmol) was added drop wise to a cooled solution (-60 °C) of the dihydride **1** (0.351 g, 1.26 mmol) in 15 ml of *n*-hexane. The mixture was slowly warmed to room temperature and stirred for 30 min. The solution was concentrated and cooled to -15 °C to obtain bright yellow crystals of **5**. Yield: 0.252 g (56%). Mp (argon, sealed capillary): 204 °C. ¹H NMR (C₆D₆, 400 MHz, 298 K): = 7.24 (8 H, pseudo-*o*, *o*-H of phenyl), 7.13 (8 H, *m*, *m*-H of phenyl), 6.99 (4 H, *m*, *p*-H of phenyl), 4.82 (2 H, s, CH of the chelate), 1.66 (12 H, s, CH₃ of the chelate), 1.06 (18 H, s, CMe₃). ¹³C NMR (C₆D₆, 100 MHz, 298 K): δ = 167.3 (C=N), 146.2 (*i*-C of phenyl), 128.7 (*m*-C of phenyl), 127.1 (*o*-C of phenyl), 125.6 (*p*-C of phenyl), 96.3 (CH of the chelate), 33.9 (CMe₃), 26.8 (CMe₃), 23.1 (CH₃ of the chelate). IR (cm⁻¹; paraffin; CsBr): 1578 s, 1560 m, 1530 w νCN, (phenyl); 1458 vs (paraffin); 1300 w δCH₃; 1377 s (paraffin); 1302 w, 1256 w δCH₃; 1217 w, 1112 w, 1047 m, 1024 m, 984 w, 943 w, 918 w δCH₃, νCC, νNC; 861 w, 851 w, 814 vw, 754 m; 721 m (paraffin); 642 w, 590 w, 561 w, 522 w, 470 m, br. νAlC, νAlN, νAlO, (phenyl). MS (EI, 20 eV): *m/z* (%) = 714 (9) M⁺; 641 (100) M⁺ - OCMe₃, 585 (9) M⁺ - OCMe₃ - butene, 250 (25) LH. Anal. Calc. for C₄₂H₅₂N₄O₃Al₂ (714.8): C, 70.6; H, 7.3; N, 7.8. Found: C, 70.2; H, 7.3; N, 7.6%.

3.5. Synthesis of the compound {LAl(CH₂SiMe₃)₂O} [6, L = {H₅C₆-N=C(Me)₂CH}]

A solution of Me₃C-O-O-H in nonane (5.5 M, 0.21 ml, 1.16 mmol) was added drop wise to a cooled solution (-60 °C) of

the hydride **2** (0.432 g, 1.18 mmol) in 10 ml of *n*-hexane. The mixture was slowly warmed to -20 °C and concentrated at this temperature to approximately 8 ml. Colorless crystals of the dialuminoxane **6** were obtained after storing of the solution at -15 °C over night. Yield: 0.367 g (83%). Mp (argon, sealed capillary): 179 °C. ¹H NMR (C₆D₆, 400 MHz, 298 K): = 7.26 (8 H, pseudo-*d*, *o*-H of phenyl), 7.17 (8 H, pseudo-*t*, *m*-H of phenyl), 6.99 (4 H, *m*, *p*-H of phenyl), 4.91 (2 H, s, CH of the chelate), 1.76 (12 H, s, CH₃ of the chelate), -0.02 (18 H, s, SiMe₃), -0.94 (4 H, s, AlCH₂). ¹³C NMR (C₆D₆, 100 MHz, 298 K): δ = 166.9 (C=N), 146.6 (*i*-C of phenyl), 129.1 (*m*-C of phenyl), 126.9 (*o*-C of phenyl), 125.6 (*p*-C of phenyl), 97.9 (CH of the chelate), 23.4 (CH₃ of the chelate), 2.7 (SiMe₃), -6.0 (AlCH₂). ²⁹Si NMR (C₆D₆, 79.5 MHz, 298 K): δ = -0.5. IR (cm⁻¹; paraffin; CsBr): 1940 w, 1879 w, 1798 w, 1750 w, 1630 w, 1595 m, 1575 m, 1558 s, 1517 w νCN, (phenyl); 1458 vs, 1375 s (paraffin); 1298 w, 1260 w δCH₃; 1239 m, 1193 w, 1168 w, 1070 m, 1022 s, 984 s, 970 s, 935 m, 918 m δCH₃, νCC, νNC; 854 s, 822 s, 746 s ρCH₃(Si); 723 s (paraffin); 698 s ν_{as}-SiC; 640 w, 604 w ν_sSiC; 551 s, 540 m, 519 s, 495 w, 465 m νAlC, νAlN, νAlO, (phenyl). MS (EI, 20 eV): *m/z* (%) = 727 (3) M⁺ - CH₃; 655 (100) M⁺ - CH₂SiMe₃; 250 (45) LH. Anal. Calc. for C₄₂H₅₆N₄OAl₂Si₂ (743.1): C, 67.9; H, 7.6; N, 7.5. Found: C, 67.5; H, 7.4; N, 7.4%.

3.6. Synthesis of the compound {LAl(CH₂CMe₃)₂O} [7, L = {H₅C₆-N=C(Me)₂CH}]

A solution of Me₃C-O-O-H in nonane (5.5 M, 0.08 ml, 0.44 mmol) was added drop wise to a cooled solution (-78 °C) of the hydride **3** (0.149 g, 0.43 mmol) in 10 ml of *n*-hexane. The mixture was slowly warmed to -10 °C and concentrated at this temperature to approximately 6 ml. Colorless crystals of the dialuminoxane **7** were obtained by storing of the solution at -15 °C for 2 d. Yield: 0.123 g (79%). Mp (argon, sealed capillary): 214 °C. ¹H NMR (C₆D₆, 400 MHz, 298 K): = 7.31 (8 H, br., *o*-H of phenyl), 7.15 (4 H, *m*, *p*-H of phenyl), 6.97 (4 H, *m*, *m*-H of phenyl), 4.91 (2 H, s, CH of the chelate), 1.79 (12 H, s, CH₃ of the chelate), 0.98 (18 H, s, CMe₃), 0.15 (4 H, s, AlCH₂). ¹³C NMR (C₆D₆,

100 MHz, 298 K): δ = 166.8 (C=N), 147.0 (*i*-C of phenyl), 129.0 (*m*-C of phenyl), 126.9 (*o*-C of phenyl), 125.6 (*p*-C of phenyl), 98.1 (CH of the chelate), 34.7 (CMe₃), 30.6 (GaC), 29.0 (CMe₃), 23.6 (CH₃ of the chelate). IR (cm⁻¹; paraffin; CsBr): 1558 s, 1524 s ν CN, (phenyl); 1456 vs (paraffin); 1402 w δ CH₃; 1377 s (paraffin); 1300 w, 1263 w δ CH₃; 1227 w, 1194 w, 1153 w, 1123 w, 1070 w, 1022 w, 980 w δ CH₃, ν CC, ν NC; 920 w, 858 w, 814 w, 752 m; 719 m (paraffin); 698 m, 656 w, 640 vw, 613 w; 559 m, 527 w, 471 m ν AlC, ν AlN, (phenyl). MS (EI, 20 eV): m/z (%) = 640 (100) M⁺ – CHCMe₃; 583 (2) M⁺ – CH₂CMe₃ – CMe₃; 250 (7) LH. Anal. Calc. for C₄₄H₅₆N₄OAl₂ (710.9): C, 74.3; H, 7.9; N, 7.9. Found: C, 74.0; H, 8.1; N, 7.8%.

3.7. Crystal structure determinations of compounds **2** and **4** to **7**

Single crystals were obtained from toluene at room temperature (**2**) or from the concentrated reaction mixtures on cooling to –15 °C (**5–7**); crystals of **4** from saturated solutions in *n*-hexane (–15 °C). The crystallographic data were collected with a BRUKER apex diffractometer. The structures were solved by direct methods and refined with the program SHELXL-97 [18] by a full-matrix least-squares method based on F^2 . Crystal data, data collection parameters and structure refinement details are given in Table 1. The crystals of **2** showed a disorder. The Al(H)–CH₂SiMe₃ group occupied two positions. Their atoms were refined with occupancy factors of 0.88 and 0.12; the last ones with isotropic displacement parameters. Only very small crystals of compound **4** were obtained. Therefore, data were collected only up to $2\theta = 39.4^\circ$. The asymmetric unit of **5** contains two independent molecules. Two *tert*-butyl groups of **5** were disordered (CT2 and CT6); the methyl groups were refined with occupancy factors of 0.7 and 0.3.

4. Supplementary material

CCDC numbers 696067, 696068, 696069, 696070 and 696071 contain the supplementary crystallographic data for compounds **2**, **4–7**. 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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