

The Methylene-bridged Dialuminium Compound $R_2Al-CH_2-AlR_2$ [$R = CH(SiMe_3)_2$] as an Effective Chelating Lewis Acid – Adducts with Halides, Perchlorate and Isopropylamide

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Dedicated to Professor Heribert Offermanns on the occasion of his 75th birthday

The new methylene-bridged dialuminium compound $Aryl_2Al-CH_2-AlAryl_2$ **1b** was synthesised from $Cl_2Al-CH_2-AlCl_2$ and four equivalents of $LiAryl$ [$Aryl = C_6H_2(2,4,6-i-Pr)_3$]. A 1 : 2 stoichiometric ratio of the starting compounds afforded the dimeric aluminium halide $(Aryl_2AlCl)_2$ (**2**) by dismutation. The coordination behaviour of the related, but more easily available dialuminium compound $R_2Al-CH_2-AlR_2$ [$R = CH(SiMe_3)_2$] **1a** was explored. It yields the Lewis acid base adducts $[M][R_2Al-CH_2-AlR_2(\mu-X)]$ [**3a**, $M = Li(TMEN)_2$, $X = Cl$; **3b**, $M = Li(TMEN)_2$, $X = Br$; **3c**, $M = K(18-crown-6)$, $X = ClO_4$; **3d**, $M = Li(TMEN)_2$, $X = NH(i-Pr)$] with X residing in a bridging position between the two Al atoms as evident from NMR spectroscopy and X-ray crystallography (**3b**, **3c**, **3d**). Compound **3c** is a unique example of a stable, in organic solvents soluble adduct that features a ClO_4^- anion coordinated by an alkylaluminium compound *via* two of its oxygen atoms.

Key words: Aluminium, Lithium, Chelating Lewis Acids, Anion Receptors, Perchlorate

Introduction

Oligoacceptors based on coordinatively unsaturated metal or semi-metal atoms of main group elements have found considerable interest in recent years because of their potential applicability in phase transfer processes, in catalysis or as anion receptors in analytical sensor systems (anion recognition) [1–8]. In this context methylene-bridged dialuminium compounds, $R_2Al-CH_2-AlR_2$, are of some importance as they proved to be effective chelating acceptor molecules with their two strongly Lewis acidic three-coordinate aluminium atoms bridged by a CH_2 group. $Cl_2Al-CH_2-AlCl_2$, which has been known since the 1960s [9], is a facile starting material for the synthesis of the corresponding organometallic derivatives by salt elimination. Nevertheless, only a few neutral compounds have so far been synthesised and fully characterised. These include $R_2Al-CH_2-AlR_2$ [$R = CH(SiMe_3)_2$ (**1a**) [10], $R = N(SiMe_3)_2$ [11], $R = N(CMe_2-CH_2)_2CH_2$ [11]] and the mixed deriva-

tive $R(Cl)Al-CH_2-AlR(Cl)$ [$R = CH(SiMe_3)_2$] [12]. The use of sterically less demanding ligands resulted in dismutation reactions with the formation of the mononuclear trialkylaluminium derivatives and a mixture of unknown secondary products [13]. The potential of the above dialuminium compounds to react as chelating Lewis acids in the presence of an auxiliary base (*e. g.* TMEN) was demonstrated for **1a** by the synthesis and characterisation of a range of mono-adducts $[Li(base)_n][1a(X)]$ ($X = NO_2$ [14], NO_3 [14], N_3 [15], CH_3CO_2 [15], $Me_2PCHPMe_2$ [16]) and $[Li(base)_n][1a(R')]$ ($R' = H$ [17], CH_2-t-Bu [18], Me [19], $n-Bu$ [19], $C\equiv C-SiMe_3$ [19], $C\equiv C-t-Bu$ [19], $C\equiv C-Ph$ [19], $C\equiv C-PPh_2$ [19]). In the solid state the anions X^- are chelated by the two aluminium atoms *via* two of their heteroatoms thereby forming five- or six-membered heterocycles, while in most cases the R' anions are bound in a terminal fashion to only one aluminium atom. Small substituents with lower steric demand show in the solution NMR spectra dynamic behaviour at room temperature with the R'

Table 1. Selected structural parameters (pm, deg) of compound **2** and methylene-bridged dialuminium compounds.

Parameter ^a	1a [3]	1b	R' = H [17]	3b	3c (OEt ₂)	3d	2
Al-CH ₂	193.8(1)	194.3 (av.)	197.0 (av.)	212.1 (av.)	196.4 (av.)	198.5 (av.)	–
Al-C(ligand)	195.7 (av.)	198.0 (av.)	202.3 (av.)	201.1 (av.)	201.7 (av.)	206.1 (av.)	196.9 (av.)
Al1-CH ₂ -Al2	129.6(2)	129.9(2)	88.4 (av.)	96.0 (av.)	120.18(9)	92.3(1)	–
Al-X	–	–	–	260.8 (av.)	202.8 (av.)	202.9 (av.)	232.5 (av.)
Al-X-Al	–	–	–	74.2 (av.)	–	–	94.5 (av.)
<i>d</i> [Al to C ₃] ^b	1.6	5.8/4.6	–	–	–	–	–
Puckering angle ^c	–	–	21	17.4	–	24.5	0.06
H3'-CH-Al2-C ^d	–	–	–	147, 155	-172, 166	156, 156	–
Al···Al	351	352	275	315	341	286	342

^a Atomic labels for previously reported compounds **1a** and R' = H, differ from the reported ones, structural parameters have been allocated appropriately; ^b deviation of Al from the average plane of the connecting carbon atoms; ^c across C3-X or Cl-Cl; ^d only torsion angle to that Al-C bond whose σ* orbitals are orientated appropriately for hyperconjugation.

CH₂-Al{CH(SiMe₃)₂}₂(μ-X) [**3a**, M = Li(TMEN)₂, X = Cl; **3b**, M = Li(TMEN)₂, X = Br; **3c**, M = K(18-crown-6)(Et₂O), X = ClO₄; **3d**, M = Li(TMEN)₂, X = NH(*i*-Pr)] in moderate (**3c**) to good yields (Eq. 2). **3d** was easily converted into its DME (dimethoxyethane) derivative **3e** [M = Li(DME)₃, X = NH(*i*-Pr)] by recrystallisation from DME.

The overall geometry of compound **1b** in the solid state (Fig. 1) in terms of the relative orientation of the ligands on the two aluminium atoms closely resembles that of the previously characterised amides R₂Al-CH₂-AlR₂ [R = N(SiMe₃)₂, N(CMe₂-CH₂)₂CH₂] [4]. The

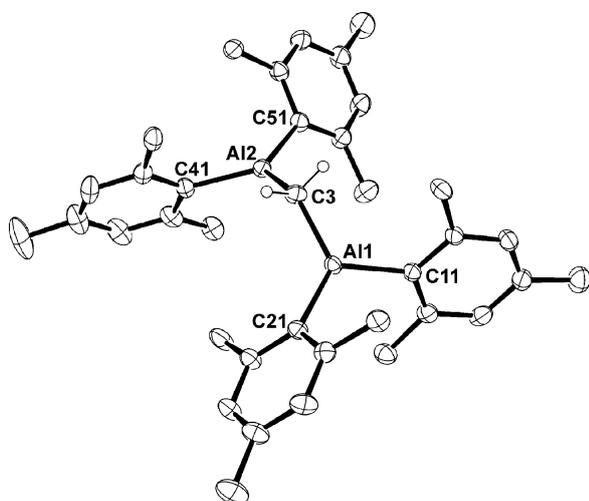


Fig. 1. Molecular structure and atomic numbering scheme of compound **1b**. Displacement ellipsoids are drawn at the 40% level, hydrogen atoms with an arbitrary radius. Hydrogen atoms (except for CH₂Al₂) and methyl groups of the isopropyl substituents have been omitted for clarity.

four *ipso*-C atoms of the aryl ligands are approximately in the same plane as evident from C-Al···Al-C torsion angles close to 0° (−8.8, −9.1°). This contrasts with the situation in compound **1a** where the ligands on one aluminium atom are rotated relative to the ligands on the second aluminium atom and are essentially perpendicular to each other with relevant C-Al···Al-C torsion angles around 86°. Each of the CH bonds of the methylene bridge in **1a** is thereby arranged parallel to an empty *p* orbital of one of the aluminium atoms (see also H-C-Al-C torsion angles in Table 1). This orientation is ideal for potential hyperconjugation, which has been discussed for **1a** and some related acid base adducts of **1a** as an important contributing factor to the observed relatively short Al-C(H₂) bond lengths in bis(trimethylsilyl)methyl-substituted methylene-bridged dialuminium compounds (Table 1). Another important aspect is the significant charge separation between the central carbon atom and the two electropositive aluminium atoms which may result in additional electrostatic contributions. In particular the latter point may help to explain why the Al-CH₂ bond lengths in **1a** and **1b** are identical within experimental error, while the Al-C distances to the substituents are slightly longer for **1b** (Table 1). The Al-C-Al angles in both compounds are comparable and with 130° very large as a consequence of steric effects and the electrostatic repulsion between the electropositive Al atoms. The coordination sphere of the metal atoms is planar (*c.f.* *d* [Al to C₃] in Table 1) as expected for three-coordinate aluminium atoms. The aromatic rings of each of the Al atoms are orientated such that there is an intermolecular CH···π interaction between an isopropyl group of one aromatic ring and the

isopropyl- and *ortho*-C atom of the second ring (CH...C 295–317 pm).

The molecular structures of the anions of the mono-adducts **3b** and **3d** feature a bridging heteroatom which is part of a four-membered, slightly puckered (*ca.* 20°) C–Al–X–Al (X = Br, N) heterocycle (Figs. 2 and 4). The compounds are similar to the hydrido-complex $[R_2Al-CH_2-AlR_2(\mu-H)]^-$ [17], but differ from a series of alkyl or alkynyl adducts $[R_2Al-CH_2-AlR_2R']^-$ ($R' = CH_2-t-Bu$ [18], Me [19], *n*-Bu [19], $C\equiv C-SiMe_3$ [19], $C\equiv C-Ph$ [19], $C\equiv C-PPh_2$ [19]) in which the Lewis base coordinates in a terminal fashion to only one of the aluminium atoms. The larger tendency of Br^- or $NH(i-Pr)^-$ to coordinate in a bridging fashion may be attributed to the energetically favoured formation of two 2e-2c bonds as compared to a 3c-2e bond required in the hypothetical derivatives containing bridging alkyl groups. The unique ability of H^- to coordinate in a bridging fashion has been discussed previously [25–28]. The Al–C bond lengths are comparable and, as was to be expected, significantly longer than in the neutral compounds **1** with three-coordinate aluminium atoms (Table 1). The formation of the heterocycles result in much more acute Al–C–Al angles in the adducts as compared to those of the open chain derivatives **1**. Al–X bonds are unexceptional for X = N (206 pm), but rather on the

long side for the bridging Br^- anion (261 pm) [*c.f.* Al_2Br_6 (241 pm) [29], $Br_2Al_2\{(C_6H_2(2,4,6-i-Pr)_3)_4$ (av. 250 pm) [30]]. It should be noted, that crystals of **3b** were twinned and caused problems in the refinement of the structure. The results are therefore somewhat preliminary. While the overall geometry is certainly reliable, individual bond lengths and angles should be treated with some caution.

The ClO_4^- anion in compound **3c**(OEt_2) coordinates to the two aluminium atoms *via* two oxygen atoms and forms a six-membered C–Al–O–Cl–O–Al heterocycle in a boat conformation (Fig. 3; schematic drawing in Eq. 2) that resembles the related adducts of **1a** with NO_3^- [14] and $H_3C-CO_2^-$ [15]. The reduced strain in the larger ring results in a much larger Al–C–Al angle of 120.18(9)°. The Al–C bond lengths of 196.4(2) and 201.8(2) pm are similar to those of $[R_2Al-CH_2-AlR_2(\mu-H)]^-$ [17], but are slightly shorter than those of **3b** and **3d** or the comparable bonds to the four-coordinate aluminium atoms in the alkyl adducts [19]. This is attributed to the lower ring strain in the six-membered ring. The short Al–C(H_2) bond lengths may further be influenced by hyperconjugation ($CH-\sigma^*$) between the C3–H3B bond and one of the terminal Al–C bonds as evident from the coplanar orientation of these bonds with H–C–Al–C torsion angles close to 180° (Table 1). The potassium

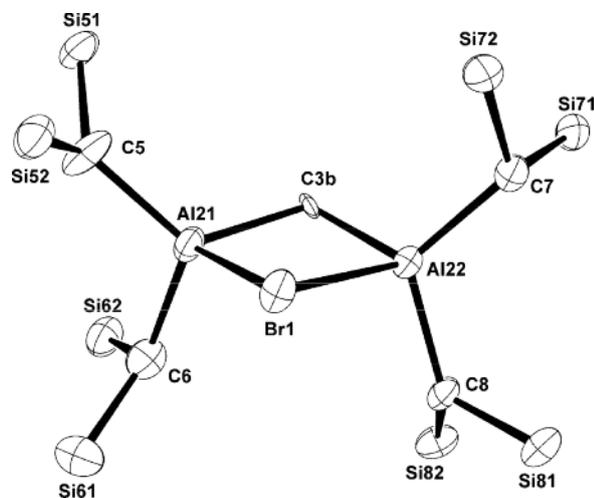


Fig. 2. Molecular structure and atomic numbering scheme of one anion of compound **3b**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms and methyl groups of the bis(trimethylsilyl)methyl substituents have been omitted for clarity.

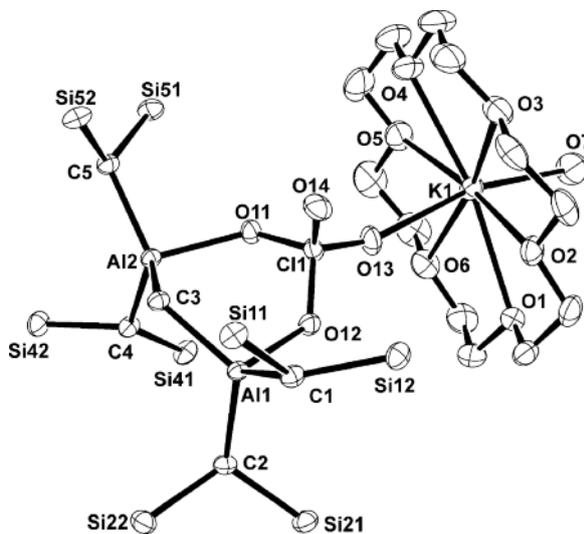


Fig. 3. Molecular structure and atomic numbering scheme of compound **3c**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms, methyl groups of the $SiMe_3$ substituents and ethyl groups of Et_2O (O7) have been omitted for clarity.

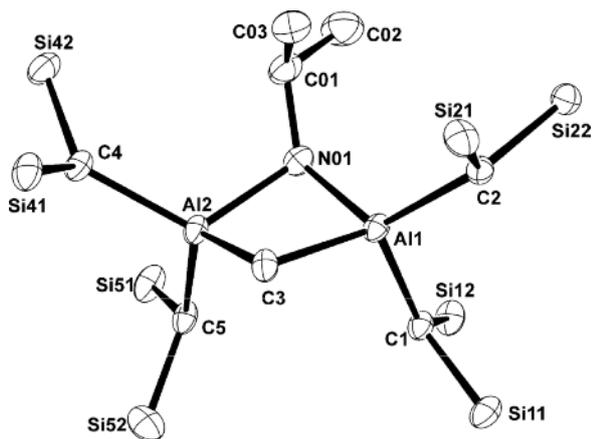


Fig. 4. Molecular structure and atomic numbering scheme of the anionic part of compound **3d**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms and methyl groups of the SiMe₃ groups have been omitted for clarity.

counter-ion is coordinated by six oxygen atoms of the crown ether and perpendicular to the hexagonal plane of these atoms by an oxygen atom of the perchlorate anion and a diethyl ether molecule in an approximately linear fashion. The Cl–O distances to the oxygen atoms that are bound to aluminium atoms of 147 pm are significantly longer than those to the remaining oxygen atoms (Cl–O 141 pm) as a consequence of the higher coordination number and the formation of polar covalent bonds. The coordination sphere of the potassium cation is typical for crown ethers as found in simple coordination compounds such as [K(18-crown-6)][ClO₄] [31], [K(18-crown-6)(OPPh₃)] [ClO₄] [32] or related dibenzo-18-crown-6 derivatives [33]. Compound **3c** is very unusual as a rare example of a stable organometallic main group metal perchlorate adduct soluble in organic solvents, and it is the first Group 13 derivative of this type. So far only a few Group 14 element complexes [34–36] are known. By contrast, related organometallic complexes of the electron-rich transition metals, especially those of Cu⁺ and Ag⁺, are much more common [37–52]. Inorganic aluminium perchlorate complexes have been reported for solvent-stabilised [Al(sol)₆]³⁺ (sol = H₃C(O)NMe₂ [53], DMSO [54], H₂O [55], HC(O)NMe₂ [56], C(O)(NH₂)₂ [57]).

The dismutation product **2** is a dimer in the solid state and features an essentially planar Al₂Cl₂ heterocycle (Fig. 5) with the organic substituents arranged above and below that plane. The aryl substituents

on the aluminium atoms are rotated (angle between AlC₂ planes 20.8°) against each other to minimise steric repulsion. As already discussed for compound **1b** there are CH···π interactions between hydrogen atoms of isopropyl groups and *ipso*- and *ortho*-C atoms of an adjacent aryl substituent (CH···π 303–309 pm). Al–Cl and Al–C bond lengths and angles (Table 1) as well as the overall geometry are unexceptional and compare well with those of the Br analogue of **2** [30] and of related dimeric chloro compounds such as (*t*-Bu₂AlCl)₂ [58], [(Me₃Si)₃C(Me)AlCl]₂ [59] or (Aryl₂AlCl)₂ (Aryl = Mes [60], C₆F₅ [61]). A monomeric chloroalane has been reported with the bulky C₆H₃(2,6-mes)₂ substituent [62].

Solution NMR spectroscopic parameters of the presented methylene-bridged compounds are summarised in Table 2. Owing to the electronic influence of the aryl groups the signals of the CH₂ protons of **1b** are shifted considerably to lower field relative to those of

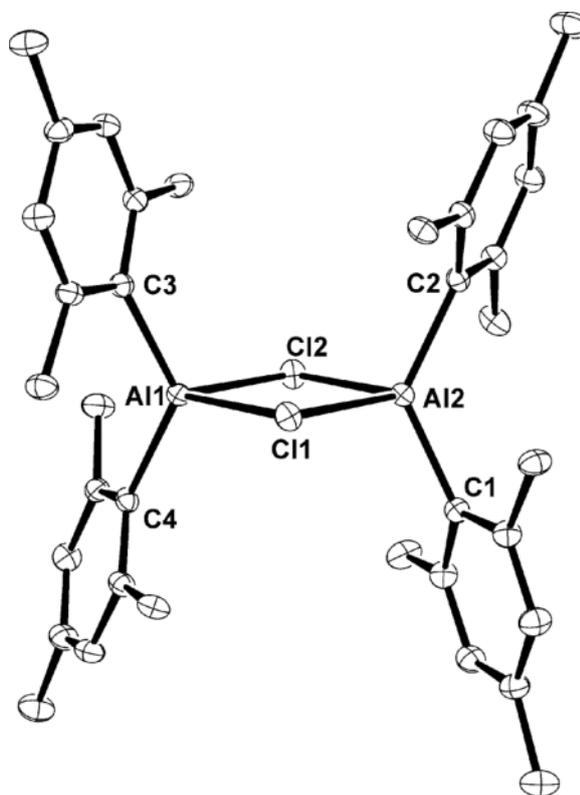


Fig. 5. Molecular structure and atomic numbering scheme of compound **2**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms and methyl groups of the isopropyl substituents have been omitted for clarity.

Table 2. Selected NMR parameters of methylene-bridged dialuminium compounds.

Compound	AlCH ₂ Al (¹ H)	AlCHSi ₂ (¹ H)	AlCH ₂ Al (¹³ C)	AlCHSi ₂ (¹³ C)	⁷ Li	CHSi ₂ (²⁹ Si)
1 [10]	-0.50	-0.22	n. o.	13.2	–	–
Aryl ₂ Al-CH ₂ -AlAryl ₂ (1b)	0.66	–	13.6	–	–	–
R' = H [17]	-1.32	-1.03	1.2	2.4	-0.5	-1.8
X = ClO ₄ [3c (Et ₂ O)]	-1.28	-1.03	2.8	5.1	–	-2.3
R' = Me [19]	-1.02	-0.84	15.3	7.5	-2.3	-5.2
X = Cl (3a)	-0.83	-0.92	11.5	6.1	0.2	-2.3
X = Br (3b)	-0.63	-0.83	13.7	6.3	-0.3	-2.3
X = NH(<i>i</i> -Pr) (3d)	-1.08	-1.08	17.4	5.1	-0.5	-2.8

1a. NMR parameters of the new mono-adducts [R₂Al-CH₂-AlR₂(μ-X)]⁻ [X = Cl, Br, NH(*i*-Pr)] are similar to that of the related alkyl or alkynide derivatives (Table 2 and ref. [19]), although the CH₂ signals (¹H) are shifted slightly to lower field, while conversely the CH signals are shifted to higher field. The alterations in the shifts result in a reversion of the relative position of the signals of the protons in the case of compounds **3a** and **3b**. The corresponding ¹H and ¹³C NMR signals of the ClO₄ derivative **3c** compare much better to those of the hydride than those of the methyl derivative. This correlates with the observation that structural parameters (Al–C distances) of **3c** in the solid state are closer to those of the hydride than to those of alkyl and alkynide derivatives [19] or of the compounds **3a**, **3b** and **3d** (Table 1).

Experimental Section

All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane and *n*-pentane with LiAlH₄; THF and DME with Na/benzophenone; TMEN with Na). NMR spectra were recorded in C₆D₆ or [D₈]THF at ambient probe temperature using the following Bruker instruments: Avance I (¹H, 400.13; ¹³C, 100.62; ⁷Li 155.51, ²⁹Si, 79.49 MHz) or Avance III (¹H, 400.03; ¹³C, 100.59; ⁷Li 155.46, ²⁹Si 79.47 MHz) and referenced internally to residual solvent resonances. Chemical shift data δ are given in ppm. ¹³C NMR spectra were all proton decoupled. IR spectra were recorded of Nujol mulls between KBr, CsBr or CsI plates on a Shimadzu Prestige 21 spectrometer. Cl₂Al-CH₂-AlCl₂ [9], [(Me₃Si)₂HC]₂Al-CH₂-Al[CH(SiMe₃)₂]₂ (**1a**) [10] and LiC₆H₂(2,4,6-*i*-Pr)₃ [63] were obtained according to literature procedures. Commercially available LiCl (anhydrous), LiBr (anhydrous), KClO₄ and H₂N(*i*-Pr) were used without further purification. 18-Crown-6 was sublimed *in vacuo* and stored under argon. The assignment of NMR spectra is based on HMBC, HSQC and DEPT135 data.

Synthesis of

[(2,4,6-*i*-Pr)₃H₂C₆]₂Al-CH₂-Al[C₆H₂(2,4,6-*i*-Pr)₃]₂ (**1b**)

A solution of LiC₆H₂(2,4,6-*i*-Pr)₃ (0.477 g, 2.27 mmol) in *n*-pentane (25 mL) was added slowly at -50 °C to a suspension of Cl₂Al-CH₂-AlCl₂ (0.119 g, 0.57 mmol) in *n*-pentane (25 mL). The mixture was allowed to warm to room temperature and stirred for 24 h. LiCl was removed by filtration. The filtrate was concentrated and kept at -15 °C to give colourless crystals of compound **1b** that were contaminated with about 5% of compound **2**. Yield: 0.174 g (35%); m. p. (under argon; sealed capillary): 197 °C (dec.). – IR (CsI, paraffin): ν = 1599 s, 1546 w (phenyl), 1458 vs, 1379 vs (paraffin), 1313 m, 1263 vw, 1240 vw δ(CH₃), 1188 w, 1166 vw, 1093 m, 1070 m, 1053 m, 1035 m, 945 m, 870 s, 835 vw, 773 vw ν(CC), δ(CH), 715 s (paraffin), 624 w, 530 w, 462 w cm⁻¹ ν(AlC). – ¹H NMR (400 MHz, C₆D₆): δ = 7.02 (s, 8 H, *m*-H), 3.01 (sep, 8 H, ³J_{H-H} = 6.3 Hz, *o*-CHMe₂), 2.78 (sep, 4 H, ³J_{H-H} = 6.8 Hz, *p*-CHMe₂), 1.23 (overlap d, 24 H, *p*-CHMe₂), 1.22 (overlap d, 48 H, *o*-CHMe₂), 0.66 (s, 2 H, AlCH₂Al). – ¹³C NMR (100 MHz, C₆D₆): δ = 156.1 (*o*-C), 150.3 (*p*-C), 144.7 (*ipso*-C), 120.4 (*m*-C), 41.0 (*o*-CHMe₂), 34.9 (*p*-CHMe₂), 25.3 (*o*-CHMe₂), 24.3 (*p*-CHMe₂), 13.6 (AlCH₂Al).

Synthesis of [(2,4,6-*i*-Pr)₃H₂C₆]₂Al-Cl] (**2**)

A solution of LiC₆H₂(2,4,6-*i*-Pr)₃ (0.385 g, 1.83 mmol) in toluene (20 mL) was added slowly at -50 °C to a suspension of Cl₂Al-CH₂-AlCl₂ (0.192 g, 0.92 mmol) in toluene (25 mL). The mixture was allowed to warm to room temperature and stirred for 48 h. The solvent was removed *in vacuo*, the remaining colourless solid was treated with *n*-pentane (50 mL), the mixture was filtered, and the filtrate was concentrated and kept at -15 °C to give colourless crystals of compound **2**. Yield: 0.350 g (82%); m. p. (under argon; sealed capillary): 173 °C. – IR (CsI, paraffin): ν = 1599 s, 1548 m (phenyl), 1462 vs, 1379 vs (paraffin), 1305 m, 1236 w δ(CH₃), 1188 w, 1165 m, 1130 w, 1099 m, 1070 w, 1033 w, 937 s, 875 s, 837 w ν(CC), δ(CH), 719 s (paraffin), 642 m, 570 w, 515 m, 478 w cm⁻¹ ν(AlC), ν(AlCl). – ¹H NMR (400 MHz, C₆D₆): δ = 7.05 (s, 4 H, *m*-H),

3.23 (sep, 4 H, ³J_{H-H} = 7.1 Hz, *o*-CHMe₂) 2.77 (sep, 2 H, ³J_{H-H} = 7.0 Hz, *p*-CHMe₂), 1.26 (d, 24 H, ³J_{H-H} = 7.1 Hz, *o*-CHMe₂), 1.21 (d, 12 H, ³J_{H-H} = 7.0 Hz, *p*-CHMe₂). – ¹³C NMR (100 MHz, C₆D₆): δ = 156.3 (*o*-C), 151.0 (*p*-C), 139.1 (*ipso*-C), 120.6 (*m*-C), 40.2 (*o*-CHMe₂), 34.4 (*p*-CHMe₂), 24.8 (*o*-CHMe₂), 23.7 (*p*-CHMe₂). – MS (EI, 20 eV, 413 K): *m/z* (%) = 468 (20) [M]⁺, 264 (68) [M-C₆H₃(2,4,6-*i*-Pr)₃-H]⁺.

Synthesis of [Li(TMEN)₂]{(Me₃Si)₂CH₂Al-CH₂-Al{CH(SiMe₃)₂}₂(μ-Cl)] (3a)

A solution of **1a** (0.512 g, 0.73 mmol) was added at room temperature to a suspension of anhydrous LiCl (0.031 g, 0.73 mmol) in Et₂O (20 mL) and TMEN (0.44 mL, 2.93 mmol). After the solution had been stirred for 18 h at room temperature, a colourless, voluminous precipitate had formed that was filtered and recrystallised from Et₂O to yield colourless crystals of **3a**. Yield: 0.627 g (88 %); m. p. (under argon; sealed capillary): 146 °C (dec.). – IR (CsI, paraffin): ν = 1458 vs, 1377 vs (paraffin), 1309 w, 1290 w, 1242 m δ(CH₃), 1182 w, 1157 w, 1128 w, 1098 w (TMEN), 1069 w, 1030 w ν(CN), ν(CC), 1015 w δ(CHSi₂), 984 w, 920 w, 845 m, 748 w ρ(CH₃(Si)), 721 w (paraffin), 669 w, 633 w, 610 vw νSiC, 557 w, 509 w, 474 w, 463 w, 437 w cm⁻¹ ν(AlC), ν(AlCl), ν(LiN). – ¹H NMR (400 MHz, [D₈]THF): δ = 2.30 (s, 8 H, NCH₂), 2.15 (s, 24 H, NMe), 0.12 (s, 76 H, SiMe₃), –0.83 (s, 2 H, AlCH₂Al), –0.92 (s, 4 H, CHSi). – ¹³C NMR (100 MHz, [D₈]THF): δ = 58.9 (NCH₂), 46.2 (NMe), 11.5 (br., AlCH₂Al), 6.1 (SiMe₃), 6.06 (CHSi). – ²⁹Si NMR (79.5 MHz, [D₈]THF): δ = –2.3. – ⁷Li NMR (155.5 MHz, [D₈]THF): δ = 0.2.

Synthesis of [Li(TMEN)₂]{(Me₃Si)₂CH₂Al-CH₂-Al{CH(SiMe₃)₂}₂(μ-Br)] (3b)

Compound **3b** was obtained in an analogous manner to compound **3a** by stirring a mixture of **1a** (0.69 g, 0.98 mmol), anhydrous LiBr (0.086 g, 0.99 mmol) and TMEN (0.45 mL, 3.00 mmol) in Et₂O (20 mL) for 18 h at room temperature. Recrystallisation of the crude product gave colourless crystals of **3b**. Yield: 0.789 g (79 %); m. p. (under argon; sealed capillary): 158–168 °C (dec.). – IR (CsI, paraffin): ν = 1452 m, 1375 w (paraffin), 1288 m, 1240 m δ(CH₃), 1182 w, 1157 m, 1128 m, 1098 w (TMEN), 1069 w ν(CN), ν(CC), 1020 m δ(CHSi₂), 947 w, 922 vw, 845 s, 775 vw, 748 vw ρ(CH₃(Si)), 719 w (paraffin), 667 w, 625 w νSiC, 588 w, 554 vw, 527 vw, 509 w, 453 w, 442 w cm⁻¹ ν(AlC), ν(AlBr), ν(LiN). – ¹H NMR (400 MHz, [D₈]THF): δ = 2.30 (s, 8 H, NCH₂), 2.14 (s, 24 H, NMe), 0.14 (s, 76 H, SiMe₃), –0.63 (s, 2 H, AlCH₂Al), –0.83 (s, 4 H, CHSi). – ¹³C NMR (100 MHz, [D₈]THF): δ = 58.9 (NCH₂), 46.2 (NMe), 13.7 (br., AlCH₂Al), 6.3 (CHSi), 6.2 (SiMe₃). – ²⁹Si NMR

(79.5 MHz, [D₈]THF): δ = –2.3. – ⁷Li NMR (155.5 MHz, [D₈]THF): δ = –0.3.

Synthesis of [K(18-crown-6)(OEt₂)]{[(Me₃Si)₂CH₂Al-CH₂-Al{CH(SiMe₃)₂}₂(μ-ClO₄)] (3c(OEt₂))

A solution of **1a** (0.666 g, 0.95 mmol) in Et₂O (15 mL) was added quickly by means of a pipette to a suspension of KClO₄ (0.262 g, 1.89 mmol) and 18-crown-6 (0.250 g, 0.95 mmol). The colour of the reaction mixture changed from colourless to pale yellow. Stirring was continued for 18 h. The suspension was filtered, the filtrate was concentrated and kept at 2 °C to yield colourless crystals of **3c(OEt₂)**. Yield: 0.387 g (35 %); m. p. (under argon; sealed capillary): 142 °C (dec.). – IR (CsI, paraffin): ν = 1466 vs, 1454 vs, 1377 s (paraffin), 1352 w, 1248 s δ(CH₃), 1117 m ν_{as}(ClO₄), 1007 w δ(CHSi₂), 962 vw, 937 vw ν_s(ClO₄), 926 vw, 918 vw, 843 vs, 777 w, 752 w ρ(CH₃(Si)), 723 w (paraffin), 671 w, 611 vw ν(SiC), 563 vw, 501 vw cm⁻¹ ν(AlC), ν(AlO). – ¹H NMR (400 MHz, [D₈]THF): δ = 3.61 (s, 24 H, OCH₂), 3.38 (q, 4 H, ³J_{H-H} = 7.0 Hz, OCH₂, Et₂O), 1.10 (t, ³J_{H-H} = 7.0 Hz, CH₃, Et₂O), 0.12 (s, 76 H, SiMe₃), –1.03 (s, 4 H, CHSi), –1.28 (s, 2 H, AlCH₂Al). – ¹³C NMR (100 MHz, [D₈]THF): δ = 71.1 (OCH₂, crown ether), 66.3 (OCH₂, Et₂O) 16.4 (CH₃, Et₂O), 5.9 (SiMe₃), 5.1 (CHSi), 2.8 (br., AlCH₂Al). – ²⁹Si NMR (79.5 MHz, [D₈]THF): δ = –2.3.

*Synthesis of [Li(TMEN)₂]{[(Me₃Si)₂CH₂Al-CH₂-Al{CH(SiMe₃)₂}₂(μ-N(H)*i*-Pr)] (3d)*

A solution of H₂N(*i*-Pr) (0.042 g, 0.061 mL, 0.71 mmol) in Et₂O (10 mL) was treated with *n*-BuLi (0.441 mL, 0.71 mmol, 1.6 M in *n*-hexane) and stirred for 16 h at room temperature. Upon addition of TMEN (0.5 mL, 3.3 mmol) and a solution of **1a** (0.498 g, 0.71 mmol) in *n*-pentane (20 mL) pure **3d** precipitated as a colourless solid and was isolated. Yield: 0.504 g (71 %). – ¹H NMR (400 MHz, [D₈]THF): δ = 3.53 (m, br., 1 H, NCH), 2.31 (s, 8 H, NCH₂), 2.15 (s, 24 H, NMe), 1.29 (d, 6 H, ³J_{H-H} = 6.4 Hz, CHMe), 0.15 (s, 76 H, SiMe₃), –1.06 (s, 6 H, CHSi and AlCH₂Al); NH not detected. – ¹³C NMR (100 MHz, [D₈]THF): δ = 58.9 (NCH₂), 46.2 (NMe), 45.7 (NCH), 30.6 (CHMe₂), 17.5 (br., AlCH₂Al), 6.8 (SiMe₃), 5.1 (CHSi). – ²⁹Si NMR (79.5 MHz, [D₈]THF): δ = –2.7. – ⁷Li NMR (155.5 MHz, [D₈]THF): δ = –0.5.

*Synthesis of [Li(DME)₃]{[(Me₃Si)₂CH₂Al-CH₂-Al{CH(SiMe₃)₂}₂(μ-N(H)*i*-Pr)] (3e)*

Recrystallisation of **3d** in DME yielded **3e** as colourless crystals. – IR (KBr, paraffin): ν = 1601 w δ(NH), 1462 vs, 1377 vs (paraffin), 1288 m, 1238 s δ(CH₃), 1179 m, 1159 m, 1128 m, 1096 w, 1069 vw ν(CN), ν(CC), 1013 s δ(CHSi₂), 972 vw, 947 m, 922 m, 843 s, 775 w ρ(CH₃(Si)),

Table 3. Crystal data and structure refinement for compounds **1b**, **2**, **3b–3d**.

	1b	2	3b	3c(OEt₂)	3d
<i>Crystal data</i>					
Empirical formula	C ₆₁ H ₉ 49Al ₂	C ₆₀ H ₉ 2Al ₂ Cl ₂	C ₄₁ H ₁₁₀ Al ₂ BrLiN ₄ Si ₈	C ₄₅ H ₁₁₂ Al ₂ ClKO ₁₁ Si ₈	C ₄₄ H ₁₁₈ Al ₂ LiN ₅ Si ₈
<i>M_r</i>	881.32	938.20	1024.86	1182.58	1003.05
Crystal system	monoclinic	triclinic	orthorhombic	orthorhombic	triclinic
Spacegroup	<i>P</i> 2 ₁	<i>P</i> $\bar{1}$	<i>I</i> ba2	<i>P</i> na2 ₁	<i>P</i> $\bar{1}$
<i>a</i> , pm	1347.11(3)	1231.98(9)	2914.03(4)	2863.2(2)	1404.39(2)
<i>b</i> , pm	1609.21(3)	1354.5(1)	3045.49(4)	1151.03(8)	1464.38(3)
<i>c</i> , pm	1350.70(3)	1920.1(1)	2908.98(4)	2132.9(2)	1739.92(4)
α , deg	90	100.513(1)	90	90	81.647(1)
β , deg	90.158(1)	107.732(1)	90	90	68.501(1)
γ , deg	90	97.271(1)	90	90	86.672(1)
<i>V</i> , × 10 ⁻³⁰ m ³	2928.0(1)	2943.3(4)	25816.2(6)	7029.3(9)	3293.9(1)
ρ_{calc} , g · cm ⁻³	1.00	1.06	1.06	1.12	1.01
<i>Z</i>	2	2	16	4	2
<i>F</i> (000), e	972	1024	8960	2576	1116
μ , mm ⁻¹	0.7 (CuK α)	0.2 (MoK α)	0.8 (MoK α)	0.3 (MoK α)	2.0 (CuK α)
<i>Data collection</i>					
<i>T</i> , K	153(2)	153(2)	153(2)	153(2)	153(2)
Unique reflections	8703	15064	28510	16649	10238
Reflections <i>I</i> > 2 σ (<i>I</i>)	8090	10047	18148	15299	7408
<i>Refinement</i>					
Refined parameters	644	601	1087	650	599
Final <i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0443	0.0583	0.0684	0.0342	0.0576
Final <i>wR</i> 2 (all data) ^b	0.1189	0.1553	0.1882	0.0867	0.1622
$\Delta\rho_{\text{fin}}$ (max / min), e · Å ⁻³	3.09 / -2.36	4.61 / -5.17	14.18 / -6.33	6.41 / -3.00	4.47 / -4.80

^a $R1 = \sum |F_o - F_c| / \sum F_o$; ^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$.

723 s (paraffin), 665 s, 621 s ν (SiC), 583 s, 548 w, 500 m, 476 m, 455 s cm⁻¹ ν (AlC), ν (AlN), ν (LiO). - ¹H NMR (400 MHz, [D₈]THF): δ = 3.54 (m, br., 1 H, NCH), 3.42 (s, 6 H, OCH₂), 3.28 (s, 18 H, OMe), 1.28 (br, coupling not resolved, 6 H, CHMe), 0.12 (s, 76 H, SiMe₃), -1.08 (s, 6 H, CHSi and AlCH₂Al); NH not detected. - ¹³C NMR (100 MHz, [D₈]THF): δ = 72.7 (OCH₂), 58.9 (OMe), 45.7 (NCH), 28.2 (CHMe₂), 17.4 (br., CH₂Al), 6.8 (SiMe₃), 5.1 (CHSi). - ²⁹Si NMR (79.5 MHz, [D₈]THF): δ = -2.8. - ⁷Li NMR (155.5 MHz, [D₈]THF): δ = -0.5.

X-Ray crystallography

Crystals suitable for X-ray crystallography were obtained by recrystallisation from *n*-pentane (**1b**, **2**) or Et₂O (**3b**, **3c(OEt₂)**, **3d**). Intensity data were collected on a Bruker APEX II diffractometer with monochromated MoK α [**2**, **3b**, **3c(OEt₂)**] or CuK α (**1b**, **3d**) radiation. The collection method involved ω scans. Data reduction was carried out using the program SAINT+ [64]. The crystal structures were solved by Direct Methods using SHELXTL [65]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculation based on *F*² using SHELXTL. Hydrogen atoms

were positioned geometrically and allowed to ride on their respective parent atoms, except H01 (**3d**) which was refined isotropically. **1b** was twinned across the crystallographic 2 (*C*₂) axis and refined using TWIN (100 0 $\bar{1}$ 00 $\bar{1}$) and BASF (0.12). Compound **3b** was also twinned but the TWIN and BASF instructions (TWIN 001 0 $\bar{1}$ 0 100, BASF 0.015) did not solve all associated problems completely and bond lengths and angles may be unreliable. Three isopropyl groups (**1b**), one methyl group (Et₂O, **3c(OEt₂)**) and one TMEN (**3d**) were disordered and refined in split positions (**1b**: C241 0.52 : 0.48; C441 0.68 : 0.32; C541 0.31 : 0.69; **3c(OEt₂)**: C74 0.80 : 0.20; **3d**: N4, C41, C42, C43 0.32 : 0.68). Further crystallographic data is summarised in Table 3.

CCDC 883419 (**1b**), 883420 (**2**), 883421 (**3b**), 883422 (**3c(OEt₂)**) and 883423 (**3d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data_request/cif.

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