Sterically crowded monomeric neutral bis(benzamidinato) compounds of aluminium, $[PhC(NSiMe_3)_2]_2AlX$ ($X = Cl, H$); X-ray crystal structure of $[PhC(NSiMe_3)_2]_2AlH$

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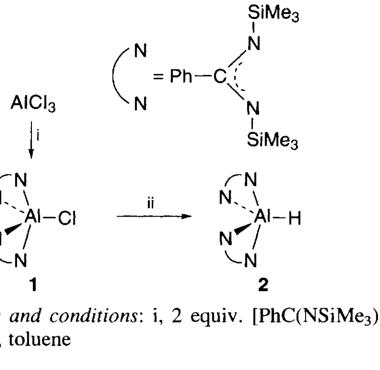
$AlCl_3$ reacts with $[PhC(NSiMe_3)_2]Li(OEt_2)$ to afford the bis(*N*,N′-bis(trimethylsilyl)benzamidinato)aluminium chloro compound which, on treatment with $KBEt_3H$, yields the structurally characterized monomeric hydrido derivative, $[PhC(NSiMe_3)_2]_2AlH$, whose reactivity towards unsaturated hydrocarbons illustrates the low electrophilicity of the aluminium and high basic character of the hydrido group.

Aluminium hydrides have interesting applications in hydrogenation and hydroalumination,[1] reduction of metal complexes[2] and as precursors in chemical vapour deposition techniques.[3] Normally aluminium hydrides are available either as Lewis-base adducts *e.g.* $AlH_3{\cdot}L_n$,[4] or as anionic species, $[X_nAlH_{4-n}]^-$ ($X = OR, NR_2$).[5] Neutral, monomeric mixed-ligand hydrides like alkoxohydrides, $(RO)_nAlH_{3-n}{\cdot}L$,[6] or amidohydrides, $(R_2N)_nAlH_{3-n}{\cdot}L$ (L = amine),[7] are rare and they tend to form Lewis-base adducts or oligomeric structures.

We decided to attempt to synthesize monomeric neutral aluminium hydrides by using benzamidinato ligands, $[PhC(NSiMe_3)_2]^-$ which we have used successfully for opening up a new field of monomeric organoyttrium derivatives.[8] Starting from $AlCl_3$ and 2 equiv. of $[PhC(NSiMe_3)_2]Li(OEt_2)$ the bis(*N*,*N*′-bis(trimethylsilyl)benzamidinato)aluminium chloride, $[PhC(NSiMe_3)_2]_2AlCl$ **1** was obtained in high yield (Scheme 1, step i).† Consequent reaction with potassium triethylborohydride, $KBEt_3H$, yielded the neutral, monomeric hydride $[PhC(NSiMe_3)_2]_2AlH$ **2** (Scheme 1, step ii).† Complexes **1** and **2** are thermally robust and show no sign of disproportionation or decomposition after 24 h at 80 °C in benzene. The singlet resonances for the $SiMe_3$ groups in the ^1H and ^{13}C NMR spectra of both **1** and **2** indicate fluxional behaviour of the benzamidinato ligands at room temperature and suggest a bidentate coordination of both ligands in these electron rich (10 valence electrons) five-coordinate aluminium species. Due to the large quadrupole moment of ^{27}Al,[9] the ^1H NMR Al–H resonance (δ 1.11) is very broad. The IR spectrum of **2** shows ν_{Al-H} at 1773 cm^{-1}, *i.e.* in the lower wavenumber range of values observed for other aluminium amidohydrides,[5,7,10] but comparable to the Al–H stretching vibrations found for Lewis-base adducts of alane, $AlH_3{\cdot}L_n$ ($L = thf, NR_3, PR_3$; R = alkyl).[4]



Scheme 1 *Reagents and conditions*: i, 2 equiv. $[PhC(NSiMe_3)_2]Li{\cdot}OEt_2$, toluene; ii, $KBEt_3H$, toluene

The molecular structure of **2** is shown in Fig. 1.‡ All hydrogen atom positions could reliably be located. The arrangement around aluminium is best described as distorted trigonal bipyramidal (tbp). The distortion is mainly caused by the rigid geometry of the benzamidinato ligands [bite angle: *e.g.* N(1)–Al–N(2) 68.69(7)°] which prevents them from occupying exact tbp positions. As a result, the hydrido ligand and one nitrogen atom of each benzamidinato ligand [H(1)–Al–N(1) 124.1(7); H(1)–Al–N(3) 121.7(7), N(1)–Al–N(3) 114.21(7)°] are in a tilted equatorial plane, while N(2) and N(4) occupy axial positions [N(2)–Al–N(4) 169.71(7), N(2)–Al–H(1) 94.2(7), N(4)–Al–H(1) 96.0(7)°]. Not unexpectedly for a tbp geometry, the axial Al–N bonds [Al–N(2) 2.0327(16), Al–N(4) 2.0309(16) Å] are longer than the equatorial ones [Al–N(1) 1.9356(17), Al–N(3) 1.9285(16) Å]. All Al–N bond distances in **2** are longer than in the related $[PhC(NSiMe_3)_2]AlCl_2$ (Al–N 1.882(3) Å)[11] and most amidoalanes, containing monodentate amido ligands

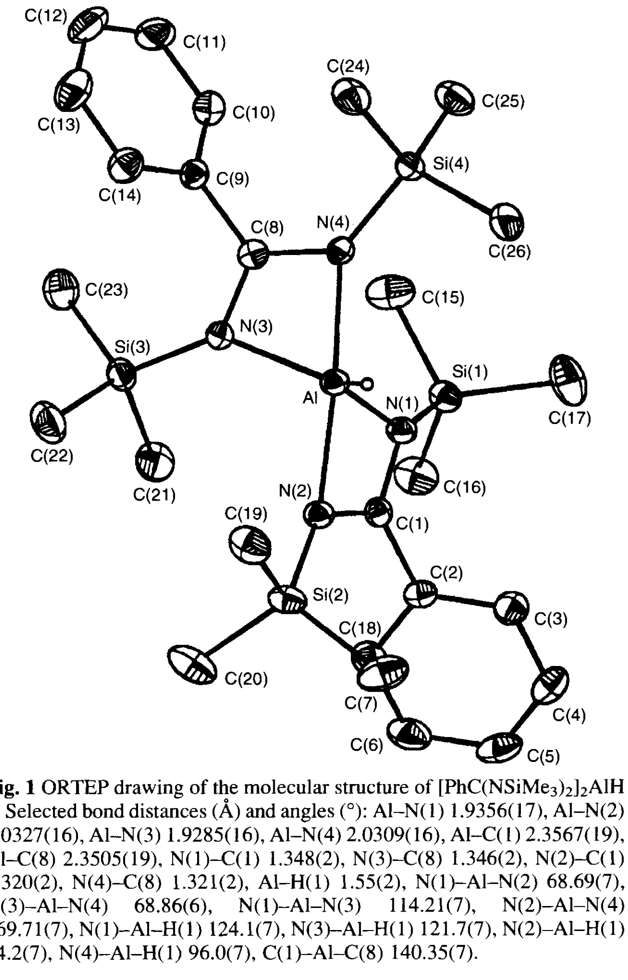
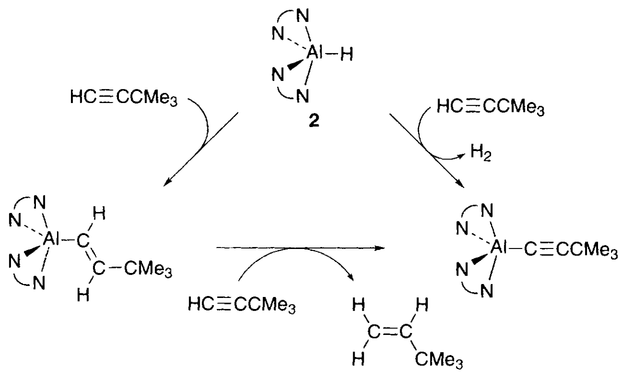


Fig. 1 ORTEP drawing of the molecular structure of $[PhC(NSiMe_3)_2]_2AlH$ **2**. Selected bond distances (Å) and angles (°): Al–N(1) 1.9356(17), Al–N(2) 2.0327(16), Al–N(3) 1.9285(16), Al–N(4) 2.0309(16), Al–C(1) 2.3567(19), Al–C(8) 2.3505(19), N(1)–C(1) 1.348(2), N(3)–C(8) 1.346(2), N(2)–C(1) 1.320(2), N(4)–C(8) 1.321(2), Al–H(1) 1.55(2), N(1)–Al–N(2) 68.69(7), N(3)–Al–N(4) 68.86(6), N(1)–Al–N(3) 114.21(7), N(2)–Al–N(4) 169.71(7), N(1)–Al–H(1) 124.1(7), N(3)–Al–H(1) 121.7(7), N(2)–Al–H(1) 94.2(7), N(4)–Al–H(1) 96.0(7), C(1)–Al–C(8) 140.35(7).



Scheme 2 i, insertion, ii, iii, C–H bond activation

[ranging from 1.78(2) Å[12] to 1.951(3) Å[7]]. Both benzamidinates form an almost planar four-membered ring with the aluminium atom [torsion angle N(2)–Al–N(1)–C(1) −4.96(10), N(4)–Al–N(3)–C(8) −4.83(10)°]. Within each benzamidinato ligand, the C–N distances are significantly different, with a short bond [*e.g.* C(1)–N(2) 1.320(2) Å] to the axial and a long bond [*e.g.* C(1)–N(1) 1.348(2) Å] to the equatorial position. This indicates that the charge within the benzamidinato ligands is not fully delocalized.[13] The Al–H(1) bond distance of 1.55(2) Å is within the wide range of values observed for other crystallographically characterized aluminium hydrides (1.37–1.88 Å).[5–7]

In exploratory reactivity studies, $[PhC(NSiMe_3)_2]_2AlH$ **2** was treated with olefins (ethylene, propylene, hex-1-ene) and $HC\equiv CCMe_3$. While with ethylene (4 atm, 40 °C, 2 h) a small amount of polyethylene was obtained, no reaction could be observed with propylene (4 atm, 40 °C, 2 h) or hex-1-ene (neat, 60 °C, 24 h). With *tert*-butylacetylene, $HC\equiv CCMe_3$ (2.5 equiv, 80 °C), **2** gave H_2, $CH_2{=}C(H)CMe_3$ and $[PhC(NSiMe_3)_2]_2AlC\equiv CCMe_3$ (NMR).§ H_2 formation indicates that the acetylide derivative, $[PhC(NSiMe_3)_2]_2AlC\equiv CCMe_3$, is formed by protolysis of **2** with $HC\equiv CCMe_3$ (Scheme 2), similarly to $[\{PhC(NSiMe_3)_2\}_2Y(\mu\text{-}H)]_2$.[8] $[PhC(NSiMe_3)_2]_2AlC\equiv CCMe_3$ itself is not active in hydrogenation of alkynes and it is probable that $CH_2{=}C(H)CMe_3$ is formed by protonation of $[PhC(NSiMe_3)_2]_2AlC(H){=}C(H)CMe_3$ formed by insertion of $HC\equiv CCMe_3$ in **2** (Scheme 2). The absence of resonances characteristic for $[PhC(NSiMe_3)_2]_2AlC(H){=}C(H)CMe_3$ in the ^1H NMR spectrum of the reaction mixture suggests that protonation of this vinyl derivative with an excess of $HC\equiv CCMe_3$, yielding $CH_2{=}C(H)CMe_3$ and $[PhC(NSiMe_3)_2AlC\equiv CCMe_3$, is fast compared to the initial insertion (Scheme 2). The reactivity of **2** towards unsaturated hydrocarbons such as alkenes and alkynes is quite different compared with known aluminium hydrides, which normally give insertion/hydroalumination products.[14] C–H bond activation such as the reaction of **2** with $HC\equiv CCMe_3$, is characteristic for organolanthanide and group 3 metal chemistry.[8,15] The preference of **2** to undergo protonation (C–H bond activation) over insertion of alk-1-ynes is most probably due to electronic factors. As observed for the analogous bis(benzamidinato)yttrium complexes,[8] the benzamidinato ligands are expected to render the aluminium centre in **2** rather ionic, favouring Brønsted-base reactivity of the hydrido group. Furthermore, the steric congestion around the aluminium centre will definitely hamper a side-on approach of an incoming alkene or alkyne (necessary for insertion).

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Footnotes

† Compound **1**: $[PhC(NSiMe_3)_2]Li(OEt_2)$ (10.4 g, 30.2 mmol) was added to a cooled (−40 °C) suspension of $AlCl_3$ (2.0 g, 15.0 mmol) in toluene (50 ml). The mixture was warmed to room temp. and stirred for 2 h; after evaporation of the volatiles the product was extracted with pentane (100 ml). Concentration and cooling to −30 °C yielded **1** (7.2 g, 12.2 mmol, 81%) as large colourless crystals. ^1H NMR (300 MHz, C_6D_6): δ 7.16 (m, 4H, Ar), 6.95 (m, 6H, Ar), 0.14 {s, 36H, $PhC[NSi(CH_3)_3]_2$}. ^{13}C NMR (300 MHz, C_6D_6): δ 183.8 [s, $PhC(NSiMe_3)_2$], 138.9 (s, Ar), 129.4 (dt, Ar, $^1J_{C-H}$ 165 Hz, $^2J_{C-H}$ 8 Hz), 127.6 (dd, Ar, $^1J_{C-H}$ 162 Hz, $^2J_{C-H}$ 7 Hz), 2.1 {q, $PhC[NSi(CH_3)_3]_2$, $^1J_{C-H}$ = 119 Hz}.

Compound **2**: A toluene solution (40 ml) of **1** (1.7 g, 2.9 mmol) was treated with $KBEt_3H$ (3.0 ml, 1 mol dm^{-3} in THF, 3.0 mmol) at room temperature. After stirring for 2 h, the volatiles were evaporated and the product was stripped twice with pentane (10 ml). The crude product was redissolved in pentane (50 ml) and, after filtration, the solution was concentrated and cooled to −30 °C for crystallization, yielding **2** (0.7 g, 1.3 mmol, 44%) as colourless, extremely air sensitive, crystals. Further concentration and cooling to −80 °C of the mother-liquor gave a second crop of **2** (0.4 g, 0.7 mmol, 25.0%). IR: δ_{Al-H} 1773 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 723 (m, 4H, Ar), 7.00 (m, 6H, Ar), 0.14 {s, 36 H, $PhC[NSi(CH_3)_3]_2$}. ^{13}C NMR (300 MHz, C_6D_6): δ 181.8 [s, $PhC(NSiMe_3)_2$], 140.5 (s, Ar), 129.3 (dt, Ar, $^1J_{C-H}$ 163 Hz, $^2J_{C-H}$ 7 Hz), 128.0 (dd, Ar, $^1J_{C-H}$ 163 Hz, $^2J_{C-H}$ 7 Hz), 127.3 (dt, $^1J_{C-H}$ 160 Hz, $^1J_{C-H}$ 6 Hz), 2.0 {q, $PhC[NSi(CH_3)_3]_2$, $^1J_{C-H}$ = 119 Hz}. Satisfactory analytical data have been obtained for both compounds.

‡ *Crystal data* for **2**: $C_{26}H_{47}AlN_4Si_4$, M = 555.01, monoclinic, space group $P2_1/a$, a = 11.948(3), b = 18.173(4), c = 15.540(2) Å, β = 98.24(1)°, U = 3339.4(12) Å^3, Z = 4, D_c = 1.104 g cm^{-3}, $F(000)$ = 1200, T = 130 K, μ(Mo-Kα) = 2.2 cm^{-1}. Full-matrix least-squares refinement for 5647 unique reflections with $I > 2.5\sigma(I)$ and 505 parameters converged at R = 0.037 and R_w = 0.037. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELX86). The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with full-matrix least-squares procedures (QRYLSQ) minimizing the function $Q = \Sigma_h\ [w(|F_o|-k|F_c|)^2]$. All hydrogen atom positions could be located from a subsequent difference Fourier map and they refined smoothly. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ ^1H NMR (300 MHz, C_6D_6) data for $[PhC(NSiMe_3)_2]_2AlC\equiv CCMe_3$: δ 7.24 (m, 4H, Ar), 7.01 (m, 6H, Ar), 1.38 [s, 9H, $C\equiv CC(CH_3)_3$], 0.21 {s, 36H, $PhC[NSi(CH_3)_3]_2$}.

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