

Preparation of a monomeric aluminium–diazabutadiene complex via an oxidative addition reaction

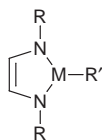
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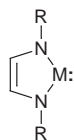
Oxidative addition of MesN=CH–CH=NMe (Mes = mesityl) to the aluminium(i) tetramer, [Al(C₅Me₅)₄], results in the monomeric aluminium(III) derivative,

[(η⁵-C₅Me₅)Al(N(Mes)CH=CHN(Mes))], which has been characterised by X-ray crystallography.

Interest in Group 13 diazabutadiene (DAB) complexes of the general type **1** has been stimulated largely by their isoelectronic relationship to the corresponding silylenes¹ and germylenes² (**2**). Since both **1** and **2** feature six π electrons, important questions arise regarding circumannular delocalisation and possible aromatic character. Previous examples of **1** (M = Al, Ga) have been stabilised by either dimerisation or intramolecular Lewis-base intervention.^{3,4} Since the foregoing examples were the products of metathetical reactions, we opted for a new synthetic approach, viz. oxidative addition to an aluminium(i) species.

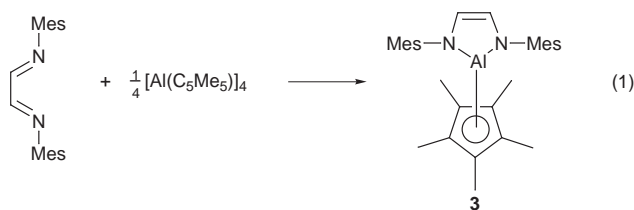


1 (M = Al, Ga)



2 (M = Si, Ge)

The reaction of [Al(C₅Me₅)₄]^{5,6} with MesN=CH–CH=NMe (Mes = mesityl) takes place at 60 °C in toluene and affords, upon work-up, yellow crystals of **3** [equation (1)], isolated in 39% yield.† Elemental analysis and HRMS data‡



† Experimental procedures: a solution of MesN=CH–CH=NMe (0.53 g, 1.81 mmol) in 30 cm³ of toluene was added dropwise to a stirred suspension of [Al(C₅Me₅)₄] (0.30 g, 0.46 mmol) in 20 cm³ of toluene at 25 °C. The mixture was warmed to 60 °C for 2 h during which time the solids dissolved. The reaction mixture was cooled to 25 °C and stirred for an additional 12 h. The resulting amber solution was filtered, then concentrated under reduced pressure until the volume was ca. 20 cm³; slow cooling to –20 °C afforded a crop of yellow crystals of **3** (0.32 g, 0.70 mmol, 39%) m.p. 213–226 °C (decomp.).

‡ Spectroscopic data for **3**. NMR (C₆D₆): ¹H δ 6.91 (s, CH_{Mes}, 4H), 5.15 (s, NCH, 2H), 2.42 (s, *o*-CH₃, 12H), 2.25 (s, *p*-CH₃, 6H), 1.65 [s, C₅(CH₃)₅, 15H]; ¹³C-{¹H} δ 146.6 (s, *ipso*-C_{Mes}), 136.5 (s, *o*-C_{Mes}), 133.2 (s, *p*-C_{Mes}), 128.8 (s, *m*-C_{Mes}), 116.1 (s, NCC), 115.1 [s, C₅(CH₃)₅], 21.1 (s, *p*-CH₃), 18.8 (s, *o*-CH₃), 9.9 [s, C₅(CH₃)₅]; ²⁷Al-{¹H} δ 45 (ω₁ = 6200 Hz). MS (CI⁺): *m/z* 507 (M⁺, 100%); HRMS (CI⁺) calculated for C₃₀H₂₉AlN₂ (M⁺), 454.2929; found 454.2928.

for **3** correspond to the formula above. Moreover, the ¹H and ¹³C NMR spectra are consistent with the formation of a symmetrical ring and the development of a double bond between the ring carbon atoms.‡ The equivalence of the Me₅C₅ methyl groups down to –78 °C is indicative of an η⁵-bonding mode to aluminium. However, since such an observation does not rule out facile sigmatropic migration of, e.g., an η¹-attached species, an X-ray crystal structure determination was desirable. The ²⁷Al NMR spectrum of **3** exhibits a single broad peak at δ 45 (ω₁ = 6200 Hz) which is within the region anticipated for three-coordinate aluminium.⁷

Compound **3** crystallises in the space group P2₁/n and there are no unusually short contacts between individual molecules (Fig. 1).§ The Me₅C₅ group is η⁵-bonded to aluminium, as reflected by the near equivalence of the Al–C distances [2.212(2)–2.257(2) Å], and the AlN₂C₂ ring is planar within experimental error. Based on the Me₅C₅ ring centroid, the sum of angles at aluminium is 360° within experimental error. The nitrogen atoms also adopt a trigonal planar geometry and the appended mesityl rings are arranged such that they are approximately parallel to the C₅Me₅ ring.

The metrical parameters for the AlN₂C₂ ring are pertinent to the question of electron delocalisation in this and related DAB systems. The following points are noteworthy: (i) the carbon–carbon [1.331(2) Å] and average carbon–nitrogen [1.406(2) Å] distances correspond to bond orders of two and one, respectively, and (ii) the average aluminium–nitrogen distance

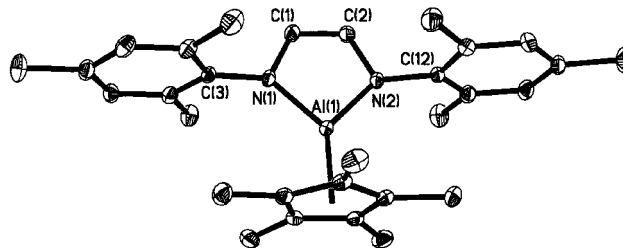


Fig. 1 Molecular structure of **3** showing the numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–N(2) 1.826(1), Al(1)–N(1) 1.827(1), Al(1)–Cp 1.877(2), N(1)–C(1) 1.401(2), N(1)–C(3) 1.429(2), N(2)–C(2) 1.412(2), N(2)–C(12) 1.430(2), C(1)–C(2) 1.331(2); N(2)–Al(1)–N(1) 89.79(6), Cp–Al(1)–N(1) 135.9(1), Cp–Al(1)–N(2) 134.2(1), C(1)–N(1)–C(3) 116.8(1), C(1)–N(1)–Al(1) 108.9(1), C(3)–N(1)–Al(1) 133.8(1), C(2)–N(2)–C(12) 115.8(1), C(2)–N(2)–Al(1) 108.7(1), C(12)–N(2)–Al(1) 133.4(1), C(1)–C(2)–N(2) 116.2(2), C(2)–C(1)–N(1) 116.5(2); Cp is defined as the centroid of the pentamethylcyclopentadienyl ring

§ Crystal data for **3**: C₃₀H₂₉AlN₂, *M* = 454.61, monoclinic, space group P2₁/n, *a* = 9.8413(9), *b* = 12.328(1), *c* = 22.244(3) Å, β = 102.18(1)°, *U* = 2637.9(5) Å³, *Z* = 4, *D_c* = 1.145 g cm^{–3}, μ = 0.97 mm^{–1}, *F*(000) = 984, *T* = 179(2) K. 6054 Independent reflections were collected on a Siemens P4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å, 1.87 < θ < 27.51°), an absorption correction was not applied: 100*w*R₂ = {Σ[w(*F_o*² – *F_c*²)]/Σ[w(*F_o*²)]} = 11.7 and 100*R* = [|*F_o*| – |*F_c*|]/Σ|*F_o*| = 4.60 for reflections with *I* > 2σ(*I*). CCDC reference number 186/998.

[1.827(1) Å] falls within the single bond range.⁸ The observed pattern of bond distances therefore points towards a relatively localised electronic structure.

Finally, we note a sensitivity to the choice of ring substituents on the DAB fragment. If Bu^tN=CH-CH=NBu^t (Bu^tDAB) is treated with [Al(C₅Me₅)₄] under virtually identical conditions to those described above, the sole isolated product is the known complex [Al(Bu^tDAB)₂],⁹ thus implying the facile elimination of the C₅Me₅ moiety.

In conclusion, an oxidative addition reaction of a diimide to an aluminium(i) derivative has been described. The reaction product is the first example of a monomeric aluminium diazabutadiene complex, and based on metrical parameters, the bonding within the metallacycle is best described as localised.

Acknowledgements

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