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

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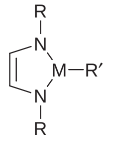
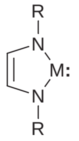
Oxidative addition of MesN=CH−CH=NMes (Mes = mesityl) to the aluminium(I) tetramer, $[Al(C_5Me_5)]_4$, results in the monomeric aluminium(III) derivative, $[(\eta^5\text{-}C_5Me_5)\overline{AlN(Mes)CH{=}CHN}(Mes)]$, which has been characterised by X-ray crystallography.

Interest in Group 13 diazabutadiene (DAB) complexes of the general type **1** has been stimulated largely by their isoelectronic relationship to the corresponding silylenes[1] and germylenes[2] (**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.

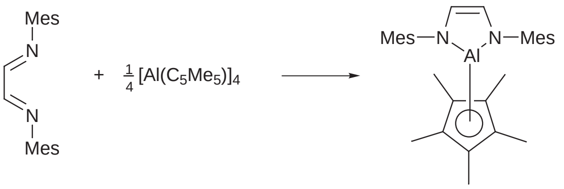


1 (M = Al, Ga)



2 (M = Si, Ge)

The reaction of $[Al(C_5Me_5)]_4$[5,6] with MesN=CH−CH=NMes (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 ‡ for **3** correspond to the formula above. Moreover, the ^1H and ^{13}C 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 Me_5C_5 methyl groups down to −78 °C is indicative of an η^5-bonding mode to aluminium. However, since such an observation does not rule out facile sigmatropic migration of, *e.g.*, an η^1-attached species, an X-ray crystal structure determination was desirable. The ^{27}Al NMR spectrum of **3** exhibits a single broad peak at δ 45 ($\omega_{\frac{1}{2}}$ = 6200 Hz) which is within the region anticipated for three-co-ordinate aluminium.[7]



(1)

3

Compound **3** crystallises in the space group $P2_1/n$ and there are no unusually short contacts between individual molecules (Fig. 1).§ The Me_5C_5 group is η^5-bonded to aluminium, as reflected by the near equivalence of the Al–C distances [2.212(2)–2.257(2) Å], and the AlN_2C_2 ring is planar within experimental error. Based on the Me_5C_5 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 C_5Me_5 ring.

The metrical parameters for the AlN_2C_2 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

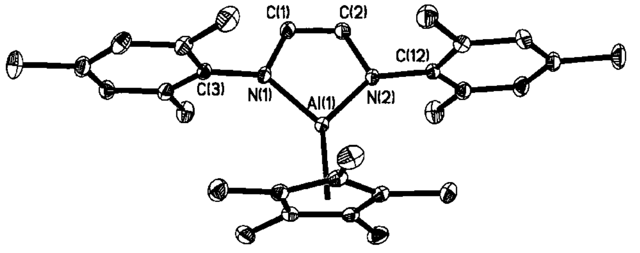


Fig. 1 Molecular structure of **3** showing the numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Al(1)–N(2) 1.826(1), Al(1)–N(1) 1.827(1), Al(1)–Cp 1.877(2), N(1)–C(1) 1.401(2), N(1)–C(3) 1.429(2), N(2)–C(2) 1.412(2), N(2)–C(12) 1.430(2), C(1)–C(2) 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

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† Experimental procedures: a solution of MesN=CH−CH=NMes (0.53 g, 1.81 mmol) in 30 cm³ of toluene was added dropwise to a stirred suspension of $[Al(C_5Me_5)]_4$ (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 (C_6D_6): ^1H δ 6.91 (s, CH_{Mes}, 4 H), 5.15 (s, NCH, 2 H), 2.42 (s, *o*-CH_3, 12 H), 2.25 (s, *p*-CH_3, 6 H), 1.65 [s, $C_5(CH_3)_5$, 15 H]; $^{13}C\text{-}\{^1H\}$ 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, N*C*C), 115.1 [s, $\mathit{C}_5(CH_3)_5$], 21.1 (s, *p*-CH_3), 18.8 (s, *o*-CH_3), 9.9 [s, $C_5(\mathit{CH}_3)_5$]; $^{27}Al\text{-}\{^1H\}$ δ 45 ($\omega_{\frac{1}{2}}$ = 6200 Hz). MS (CI+): *m*/*z* 507 (M^+, 100%); HRMS (CI^+) calculated for $C_{30}H_{29}AlN_2$ (M^+), 454.2929; found 454.2928.

§ Crystal data for **3**: $C_{30}H_{29}AlN_2$, $M = 454.61$, monoclinic, space group $P2_1/n$, $a = 9.8413(9)$, $b = 12.328(1)$, $c = 22.244(3)$ Å, $\beta = 102.18(1)°$, $U = 2637.9(5)$ Å³, $Z = 4$, $D_c = 1.145$ g cm⁻³, $\mu = 0.97$ 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: $100wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{\frac{1}{2}} = 11.7$ and $100R = |F_o| - |F_c|/\Sigma|F_o| = 4.60$ for reflections with $I > 2\sigma(I)$. 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 $[Al(C_5Me_5)]_4$ 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 C_5Me_5 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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References

1 M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, *J. Am. Chem. Soc.*, 1994, **116**, 2691.

2 W. A. Hermann, M. Denk, J. Behm, W. Scherer, F. R. Klingan, H. Bock, M. Soluki and M. Wagner, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1485.

3 D. S. Brown, A. Decken, C. A. Schnee and A. H. Cowley, *Inorg. Chem.*, 1995, **34**, 6415.

4 D. S. Brown, A. Decken and A. H. Cowley, *J. Am. Chem. Soc.*, 1995, **117**, 5421.

5 S. Schulz, H. W. Roesky, H. J. Koch, G. M. Sheldrick, D. Stalke and A. Kuhn, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1729.

6 For a review of the chemistry of $[Al(C_5Me_5)]_4$ and related systems, see C. Dohmeier, D. Loos and H. Schnöckel, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 129. For earlier work on aluminium atom chemistry, see J. H. B. Chenier, J. A. Howard and B. Mile, *J. Am. Chem. Soc.*, 1987, **109**, 4109 and refs. therein.

7 J. W. Akitt, in *Multinuclear NMR*, Plenum Press, New York, 1987, pp. 259–292.

8 M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood, West Sussex, 1980, pp. 105–114.

9 F. G. N. Cloke, C. I. Dalby, M. J. Henderson, P. B. Hitchcock, C. H. L. Kennard, R. N. Lamb and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1990, 1394; F. G. N. Cloke, C. I. Dalby, P. J. Daff and J. C. Green, *J. Chem. Soc., Dalton Trans.*, 1991, 181.

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