

Paramagnetic Aluminium–1,4-Di-*t*-butyl-1,4-diazabutadiene (dbdab) Complexes Derived from Metal Vapours and/or Metal Hydrides: Crystal Structures of $[\text{Al}(\text{dbdab})_2]$ and $[\text{Al}(\text{dbdab})\{\text{N}(\text{Bu}^t)\text{CH}_2\}_2]$

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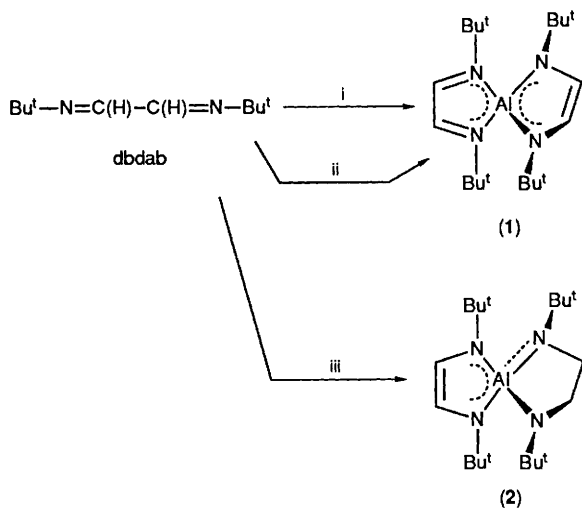
Reaction of aluminium vapour or LiAlH_4 –aluminium metal–hexane with 1,4-di-*t*-butyl-1,4-diazabutadiene (dbdab) yields dark green $[\text{Al}(\text{dbdab})_2]$ (**1**), whereas $\text{AlH}_3\cdot\text{NMe}_3$ with dbdab in hexane at -80°C yields the corresponding hydroalumination product $[\text{Al}(\text{dbdab})\{\text{N}(\text{Bu}^t)\text{CH}_2\}_2]$ (**2**) as a yellow solid; although both compounds are paramagnetic, XPS (solid) and EPR (solution) spectroscopy, and X-ray structure determinations support formally Al^{III} centres with the unpaired electron ligand-centred.

Diazabutadienes have been shown to stabilize low-valent homoleptic compounds of transition metals,^{1,2} and more recently some lanthanoid and main group elements.^{2,3} Low-valent complexes of aluminium are known for systems possessing bulky alkyl ligands, either as paramagnetic, monomeric species⁴ or diamagnetic, dimeric species with metal–metal bonding.⁵ We have attempted to prepare low-valent aluminium complexes using 1,4-di-*t*-butyl-1,4-diazabutadiene (dbdab) along the lines developed for gallium, which yielded the first example of a monomeric, formally gallium(II) complex, $[\text{Ga}(\text{dbdab})_2]$.^{3,6}

Noteworthy findings include (i) cocondensation of aluminium vapour and dbdab, or treating dbdab with lithium

aluminium hydride–aluminium powder mixture in hexane both lead to the homoleptic complex $[\text{Al}(\text{dbdab})_2]$ (**1**); (ii) reaction of the trimethylamine adduct of alane, $\text{AlH}_3\cdot\text{NMe}_3$, with dbdab gives the novel partially hydrogenated analogue of (**1**), viz. $[\text{Al}(\text{dbdab})\{\text{N}(\text{Bu}^t)\text{CH}_2\}_2]$, (**2**) via hydroalumination; (iii) compounds (**1**) and (**2**) are thermally robust, sublimable at ca. 130 – 155°C , and are paramagnetic but with the metal centres in the trivalent state [X-ray structure, EPR (solution) spectroscopy, and XPS (solid)]; and (iv) the crystal structure of (**2**) reveals that the hydrogenated ligand is unsymmetrically bound to the metal centre.

Details of the syntheses are summarized in Scheme 1.† The



Scheme 1. Reagents and conditions: i, Al vapour, condensation at -196°C ; ii, LiAlH_4 , Al, hexane, 20°C , $-\text{H}_2$, $-\text{LiH}$; iii, $\text{AlH}_3\cdot\text{NMe}_3$, hexane, -80°C , $-\text{NMe}_3$, $-\text{H}_2$.

† *Synthesis and characterization.* Compound (**1**): Method A. Aluminium vapour (50 mmol), generated from a resistively heated boron nitride crucible, was cocondensed with an excess of dbdab (180 mmol) at -196°C during 2 h. After warming to room temperature the dark green product was extracted from the reactor in toluene (1000 ml), filtered, and solvent and excess of dbdab removed *in vacuo*. Recrystallization of the residue from toluene–pentane (30 ml) at -30°C afforded deep green crystals of (**1**) (yield 5 g, 30%). Method B. A slurry of LiAlH_4 (8.4 mmol) in hexane (30 ml) was added to a stirred mixture of dbdab (22 mmol) and aluminium metal (10 mmol) in hexane (30 ml) at room temperature. After 2 h solvent and excess of dbdab were removed *in vacuo* yielding a brown solid that was taken up in toluene–hexane (3:2). On cooling to -30°C the red solution became deep green affording a green precipitate of (**1**) (0.56 g, 20%); m.p. 187°C (sublimes at 155°C , 3 mmHg); m/z 363 (M^+); g_{av} (hexane) 2.0012.

Compound (**2**): To a solution of $\text{AlH}_3\cdot\text{NMe}_3$ (8.54 mmol) in hexane (30 ml) at -80°C was added sublimed dbdab (17.08 mmol) in hexane (10 ml) over 20 min. On warming to 0°C a gas was evolved from a pale green solution yielding an orange solution. After gas evolution had ceased the mixture was filtered and volatile material removed *in vacuo*. The resulting yellow powder was recrystallized from hexane (1.19 g, 38% yield); m.p. 153°C (sublimes at 129°C , 3 mmHg); m/z 365 (M^+); g_{av} (hexane) 2.0018.

Satisfactory elemental analyses were obtained for both compounds.

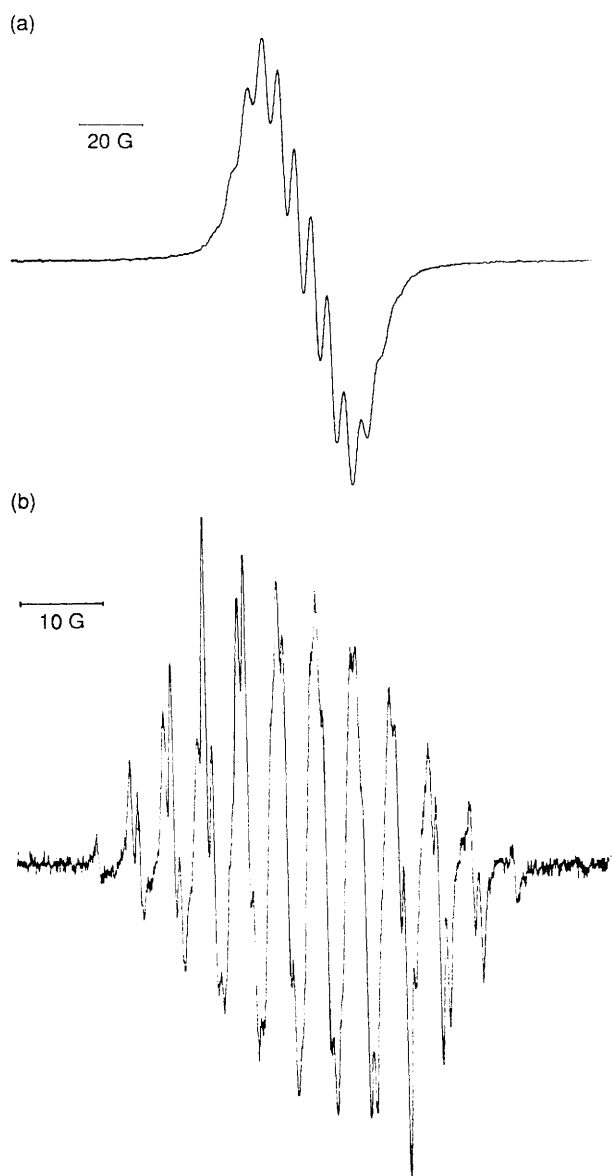


Figure 1. EPR spectra of (a) $[\text{Al}(\text{dbdab})_2]$ (**1**), and (b) $[\text{Al}(\text{dbdab})\{\text{N}(\text{Bu}^t)\text{CH}_2\}_2]$ (**2**) ($1 \text{ G} = 10^{-4} \text{ T}$).

metal powder– LiAlH_4 mixture that features in the synthesis of (**1**) seemingly delivers an activated source of aluminium and has exciting potential for reactions with other organic substrates; aluminium powder alone gave no reaction, and LiAlH_4 in the absence of metal gave an intractable red–brown oil. It is possible that the aluminium metal catalyses decomposition of LiAlH_4 to finely divided aluminium, which then undergoes electron transfer with dbdab, rather than initial complexation of dbdab to AlH_4^- which would tend to favour hydrometallation. The formation of complex (**2**) from $\text{AlH}_3 \cdot \text{NMe}_3$ with dbdab most likely involves NMe_3 displacement as the primary process. The product differs from the analogous reaction of $\text{GaH}_3 \cdot \text{NMe}_3$ where a diamagnetic gallium(III) species, $[\{\text{GaH}_2\}_2\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\}_2]$ is obtained.⁶

EPR spectra for (**1**) and (**2**) showing hyperfine coupling are presented in Figure 1; neither is dominated by the expected six lines corresponding to coupling to ^{27}Al (100%, $I = 5/2$), suggesting that the unpaired electron is mainly ligand-centred with the metal formally in a trivalent state. In contrast, the gallium analogue of compound (**1**) is dominated by coupling to

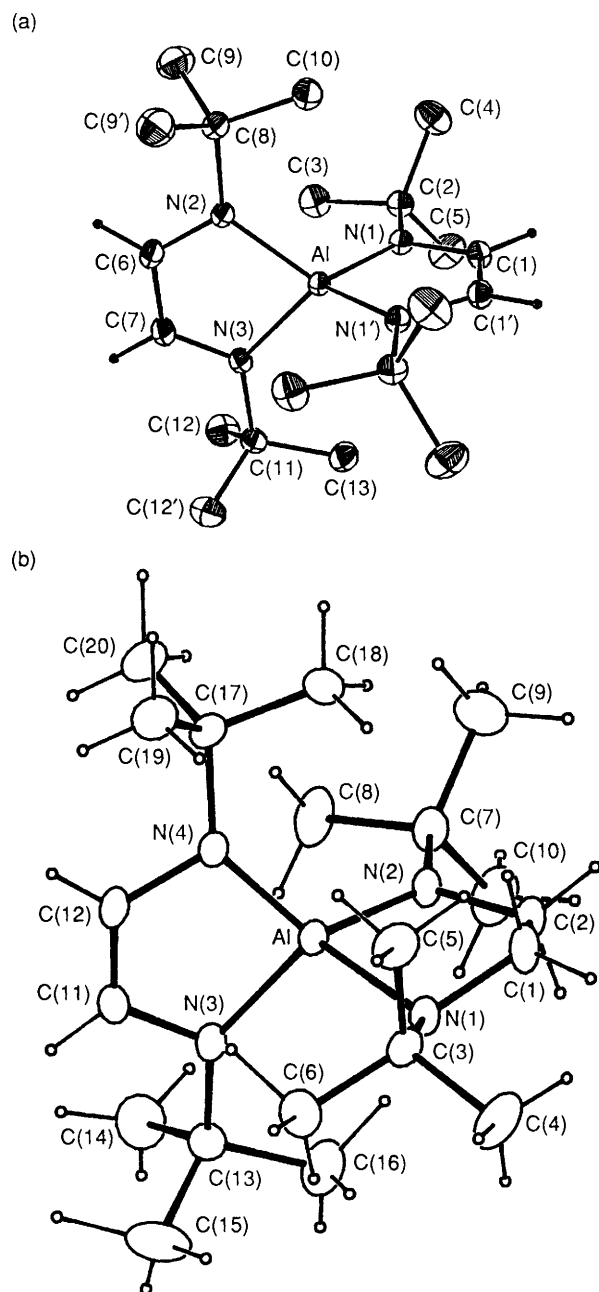


Figure 2. Molecular projection of (a) $[\text{Al}(\text{dbdab})_2]$ (**1**), and (b) $[\text{Al}(\text{dbdab})\{\text{N}(\text{Bu}^t)\text{CH}_2\}_2]$ (**2**), with arbitrary radii hydrogen atoms. Selected bond distances (\AA) and angles ($^\circ$): (**1**); $\text{Al}-\text{N}(1)$ 1.823(2), $\text{Al}-\text{N}(2)$ 1.916(3), $\text{Al}-\text{N}(3)$ 1.924(3), $\text{N}(1)-\text{C}(1)$ 1.415(3), $\text{N}(2)-\text{C}(6)$ 1.346(5), $\text{N}(3)-\text{C}(7)$ 1.331(5), $\text{C}(1)-\text{C}(1')$ 1.343(5), $\text{C}(6)-\text{C}(7)$ 1.395(6), $\text{N}(1)-\text{Al}-\text{N}(1')$ 92.3(1), $\text{N}(2)-\text{Al}-\text{N}(3)$ 86.1(1), $\text{N}(1)-\text{Al}-\text{N}(3)$ 120.5(1), $\text{N}(1)-\text{Al}-\text{N}(2)$ 120.4(1); (**2**); $\text{Al}-\text{N}(1)$ 2.057(4), $\text{Al}-\text{N}(2)$ 1.813(3), $\text{Al}-\text{N}(3)$ 1.839(4), $\text{Al}-\text{N}(4)$ 1.831(4), $\text{N}(1)-\text{C}(1)$ 1.487(6), $\text{N}(2)-\text{C}(2)$ 1.443(6), $\text{C}(1)-\text{C}(2)$ 1.470(6), $\text{N}(3)-\text{C}(11)$ 1.408(5), $\text{N}(4)-\text{C}(12)$ 1.419(6), $\text{C}(11)-\text{C}(12)$ 1.311(8), $\text{N}(1)-\text{Al}-\text{N}(2)$ 86.7(1), $\text{N}(3)-\text{Al}-\text{N}(4)$ 92.4(2), $\text{N}(1)-\text{Al}-\text{N}(3)$ 108.1(2), $\text{N}(1)-\text{Al}-\text{N}(4)$ 117.4(2), $\text{N}(2)-\text{Al}-\text{N}(3)$ 127.5(2), $\text{N}(2)-\text{Al}-\text{N}(4)$ 125.6(2), $\text{Al}-\text{N}(1)-\text{C}(2)$ 103.0(3), $\text{Al}-\text{N}(2)-\text{C}(2)$ 114.2(3), $\text{Al}-\text{N}(3)-\text{C}(11)$ 105.4(3), $\text{Al}-\text{N}(4)-\text{C}(12)$ 105.6(3).

the metal centre in a divalent state.⁶ XPS on solid samples of (**1**) and (**2**) also supports the presence of trivalent aluminium, the Al 2p region being dominated by peaks with binding energies at 73.7 and 73.9 eV respectively, which are in the normal Al^{3+} region.⁷

Compound (1) has two crystallographically independent ligands,‡ with different geometries [Figure 2(a)], in accordance with two types of nitrogen environments from XPS studies (N_{1s} 398.1, 399.1 eV). The C–C and C–N distances suggest a dianion and a neutral ligand as for the gallium analogue with which it is isostructural.⁶ In fact, corresponding distances for the two compounds are within three standard deviations. Metal–N distances, however, all differ by *ca.* 10 standard deviations, with those for the aluminium compound the shortest. Given that gallium and aluminium have the same covalent radius, this is consistent with different formal oxidation states, Al^{III} vs. Ga^{II} , *viz.* greater positive charge on the aluminium centre. A picture of bonding that emerges is

‡ *Crystal structure determinations.* Compound (1) ($T = 296$ K; Enraf-Nonius CAD4 diffractometer, crystals mounted in capillaries): $C_{20}H_{40}AlN_4$, $M = 363.6$, orthorhombic, space group $Pnma$, $a = 18.239(2)$, $b = 13.528(1)$, $c = 9.3669(9)$ Å, $U = 2311.1(4)$ Å³, $F(000) = 804$; $Z = 4$, $D_c = 1.04$ g cm⁻³, $\mu(Mo-K\alpha) = 1.02$ cm⁻¹, specimen $0.4 \times 0.3 \times 0.15$ mm, 1955 unique reflections, 1386 with $|F^2| > 2.5\sigma(F^2)$ used in the refinement where $\sigma(F^2) = [1.1\sigma^2(I) + (0.002I)^2]^{1/2}/LP$, $S = 1.2$, $2\theta_{max} = 50^\circ$. Data were corrected for crystal decay (3.8% drop in standards), and no absorption corrections were applied. Compound (2) ($T = 296$ K; Enraf-Nonius CAD4 diffractometer, crystals mounted in capillaries): $C_{20}H_{42}AlN_4$, $M = 365.6$, monoclinic, space group $P2_1/c$, $a = 11.575(2)$, $b = 9.403(8)$, $c = 22.423(4)$ Å, $\beta = 104.41(1)^\circ$, $U = 2363.8$ Å³, $F(000) = 812$; $Z = 4$, $D_c = 1.03$ g cm⁻³, $\mu(Mo-K\alpha) = 0.9$ cm⁻¹, specimen $0.6 \times 0.3 \times 0.2$ mm, 4433 unique reflections, 1907 with $|F^2| > 3\sigma(F^2)$ used in the refinement where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/LP$, $2\theta_{max} = 50^\circ$. There was no crystal decay and no absorption corrections were applied.

Structure (2) was solved by direct methods using MULTAN and refined by full-matrix least-squares analysis with non-hydrogen atoms anisotropic. Structure (1) was refined similarly, but the starting parameters were those of the isostructural gallium analogue. Hydrogen atoms were located from a difference map and refined in x , y , z , U_{iso} , methyl groups (2) excepted, where U_{iso} were constrained to $1.3 U_{equiv}$ for the associated atom. The weighting scheme was $w = 1/\sigma^2(F)$ and the final residuals were $R = 0.043$, 0.058 , $R'_w = 0.049$, 0.079 for (1) and (2) respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

shown in Scheme 1, with some N_p -Al interaction associated with planar N centres, and the unpaired electron ligand-centred. The X-ray crystal structure of (2),‡ Figure 2(b), reveals Al–N, C–C, and N–C ring distances for dbdab to be close to the reduced ligand in (1); the hydrogenated ligand is bound unsymmetrically, with a difference in Al–N distances, 0.24 Å, and angular geometry about the N-centres consistent with trigonal N(2), $\Sigma_{angles} 359.8^\circ$, and pyramidal N(1), $\Sigma_{angles} 341.6^\circ$, so that only N(1) has a significant N_p -Al interaction. A picture of bonding for molecules of (2) with trivalent metal centres is then as presented in Scheme 1, with the unpaired electron ligand-centred. The presence of three different N-centres in (2) is reflected in the XPS for nitrogen with N 1s peaks, 398.1, 399.3, and 400.9 eV. Moreover, the peak at 398.1 eV matches a peak for (1) and is tentatively assigned to that of the nitrogens of the dianion ligand; the 400.9 eV peak most likely corresponds to the pyramidal nitrogen. Finally, the compounds have different colours, dark green and yellow for (1) and (2) respectively, in line with more delocalization of spin density in (1).

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