

A bridging ethyl complex of aluminium

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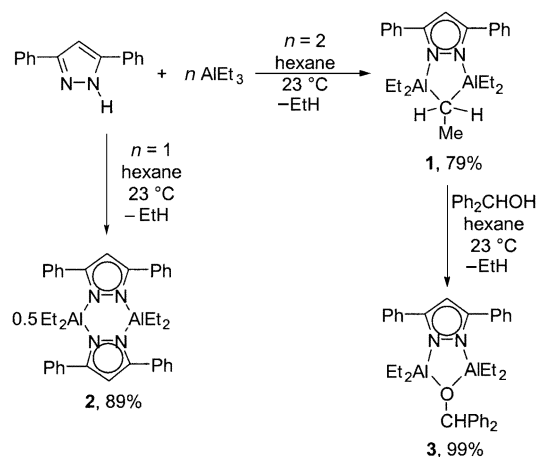
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Treatment of triethylaluminium (2 equiv.) with diphenylpyrazole (1 equiv) affords a pyrazolate-bridged dialuminium complex that contains a bridging ethyl group between the two aluminium centers; this complex has been structurally characterized and its reactivity and properties are described.

The bridging of saturated hydrocarbon groups between two aluminium ions is widely recognized.^{1,2} Despite widespread interest in this phenomenon, there are actually very few such compounds that have been structurally characterized and nearly all contain methyl bridges.² Hexakis(cyclopropyl)dialuminium has been structurally characterized and contains two bridging cyclopropyl groups per dimeric unit.³ In addition to homo-bimetallic complexes, there is a small family of structurally characterized complexes in which methyl⁴ or ethyl⁵ groups act as bridges between aluminium and a different metal center [mostly lanthanide(III) ions]. The degree of association of several saturated higher alkyl derivatives of aluminium has been investigated in solution and in the gas phase by several different techniques.^{6–9} Triethylaluminium and tri-*n*-propylaluminium were found to be dimeric by freezing point depression measurements in benzene, while triisopropylaluminium and triisobutylaluminium are predominantly monomeric in this medium apparently due to steric hindrance to dimerization.⁷ Triethylaluminium was reported to be predominantly dimeric in the gas phase, as determined by vapor density measurements.⁸ The low-temperature ¹H NMR spectrum of triethylaluminium has been interpreted in terms of a dimeric structure similar to that of trimethylaluminium dimer.⁹ However, despite extensive investigation of aluminium alkyls over many years, there have been no reports of structurally characterized complexes in which an *n*-alkyl group other than methyl serves as the bridging group. In this context, we report the synthesis, structure, properties and reactivity of an aluminium pyrazolate complex that contains an ethyl group bridging between two aluminium atoms.

Treatment of diphenylpyrazole with triethylaluminium (2 equiv.) in hexane at ambient temperature led to slow ethane evolution over 18 h. The bridging ethyl complex **1** was isolated as colorless needles after crystallization of the crude residue from hexane (Scheme 1).[†] The formulation of **1** as the ethyl-bridged structure was suggested initially by the ¹H and ¹³C{¹H} NMR spectra. At –40 °C in toluene-*d*₈, resonances due to terminal ethyl groups were observed in the ¹H NMR spectrum at δ 1.27 (t) and –0.30 (q) while another set of ethyl resonances appeared at δ 1.00 (t) and 0.93 (q). The ratio of these two sets of peaks (δ 1.27, –0.30 and 1.00, 0.93) was 4:1, suggesting that the presence of a bridging ethyl ligand. In the ¹³C{¹H} NMR spectrum at –40 °C, the terminal ethyl carbons resonated at δ 9.79 and 1.79, while sharp bridging ethyl ligand resonances were observed at δ 7.35 and 4.08. At or below –40 °C in toluene-*d*₈, static NMR spectra with sharp resonances were obtained for **1**. Upon warming from –40 to 20 °C in toluene-*d*₈, the methyl and methylene resonances of the bridging ethyl resonance gradually broadened and shifted downfield slightly. Above 20 °C, only one type of ethyl group was observed, suggesting rapid exchange of terminal and bridging ethyl sites. The bridged ethyl structure of **1** was established in the solid state by X-ray crystallography, as described below.



Scheme 1

Other reactions relating to **1** are outlined in Scheme 1. Treatment of diphenylpyrazole with triethylaluminium (1 equiv.) afforded the dimeric pyrazolato complex **2** (89%) as colorless crystals after crystallization from hexane. Protonolysis of **1** with diphenylmethanol in hexane at 23 °C was complete within 0.25 h to afford the diphenylmethoxy complex **3** (99%) as colorless crystals. The structures of **2** and **3** were established by a combination of spectral and analytical techniques.

The X-ray crystal structure of **1** was determined.[‡] Fig. 1 shows a perspective view of **1** along with selected bond lengths and angles. Consistent with the NMR analysis, the molecule consists of a diphenylpyrazolato ligand with a diethylaluminumo group bonded to each nitrogen atom. An ethyl group acts as a bridge between the two aluminium atoms. The two nitrogen atoms and two aluminium atoms occupy an approximate plane, but the methylene carbon of the bridging ethyl group is situated 0.95 Å above this plane. The aluminium–nitrogen bond lengths are 1.928(2) and 1.936(2) Å. The aluminium–carbon bond lengths lie in the range 1.942(4)–1.967(3) Å for the terminal ethyl groups and are 2.144(4) and 2.150(4) Å for the bridging ethyl group. These aluminium–carbon bond lengths are very similar to the related values in structurally characterized aluminium complexes with bridging methyl groups.² The carbon–carbon bond length of the bridging ethyl group [1.535(4) Å] is within the normal range for such bonds and does not differ significantly from the values for the terminal ethyl groups. The geometry about the aluminium centers is distorted tetrahedral.

The crystal structure of **1** provides the first structural documentation of a saturated *n*-alkyl group other than methyl bridging between two aluminium centers. The bridging ethyl ligand in **1** appears to be far more stable than the analogous group in triethylaluminium. In the ¹H NMR spectrum of triethylaluminium the bridging methylene resonance is only resolved below –60 °C, suggesting that bridge–terminal ethyl group exchange is fast on the NMR timescale above this temperature.⁹ In **1**, the bridging ethyl resonance is resolved at temperatures as high as 20 °C. We have recently reported the synthesis, structure and molecular orbital calculations of pyrazolate-bridged dialuminium complexes that contain bridging

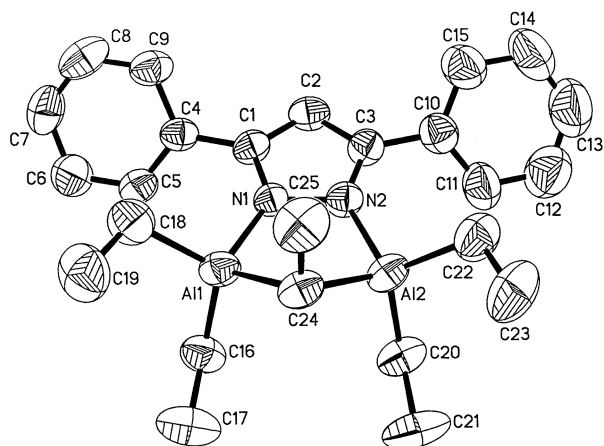


Fig. 1 Perspective view of **1**. Selected bond lengths (Å) and angles (°): Al(1)–N(1) 1.928(2), Al(2)–N(2) 1.936(2), Al(1)–C(16) 1.942(4), Al(1)–C(18) 1.967(3), Al(2)–C(20) 1.947(3), Al(2)–C(22) 1.942(4), Al(1)–C(24) 2.144(4), Al(2)–C(24) 2.150(4), C(16)–C(17) 1.496(5), C(18)–C(19) 1.533(5), C(20)–C(21) 1.508(5), C(22)–C(23) 1.544(5), C(24)–C(25) 1.535(4), N(1)–N(2) 1.378(2), N(1)–Al(1)–C(16) 111.93(14), N(1)–Al(1)–C(18) 109.79(13), N(1)–Al(1)–C(24) 100.54(13), C(16)–Al(1)–C(18) 117.67(19), C(16)–Al(1)–C(24) 110.75(17), C(18)–Al(1)–C(24) 104.56(16), N(2)–Al(2)–C(20) 110.38(13), N(2)–Al(2)–C(22) 112.18(14), N(2)–Al(2)–C(24) 100.92(12), C(20)–Al(2)–C(22) 116.23(19), C(20)–Al(2)–C(24) 112.12(17), C(22)–Al(2)–C(24) 103.79(18), Al(1)–C(24)–C(25) 112.6(2), Al(2)–C(24)–C(25) 112.0(2), Al(1)–C(24)–Al(2) 90.44(12).

ing methyl groups.¹⁰ The bridging aluminium–carbon bond strengths in these complexes are 6–7 kcal mol⁻¹ stronger than the analogous bonds in trimethylaluminium dimer, and calculations indicate that this increased bond strength is due to extended bonding interactions involving pyrazolate π -orbitals. Similar extended bonding interactions in **1** could account for the slower bridge–terminal exchange of the ethyl groups, compared to triethylaluminium. The preparation of **1** suggests that other main group metal complexes with bridging *n*-alkyl ligands may be accessible synthetically by inclusion of pyrazolate or other unsaturated groups in the cyclic array incorporating the bridging alkyl.

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Notes and references

† *Spectroscopic data*: for **1**: mp 66–67 °C; ¹H NMR (300 MHz, C₆D₆, 298 K): δ 7.42 (m, 4 H, CH of phenyl rings), 7.09 (m, 6 H, CH of phenyl rings), 6.24 (s, 1 H, pz ring CH), 1.13 (t, *J* 7.8 Hz, 15 H, CH₂CH₃), 1.04 (br s, 2 H, bridging CH₂CH₃), 0.21 (q, *J* 7.5 Hz, 8 H, terminal CH₂CH₃); ¹³C{¹H} NMR (75 MHz, C₆D₆, 298 K): δ 155.38 (s, pz ring C-Ph), 131.35 (s, *ipso*-C of phenyl rings), 129.43 (s, *para*-CH of phenyl rings), 128.74 (s, *ortho*-CH of phenyl rings), 128.54 (s, *meta*-CH of phenyl rings), 107.13 (s, pz ring CH), 9.40 (s, terminal CH₂CH₃), 7.4 (br s, bridging CH₂CH₃), 3.9 (br s, bridging CH₂CH₃), 1.80 (s, terminal CH₂CH₃); MS (EI, 70 eV) *m/z* 304 ([M – AlEt₃]⁺, 16%), 220 ([Ph₂pZ]⁺, 100%). Anal. Calc. for C₂₅H₃₆Al₂N₂: C, 71.74; H, 8.67; N, 6.69. Found: C, 71.48; H, 8.60; N, 6.52%. For **2**: mp. 117–118 °C; ¹H NMR (300 MHz, C₆D₆, 298 K): δ 7.49 (m, 8 H, CH of phenyl rings), 7.05 (m, 12 H, CH of phenyl rings), 6.26 (s, 2 H, pz ring CH), 0.86 (t, *J* 7.8 Hz, 12 H, CH₂CH₃), –0.16 (q, *J* 7.8 Hz, 8 H, CH₂CH₃); ¹³C{¹H} NMR (75 MHz, C₆D₆, 298 K): δ 158.71 (s, pz ring C-Ph), 131.91 (s, *ipso*-C of phenyl rings), 129.53 (s, *ortho*-CH of phenyl rings), 129.41 (s, *para*-CH of phenyl rings), 128.40 (s, *meta*-CH of phenyl rings), 109.56 (s, pz ring CH), 8.74 (s, CH₂CH₃), 2.91 (s, CH₂CH₃); MS (EI, 70 eV) *m/z* 220 ([Ph₂pZ]⁺, 100%). Anal. Calc. for C₃₈H₄₂Al₂N₄: C, 74.98; H, 6.95; N, 9.20. Found: C, 74.67; H, 7.02; N, 9.29%. For **3**: decomp. pt. 122 °C; ¹H NMR (300 MHz, C₆D₆, 298 K): δ 7.56 (m, 4 H, CH of pz phenyl rings), 7.37 (m, 8 H, CHPh₂), 7.12 (m, 12 H, CHPh₂), 7.01 (m, 6 H, CH of pz phenyl rings), 6.40 (s, 1 H, OCH), 6.37 (s, 1 H, pz ring CH), 0.98 (t, *J* 7.8 Hz, 12 H, CH₂CH₃), 0.00 (m, 8 H, CH₂CH₃); ¹³C{¹H} NMR (75 MHz, C₆D₆, 298 K): δ 155.59 (s, pz ring C-Ph), 140.18 (s, *ipso*-C of CHPh₂), 131.81 (s, *ipso*-C of pz phenyl rings), 129.30 (s, CH of phenyl rings), 128.94 (s, CH of

phenyl rings), 128.81 (s, CH of phenyl rings), 128.74 (s, CH of phenyl rings), 128.59 (s, 2 CH of phenyl rings), 107.33 (s, pz ring CH), 79.91 (s, OCHPh₂), 9.16 (s, CH₂CH₃), 2.03 (s, CH₂CH₃); MS (EI, 70 eV) *m/z* 347 ([M – Ph₂CH – 2Et]⁺, 6%), 105 (100%). Anal. Calc. for C₃₆H₄₂Al₂N₂O: C, 75.50; H, 7.39; N, 4.89. Found: C, 75.27; H, 7.42; N, 4.87%.

‡ Single crystals suitable for X-ray diffraction analysis were grown from hexane at –20 °C. Data were collected on a Siemens/Bruker P4-CCD diffractometer. *Crystal data* for **1**: C₂₅H₃₆Al₂N₂, *M_r* = 418.52, monoclinic, space group *P*1, *a* = 12.0348(14), *b* = 11.7684(12), *c* = 18.159(2) Å, β = 101.661(2)°, *V* = 2518.8(5) Å³, *T* = 296 K, *Z* = 2, μ (Mo-K α) = 0.126 mm⁻¹, 5850 independent reflections harvested from 1650 frames of data containing 9276 integrated intensities, *R_{int}* = 0.050. All data were included in the refinement. For *I* \geq 2 σ (*I*), *R*₁ = 0.0392, *wR*₂ = 0.0615. Including weak data *R*₁ = 0.2215, *wR*₂ = 0.0808. CCDC 182/1888. See <http://www.rsc.org/suppdata/cc/b0/b008047k/> for crystallographic files in .cif format.

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