A valence isomer of a dialane

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The compound (η^5-C_5Me_5)Al→Al(C_6F_5)$_3$, which is the first valence isomer of a dialane, has been prepared by treatment of [Al(η^5-C_5Me_5)]$_4$ with Al(C_6F_5)$_3$ and characterized by X-ray crystallography and NMR spectroscopy.

Compounds with aluminium–aluminium bonds are attracting considerable recent attention. The simplest such compounds are the dialanes, R_2AlAlR_2, and a number of these have now been structurally authenticated.[1] It occurred to us that valence isomers of dialanes, *viz.* RAl→AlR_3, might be capable of existence if the appropriate substituents were employed. DFT calculations[2] on the prototypical dialane, H_2AlAlH_2, revealed that the valence isomer HAl→AlH_3, is less stable than H_2AlAlH_2 by 9.17 kcal mol^{-1}. However, replacement of one of the dialane hydride substituents by cyclopentadienide inverted this order and (η^5-C_5H_5)Al→AlH_3 **1** is more stable than the dialane (η^2-C_5H_5)(H)Al→AlH_2 by 10.79 kcal mol^{-1}. In view of the foregoing, [Al(η^5-C_5Me_5)]$_4$ [65 mg, 0.40 mmol of Al(η^5-C_5Me_5) units][3] was treated with Al(C_6F_5)$_3$·$PhCH_3$[4] (250 mg, 0.40 mmol) in 30 mL of toluene at 25 °C. After being stirred for 4 h at 25 °C, the yellow reaction mixture was heated to 50 °C for 30 min. Upon cooling to 25 °C, the reaction mixture was filtered and the solvent and volatiles were removed from the filtrate to afford a dark amber oil from which yellow crystalline (η^5-C_5Me_5)Al→Al(C_6F_5)$_3$ **2** (220 mg, 80% yield, mp 131–133 °C) deposited over a period of 24 h. The mass spectral data† for **2** are consistent with the proposed dialane isomer formulation. The presence of (η^5-C_5Me_5)Al and Al(C_6F_5)$_3$ moieties in **2** is evident from the ^1H, ^{13}C, and ^{19}F NMR spectroscopic data,† noting however that the equivalence of the C_5Me_5 ring carbon and Me resonances could be due to the well known fluxional behaviour of cyclopentadienyl–aluminium systems.[5] The ^{27}Al NMR spectrum of **2** comprises singlet resonances at δ −115.7 and 106.9. Given that the ^{27}Al chemical shifts for the model compound **1**, as computed by the GAIO method,[2b,6] are δ −107.9 and 109.0 for the (η^5-C_5Me_5)Al and AlH_3 centres, respectively, analogous assignments have been made for **2**.† Further support for the proposed assignments stems from the experimentally observed ^{27}Al chemical shifts for monomeric (η^5-C_5Me_5)Al (δ −150)[7] and Al(C_6F_5)$_3$·arene [δ 52 (benzene); δ 61 (toluene)].[4] The overall trend of ^{27}Al chemical shifts is consistent with the transfer of electron density from the alanediyl to the Al(C_6F_5)$_3$ fragment upon formation of the Al→Al donor acceptor bond of **2**.

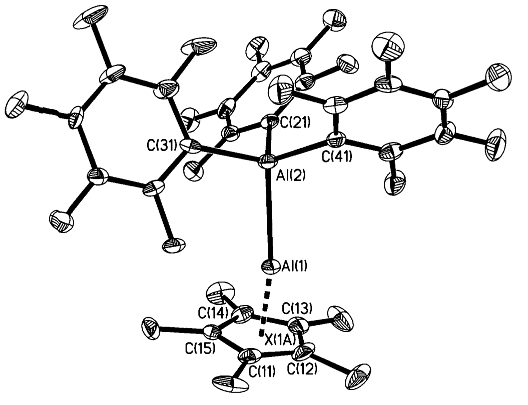

Fig. 1 Thermal ellipsoid plot (30% probability level) for (η^5-C_5Me_5)-Al→Al(C_6F_5)$_3$ **2**. Selected bond lengths (Å) and bond angles (°): Al(2)–Al(1) 2.591(2), Al(1)–X(1A) 2.591(8), Al(1)–C(11) 2.172(7), Al(1)–C(12) 2.162(6), Al(1)–C(13) 2.165(7), Al(1)–C(14) 2.200(7), Al(1)–C(15) 2.189(6), Al(2)–C(21) 1.982(7), Al(2)–C(31) 1.999(7); Al(2)–C(41) 1.997(7); Al(2)–Al(1)–X(1A) 170.1(3), C(21)–Al(2)–C(41) 111.0(3), C(21)–Al(2)–C(31) 108.5(3), C(41)–Al(2)–C(31) 113.5(3), C(21)–Al(2)–Al(1) 104.1(2), C(41)–Al(2)–Al(1) 111.2(2), C(31)–Al(2)–Al(1) 108.0(2).

The foregoing spectroscopic conclusions were confirmed by X-ray crystallography.‡ Compound **2** crystallizes in the *C*2/*c* space group with $Z = 8$; the solid state consists of individual molecules of the dialane isomer and there are no unusually short intermolecular contacts. The pentamethylcyclopentadienyl substituent is attached in an η^5 fashion and the ring centroid–Al–Al moiety deviates only modestly from linearity [170.1(3)°]. The Al–Al bond length in **2** [2.591(3) Å] is shorter than those in the dialanes {$(Me_3Si)_2CH$}$_4Al_2$ [2.660(1) Å],[1a] {2,4,6-Pr^i_3-C_6H_2}$_4Al_2$ [2.647(3) Å],[1b] and {Bu^t_3Si}$_4Al_2$ [2.751(2) Å][1c] but identical to that in [RIAl–AlClR] {R = [$(Me_3Si)_2C(Ph)C(Me_3Si)N$]} [2.593(2) Å]}[1d] within experimental error. The average Al(1)–C bond length of 2.178(7) Å [Al–centroid 1.810(8) Å] is considerably shorter than those reported for Al(η^5-C_5Me_5) [2.388(7) Å][8] and [Al(η^5-C_5Me_5)]$_4$ (2.344 Å, av. Al–centroid 2.011 Å).[7] Such a shortening is anticipated as the partially antibonding aluminium 'lone pair' orbital of Al(η^5-C_5Me_5) is transformed into the donor–acceptor bond with the concomitant development of positive and negative charges on the aluminium centres.[9] The same trend is evident for other group 13 (η^5-C_5Me_5)M→acceptor complexes[10] and is true for both main-group and transition element acceptors.

In conclusion, we have prepared (η^5-C_5Me_5)Al→Al(C_6F_5)$_3$, a valence isomer of a dialane. This compound also features the first example of an Al→Al donor acceptor bond.

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Notes and references

† **2**: HRMS (CI, CH_4) calc. for $C_{28}H_{15}Al_2F_{15}$ *m/z* 690.0565; found 690.0572. ^1H NMR (499.35 MHz, 295 K, C_6D_6) δ 1.49 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (125.69 MHz, 295 K, C_6D_6) δ 149.99 (d, *o*-C_6F_5, $^1J_{CF}$ 224 Hz), 141.83 (d, *p*-C_6F_5, $^1J_{CF}$ 239 Hz), 137.34 (d, *m*-C_6F_5, $^1J_{CF}$ 226 Hz), 129.28 (s, *ipso*-C_6F_5), 115.94 [s, $\mathit{C}_5(CH_3)_5$], 8.44 [s, $C_5(\mathit{C}H_3)_5$]. ^{19}F NMR (469.81 MHz, 295 K, C_6D_6) δ −122.03 (s, *m*-C_6F_5), −153.19 (s, *p*-C_6F_5), 161.77 (s, *o*-C_6F_5). ^{27}Al NMR (130.25 MHz, 295 K, C_6D_6) δ 106.9 [br, $(C_6F_5)_3\mathit{Al}AlC_5Me_5$, $w_{1/2}$ 6122 Hz], −115.7 [s, $(C_6F_5)_3Al\mathit{Al}C_5Me_5$].

‡ *Crystal data* for **2**: $C_{28}H_{15}Al_2F_{15}$, monoclinic, space group *C*2/*c*, $a = 30.635(6)$, $b = 9.814(2)$, $c = 20.236(4)$ Å, $\beta = 111.10(3)$, $V = 5676(2)$ Å^3, $Z = 8$, $D_c = 1.616$ g cm^{-3}, μ(Mo-Kα) = 0.220 mm^{-1}. A suitable single crystal of **2** was covered with mineral oil and mounted on a Nonius-Kappa CCD diffractometer at 123 K. A total of 8481 independent reflections were collected in the range $5.96 < 2\theta < 50.20°$ using Mo-Kα radiation ($\lambda = 0.71073$ Å). Of these, 3815 were considered observed [$I > 2.0\sigma(I)$] and were used to solve (direct methods) and refine (full matrix, least squares on F^2) the structure of **2**; $R = 0.0767$, $wR2 = 0.1944$.

CCDC 182/1856. See http://www.rsc.org/suppdata/cc/b0/b007341p/ for crystallographic files in .cif format

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