A valence isomer of a dialane

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The compound (η⁵-C₅Me₅)Al→Al(C₆F₅)₂, which is the first valence isomer of a dialane, has been prepared by treatment of [Al(η⁵-C₅Me₅)₂] with Al(C₆F₅)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, R₂AlAlR₂, and a number of these have now been structurally authenticated. It occurred to us that valence isomers of dialanes, viz. RAlAIr₅, might be capable of existence if the appropriate substituents were employed. DFT calculations on the prototypical dialane, H₂AlAlH₂, revealed not only that the equivalence of the C₅Me₅ ring carbon atoms is an artefact of the calculations but that the Al–Al single bond length of 2.178(7) Å is considerably shorter than those reported for Al(H₂)₃. The Al–Al bond length in [2.591(1) Å] is shorter than those in the dialanes [(Me₅C₅)₂CH]₂Al₂ [2.660(1) Å] and [Bu₅Sn]₂Al₂ [2.751(2) Å] but identical to that in RAl₂AlC[MeC(C(Me)₃)₂Si]²[2.592(2) Å] within experimental error. The average Al–Al bond length of 2.178(7) Å [Al–centroid 1.810(8) Å] is considerably shorter than those reported for Al(η⁵-C₅Me₅)₂[2.388(7) Å] and [Al(η⁵-C₅Me₅)₂]₂[2.344 Å, av. Al–centroid 2.011 Å]. Such a shortening is anticipated as the partially antibonding aluminium lone pair orbital of Al(η⁵-C₅Me₅)₂ is transformed into the donor–acceptor bond with the concomitant development of positive and negative charges on the aluminium centres. The same trend is evident for other group 13 Al(η⁵-C₅Me₅)₂acceptor complexes and is true for both monogroup and transition element acceptors.

In conclusion, we have prepared (η⁵-C₅Me₅)Al→Al(C₆F₅)₂, 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

1. Z. HRMS (CI, CH₄) calc. for C₂₅H₁₅Al₂F₁₅, m/z 690.0565; found 690.0572. 'H NMR (499.35 MHz, 295 K, C₆D₆) δ 1.49 (s, 15H, C₅Me₅). ¹³C{¹H} NMR (125.69 MHz, 295 K, C₆D₆) δ 149.99 (d, o-C₆F₅, J₆CF₂ = 224 Hz), 141.83 (d, p-C₆F₅, J₆CF₂ = 239 Hz), 137.34 (d, m-C₆F₅, J₆CF₂ = 226 Hz), 129.28 (s, ipso-C₆F₅), 2, 115.94 [s, (C₆F₅)₃Al], 8.44 [s, (C₆F₅)₃Al]. ¹⁹F NMR (469.81 MHz, 295 K, C₆D₆) δ −122.03 (s, C₆F₅), −153.19 (s, C₆F₅), 161.77 (s, o-C₆F₅). ²⁷Al NMR (130.25 MHz, 295 K, C₆D₆) δ 106.9 [br, (C₆F₅)₃Al] = 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 ⩽ 2θ ⩽ 50.20° using Mo-Kα radiation (λ = 0.71073 Å). Of these, 3815 were considered observed (I > 2σ(I)) and were used to solve (direct methods) and refine (full matrix, least squares on F²) the structure of 2: R = 0.0767, wR2 = 0.1944. CCDC 1821856. See http://www.ccdc.cam.ac.uk/suppdata/cc/c60/b007341p/ for crystallographic files in cif format

Fig. 1 Thermal ellipsoid plot (30% probability level) for (η⁵-C₅Me₅)Al→Al(C₆F₅)₂. 2. Selected bond lengths (Å) and bond angles (°): Al(1)–Al(2) 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) 1.997(7), Al(2)–Al(2)–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).

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2 B3LYP: (a) A. D. Becke, _J. Chem. Phys._, 1993, 98, 5648; (b) A. D. Becke, _Phys. Rev. A_, 1988, 38, 3098; (c) C. Lee, W. Yang and R. G. Parr, _Phys. Rev. B_, 1988, 37, 785; (d) S. H. Vosko, L. Wilk and M. Nusair, _Can. J. Phys._, 1980, 58, 1200. All DFT calculations were performed using the Gaussian 94 (revision B2) suite of programs. All-electron basis sets were used for C, H [6-31G(d)] and the group 13 elements [6-31 + G(d)].


