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1,2-Bis(chloromethylalumino)tetrafluorobenzene, an aluminium-based bifunctional Lewis acid with a perfluorinated backbone

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1,2-Bis(trimethylstannyl)tetrafluorobenzene reacts with chlorodimethylaluminium(III) to afford dimeric 1,2-bis(chloromethylalumino)tetrafluorobenzene the structure of which has been determined by X-ray analysis.

Bidentate aluminium Lewis acids have recently emerged as promising tools for organic reaction catalysis[1] as well as for anion[2] and molecular recognition.[3] Experience gained in boron chemistry indicates that this class of compounds could also prove useful as activators for olefin polymerization with d^0-transition metal catalysts.[4,5] In this latter case, the use of strongly electron withdrawing substituents[6,7] appears to be required in order to yield very stable weakly coordinating anions.[8] As part of our continuing effort[9] in this direction, we now report the synthesis and characterization of dimeric 1,2-bis(chloromethylalumino)tetrafluorobenzene, a bidentate Lewis acid bearing a perfluorinated backbone.

1,2-Bis(trimethylstannyl)benzene has been shown to react with aluminium chlorides to yield 1,2-bis(alumino)benzene complexes.[10] In order to determine if a similar synthetic strategy could be applied to the preparation of perfluorinated systems, bis(trimethylstannyl)tetrafluorobenzene **1**[11] was allowed to react with chlorodimethylaluminium(III) in hexane (Scheme 1).† After 96 h, complete removal of the volatile components afforded a quantitative yield of **2**, which could be crystallized by slow evaporation of the solvent from a hexane solution. The identity of **2** was first inferred from the following salient NMR spectroscopic features.‡ ^{27}Al NMR indicated the presence of a tetra-coordinated aluminium center (δ 150, $\omega_{1/2}$ = 2700 Hz). The ^{19}F NMR spectrum allowed the possibility of fluoride activation[8] to be eliminated since two signals with multiplicity consistent with a AA′BB′ higher order spin system were observed. A high field singlet in both the ^{1}H and ^{13}C NMR spectrum could be assigned to the methylaluminium groups. While EI mass spectrometry allowed the detection of a peak corresponding to 1,2-bis(methylchloroalumino)tetrafluorobenzene, definitive identification of **2** was provided by a single crystal structure analysis (*vide infra*), which revealed its dimeric nature. In this respect, **2** differs from its perprotio analog 1,2-bis(methylchloroalumino)benzene which has been formulated as a monomer.[10] By analogy with the reaction of 1,2-bis(trimethylstannyl)benzene with chlorodimethylaluminium(III),[10] the formation of 1,2-bis(dimethylalumino)tetrafluorobenzene through trimethylstannyl chloride elimination could have been expected. In the present case however, the isolation of **2** is accompanied by formation of tetramethylstannane which was found among the volatile components of the reaction.

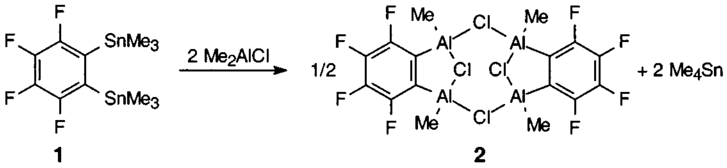
Table 1 Important bond lengths (Å) and angles (°) in the structure of **2**

Al(1)–C(11)	1.954(4)	Al(2)–Cl(24)	2.2778(14)	Al(3)–Cl(13)	2.2894(14)
Al(1)–Cl(12)	2.2808(15)	Al(2)–Cl(12)	2.2784(14)	Al(4)–C(22)	1.966(3)
Al(1)–Cl(13)	2.2812(16)	Al(3)–C(21)	1.959(4)	Al(4)–Cl(34)	2.720(14)
Al(2)–C(12)	1.955(4)	Al(3)–Cl(34)	2.2884(14)	Al(4)–Cl(24)	2.3003(15)

C(11)–Al(1)–Cl(12)	98.90(12)	Al(2)–Cl(12)–Al(1)	98.25(5)
Cl(12)–Al(1)–Cl(13)	101.73(6)	Al(1)–Cl(13)–Al(3)	120.12(6)
C(12)–Al(2)–Cl(12)	99.17(12)	Al(2)–Cl(24)–Al(4)	118.79(5)
Cl(24)–Al(2)–Cl(12)	99.63(6)	Al(4)–Cl(34)–Al(3)	99.11(5)
C(21)–Al(3)–Cl(34)	98.33(11)	C(12)–C(11)–Al(1)	121.8(3)
Cl(34)–Al(3)–Cl(13)	100.23(5)	C(11)–C(12)–Al(2)	120.2(3)
C(22)–Al(4) Cl(34)	99.20(11)	C(22)–C(21)–Al(3)	122.0(2)
Cl(34)–Al(4)–Cl(24)	100.75(5)	C(21)–C(22)–Al(4)	120.7(3)

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell.§ Important bond length and angles are listed in Table 1. As shown in Fig. 1, the complex approachs C_{2v} symmetry and adopts a conformation reminiscent of a wings-up butterfly. Each aluminium center is tetrahedrally coordinated and lies close to the plane containing its corresponding phenylene ligand [Al(1) 0.129 Å, Al(2) −0.144 Å,Al(3) 0.179 Å, Al(4) 0.018 Å]. There are two types of bridging chlorine atoms in the coordination sphere of each aluminium center. The chlorine atoms Cl(12) and Cl(34) bridge neighboring aluminium centers within the 1,2-bis(alumino)tetrafluorobenzene sub-units. They are thus responsible for the formation of [C_2AlClAl] five-membered rings which approach planarity [Σ(endocyclic angles) 538.32 and 539.33°]. The chloride coordination angles Al(1)–Cl(12)–Al(2) and Al(3)–Cl(34)–Al(4) of 98.25(5) and 99.11(5)° can be compared to the value of 94.83(4)° observed in the structure of the related tin-based bidentate complex 1,2-bis(dimethylchlorostannyl)benzene·HMPA.[12] The Al–Cl bond distances of **2** fall within the narrow range of 2.272(1)–2.300(1) Å with an average value of 2.28 Å. The chlorine atoms Cl(13) and Cl(24) connect the two 1,2-bis(alumino)tetrafluorobenzene sub-units into a symmetrical dimer and form an eight-membered $(AlCl)_4$ ring which adopts a crown conformation. The cofacial tetrafluorophenylene rings are essentially parallel (dihedral angle 6.4°). The distance between their respective centroids is relatively short (3.56 Å) and indicates the presence of an interaction.

In view of the low stability and sometimes explosive behavior of perfluoroaryl aluminium derivatives,[6] the isolation



Scheme 1

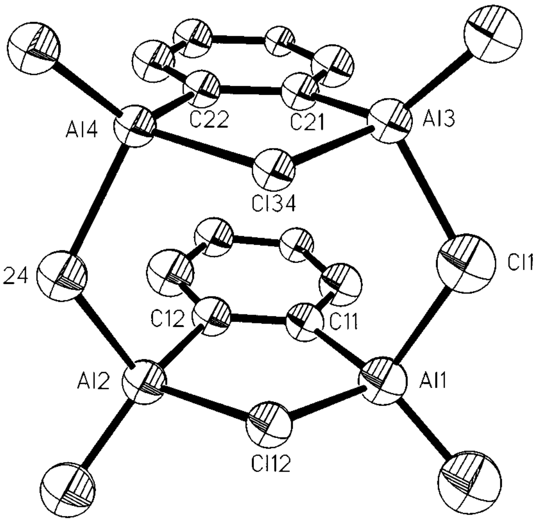


Fig. 1 ORTEP drawing of **2** with 50% probability ellipsoids; H and F atoms omitted for clarity.

of **2** is especially noteworthy. Analogous boron complexes such as 1,2-bis[bis(pentafluorophenyl)boryl]tetrafluorobenzene have been only very recently isolated.[13] Current studies are focussed on the use of 1,2-bis(alumino)tetrafluorobenzene complexes to abstract halides from a variety of substrates.

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Notes and references

† *Synthesis of* 2: *great caution should be exercised as aluminium complexes with perfluorinated aryl substituents have been reported to spontaneously explode.*[6] Chlorodimethylaluminium (374 mg, 4.04 mmol) was added to a solution of **1** (961 mg, 2.02 mmol) in hexane (5 mL) at room temp. The resulting solution was stirred for four days and filtered to remove traces of insoluble material. Evaporation of the solvent left a white residue that was exposed to a dynamic vacuum for 6 h at 50 °C. This procedure afforded a 95% yield (580 mg) of **2** (mp 79–80 °C). Elemental analysis. Calc. for $C_{16}H_{12}Al_4Cl_4F_8$: C, 31.69; H, 1.98. Found C, 31.05; H, 2.15%.

‡ *NMR data for* **1**, ^{1}H NMR (300 MHz, [$^2H_6$]benzene): δ −0.25 (s, 12 H, CH_3). ^{13}C NMR (75.4 MHz, [$^2H_6$]benzene: δ −8.4 (s, CAl) 126.8 (s, C-1/2) 140.7 (d, $^1J_{CF}$ 241.7 Hz, C-3/6) 152.1 (d, $^1J_{CF}$ 236.6 Hz, C-4/5). ^{19}F NMR (282.2 MHz, [$^2H_6$]benzene, $CFCl_3$ ext.); δ −121.22 (pseudo d, J_{FF} 19.5 Hz, 4 F, F-3/6) −151.88 (pseudo, d, J_{FF} 19.5 Hz, 4 F, F-4/5). ^{27}Al NMR (104.2 MHz, [$^2H_6$]benzene, $AlCl_3\cdot 6H_2O$ ext.) δ 150 ($\omega_{1/2}$ 2700 Hz).

§ *Crystal and structure determination data for* **2**: X-ray data for **2** were collected at −100 °C on a Siemens SMART-CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). An irregularly shaped colorless plate of **2** *ca.* 0.1 × 0.3 × 0.4 mm in size was selected and mounted on a glass fiber with epoxy. The data were collected using 0.3°-wide ω-scans with a crystal to detector distance of 5.0 cm to yield a sphere (98% complete) of data to a resolution of 0.75 Å (2θ = 56.6°). The data was then truncated, on the basis of intensity statistics, at a resolution of 0.90 Å to yield a sphere (99.8% complete) of data ($2.08 \leqslant 2\theta \leqslant 23.23°$) composed of 19775 reflections (3549 unique, R_{int} = 0.0522). Other key crystallographic parameters are as follows: $C_{16}H_{12}Al_4Cl_4F_{12}$, M = 605.98, monoclinic, space group $P2_1/c$, a = 9.832(2), b = 9.855(2), c = 25.692(6) Å, V = 2484.9(9) Å^3, Z = 4, μ = 0.681 mm^{-1}. The structure was solved by direct methods and refined by full-matrix least squares against F^2 using the SHELXTL/PC (ver. 5.10) package. The refinement converged with residuals of $R1$ ($wR2$) = 0.0359 (0.0779) for 293 refined parameters and 3549 unique reflections [2505 with $I > 2\sigma(I)$].

CCDC 182/1273. See http://www.rsc.org/suppdata/cc/1999/1367/ for crystallographic files in .cif format.

1 T. Ooi, M. Tomoya and K. Maruoka, *Angew. Chem., Int. Ed.*, 1998, **37**, 2347.
2 W. Uhl, F. Hannemann, W. Saak and R. Wartchow, *Eur. J. Inorg. Chem.*, 1998, 921.
3 O. Saied. M. Simard and J. D. Wuest, *Organometallics*, 1998, **17**, 1128.
4 L. Jia, X. Yang, C. Stern and T. J. Marks, *Organometallics*, 1994, **13**, 3755.
5 K. Köhler, W. E. Piers, A. P. Jarvis, S. Xin, Y. Feng, A. M. Bravakis, S. Collins, W. Clegg, G. P. A. Yap and B. Marder, *Organometallics*, 1998, **17**, 3557.
6 T. Belgardt, J. Storre, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Inorg. Chem.*, 1995, **34**, 3821.
7 A. H. Cowley, G. S. Hair, B. G. McBurnett and R. A. Jones, *Chem. Commun.*, 1999, 437.
8 Y.-X. Chen, M. V. Metz, L. Li, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1998, **120**, 6287.
9 M. Tschinkl, A. Schier, J. Riede and F. P. Gabbaï, *Inorg. Chem.*, 1998, **37**, 5097.
10 J. J. Eisch, K. Mackenzie, H. Windisch and C. Krüger, *Eur. J. Inorg. Chem.*, 1998, 153.
11 T. Chivers, *J. Organomet. Chem.*, 1969, **19**, 75.
12 R. Altmann, K. Jurkschat and M. Schürmann, *Organometallics*, 1998, **17**, 5858.
13 V. C. Williams, W. E. Piers, W. Clegg, M. R. J. Elsegood, S. Collins and T. B. Marder, *J. Am. Chem. Soc.*, 1999, **121**, 3244.

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