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A dimeric aluminium amide, bis(*trans*-μ_2-pentafluoroanilino-κ^2*N*:*N*)bis[dimethylaluminium(III)]

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Key indicators

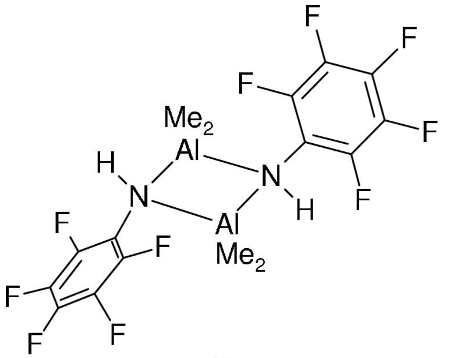
Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.002 Å
R factor = 0.037
wR factor = 0.107
Data-to-parameter ratio = 16.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title dimeric aluminium amide, $[Al_2(CH_3)_4(C_6HF_5N)_2]$, contains a folded Al_2N_2 ring with four-coordinate Al atoms [mean Al—N = 1.9910 (14) Å and mean Al—C = 1.9452 (19) Å]. The pentafluorophenyl substituents on the N atoms adopt a *trans* configuration.

Comment

In the last decade, a major theme of organometallic chemistry has been the design and development of alternative ligand systems capable of stabilizing monomeric metal complexes while provoking novel reactivity. Exploration of this field is driven by the potential use of these complexes in catalysis and organic synthesis. We recently succeeded in the preparation of aryl-substituted sterically crowded triazenes, which were used to stabilize the first examples of structurally characterized aryl compounds of the heavier alkaline earth metals Ca, Sr and Ba (Hauber *et al.*, 2005).



(I)

As a continuation of this work, we have examined the reaction between the bulky dialkylaluminiumtriazenide [{Dmp(Tph)N$_3$}AlMe$_2$] (Dmp is 2,6-Mes$_2$C$_6$H$_3$, where Mes is 2,4,6-Me$_3$C$_6$H$_2$, and Tph is 2-TripC$_6$H$_4$, where Trip is 2,4,6-^{i}Pr$_3$C$_6$H$_2$) and pentafluorophenylaniline. However, instead of an expected triazenidoaluminium amido or imido species, the title compound, (I), was isolated in good yield. It should be noted that earlier attempts to synthesize (I) by direct reaction of trimethylaluminium with pentafluorophenylaniline have failed (Belgardt *et al.*, 1994).

The molecular structure of (I) consists of a C_1-symmetric dimeric unit, in which the dimethylaluminium fragments are bridged by –NHC$_6$F$_5$ groups. Both metal atoms have distorted tetrahedral environments, with angles ranging from 85.11 (5) to 123.49 (9)°. The Al1$\cdots$Al2 separation is 2.8728 (11) Å and the internal angles in the Al_2N_2 core are very similar, with an average of 85.20 (6)° at Al and 92.36 (6)° at N. The average

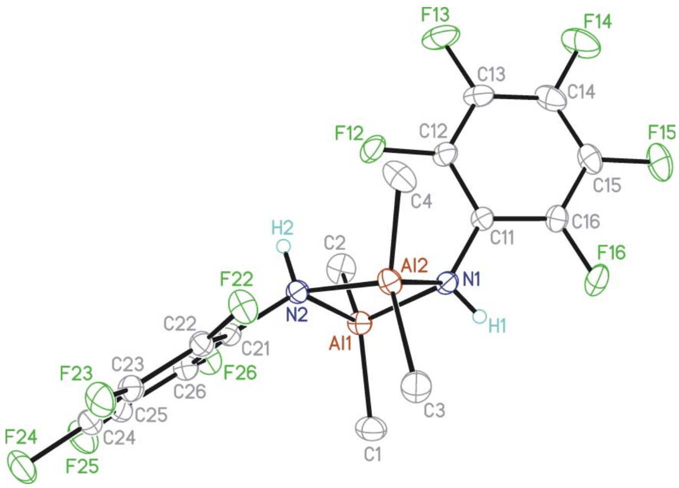


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and the H atoms on the methyl groups have been omitted for clarity.

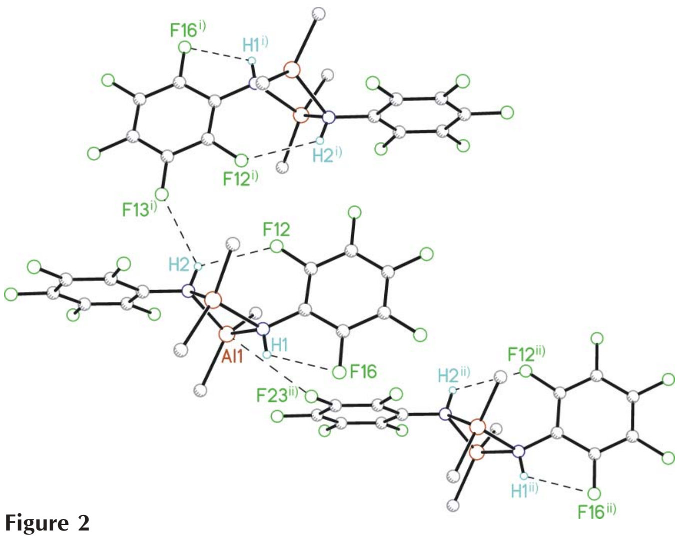


Figure 2
Intra- and intermolecular contacts in the structure of (I). Dashed lines indicate intra- and intermolecular N—H···F hydrogen bonds and Al···F contacts. [Symmetry codes: (i) (i) $-x$, $-y + 2$, $-z$; (ii) x, $y + 1$, z.]

Al—N bond length of 1.9910 (14) Å is very close to the values in other structurally characterized dimeric dimethylaluminium arylamides {examples are [$Me_2AlNHDip$]$_2$ [1.987 (12) Å; Dip is 2,6-$^{i}Pr_2C_6H_3$; Waggoner & Power, 1991] and [Me_2AlNH-3,5-$F_2C_6H_3$]$_2$ (1.980 Å; Gordon *et al.*, 2002)}.

The Al_2N_2 core is not planar but has a fold angle of 155.66 (9)° between the Al_2N planes. The angles between the C1*n*- or C2*n*-aromatic ring planes of the pentafluorophenyl substituents on the N atoms, which adopt a *trans* configuration, and the Al1···Al2 vector are 2.2 and 86.6°, respectively. In addition, the aryl rings show a perpendicular orientation relative to each other, with an interplanar angle of 84.41 (5)°.

There are two weak to medium-strong intramolecular N—H···F hydrogen bonds present in the structure (Table 2). Important interactions that contribute to the crystal packing (Fig. 2) are another weak intermolecular N—H···F hydrogen bond and an Al1···F23^{ii} contact [symmetry code: (ii) x, $y + 1$, z].

Experimental

The synthesis of [{Dmp(Tph)N_3}$AlMe_2$] was carried out as follows. Under an atmosphere of purified argon, $AlMe_3$ (1.1 ml, 2 *M* in *n*-hexane, 2.2 mmol) was added with stirring to a solution of the triazene HN_3Dmp(Tph) (1.36 g, 2.14 mmol) in *n*-heptane (40 ml). After 30 min, all volatile materials were removed under reduced pressure to afford the product as a viscous yellow oil in quantitative yield. Spectroscopic analysis: ^{1}H NMR (C_6D_6, 250.1 MHz, δ, p.p.m.): −1.31 (*s*, 6H, $AlMe_2$), 0.96, 1.13, 1.23 [3*d*, $^{3}J_{HH}$ = 6.9 Hz, 3 × 6H, *o*+*p*-CH(CH_3)$_2$], 2.09 (*s*, 12H, *o*-CH_3), 2.18 (*s*, 6H, *p*-CH_3), 2.51 [*sep*, $^{3}J_{HH}$ = 6.9 Hz, 2H, *o*-CH(CH_3)$_2$], 2.78 [*sep*, $^{3}J_{HH}$ = 6.9 Hz, 1H, *p*-CH(CH_3)$_2$], 6.33–7.11 (*m*, 7H, various Aryl-H), 6.84 (*s*, 4H, *m*-Mes), 7.07 (*s*, 2H, *m*-Trip); ^{13}C NMR (C_6D_6, 62.9 MHz, δ, p.p.m.): −11.2 ($AlMe_2$), 21.0 (*o*-CH_3), 21.1 (*p*-CH_3), 23.4, 24.3, 25.6 [*o*+*p*-CH(CH_3)$_2$], 30.7 [*o*-CH(CH_3)$_2$], 34.9 [*p*-CH(CH_3)$_2$], 120.5, 121.5, 125.0, 125.9, 127.9, 129.0, 130.7, 131.9, 132.1, 133.6, 134.1, 135.9, 136.8, 138.2, 141.0, 144.2, 147.1, 149.0 (aromatic C). The synthesis of (I) was carried out as follows. $C_6F_5NH_2$ (0.27 g, 1.50 mmol) was added to a solution of [{Dmp(Tph)N_3}$AlMe_2$] (1.04 g, 1.50 mmol) in *n*-heptane (40 ml) and stirring was continued for 14 h, after which half of the solvent was removed under reduced pressure. Storage in a freezer at 253 K afforded colourless plates of (I) suitable for X-ray crystallographic studies [yield 0.27 g, 74%; m.p. 374–390 K (decomposition)]. Spectroscopic analysis: ^{1}H NMR (C_6D_6, 250.1 MHz, δ, p.p.m.): −0.61 (*s*, 6H, $AlMe_2$), 2.94 (*s*, 2H, NH); ^{13}C NMR (C_6D_6, 62.9 MHz, δ, p.p.m.): −11.0 (*s*, $AlMe_2$); ^{19}F NMR (C_6D_6, 235.4 MHz, δ, p.p.m.): −163.0 (*m*, *m*-C_6F_5), −161.5 (*m*, *p*-C_6F_5), −148.8 (*m*, *o*-C_6F_5). At 333 K, a solution of (I) in C_6D_6 slowly decomposes to the imido cluster [($MeAlNC_6F_5$)$_4$] [δ(^{1}H) −0.45 p.p.m.] (Belgardt *et al.*, 1994).

Crystal data

[$Al_2(CH_3)_4(C_6HF_5N)_2$]
M_r = 478.25
Triclinic, $P\overline{1}$
a = 9.651 (3) Å
b = 10.584 (3) Å
c = 10.681 (3) Å
α = 82.24 (2)°
β = 84.87 (2)°
γ = 68.06 (2)°
V = 1001.8 (5) Å^3
Z = 2
D_x = 1.585 Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 39 reflections
θ = 7.9–12.5°
μ = 0.24 mm^{-1}
T = 173 (2) K
Block, colourless
0.75 × 0.60 × 0.60 mm

Data collection

Rebuilt Syntex $P2_1$/Siemens $P3$ four-circle diffractometer
Wyckoff scans
Absorption correction: none
5088 measured reflections
4809 independent reflections
4472 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 28.0°
h = −12 → 12
k = −12 → 13
l = −14 → 14
2 standard reflections every 198 reflections intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.107
S = 1.08
4809 reflections
295 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2 + 0.3866P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Al1—N1	1.9971 (14)	Al2—C4	1.9417 (19)
Al1—N2	1.9883 (14)	Al1—Al2	2.8728 (11)
Al2—N1	1.9996 (14)	N1—C11	1.4159 (18)
Al2—N2	1.9788 (14)	N2—C21	1.4306 (17)
Al1—C1	1.9473 (19)	N1—H1	0.83 (2)
Al1—C2	1.9358 (18)	N2—H2	0.86 (2)
Al2—C3	1.9561 (18)		
N1—Al1—N2	85.11 (5)	Al1—N1—Al2	91.91 (6)
N1—Al2—N2	85.29 (6)	Al1—N2—Al2	92.80 (6)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···F16	0.83 (2)	2.30 (2)	2.7676 (16)	116 (2)
N2—H2···F12	0.86 (2)	2.52 (2)	3.0784 (17)	123 (2)
N2—H2···F13^{i}	0.86 (2)	2.51 (2)	3.0949 (19)	126 (2)

Symmetry code: (i) $-x, -y+2, -z$.

Atoms H1 and H2 were located in a difference Fourier map and allowed to refine freely. The remaining H atoms were positioned geometrically at C—H distances of 0.98 Å (CH_3) and refined in a riding-model approximation, including free rotation for methyl groups and variable isotropic displacement parameters.

Data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL*.

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