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Bis[μ-1-(2,4,6-trimethylphenyl)ethanolato-*O*:*O*]-bis(dimethylaluminium)

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Key indicators

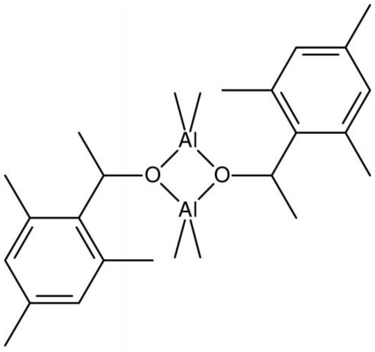
Single-crystal X-ray study
T = 160 K
Mean σ(C–C) = 0.005 Å
R factor = 0.076
wR factor = 0.216
Data-to-parameter ratio = 15.4

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

The title compound, $[\{Al(CH_3)_2\}_2(C_{12}H_{18}O)_2]$, formed by the Me_3Al-mediated alkylation of mesitylaldehyde, is dimeric in the solid state, with a central Al_2O_2 planar ring core residing on an inversion centre.

Comment

For many years, aluminium alkoxides and aryloxides have been utilized as reagents in organic synthesis (Zietz *et al.*, 1983). However, the development of heterobimetallic reagents for use in asymmetric transformations has led to an increased awareness of the importance of aluminium in synthesis (Yamamoto & Maruoka, 1988; Saito & Yamamoto, 1997; Saito *et al.*, 1998; Saito *et al.*, 1999; Cogan & Ellman, 1999). In this regard, we have recently reported the syntheses and solid-state structures of dimethylaluminium enolates and aryloxides, produced from the reactions of trimethylaluminium and aromatic methyl ketones (Allan *et al.*, 2000). The unexpected formation of enolate species was found to be a consequence of steric crowding in the ketones, when both the 2- and 6-positions of the aromatic rings carried methyl groups. We report here the structure of the title compound, (I), which is produced from the addition reaction between trimethylaluminium and 2,4,6-trimethylbenzaldehyde (mesitylaldehyde).



(I)

As can be seen from Fig. 1, complex (I) adopts a dimeric structure with a planar central Al_2O_2 ring core. The molecule is crystallographically centrosymmetric. Each Al atom is tetracoordinate by bonding to two methyl groups and two bridging O atoms. Although the average of the angles around each metal is 108.4°, these vary from 80.20 (9)° for $O—Al—O^i$ to 119.49 (16)° for C1—Al—C2, giving a highly distorted pseudo-tetrahedral geometry at aluminium [symmetry code: (i) $1-x$, $1-y$, $-z$]. The internal Al_2O_2 ring angles at the metal atoms are smaller than at the O atoms [80.20 (9) and 99.80 (9)°, respectively], which is consistent with sp^2 hybridi-

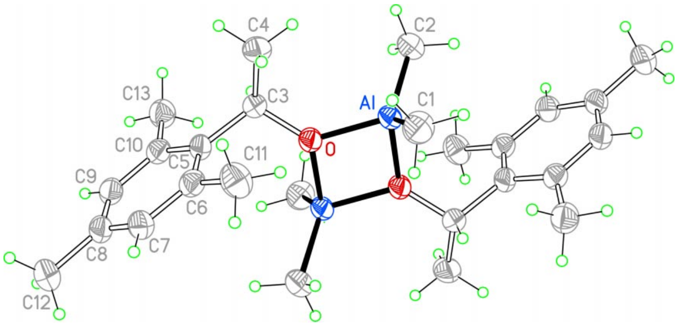


Figure 1
The molecular structure of (I) with unique atom labels and 50% probability ellipsoids for non-H atoms.

zation for the bridging O atoms (van der Steen *et al.*, 1991). The two independent Al—O distances are essentially the same at 1.844 (2) and 1.848 (2) Å for Al—O and Al—O^i respectively. Similarly, the remaining bond lengths and angles within (I) are in accord with those found in related systems (Schumann *et al.*, 1996; Hitchcock *et al.*, 1990; Sierra *et al.*, 1989).

It is notable that the α-C atom C3 lies 0.434 Å out of the Al_2O_2 ring plane, and that the groups attached to this atom are staggered with respect to the ring, with torsion angles of −30.5 (4), 86.3 and −157.3 (2)° for Al—O—C3—C4, Al—O—C3—H3, Al—O—C3—C5, respectively. These differ markedly from those found in the closely related enolate analogue $[Me_2AlOC(2,4,6\text{-}Me_3C_6H_2){=}CH_2]$, (II), where the olefin bond lies close to the Al_2O_2 ring plane (Allan *et al.*, 2000). This difference is most likely a consequence of the sp^3 *versus* sp^2 hybridization of the α-C atoms in (I) and (II), respectively, which alters the minimum energy orientation of the attached groups.

Experimental

Under an inert atmosphere of argon gas, mesitylaldehyde (0.35 g, 2.36 mmol) was added dropwise to a 195 K cooled solution of Me_3Al (2.4 mmol of a 2 *M* solution in toluene) in 3 ml of toluene, producing a yellow solution. The reaction mixture was allowed to warm slowly to ambient temperature with constant stirring and stirred for a further 20 h. All toluene was removed *in vacuo*, the residue was dissolved in 5 ml of hexane and a crystalline product was obtained on cooling the mixture to 245 K for 24 h. Yield: 0.153 g, 29.5%; m.p. 417–419 K. ^1H NMR (C_6D_6, 400 MHz): δ 6.66 (broad *s*, 2H, *m*-H, Ph), 5.58 (*q*, *J* = 6.8 Hz, 1H, HCO), 2.54 (broad *s*, 3H, *o*-Me, Ph), 2.14 (broad *s*, 3H, *o*-Me, Ph), 2.01 (*m*, 3H, *p*-Me, Ph), 1.36 (*m*, 3H, Me), −0.44, −0.53, −0.62 (*s*, 6H, Me-Al). The presence of three signals for the methyl groups attached to the metal and the broad resonances obtained for some of the ligand H atoms indicates that a dynamic process is in operation in solution.

Crystal data

$[Al_2(CH_3)_4(C_{12}H_{18}O)_2]$
M_r = 440.56
Monoclinic, $P2_1/c$
a = 7.224 (3) Å
b = 15.380 (6) Å
c = 12.204 (5) Å
β = 103.48 (4)°
V = 1318.6 (9) Å^3
Z = 2
D_x = 1.110 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 32 reflections
θ = 19.0–28.0°
μ = 1.12 mm^{-1}
T = 160 (2) K
Block, colourless
0.7 × 0.7 × 0.6 mm

Data collection

Stoe–Siemens diffractometer
ω/θ scans
2201 measured reflections
2201 independent reflections
1912 reflections with $I > 2\sigma(I)$
θ_{max} = 67.5°
$h = -7 \rightarrow 8$
$k = -14 \rightarrow 18$
$l = -10 \rightarrow 14$
5 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.077
$wR(F^2)$ = 0.217
S = 1.05
2201 reflections
143 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1463P)^2 + 0.8656P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.84 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.011 (2)

Table 1
Selected geometric parameters (Å, °).

Al—O	1.844 (2)	Al—C2	1.950 (4)
Al—O^i	1.848 (2)	O—C3	1.448 (3)
Al—C1	1.950 (3)		
O—Al—O^i	80.20 (9)	C1—Al—C2	119.49 (16)
O—Al—C1	111.46 (13)	C3—O—Al	132.26 (17)
O^i—Al—C1	110.88 (13)	C3—O—Al^i	123.53 (16)
O—Al—C2	113.67 (13)	Al—O—Al^i	99.80 (9)
O^i—Al—C2	114.63 (13)		

Symmetry code: (i) $1-x, 1-y, -z$.

The high-angle data (θ = 60–67.5°) are incomplete because of restrictions imposed by the low-temperature device; data up to θ = 60° are 98% complete. H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds), and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Data collection: *DIF*4 (Stoe & Cie, 1988); cell refinement: *DIF*4; data reduction: local programs; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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m388 William Clegg *et al.* • $[Al_2(CH_3)_4(C_{12}H_{18}O)_2]$ *Acta Cryst.* (2001). E**57**, m387–m389

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