

# Bis[ $\mu^2$ -bis(diphenylphosphinoyl)methanido- $\kappa^2$ O:O']-hexamethyldi- $\mu^3$ -oxo-tetraaluminium(III) tetrahydrofuran disolvate

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## Key indicators

Single-crystal X-ray study

$T = 100$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å

$R$  factor = 0.062

$wR$  factor = 0.173

Data-to-parameter ratio = 20.5

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

The title centrosymmetric alumoxane compound,  $[\text{Al}_4(\text{CH}_3)_6(\mu^3\text{-O})_2(\mu\text{-}\{\text{Ph}_2\text{P}(\text{O})\}_2\text{CH})_2]\cdot\text{C}_4\text{H}_8\text{O}$ , is dimeric in the solid state as its THF disolvate, with a central  $\text{Al}_2\text{O}_2$  ring core connected to terminal  $\text{Me}_2\text{Al}$  units through oxo and non-chelating phosphinate anions.

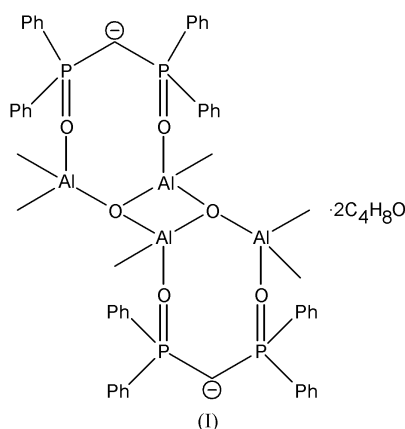
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## Comment

Carbanions stabilized by two  $\alpha,\alpha'$ -electron-withdrawing groups constitute an important class of reagents in C–C bond-forming reactions (Johnson, 1993). We are interested in the emerging structure–reactivity relationships of doubly stabilized carbanions with various metallic partners (Nassar *et al.*, 2003; Henderson *et al.*, 2000, 2002, 2003). During our studies, the unexpected title compound, (I), was prepared as colourless crystals from a reaction mixture containing  $\{\text{Ph}_2\text{P}(\text{O})\}_2\text{CH}_2$ ,  $\text{AlMe}_3$  and  $^t\text{BuLi}$ . The formation of the alumoxane fragment was most likely due to adventitious exposure to air. Nevertheless, compound (I) was isolated in sufficient yield to enable characterization by  $^1\text{H}$  NMR spectroscopy and single-crystal X-ray diffraction. The use of methylalumoxane (MAO) as a highly active cocatalyst in olefin polymerization reactions has led to significant interest in the structural characterization of this class of compounds (Uhl & Roesky, 2004).



Compound (I) is centrosymmetric and crystallizes with two non-coordinating tetrahydrofuran (THF) molecules per dimer within the crystal structure. The core is an  $\text{Al}_2\text{O}_2$  ring where each  $\text{O}^{2-}$  unit is bound to three Al atoms, two of which carry single methyl groups (central Al) and one is bound to a pair of methyl groups (terminal Al) (Fig. 1). Each bis(diphenylphosphinoyl)methanide anion bridges between a terminal and a central aluminium *via* coordination of individual  $\eta^1$ -phosphoryl units, with no metal–carbanion contacts present.

The coordination geometry around the O atoms at the core of the structure is perfectly planar (sum of angles = 360°) and that around all the Al atoms is pseudo-tetrahedral. The Al—O bond lengths range between 1.749 (2) and 1.808 (3) Å and are similar to Al—O distances in comparable alumoxane compounds (Gibson *et al.*, 2001).

### Experimental

The phosphine oxide  $\{\text{Ph}_2\text{P}(\text{O})\}_2\text{CH}_2$  (0.150 g, 0.36 mmol) was placed in a 25 ml Schlenk flask and suspended in 5 ml dry hexane. The mixture was cooled to 273 K and 1.5 molar equivalents of  $\text{AlMe}_3$  (0.27 ml, 0.54 mmol, 2 M solution in heptane) were added dropwise. The solution was heated to reflux for 3 h, cooled to 273 K and one equivalent  $t\text{-BuLi}$  (0.21 ml, 0.36 mmol, 1.7 M solution in pentane) was added dropwise. The resulting mixture was stirred for 10 min at room temperature before the addition of 5 ml dry THF to complete dissolution. Colourless crystals of (I) were isolated after storage at 229 K over a period of 4 d.  $^1\text{H}$  NMR (300 MHz,  $d^6$ -benzene, 298 K):  $\delta$  7.84 (*m*, 16H, *ortho*-Ar H), 6.94 (*m*, 24H, *m*- and *p*-Ar H), 3.57 (*m*, 4H, THF), 2.86 (*t*,  $^2J_{\text{H-P}} = 6$  Hz, 2H, PCHP), 1.41 (*m*, 4H, THF),  $-0.03$  [*s*, 6H,  $\text{Al}(\text{CH}_3)_3$ ],  $-0.10$  [*s*, 6H,  $\text{Al}(\text{CH}_3)_3$ ],  $-0.23$  [*s*, 6H,  $\text{Al}(\text{CH}_3)_3$ ].

#### Crystal data

$[\text{Al}_4(\text{CH}_3)_6\text{O}_2(-\text{C}_{25}\text{H}_{21}\text{O}_2\text{P}_2)] \cdot \text{C}_4\text{H}_8\text{O}$   
 $M_r = 1205.12$   
 Monoclinic,  $P2_1/n$   
 $a = 13.0087$  (2) Å  
 $b = 18.5644$  (3) Å  
 $c = 13.7312$  (2) Å  
 $\beta = 102.117$  (1)°  
 $V = 3242.19$  (9) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.234$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 5174 reflections  
 $\theta = 2.2$ – $23.8^\circ$   
 $\mu = 0.22$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
 Block, colourless  
 $0.19 \times 0.14 \times 0.14$  mm

#### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (Blessing, 1995)  
 $T_{\text{min}} = 0.960$ ,  $T_{\text{max}} = 0.971$   
 47479 measured reflections

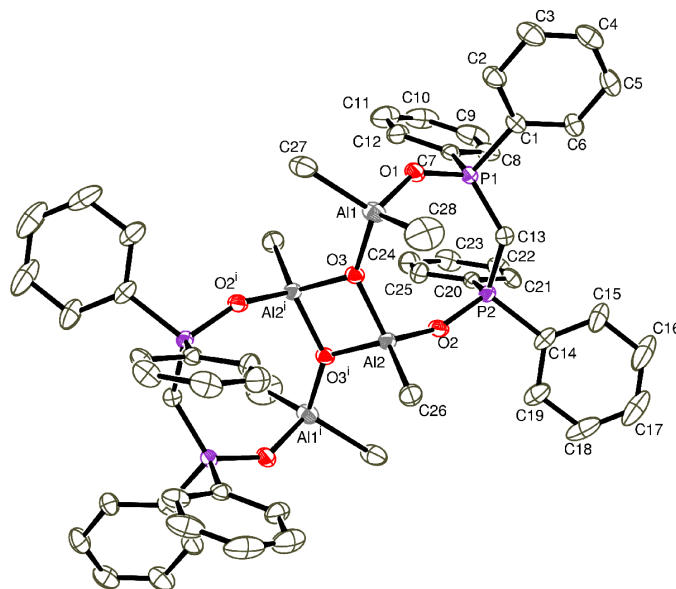
6623 independent reflections  
 5264 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.035$   
 $\theta_{\text{max}} = 26.4^\circ$   
 $h = -16 \rightarrow 13$   
 $k = -23 \rightarrow 23$   
 $l = -17 \rightarrow 17$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.062$   
 $wR(F^2) = 0.173$   
 $S = 1.05$   
 6623 reflections  
 323 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0936P)^2 + 2.8045P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 0.89$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.38$  e Å<sup>-3</sup>

H atoms were placed at calculated geometries and allowed to ride on the positions of parent atoms. The H atom attached to C13 was located in a difference map and was freely refined in subsequent cycles of least-squares refinement. The solvent tetrahydrofuran molecule was completely disordered and was treated with SQUEEZE (Spek, 2003)



**Figure 1**  
 ORTEP-3 (Farrugia, 1997) view of complex (I). THF molecules and H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with (i) are at the symmetry position  $(-x, -y, -z)$ .

Data collection: APEX2 (Bruker–Nonius, 2004); cell refinement: APEX2 and SAINT (Bruker–Nonius, 2004); data reduction: SAINT and XPREP (Sheldrick, 2003); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL (Sheldrick, 2001); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXTL.

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