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A dimeric constrained-geometry titanium complex linked by double Ti–CH_2–Al–CH_2 heterocycles

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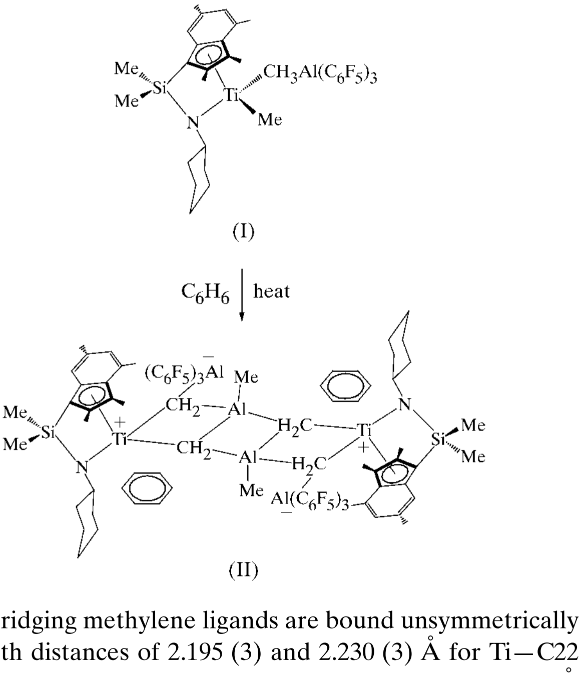
In the structure of bis({*N*-[dimethyl(1η^5-2,3,4,6-tetramethylindenyl)silyl]cyclohexylamido-1κN}(methyl-3κC)-di-μ_3-methylene-1:2:3κ^3C;1:3:3$'\kappa^3C$-tris(pentafluorophenyl-2κC)titanium) benzene disolvate, $[Me_2Si(\eta^5\text{-}2,3,4,6\text{-}Me_4C_9H_2)(C_6H_{11}N)]Ti[(\mu_3\text{-}CH_2)Al(C_6F_5)_3][AlMe(\mu_3\text{-}CH_2)]_2$ or $[Ti_2(C_{21}H_7AlF_{15})_2(C_{21}H_{31}NSi)_2]\cdot 2C_6D_6$, the dimer is located on an inversion center, and the two Ti centers are linked by double $Ti(\mu_3\text{-}CH_2)Al(C_6F_5)_3AlMe(\mu_3\text{-}CH_2)$ heterocycles. The electron-deficient Ti centers are further stabilized by two α-agostic interactions between Ti and one H atom of each bridging methylene group.

Comment

Catalyst decomposition of activated metallocene and constrained-geometry complexes is a key contribution to catalyst activity decay in catalytic homogeneous olefin polymerization (Chen & Marks, 2000). We were interested in the thermal stability of an activated catalyst, $Me_2Si(\eta^5\text{-}2,3,4,6\text{-}Me_4C_9H_2)(C_6H_{11}N)Ti(CH_3)[\mu\text{-}CH_3Al(C_6F_5)_3]$, (I), an example of the constrained geometry catalyst family (McKnight & Waymouth, 1998). Upon heating a C_6D_6 solution of (I) in a sealed NMR tube under an argon atmosphere at 333 K for 12 h, we found that dimer (II) was formed, the structure of which is reported here.

The molecular structure of compound (II) is depicted in Fig. 1 and selected geometric parameters are given in Table 1. Complex (II) crystallizes as a dimer having an inversion center. Each Ti metal center is coordinated in a distorted tetrahedral geometry [N1—Ti—C22 = 110.4 (2)°, N1—Ti—C23 = 105.6 (2)° and C22—Ti—C23 = 89.8 (2)°] by the η^5-substituted indenyl ligand, the dimethylsilyl-bridged *N*-cyclohexyl amide, and two anionic methylene ligands. The openness of the coordination sphere about Ti is manifested by an obtuse Cp(centroid)—Ti—N angle of 108.1 (2)°. In addition to the above ligands coordinated to Ti, one H atom of each bridging methylene group (H22*B* and H23*A*) exhibits a relatively close contact to Ti, with Ti—H22*B* and Ti—H23*A* distances of 2.19 (3) and 2.26 (3) Å and acute Ti—C22—H22*B* and Ti—C23—H23*A* angles of 77 (2) and 80 (2)°, respectively, indicative of two α-agostic interactions to each Ti atom.



Two bridging methylene ligands are bound unsymmetrically to Ti, with distances of 2.195 (3) and 2.230 (3) Å for Ti—C22 and Ti—C23, respectively, which are approximately 0.2 Å (average) longer than the $Ti(\mu\text{-}CH_2)$ distances in $[(Cy_2N)_2Ti(\mu\text{-}CH_2)]_2$ (Scoles *et al.*, 1994). These distances are slightly shorter than the Ti—CH_3 bond in $[CpTi(\mu_2\text{-}Me)(\mu_2\text{-}NPiPr_3)(\mu_4\text{-}C)(\mu_2\text{-}AlMe_2)_2(AlMe_2)]$, but substantially longer than the Ti—C(carbide) bond in the same molecule (Kickham *et al.*, 2000). Linking the two Ti centers are three fused four-membered metallacycles, with torsion angles of 126.5 (2) and

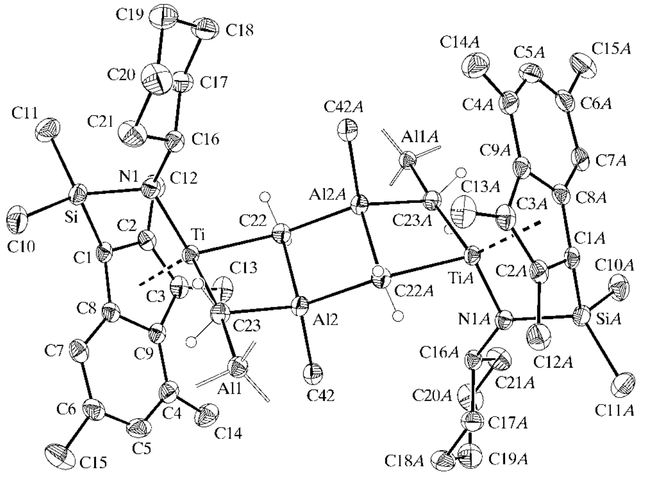


Figure 1
The molecular structure of (I) showing 40% probability displacement ellipsoids and the atom-numbering scheme. Atoms Al1 and Al1*A* (where *A* = 1 − *x*, 1 − *y*, −*z*) have three open bonds around them, representing C_6F_5 groups, which are not shown for clarity. The benzene solvent molecules have also been removed for clarity.

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144.3 (2)° for C23—Al2—C22—Al2*A* and Ti—C22—Al2—C22*A*, respectively (Al2*A* and C22*A* are derived from Al2 and C22 by $1 - x$, $1 - y$, $-z$). The middle four-membered ring is coplanar (C22—Al2—C22*A*—Al2*A* = 0°), while the other two adopt a 'puckered' conformation [Ti—C22—Al2—C23 = −17.8 (2)°]. Due to the presence of strain arising from the metallacycles, the geometry at the Al center on the ring (Al2) is that of a highly distorted tetrahedron. The largest deviations from tetrahedral geometry are found in the obtuse C22—Al2—C23 angle of 99.2 (2)° and the significantly larger C23–Al2–C22*A* angle of 123.5 (2)°.

There is an $Al(C_6F_5)_3$ group attached to C23 (and C23*A*) and the Ti—C23—Al1 vector is close to linearity [170.7 (2)°], suggesting some degree of dipole–dipole component to the ion–ion interaction in this complex. Compared to the Ti—C22 bond distance, the Ti—C23 bond is only slightly elongated as a result of the attached strongly Lewis acidic $Al(C_6F_5)_3$ group, presumably due to the metallacycle formation. The C23—$Al(C_6F_5)_3$ distance of 2.048 (3) Å is comparable to those in the μ-CH_3-$Al(C_6F_5)_3^-$ anion [2.084 (2) and 2.059 (2) Å] in a 'doubly activated' *ansa*-zirconocene complex (Chen, 2000) and to that in the μ-CH_3-$Al(C_6F_5)_3^-$ anion [2.033(3) Å] in a 'constrained-geometry' Ti complex (Chen *et al.*, 2001).

Experimental

All syntheses and manipulations of air-sensitive materials were carried out under an inert atmosphere (argon) glove-box. NMR scale reactions were conducted in Teflon-valve-sealed sample J-Young tubes. Solvents were first saturated with nitrogen and then dried by passage through activated alumina and *Q*-5^{TM} catalyst prior to use. Deuterated NMR solvents were dried over sodium/potassium alloy and distilled and/or filtered prior to use. $Me_2Si(\eta^5$-2,3,4,6-Me_4-$C_9H_2)(C_6H_{11}N)Ti(CH_3)[\mu$-$CH_3Al(C_6F_5)_3]$, (I), was prepared from the reaction on $Me_2Si(\eta^5$-2,3,4,6-Me_4-$C_9H_2)(C_6H_{11}N)Ti(CH_3)_2$ with $Al(C_6F_5)_3$ in toluene or benzene at room temperature using a procedure similar to that described previously by Chen *et al.* (2001). Compound (I) was dissolved in benzene-d_6 in a J-Young NMR tube and the solution was heated in an oil bath at 333 K for 12 h. The resulting dark-red solution was stored at room temperature in a glove-box for 5 d, after which time, black crystals of (II) had formed.

Crystal data

$[Ti_2(C_{21}H_7AlF_{15})_2(C_{21}H_{31}$-$NSi)_2]\cdot 2C_6D_6$
$M_r = 2099.58$
Triclinic, $P\overline{1}$
$a = 12.8651$ (7) Å
$b = 13.7422$ (7) Å
$c = 15.2642$ (9) Å
$\alpha = 70.595$ (2)°
$\beta = 70.795$ (2)°
$\gamma = 71.944$ (2)°
$V = 2341.9$ (2) Å^3
$Z = 1$
$D_x = 1.489$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4099 reflections
$\theta = 2.0$–27.5°
$\mu = 0.34$ mm^{-1}
$T = 173$ (2) K
Needle, black
0.27 × 0.11 × 0.06 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: integration based on measured indexed crystal faces (*SHELXTL*; Bruker, 1998)
$T_{min} = 0.925$, $T_{max} = 0.985$
15 647 measured reflections
10 542 independent reflections
5884 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 27.5°$
$h = -15 \rightarrow 16$
$k = -10 \rightarrow 17$
$l = -17 \rightarrow 19$

Table 1
Selected geometric parameters (Å, °).

Ti—N1	1.898 (2)	Ti—H22*B*	2.19 (3)
Ti—C22	2.195 (3)	Ti—H23*A*	2.26 (3)
Ti—C23	2.230 (3)	Al1—C23	2.048 (3)
Ti—C1	2.256 (3)	Al2—C42	1.950 (3)
Ti—C2	2.333 (3)	Al2—C23	2.015 (3)
Ti—C8	2.395 (3)	Al2—C22	2.085 (3)
Ti—C3	2.474 (3)	Al2—C22^i	2.086 (3)
Ti—C9	2.556 (3)	Al2—Al2^i	2.695 (2)
N1—Ti—C22	110.38 (12)	Al2^i—C22—Ti	140.60 (19)
N1—Ti—C23	105.62 (12)	Ti—C22—H22*B*	77.5 (19)
C22—Ti—C23	89.82 (12)	Al2—C23—Ti	83.33 (12)
C22—Al2—C22^i	99.48 (12)	Ti—C23—H23*A*	80 (2)
Al2—C22—Ti	82.62 (12)		

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.123$
$S = 0.96$
10 542 reflections
636 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

C—H distances of 0.98 and 0.99 Å were used for methyl and secondary C atoms, respectively. A distance of 0.95 Å was used for aromatic C atoms. The H-atom displacement parameters were set at $1.2U_{eq}$ of the parent C atom or $1.5U_{eq}$ for the methyl atoms. The H atoms on C22 and C23 were obtained from a difference Fourier map and refined without constraint. In addition to the complex, a molecule of benzene was found in a general position. Full data-collection details are in the archived CIF and also reported elsewhere (Abboud *et al.*, 1997).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART* and *SAINT* (Bruker, 1998); data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: Bruker *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1315). Services for accessing these data are described at the back of the journal.

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