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μ_2-Oxo-bis[bis(η^5-1,3-di-*tert*-butylcyclopentadienyl)titanium(III)]

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Key indicators

Single-crystal X-ray study
T = 164 K
Mean σ(C–C) = 0.006 Å
R factor = 0.065
wR factor = 0.174
Data-to-parameter ratio = 14.6

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

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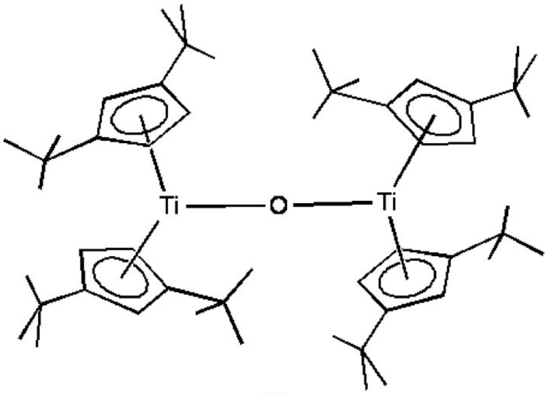
The title compound, $[Ti_2O(C_{13}H_{21})_4]$ or $\{[(1,3\text{-}^t\text{Bu}_2\text{-}C_5H_3)_2Ti\}_2(\mu_2\text{-O})\}$, crystallizes as a centrosymmetric molecule, in which the two metallocene fragments are bridged by an O atom. The trigonal planar coordination around each metal consists of two 1,3-^{t}Bu$_2$C$_5$H$_3$ ligands and the bridging O atom. The O atom is located on a crystallographic inversion center, resulting in a linear Ti—O—Ti linkage.

Comment

The title compound, (I), was prepared as part of an extensive study of titanium complexes containing the sterically demanding 1,3-di(*tert*-butyl)cyclopentadienyl (Cp^t) ligand. Although several μ-oxo complexes of Ti^{IV} are known, their Ti^{III} analogs, $\{[(C_5H_{5-n}R_n)_2Ti]_2(\mu\text{-O})\}$ (*R* is alkyl or aryl), are still rare, with the exceptions of the structurally characterized $\{[(C_5H_5)_2Ti]_2(\mu\text{-O})\}$ (Honold *et al.*, 1986), in which weak inter- and intramolecular ferromagnetic coupling has been observed (Lukens & Andersen, 1995), and the tetrahydroindenyl derivative, $\{[(C_9H_{11})_2Ti]_2(\mu\text{-O})\}$ (Kempe *et al.*, 1998).



(I)

Complex (I) crystallizes in the triclinic space group $P\overline{1}$ with two half-molecules in the asymmetric unit. The O atom of each molecule is located on an inversion center. The coordination around the Ti center is trigonal planar and the sum of the bond angles is 360° (the cyclopentadienyl ligands are represented by their centroids: *Cg*1, *Cg*2, *Cg*3 and *Cg*4 are the centroids of rings C1–C5, C6–C10, C11–C15 and C16–C20, respectively). A similar trigonal–planar geometry can be found in the dinuclear complexes $\{[(C_5H_5)_2Ti]_2(\mu\text{-O})\}$ (Honold *et al.*, 1986), $\{[(C_5Me_5)_2Ti]_2(\mu\text{-N}_2)\}$ (Sanner *et al.*, 1976), $\{[(C_5HMe_4)_2Ti]_2(\mu\text{-N}_2)\}$ (de Wolf *et al.*, 1996) and $\{[(1,3\text{-}(SiMe_3)_2C_5H_3)_2Ti]_2(\mu\text{-N}_2)\}$ (Hanna *et al.*, 2004). The average *Cg*—Ti—*Cg* angle between the cyclopentadienyl ligands of 132.3 (1)° in (I) is slightly smaller than the value of 136° in the

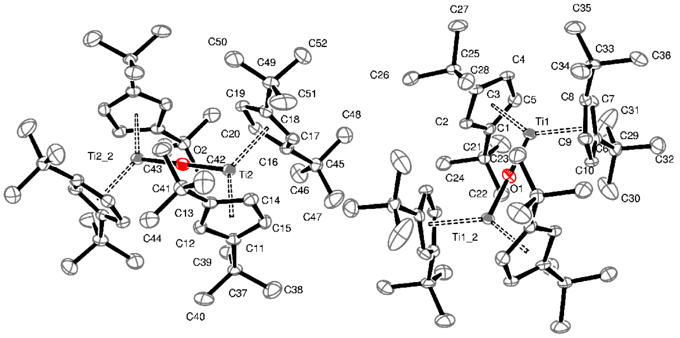


Figure 1

A view of the two independent centrosymmetric molecules of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

C_5H_5 case (Honold *et al.*, 1986) and the value of 134.4° in the C_9H_{11} case (Kempe *et al.*, 1998).

The *tert*-butyl substituents on the cyclopentadienyl ligands adopt a common orientation in which the *tert*-butyl groups 'gear' in an alternating 'backwards–forwards' fashion with respect to the μ-oxo ligand. Similar conformations are observed in $\{[\{1,3\text{-}(SiMe_3)_2C_5H_3\}_2Ti]_2(\mu\text{-}N_2)\}$ (Hanna *et al.*, 2004) and $\{[(1,3\text{-}{}^tBu_2C_5H_3)_2UO]_2\}$ (Lukens *et al.*, 1999).

The average Ti—O distance in (I) of 1.8769 Å is on the upper limit (1.83–1.86 Å) expected for oxo-bridged dicyclopentadienyl–Ti complexes (Honold *et al.*, 1986, and references therein). A linear Ti—O—Ti linkage for this type of complex has not been observed to date. However, linearity has been observed in the Ti^{IV} complexes $\{[(C_5H_5)_2TiCl_2](\mu\text{-}O)\}$ (Thewalt & Schomburg, 1977) and $\{[benzyl_3Ti]_2(\mu\text{-}O)\}$ (Cetinkaya *et al.*, 1980). According to the model developed by Lauher & Hoffman (1976) for complexes of the type $(C_5H_5)_2ML_n$ (n = 1, 2, 3), the b_2 fragment orbital has suitable symmetry to interact with the p orbital of the oxygen bridge, forming a π bond. The orientation of the Cp^t rings allows the empty b_2 symmetry orbital on each metallocene fragment to interact with a p orbital (either p_x or p_y) of the bridging O atom. In compound (I), the metallocene fragments are related by an inversion center, in contrast with $\{[(C_5H_5)_2Ti)]_2(\mu\text{-}O)\}$ (Honold *et al.*, 1986) and $\{[(C_9H_{11})_2Ti]_2(\mu\text{-}O)\}$ (Kempe *et al.*, 1998), in which the metallocene fragments are rotated relative to each other by 90° and 63°, respectively, thereby maximizing the metallocene orbital overlap with that of O. This behavior is presumably due to the severe steric restrictions imposed on the molecule by the bulky *tert*-butyl groups.

Experimental

Compound (I) was synthesized by the reaction of base-free $[(1,3\text{-}{}^tBu_2C_5H_3)_2Ti]$ (1.0 g, 2.5 mmol) in n-hexane with N_2O (1 atm) at room temperature. The color of the solution changed from blue to red–brown. After stirring the solution for 12 h, it was filtered, and crystallization from a saturated n-hexane solution at 253 K yielded red–brown crystals of (I) in 45% yield (m.p. 480–482 K). The crystal was handled under a nitrogen atmosphere, mounted on a glass fiber with Paratone-*N* oil and cooled to 164 (2) K for data collection.

Crystal data

$[Ti_2O(C_{13}H_{21})_4]$
M_r = 820.93
Triclinic, $P\bar{1}$
a = 10.6900 (8) Å
b = 11.7225 (8) Å
c = 20.2272 (13) Å
α = 90.196 (2)°
β = 101.945 (2)°
γ = 103.992 (2)°
V = 2402.5 (3) Å^3
Z = 2
D_x = 1.135 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2932 reflections
θ = 2–25°
μ = 0.37 mm^{-1}
T = 164 (2) K
Block, red–brown
0.30 × 0.25 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.898, T_{max} = 0.964
10 782 measured reflections
7637 independent reflections
4690 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 25.6°
h = −12 → 12
k = −14 → 12
l = −20 → 24

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.174
S = 0.99
7637 reflections
523 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0907P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

*Cg*1, *Cg*2, *Cg*3 and *Cg*4 are the centroids of the rings C1–C5, C6–C10, C11–C15 and C16–C20, respectively.

Ti1—C1	2.470 (4)	Ti2—C11	2.485 (4)
Ti1—C2	2.456 (4)	Ti2—C12	2.455 (4)
Ti1—C3	2.479 (4)	Ti2—C13	2.450 (4)
Ti1—C4	2.418 (4)	Ti2—C14	2.407 (4)
Ti1—C5	2.416 (4)	Ti2—C15	2.421 (4)
Ti1—C6	2.499 (4)	Ti2—C16	2.514 (4)
Ti1—C7	2.516 (4)	Ti2—C17	2.523 (4)
Ti1—C8	2.495 (4)	Ti2—C18	2.516 (4)
Ti1—C9	2.396 (4)	Ti2—C19	2.398 (4)
Ti1—C10	2.393 (4)	Ti2—C20	2.391 (4)
Ti1—*Cg*1	2.134	Ti2—*Cg*3	2.159
Ti1—*Cg*2	2.146	Ti2—*Cg*4	2.128
Ti1—O1	1.8780 (8)	Ti2—O2	1.8760 (8)
Ti1—O1—Ti1^i	180	*Cg*1—Ti1—*Cg*2	132.43
Ti2—O2—Ti2^{ii}	180	*Cg*3—Ti2—*Cg*4	132.23

Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $-x, 2 - y, -z$.

Methyl H atoms were placed in calculated positions and refined using a riding model, with C—H distances of 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. For each methyl group, the torsion angle which defines the orientation about the C—C bond was refined. The remaining methine H atoms were included in the model at calculated positions using a riding model, with C—H distances of 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Two maxima of residual unassigned electron density greater than 1 e Å^{-3} were observed at 1.83 Å from atom C20 and at 1.76 Å from atom C9. Due to poor crystal quality, diffraction was only observed up to θ_{max} = 25.6° with 0.85 data completeness, but the data were virtually complete up to θ = 23.0°.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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