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$[(\eta^5\text{-C}_5R_5)\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)]_2\text{O}\cdot n\text{CH}_2\text{Cl}_2$[1] ($R$ = H, Me; n = 1, 0)

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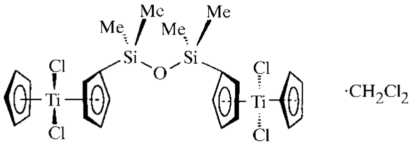
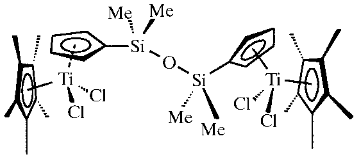
The first title metallocene, 1,3-bis(dichlorotitanocene)-1,1,3,3-tetramethyldisiloxane dichloromethane solvate, $[(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)]_2\text{O}\cdot\text{CH}_2\text{Cl}_2$, (I), crystallizes in space group $P2_1/c$. Compound (I) represents the first crystal structure of a bimetallic siloxy-bridged titanocene. The geometric parameters of (I) are similar to those of the parent titanocene; however, the disiloxane substituents adopt an unexpected eclipsed conformation. The second title metallocene, 1,3-bis[(pentamethylcyclopentadienyl)(cyclopentadienyl)titanium dichloride]-1,1,3,3-tetramethyldisiloxane, $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiCl}_2(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2)]_2\text{O}$, (II), represents the second crystal structure of a bimetallic siloxy-bridged titanocene and crystallizes in the space group $P2_1/n$. Compound (I) possesses non-crystallographic twofold molecular symmetry and both metal centers adopt pseudo-tetrahedral geometries. The geometric parameters of (II) are similar to those of the mixed titanocene $\text{Cp}^*\text{CpTiCl}_2$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) and the disiloxane substituents adopt a staggered conformation.

Comment

The title compounds, (I) and (II), were obtained as by-products in the synthesis of [η^5-(dimethylfenchoxysilyl)-cyclopentadienyl](η^5-cyclopentadienyl)titanium dichloride, $(\text{C}_{10}\text{H}_{17}\text{OSiMe}_2\text{C}_5\text{H}_4)\text{C}_5\text{H}_5\text{TiCl}_2$ (Grimmond & Corey, 1998), and [η^5-(dimethylfenchoxysilyl)cyclopentadienyl](η^5-pentamethylcyclopentadienyl)titanium dichloride, $(\text{C}_{10}\text{H}_{17}\text{OSiMe}_2\text{C}_5\text{H}_4)\text{C}_5\text{Me}_5\text{TiCl}_2$, respectively, upon crystallization from ethyl acetate at 298 K. A search of the Cambridge Structural Database (Version 5.14; Allen & Kennard, 1993) indicated that these substituted metallocenes are the first crystallographically characterized examples of bimetallic siloxy-bridged titanocenes, although other structures of cyclopentadienyl transition metal complexes involving siloxane bridges are known (Schubert & Grubert, 1998; Ciruelos *et al.*, 1998). The synthesis of compound (I) by alternative means has also been described by Noh *et al.* (1996). There is one CH_2Cl_2 molecule of solvation per molecule for metallocene (I) and no solvation for (II). Neither structure exhibits molecular disorder. For both compounds, there are no significant intermolecular close contacts resulting from crystal packing. Selected bond lengths and angles for (I) and (II) are listed in Tables 1 and 2, and perspective views of the two metallocenes are presented in Figs. 1 and 2.



(I)



(II)

In compounds (I) and (II), the cyclopentadienyl rings are planar within experimental error and adopt η^5 bonding modes with respect to each Ti atom. The following geometric parameters described for (I) are compared in parentheses with the corresponding values for the parent titanocene dichloride

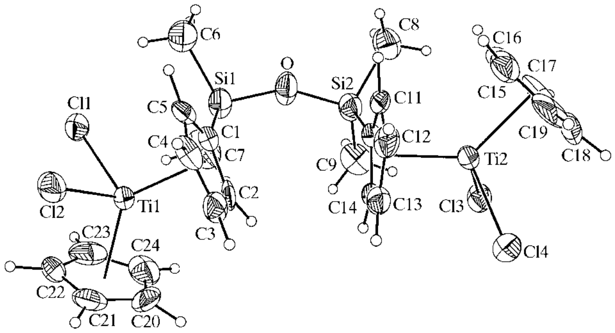


Figure 1
View of (I) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels, H atoms are drawn as spheres of arbitrary radii and the dichloromethane solvate has been omitted.

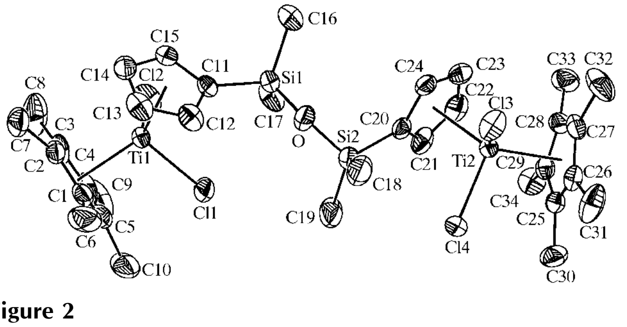


Figure 2
View of (II) showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as spheres of arbitrary radii.

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[1] Systematic names: [μ-1,2(η^5)-1,3-dicyclopentadienyl-1,1,3,3-tetramethyldisiloxanyl]bis[dichloro(η^5-cyclopentadienyl)titanium] dichloromethane solvate and [μ-1,2(η^5)-1,3-dicyclopentadienyl-1,1,3,3-tetramethyldisiloxanyl]-bis[dichloro(η^5-pentamethylcyclopentadienyl)titanium].

(Clearfield *et al.*, 1975). The average *Cp*—Ti distance is 2.06 Å (2.06 Å; *Cp* is the cyclopentadienyl ring centroid) and the *Cp*—Ti—*Cp* angle is 130.70° (130.98°). Additionally, compound (I) has a mean Ti—Cl bond length of 2.37 Å (2.36 Å) with a Cl—Ti—Cl angle of 93.25° (94.52°), indicating that all major aspects of the substituted metallocene architecture compare well with those of titanocene dichloride.

A similar comparison of (II) with the parent mixed titanocene dichloride $Cp^*CpTiCl_2$ ($Cp^* = C_5Me_5$) indicated no significant deviations in the geometry of (II) from the base structure. The following geometric parameters described for (II) are compared in parentheses with the corresponding values for the parent mixed titanocene dichloride (Rodgers *et al.*, 1985). The average *Cp*—Ti distance is 2.07 Å (2.07 Å), while the mean *Cp**—Ti distance is 2.10 Å (2.10 Å; *Cp** is the tetramethylcyclopentadienyl ring centroid). The *Cp**—Ti—*Cp* angle is 132.60° (131.98°). Additionally, compound (II) has a mean Ti—Cl bond length of 2.35 Å (2.35 Å) with a slightly extended Cl—Ti—Cl angle of 95.94° (94.44°).

The conformations of the siloxy chains within (I) and (II) are different. The conformational geometry of the siloxy linkage in (I) is *cisoid*, in contrast to the *transoid* siloxy conformation observed in (II). In (I), a nearly eclipsed geometry for the Si1—O—Si2 linkage is observed in the crystal structure and this is highlighted by the C6—Si1···Si2—C8 torsion angle of 8.30°. Indeed, the C_5H_4 groups are also disposed in a periplanar or *cis* conformation with respect to one another, and the C1—Si1···Si2—C10 torsion angle of 6.20° emphasizes the nearly ideal eclipsed conformation of the silicon substituents. However, for (II), a staggered geometry of the substituents about the Si1—O—Si2 linkage is observed in the crystal structure in the solid state, which is highlighted by the C6—Si1···Si2—C9 torsion angle of 160.1°. The C_5H_4 groups are also disposed in an antiperiplanar or *trans* conformation with respect to one another, and the C1—Si1···Si2—C10 torsion angle is 168.3°, further emphasizing the staggered conformation of the Si substituents.

In compound (I), the two monosubstituted C_5 planes are aligned in a nearly parallel fashion with a C_5H_4–centroid–C_5H_4–centroid distance of 3.86 Å, suggesting that a small degree of π-stacking may also be responsible for the observed geometry. However, in (II), a staggered conformation of the Si1—O—Si2 bridge substituents appeared to be a conformational energy minimum. Presumably, the steric repulsion of the Cp* ligands was too great to allow the *cis* conformation of the siloxane substituents which was observed for (I). It is also possible that net packing forces contributed to the opposing conformations observed between (I) and (II). For (I) and (II), all Si—C bond lengths approximate to the average $Sisp^3$—Csp^n (n = 2 or 3) distance within the margins of experimental error (Orpen *et al.*, 1989).

All other cases of metallocenes that involve the same siloxane bridging unit are ansa-metallocenes, wherein both Cp units of the same ligand are bound to the same metal (Curtis *et al.* 1983; Angelokos *et al.*, 1994; Ciruelos *et al.*, 1995). For such ansa-metallocenes, the siloxane methyl substituents are constrained to be eclipsed in order to accommodate the metal center and so do not offer a legitimate comparison with the title compounds where free rotation about the Si1—O—Si2 axis is possible.

Experimental

Compounds (I) and (II) were generated by slow hydrolysis of the corresponding alkoxysilane precursor in CH_2Cl_2. X-ray quality crystals of both (I) and (II) were obtained by slow evaporation of ethyl acetate solutions at ambient temperature.

Compound (I)

Crystal data

$[Ti_2(C_{10}H_{15})_2(C_{14}H_{20}OSi_2)Cl_4]$
$M_r = 713.19$
Monoclinic, $P2_1/c$
$a = 13.6494$ (2) Å
$b = 12.8573$ (2) Å
$c = 18.4995$ (3) Å
$\beta = 103.977$ (1)°
$V = 3150.44$ (8) Å^3
$Z = 4$
$D_x = 1.504$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4922 reflections
$\theta = 2$–24°
$\mu = 1.11$ mm^{-1}
$T = 223$ (2) K
Needle, red
0.40 × 0.18 × 0.10 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Blessing, 1995)
$T_{min} = 0.67, T_{max} = 0.90$
27 882 measured reflections
4950 independent reflections
2810 reflections with $I > 2\sigma(I)$
$R_{int} = 0.13$
$\theta_{max} = 24°$
$h = -15 \rightarrow 15$
$k = -14 \rightarrow 14$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.179$
$S = 1.05$
4950 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0647P)^2 + 10.5834P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Ti1—Cl1	2.360 (2)	Si1—C1	1.876 (8)
Ti1—Cl2	2.373 (2)	C1—C2	1.415 (10)
Si1—O	1.633 (5)	C2—C3	1.411 (10)
Si1—C6	1.849 (8)	C3—C4	1.404 (11)
Si1—C7	1.852 (9)		
Cl1—Ti1—Cl2	93.25 (9)	C2—C1—C5	105.5 (7)
C6—Si1—C7	112.9 (4)	C3—C2—C1	109.3 (7)
Si2—O—Si1	151.5 (4)	C4—C3—C2	107.0 (7)

Table 2
Selected geometric parameters (Å, °) for (II).

Ti1—Cl1	2.3291 (12)	Si1—C1	1.874 (4)
Ti1—Cl2	2.3687 (12)	C1—C2	1.410 (5)
Si1—O	1.625 (3)	C2—C3	1.397 (6)
Si1—C7	1.849 (4)	C3—C4	1.408 (6)
Si1—C6	1.861 (4)		
Cl1—Ti1—Cl2	95.94 (5)	C2—C1—C5	105.1 (3)
C7—Si1—C6	109.9 (2)	C3—C2—C1	110.3 (4)
Si1—O—Si2	153.9 (2)	C2—C3—C4	107.2 (4)

Compound (II)

Crystal data

$[Ti_2(C_5H_5)_2(C_{14}H_{20}OSi_2)Cl_4]\cdot$-
CH_2Cl_2
$M_r = 768.52$
Monoclinic, $P2_1/n$
$a = 8.1319$ (1) Å
$b = 22.2503$ (3) Å
$c = 21.6970$ (3) Å
$\beta = 97.97$ (1)°
$V = 3887.84$ (9) Å^3
$Z = 4$

$D_x = 1.313$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2$–25°
$\mu = 0.77$ mm^{-1}
$T = 223$ (2) K
Plate, brown
$0.38 \times 0.20 \times 0.10$ mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Blessing, 1995)
$T_{\min} = 0.76, T_{\max} = 0.93$
62 999 measured reflections

6849 independent reflections
4852 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.11$
$\theta_{\max} = 25°$
$h = -9 \rightarrow 9$
$k = -26 \rightarrow 26$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.122$
$S = 1.02$
6849 reflections
388 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 6.1721P]$
where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max} = 0.72$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ e Å^{-3}

Only data up to $2\theta_{\max} = 48.0°$ could be used for (I) as the crystals were very weak diffractors (mean $I/\sigma = 1.8$ for a resolution of 0.90 Å). For (I), intensity data were collected using a longer exposure time of 60 s per frame to improve data quality.

For both compounds, data collection: *SMART* (Bruker, 1997*a*); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997*a*); program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1999); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL* (Bruker, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1495). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (2000). C**56**, 53–55 Brian J. Grimmond *et al.* • $[Ti_2(C_5R_5)_2(C_{14}H_{20}OSi_2)Cl_4]\cdot nCH_2Cl_2$ **55**