

## A ferrocenyl-substituted pseudotitanocene complex

Petr Štěpnička,<sup>a\*</sup> Ivana Čísařová,<sup>a</sup> Michal Horáček<sup>b</sup> and Karel Mach<sup>b</sup>

<sup>a</sup>Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic, and <sup>b</sup>J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic

Correspondence e-mail: stepnic@natur.cuni.cz

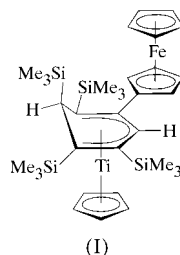
Received 19 June 2000

Accepted 20 July 2000

The title compound, ( $\eta^5$ -cyclopentadienyl)[(1,2,3,4,5- $\eta$ )-4-ferrocenyl-1,2,5,6-tetrakis(trimethylsilyl)cyclohexa-2,4-dien-1-yl]titanium(II),  $[\text{TiFe}(\text{C}_5\text{H}_5)_2(\text{C}_{23}\text{H}_{42}\text{Si}_4)]$  or  $[\text{Ti}\{\eta^5\text{-C}_6\text{H}_2\text{-}[\text{Fe}(\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)]\{\text{Si}(\text{CH}_3)_3\}_4\}(\eta^5\text{-C}_5\text{H}_5)]$ , possesses two directly linked metallocene units that subtend an angle of  $52.9(1)^\circ$  (defined by the least-squares planes of the directly connected  $\pi$ -ligands) associated with the steric requirements of the bulky trimethylsilyl substituents. The cyclohexadienyl ligand adopts an envelope conformation; the perpendicular distance of its  $\eta^5$ -plane to the Ti atom is  $1.512(1) \text{ \AA}$ .

### Comment

Multinuclear organometallic compounds having two or more metallic centres bonded by hydrocarbon ligands often exhibit interesting properties that arise from interactions of the metals. As the properties of such complexes change dramatically with the nature of the bridging ligand(s), any structural information is of importance since it provides the possibility of its comparison with indirect, *e.g.* spectral and electrochemical, data. There are numerous reports on the structures of such compounds available in the literature, including some titanocene–ferrocene complexes (Zakharov *et al.*, 1979; Back *et al.*, 1998; Štěpnička, Gyepes, Čísařová, Varga *et al.*, 1999; Štěpnička, Gyepes, Čísařová, Kubišta *et al.*, 1999). However, to the



best of our knowledge, the title compound, ( $\eta^5$ -cyclopentadienyl)[(1,2,3,4,5- $\eta$ )-4-ferrocenyl-1,2,5,6-tetrakis(trimethylsilyl)cyclohexa-2,4-dien-1-yl]titanium(II), (I), is the first

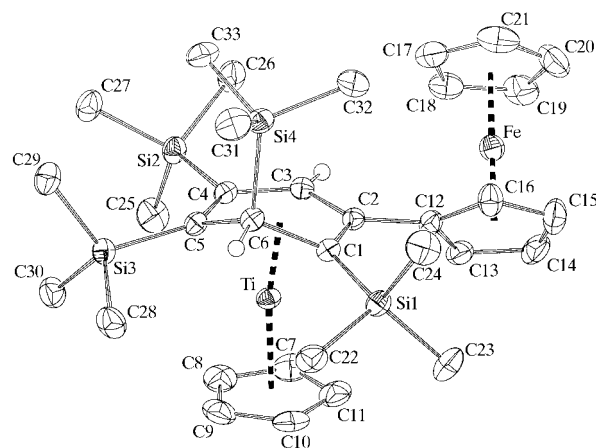
example of a structurally characterized directly linked metalocene–pseudometallocene complex.

The molecular structure of the complex is depicted in Fig. 1 and selected geometric parameters are given in Table 1. The metallocene units are rotated by  $52.9(1)^\circ$  as defined by the dihedral angle between the C1–C5 and C12–C16 least-squares ring planes. The ferrocenyl moiety is inclined towards the unsubstituted C3 atom. Such a deviation of the directly linked  $\pi$ -ligands from a coplanar arrangement is probably a result of steric constraints imposed by the bulky trimethylsilyl groups and prevents conjugation of the metallocene units. The  $\text{Ti}\cdots\text{Fe}$  distance of  $5.1562(2) \text{ \AA}$  also excludes any direct interaction between the metal centres.

The ferrocene framework does not exhibit unexpected features: the  $\text{Fe}-\text{C}_g$  distances (where  $\text{C}_g$  represents a ring centroid) are  $1.651(1)$  (ring C12–C16) and  $1.653(1) \text{ \AA}$  (ring C17–C21), and the mean  $\text{Fe}-\text{C}$  and  $\text{C}-\text{C}$  distances are  $2.047(9)$  and  $1.42(1) \text{ \AA}$ , respectively. The cyclopentadienyl (Cp) rings of the ferrocene unit are parallel [dihedral angle of the least-squares cyclopentadienyl planes  $1.7(2)^\circ$ ] and adopt a conformation between staggered and eclipsed, as demonstrated by the torsion angle  $\text{C12}-\text{C}_g(\text{C12}-\text{C16})-\text{C}_g(\text{C17}-\text{C21})-\text{C17}$  of  $10.6(2)^\circ$ .

Similarly, the  $\eta^5$ -ligand planes within the pseudotitanocene moiety are tilted only slightly [dihedral angle  $2.9(2)^\circ$ ]. The mean  $\text{Ti}-\text{C}_{\text{Cp}}$  and  $\text{C}-\text{C}_{\text{Cp}}$  distances are  $2.36(2)$  and  $1.406(6) \text{ \AA}$ , respectively, while the corresponding  $\text{Ti}$ -centroid distance is  $2.032(1) \text{ \AA}$ . For the cyclohexadienyl ligand, the perpendicular distance of the  $\text{Ti}$  atom from the least-squares C1–C5 plane is  $1.512(1) \text{ \AA}$ , with the respective  $\text{Ti}-\text{C}$  distances varying in the range  $2.064(2)$ – $2.230(2) \text{ \AA}$  [*cf.*  $\text{Ti}-\text{C6}$   $2.412(2) \text{ \AA}$ ]. The  $\eta^5$ -cyclohexadienyl moiety is slipped by as much as  $0.51 \text{ \AA}$ , the corresponding angle between the  $\text{Ti}-\text{C}_g$  vector and the normal from the  $\text{Ti}$  atom to the least-squares plane being  $19^\circ$  (note that the pseudotitanocene cyclopentadienyl ring is slipped by only *ca*  $0.06 \text{ \AA}$ ).

The conformation of the cyclohexadienyl ring is best described as a regular envelope, with ring-puckering coordi-



**Figure 1**

A view of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Methyl and cyclopentadienyl H atoms have been omitted for clarity.

nates  $Q = 0.465$  (3) Å,  $\theta = 59.9$  (2)° and  $\varphi = 299.1$  (4)° (Cremer & Pople, 1975). All  $\pi$ -coordinated C atoms of the dienyli moiety (C1–C5) are  $sp^2$  hybridized, nearly coplanar (sum of angles close to 360°) and their bonding distances are in the range 1.428 (3)–1.485 (3) Å. The  $sp^3$  hybridized C6 atom is disposed above the  $\eta^5$ -plane by 0.643 (3) Å and its adjacent Si4 atom is bonded to the cyclohexadienyl ring in an axial position (contrary to the structure predicted earlier by ZINDO calculations). The other atoms bonded to the plane of the  $\pi$ -donor are bent towards the Ti centre, their perpendicular distances from the least-squares plane being between 0.001 (3) Å for Si2 and 0.285 (4) Å for Si3.

The overall arrangement of the pseudotitanocene unit resembles the structure of an analogous compound bearing a trimethylsilyl substituent in place of the ferrocenyl group: *cf.* Ti–Cg 2.047 (9) Å, dihedral angle of the ligand planes 4.9° and cyclohexadienyl C<sub>5</sub>-ring slippage of 0.51 Å (or 19°), but a slightly longer Ti–Cg distance of 1.582 (4) Å (Varga *et al.*, 1996).

The molecule of the title complex displays planar chirality, but the compound crystallizes as a racemic mixture. No intermolecular distances shorter than van der Waals contacts were detected.

## Experimental

The complex was obtained as the only pseudotitanocene compound by a cyclohexadienyl ring-forming reaction from  $[(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\mu\text{-}\eta^2\text{-}\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)_2\text{Mg}(\eta^5\text{-C}_5\text{H}_5)]$  and ethynylferrocene, as described previously by Štěpnička, Podlaha *et al.* (1999). Extremely air-sensitive brown prismatic crystals suitable for X-ray analysis were obtained by very slow evaporation of a hexane solution on a vacuum line. The selected crystal was inserted into a Lindemann glass capillary under a nitrogen atmosphere, fixed with wax and sealed (in a glove box).

### Crystal data

$[\text{TiFe}(\text{C}_5\text{H}_5)_2(\text{C}_{23}\text{H}_{42}\text{Si}_4)]$	$Z = 2$
$M_r = 664.86$	$D_x = 1.275 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.1311$ (3) Å	Cell parameters from 51 022 reflections
$b = 12.2128$ (4) Å	$\theta = 1.0\text{--}27.5^\circ$
$c = 14.3972$ (5) Å	$\mu = 0.809 \text{ mm}^{-1}$
$\alpha = 82.423$ (2)°	$T = 150.0$ (1) K
$\beta = 80.855$ (3)°	Prism, dark brown
$\gamma = 82.344$ (2)°	$0.33 \times 0.25 \times 0.18 \text{ mm}$
$V = 1731.85$ (10) Å <sup>3</sup>	

### Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.044$
$\omega$ scans	$\theta_{\text{max}} = 27.56^\circ$
66 966 measured reflections	$h = 0 \rightarrow 13$
7859 independent reflections	$k = -15 \rightarrow 15$
6660 reflections with $I > 2\sigma(I)$	$l = -18 \rightarrow 18$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 2.8301P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.069$	$\Delta\rho_{\text{max}} = 1.15 \text{ e \AA}^{-3}$
7859 reflections	$\Delta\rho_{\text{min}} = -0.60 \text{ e \AA}^{-3}$
360 parameters	
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**

Selected geometric parameters (Å, °).

Ti–C1	2.088 (2)	Ti–C10	2.333 (3)
Ti–C2	2.191 (2)	Ti–C11	2.363 (3)
Ti–C3	2.230 (2)	C1–C2	1.452 (3)
Ti–C4	2.183 (2)	C1–C6	1.578 (3)
Ti–C6	2.412 (2)	C2–C3	1.428 (3)
Ti–C5	2.064 (2)	C2–C12	1.485 (3)
Ti–C7	2.385 (3)	C3–C4	1.442 (3)
Ti–C8	2.370 (3)	C4–C5	1.471 (3)
Ti–C9	2.341 (3)	C5–C6	1.588 (3)
C2–C1–C6	110.94 (19)	C4–C5–C6	110.6 (2)
C1–C2–C3	118.7 (2)	C1–C6–C5	113.72 (19)
C2–C3–C4	126.6 (2)	C1–C6–Si4	109.86 (16)
C3–C4–C5	117.7 (2)	C5–C6–Si4	110.33 (16)
C6–C1–C2–C3	−21.2 (3)	C3–C4–C5–C6	21.8 (3)
Ti–C2–C3–C4	41.6 (2)	C4–C5–C6–C1	−50.4 (3)
C2–C3–C4–C5	7.3 (4)	C5–C6–C1–C2	50.1 (3)

The H atoms, except H3 and H6, which were identified on difference electron-density maps and refined isotropically, were refined in fixed positions with C–H distances of 0.96 (methyl) and 0.93 Å (aromatic), and assigned  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: COLLECT (Nonius, 1997–2000); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO and SCALEPACK; program used to solve structure: SIR92 (Altomare *et al.*, 1994); program used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 1999); software used to prepare material for publication: SHELXL97 and PLATON.

This study was supported by the Grant Agency of the Czech Republic (grant No. 203/99/0846).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1420). Services for accessing these data are described at the back of the journal.

## References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Back, S., Pritzkow, H. & Lang, H. (1998). *Organometallics*, **17**, 41–44.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Nonius (1997–2000). COLLECT. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
- Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.
- Spek, A. L. (1999). PLATON. Version of 1999. Utrecht University, The Netherlands.
- Štěpnička, P., Gyepes, R., Císařová, I., Kubišta, J., Horáček, M. & Mach, K. (1999). *Organometallics*, **18**, 4869–4880.
- Štěpnička, P., Gyepes, R., Císařová, I., Varga, V., Poláček, M., Horáček, M. & Mach, K. (1999). *Organometallics*, **17**, 627–633.
- Štěpnička, P., Podlaha, J., Horáček, M., Hanuš, V. & Mach, K. (1999). *J. Organomet. Chem.* **580**, 210–213.
- Varga, V., Poláček, M., Hiller, J., Thewalt, U., Sedmera, P. & Mach, K. (1996). *Organometallics*, **15**, 1268–1274.
- Zakharov, L. N., Struchkov, Y. T., Sharutin, V. V. & Suvorova, O. N. (1979). *Cryst. Struct. Commun.* **8**, 439–444.