Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

[μ-1κ^2*O*,*O*′:2(η^5)-Cyclopentadienylcarboxylato][2(η^5)-diphenylphosphinocyclopentadienyl]bis[1,1(η^5)-tetramethylcyclopentadienyl]iron(II)titanium(III)

Karel Mach,[a] Jiří Kubišta,[a] Ivana Císařová[b] and Petr Štěpnička[b]*

[a]J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic, and [b]Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic
Correspondence e-mail: stepnic@mail.natur.cuni.cz

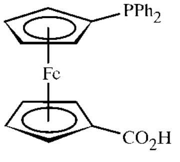
Received 2 November 2001
Accepted 13 November 2001
Online 23 January 2002

Reacting stoichiometric amounts of 1-(diphenylphosphino)ferrocenecarboxylic acid and [Ti(η^5-C$_5$HMe$_4$)$_2$(η^2-Me$_3$SiC$\equiv$CSiMe$_3$)] produced the title carboxylatotitanocene complex, [{μ-1κ^2*O*,*O*′:2(η^5)-C$_5$H$_4$CO$_2$}{2(η^5)-C$_5$H$_4$P(C$_6$H$_5$)$_2$}{1(η^5)-C$_5$H(CH$_3$)$_4$}$_2$Fe^{II}Ti^{III}] or [FeTi(C$_9$H$_{13}$)$_2$(C$_6$H$_4$O$_2$)(C$_{17}$H$_{14}$P)]. The angle subtended by the Ti/O/O′ plane, where O and O′ are the donor atoms of the κ^2-carboxylate group, and the plane of the carboxyl-substituted ferrocene cyclopentadienyl is 24.93 (6)°.

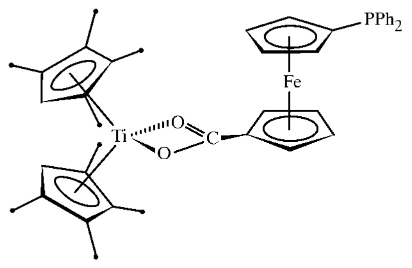
Comment

Multidentate ligands possessing donor groups of different natures according to Pearson's hard and soft acid and base concept (so-called hybrid ligands) are capable of hemilabile coordination and of linking (different) transition metals into multinuclear complexes. Whereas the former property plays an important role in homogeneous catalysis, the latter is relevant mainly to fundamental research and material chemistry.

We have recently reported the synthesis of a ferrocene carboxyphosphine ligand, 1-(diphenylphosphino)ferrocenecarboxylic acid (Hdpf; Podlaha *et al.*, 1995), and its coordination properties towards various metals (Štěpnička *et al.*, 1999; Pinkas *et al.*, 2001). In order to obtain novel titanocene–ferrocene complexes, which to date are represented mostly by compounds having the metallocene units directly connected or separated by hydrocarbon bridges (Štěpnička *et al.*, 2000), we have studied the reactivity of Hdpf towards Ti^{II} complexes [Ti(η^5-C$_5$*R*$_5$)$_2$(η^2-Me$_3$SiC$\equiv$CSiMe$_3$)] (*R* is H or Me), which behave as a source of reactive titanocenes, [Ti(η^5-C$_5$*R*$_5$)$_2$] (Varga *et al.*, 1996). The reaction of [Ti(η^5-C$_5$HMe$_4$)$_2$(η^2-Me$_3$SiC$\equiv$CSiMe$_3$)] with one molar equivalent of Hdpf produced a novel paramagnetic titanocene–ferrocene complex, namely the title compound, (I), in high yield. The title complex has been characterized by spectral methods and its structure determined. The results are presented here.



Hdpf



(I)

The molecular structure is shown in Fig. 1 and selected geometric parameters are given in Table 1. Both metallocene units exhibit the expected arrangement. The titanocene moiety is bent, with a dihedral angle between the least-squares cyclopentadienyl planes Cp3 and Cp4 of 46.24 (5)°, and is very nearly bisected by the TiO$_2$ plane [angle between Cp3 and TiO$_2$ 22.88 (4), and between Cp4 and TiO$_2$ 23.46 (5)°]. The planes are defined as follows: Cp1 = C1–C5, Cp2 = C6–C10, Cp3 = C30–C34, Cp4 = C40–C44, Ph1 = C12–C17, Ph2 = C18–C23, TiO$_2$ = Ti/O1/O2 and CO$_2$ = C11/O1/O2. *Cg* denotes the ring centroid of the corresponding least-squares cyclopentadienyl plane. The *Cg*3—Ti—*Cg*4 angle is 137.09 (4)°; the Ti—*Cg* distances differ only slightly: Ti—*Cg*3 = 2.0513 (8) Å and Ti—*Cg*4 = 2.0567 (8) Å. The titanocene cyclopentadienyls are staggered [τ(C30—*Cg*3—*Cg*4—C40) = 39.1 (1)°; ideal value = 36°], with the non-substituted ring C atoms located at the hinge position. The methyl substituents are disposed from the cyclopentadienyl planes outwards from the Ti centre, the maximum perpendicular distance being 0.100 (3) Å for atom C45 and the Cp4 plane.

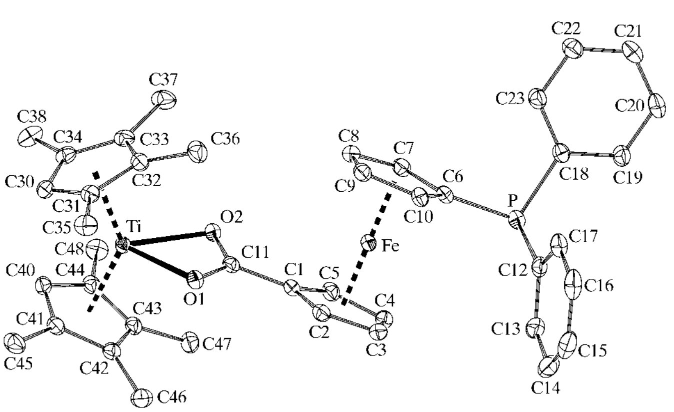


Figure 1
A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level. For clarity, H atoms have been omitted.

DOI: 10.1107/S0108270101019370

The cyclopentadienyl rings of the bridging ferrocene unit are nearly parallel [Cp1/Cp2 = 1.1 (1)°] and, as indicated by the torsion angle τ(C1—*Cg*1—*Cg*2—C6) of −163.4 (1)°, adopt a conformation halfway between anticlinal eclipsed (τ = 144°) and antiperiplanar staggered (τ = 180°). The distances of the Fe atom to the cyclopentadienyl ring centroids, Fe—*Cg*1 = 1.6513 (8) and Fe—*Cg*2 = 1.6476 (8) Å, correspond well to the Fe—*Cg* distances in uncoordinated Hdpf (Podlaha *et al.*, 1995). Likewise, the arrangement at the phosphino substituent, which remains unaffected by coordination, resembles that of Hdpf [dihedral angles: Ph1/Ph2 = 82.85 (5)°, Cp2/Ph1 = 75.31 (6)° and Cp2 = Ph2 84.06 (6)°].

The two metallocene units are mutually rotated, as defined by the dihedral angle of 24.93 (6)° between the Cp1 and TiO_2 planes. Although the pseudo-tetrahedral arrangement around the Ti atom is severely distorted due to the steric requirements of the carboxylate and cyclopentadienyl ligands [O1—Ti—O2 = 60.85 (4)° and *Cg*3—Ti—*Cg*4 = 46.24 (5)°], the carboxylate ligand is bonded in a symmetric fashion. The Ti—O bond lengths differ by only 0.014 Å, whilst the lengths of the carboxylic C—O bonds are identical within the precision of measurement. The four-membered Ti/O1/O2/C11 ring is slightly bent along the O1···O2 diagonal, with the carboxylic C11 atom disposed by 0.124 (2) Å from the TiO_2 plane, though without deformation of the planar arrangement at C11, as evidenced by the sum of the bond angles being 359.9°.

The arrangement of the carboxylate moiety is similar to the titanocene complex with chelating benzoate, $[Ti(\eta^5\text{-}C_5H_5)_2(PhCO_2\text{-}\kappa^2 O,O')]$ (Clauss *et al.*, 1983), which exhibits Ti—O bond lengths of 2.134 (3), 2.147 (3), 2.152 (4) and 2.155 (3) Å (two independent molecules), and C—O distances in the range 1.254 (6)–1.271 (5) Å. As a comparison, the monodentate phosphinocarboxylate in $[Ti(\eta^5\text{-}C_5H_5)_2(Ph_2PCH_2CO_2\text{-}\kappa O)_2]$ (Edwards *et al.*, 2000) shows similar Ti—O bond lengths of 1.925 (5) and 1.972 (4) Å, but clearly distinct C—O distances within the carboxylate moiety of 1.282 (8) and 1.300 (7) Å for C—O, and 1.189 (8) and 1.216 (6) Å for C═O.

The Cp1 and CO_2 planes in (I) are rotated by as much as 19.3 (1)° from a coplanar arrangement, and the C1—C11 bond is slightly shorter than the corresponding distance in Hdpf (1.452 and 1.458 Å). Nevertheless, it is likely that conjugation between the Cp1 ring and the carboxylate group remains active, since it has been shown for ferrocenoyl derivatives of the general formula $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4C(O)X)]$ (*X* is OH or NH_2) that the π systems interact even at Cp-to-CO*X* twist angles of 40–50° (Lin *et al.*, 1998). Hence, the rotation as well as the bending of the Ti/O1/O2/C11 ring can be ascribed to inter- and intramolecular steric interactions of the bulky octamethyltitanocene and (diphenylphosphino)ferrocene moieties. An inspection of intermolecular contacts has revealed that the solid-state packing in (I) is dictated mostly by steric requirements. The only notable exception is edge-to-face interaction between H21 and the ferrocene cyclopentadienyl Cp1 ring in a neighbouring molecule [H21···*Cg*1^{i} = 2.845 Å, C21···*Cg*1^{i} = 3.708 (2) Å and C21—H21···*Cg*1^{i} = 155.0°; symmetry code: (i) $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$].

Table 1
Selected geometric parameters (Å, °).

Fe—C1	2.0409 (15)	Ti—C32	2.3718 (16)
Fe—C2	2.0566 (17)	Ti—C33	2.4166 (16)
Fe—C3	2.0569 (17)	Ti—C34	2.4095 (17)
Fe—C4	2.0478 (17)	Ti—C40	2.3256 (16)
Fe—C5	2.0360 (17)	Ti—C41	2.3771 (16)
Fe—C6	2.0435 (16)	Ti—C42	2.4440 (16)
Fe—C7	2.0380 (17)	Ti—C43	2.4189 (16)
Fe—C8	2.0484 (17)	Ti—C44	2.3493 (16)
Fe—C9	2.0512 (17)	P—C6	1.8122 (17)
Fe—C10	2.0457 (16)	P—C12	1.8359 (18)
Ti—O1	2.1582 (12)	P—C18	1.8349 (17)
Ti—O2	2.1658 (11)	O1—C11	1.2697 (19)
Ti—C30	2.3489 (16)	O2—C11	1.2693 (19)
Ti—C31	2.3435 (16)	C1—C11	1.474 (2)
O1—Ti—O2	60.85 (4)	C11—O2—Ti	89.35 (9)
C6—P—C12	100.71 (8)	O2—C11—O1	119.18 (14)
C6—P—C18	100.52 (8)	O2—C11—C1	121.10 (14)
C12—P—C18	101.96 (8)	O1—C11—C1	119.59 (14)
C11—O1—Ti	89.68 (9)		
Ti—O1—C11—C1	−166.29 (13)	C2—C1—C11—O1	−19.0 (2)
Ti—O2—C11—C1	166.26 (13)	C5—C1—C11—O2	−17.7 (2)

Experimental

On a vacuum line, a solution of Hdpf (207 mg, 0.50 mmol) in toluene (20 ml) was added to solid $[Ti(\eta^5\text{-}C_5HMe_4)_2(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ (235 mg, 0.51 mmol; Varga *et al.*, 1996) and the resulting green–brown solution was heated to 333 K for 1 h. All volatiles were then removed under vacuum and the residue was extracted with hexane (50 ml). The extracts were concentrated to crystallization and kept at 273 K overnight to afford compound (I) as thin brown crystals. The mother liquor was concentrated and crystallized as above to provide an additional crop of crystals (combined yield: 307 mg, 84%; m.p. 398 K). Spectroscopic analysis: electron-spin resonance (toluene, 295 K): *g* = 1.9793, *H* = 3.0 G, a_{Ti} = 7.3 G; IR (KBr, cm^{-1}): 3068 (*w*), 3050 (*w*), 2943 (*m*), 2907 (*s*), 2858 (*m*), 1585 (*m*), 1506 (*s*) [$\nu_{as}(CO_2)$], 1434 (*m*), 1396 (*s*) [$\nu_s(CO_2)$], 1358 (*m*), 1190 (*w*), 1163 (*m*), 1092 (*w*), 1027 (*s*), 828 (*s*), 812 (*s*), 798 (*m*), 744 (*s*), 697 (*s*), 634 (*m*), 506 (*m*), 486 (*w*), 451 (*m*), 422 (*m*); MS [*m*/*z* (relative abundance)]: 706 (6), 705 (21), 704 (53), 703 (100, $M^{+\cdot}$), 702 (18), 701 (17), 582 (4), 352 (7), 305 (4), 292 (11), 290 (14), 289 {14, $[(C_5Me_4H)_2Ti - H]^+$}, 287 (4), 105 (7).

Crystal data

$[FeTi(C_9H_{13})_2(C_6H_4O_2)(C_{17}H_{14}P)]$
M_r = 703.48
Monoclinic, $P2_1/c$
a = 8.4660 (1) Å
b = 29.5260 (3) Å
c = 14.1002 (1) Å
β = 97.3941 (5)°
V = 3495.28 (6) Å^3
Z = 4

D_x = 1.337 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 97 200 reflections
θ = 1.0–27.5°
μ = 0.72 mm^{-1}
T = 150 K
Prism, dark red–brown
0.75 × 0.50 × 0.40 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
T_{min} = 0.606, T_{max} = 0.757
47 188 measured reflections

7976 independent reflections
6981 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 27.5°
$h = 0 \rightarrow 10$
$k = -38 \rightarrow 38$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2 + 1.8480P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$(\Delta/\sigma)_{\max} = 0.001$
$wR(F^2) = 0.085$	$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{\min} = -0.34$ e Å^{-3}
7976 reflections	
415 parameters	
H-atom parameters constrained	

All H atoms were treated as riding, with C—H distances of 0.96 (methyl) and 0.93 Å (aromatic).

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97 and *PLATON*.

Financial support from the Grant Agency of the Czech Republic is gratefully acknowledged (grant Nos. 203/01/P002, 203/99/0846 and 203/99/M037).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1183). 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.

Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.

Clauss, A. W., Wilson, S. R., Buchanan, R. M., Pierpont, C. G. & Hendrickson, D. A. (1983). *Inorg. Chem.* **22**, 628–636.

Edwards, D. A., Mahon, M. F. & Paget, T. J. (2000). *Polyhedron*, **19**, 757–764.

Lin, L., Berces, A. & Kraatz, H.-B. (1998). *J. Organomet. Chem.* **556**, 11–20.

Nonius (1997–2000). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.

Pinkas, J., Bastl, Z., Šlouf, M., Podlaha, J. & Štěpnička, P. (2001). *New J. Chem.* **25**, 1215–1220, and references therein.

Podlaha, J., Štěpnička, P., Ludvík, J. & Císařová, I. (1995). *Organometallics*, **15**, 543–550.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1999). *PLATON*. University of Utrecht, The Netherlands.

Štěpnička, P., Císařová, I., Horáček, M. & Mach, K. (2000). *Acta Cryst.* C**56**, 1204–1205, and references therein.

Štěpnička, P., Císařová, I., Podlaha, J., Ludvík, J. & Nejezchleba, M. (1999). *J. Organomet. Chem.* **582**, 319–327, and references therein.

Varga, V., Mach, K., Polášek, M., Sedmera, P., Hiller, J., Thewalt, U. & Troyanov, S. I. (1996). *J. Organomet. Chem.* **506**, 241–251.