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Synthesis and characterization of Group IV metal–iron complexes bridged by carboxylate substituted cyclopentadienyl group. The structure of $Cp_2Ti[(\mu\text{-}O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$

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Abstract

The complexes, $(\eta^5\text{-}C_5H_5)_2M[(\mu\text{-}O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$ ($M = Ti$ or Zr), were prepared by reacting 1 molar equivalent of $(\eta^5\text{-}C_5H_5)_2MCl_2$ and 2 molar equivalents of $(NaO_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)$ in dichloromethane. These complexes have been characterized by elemental analysis, IR, ^1H, and ^{13}C NMR spectroscopy. $(\eta^5\text{-}C_5H_5)_2Ti[(\mu\text{-}O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.010(2)$, $b = 12.39(1)$, $c = 17.987(2)$ Å, $\alpha = 104.006(8)$, $\beta = 90.00(2)$, $\gamma = 93.97(1)°$, $V = 1728.1(5)$ Å^3, $D_{calc} = 1.630$ g/cm^3, and $Z = 2$. The spectral data of the complexes and the solid state structure of $(\eta^5\text{-}C_5H_5)_2Ti[(\mu\text{-}O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$ show that the coordination of the carboxylates to the early transition metal centre is not perturbed by the iron metal.

Introduction

Recently the synthesis and chemistry of complexes containing both early and late transition metal centres have attracted considerable attention [1]. One of the methods for the preparation of early-late heterobimetallic complexes is to use difunctional ligands to bridge two metals in a complex [2]. These hetero-difunctional ligands are usually phosphine-based ligands, such as OCH_2PPh_2 [3], CH_2PR_2 [4], $S(CH_2)_nPPh_2$ [5], $C_5H_4(CH_2)_nPPh_2$ [6], $C_5H_4SiMe_2CH_2CH_2PPh_2$ [7], and $C_7H_6PPh_2$ [8]. However the difunctional ligands used to bridge early-late transition metals without phosphine donor end are found in a few cases. They are

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C_5H_4 [9], $CH_2CH_2C_5H_4$ [9(f)], and SeC_5H_4 [10]. Moreover the carboxylate substituted cyclopentadienyl is also a suitable difunctional ligand to bridge early and late transition metals. The carboxylate substituted cyclopentadienyl is capable of coordinating to many transition metals using their π electrons and leaves the carboxylate group for further reaction to the oxophilic early transition metals. Some of the ring substituted cyclopentadienyl metal complexes [11] are known and they offer us a good starting point for the preparation of early-late bimetallic complexes.

Here we report the synthesis, characterizations, and X-ray structure of Group IV transition metal–iron complexes bridged by the difunctional carboxylate substituted cyclopentadienyl group ($O_2CC_5H_4$). The formula of the prepared complexes is $Cp_2M[(\mu\text{-}O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$ ($Cp = \eta^5\text{-}C_5H_5$; M = Ti or Zr). The spectral data of the complexes and the solid state structure of $(\eta^5\text{-}C_5H_5)_2Ti[(\mu\text{-}O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$ show that the coordination of the carboxylates to the early transition metal centre is not perturbed by the iron atom.

Experimental section

Reagents and general techniques

The compounds $(HO_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)$ [11c] and Cp_2ZrCl_2 [12] were prepared according to literature procedures. $(NaO_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)$ was obtained by reacting $(HO_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)$ with NaH in dichloromethane. Cp_2TiCl_2 (Aldrich) and NaH (Aldrich) were used without further purification. Solvents were dried by refluxing (at least 24 h) over P_2O_5 (dichloromethane) or sodium/benzophenone (benzene, diethyl ether, hexane); all solvents were freshly distilled prior to use. Deuterated solvents (Aldrich) were dried over molecular sieves. All syntheses and manipulations were carried out under a dry dinitrogen atmosphere.

Synthesis of $Cp_2Ti[(\mu\text{-}O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$ (1)

A mixture of $(NaO_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)$ (0.668 g, 2 mmol) and Cp_2TiCl_2 (0.249 g, 1 mmol) in 20 mL of dichloromethane at 0°C was stirred under a dry dinitrogen atmosphere for 12 h. The resulting red solution was filtered and the filtrate was pumped to dryness *in vacuo* to give a brown solid of almost quantitative yield with a very trace of impurities. The solid was washed with 10 mL of diethyl ether to afford a brown product (0.76 g, 92.6% yield), m.p. 147.3–149.3°C dec. Anal. Found: C, 59.34; H, 4.05. $C_{40}H_{32}O_8TiFe_2$ calc.: C, 60.04; H, 4.03. IR (Nujol mull) (cm^{-1}): 2001 s, 1949 s, 1941 s, 1639 s, 1591 w, 1584 w, 1485 w, 1416 w, 1355 w, 1321 s, 1299 s, 1193 sh, 1179 s, 1071 w, 1060 w, 1019 m, 964 vw, 919 w, 859 w, 835 m, 824 s, 782 m, 775 m, 756 m, 749 m, 727 sh, 697 s, 631 s, 601 sh, 587 s, 560 m, 517 w, 464 m, 450 w, 418 w.

Synthesis of $Cp_2Zr[(\mu\text{-}O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$ (2)

A mixture of $(NaO_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)$ (0.668 g, 2 mmol) and Cp_2ZrCl_2 (0.292 g, 1 mmol) in 20 mL of dichloromethane at 0°C was stirred under a dry dinitrogen atmosphere for 12 h. The resulting precipitate of NaCl was filtered off and the filtrate was pumped to dryness to give a yellow solid of almost quantitative yield. The solid was washed with 10 mL of diethyl ether to give the yellow product (0.82 g, 95.3% yield), m.p. 145.0–147.5°C dec. Anal. Found: C, 56.56; H, 3.91. $C_{40}H_{32}O_8ZrFe_2$ calc.: C, 56.93; H, 3.82. IR (Nujol mull) (cm^{-1}): 2017 s, 1995 s, 1971 s, 1939 s, 1643 s, 1600 w, 1529 m, 1503 m, 1494 w, 1422 sh, 1408 m, 1325 s, 1217 w, 1196 m, 1072 w, 1059 w, 1140 w, 1027 m, 937 w, 859 w, 826 m, 808 m, 795 m, 757 m, 729 w, 635 m, 589 s, 561 m, 515 vw, 485 w, 452 w.

Physical measurements

Infrared spectra were recorded on a Hitachi 270-30 spectrometer in the region of 4000–400 cm^{-1}; the peak positions were calibrated with the 1601.4 cm^{-1} peak of polystyrene. ^1H NMR spectra were obtained with a Varian Gemini-200 (200 MHz) or a Varian VXR-300 (300 MHz) spectrometer and ^{13}C NMR spectra were recorded with the Varian VXR-300 (75.43 MHz) spectrometer. The ^1H and ^{13}C chemical shifts were measured relative to TMS as the internal reference. Melting points were measured under a nitrogen atmosphere using a Büchi 535 instrument and were not corrected. Elemental analyses of complexes were performed using a Heraeus CHN-O-RAPID instrument.

Crystal structure determination

A red crystal of **1** of size 0.50 × 0.31 × 0.15 mm grown from dichloromethane/hexane was used for X-ray diffraction. Cell dimensions were obtained from 25 reflections with 2θ angle in the range of 19.84–32.4°. The diffraction intensities were collected on a Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo-K_α radiation, $\lambda = 0.70930$ Å. All calculations were carried out using the NRCC package [13] on a Vax 780 computer. Atomic scattering factors were taken from reference 14. The crystallographic data of **1** are summarized in Table 1.

Results and discussion

Synthesis and characterization

The complexes, $Cp_2M[(\mu\text{-}O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$ (M = Ti (**1**) or Zr (**2**)), were prepared in high yield by reacting 1 molar equivalent of Cp_2MCl_2 and 2 molar equivalents of $(NaO_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)$ in dichloromethane (eq. 1). Complex **1** is a brown, and complex **2** is a yellow solid.

$$Cp_2MCl_2 + 2\ (NaO_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5) \rightarrow Cp_2M[(\mu\text{-}O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2 + 2\ NaCl \quad (1)$$

Both complexes are soluble in dichloromethane or benzene, but not soluble in diethyl ether or hexane.

We have also attempted to synthesize the mono-substituted complexes, $Cp_2MX[(\mu\text{-}O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]$ (M = Ti or Zr; X = Cl or Br), by reaction of 1 molar equivalent of $(NaO_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)$ with Cp_2MX_2. The reaction mixtures were analyzed by ^1H NMR and were shown to contain a major product, a minor product of the di-substituted complex, and the unreacted metallocene dichloride. Although the major product is believed to be the mono-substituted complexes, we are unable to isolate them in pure form.

Table 1

Crystallographic data of $Cp_2Ti[(\mu\text{-}O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$

Formula	$C_{40}H_{32}Fe_2O_8Ti$
FW	800.26
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	8.010(2)
b, Å	12.393(1)
c, Å	17.987(2)
α, deg	104.006(8)
β, deg	90.00(2)
γ, deg	93.97(2)
V, Å^3	1728.1(5)
Z	2
D_{calcd}, $g \cdot cm^{-3}$	1.630
$\mu(Mo\text{-}K_\alpha)$, cm^{-1}	11.0
Min transmission factor	0.825
Scan mode	$\theta/2\theta$
2θ(max), deg	44.9
No. of reflections measured	4918
No. of unique reflections with $I > 2.5\sigma(I)$	2794
No. of refined parameters	588
R_f for significant reflections [a]	0.032
R_w for significant reflections [b]	0.034
GoF [c]	1.33

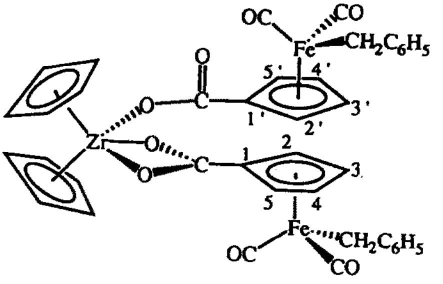
[a] $R_f = [\Sigma|F_o - F_c|/\Sigma|F_o|]$. [b] $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$. [c] $GoF = [\Sigma w(F_o - F_c)^2/(N_{rflns} - N_{params})]^{1/2}$.

The complexes **1** and **2** were characterized by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy. IR stretching bands of carbonyl and carboxylate group are listed in Table 2. The IR spectra of the complexes in the solid state as Nujol mull show three $\nu(CO)$ bands for **1** and four $\nu(CO)$ bands for **2**. This may indicate that

Table 2

CO and CO_2 IR stretching bands of **1**, **2** and $(\eta^5\text{-}C_5H_4COOH)Fe(CO)_2(CH_2C_6H_5)$

Vibration mode	$(\eta^5\text{-}C_5H_4COOH)Fe(CO)_2$-$(CH_2C_6H_5)$		**1**		**2**	
	Nujol mull	CH_2Cl_2	Nujol mull	CH_2Cl_2	Nujol mull	CH_2Cl_2
$\nu(CO)$	2013	2021	2001	2012	2017	2017
	1949	1969	1949	1960	1995	1965
			1941		1971	
					1939	
monodentate CO_2						
$\nu(CO_2(asym))$	1681	1689	1639	1639	1643	1641
$\nu(CO_2(sym))$	1353	1257	1321	1321	1325	1317
bidentate CO_2						
$\nu(CO_2(asym))$					1529	1512
$\nu(CO_2(sym))$					1408	1398



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two $(O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)$ moieties in the solid state are environmentally different. However the IR spectra of the complexes **1** and **2** in dichloromethane solution show only two $\nu(CO)$ bands. For the complex **1**, the $\nu(CO_2(asym))$ at ~ 1640 cm^{-1} and $\nu(CO_2(sym))$ at ~ 1320 cm^{-1} with $\Delta\nu$ of ~ 320 cm^{-1} suggests monodentate binding mode [15] for both carboxylate groups. However for the complex **2**, one of the carboxylate groups is monodentate with $\nu(CO_2(asym))$ at ~ 1640 cm^{-1} and $\nu(CO_2(sym))$ at ~ 1330 cm^{-1} and another carboxylate group is bidentate with $\nu(CO_2(asym))$ at ~ 1525 cm^{-1} and $\nu(CO_2(sym))$ at ~ 1400 cm^{-1} [16]. It is conceivable that the bigger zirconium metal is capable of accommodating one monodentate and one bidentate carboxylate simultaneously to achieve 18 electrons (structure I).

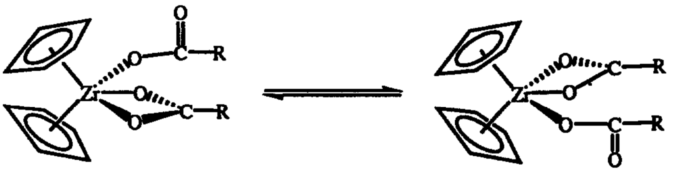
Results of ^1H NMR of the complexes **1** and **2** and of $(\eta^5\text{-}C_5H_4CO_2H)Fe(CO)_2(CH_2C_6H_5)$ are listed in Table 3. ^1H chemical shifts of $CH_2C_6H_5$ groups do not vary much for the complexes **1** and **2**. From the IR spectrum of the complex **2**, two carboxylates are different in binding mode and the protons (2,5) and (2',5') (structure I) are expected to be different in NMR environments, as also protons (3,4) and (3',4'). However only one ^1H NMR signal is observed for the corresponding protons in $CDCl_3$ at ambient temperature and in CD_2Cl_2 at −90°C. This indicates a fast interconversion between monodentate and bidentate carboxylates as shown in Fig. 1 [16b]. For further support of the fast interconversion mechanism, the ^{13}C NMR of the complex **2** in CD_2Cl_2 at −90°C was carried out and still a single resonance for the carboxylate carbons is observed.

Table 3

^1H NMR data for **1**, **2**, and $(\eta^5\text{-}C_5H_4COOH)Fe(CO)_2(CH_2C_6H_5)$ [a]

	C_6H_5	C_5H_5	C_5H_4	CH_2
$(\eta^5\text{-}C_5H_4COOH)\text{-}Fe(CO)_2(CH_2C_6H_5)$	6.9–7.2 m (5H)		4.76 m (2H) 5.36 m (2H)	2.88 s (2H)
1	6.9–7.2 m (10H)	6.62 s (10H)	4.68 m (4H) 5.26 m (4H)	2.89 s (2H)
2	6.9–7.2 m (10H)	6.38 s (10H)	4.68 m (4H) 5.33 m (4H)	2.90 s (2H)

[a] Chemical shift is in ppm relative to TMS in $CDCl_3$. s, singlet; m, multiplet.



R = $(C_5H_4)Fe(CO)_2(CH_2C_6H_5)$

Fig. 1. Fast interconversion between monodentate and bidentate carboxylate groups of the zirconium complex 2.

^{13}C NMR data of the complexes **1**, **2**, and $(\eta^5\text{-}C_5H_4COOH)Fe(CO)_2(CH_2C_6H_5)$ are listed in Table 4. ^{13}C chemical shifts of $CH_2C_6H_5$ and CO groups for the complexes **1** and **2** are almost the same. The ^{13}C chemical shift of the carboxylate carbons for the titanium complex **1** at 169.5 ppm is somewhat upfield relative to the values for the monodentate carboxylate complexes of $[Cp_2Ti(\mu\text{-}OC(O)C_6H_4\text{-}C(O)O)]_4$ [17] at 171.7 ppm and of $[Cp_2Ti(\mu\text{-}OC(O)CH{=}CHC(O)O)]_2$ [18] at 172.17 ppm. However the ^{13}C chemical shift for the Cp carbons of **1** at 118.9 ppm is close to the values for $[Cp_2Ti(\mu\text{-}OC(O)C_6H_4C(O)O)]_4$ at 118.8 ppm and for $[Cp_2Ti(\mu\text{-}OC(O)CH{=}CHC(O)O)]_2$ at 118.45 ppm. For the complex **2**, the ^{13}C chemical shift of the carboxylate carbons appears somewhat downfield relative to the values for $Cp_2ZrCl(O_2CPh)$ at 171.9 ppm and for $Cp_2ZrCl(O_2CH)$ at 171.5 ppm, but it is much upfield relative to $Cp_2ZrCl(O_2CCH_3)$ at 187.1 ppm and to $Cp_2ZrCl(O_2CCMe_3)$ at 193.8 ppm [19]. It seems that the R group of the carboxylate ligands affects the ^{13}C chemical shifts of the carboxylate carbons, but, in view of the similar chemical shifts of the Cp carbons, the R group has no effect on the coordination abilities of the carboxylate oxygens. For the complexes **1** and **2**, it seems that further coordination of the C_5H_4 ring of the carboxylate ligand to iron metal has little effect on the coordination of the carboxylate oxygens to the early transition metals. That the ^{13}C chemical shift of carboxylate carbons for **2** is at downfield by 4.1 ppm relative to that of **1** suggests more electron donation from the bidentate carboxylate group to the zirconium metal centre.

Table 4

^{13}C NMR data for **1**, **2**, and $(\eta^5\text{-}C_5H_4COOH)Fe(CO)_2(CH_2C_6H_5)$ [a]

	CO	CO_2	C_6H_5	C_5H_5	C_5H_4	CH_2
$(\eta^5\text{-}C_5H_4COOH)\text{-}Fe(CO)_2(CH_2C_6H_5)$	214.7	170.0	151.7 128.3 127.6 123.8		92.1 86.7 83.0	7.2
1	216.0	169.5	152.2 128.2 127.5 123.4	118.9	90.7 89.0 86.4	6.5
2	215.6	173.6	152.2 128.2 127.6 123.5	114.4	91.3 86.9 86.5	6.6

[a] Chemical shift is in ppm relative to TMS in $CDCl_3$.

Molecular structure of $Cp_2Ti[(\mu\text{-}O_2CC_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$ *(1)*

The final coordinates of complex **1** are listed in Table 5 and the molecular structure of **1** is shown in Fig. 2. Two carboxylate groups adopt the expected monodentate attachment to the titanium metal. The Ti–O2 and Ti–O4 distances are 1.923 and 1.972 Å (average 1.948 Å). Two noncoordinated oxygen atoms are far away from titanium with distances at 3.528 and 3.652 Å. In order to achieve 18 e^-, the Ti–O bond distances in **2** are expected to be short for better π interaction. However the short Ti–O bond distances would cause severe steric hindrance in view of the rather short nonbonded distances between the coordinated oxygen atoms (O2 and O4) and some of the Cp ring carbons (Table 6). The average distance of these nonbonded C···O is 2.857 Å which is less than the van der Waals distance by 0.4 Å [20]. The shortest distance occurs between the O2 atom and C35 atom at 2.687 Å which is less than the van der Waals distance by almost 0.6 Å. The average Ti–O bond distance for the complex **1** agrees with those in $Cp_2Ti[OC(O)Ph]_2$ (1.926 Å), in $[Cp_2Ti(\mu\text{-}OC(O)C_6H_4C(O)O)]_4$ (1.94 Å), in $[Cp_2Ti(\mu\text{-}OC(O)C{\equiv}CC(O)O)]_4 \cdot 5CH_2Cl_2$ [21] (1.955 Å), in $[Cp_2Ti(\mu\text{-}OC(O)CH{=}CHC(O)O)]_2$ (1.957 Å) and in $[Cp_2Ti(\mu\text{-}OC(O)C{\equiv}CC(O)O]_2$ [21] (1.978 Å). The average Ti–Cp distance for **1** at 2.055 Å is similar to the distance in $[Cp_2Ti(\mu\text{-}OC(O)C_6H_4C(O)O)]_4$ at 2.06 Å, in $Cp_2Ti[OC(O)Ph]_2$ at 2.062 Å, and in $[Cp_2Ti(\mu\text{-}OC(O)C{\equiv}CC(O)O)]_2$ at 2.062 Å, but it is longer by 0.02 Å than the distance in $[Cp_2Ti(\mu\text{-}OC(O)C{\equiv}CC(O)O)]_4 \cdot 5CH_2Cl_2$ at 2.035 Å. The X-ray structural data of **1** show no effect of the iron metal centre on the coordination of the carboxylate groups to the titanium metal centre.

Some structural important features of $Ti(O_2CC_5)_2$ moiety with bond lengths and bond angles are shown in Fig. 3 and other selected bond lengths and bond angles are listed in Table 7. All atoms in Fig. 3 are nearly in a plane with the dihedral angle between two O_2CC_5 planes at 5.06°. Besides the sterically crowding between the coordinated oxygen atoms and the Cp ring carbons, the steric effect also reflects on the Ti–O–C angles. With shorter Ti–O distance the Ti–O2–C15 angle at 148.0° is substantially larger than the Ti–O4–C30 angle at 139.4°. In $[Cp_2Ti(\mu\text{-}OC(O)C{\equiv}CC(O)O)]_2$, these angles are 138.6 and 144.1° with Ti–O distances of 1.980 and 1.976 Å. The bond angles of the carboxylate C–C(O)O groups are also inequivalent with the largest O–C–O angles at 125.9 and 126.0° which are due to the geometrically closer of oxygen atoms to Cp rings. The C–C bond distances of C_5H_4 rings are inequivalent with short distances of C2–C3 (1.380 Å), C4–C5 (1.387 Å), C17–C18 (1.403 Å), and C19–C20 (1.385 Å). Other C–C bond distances are all above 1.410 Å with the longest C16–C20 bond at 1.441 Å. This localization effect may be due to electron withdrawing of carboxylate group and the coordination of C_5H_4 ring to the iron metal centre [22].

Regarding the $Fe(CO)_2(CH_2C_6H_5)$ moieties, one is pointed up geometrically and the other is down. Two $CH_2C_6H_5$ groups are located inside with structural different orientations. The average distance of Fe–C_5H_4 ring centroid at 1.737 Å is comparable to the distance of Fe–Cp ring centroid in $[CpFe(CO)_2]_2C_4H_4$ [23] at 1.731 Å. However this distance is longer than the distance of Fe–Cp ring centroid in $CpFe(CO)_2(\eta^1\text{-}C_5H_5)$ [24] at 1.70 Å and in $CpFe(CO)_2(\eta^1\text{-}SO_2C_5H_4)$ [25] at 1.722 Å, but shorter than that in $CpFe(CO)_2(CH_2CO_2H)$ [26] at 1.80 Å. The variations of these distances reflect the donating ability of R group in $CpFe(CO)_2R$ system with better σ-donating ability having shorter Fe-Cp ring centroid distance.

Table 5

Final coordinates and isotropic thermal parameters for **1**

Atom	x	y	z	B_{iso}
Fe1	0.12541(9)	0.26806(6)	0.43115(5)	2.90(4)
Fe2	−0.36620(9)	0.36470(6)	0.12922(4)	2.85(4)
Ti	−0.19409(11)	−0.03050(7)	0.18736(5)	2.59(4)
O1	0.1951(5)	−0.0233(3)	0.2948(2)	5.3(2)
O2	−0.0189(4)	0.0557(3)	0.2534(2)	3.4(2)
O3	−0.5631(5)	0.0700(3)	0.1309(2)	5.5(2)
O4	−0.3229(4)	0.1023(3)	0.1986(2)	3.5(2)
O6	0.1091(6)	0.4442(3)	0.5686(2)	5.7(2)
O7	0.1243(6)	0.1061(4)	0.5226(3)	6.4(3)
O21	−0.3737(5)	0.2081(4)	−0.0187(2)	5.7(2)
O22	−0.3353(6)	0.5558(3)	0.0628(2)	5.7(2)
C1	0.1930(6)	0.1729(4)	0.3239(3)	2.8(3)
C2	0.1289(7)	0.2722(5)	0.3146(3)	3.2(3)
C3	0.2257(8)	0.3631(5)	0.3563(3)	4.0(3)
C4	0.3574(8)	0.3219(6)	0.3919(3)	4.5(3)
C5	0.3397(7)	0.2063(6)	0.3718(3)	3.6(3)
C6	0.1124(7)	0.3752(5)	0.5131(3)	3.6(3)
C7	0.1210(7)	0.1683(5)	0.4857(3)	3.7(3)
C8	−0.1350(7)	0.2557(6)	0.4177(3)	3.5(3)
C9	−0.2422(6)	0.2542(5)	0.4853(3)	3.1(3)
C10	−0.3120(7)	0.3503(5)	0.5247(3)	3.5(3)
C11	−0.4203(7)	0.3499(5)	0.5846(3)	4.3(3)
C12	−0.4593(8)	0.2536(6)	0.6072(4)	5.2(4)
C13	−0.3898(9)	0.1576(6)	0.5693(4)	5.4(4)
C14	−0.2824(8)	0.1574(6)	0.5088(4)	4.8(3)
C15	0.1233(7)	0.0574(5)	0.2895(3)	3.3(3)
C16	−0.4728(6)	0.2537(4)	0.1920(3)	3.0(3)
C17	−0.3674(7)	0.3371(5)	0.2413(3)	3.2(3)
C18	−0.4259(8)	0.4415(5)	0.2422(3)	4.1(3)
C19	−0.5724(8)	0.4237(6)	0.1954(4)	4.4(3)
C20	−0.6024(7)	0.3102(5)	0.1647(4)	3.7(3)
C21	−0.3726(7)	0.2698(5)	0.0405(3)	3.7(3)
C22	−0.3449(7)	0.4800(5)	0.0898(3)	3.7(3)
C23	−0.1051(7)	0.3578(5)	0.1301(4)	3.4(3)
C24	−0.0103(6)	0.4665(4)	0.1608(3)	2.8(2)
C25	0.0734(8)	0.5235(6)	0.1119(4)	4.5(3)
C26	0.1628(8)	0.6231(6)	0.1400(5)	5.0(4)
C27	0.1715(8)	0.6728(5)	0.2164(5)	4.9(4)
C28	0.0918(7)	0.6188(5)	0.2657(4)	4.1(3)
C29	0.0024(7)	0.5183(5)	0.2387(3)	3.6(3)
C30	−0.4584(7)	0.1319(5)	0.1709(3)	3.5(3)
C31	−0.2349(9)	−0.2046(6)	0.2185(4)	4.6(4)
C32	−0.3862(9)	−0.1816(6)	0.1918(4)	4.6(4)
C33	−0.4429(10)	−0.0908(7)	0.2422(6)	5.7(5)
C34	−0.3220(14)	−0.0569(7)	0.3002(5)	6.6(5)
C35	−0.1968(11)	−0.1300(7)	0.2841(5)	5.5(4)
C36	0.0267(12)	−0.0165(14)	0.1019(5)	8.6(7)
C37	−0.1086(17)	0.0270(7)	0.0768(4)	6.3(5)
C38	−0.2264(10)	−0.0541(11)	0.0545(4)	6.2(6)
C39	−0.1739(19)	−0.1468(8)	0.0649(5)	7.9(6)
C40	−0.0193(19)	−0.1248(14)	0.0943(6)	8.8(8)

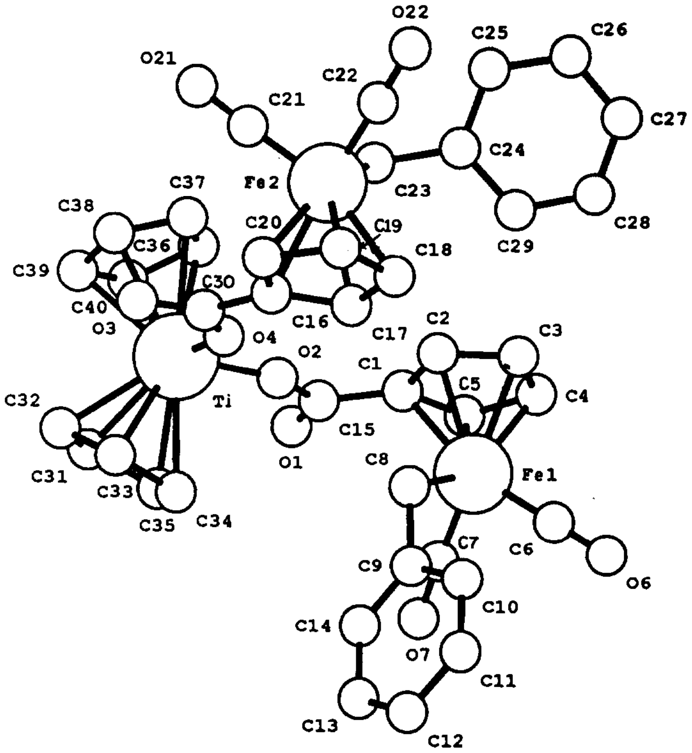


Fig. 2. Molecular structure of $Cp_2Ti[(\mu\text{-}OC(O)C_5H_4)Fe(CO)_2(CH_2C_6H_5)]_2$ (1).

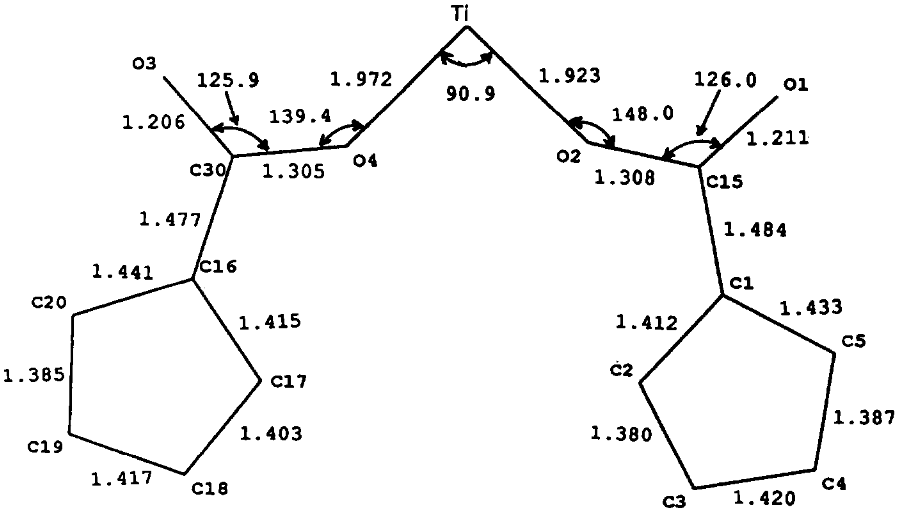


Fig. 3. Important features with bond lengths and bond angles for the $Ti(OC(O)C_5)_2$ moiety of the complex 1.

Table 6

Distances (Å) between some nonbonded atoms

Ti···O1	3.6250(3)	Ti···O3	3.5276(3)
O2···C34	2.9416(3)	O4···C33	2.8032(3)
O2···C35	2.7912(3)	O4···C34	2.9976(3)
O2···C36	2.6872(3)	O4···C37	2.8018(3)

Table 7

Selected bond lengths (Å) and bond angles (°) of the complex **1** [a]

Ti–Cp1	2.0554(9)	Ti–Cp2	2.0549(9)
C1–C15	1.484(8)	C16–C30	1.477(8)
O1–C15	1.211(7)	O3–C30	1.206(7)
O2–C15	1.308(7)	O4–C30	1.305(7)
Fe1–Cp'1	1.7370(8)	Fe2–Cp'2	1.7366(8)
Fe1–C6	1.738(6)	Fe2–C21	1.737(6)
Fe1–C7	1.735(6)	Fe2–C22	1.741(6)
Fe1–C8	2.090(6)	Fe2–C23	2.099(6)
C8–C9	1.491(7)	C23–C24	1.491(7)
C6–O6	1.147(7)	C21–O21	1.151(7)
C7–O7	1.134(7)	C22–O22	1.155(7)
Cp1–Ti–Cp2	131.48	O2–Ti–O4	90.90(15)
Fe1–C6–O6	177.2(5)	Fe2–C21–O21	178.5(5)
Fe1–C7–O7	177.0(5)	Fe2–C22–O22	178.1(5)
C6–Fe1–C7	91.4(4)	C21–Fe2–C22	93.7(4)
C6–Fe1–C8	91.3(4)	C21–Fe2–C23	87.7(4)
C7–Fe1–C8	93.3(4)	C22–Fe2–C23	90.9(4)

[a] Cp1 = C(31–35), Cp2 = C(36–40); Cp'1 = C(1–5), Cp'2 = C(16–20).

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