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Synthesis, characterization and structure of (methyl 2-butenoate)iron complexes

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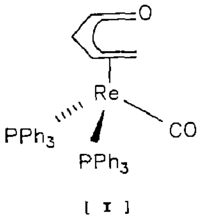
Abstract

The reaction between $CpFe(CO)_2Na$ and methyl-4-chloro-2-butenoate in tetrahydrofuran at −78 °C gives $CpFe(CO)_2(\eta^1\text{-}CH_2\text{-}CH{=}CH\text{-}CO\text{-}OCH_3)$ (**1**). Photolysis of **1** in ether at −20 °C yields $CpFe(CO)(\eta^3\text{-}CH_2\text{:::}CH\text{:::}CH\text{-}CO\text{-}OCH_3)$ (**2**). Attempts to prepare the corresponding η^5-oxapentadienyl from **2** by thermolysis or photolytic activation were unsuccessful. Photolysis of **2** in the presence of the phosphine ligands R_3P ($R_3P = PMe_3$, $P(OCH_3)_3$ gives $CpFe(PR_3)(\eta^3\text{-}CH_2\text{:::}CH\text{:::}CH\text{-}CO\text{-}OCH_3)$ ($PR_3 = PMe_3$ (**3**), $P(OCH_3)_3$ (**4**)). The molecular structure of **2** has been determined by an X-ray diffraction study. Crystallographic data: space group $P2_1/c$, *a* 8.034(2), *b* 9.430(3), *c* 14.058(4)Å, *β* 94.42(2)°, $Z = 4$, *R* 3.49%, R_w 4.05%.

Introduction

There have been few reports of transition-metal-acyclic 1-oxapentadienyl compounds [1*]. Although this class of compounds has been obtained from several chemical reactions, they were often encountered as unexpected products and isolated in low yields. The reported synthetic procedures do not find general application [2]. For example, a rhenium complex (I) was obtained from the reaction between $(PPh_3)_2ReH_7$ and furan under reflux in tetrahydrofuran (THF), in the presence of 3,3′-dimethyl-1-butene [1c]. The chemistry of metal-oxapenta-



[I]

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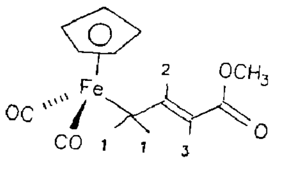
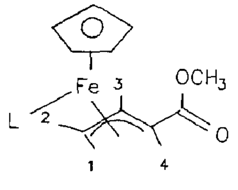
* Reference number with asterisk indicates a note in the list of references.

dienyl compounds remains largely unexplored owing to the lack of suitable reagents. Recently, we have prepared a number of metal-pentadienyl compounds from 1-halo-2,4-pentadiene [3], a reagent that is convenient in the synthesis of η^1, η^3 and η^5-metal-dienyl compounds because it can be oxidatively added to low-valence metal complexes. In order to develop the chemistry of metal-oxapentadienyl compounds, we attempted the synthesis of iron-1-oxapentadienyl complexes derived from methyl 4-chloro-2-butenoate. One intriguing feature of these complexes is the variety of geometries possible for ligand bonding to the metal center, viz., the η^3 and η^5 configurations [4]. The molecular structure of an iron-η^3-allyl ester complex is also described.

Results and discussion

A previously published procedure [5], was used to give methyl 4-chloro-2-butenoate in good yields. The Z/E isomers were obtained in ca. 28.72 molar ratio. The reaction of methyl 4-chloro-2-butenoate with $CpFe(CO)_2Na$ in THF at −78 °C gave $CpFe(CO)_2(\eta^1\text{-}CH_2\text{-}CH{=}CH\text{-}CO\text{-}OCH_3)$ (**1**) in moderate yields (29%). Compound **1** was obtained pure as a yellow oil after chromatography through an alumina column. Elemental analysis was consistent with our formulation. The mass spectrum revealed that 276 was the mass of the greatest ion and that the fragmentions resulted from the loss of a CO and then an ester group. The ^1H NMR spectra revealed the presence of only the *trans* isomer although the starting reagent chloroester is present as both the *Z* and the *E* isomers. The *trans* isomer was characterized by the proton coupling constants $J_{23} = 15.0$ Hz. Like $CpFe(CO)_2(\eta^1$-2,4-pentadienyl) [3e], this compound is fairly sensitive to air and decomposes slowly under argon at room temperature; but at −20 °C under argon it keeps for a week.





L=CO, L=PMe$_3$, L=P(OMe)$_3$

Complex **1** readily loses CO under photolytic irradiation at −20 °C in ether to give $CpFe(CO)(\eta^3\text{-}CH_2{\cdots}CH{\cdots}CH\text{-}CO\text{-}OCH_3)$ (**2**) in moderate yield. Red crystals of **2** were obtained after purification by column chromatography, followed by recrystallization from a saturated solution of **2** in pentane. The compound has been fully characterized by elemental and analysis, and mass, ^1H NMR and IR spectra. The ^1H NMR data show that the ligand is bonded to the metal in the η^3-allyl fashion rather than the oxa-allyl fashion. The $\nu(CO)$ band of the ester group occurs at 1698(s)cm^{-1} and indicates of a free carbonyl group. In the η^3-enonyl ligand, the ester group is in the *syn* position as judged from the following coupling constants, J_{13} 11.3 Hz, J_{34} 9.8 Hz and J_{32} 7.2 Hz. In the $CpFe(CO)(\eta^3$-allyl) system [6], the molecule probably exists as a mixture of *exo* and *endo* conformers owing to the differing orientations of the allyl group relative to the Cp group. Molecular structure of **2** was further characterised by an X-ray diffraction study.

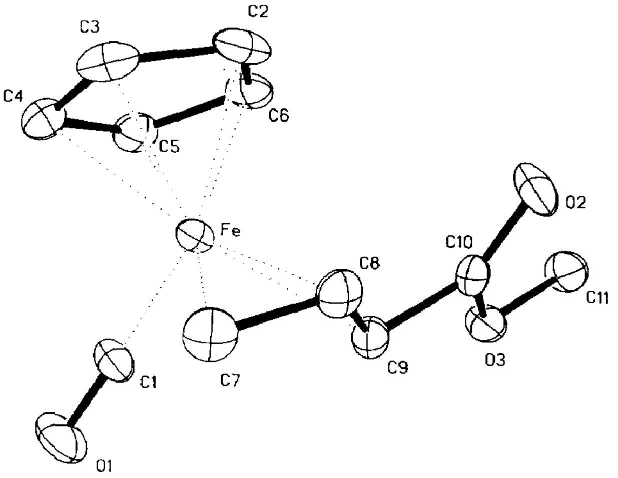


Fig. 1. Molecular structure of complex **2**.

The molecular structure of **2** is shown in Figure 1. The atomic coordinates, bond distances and angles are listed in Tables 1 and 2. The coordination geometry about the iron atom approximates a trigonal plane with the carbonyl, cyclopentadienyl, and allyl groups occupying the three coordination sites, if the cyclopentadienyl and allyl groups are regarded as unidentate ligands. The L–Fe–L angles are 123.5(2)°, 109.4(2)° and 126.9(2)° for Cp–Fe–C(1), C(1)–Fe–C(8) and Cp–Fe–C(8) respectively (Cp is the centroid of the cyclopentadienyl group). The five carbons of the cyclopentadienyl group lie 2.063–2.127 Å away from the Cp group. These values are comparable to those of CpFe(CO)(η^3-pentadienyl) [3c]. The molecule has the *exo* conformation. The allyl ester is bonded to the iron atom in an asymmetric allyl fashion with Fe–C(7) 2.127(4), Fe–C(8) 2.013(4), and Fe–C(9) 2.107(4) Å. The

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times 10^3$) [a]

	x	*y*	*z*	*U*(eq)
Fe	8448(1)	1056(1)	8340(1)	37(1)
O(1)	12016(3)	697(4)	8330(3)	82(1)
O(2)	5375(3)	−1708(3)	8481(2)	70(1)
O(3)	7703(3)	−2834(3)	9031(2)	54(1)
C(1)	10599(5)	808(4)	8326(3)	49(1)
C(2)	6217(5)	1875(5)	8753(3)	63(2)
C(3)	7211(6)	2968(5)	8478(3)	66(2)
C(4)	8681(5)	2950(4)	9060(3)	60(1)
C(5)	8602(5)	1831(5)	9716(3)	56(1)
C(6)	7075(5)	1160(5)	9536(3)	58(1)
C(7)	8279(6)	990(5)	6824(3)	60(1)
C(8)	7268(5)	−37(4)	7259(3)	52(1)
C(9)	8012(5)	−1057(4)	7902(3)	46(1)
C(10)	6862(5)	−1872(4)	8476(3)	48(1)
C(11)	6725(6)	−3633(5)	9663(3)	64(2)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

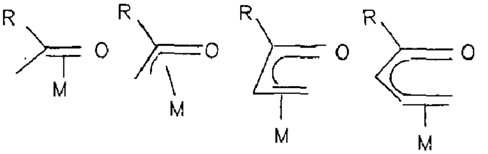
Table 2

Bond lengths (Å) and bond angles (°)

Fe-C(1)	1.745 (4)	Fe-C(2)	2.075 (4)
Fe-C(3)	2.075 (5)	Fe-C(4)	2.054 (4)
Fe-C(5)	2.063 (4)	Fe-C(6)	2.083 (4)
Fe-C(7)	2.127 (4)	Fe-C(8)	2.013 (4)
Fe-C(9)	2.107 (4)	O(1)-C(1)	1.143 (5)
O(2)-C(10)	1.205 (4)	O(3)-C(10)	1.345 (4)
O(3)-C(11)	1.443 (6)	C(2)-C(3)	1.377 (7)
C(2)-C(6)	1.422 (6)	C(3)-C(4)	1.384 (6)
C(4)-C(5)	1.406 (6)	C(5)-C(6)	1.387 (6)
C(7)-C(8)	1.430 (6)	C(8)-C(9)	1.421 (5)
C(9)-C(10)	1.486 (5)		
C(1)-Fe-C(2)	158.5(2)	C(1)-Fe-C(3)	126.8(2)
C(2)-Fe-C(3)	38.8(2)	C(1)-Fe-C(4)	94.0(2)
C(2)-Fe-C(4)	65.6(2)	C(3)-Fe-C(4)	39.2(2)
C(1)-Fe-C(5)	94.0(2)	C(2)-Fe-C(5)	66.2(2)
C(3)-Fe-C(5)	66.4(2)	C(4)-Fe-C(5)	40.0(2)
C(1)-Fe-C(6)	127.0(2)	C(2)-Fe-C(6)	40.0(2)
C(3)-Fe-C(6)	66.2(2)	C(4)-Fe-C(6)	66.1(2)
C(5)-Fe-C(6)	39.1(2)	C(1)-Fe-C(7)	88.4(2)
C(2)-Fe-C(7)	107.5(2)	C(3)-Fe-C(7)	97.2(2)
C(4)-Fe-C(7)	121.0(2)	C(5)-Fe-C(7)	160.9(2)
C(6)-Fe-C(7)	144.4(2)	C(1)-Fe-C(8)	109.4(2)
C(2)-Fe-C(8)	92.0(2)	C(3)-Fe-C(8)	108.3(2)
C(4)-Fe-C(8)	146.8(2)	C(5)-Fe-C(8)	151.7(2)
C(6)-Fe-C(8)	112.7(2)	C(7)-Fe-C(8)	40.3(2)
C(1)-Fe-C(9)	90.7(2)	C(2)-Fe-C(9)	107.8(2)
C(3)-Fe-C(9)	141.1(2)	C(4)-Fe-C(9)	166.7(2)
C(5)-Fe-C(9)	127.3(2)	C(6)-Fe-C(9)	101.2(2)
C(7)-Fe-C(9)	71.5(2)	C(8)-Fe-C(9)	40.3(1)
C(10)-O(3)-C(11)	115.9(3)	Fe-C(1)-O(1)	177.4(4)
Fe-C(2)-C(3)	70.6(3)	Fe-C(2)-C(6)	70.3(2)
C(3)-C(2)-C(6)	108.4(4)	Fe-C(3)-C(2)	70.6(3)
Fe-C(3)-C(4)	69.6(3)	C(2)-C(3)-C(4)	108.1(4)
Fe-C(4)-C(3)	71.2(3)	Fe-C(4)-C(5)	70.3(2)
C(3)-C(4)-C(5)	108.5(4)	Fe-C(5)-C(4)	69.7(2)
Fe-C(5)-C(6)	71.2(2)	C(4)-C(5)-C(6)	107.8(3)
Fe-C(6)-C(2)	69.7(2)	Fe-C(6)-C(5)	69.7(2)
C(2)-C(6)-C(5)	107.1(4)	Fe-C(7)-C(8)	65.6(2)
Fe-C(8)-C(7)	74.1(2)	Fe-C(8)-C(9)	73.4(2)
C(7)-C(8)-C(9)	120.4(4)	Fe-C(9)-C(8)	66.3(2)
Fe-C(9)-C(10)	115.3(3)	C(8)-C(9)-C(10)	116.5(3)
O(2)-C(10)-O(3)	122.5(4)	O(2)-C(10)-C(9)	126.5(4)
O(3)-C(10)-C(9)	111.0(3)		

mouth of the allyl moiety faces away from the cyclopentadienyl group and is aligned with the CO group. A similar stereochemical arrangement is present in CpFe(CO)(η^3-2,4-hexadien-1-yl) [3c]. The ester group of the η^3-ligand points away from the rest of the complex, so minimizing steric hindrance. The C(8)-C(9) bond lies *trans* to the C(10)-O(3) bond and *cis* to the C(10)-O(2) bond. The bond distances C(10)-O(3) (1.345(4) Å), and C(10)-O(2) (1.205(4) Å) reflect single and double bonds, respectively. These bond distances do not show a delocalization pattern within the enonyl ligand. The atoms on the η^3-enonyl ligand are quite planar. The dihedral angle between the plane (O(2), C(10), C(9)) and the allylic plane (C(7), C(8), C(9)) is 14.2(3)°, whereas the dihedral angle between the plane (C(9), C(10), O(3)) and allylic plane (C(7), C(8), C(9)) is 13.6(3)°.

In our previous paper [3], we have shown that the $\eta^3 \rightarrow \eta^5$ transformation is feasible in the pentadienyl system. Neither thermal activation nor photolytic activation induce $\eta^3 \rightarrow \eta^5$ conversion in **2**. A solution of **2** in toluene under reflux yielded no corresponding η^5-oxapentadienyl compounds. Irradiation of **2** in benzene solution in a vacuum-sealed pyrex tube gave a precipitate of composition. The CO group of **2** can be readily lost. Irradiation of **2** in the presence of phosphine ligands R_3P ($R_3P = PMe_3$, $P(OCH_3)_3$) gives the phosphine derivatives $CpFe(R_3P)(\eta^3\text{-}CH_2{\cdots}CH{\cdots}CH\text{-}CO\text{-}OCH_3)$ ($R_3P = PMe_3$ (**3**), $P(OCH_3)_3$ (**4**)) in high yields. Compounds **3** and **4** were obtained as red crystals after recrystallization from their saturated solutions in pentane. The crystals are fairly stable to air. Elemental analysis and the mass spectra are consistent with our formulations. Only one isomer was detected in solutions of each compound as revealed by the ^{1}H NMR spectra. A *syn*-W-configuration is assigned to the enolate ligand on the basis of its ^{1}H NMR coupling constants. **3** has been found to be the *exo* conformer, and **4** the *endo* conformer by comparison of their ^{1}H NMR data with those of **2**. The chemical shifts of the H^2 and H^3 protons in both **3** and **4** are comparable to those of **2**. Moreover, the proton resonances of H^1 and H^4 of **3** and **4** lie about 0.5–1.5 ppm more upfield than those of **2** [3b]. The *endo* isomer is expected to show greater upfield chemical shifts of the H^2 and H^3 protons and greater downfield chemical shifts of H^1 and H^4 protons than those of the *exo* isomer [6]. In our previous paper [3c], we have shown that protonation of an η^3-pentadienyl complex gives an η^4-diene cation. The protonation site is the α-carbon of the dienyl ligand. The addition of HPF_6 to solutions of **2**, **3** or **4**, however, fails to yield the corresponding $CpFe(L)(\eta^4\text{-}CH_3\text{-}CH{=}CH\text{-}CO\text{-}OCH_3)$ (L = CO, $P(OCH_3)_3$, PPh_3). For the iron system, many η^4-Fe^0-enone complexes have been reported [7], but the failure to obtain the corresponding Fe^{II} complexes can be attributed to the electron deficiency of the Fe^{II} ion. Organic carbonyls bonded to the metal in π-fashion have been reported to have the following geometries:



in addition to the η^5-1-oxa-pentadienyl structure [7–9]. One common feature of these complexes is that the metals are in a low oxidation state because the carbonyl group is a very good π acceptor. The degree of the electron transfer from the metal orbital to the vacant $\pi^\star$ orbital plays a key role in metal–ligand bonding. Similarly, the absence of the $\eta^3 \rightarrow \eta^5$ transformation in **2** can be attributed to the electron deficiency of the Fe^{II} ion. Other systems involving the synthesis of η^5-oxapentadienyl complexes bonded to low-valence metals are currently under investigation.

Experimental section

All operations were performed under argon in a Schlenk apparatus or in a glovebox. The solvents diethyl ether, tetrahydrofuran (THF) and pentane were dried with sodium/benzophenone and distilled before use.

All ^1H (100 and 400 MHz) and ^{13}C (100 MHz) NMR were recorded on either a JEOL FX-100 or a Bruker AM-400 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 781 spectrophotometer. Microanalyses were performed at the microanalytical laboratory, National Taiwan University.

Preparation of $CpFe(CO)_2(\eta^1\text{-}CH_2\text{-}CH{=}CH\text{-}CO\text{-}OCH_3)$ (1)

A solution (50 ml) of $CpFe(CO)_2Na$ (1.56 g, 8.4 mmol) in THF (50 ml) was added dropwise to methyl 4-chloro-2-butenoate (1.49 g, 10.4 mmol) in THF (20 ml) at −78 °C and the mixture was stirred for 4 h. After the insoluble sodium chloride was filtered off, the solvent was evaporated to dryness in vacuo to yield a dark red residue. This residue was extracted twice with 20 ml ether, filtered and evaporated to dryness. The residue was chromatographed on a neutral alumina column (50 g) at 23 °C with ether as the eluant. The purple band, that was eluted first, was identified as $Cp_2Fe_2(CO)_4$. The second, a gold-yellow band, was collected, the solution was evaporated to dryness, to leave the yellow oil of **1** (0.65 g, 2.45 mmol). Anal. Found: C, 52.25; H, 4.24. $C_{12}/H_{12}FeO_4$ calcd.: C, 52.17; H, 4.34%; . Mass spectrum (12 eV): m/e 276(M^+), 248($M^+ - CO$), 220($M^+ - 2CO$), 177($M^+ - C_5H_7O_2$). IR spectrum (ether): ν(CO) 2014(vs) 1956(vs) and 1699 cm^{-1}(s); ν(C=C) 1608 cm^{-1} (w). ^1H NMR (100 MHz, $CDCl_3$). δ 2.02(2H, d, H^1H^2), 3.62(3H, s, O–CH_3), 4.67(5H, s, C_5H_5), 5,50(1H, d, H^4), 7.23(1H, m, H^3), J_{13} 9.5, J_{12} 1.2, J_{34} 15 Hz.

Preparation of $CpFe(CO)(\eta^3\text{-}CH_2\text{⋯}CH\text{⋯}CH\text{-}CO\text{-}OCH_3)$ (2)

A solution of **1** (0.5 g, 1.81 mmol) in ether (25 ml), in a vacuum-sealed tube was irradiated with a 400-W mercury lamp at −20 °C for 6 h. After removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column (30 g, Merck) at 25 °C with ether as the eluant. An orange band, that was eluted first and identified as **2**, was collected and evaporated to dryness. The orange residue was dissolved in pentane and cooled to 4 °C to yield dark red cyrstals of **2** (0.38 g, 1.53 mmol). Anal. Found: C, 53.26; H, 4.92. $C_{11}H_{12}FeO_3$ calcd.: C, 53.27; H, 4.84%. Mass spectrum (12 eV): m/e 248(M^+), 220($M^+ - CO$). IR spectrum (ether) ν(CO): 1953(vs) and 1698(vs) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.90(1H, d, H^1), 1.19(1H, d, H^4) 2.96(1H, d, H^2), 3.65(3H, s, OCH_3), 4.40(5H, s, C_5H_5), 5.44(1H, ddd, H^3), J_{13} 11.37, J_{34} 9.78, J_{23} 7.25 Hz. $^{13}C\{H\}$ NMR(100 MHz, $CDCl_3$): δ 34.76(CH_2), 38.44(CH^4), 59.68(O–CH_3), 77.1(CH^3), 80.2(C_5H_5), 177.1(*C*O–OCH_3), 220.9(Fe–CO).

Preparation of $CpFe(P(CH_3)_3)(\eta^3\text{-}CH_2\text{⋯}CH\text{⋯}CH\text{-}CO\text{-}OCH_3)$ (3)

A mixture of $P(CH_3)_3$ (0.19 g, 1.3 mmol) and **2** (0.5 g, 0.20 mmol) in a vacuum-sealed tube was irradiated with a 400-W mercury lamp at −20 °C for 6 h. After removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column (30 g, Merck) with ether as the eluant. An orange band was eluted and identified as **3**. A brown purple band of $Cp_2Fe(CO)_4$ remained in the top portion of the column. Recrystallization from pentane at −20 °C gave red crystals (0.38 g, 1.29 mmol). Anal. Found: C, 52.88; H, 7.19. $C_{13}H_{21}FeO_2P$ calcd.: C, 52.70; H, 7.09%. Mass spectrum (12 eV): *m/e*: 296(M^+), 220($M^+ -$ PMe_3). IR spectrum (ether) ν(CO): 1696(s)cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ -0.22(1H, dd, H^1), -0.11(1H, dd, H^4), 1.24(9H, d, PMe_3), 2.62(1H, d, H^2), 3.12(3H, S, OCH_3), 3.95(5H, S, C_5H_5), 5.54(1H, m, H^3), J_{13} 10.5, J_{34} 9.0, J_{23} 5.8, $J(H^1P) = 17.0$, $J(H^4P)$ 14.6, $J(PMe_3$,P–H) 8.0 Hz. ^{13}C{H} NMR (400 MHz, $CDCl_3$): δ 29.54(CH^1H^2), 18.6(d, *J* 18 Hz, PMe_3), 35.6(CH^4), 50.4(OCH_3), 71.98(CH^3), 75.6(C_5H_5), 160.0(*CO*–OCH_3).

Preparation of $CpFe(P(OCH_3)_3)(\eta^3\text{-}CH_2\cdots CH\cdots CH\text{-}CO\text{-}OCH_3)$ *(4)*

This complex was prepared similarly by photolytic reaction of $P(OCH_3)_3$ and **2** in a vacuum-sealed tube. The yield was 52%. Anal. Found: C, 45.54; H, 6.24. $C_{13}H_{21}FeO_5P$ calcd.: C, 45.34; H, 6.10%. Mass spectrum (12 eV): *m/e* 344(M^+), 220($M^+ - P(OCH_3)_3$). IR spectrum (ether) ν(CO): 1697(s)cm^{-1}. ^{1}H NMR (400

Table 3

Summary of crystal data and intensity collection

Empirical formula	$C_{11}H_{12}O_3Fe$
Color; habit	orange; columnar
Crystal size (mm^3)	0.40 mm × 0.48 mm × 0.58 mm
Space group	monoclinic, $P2_1/c$
Unit cell dimensions	$a = 8.034(2)$ Å $b = 9.430(3)$ Å $c = 14.058(4)$ Å $\beta = 94.42(2)°$
Volume	1061.9(5) Å^3
Formula units/cell	4
Formula weight	248.1 AMU
Density (calc.)	1.552 g/cm^3
Absorption coefficient	1.400 mm^{-1}
F(000)	512 e$^-$
Diffractometer used	Nicolet R3m/V
Radiation	Mo-K_α ($\lambda = 0.71073$ Å)
Temperature	23° C.
Monochromator	Highly oriented graphite crystal
2θ range	2.0 to 50.0°
Scan type	$\theta/2\theta$
Scan speed	Variable; 2.93 to 14.65°/min.
Scan range	1.20° plus K_α-separation
Standard reflections	3 measured every 50 reflections
Index ranges	$-9 \leq h \leq 9$, $-1 \leq k \leq 11$, $-16 \leq l \leq 1$
Reflections collected	2228 (1687 > $3\sigma(I)$)
Unique reflections	1880 (1477 > $3\sigma(I)$)
Hydrogen atoms	Riding model, fixed isotropic *U*
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$
Final residuals (obs. data)	$R = 3.49\%$, $R_w = 4.05\%$
Goodness-of-fit	1.44
Largest and mean Δ/σ	0.037, −0.001
Data-to-parameter ratio	10.9 : 1
Largest difference peak	0.60 e$^-$/Å^3

MHz, $CDCl_3$): δ 0.27(1H, dd, H^1), 0.53(1H, dd, H^4), 2.66(1H, d, H^2), 3.60(3H, s, $-O-CH_3$), 3.53(9H, d, $P(OCH_3)_3$, 4.07 (5H, s, C_5H_5), 5.50(1H, m, H^3), J_{13} 10.3, J_{34} 9.4 J_{23} 7.4, $J(H^1P)$ 16.1, $J(H^2P)$ 13.0, $J(P-OCH_3)$ 12 Hz $^{13}C\{H\}$ NMR (400 MHz, $CDCl_3$): δ 20.6 (CH_2). 35.4(CH^4), 50.5($O-CH_3$), 50.2, (d, J 40 Hz, $P-OCH_3$), 70.0(CH^3), 76.4(C_5H_5), 178.4($CO-OCH_3$).

Crystal data for 2

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with lattice parameters: a 8.034(2), b 9.430(3), c 14.058(4) Å, β 94.42(2)°, Molecular weight 248.1, D(calcd.) 1.552 g/cm^3 and $Z = 4$. The structure was solved and refined to R and R_w values 0.0349 and 0.0405, respectively, for 1477 reflections.

X-ray diffraction study. The crystal and molecular structure determination of compound **2** was carried out. Crystal data and details of the intensity data collection are summarized in Table 3. Unit cell dimensions were determined from a least-squares refinement of fifteen carefully centered reflections (2θ ranging from 8.03° to 27.71°). The intensity data were corrected for Lorentz and polarization effects. Five reflections with 2θ angles ranging from 13.04° to 44.24° and their χ angles near 90° were scanned in 100 steps of χ, and the crystal showed transmission factors varying from 0.731 to 0.929, thus, empirical corrections were made for absorption.

The space group $P2_1/c$ was determined from the systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$. Atomic scattering factors were obtained from International Tables for X-ray Crystallography [10]. The structure was solved by direct methods. All the nonhydrogen atoms were located from E maps and then anisotropically refined by full matrix least-squares. The positions of all hydrogen atoms were calculated and refined isotropically. The final difference map showed no other features with electron densities of less than 0.60 e-Å^{-3}. All calculations were performed on a MicroVAX II based Nicolet SHELXTL PLUS system [11]. The positional and thermal parameters of all the nonhydrogen atoms are given in Table 2. Tables of anisotropic thermal parameters, hydrogen atom parameters, and structure factors are available from the authors.

References

1 A few 1-oxapentadienyl complexes have been reported, see (a) R.L. Bennett and M.I. Bruce, Aust. J. Chem., 28 (1975) 1141; (b) M. Green and R.I. Hancock, J. Chem. Soc., A. (1968) 109; (c) D. Baudry, J.C. Daran, U. Y. Dromzee, M. Ephritikhine, H. Felkin, Y. Jeannin, and J. Zakrzewski, J. Chem. Soc., Chem. Commun., (1983), 813; (d) C. White, S.J. Thompson and P.M. Maitlis, J. Organomet. Chem., 134 (1977) 319.

2 P. Powell, Adv. Organomet. Chem., 26 (1986) 125.

3 (a) T.W. Lee and R.S. Liu, Organometallics, 7 (1988) 878; (b) G.H. Lee, S.M. Peng, T.W. Lee and R.S. Liu, ibid., 7 (1988) 2378; (c) G.H. Lee, S.M. Peng, S.F. Lush, M.Y. Liao and R.S. Liu, ibid., 6 (1987) 2094; (d) S.F. Lush and R.S. Liu, ibid., 5 (1986) 1908; (e) T.W. Lee and R.S. Liu, J. Organomet. Chem., 320 (1987) 211.

4 (a) R.D. Ernst, Acc. Chem. Res., 18 (1985) 56; (b) H. Yasuda, A. Nakamura, J. Organomet. Chem., 285 (1985) 15.

5 H.O. House, V.K. Jones and J.A. Frank, J. Org. Chem., 29 (1964) 3327.

6 R.W. Fish, W.P. Giering, D. Marten and M. Rosenblum, J. Organomet. Chem., 105 (1976) 101.

7 For examples see (a) C. Cardaci, G. Bellachioma, J. Chem. Soc. Dalton Trans., (1976) 1735; (b) A.M. Brodie, B.F.G. Johnson, P.L. Josty and J. Lewis, ibid., (1972) 2031.

8 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, Principles and Application of Organotransition Metal Chemistry, University Science, 1987.

9 J.J. Doney, R.G. Bergman and C.H. Heathcock, J. Am. Chem. So., 107 (1985) 3724.

10 International Tables for X-ray Crystallography (1974), Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht).

11 Sheldrick., G.M. SHELXTL PLUS User Manual (1986). Nicolet XRD Corporation, Madison, Wisconsin, U.S.A.