GROUP 6 METAL MIXED CARBONYL COMPLEXES WITH A CARBOXYFERROCENYLPHOSPHANE

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Received November 2, 2000
Accepted December 18, 2000

A series of complexes $[M(CO)_5(Hdpf\text{-}\kappa P)]$, where M = Cr (**1**), Mo (**2**) and W (**3**), and Hdpf is 1′-(diphenylphosphanyl)ferrocenecarboxylic acid, was obtained by thermally-induced (**2**) or photochemically-assisted (**1**, **3**) displacement of carbon monoxide with Hdpf from the corresponding hexacarbonyl complexes. The complexes were characterized by NMR, UV-VIS and IR spectroscopies and further studied by cyclic voltammetry. The solid-state structure of complex **1** has been determined by single-crystal X-ray diffraction.

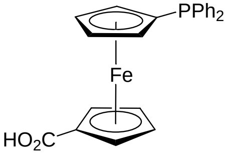
Key words: Chromium; Molybdenum; Tungsten; Ferrocenes; Phosphanes; Phosphine ligands; Carbonyl complexes; Electrochemistry; X-Ray diffraction.

Ferrocene derivatives possessing donor groups were studied as ligands in coordination compounds ever since the discovery of ferrocene – not only because of the unique properties of the ferrocene building block (flexible in rotation along the axis connecting cyclopentadienyl-ring centroids but rather rigid in tilting the cyclopentadienyl rings) but also due to its electronic properties (electron-releasing group) and the possibility of following changes in the structure of ferrocene derivatives by a variety of methods ranging from traditional spectral methods to electrochemistry and Mössbauer spectroscopy. Recent interest in ferrocene derivatives is mainly focused on the development of ferrocene-based ligands with planar, central or combined chirality for homogeneous[1] or immobilized catalysts[2], since they often proved superior to traditional components of catalytic systems.

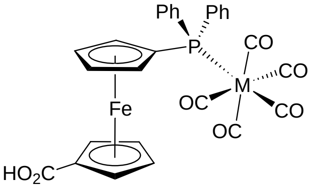
In view of these facts, it appears natural that there is a vast number of reports on transition metal complexes with ferrocene ligands in the literature. As far as group 6 carbonyls are concerned, the most frequently studied are undoubtedly mixed carbonyl complexes with 1,1′-bis(diphenylphosphanyl)ferrocene (dppf), where the ferrocene ligand acts as a simple

P-donor, *P*,*P′*-chelating[3] or μ-*P*,*P′*-bridging ligand[4]. Another example represents a series of complexes $[M(CO)_{6-x}L_x]$ (M = Cr, Mo and W; x = 1, 2) bearing phosphanes PFc_yPh_{3-y} (Fc = ferrocenyl, y = 1–3) as the ligand L (ref.[5]). Oligometallic complexes resulting from coordination of a ferrocene donor to a group 6 metal are usually studied with regard to possible electronic interaction of the ferrocene unit with the other coordination centre(s) but they may also serve as rather simple model compounds for complexes involved in molybdenum- and tungsten-catalyzed nucleophilic allylic substitution[6], which are usually generated only *in situ* from $[M(CO)_3L_3]$ precursors with good leaving ligands (*e.g.*, L_3 = 3 MeCN or η^6-cycloheptatriene) and suitable (chiral) ligands.

As the number of complexes with ferrocene ligands possessing other donor group(s) besides the phosphane moiety is still rather limited, we decided to study a series of complexes $[M(CO)_5L]$ (M = Cr, Mo and W) with 1′-(diphenylphosphanyl)ferrocenecarboxylic acid[7] (Hdpf) as a potential multifunctional hybrid donor. In this paper, we report the preparation and spectral and cyclovoltammetric study of a series of complexes $[M(CO)_5(\text{Hdpf-}\kappa P)]$, where M = Cr, Mo and W. We also present crystal structure of the chromium(0) representative.



Hdpf



1-3

	M
1	Cr
2	Mo
3	W

RESULTS AND DISCUSSION

Synthesis and Spectra

Complex $[Mo(CO)_5(\text{Hdpf-}\kappa P)]$ (**2**) has been synthesized by displacement of CO in the corresponding hexacarbonyl with Hdpf in refluxing xylenes (Eq. (*1*)). The course of the substitution reaction was followed by IR spectroscopy. As an illustration, Fig. 1 shows changes of IR spectra in the carbonyl stretching region for a model experiment in which stoichiometric amounts of $[Mo(CO)_6]$ and Hdpf were reacted in refluxing *p*-xylene ($c = 2 \cdot 10^{-3}$ mol dm^{-3}).

With $[Cr(CO)_6]$ and $[W(CO)_6]$, a similar direct substitution did not afford analogous mixed phosphane carbonyl complexes even after a much longer heating; instead, the reaction components decomposed extensively. Indeed, complexes $[Cr(CO)_5(Hdpf\text{-}\kappa P)]$ (**1**) and $[W(CO)_5(Hdpf\text{-}\kappa P)]$ (**3**) were obtained in good yields from the reaction of Hdpf with complexes $[M(CO)_5(THF)]$ (M = Cr and W) generated *in situ* by irradiating THF solutions of the hexacarbonyls with a mercury lamp (Eq. (*2*)). Although the

$$[Mo(CO)_6] + Hdpf \xrightarrow[\text{xylenes}]{\text{heating}} \mathbf{2} + CO \qquad \text{Eq. } (\mathit{1})$$

$$[M(CO)_6] + THF \xrightarrow[-CO]{\text{irradiation}} [M(CO)_5(THF)] \xrightarrow{\text{Hdpf}} [M(CO)_5(Hdpf)] \qquad \text{Eq. } (\mathit{2})$$

1 (M = Cr)
3 (M = W)

complexes **1**–**3** are stable enough to be isolated in pure form and characterized, they decompose slowly in air and daylight. The inherent instability of carbonyl complexes under ambient conditions is in the case of compounds **1**–**3** further enhanced by the presence of carboxyl group. *N.B.* $[Mo(CO)_6]$ was shown to react with weak acids such as benzoic acid[8a,8b] or even pentane-2,3-dione[8c] under evolution of carbon monoxide and concurrent oxidation of the zerovalent metal to provide benzoato and pentane-2,3-dionato molybdenum complexes, respectively. Similarly, the reaction of $[Cr(CO)_6]$ with arenes in the presence of acetic acid as the catalyst produces chromium(II) acetate as a by-product[8d]. The arene tricarbonylchromium(0) complex $[Cr(\eta^6\text{-}C_6H_5CO_2H)(CO)_3]$ is not accessible by traditional direct replacement of CO ligands in $[Cr(CO)_6]$ by benzoic acid; the carboxyl group has to be protected prior to the reaction as an ester[8e,8f].

In the present case, the decomposition of the parent carbonyls by Hdpf as an acid undoubtedly accounts for a rather low stability of complexes **1**–**3**. However, it may be reasoned that once the the Cr–P bond is formed, the association of the carboxyl group into H-bonded dimers and a long distance between the metal centre and carboxyl group of its own molecule (see below) decrease the decomposition rate.

Solid-state IR spectra of complexes **1**–**3** in the carbonyl stretching region are very similar, displaying five bands between *ca* 1 900 and 2 070 cm^{-1} (the shoulder at *ca* 1 875 cm^{-1} is not sufficiently resolved in the spectrum of compound **2**). The number of bands exceeds that expected for an idealized C_{4v} symmetry due to lowered local symmetry and, consequently, to an activation of forbidden bands and removal of their degeneracy in a solution and in the solid state. As a result of an enhanced π-back M → CO donation upon replacement of one carbonyl ligand with a better phosphane donor, the ν_{CO} bands are shifted to lower wavenumbers compared with the parent hexacarbonyls[9]. Another diagnostic feature in the IR spectra is the presence of bands at *ca* 1 299 and 1 678 cm^{-1} which arise from symmetric and asymmetric vibrations of the protonated carboxyl group, respectively. A comparison of their position with that of analogous bands in the spectrum of Hdpf (1 294 and 1 666 cm^{-1}) implies that the carboxyl group remains undissociated and does not coordinate metal centre of its own or a neighbouring molecule; however, it very likely participates in hydrogen bonding to the carboxyl group of a neigbouring complex molecule in the solid state similarly to the structure of uncoordinated Hdpf. This assumption is further corroborated by the chemical shift of the carboxyl carbon atom in ^{13}C NMR spectra of **1**–**3** (δ_C 176.2–176.9 *vs* 177.2 for Hdpf) and was unequivocally confirmed by X-ray crystallography for complex **1**. ^{31}P NMR coordination shifts ($\Delta = \delta_{complex} - \delta_{ligand}$; Δ_P: 65.3, **1**; 45.8, **2**; 28.5, **3**) follow a trend typical

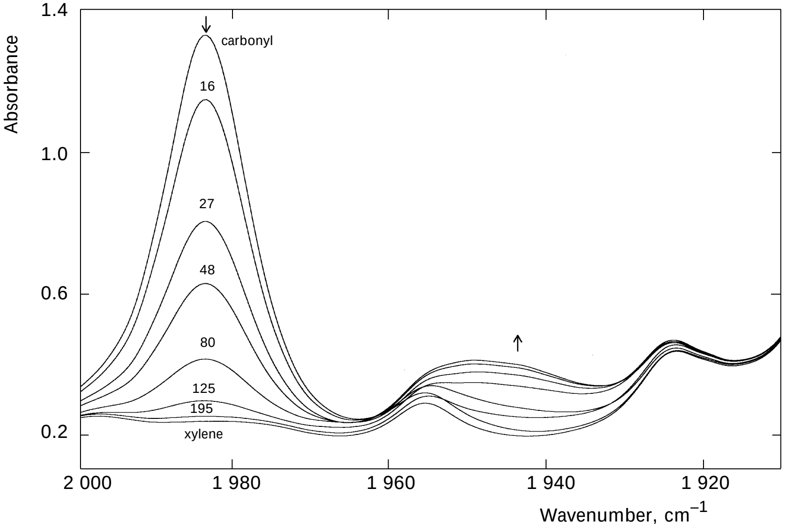


FIG. 1

IR spectra of a $[Mo(CO)_6]$–Hdpf mixture during the substitution reaction in refluxing *p*-xylene. The numbers above the curves correspond to the reaction time (in minutes after mixing the reaction components); the labels “xylene” and “carbonyl” denote spectra of the pure solvent (background) and the hexacarbonyl dissolved in *p*-xylene (without Hdpf), respectively in series of monophosphane complexes[10] $[M(CO)_5(PR_3)]$ while the actual position of the signals in the spectra of **1**–**3** is similar to that of their dppf analogues $[M(CO)_5\{Fe(\eta^5\text{-}C_5H_4PPh_2)_2\text{-}\kappa P\}]$ (M = Cr, Mo and W)[3].

Electrochemistry

The three mixed carbonyl-phosphane complexes **1**–**3** were studied by cyclic voltammetry in dichloromethane solution (Table I, Fig. 2). Upon increasing the potential, the complexes first undergo a reversible one-electron oxidation of the ferrocene ligand followed by a group-6 metal-centered redox process. The redox potential of the ferrocene/ferrocenium couple is independent of the central atom ($E_{1/2}$ = 0.50 V *vs* the ferrocene/ferrocenium standard; $E_{1/2}$ is defined as $1/2(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} denote the anodic and cathodic peak potentials) but, due to an electron density transfer from the ligand to the central atom, it is shifted by *ca* 180 mV to higher potentials compared to free Hdpf (ref.[7]). The same coordination shift was observed for the analogous complexes $[M(CO)_5(FcPPh_2)]$ (M = Mo and W): +0.17 V (Mo) and +0.19 V (W) *vs* free $FcPPh_2$ (ref.[5b]).

The complete reversibility of the first wave indicates that the complexes are stable in both the usual and oxidised form under the conditions of measurement (scan rate 100 mV s^{-1}); contrary to oxidations of free Hdpf and its mercury(II) complexes[11] that are immediately followed by chemical decay of the ferrocenium species (EC process).

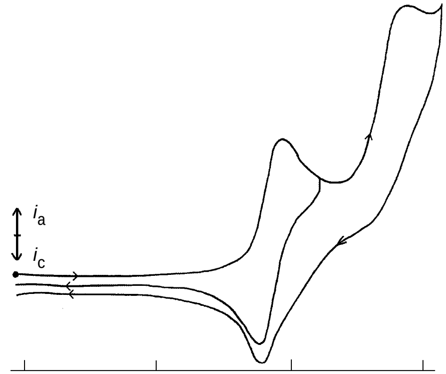


FIG. 2
Cyclic voltammogram of compound **2** (see text for conditions)

The second wave in cyclovoltammograms of compounds **1**–**3** has been assigned to group 6 metal oxidation. In the case of the chromium complex **1**, the wave is reversible and appears at $E_{1/2}$ 0.85 V (*vs* ferrocene). For compounds **2** and **3**, the second wave is shifted to a more positive potential (E_{pa} 0.98 V for both), close to the wave observed for their $FcPPh_2$ analogues (E_{pa} *ca* 1.04 V *vs* ferrocene/ferrocenium). However, it is difficult to judge the exact nature of the second wave in the latter case since it is located at the onset of base electrolyte decomposition. Hence, the reduction counterpeaks (if any) are not resolved enough to enable determination of E_{pc}. Such a behaviour corresponds well to that of analogous compounds: a reversible one-electron oxidation was reported[12] for $[Cr(CO)_5(PPh_3)]$ whilst an irreversible multielectron process was observed for the mentioned $[M(CO)_5(FcPPh_2)]$ (M = Mo and W) complexes.

Crystal and Molecular Structure of Complex 1

The solid-state structure of complex **1** was determined by single-crystal X-ray diffraction. A labelled diagram is shown in Fig. 3 and the selected geometric parameters are given in Table II. As expected, the chromium(0) centre in the structure of **1** is octahedrally coordinated. Besides non-equal distances of the donor atoms from the metal centre (Cr–P *vs* five Cr–C bonds), the only other deformation of the coordination polyhedron ap-

TABLE I
Cyclic voltammetric data[a] for complexes **1**–**3**

Complex	1st wave		2nd wave	
	E_{pa}, V	E_{pc}, V	E_{pa}, V	E_{pc}, V
Hdpf	0.28	0.36	–	
1	0.46	0.54	0.81	0.89
2	0.46	0.53	0.98[b]	
3	0.46	0.53	0.98[b]	

[a] Conditions: platium disc electrode, 100 mV s^{-1} scan rate; measured for $5 \cdot 10^{-4}$ M solutions in 0.05 M Bu_4NPF_6 in CH_2Cl_2 at room temperature. Potentials are given relative to the redox potential of the internal ferrocene/ferrocenium couple. [b] No counter-wave detected.

pears to be a very slight bending along the P–C(28) interconnection: carbon atoms C(26) and C(27) are bent outwards the ferrocene unit whereas the other atoms in the plane passing through the chromium centre, C(24) and C(25), are inclined towards the phosphane ligand. Owing to an increased Cr → *trans*-C back donation (*trans*-influence of a phosphane is lower than that of the CO ligand), the Cr–CO bond *trans* to the phosphane donor (Cr–C(28)) is by *ca* 0.03 Å (or 10 times esd) shorter than the four remaning Cr–CO bonds. However, the CrC–O bond lengths are rather uniform. Similar features can be observed in the structure of related complexes $[Cr(CO)_5(PR_3)]$, where R = Me (ref.[13]) and Ph (ref.[14]). The Cr–P bond length in **1** (2.4130(6) Å) is similar to that in $[Cr(CO)_5(PPh_3)]$ 2.422(1) or $[\{Cr(CO)_5\}_2(\mu\text{-dppf-}\kappa^2P,P')]$ 2.389(2) Å (ref.[15]) and, in accordance with a stronger donating ability and lower steric demands of PMe_3, longer than that observed for complex $[Cr(CO)_5(PMe_3)]$ (2.3664(2) Å).

A formal replacement of the lone electron pair on the phosphorus atom by the $Cr(CO)_5$ moiety upon coordination does not affect the original pseudotetrahedral arrangement around the phosphorus atom (*cf.* C–P–C angles 100.2(2)–102.4(4)° for Hdpf)[7]. The displacement of the phosphorus

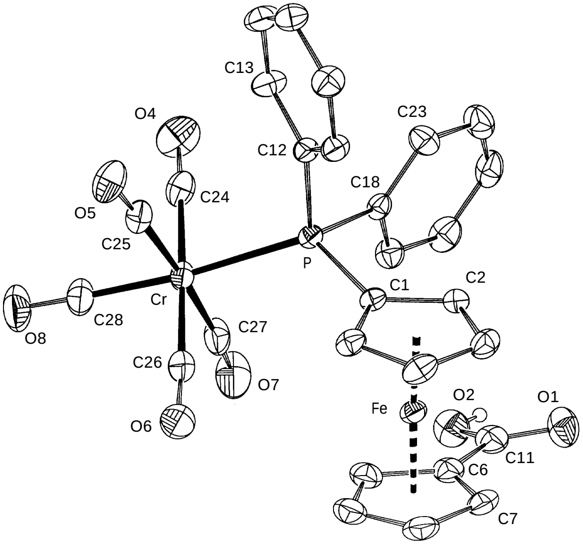


FIG. 3
Molecular structure of complex **1** showing the atom labelling scheme (30% probability level). For clarity, hydrogen atoms except the carboxyl hydrogen atom H(99) were omitted and only the pivot and its adjacent carbon atom of each aromatic ring are labelled

TABLE II
Selected bond distances (Å) and angles, dihedral[a] and torsion angles (°) for complex **1**

Cr–P	2.4130(6)		
Cr–C24	1.888(3)	O4–C24	1.143(3)
Cr–C25	1.907(3)	O5–C25	1.136(3)
Cr–C26	1.904(3)	O6–C26	1.136(3)
Cr–C27	1.884(3)	O7–C27	1.143(3)
Cr–C28	1.863(3)	O8–C28	1.144(3)
P–C01	1.815(2)	O1–C11	1.255(3)
P–C12	1.837(2)	O2–C11	1.288(3)
P–C18	1.837(2)	O2–H99	0.90(4)
C24–Cr–C25	91.0(1)	C01–P–C12	101.35(9)
C24–Cr–C27	89.3(1)	C01–P–C18	99.88(9)
C24–Cr–C28	88.5(1)	C12–P–C18	102.02(9)
C25–Cr–C26	90.7(1)	P–Cr–C01	122.01(7)
C25–Cr–C28	87.3(1)	P–Cr–C18	117.29(6)
C26–Cr–C27	89.0(1)	P-Cr–C12	111.40(7)
C26–Cr–C28	89.7(1)	O1–C11–O2	123.7(2)
C27–Cr–C28	88.5(1)	C11–O2–H99	115(3)
P–Cr–C24	87.90(8)	Cp^P,Cp^C	7.5(1)
P–Cr–C25	89.00(7)	Cp^P,Ph^1	83.45(9)
P–Cr–C26	93.98(8)	Cp^P,Ph^2	81.94(8)
P–Cr–C27	95.31(8)	Ph^1,Ph^2	74.84(8)
Fe–C(Cp) av.	2.05(1)	Cr–C–O av.	177(1)
C–C(Cp) av.	1.420(8)	C–C–Cp(Cp) av.	108.0(7)
C–C(Ph) av.	1.38(1)	C–C–Cp(Ph) av.	120(1)

[a] Least-squares planes are defined as follows: Cp^P: C01–C05, Cp^C: C06–C10, Ph^1: C12–C17, Ph^2: C18–C23.

atom from the least-squares cyclopentadienyl and phenyl ring-planes are 0.335(3), 0.047(3) and 0.103(3) Å for Cp^P, Ph^1 and Ph^2, respectively (see footnote in Table II for definition of the ring planes). Similarly, the ferrocene framework in the carboxyphosphane part remains practically unaffected by coordination. The perpendicular iron-cyclopentadienyl ring centroids are 1.653(1) and 1.656(1) Å for Cp^P and Cp^C rings, respectively. The cyclopentadienyl rings are slightly tilted (dihedral angle Cp^P, Cp^C 7.5(1)°) and unlike the conformation of uncoordinated Hdpf, which is exactly half-way between *anti*-eclipsed and *anti*-stagerred, their conformation is very close to *syn*-eclipsed (torsion angle C(1)–Cg^P–Cg^C–C(6) 68.2(2)°; the ideal value for this conformation is 72°). Similarly to Hdpf itself, the carboxyl group of the ligand participates in double hydrogen bonding to its centrosymmetric counterpart in the unitcell. Parameters of the O(2)–H(99)···$O(1)^i$ (i $1 - x$, $1 - y$, $-z$) hydrogen bonds are as follows (Å and °):

O(2)···$O(1)^i$ 2.653(3)   O(2)–H(99) 0.90(4)
H(99)···$O(1)^i$ 1.76(4)   O(2)–H(99)···$O(1)^i$ 174(3).

The formation of hydrogen bonds very likely causes the conformational change as well as a departure of the carboxyl group from an arrangement coplanar with its parent cyclopentadienyl ring. The dihedral angle of the Cp^C ring and the plane defined by atoms C(11), O(1) and O(2) is 13.4(1)°. Apart from the association into H-bonded dimers, no other intermolecular contacts were detected in the solid-state structure of complex **1**. The distances Cr···O(1) 7.141(2) and Cr···O(2) 5.800(2) Å indicate that the coordinatively saturated chromium(0) centre does not interact with the carboxyl group of the *P*-ligated Hdpf ligand. Any direct Cr···O interaction in the present case is ruled out even if the Cr···O distance becomes shorter by rotating the carboxyl group around the C(6)–C(11) bond. Nevertheless, the long Cr···O distances do not exclude possible interactions to arise in systems resulting from a replacement of the carbonyl ligand(s) by a bulky donor such as a substrate in a complex-catalyzed reaction.

EXPERIMENTAL

General Comments

Syntheses were carried out in argon atmosphere using solvents dried by refluxing with an appropriate drying agent (THF: potassium benzophenone ketyl, xylenes: potassium) and distilled under argon. Dichloromethane for cyclovoltammetric measurements was used as received (Merck, p.a.). Hdpf was prepared by the literature method[7].

NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95; ^{13}C, 100.58 MHz) in $CDCl_3$ solutions at 298 K. Chemical shifts (δ, ppm) are given relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (*J*) are given in Hz. The assignment of NMR signals is based on ^{1}H, ^{13}C{^{1}H}, ^{13}C APT, COSY-90 and ^{13}C HSQC spectra. IR spectra were measured on an FT IR Nicolet Magna 760 instrument (range 400–4 000 cm^{-1}). Solution UV-VIS spectra were measured on a UV 300 Unicam spectrometer (λ_{max} in nm, ε in m^{2} mol^{-1}) in the range 350–1 100 nm. Melting points are uncorrected. Elemental analyses were performed by standard methods. However, the complexes studied are unstable at ambient conditions and decompose partially before analysis, thus giving microanalytical results slightly different from the calculated values even for pure samples.

Electrochemical measurements were carried out on a polarograph PA4 interfaced to a XY Recorder 4103 (Laboratorní přístroje, Prague) with a standard three-electrode system: stationary platinum disc working electrode (0.5 mm diameter), a platinum wire auxiliary electrode and saturated calomel reference electrode in a special compartment separated from the analyzed solution by a bridge filled with a Bu_4NPF_6 solution in dichloromethane to ensure exclusion of water. Cyclic voltammograms were recorded for 5 · 10^{-4} M dichloromethane solutions of the complexes containing 0.05 M Bu_4NPF_6 under argon flow at room temperature and 100 mV s^{-1} scan rate. The potentials are given in volts relative to the redox potential of internal ferrocene/ferrocenium standard.

Syntheses

Pentacarbonyl[1′-(diphenylphosphanyl)ferrocenecarboxylic Acid-κ*P*]chromium(0) (**1**)

A solution of [$Cr(CO)_6$] (220 mg, 1.0 mmol) in THF (100 ml) was irradiated with a high-pressure mercury lamp (125 W, type RKW, Tesla, Czech Republic) at room temperature while the progress of substitution was monitored by IR spectra in the carbonyl stretching region (1 850–2 050 cm^{-1}). When a decrease of the band due to [$Cr(CO)_6$] at 1 978 cm^{-1} ceased (4.5 h), irradiation was terminated and solid Hdpf (104 mg, 0.25 mmol) was added to the resulting yellow solution of [$Cr(CO)_5$(THF)] intermediate. After stirring for 30 min, the solvent was removed *in vacuo* and the orange solid residue was extracted into chloroform. The extract was treated with Celite, filtered and evaporated to dryness. Unreacted [$Cr(CO)_6$] was removed by sublimation in oil-pump vacuum at 50 °C and the remaining crude complex **1** was purified by repeated crystallization by diffusion of hexane into its chloroform solution at 4 °C (four times; removal of phosphane oxide HdpfO). Finally, the crystals formed were filtered off, washed with some hexane–chloroform (5 : 1, v/v) and dried *in vacuo* in the dark to yield pure **1** as a rusty orange crystalline solid. Yield 120 mg (79%), m.p. 189–190 °C (dec.). ^{1}H NMR ($CDCl_3$): 4.18 apparent t, 2 H (C_5H_4C); 4.40 apparent q (C_5H_4P); 4.55 br apparent t, 2 H (C_5H_4P); 4.60 apparent t, 2 H (C_5H_4C); 7.40–7.51 m, 10 H (PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): 70.7 s (C_5H_4C, C_{ipso}); 71.7 s (C_5H_4C, CH); 74.1 s (C_5H_4C, CH); 74.3 d, *J*(P,C) = 6 (C_5H_4P, CH); 74.9 d, *J*(P,C) = 11 (C_5H_4P, CH); 81.3 d, ^{1}*J*(P,C) = 37 (C_5H_4P, C_{ipso}); 128.3 d, *J*(P,C) = 10 (PPh_2, CH); 130.0 d, *J*(P,C) = 2 (PPh_2, CH); 132.2 d, *J*(P,C) = 12 (PPh_2, CH); 137.5 d, ^{1}*J*(P,C) = 39 (PPh_2, C_{ipso}); 176.3 s (CO_2H); 216.6 d, ^{2}*J*(P,C) = 13 (CO); 221.1 d, ^{2}*J*(P,C) = 7 (CO). ^{31}P{^{1}H} NMR ($CDCl_3$): 47.7 s. IR (Nujol): ν(CO) 2 062 s, 1 991 s, 1 935 vs, 1 907 vs, 1 878 sh; $\nu_{as}(CO_2)$ 1 679 s; $\nu_{s}(CO_2)$ 1 299 m; 1 164 m composite, 1 092 m, 1 031 m, 834 m composite, 748 m, 695 m, 676 s, 653 s, 473–534 m. UV-VIS (CH_2Cl_2, λ_{max} (log ε)):

450 (3.5). For $C_{28}H_{19}CrFeO_7P$ (606.3) calculated: 55.47% C, 3.16% H; found: 55.69% C, 3.82% H.

Pentacarbonyl[1′-(diphenylphosphanyl)ferrocenecarboxylic Acid-κ*P*]molybdenum(0) (**2**)

[Mo(CO)$_6$] (264 mg, 1.0 mmol) and Hdpf (414 mg, 1.0 mmol) were dissolved in xylenes (30 ml). The solution was refluxed until the intensity of the ν_{CO} band of [Mo(CO)$_6$] in IR spectra did not change further (4.5 h). After cooling to room temperature, the solvent was removed *in vacuo* and the residue was dissolved in chloroform. The resulting solution was filtered (Celite), chloroform was evaporated under reduced pressure and the crude product was purified by vacuum sublimation (50 °C, oil pump; removal of the unreacted carbonyl), dissolved in chloroform and crystallized by diffussion of hexane at 4 °C for several days. The crystalline product was filtered off, washed with hexane–chloroform (5 : 1, v/v) and dried *in vacuo* in dark. Yield 424 mg (60%), orange-brown crystalline solid, m.p. 191–195 °C (dec.). ^{1}H NMR (CDCl$_3$): 4.20 apparent t, 2 H (C_5H_4C); 4.39 apparent q (C_5H_4P); 4.56 br apparent t, 2 H (C_5H_4P); 4.61 apparent t, 2 H (C_5H_4C); 7.38–7.50 m, 10 H (PPh$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): 70.9 s (C_5H_4C, C$_{ipso}$); 71.6 s (C_5H_4C, CH); 73.8 s (C_5H_4C, CH); 74.4 d, *J*(P,C) = 7 (C_5H_4P, CH); 75.1 d, *J*(P,C) = 12 (C_5H_4P, CH); 80.5 d, ^1J(P,C) = 37 (C_5H_4P, C$_{ipso}$); 128.3 d, *J*(P,C) = 10 (PPh$_2$, CH); 129.9 d, *J*(P,C) = 2 (PPh$_2$, CH); 132.3 d, *J*(P,C) = 13 (PPh$_2$, CH); 137.8 d, ^1J(P,C) = 38 (PPh$_2$, C$_{ipso}$); 176.9 s (CO$_2$H); 205.7 d, ^2J(P,C) = 9 (CO); 209.9 d, ^2J(P,C) = 23 (CO). ^{31}P{^{1}H} NMR (CDCl$_3$): 28.2 s. IR (Nujol): ν(CO) 2 070 s, 1 989 s, 1 933 vs, 1 901 vs; ν_{as}(CO$_2$) 1 679 s; ν_s(CO$_2$) 1 299 m; 1 170 m composite, 1 094 w, 1 031 m, *ca* 840 m composite, 748 m, 694 m, 602 m, 575 m, 465–537 m. UV-VIS (CH$_2$Cl$_2$, λ_{max} (log ε)): 448 (3.7). For $C_{28}H_{19}FeMoO_7P$ (650.2) calculated: 51.72% C, 2.59% H; found: 51.09% C, 3.26% H.

Pentacarbonyl[1′-(diphenylphosphanyl)ferrocenecarboxylic Acid-κ*P*]tungsten(0) (**3**)

Starting from [W(CO)$_6$] (352 mg, 1.0 mmol) and Hdpf (104 mg, 0.25 mmol), a procedure analogous to the preparation of complex **1**, except that the solution of [W(CO)$_6$] in THF had to be irradiated for 7.5 h prior to addition of Hdpf, afforded crude **3**. Repeated dissolution in chloroform and diffusion of hexane then gave pure complex **3** as a yellow-orange crystalline solid. Yield 120 mg, 65%, m.p. 206–208 °C (dec.). ^{1}H NMR (CDCl$_3$): 4.20 apparent t, 2 H (C_5H_4C); 4.39 br apparent q (C_5H_4P); 4.58 br apparent t, 2 H (C_5H_4P); 4.61 apparent t, 2 H (C_5H_4C); 7.40–7.50 m, 10 H (PPh$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): 71.0 s (C_5H_4C, C$_{ipso}$); 71.7 s (C_5H_4C, CH); 73.9 s (C_5H_4C, CH); 74.5 d, *J*(P,C) = 7 (C_5H_4P, CH); 75.2 d, *J*(P,C) = 12 (C_5H_4P, CH); 80.7 d, ^1J(P,C) = 43 (C_5H_4P, C$_{ipso}$); 128.3 d, *J*(P,C) = 10 (PPh$_2$, CH); 130.2 s (PPh$_2$, CH); 132.4 d, *J*(P,C) = 12 (PPh$_2$, CH); 137.5 d, ^1J(P,C) = 44 (PPh$_2$, C$_{ipso}$); 176.2 s (CO$_2$H); 191.1 d with ^{183}W satellites, ^2J(P,C) = 13, ^1J(W,C) = 126 (*trans*-CO); 197.2 d with ^{183}W satellites, ^2J(P,C) = 7, ^1J(W,C) = 126 (*cis*-CO). ^{31}P{^{1}H} NMR (CDCl$_3$): 10.9 s with ^{183}W satellites, ^1J(W,P) = 247. IR (Nujol): ν(CO) 2 071 s, 1 997 s, 1 939 vs, 1 912 vs, 1 874 sh; ν_{as}(CO$_2$) 1 676 s; ν_s(CO$_2$) 1 298 m; 1 165 m composite, 1 094 w, 1 030 m, *ca* 840 m composite, 748 m, 694 m, 584 m, 465–534 m. UV-VIS (CH$_2$Cl$_2$, λ_{max} (log ε)): 449 (3.7). For $C_{28}H_{19}FeO_7PW$ (738.1) calculated: 45.56% C, 2.59% H; found: 44.88% C, 2.67% H.

X-Ray Crystallography

Single crystals of **1** suitable for X-ray analysis were obtained by slow diffusion of hexane into a chloroform solution of the complex. Diffraction data (Table III) were collected on a

TABLE III
Crystallographic data, data collection and structure refinement for complex **1**

Formula	$C_{28}H_{19}CrFeO_7P$
M, g mol^{-1}	606.25
Crystal size, mm^3	0.15 × 0.50 × 0.80
Crystal description	orange plate
T, K	296(1)
Crystal system, space group	triclinic, $P\text{-}\bar{1}$ (No. 2)
a, Å; α, °	9.1808(2); 100.754(1)
b, Å; β, °	11.9808(3); 109.749(2)
c, Å; γ, °	12.8029(3); 90.766(2)
V, Å^3; Z	1 297.67(5); 2
D_c, g cm^{-3}	1.552
F(000); μ(MoKα), mm^{-1}	616; 1.085
θ range, deg; data completness, %	1.0–27.5; 99.3
hkl range	–11/11, –15/15, –16/16
No. of unique diffractions	5 938
No. of observed diffractions[a]	4 544
No. of parameters	419
w_1, w_2[b]	0.0463, 0.2663
R, wR for observed diffractions[c], %	3.57, 8.47
R, wR for all data[c], %	5.49, 9.32
GOF for all data[d]	1.024
$(\Delta/\sigma)_{max}$	0.001
Residual electron density, e Å^{-3}	0.28, –0.41

[a] Diffractions with $F_o > 4\sigma(F_o)$. [b] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, $P = 1/3[\max(F_o^2) + 2F_c^2]$. [c] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$. [d] GOF $= [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$.

Nonius KappaCCD image plate diffractometer at 296(1) K using graphite monochromated MoKα radiation (λ = 0.71073 Å): 234 frames were measured (2° oscillation and 50 s counting time for each, total rotation ϕ 182° and ω 286°, 22 344 integrated diffractions) and analyzed by HKL program package[16]. Cell parameters were determined from 11 982 partial diffractions with $1.0 \le \theta \le 27.5°$. The structure was solved by direct methods (SIR92, ref.[17]) and refined by full-matrix least-squares on F^2 (SHELXL97, ref.[18]). Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were identified on difference electron density maps and isotropically refined.

Crystallographic data for the structure **1** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-151592. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

We thank Prof. J. Podlaha for helpfull discussions. This work was financially supported by the Ministry of Education, Youth and Sports of the Czech Republic. An access to the Cambridge Crystallographic Data Centre was sponsored by Grant Agency of the Czech Republic (grant No. 203/99/0067).

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