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Synthesis, structure, and chemistry of heterobimetallic phosphido-bridged complexes $CpFe(CO)_2(\mu\text{-}PPh_2)M(CO)_5$ (M = Cr, Mo, W)

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Abstract

A series of new non-metal–metal bonded heterobimetallic phosphido-bridged complexes $CpFe(CO)_2(\mu\text{-}PPh_2)M(CO)_5$ (M = Cr, Mo, W) was synthesized by reaction of $LiPPh_2M(CO)_5$ (M = Cr, Mo, W) with $CpFe(CO)_2I$. Results from single-crystal X-ray diffraction studies of the Fe–Mo and Fe–Cr complexes indicated that Fe was ligated by one C_5H_5 and two terminal CO. Five CO groups were coordinated to M (M = Cr, Mo). The long distances between Fe and M in phosphido-bridged complexes indicated no metal–metal bond to exist. Removal by photolysis of one CO from the Fe–W complex produced $\overline{CpFe(CO)(\mu\text{-}CO)(\mu\text{-}PPh_2)W}(CO)_4$. The corresponding Fe–Cr and Fe–Mo analogues were found to be inert to UV radiation.

1. Introduction

One interesting cooperative interaction between adjacent metals with different chemical properties in phosphido-bridged heterobimetallic complexes is the breakage and formation of the metal–metal bond in the complexes during reaction [1–6]. Metal–metal bonds in these complexes are usually not entirely covalent; they may have significant donor-acceptor character [3,5,6]. The breakage and formation of the metal–metal bond are similar to the reversible coordination of ligand to metal such that the metal–metal bond is considered to follow the usual donor-acceptor mode of ligand–metal binding with electron lone pair localized on the ligand. Thus, whether a metal–metal bond is formed or broken depends on the electronic and steric requirements of the ligand–metal fragments involved. We report the syntheses, structural and preliminary reactivity studies of a series of non-metal–metal bonded phosphido-bridged complexes which link Fe and Group VI transition metal (Cr, Mo, W), and which undergo reversible ligand addition resulting in the breakage and formation of the metal–metal bond.

2. Experimental details

Unless otherwise stated, all reactions and manipulations of air-sensitive compounds were carried out with standard procedures at ambient temperature under purified nitrogen. Infrared (IR) spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. ^1H NMR spectra were obtained on a Bruker AC-200 spectrometer and ^{13}C NMR spectra on a Bruker MSL-200 at 50.32 MHz or on a Bruker ASM-500 spectrometer at 125.76 MHz. Both ^1H and ^{13}C chemical shifts are given in ppm downfield from the internal standard Me_4Si. ^{31}P NMR spectra were obtained on the Bruker MSL-200 at 81.00 MHz; chemical shifts are reported with reference to 85% H_3PO_4. Except as noted, NMR spectra were collected at room temperature. Electron impact (EI) mass spectra were recorded on a VG 70-250S mass spectrometer. Elemental analyses were performed by use of a Perkin-Elmer 2400 CHN elemental analyzer.

2.1. Materials

Tetrahydrofuran (THF) was distilled from Na and benzophenone under nitrogen immediately before use. Other solvents were purified according to established procedures [7].

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n-Butyllithium (2.0 M in cyclohexane) was from Aldrich. M(CO)$_6$ (M = Cr, Mo, W), PPh$_2$H were from Strem. ^{13}CO (99 atom% ^{13}C) was from Isotec. Other reagents and solvents were from various commercial sources and used as received. The complexes M(CO)$_5$PPh$_2$H (M = Cr, Mo, W) were prepared by general methods [8], and their IR, ^{1}H and ^{31}P NMR spectra compared with those in the literature [9–11]. FeCp(CO)$_2$I was prepared by literature procedures [12].

2.2. Preparation of CpFe(CO)$_2$(μ-PPh$_2$)Cr(CO)$_5$ (1-Cr)

To a solution of Cr(CO)$_5$PPh$_2$H (1.89 g, 5.00 mmole) in 30 ml of THF was added 3.00 ml of n-butyllithium (2.0 M in cyclohexane). The colour of the solution changed to orange. A dark brown solution of FeCp(CO)$_2$I (1.52 g, 5.00 mmol) in THF (30 ml) was transferred to the above solution. A deep brown solution was obtained which was stirred overnight. The solvent was removed under vacuum and the residue chromatographed on silica gel. Elution with benzene : hexane (1 : 4) afforded a yellow fraction. Solvent was removed by rotary evaporator and a yellow solid was obtained which was dried further under vacuum, yield 1.67 g (60%). Anal. Found: C, 51.90; H, 2.77. C$_{24}$H$_{15}$CrFeO$_7$P calc.: C, 51.99; H, 2.71%. IR spectrum (THF, ν(CO)): 2053m, 2020w, 1974m, 1926s, 1915 (sh) cm^{-1}. ^{1}H NMR spectrum (CDCl$_3$): δ 7.6 (m, 4H), 7.3 (m, 6H), 4.6 (d, J(PH) = 1.4 Hz, 5H). ^{13}C{^{1}H} NMR spectrum (CDCl$_3$): δ 223.34 (d, J(P–C) = 6.69 Hz), 217.53 (d, J(P–C) = 11.02 Hz), 213.70 (d, J(P–C) = 14.74 Hz), 146.61 (d, J(P–C) = 10.16 Hz), 132.32 (d, J(P–C) = 8.70 Hz), 128.10 (s), 127.90 (d, J(P–C) = 7.9 Hz), 87.88 (s). ^{31}P{^{1}H} NMR spectrum (THF): δ 45.9. MS (EI), M^{+1} m/z = 554.

2.3. Preparation of CpFe(CO)$_2$(μ-PPh$_2$)Mo(CO)$_5$ (1-Mo)

Similar reaction conditions as 1-Cr were applied to prepare 1-Mo. Yield 54.38%. Anal. Found: C, 48.25; H, 2.40. C$_{24}$H$_{15}$MoFeO$_7$P calc.: C, 48.16; H, 2.51%. IR spectrum (THF, ν(CO)): 2064w, 2020w, 1978m, 1937s, 1914(sh) cm^{-1}. ^{1}H NMR spectrum (CDCl$_3$): δ 7.6 (m, 4H), 7.3 (m, 6H), 4.6 (d, J(P–H) = 1.5 Hz, 5H). ^{13}C{^{1}H} NMR spectrum (CDCl$_3$): δ 213.83 (d, J(P–C) = 14.89 Hz), 212.91 (d, J(P–C) = 21.69 Hz), 206.48 (d, J(P–C) = 7.70 Hz), 146.40 (d, J(P–C) = 8.65 Hz), 132.41 (d, J(P–C) = 9.7 Hz), 127.97 (s, br), 87.97 (s). ^{31}P{^{1}H} NMR spectrum (THF): δ 23.0. MS(EI), M^{+1} m/z = 600 (^{98}Mo).

2.4. Preparation of CpFe(CO)$_2$(μ-PPh$_2$)W(CO)$_5$(1-W)

Similar reaction conditions as for 1-Cr were applied to prepare 1-W. Yield 66.0%. Anal. Found: C, 42.13; H, 2.06. C$_{24}$H$_{15}$WFeO$_7$P calc.: C, 41.98; H, 2.19%. IR spectrum (THF, ν(CO)): 2063w, 2021w, 1975m, 1925s, 1910(sh) cm^{-1}. ^{1}H NMR spectrum (CDCl$_3$): δ 7.60 (m, 4H), 7.32 (m, 6H), 4.63 (d, J(P–H) = 1.5 Hz, 5H). ^{13}C{^{1}H} NMR spectrum (CDCl$_3$): δ 214.04 (d, J(P–C) = 15.85 Hz), 201.48 (d, J(P–C) = 20.18 Hz), 199.04 (d, J(P–C) = 5.58 Hz, J(W–C) = 121.29 Hz), 145.93 (d, J(P–C) = 14.94 Hz), 132.51 (d, J(P–C) = 10.02 Hz), 128.22 (s), 127.91 (d, J(P–C) = 8.30 Hz), 88.01 (s). ^{31}P{^{1}H} NMR spectrum (THF): δ 0.1 (J(P–W) = 209 Hz). MS(EI), M^{+1} m/z = 686.

2.5. Preparation of $CpF\overline{e(CO)(\mu\text{-}CO)(\mu\text{-}PPh_2)W}(CO)_4$ (2)

A brown solution of 1-W was prepared by addition of 15 ml of THF into a Schlenk tube which contained 0.17 g of 1-W. The solution was than degassed by freeze-thaw cycles. A 450 watt Hanovia medium-pressure quartz mercury-vapour lamp (Ace Glass) was used to irradiate the solution. Freeze-thaw cycles removed the CO generated from the photoreaction during irradiation. Total irradiation time was 70 min and the colour of the solution changed to dark brown. Complex 2 was obtained quantitatively according to different spectroscopic measurements (IR, ^{31}P NMR and ^{1}H NMR). Anal. Found: C, 41.93; H, 2.09. C$_{23}$H$_{15}$WFeO$_6$P calc: C, 41.94; H, 2.27%. IR spectrum (THF, ν(CO)): 2054m, 1958s, 1927s, cm^{-1}; (Nujol, ν(CO)): 2049m, 2022w, 1967s, 1951s, 1917s, 1836m cm^{-1}. ^{1}H NMR spectrum (CDCl$_3$): δ 7.8 (m, 4H), 7.4 (m, 6H), 4.46 (d, J(PH) = 1.1 Hz, 5H). ^{31}P{^{1}H} NMR spectrum (THF): δ 160.8 (J(P–W) = 201 Hz). MS (EI), M^{+1} m/z = 658.

2.6. Reaction of 2 with CO

Complex 2 was prepared *in situ* by irradiation of the THF solution of 1-W for a total of 75 min between freeze-thaw cycles. ^{31}P NMR spectrum of the solution indicated 2 was obtained and only a trace amount of 1-W was left in the solution. After CO was bubbled through the above solution for an hour, the colour changed from dark brown to brown. ^{31}P NMR of the solution showed 1-W was obtained with only a trace amount of intact 2.

2.7. Preparation of ^{13}CO-enriched 2

Complex 2 was freshly prepared by irradiation of a solution of 1-W (0.174 g, 0.25 mmol) in 15 ml of THF. After 75 min of irradiation, about 20 ml of ^{13}CO was introduced into the system. The solution was stirred for 3 h. ^{31}P NMR of the solution indicated all 2 was converted to 1-W. The solution was then irradiated again for a total of 50 min, and again, only 2 was observed by ^{31}P NMR.

TABLE 1. Crystal and intensity collection data for 1-Cr and 1-Mo

Molecular formula	$C_{24}H_{15}FeMoO_7P$	$C_{24}H_{15}CrFeO_7P$
Mol. wt.	598.14	554.20
Space group	$P2_1/n$	$P2_1/n$
a (Å)	9.1748(7)	9.0781(15)
b (Å)	17.5902(15)	17.4634(19)
c (Å)	14.7446(11)	14.6105(23)
α (°)	–	–
β (°)	95.097(6)	94.842(14)
γ (°)	–	–
V (Å^3)	2370.2(3)	2308.0(6)
calc. ρ (mg m^{-3})	1.676	1.595
Z	4	4
Crystal dimensions (mm)	0.38×0.19×0.31	0.5×0.31×0.25
Absolute coefficient μ (Mo Kα) (mm^{-1})	1.24	1.20
Temperature	Room temperature	Room temperature
Radiation	Mo Kα (λ = 0.70930 Å)	Mo Kα (λ = 0.7093 Å)
2θ range	45°	45°
Scan type	$2\theta-\omega$	$2\theta-\omega$
No. of reflections	3303	3236
No. of observed reflections	2528 ($> 2.0\sigma$)	2448 ($> 2.0\sigma$)
Variables	367	367
R	0.025	0.036
R_w	0.029	0.045
S	1.44	2.12
ΔF (e/Å^3)	< 0.320	< 0.400
$(\Delta/\sigma)_{max}$	0.051	0.050

2.8. Crystallographic analyses of $CpFe(CO)_2(\mu\text{-}PPh_2)M(CO)_5$ (1-Cr, 1-Mo)

Suitable crystals of **1-Cr** and **1-Mo** were obtained by slow diffusion of hexanes into a saturated solution of the corresponding complexes in benzene under vacuum at 0°C. Diffraction measurements were carried out on an Enraf-Nonius CAD-4 fully automated diffractometer. Space group and crystal collection data for **1-Cr** and **1-Mo** are given in Table 1.

3. Results and discussion

3.1. Preparation and characterization of $CpFe(CO)_2(\mu\text{-}PPh_2)M(CO)_5$ (1-Cr, 1-Mo, 1-W)

We prepared the new complexes $CpFe(CO)_2(\mu\text{-}PPh_2)M(CO)_5$ (**1-Cr**, **1-Mo**, and **1-W**) by adding $CpFe(CO)_2I$ [12] to the solution of the corresponding $LiPPh_2M(CO)_5$ (M = Cr, Mo and W) in THF [13] under nitrogen (eqn. (1)). The nucleophilic phosphido ligand of $[M(CO)_5PPh_2]^-$ substituted the iodide in $CpFe(CO)_2I$ and bridged the metals to form the phosphido-bridged heterobimetallic complex. Deprotonation of $W(CO)_5PPh_2H$ with n-butyllithium at 0°C produced $[W(CO)_5PPh_2]^-$, which reacted further with itself at elevated temperature to produce $[W(CO)_4(\mu\text{-}PPh_2)]_2^-$ and $[(CO)_5W(\mu\text{-}PPh_2)W(CO)_4(PPh_2H)]^-$[14]. However, deprotonation of $Mo(CO)_5PPh_2H$ with n-butyllithium in THF generated $[Mo(CO)_4(\mu\text{-}PPh_2)]_2^-$ and $[(CO)_5Mo(\mu\text{-}PPh_2)Mo(CO)_4(PPh_2H)]^-$ within 10 min at room temperature [14b]. In order to avoid these side reactions, we added $CpFe(CO)_2I$ within 5 min after $M(CO)_5PPh_2H$ (especially M = Mo) was deprotonated with n-butyllithium.

$$Li[PPh_2M(CO)_5] + CpFe(CO)_2I \xrightarrow[\text{THF}]{25°\text{C}} CpFe(CO)_2(\mu\text{-}PPh_2)M(CO)_5 \quad (1)$$

M = Cr (60%); Mo (54%); W (66%)

3.2. Molecular structures of $CpFe(CO)_2(\mu\text{-}PPh_2)M(CO)_5$ (1-Cr, 1-Mo)

Orange-brown crystals of **1-Cr** and **1-Mo** were obtained by slow diffusion of hexanes into the saturated solution of the corresponding complex in benzene at 0°C. Single X-ray diffraction studies of these complexes were obtained. Their atomic positional parameters are listed in Tables 2 and 3. Their ORTEP plots are shown in Fig. 1.

The long distances between Fe and M in complexes of **1-Cr** and **1-Mo** indicated that there was no metal–metal bond there (Table 4). The phosphorus atoms of phosphido-bridge ligands in these complexes may donate two electrons to M. Thus both Fe and M could be saturated coordinatively with 18 valence electrons.

$CpFe(CO)_2PPh_2$ may be considered as a ligand similar to PR_3. The M–P distances in **1-Cr** and **1-Mo** are longer than the usual M–P distances in the corresponding $M(CO)_5PR_3$ (R = Ph) [15]. This indicates that the partial double bond character between metal and phosphorus was less for $CpFe(CO)_2PPh_2$ than for PPh_3 when they coordinated to $M(CO)_5$. This is consistent with the observations that the M–C distances of the CO *trans* to the phosphido-bridge ligands in **1** had shorter bond distances than the corresponding M–C distance of *trans* CO in $M(CO)_5PPh_3$, which implies that $CpFePPh_2$ is a poorer d-π acceptor than PPh_3.

3.3. Spectroscopic data of 1 and molecular structure of $CpFe(CO)_2(\mu\text{-}PPh_2)W(CO)_5$ (1-W)

The $^{31}P\{^1H\}$ NMR spectra of **1** showed relative upfield resonance, which is consistent with the observation that no metal–metal bond was formed in the compounds [16]. For **1-W**, the ratio of the intensity of the signal to the intensity of the $J(^{31}P-^{183}W)$ satellites was 1 : 11 : 1. This indicated that phosphorus was coor-

TABLE 2. Atomic coordinates and isotropic thermal parameters (Å^2) for **1**-Cr

Atom	x	y	z	B_{iso}
Cr	0.29165(8)	0.38437(4)	0.01970(5)	2.83(3)
Fe	0.04616(7)	0.25002(4)	0.18270(4)	3.03(3)
P	0.27518(12)	0.29814(6)	0.15189(7)	2.54(5)
O1	−0.0402(4)	0.4083(2)	−0.0115(3)	6.6(2)
O2	0.2579(4)	0.2660(2)	−0.1311(2)	5.4(2)
O3	0.6233(4)	0.3586(2)	0.0444(3)	5.0(2)
O4	0.3288(4)	0.4862(2)	−0.1423(2)	5.3(2)
O5	0.3137(5)	0.5242(2)	0.1453(3)	5.4(2)
O6	−0.0845(4)	0.3996(2)	0.2070(3)	6.5(2)
O7	0.1403(5)	0.2315(3)	0.3759(3)	6.8(2)
C1	0.0837(7)	0.3988(3)	0.0033(3)	4.3(3)
C2	0.2704(5)	0.3081(3)	−0.0696(3)	3.6(2)
C3	0.4995(6)	0.3681(2)	0.0366(3)	3.2(2)
C4	0.3144(5)	0.4493(3)	−0.0785(3)	3.5(2)
C5	0.3066(5)	0.4707(3)	0.1013(3)	3.6(2)
C6	−0.0306(5)	0.3425(3)	0.1969(3)	3.9(2)
C7	0.1063(6)	0.2396(3)	0.2988(4)	4.0(2)
C8	0.0430(7)	0.1865(3)	0.0615(4)	5.0(3)
C9	0.0601(7)	01374(3)	0.1362(5)	5.2(3)
C10	−0.0658(7)	0.1443(3)	0.1835(5)	5.3(3)
C11	−0.1554(7)	0.1993(4)	0.1390(5)	5.6(4)
C12	−0.0912(7)	0.2254(3)	0.0628(4)	5.0(3)
C21	0.3651(5)	0.3498(2)	0.2525(3)	2.8(2)
C22	0.2868(6)	0.3935(3)	0.3106(3)	3.8(2)
C23	0.3581(6)	0.4392(3)	0.3778(3)	4.1(2)
C24	0.5093(7)	0.4423(3)	0.3880(3)	4.1(3)
C25	0.5890(6)	0.3988(3)	0.3312(3)	3.8(2)
C26	0.5177(6)	0.3527(3)	0.2655(3)	3.4(2)
C31	0.3913(5)	0.2104(2)	0.1527(3)	2.8(2)
C32	0.4363(6)	0.1798(3)	0.0725(4)	3.6(2)
C33	0.5071(6)	0.1097(3)	0.0722(4)	4.6(3)
C34	0.5366(6)	0.0694(3)	0.1513(5)	4.9(3)
C35	0.4990(6)	0.1004(3)	0.2319(4)	4.5(3)
C36	0.4283(6)	0.1697(3)	0.2328(4)	3.8(2)
H8	0.1075(45)	0.1935(23)	0.0224(26)	2.2(9)
H9	0.1383(59	0.1084(29)	0.1525(35)	5.5(15)
H10	−0.0968(55)	0.1204(29)	0.2373(35)	5.3(13)
H11	−0.2451(49)	0.2112(26)	0.1622(30)	2.6(12)
H12	−0.1189(51)	0.2605(25)	0.0205(31)	3.6(11)
H22	0.1869(48)	0.3958(23)	0.3025(27)	2.9(10)
H23	0.2983(51)	0.4664(26)	0.4175(30)	4.5(12)
H24	0.5550(52)	0.4692(26)	0.4315(31)	4.3(12)
H25	0.6979(51)	0.3973(24)	0.3360(28)	3.5(10)
H26	0.5598(37)	0.3293(20)	0.2274(23)	0.7(8)
H32	0.4278(47)	0.2046(25)	0.0253(28)	2.9(11)
H33	0.5391(50)	0.0898(25)	0.0173(31)	4.3(12)
H34	0.5902(56)	0.0220(29)	0.1462(33)	5.5(13)
H35	0.5142(52)	0.0785(27)	0.2843(32)	4.0(12)
H36	0.3975(49)	0.1868(26)	0.2850(30)	3.8(11)

TABLE 3. Atomic coordinates and isotropic thermal parameters (Å^2) for **1**-Mo

Atom	x	y	z	B_{iso}
Mo	0.29305(3)	0.11566(2)	0.01779(2)	2.74(1)
Fe	0.04931(6)	0.25303(3)	0.18440(4)	3.25(2)
P	0.27623(10)	0.20545(5)	0.15613(6)	2.68(4)
O1	0.2636(4)	0.2390(2)	−0.1377(2)	5.5(2)
O2	−0.0496(4)	0.0911(2)	−0.0150(2)	6.7(2)
O3	0.3185(4)	−0.0281(2)	0.1508(2)	5.7(2)
O4	0.3279(3)	0.0091(2)	−0.1493(2)	5.3(1)
O5	0.6368(3)	0.1429(2)	0.0465(2)	5.1(2)
O6	−0.0785(4)	0.1046(2)	0.2076(2)	6.9(2)
O7	0.1416(4)	0.2724(2)	0.3761(2)	7.1(2)
C1	0.2738(4)	0.1974(2)	−0.0782(3)	3.6(2)
C2	0.0708(5)	0.1005(2)	−0.0009(3)	4.1(2)
C3	0.3087(4)	0.0236(2)	0.1056(3)	3.6(2)
C4	0.3161(4)	0.0455(2)	−0.0866(3)	3.5(2)
C5	0.5150(5)	0.1326(2)	0.0361(2)	3.3(2)
C6	−0.0249(4)	0.1617(3)	0.1978(3)	4.3(2)
C7	0.1073(5)	0.2642(2)	0.3000(3)	4.5(2)
C8	0.0502(6)	0.3149(3)	0.0627(3)	5.0(2)
C9	−0.0824(6)	0.2771(3)	0.0638(4)	5.3(3)
C10	−0.1512(6)	0.3028(3)	0.1384(4)	5.7(3)
C11	−0.0630(6)	0.3573(3)	0.1830(4)	5.6(3)
C12	0.0628(6)	0.3641(3)	0.1374(4)	5.3(3)
C21	0.3640(4)	0.1530(2)	0.2554(2)	2.8(1)
C22	0.2874(5)	0.1101(2)	0.3130(3)	4.0(2)
C23	0.3571(5)	0.0635(2)	0.3789(3)	4.5(2)
C24	0.5062(5)	0.0590(2)	0.3878(3)	4.4(2)
C25	0.5844(5)	0.1014(2)	0.3318(3)	4.3(2)
C26	0.5145(5)	0.1485(2)	0.2671(3)	3.7(2)
C31	0.3917(4)	0.2918(2)	0.1573(2)	3.0(2)
C32	0.4292(5)	0.3325(2)	0.2363(3)	4.0(2)
C33	0.5009(5)	0.4012(3)	0.2355(4)	4.8(2)
C34	0.5398(5)	0.4306(3)	0.1549(4)	5.4(3)
C35	0.5079(5)	0.3909(3)	0.0763(4)	5.1(2)
C36	0.4351(5)	0.3217(2)	0.0770(3)	4.0(2)
H8	0.1180(50)	0.3083(26)	0.0209(29)	6.4(13)
H9	−0.1039(51)	0.2425(25)	0.0231(30)	6.1(13)
H10	−0.2297(53)	0.2869(27)	0.1592(31)	6.7(14)
H11	−0.0721(46)	0.3847(24)	0.2368(29)	5.6(11)
H12	0.1381(46)	0.3938(23)	0.1496(27)	4.9(11)
H22	0.1922(40)	0.1110(19)	0.3078(23)	3.1(9)
H23	0.2954(42)	0.0337(22)	0.4162(25)	4.8(10)
H24	0.5487(43)	0.0255(22)	0.4316(25)	4.9(10)
H25	0.6877(45)	0.0993(21)	0.3416(25)	4.6(10)
H26	0.5608(34)	0.1742(18)	0.2309(21)	2.1(8)
H32	0.4062(35)	0.3162(18)	0.2868(21)	2.3(8)
H33	0.5186(46)	0.4238(24)	0.2938(29)	5.9(11)
H34	0.5893(44)	0.4777(24)	0.1555(26)	5.4(10)
H35	0.5330(50)	0.4086(25)	0.0177(30)	6.8(12)
H36	0.4182(32)	0.2952(17)	0.0254(20)	1.8(7)

dinated to one tungsten atom only [17*] and **1**-W, **1**-Cr and **1**-Mo had similar structures.

The ^{13}C NMR spectra of **1** showed resonances of C in CO ligands in the complexes at around 200 ppm. A doublet at 214.04 ppm was assigned to CO coordinated to Fe [18]. The other two sets of doublets were assigned to CO coordinated to the Group VI elements [19]. These assignments were clearly revealed by the observation of J(W–C) satellites in the spectrum of **1**-W (Fig. 2). The doublet at 199.04 ppm was assigned to the *cis* CO and the other doublet at 201.48 was assigned to the *trans* CO. These assignments were based on the observations that the intensity ratio of the

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

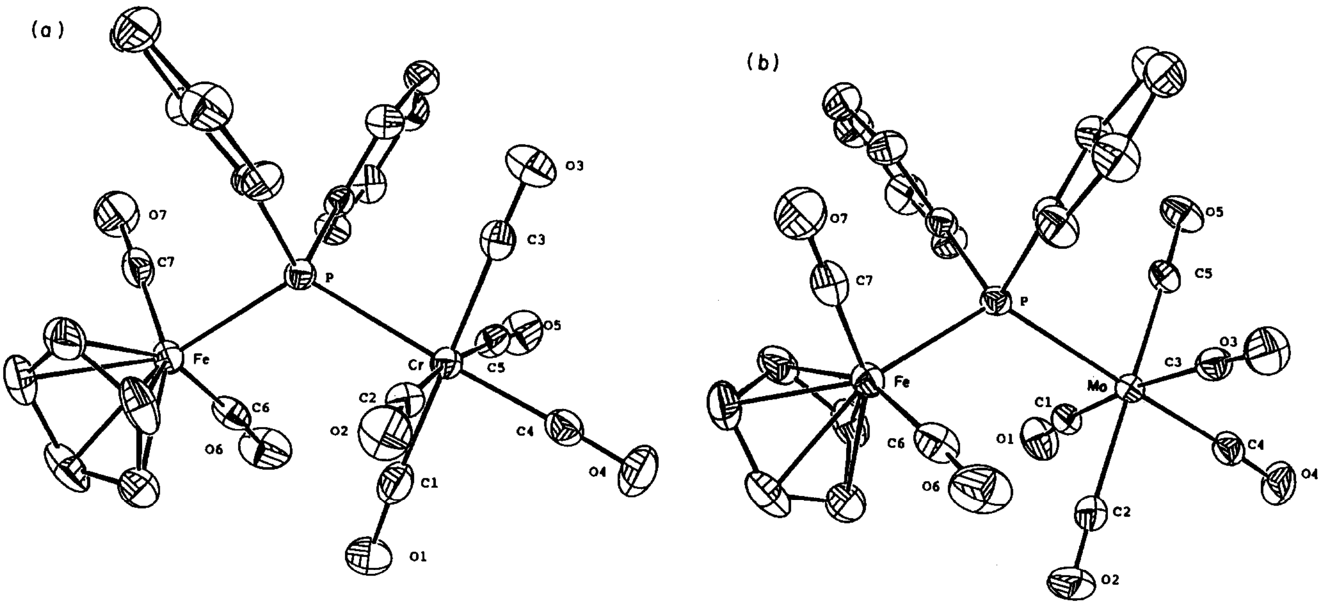


Fig. 1. ORTEP plots of (a) 1-Cr and (b) 1-Mo. Hydrogen atoms are omitted.

TABLE 4. Selected bond lengths (Å) and angles (°) in complexes 1-Cr and 1-Mo

Bond length		Bond angle	
Complex 1-Cr			
Cr–Fe	4.1278(10)	Cr–P–Fe	119.20(5)
Cr–P	2.4636(13)	P–Cr–C(1)	93.13(15)
Cr–C(1)	1.899(6)	P–Cr–C(2)	95.85(14)
Cr–C(2)	1.863(5)	P–Cr–C(3)	86.10(14)
Cr–C(3)	1.904(5)	P–Cr–C(4)	177.10(15)
Cr–C(4)	1.855(5)	P–Cr–C(5)	89.93(14)
Cr–C(5)	1.920(5)	Cr–C(1)–O(1)	176.2(5)
Fe–P	2.3214(13)	Cr–C(2)–O(2)	173.5(4)
O(1)–C(1)	1.140(7)	Cr–C(3)–O(3)	178.3(4)
O(2)–C(2)	1.159(6)	Cr–C(4)–O(4)	176.4(4)
O(3)–C(3)	1.132(6)	Cr–C(5)–O(5)	176.1(4)
O(4)–C(4)	1.149(6)	Fe–C(6)–O(6)	177.0(4)
O(5)–C(5)	1.132(6)	Fe–C(7)–O(7)	177.1(4)
Complex 1-Mo			
Mo–Fe	4.2250(6)	Mo–P–Fe	118.59(4)
Mo–P	2.5952(10)	P–Mo–C(1)	96.33(11)
Mo–C(1)	2.015(4)	P–Mo–C(2)	93.26(11)
Mo–C(2)	2.051(4)	P–Mo–C(3)	89.43(11)
Mo–C(3)	2.070(4)	P–Mo–C(4)	177.23(11)
Mo–C(4)	1.999(4)	P–Mo–C(5)	86.30(11)
Mo–C(5)	2.052(4)	Mo–C(1)–O(1)	174.3(3)
Fe–P	2.3158(11)	Mo–C(2)–O(2)	176.8(4)
O(1)–C(1)	1.140(5)	Mo–C(3)–O(3)	177.5(3)
O(2)–C(2)	1.118(5)	Mo–C(4)–O(4)	176.1(3)
O(3)–C(3)	1.126(5)	Mo–C(5)–O(5)	179.1(3)
O(4)–C(4)	1.137(5)	Fe–C(6)–O(6)	176.7(4)
O(5)–C(5)	1.129(5)	Fe–C(7)–O(7)	178.1(4)

two doublets was 1 to 4 and the J(W–C) of *trans* CO was larger than J(W–C) of *cis* CO[20].

IR of **1** in THF showed absorption of the terminal CO units at around 2000 cm^{-1}. The 2020(m) and 1974(s) bands were assigned to the iron cyclopentadi-

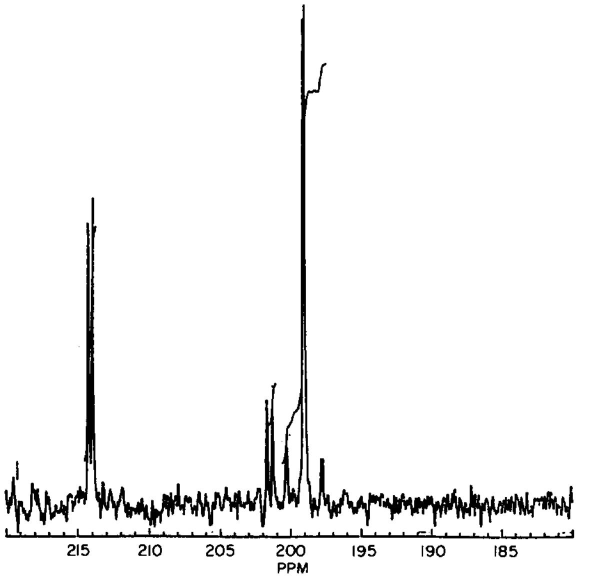


Fig. 2. $^{13}C\{^1H\}$ NMR spectrum of 1-W. Only the terminal carbonyl region is shown.

ene carbonyls because these compared well with the 2020(s), 1975(s, br) bands reported for $CpFe(CO)_2PPh_2$[21]. The remaining bands were assigned to the group VI metal(Cr, Mo, W) carbonyls and compared in position to the corresponding $M(CO)_5PPh_2H$ [9,10,11].

3.4. Spectroscopic data and molecular structure of $CpFe(CO)(\mu\text{-}Co)(\mu\text{-}PPh_2)W(CO)_4$ (2)

When the THF solution of **1-W** was irradiated with UV under vacuum, the colour of the solution turned from yellow to dark brown. After the solvent was removed, an air sensitive brown compound, **2**, was obtained. No reaction was observed when THF solutions of **1-Cr** and **1-Mo** were irradiated with UV light under similar conditions.

The phosphorus NMR of **2** in THF at room temperature showed resonance at 160.8 ppm with $J(^{31}P-^{183}W)$ 201.4 Hz. This relatively low field resonance indicated that a metal–metal bond formed in the complex [16]. The intensity ratio to the $J(^{31}P-^{183}W)$ satellites of the phosphorus signal was 1 : 11 : 1, which indicated that phosphorus was coordinated to only one tungsten. The mass spectrum of the complex showed parent peak with m/z at 658, which was inconsistent with the empirical formula of $CpFe(CO)(\mu\text{-}PPh_2)W(CO)_5$. No bridging carbonyl was observed in the solution IR spectrum of **2**. However, absorption at 1836 cm^{-1} was observed in the solid state IR spectrum. Bridging CO or semibridging CO may exist in the solid form of the complex [22].

The absence of bridging CO absorption in solution IR and the observation of bridging CO or semibridging CO absorption in solid state IR indicated that in solution complex **2** may exist in two forms, one with bridging or semibridging carbonyl and the other without. These two forms of structure exchanged with each other in solution at room temperature. In solid state, only one isomer existed. In order to understand this exchange, we obtained a variable temperature ^{13}C NMR of complex **2**.

We prepared the ^{13}CO enriched complex **2** by reacting ^{13}CO with **2** to produce enriched **1-W**. This enriched **1-W** was then further photolyzed to reproduce **2**. About 20% enrichment was obtained according to the parent peak pattern of the mass spectrum of enriched **1-W**. Figure 3 shows the variable temperature ^{13}C NMR spectra of **2** in CD_2Cl_2.

At 308 K, two doublets at 212.6 and 199.1 ppm were observed. That at 212.6 was assigned to CO on Fe, and the other was assigned to CO on W on the basis of the $J(W-C)$ satellite with peak intensity to satellite intensity ratio 11 : 1. At 280 K, a very broad hump was observed at around 192 ppm. At 260 K, a broad peak at 246 ppm appeared. At 240 K, broad peaks at 247.1,

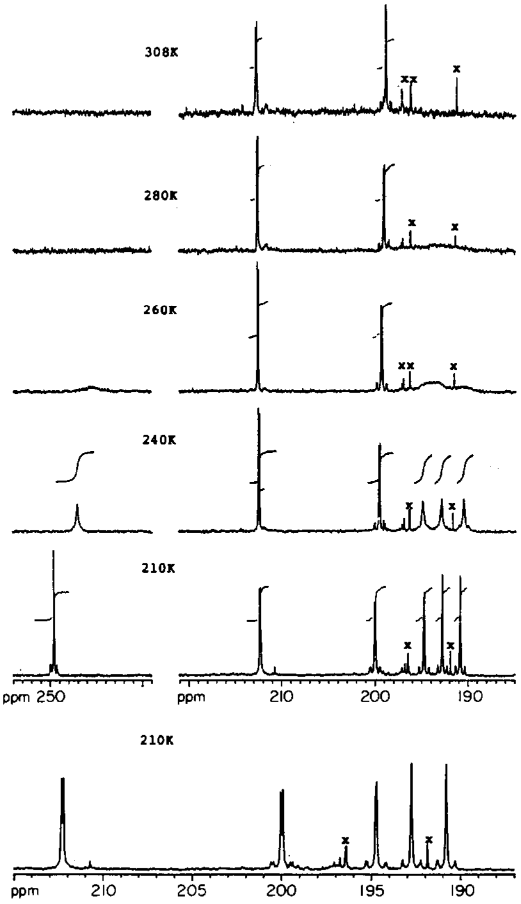
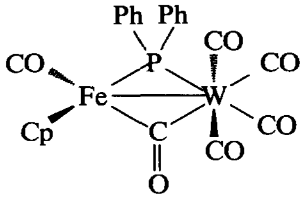


Fig. 3. Variable temperature $^{13}C\{^1H\}$ NMR spectrum of **2**. Only carbonyl region is shown. Signals due to impurities are marked x.

194.8, 192.8 and 190.4 ppm were observed. At 210 K, the above peaks were sharpened and $J(W-C)$ and $J(P-C)$ were clearly shown. The 247.1 ppm peak was assigned to bridging (or semibridging) carbonyl which bridged the Fe and W in the complex because bridging carbonyl of Fe complexes was downfield relative to the corresponding terminal carbonyl [19]. This assignment received further clear support from the observed $J(W-C)$ satellites, which indicated that the carbon on the CO was attached to one W. Intensity ratios of all these carbonyls were 1 : 1 : 1 : 1 : 1 : 1, which indicated that there was one carbonyl on Fe, one carbonyl bridging Fe and W, and four carbonyls on W. Of the four tungsten terminal carbonyl resonances at low temperature, the doublet at 199.1 pm was assigned to the CO *trans* to the phosphido phosphorus atom based on its $J(P-C)$ value being larger than the $J(P-C)$ values of the other CO ligands. The other tungsten terminal CO signals were assigned to the CO *cis* to the phosphido bridge. Based on these observations, we tentatively assigned the structure of **2** thus:



We interpret the ^{13}C NMR observations as follows. Below 240 K, all carbonyls were rigid and no intramolecular exchange of carbonyl ligands occurred. Above 260 K, exchanges of the carbonyl groups took place among the three *cis* tungsten CO ligand and the bridging CO (with signal at 250 ppm). The signal of the *trans* CO ligand and the iron terminal carbonyl ligand remained unchanged at room temperature indicating that these two ligands were not involved in the exchange with the bridging CO throughout the process. At room temperature, fluxional behaviour was clearly revealed by the observation of the broadening of all three *cis* CO and the bridging CO signals.

After bubbling CO through a stirred solution of **2** in THF, we recovered the complex **1-W** quantitatively based on ^{31}P NMR. We consider this as a ligand substitution reaction, in which the incoming CO replaced the metal–metal donor–acceptor bond [23]. This indicated that the metal–metal donor–acceptor bond was relatively weak and compound **2** could be a convenient source for the preparation of $CpFe(CO)_2(\mu\text{-}PPh_2)M(CO)_4L$.

3.5. Supplementary material available

Tables of experimental and crystal data, atomic coordinates, anisotropic thermal parameters, bond distances and angles, and a list of structure factors are available from the authors.

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References and notes

1 R. Regragui, P. H. Dixneuf, N. J. Taylor and A. J. Carty, *Organometallics, 9* (1990) 2234.
2 S. G. Shyu and A. Wojcicki, *Organometallics, 4* (1985) 1457.
3 W. C. Mercer, R. R. Whittle, E. W. Burkhardt and G. L. Geoffroy, *Organometallics, 4* (1985) 68.
4 S. Rosenberg, G. L. Geoffroy and A. L. Rheingold, *Organometallics, 4* (1985) 1184.
5 D. A. Roberts, G. R. Steinmetz, M. J. Breen, P. M. Shulman, E. D. Morrison, M. R. Duttera, C. W. DeBrosse, R. R. Whittle and G. L. Geoffroy, *Organometallics, 2* (1983) 846.
6 M. J. Breen, M. R. Duttera, G. L. Geoffroy, G. C. Novotnak, D. A. Roberts, P. M. Shulman and G. R. Steinmetz, *Organometallics, 1* (1982) 1008.
7 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals* Pergamon, Oxford, 1966.
8 S. O. Grim, D. A. Wheatland and W. McFarlane, *J. Am. Chem. Soc., 89* (1967) 5573.
9 J. G. Smith and T. D. Thompson, *J. Chem. Soc. A*, (1967) 1694.
10 R. L. Keiter, S. L. Kaiser, N. P. Hansen, J. W. Brodak and L. W. Cary, *Inorg. Chem., 20* (1981) 283.
11 R. L. Keiter, Y. Y. Sun, J. W. Broadack and L. W. Cray, *J. Am. Chem. Soc., 106* (1979) 2636.
12 R. B. King and F. G. Stone, *Inorg. Synth., 7* (1963) 110.
13 P. M. Treichel, W. K. Dean and W. M. Douglas, *J. Organomet. Chem., 42* (1972) 145.
14 (a) R. L. Keiter and M. J. Madigan, *Organometallics, 1* (1982) 409; (b) S. G. Shyu, *Ph.D. thesis*, Ohio State University, 1986.
15 S. W. Kirtley, in G. Wilkinson, F. G. A. Stone, and E. Abel, (eds.), *Comprehensive Organometallic Chemistry,* Pergamon, Oxford, 1982, Chap. 26.
16 (a) A. J. Carty, *Adv. Chem. Ser., 196* (1982) 163; (b) P. E. Garrou, *Chem. Rev., 81* (1981) 229.
17 Natural abundance of ^{183}W is 14.28%.
18 O. A. Gansow, D. A. Schexanayder and B. Y. Kimura, *J. Am. Chem. Soc., 94* (1971) 3406.
19 O. A. Gansow and W. D. Vernon, *Top. Carbon-13 NMR Spectrosc., 2* (1972) 269.
20 B. E. Mann, *Adv. Organomet. Chem., 12* (1974) 135.
21 J. C. T. R. Burckett-St. Laurent, R. J. Haines, C. R. Nolte and N. D. C. T. Steen, *Inorg. Chem., 19* (1980) 577.
22 H. Schafer and W. Leske, *Z. Anorg. Allg. Chem., 550* (1987) 57.
23 T. Kawamura, T. Sowa, T. Yonezawa, T. Yamabe, H. Masuda, T. Taga and K. Machida, *J. Organomet. Chem., 276* (1984) C10.