

Synthesis and structural characterization of a phosphido-bridged heterobimetallic transition metal complex, $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Mo}(\text{CO})_4$

Song-Lin Li, Zheng-Zhi Zhang¹, Jerry C.C. Chan, Steve C.F. Au-Yeung,
Thomas C.W. Mak^{*}

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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Abstract

A heterobimetallic transition metal complex $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Mo}(\text{CO})_4$ (2) has been synthesized by the direct reaction of *trans*-($\text{CO})_3\text{Fe}(\text{Ph}_2\text{PH})_2$ (1) with $\text{Mo}(\text{CO})_6$ in benzene, and fully characterized by single-crystal X-ray analysis. Complex 2 crystallizes in the space group C2 (No. 5) with $a = 20.688(4)$, $b = 8.809(2)$, $c = 17.081(3)$ Å, $\beta = 102.60(3)^\circ$, $V = 3038(2)$ Å³ and $Z = 4$. The structure has been refined to $R_F = 0.032$ and $R_{w,F} = 0.041$ for 2579 Mo K α reflections with $F > 4\sigma(F)$. The two metal carbonyl fragments are bridged by a pair of $\mu\text{-PPh}_2$ ligands. Although the Fe–Mo distance of 2.854(1) Å in 2 is much longer than the sum of the metallic radii of Fe and Mo atoms [2.66 Å], the existence of metal–metal bonding between the Fe and Mo atoms has been deduced from spectroscopic and structural data.

Keywords: Iron; Molybdenum; Phosphido complex; Heterobimetallic complex; Carbonyl; Crystal structure

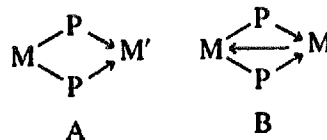
1. Introduction

Heterobimetallic complexes have been the subject of extensive studies because two different transition metals brought into close proximity in a bimetallic complex may display chemistry unique from that found in the individual separated fragments [1–4]. In particular, interest has focused on the complexes containing electron-deficient and electron-rich metal centers. Such systems offer a synergistic interaction when they are used as catalysts in some catalytic reactions [5], such as in the reactions of Group 9 metal carbonylates with Group 4 metallocene alkyls [6], hydroformylation catalyzed by a Zr–Rh heterobimetallic species in which enhanced activity was attributed to Lewis acid activation of CO by the Zr [7,8], and hydroformylation of 1-hexene catalyzed by $\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{RhH}(\text{CO})\text{PPh}_3$ [9].

Several factors contribute to the occurrence and sta-

bility of heterobimetallic compounds: formation of metal–metal bonds, ligand bridges, or a combination of both structural features. Among the phosphine ligands that are capable of serving as bridging agents, diorganophosphide (PR_2^-) ligands have been used extensively to synthesize heterobimetallic complexes because they not only provide particularly stable bridge anchors, which retard fragmentation of the bimetallic unit [10–12], but also constitute systems in which steric and electronic factors can be finely tuned. For example, in bis- PR_2^- -bridged complexes that have been structurally characterized, the M–P–M' angles and M–M' distances range from 54 to 104° and 2.21 (multiple M–M' bond) to 3.70 Å (M–M' non-bonding) respectively [13,14].

For the phosphido-bridged bimetallic complexes containing early and late transition metals (M and M' respectively), two bonding modes have been established structurally and spectroscopically [15]:



^{*} Corresponding author.

¹ On sabbatical leave from the Elemento-Organic Chemistry Laboratory, Nankai University, Tianjin, People's Republic of China.

In type A, there is no interaction between the metal centers, and the $M(PR_2)_2$ unit simply acts as a bidentate phosphine ligand to coordinate with M' [16]. In type B, bonding between the M and M' fragments occurs via lone-pair donation from the bridging phosphido groups to the late transition metal, with a weak secondary interaction comprising back-donation from the late transition metal M' to the empty low-lying orbitals on the early transition metal M.

In the present study, a phosphido-bridged heterobimetallic transition metal complex $(CO)_3Fe(\mu-PPh_2)_2Mo(CO)_4$ (**2**) was synthesized from the direct reaction of $trans-(CO)_3Fe(Ph_2PH)_2$ with $Mo(CO)_6$ and fully characterized by single-crystal X-ray analysis. Although the Fe–Mo distance of 2.853(1) Å in **2** is much longer than the sum of the atomic radii of Fe and Mo atoms, bonding between these two metal atoms has been established spectroscopically and structurally.

2. Experimental section

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. The solvent tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled before use. Ph_2PH was prepared from reaction of Ph_3P and lithium chips followed by hydrolysis. Other solvents and chemicals were used as purchased without further purification. Infrared spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 205 FT-IR spectrometer. The solid ^{31}P NMR spectra were measured on a Bruker ASX-300 solid-state FT-NMR spectrometer using 85% H_3PO_4 as reference standard.

2.1. Synthesis of $trans-Fe(CO)_3(Ph_2PH)_2$ **1**

Sodium hydroxide (1.5 g, 37.5 mmol) was ground and dissolved in *n*-butanol (80 cm^{-1}), to which $Fe(CO)_5$ (2.1 cm^{-1} , 16 mmol) was added. After the mixture was stirred for 30 min at ambient temperature, Ph_2PH (5.3 g, 28 mmol) in *n*-butanol (10 cm^{-1}) was added. The mixture was refluxed for 4 h, then cooled to room temperature and filtered. The product obtained was dissolved in CH_2Cl_2 and filtered to remove the insoluble solid. Methanol was added to the filtrate and the solvent was removed under reduced pressure to give a yellow crystalline solid. Recrystallization from CH_2Cl_2 /MeOH afforded the orange complex **1** (5.3 g, 74%). IR $\nu(CO)$: 1878 cm^{-1} . Solid ^{31}P NMR exhibits two peaks: $\delta_{11} = -85$, $\delta_{22} = 17$, $\delta_{33} = 243$ ppm; $\delta_{11} = -56$, $\delta_{22} = 78$, $\delta_{33} = 148$ ppm.

2.2. Synthesis of $(CO)_3Fe(\mu-PPh_2)_2Mo(CO)_4$ **2**

$trans-(CO)_3Fe(Ph_2PH)_2$ (0.52 g, 1.0 mmol) and $Mo(CO)_6$ (0.26 g, 1.0 mmol) were dissolved in benzene (25 cm^{-1}). After the mixture was refluxed for 3 days, the solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of benzene. After standing for 1 day at $-15^\circ C$, air-stable purple–red plate-like crystals of **2** were formed, collected and dried in air (0.43 g, 60%). Anal. Found: C, 51.70; H, 2.87; P, 8.33. $C_{31}H_{20}FeMoP_2$ ($M_r = 718.2$) Calc.: C, 51.81; H, 2.79; P, 8.64%. IR ($\nu(CO)$): 2028s, 1970s, 1930s, 1879s cm^{-1} . Solid ^{31}P NMR $\delta_{11} = 5$, $\delta_{22} = 122$, $\delta_{33} = 499$ ppm.

2.3. Structure determination of $(CO)_3Fe(\mu-PPh_2)_2Mo(CO)_4$ **2**

Purple–red crystals of **2** were obtained by recrystallization from benzene. A suitable crystal was selected and affixed to a glass fiber. Information concerning X-ray data collection and structure refinement is summarized in Table 1. The intensities were collected at 290 K in the ω -scan mode [17] on a Rigaku AFC7 diffractometer, using Mo K α radiation ($\lambda = 0.71073$ Å) from a rotating-anode generator operating at 50 kV and 90 mA. Unit-cell parameters were calculated from

Table 1
Crystallographic summary for $(CO)_3Fe(\mu-PPh_2)_2Mo(CO)_4$ **2**

Formula	$C_{31}H_{20}O_7P_2FeMo$
M	718.2
Crystal system	monoclinic
Space group	C_2 (No. 5)
Crystal size (mm ³)	0.10–0.20 × 0.20
a (Å)	20.668(4)
b (Å)	8.809(2)
c (Å)	17.081(3)
β (deg)	102.60(3)
U (Å ³)	3038(2)
Z	4
D_c (g cm ^{−3})	1.570
$F(000)$	1440
μ (cm ^{−1})	10.41
2θ range (deg)	4–50
No. of data collected	2958
No. of independent data	2870
No. of data used, n	2579 [$F > 4\sigma(F)$]
No. of variables, p	379
R	0.032
R'	0.041
S	1.16
Extrema in final difference map (e Å ^{−3})	+0.41, −0.64
Mean shift/eds max	0.001

$R = \sum \Delta / \sum |F_o|$, $R' = [\sum w \Delta^2 / \sum |F_o|^2]^{1/2}$ and $S = [\sum w \Delta^2 / (n - p)]^{1/2}$ where $w = [\sigma^2(F_o) + K |F_o|^{-4}]^{-1}$, $\Delta = |F_o| - |F_c|$; $K = 4 \times 10^4$. Extinction parameter $\chi = 0.00016$ where the 'corrected' calculated structural factor $F_{corr} = F_c(1 + 0.002\chi F_c^2 / \sin 2\theta)^{-1/4}$.

least-squares fitting of the 2θ angles for 25 selected strong reflections. Crystal stability was monitored by recording three check reflections at intervals of 100 data measurements, and no significant variation was detected.

The crystal structure of **2** was solved by direct methods. All non-hydrogen atoms other than one two-fold disordered carbonyl group [represented by C(6)O(6) and C(6')O(6')] which are subjected to soft restraints of Fe–C 1.73 ± 0.005 and C–O 1.18 ± 0.005 Å] were refined anisotropically by full-matrix least-squares. The hydrogen atoms of the ligands were placed in their calculated positions with C–H 0.96 Å, assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms. These hydrogen atoms were included in the structure factor calculations, but their positions were not refined. Assignment of the absolute structure [18] (here the direction of the polar axis in space group C2) was verified by refining a parameter η as a factor, multiplying by all imaginary components $\Delta f''$ of the anomalous dispersion terms of the atomic scattering factors, which converged towards a value of +1 [19].

All calculations were carried out on a PC 486 using the SHELXTL PC program package [20]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [21].

Final atomic coordinates and equivalent isotropic thermal parameters, along with their estimated standard deviations, are presented in Table 2 and selected bond lengths and angles in Table 3. A listing of observed and calculated structure factors, anisotropic thermal parameters and H-atom coordinates is available as supplementary material.

3. Results and discussion

Reaction of Ph_2PH with $\text{Fe}(\text{CO})_5$ led to the formation of **1**, and a phosphido-bridged heterobimetallic complex $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Mo}(\text{CO})_4$ **2** was obtained via direct reaction of *trans*- $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PH})_2$ **1** with $\text{Mo}(\text{CO})_6$, as shown in Scheme 1.

3.1. Synthesis and spectroscopic characterization

Complex **2** was synthesized by adapting the literature method for the preparation of *trans*-($\text{CO})_3\text{Fe}(\text{Ph}_2\text{Ppy})_2$ [22]. Similar to that of *trans*-($\text{CO})_3\text{Fe}(\text{Ph}_2\text{Ppy})_2$, the IR spectrum of *trans*-($\text{CO})_3\text{Fe}(\text{Ph}_2\text{PH})_2$ exhibits only one intense carbonyl stretching frequency, at 1878 cm^{-1} , which indicates D_{3h} molecular symmetry consistent with the two Ph_2PH ligands occupying *trans*-positions. The solid ^{31}P NMR spectrum of **1** shows a doublet at $\delta_{\text{iso}} \equiv (\delta_{11} + \delta_{22} + \delta_{33})/3$ of 58 and 57 ppm, caused by

Table 2

Atomic coordinates ($\times 10^5$ for Mo and Fe, $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients U_{eq} ($\text{\AA}^2 \times 10^4$ for Mo and Fe, $\text{\AA}^2 \times 10^3$ for other atoms) for complex **2**

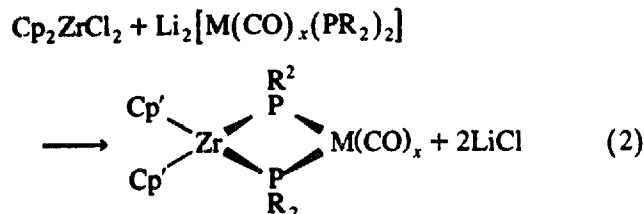
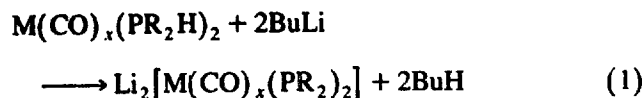
Atom	x	y	z	U_{eq}
Mo(1)	41363(2)	50000	32445(3)	402(2)
C(1)	3475(3)	6701(8)	2799(4)	48(2)
O(1)	3136(3)	7682(7)	2589(3)	76(2)
C(2)	3998(3)	5247(9)	4368(4)	55(2)
O(2)	3934(3)	5341(8)	5016(3)	81(2)
C(3)	4873(4)	3483(9)	3690(4)	54(2)
O(3)	5300(3)	2704(8)	3952(4)	79(2)
C(4)	4813(4)	6690(10)	3508(5)	59(3)
O(4)	5183(3)	7633(9)	3674(4)	95(3)
Fe(1)	35491(4)	30066(12)	19703(5)	43(1)
C(5)	4098(3)	1464(8)	2332(4)	48(2)
O(5)	4426(3)	434(6)	2532(3)	74(2)
C(6)	3081(6)	1626(14)	1382(8)	48(3)
O(6)	2753(6)	687(15)	989(8)	90(4)
C(6')	3239(8)	1961(19)	1119(8)	65(4)
O(6')	2985(8)	1143(19)	596(9)	121(5)
C(7)	2979(3)	4432(9)	1463(4)	53(2)
O(7)	2611(3)	5242(9)	1113(3)	84(2)
P(1)	3187(1)	3202(2)	3093(1)	43(1)
C(8)	2598(4)	921(9)	3868(4)	63(3)
C(9)	2600(5)	−367(10)	4325(5)	79(4)
C(10)	3191(5)	−1042(10)	4683(5)	83(4)
C(11)	3760(4)	−429(11)	4593(5)	79(4)
C(12)	3771(4)	867(11)	4129(5)	71(3)
C(13)	3183(3)	1566(8)	3752(3)	49(2)
C(14)	1834(3)	3415(10)	2440(4)	64(3)
C(15)	1195(3)	4008(13)	2408(5)	78(3)
C(16)	1101(3)	5135(13)	2924(5)	75(3)
C(17)	1610(3)	5702(10)	3471(5)	69(3)
C(18)	2246(3)	5134(10)	3517(4)	57(2)
C(19)	2361(3)	3998(8)	3015(3)	45(2)
P(2)	4389(1)	4557(2)	1902(1)	43(1)
C(20)	5778(3)	4390(9)	2257(4)	60(3)
C(21)	6393(4)	3914(11)	2116(5)	73(3)
C(22)	6411(4)	2905(11)	1519(5)	76(3)
C(23)	5842(4)	2335(10)	1073(5)	73(3)
C(24)	5224(3)	2765(8)	1201(4)	55(2)
C(25)	5195(3)	3828(8)	1795(4)	46(2)
C(26)	4054(4)	5604(10)	327(4)	79(3)
C(27)	3959(5)	6671(11)	−270(5)	91(4)
C(28)	4042(5)	8169(11)	−89(5)	88(4)
C(29)	4241(5)	8584(10)	697(6)	95(4)
C(30)	4342(4)	7530(9)	1294(5)	69(3)
C(31)	4250(3)	6017(7)	1121(4)	47(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Atoms C(6), O(6) and C(6'), O(6') represent a two-fold disordered carbonyl group and each has a site occupancy of 0.5.

dipolar coupling between the directly bonded P and H atoms [23]. These spectral data are similar to those reported previously for $(\text{CO})_3\text{Fe}(\text{Ph}_2\text{PH})_2$ prepared using a photochemical method, whose IR spectrum showed three carbonyl stretching frequencies at 1964w, 1873s, 1844w cm^{-1} in THF, and whose ^{31}P NMR spectrum showed a chemical shift at δ 54 ppm in C_6D_6 [24].

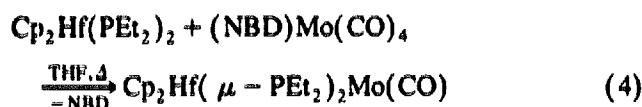
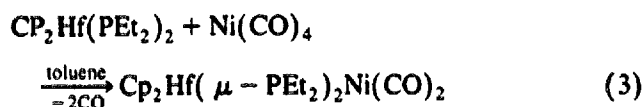
The most widely used synthetic routes to diorganophosphido-bridged heterobimetallic complexes involve the deprotonation of metal-coordinated sec-

ondary phosphines and reaction of the resulting anions with a transition-metal halide. A typical example is shown in Eqs. (1) and (2) [25]:



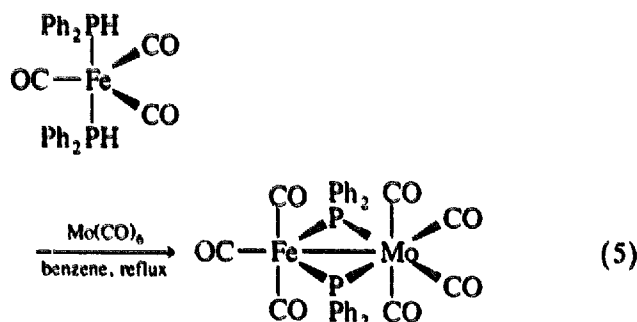
$\text{M} = \text{Fe}$, $x = 3$, $\text{R} = \text{Ph}$, Cy ; $\text{M} = \text{W}$, $x = 4$, $\text{R} = \text{Ph}$

Such complexes can also be prepared from the reaction of a neutral complex containing two secondary phosphine groups, which functions as a bidentate phosphine ligand, and another metal complex containing easily leaving coordination groups, as shown in Eqs. (3) and (4) [16]:

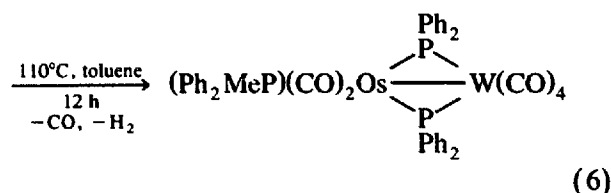
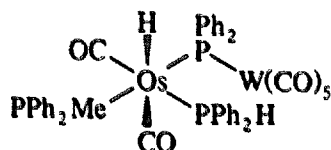


$\text{NBD} = \eta^4\text{-norbornadine}$

However, in the present case complex **2** was prepared by direct reaction of *trans*- $\text{Fe}(\text{CO})_3(\text{Ph}_2\text{PH})_2$ with $\text{Mo}(\text{CO})_6$:



The yield is almost quantitative after refluxing for 6 days. A similar reaction was observed in the following example [25]:

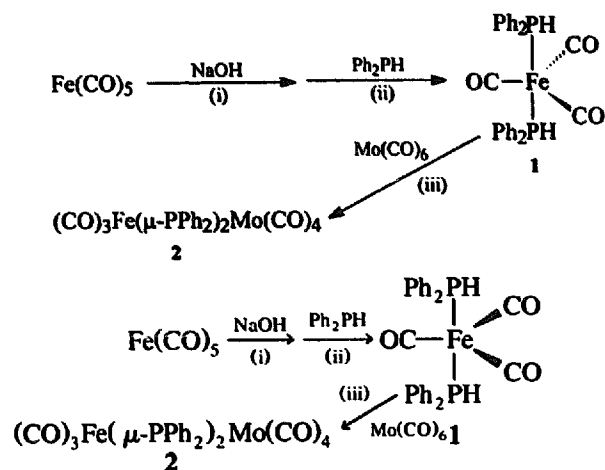


The IR spectrum of complex **2** shows an extensive absorption band in the range of terminal carbonyl group stretching vibration, and only four peaks of $\nu(\text{CO})$ 2028s, 1970s, 1930s, 1879s cm^{-1} can be distinguished. The solid ^{31}P NMR spectrum of **2** exhibits one peak at δ_{iso} 209 ppm, which is consistent with the chemical equivalence of the two bridging phosphorus atoms.

3.2. Crystal structure of $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Mo}(\text{CO})_4$ **2**

The X-ray crystallographic study of $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Mo}(\text{CO})_4$ (**2**) reveals that it exists as a discrete dinuclear molecule in which the iron and molybdenum centers are linked by two phosphido groups (Fig. 1). The Fe–Mo distance of 2.854(1) Å is not only markedly longer than the sum of the atomic radii of iron and molybdenum [$r(\text{Fe}) + r(\text{Mo}) = 2.66$ Å] [26], but also significantly longer than those found in the complex $\eta^3\text{-}[(2,4,6\text{-}^i\text{Bu}_3\text{-C}_6\text{H}_2\text{O})[(\text{Ph})(\text{H})\text{C}=\text{CH})\text{P}-\text{Fe}(\text{CO})_3-\text{C}(\text{Ph})-\text{CH}]\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$] [2.804(1) Å] [27], in the heterotrinuclear cluster $(\mu_3\text{-S})\text{FeMoNi}(\eta^5\text{-RC}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5$ [2.782(1) Å] [28], and in $\text{Cp}_3\text{Co}_2\text{MoFe}(\text{CO})_5\text{CCO}_2\text{CH}(\text{CH}_3)_2$ [2.773(1) Å] [29]. If the Fe–Mo interaction is ignored, the coordination environment of the Fe atom can be regarded as a trigonal bipyramid with two carbonyl groups occupying the axial positions and one carbonyl group and two phosphorus atoms in the equatorial plane. This coordination environment is similar to that found in $\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)_2$ [30] [Fe–P 2.234(3), 2.228(3) Å]. The *cis*-octahedral coordination environment around the molybdenum atom is similar to that found in $\text{Cp}_2\text{Hf}(\mu\text{-PPh}_2)_2\text{Mo}(\text{CO})_4$ [16]. The Mo–P distances of 2.492(2) and 2.491(2) Å are somewhat shorter than those found in $\text{Cp}_2\text{Hf}(\mu\text{-PPh}_2)_2\text{Mo}(\text{CO})_4$ [2.538(1), 2.534(1) Å] [16], and similar to that in $[\text{Mo}(\text{CO})_4(\mu\text{-PEt}_2)_2]_2$ [av. Mo–P 2.51(1) Å] [31]. The Mo–C distances lie in the range of other normal molybdenum carbonyl compounds. The planar FeP_2Mo ring is similar to the HfP_2Mo unit in $\text{Cp}_2\text{Hf}(\mu\text{-PPh}_2)_2\text{Mo}(\text{CO})_4$ [16]. The Mo(1)–Fe(1)–C(6) and Mo(1)–Fe(1)–C(6') angles are 164.9(5) and 172.3(3)° respectively.

For the phosphido-bridged bimetallic complexes, structural and spectroscopic rules have been established to determine the existence of metal–metal bonding between the bridged metal centers: (1) for phosphido-bridged transition-metal systems $\text{M}-\text{P}-\text{M}'$ angles in the range 70–85° have invariably been associated with some degree of metal–metal bonding, as exemplified by



Scheme 1. Conditions: (i) *n*-butanol, 25°C, 30 min; (iv) reflux, 4 h; (v) benzene, reflux, 3 days.

$(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Fe(CO)}_3$ [Fe–Fe 2.613(2) Å, av. Fe–P–Fe 72.0(1)°] [30] and $\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{W(CO)}_4$ [Zr–W 3.289(1) Å, av. Zr–P–Mo 79.21°] [24]; (2) in

closely related phosphido-bridged transition-metal complexes the ^{31}P NMR chemical shift for $\mu\text{-PR}_2$ ligands bridging two metals linked by a metal–metal bond often appears downfield (δ 300 to 50), whereas upfield resonances (δ 50 to –300) are commonly observed for compounds without a metal–metal bond [22–34]. Although exceptions to these correlations are known [10,35], they are important criteria for judging the existence of metal–metal bonding in the phosphido-bridged transition-metal complexes.

In complex 2 the formulation of a single bond between the iron and molybdenum centers, which satisfies the 18-electron rule, is derived from the following structural features and spectroscopic data: (i) the Fe–P–Mo angles of 74.4(1) and 74.1(1)° in complex 2 fall well within the range of 70–85°; (ii) a downfield chemical shift δ 151 was observed in the solid ^{31}P NMR of compound 2, a value downfield of the resonance at δ 58 ppm in 1.

Although the Fe–C bond length *trans* to the Mo atom is significantly shorter than the other two Fe–C

Table 3
Selected bond lengths (Å) and angles (deg) for complex 2

Mo(1)–C(1)	2.059(7)	Mo(1)–C(2)	2.012(7)
Mo(1)–C(3)	2.045(7)	Mo(1)–C(4)	2.025(8)
Mo(1)–Fe(1)	2.854(1)	Mo(1)–P(1)	2.492(2)
Mo(1)–P(2)	2.491(2)	C(1)–O(1)	1.121(9)
C(2)–O(2)	1.146(9)	C(3)–O(3)	1.132(9)
C(4)–O(4)	1.124(11)	Fe(1)–C(5)	1.791(7)
Fe(1)–C(6)	1.733(12)	Fe(1)–C(6')	1.722(14)
Fe(1)–C(7)	1.809(7)	Fe(1)–P(1)	2.212(2)
Fe(1)–P(2)	2.233(2)	C(5)–O(5)	1.141(9)
C(6)–O(6)	1.181(17)	C(6')–O(6')	1.179(20)
C(7)–O(7)	1.117(9)		
C(1)–Mo(1)–C(2)	93.0(3)	C(1)–Mo(1)–C(3)	173.7(3)
C(2)–Mo(1)–C(3)	88.0(3)	C(1)–Mo(1)–C(4)	85.3(3)
C(2)–Mo(1)–C(4)	86.8(3)	C(3)–Mo(1)–C(4)	88.6(3)
C(1)–Mo(1)–Fe(1)	91.6(2)	C(2)–Mo(1)–Fe(1)	131.9(2)
C(3)–Mo(1)–Fe(1)	92.3(2)	C(4)–Mo(1)–Fe(1)	141.3(2)
C(1)–Mo(1)–P(1)	88.8(2)	C(2)–Mo(1)–P(1)	84.0(2)
C(3)–Mo(1)–P(1)	97.4(2)	C(4)–Mo(1)–P(1)	168.8(3)
Fe(1)–Mo(1)–P(1)	48.3(1)	C(1)–Mo(1)–P(2)	91.7(2)
C(2)–Mo(1)–P(2)	175.2(2)	C(3)–Mo(1)–P(2)	87.2(2)
C(4)–Mo(1)–P(2)	92.6(2)	Fe(1)–Mo(1)–P(2)	48.8(1)
P(1)–Mo(1)–P(2)	97.1(1)	Mo(1)–C(1)–O(1)	176.0(6)
Mo(1)–C(2)–O(2)	177.4(6)	Mo(1)–C(3)–O(3)	176.4(7)
Mo(1)–C(4)–O(4)	177.8(8)	Mo(1)–Fe(1)–C(5)	94.1(2)
Mo(1)–Fe(1)–C(6)	164.9(5)	C(5)–Fe(1)–C(6)	84.3(4)
Mo(1)–Fe(1)–C(6')	172.3(5)	C(5)–Fe(1)–C(6')	88.6(6)
Mo(1)–Fe(1)–C(7)	93.6(2)	C(5)–Fe(1)–C(7)	171.6(3)
C(6)–Fe(1)–C(7)	89.2(5)	C(6')–Fe(1)–C(7)	83.3(6)
Mo(1)–Fe(1)–P(1)	57.3(1)	C(5)–Fe(1)–P(1)	94.0(2)
C(6)–Fe(1)–P(1)	107.8(5)	C(6')–Fe(1)–P(1)	129.7(6)
C(7)–Fe(1)–P(1)	93.1(2)	C(5)–Fe(1)–P(2)	92.3(2)
C(6)–Fe(1)–P(2)	137.9(5)	C(6')–Fe(1)–P(2)	115.7(2)
C(7)–Fe(1)–P(2)	89.1(2)	Mo(1)–Fe(1)–P(2)	57.1(1)
Fe(1)–C(7)–O(7)	175.5(7)	Mo(1)–P(1)–Fe(1)	74.4(1)
Mo(1)–P(2)–Fe(1)	74.1(1)		

Atoms C(6), O(6) and C(6'), O(6') represent a two-fold disordered carbonyl group and each has a site occupancy of 0.5.

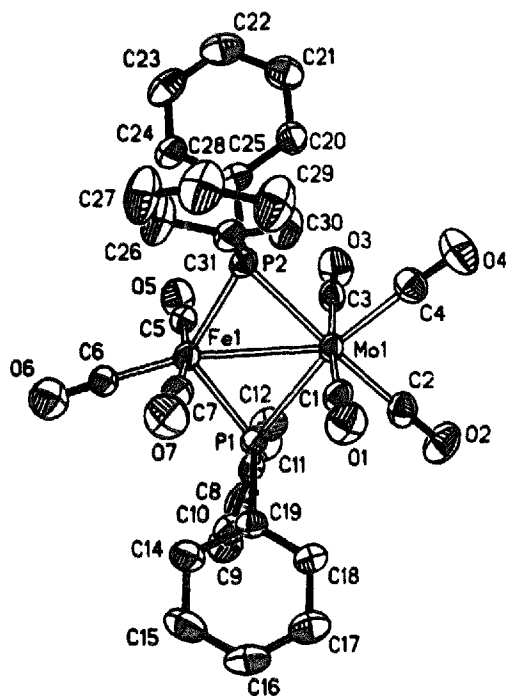


Fig. 1. Molecular structure and atom numbering scheme of $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)\text{Mo}(\text{CO})_4$. H-atoms and one component of the disordered carbonyl group are omitted for the sake of clarity. The thermal ellipsoids are drawn at the 35% probability level.

bond lengths, it cannot be definitely associated with the *trans* influence of Mo upon C(6)O(6) [or C(6')O(6')] owing to the manifestation of two-fold disorder of the *trans* carbonyl group.

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References

- [1] W.L. Gladfelter and G.L. Geoffroy, *Adv. Organomet. Chem.*, **18** (1980) 207.
- [2] D.A. Roberts and G.L. Geoffroy, in G. Wilkinson, F.G.A. Stone and W.E. Abel (eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, Chapter 40.
- [3] H.C. Foley, W.C. Finch, C.G. Pierpont and G.L. Geoffroy, *Organometallics*, **1** (1982) 1379.
- [4] P.T. Barger and J.E. Bercaw, *Organometallics*, **3** (1984) 279.
- [5] P. Braunstein, R. Bender and J. Kervennal, *Organometallics*, **1** (1982) 1236.
- [6] C.P. Cassey, R.F. Jordan and A.L. Rheingold, *J. Am. Chem. Soc.*, **105** (1983) 665.
- [7] R. Choukroum, D. Gervais, J. Jaud, P. Kalck and F. Senocq, *Organometallics*, **5** (1986) 67.
- [8] R. Choukroum and D. Gervais, *J. Organomet. Chem.*, **266** (1984) C37.
- [9] L. Gelmini and D.W. Stephan, *Organometallics*, **7** (1988) 849.
- [10] D. Nucciarone, N.J. Taylor and A.J. Carty, *Organometallics*, **3** (1984) 177.
- [11] R.P. Rosan, J.B. Hoke, R.R. Whittle, G.L. Geoffroy, J.P. Hutchinson and J.A. Zubieta, *Organometallics*, **3** (1984) 846.
- [12] G.N. Mott and A.J. Carty, *Inorg. Chem.*, **22** (1983) 2726.
- [13] R.A. Jones, J.G. Lasch, N.C. Norman, B.R. Whittlesey and T.C. Wright, *J. Am. Chem. Soc.*, **105** (1983) 6184.
- [14] A.J. Carty, F. Hartstock and N.J. Taylor, *Inorg. Chem.*, **21** (1982) 1349.
- [15] R.T. Baker, W.C. Fultz, T.B. Marder and I.D. Williams, *Organometallics*, **9** (1990) 2357.
- [16] R.T. Baker, T.H. Tulip and S.S. Wreford, *Inorg. Chem.*, **24** (1985) 1379.
- [17] R.A. Sparks, in R.F. Ahmed (ed.), *Crystallographic Computing Techniques*, Munksgaard, Copenhagen, 1971, p. 452.
- [18] P.G. Jones, *Acta Crystallogr.*, **A40** (1984) 660.
- [19] D. Rogers, *Acta Crystallogr.*, **A37** (1981) 731.
- [20] G.M. Sheldrick, in D. Sayre (ed.), *Computational Crystallography*, Oxford University Press, New York, 1982, pp. 506–514.
- [21] *International Tables for X-Ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, UK, 1974, pp. 55, 99, 149.
- [22] Z.Z. Zhang, H.P. Xi, W.J. Zhao, K.Y. Jiang, R.J. Wang, H.G. Wang and Y. Wu, *J. Organomet. Chem.*, **454** (1993) 221.
- [23] K. Eichele and R.E. Wasylshen, *J. Magn. Reson. A*, **106** (1994) 46.
- [24] T.S. Targos, R.P. Rosen, R.R. Whittle and G.L. Geoffroy, *Inorg. Chem.*, **24** (1985) 1375.
- [25] S. Rosenberg and G.L. Geoffroy, *Organometallics*, **4** (1985) 1184.
- [26] A.F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 5th edn., 1984, p. 1288.
- [27] H. Lang, M. Leise and L. Isolnai, *J. Organomet. Chem.*, **447** (1993) C1.
- [28] L.-C. Song, Y.-B. Dong, Q.-M. Hu, B.-M. Wu and T.C.W. Mak, *Chin. J. Struct. Chem.*, **14** (1995) 393.
- [29] M. Mlekuz, P. Bougeard, B.G. Sayer, R. Faggiani, C.J.L. Lock, M.J. McGlinchey and G. Jaouen, *Organometallics*, **4** (1985) 2046.
- [30] R.E. Ginsburg, R.K. Rothrock, R.G. Finke, J.P. Collman and L.F. Dahl, *J. Am. Chem. Soc.*, **101** (1979) 6550.
- [31] M.H. Linck and L.R. Nassimbeni, *Nucl. Chem. Lett.*, **9** (1973) 1105.
- [32] J.L. Petersen and R.P. Stewart, Jr., *Inorg. Chem.*, **19** (1980) 186.
- [33] A.J. Carty, S.A. MacLaughlin and N.J. Taylor, *J. Organomet. Chem.*, **204** (1981) C27.
- [34] P. Garrou, *Chem. Rev.*, **81** (1981) 229.
- [35] R.A. Jones, J.C. Wright, J.C. Atwood and W.E. Hunter, *Organometallics*, **2** (1983) 469.