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Metal−Metal-Bond-Assisted Substitution Reaction of a Heterobimetallic Phosphido-Bridged Mo−Fe Complex

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The heterobimetallic phosphido-bridged complexes $Cp\overline{Mo(CO)_2(\mu\text{-}PPh_2)Fe}(CO)_4$ (**1**) and $CpMo(CO)_3(\mu\text{-}PPh_2)Fe(CO)_4$ (**2**) were prepared by the reaction of $CpMo(CO)_3PPh_2$ with $Fe_2(CO)_9$. The reaction between **1** and Lewis bases L (L = $P(OMe)_3$, PPh_2H, PPh_3) at ambient temperatures produced $Cp\overline{Mo(CO)_2(\mu\text{-}PPh_2)Fe}(CO)_3(L)$ (**3**) with L regiospecifically coordinated to Fe. However, **2** did not react with L under similar conditions.

An interesting cooperativity effect between metals in bimetallic phosphido-bridged complexes is that a metal can activate the substitution reaction of its adjacent metal carbonyl through the formation of a metal−metal bond.[1,2] The metal−metal bond was proposed to influence the reactivity of the bimetallic complex in two ways. One way is the electron donation from one metal to its adjacent metal through the metal−metal bond.[1] The second way is that the metal−metal bond can bring two metals together. The metal carbonyl is thus activated by its adjacent metal to form a semibridging carbonyl through the donation of the electron from this electron-rich adjacent metal atom to the π^* orbital of the metal CO to form a semibridging carbonyl.[1] To date, all the reported bimetallic phosphido-bridged complexes which show metal carbonyl substitution enhancement all have semibridging carbonyl ligands which are primarily coordinated to the metals where substitution occurs.[1,3] However, in the $(CO)_4\overline{Ru(\mu\text{-}PPh_2)Co}(CO)_3$ system, substitution of the Co carbonyl by Lewis base was proposed to be enhanced by the metal−metal bond.[2a] In that complex, no semibridging carbonyl ligand was present. Since its non-metal−metal-bonded analogue had not been reported, a reactivity comparison between metal−metal-bonded and non-metal−metal-bonded complexes could not be made and substitution enhancement by the metal−metal bond could not be concluded without reservation. However, whether a semibridging carbonyl ligand is a necessary structural criterion for substitution enhancement in bimetallic complexes is still interesting in the understanding of this kind of cooperativity effect.

To investigate whether a semibridging carbonyl ligand is a necessary structural criterion in bimetallic carbonyl substitution enhancement, we studied the substitution reaction of $Cp\overline{Mo(CO)_2(\mu\text{-}PPh_2)Fe}(CO)_4$ (**1**).[4] First, this complex is similar in molecular construction to previously reported bimetallic phosphido-bridged systems: $Cp\overline{W(CO)_2(\mu\text{-}PPh_2)W}(CO)_5$,[1d] $Cp\overline{Fe(CO)(\mu\text{-}CO)(\mu\text{-}PPh_2)W}(CO)_4$,[1a] $Cp\overline{W(CO)_2(\mu\text{-}PPh_2)Mo}(CO)_5$,[3c] and $Cp\overline{W(CO)_2(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe}(CO)_3$.[2b,4] Enhancement of the substitution of the Fe carbonyl in this complex can be expected. Second, its non-metal−metal-bonded analogue $CpMo(CO)_3(\mu\text{-}PPh_2)Fe(CO)_4$ (**2**) can be prepared and serves as a standard for the comparison of their reactivities to reveal the influence of the metal−metal bond in $Cp\overline{Mo(CO)_2(\mu\text{-}PPh_2)Fe}(CO)_4$. Third, and most important, the structure of this complex has been reported, which shows that it has no semibridging or bridging carbonyl ligand.[4]

$Cp\overline{Mo(CO)_2(\mu\text{-}PPh_2)Fe}(CO)_4$ (**1**) and $CpMo(CO)_3(\mu\text{-}PPh_2)Fe(CO)_4$ (**2**) were prepared by the reaction between $CpMo(CO)_3PPh_2$[5] and $Fe_2(CO)_9$ with **2** as a major product.[6,7] Because photolysis and thermolysis of **2** can produce **1**, complex **1** obtained in the reaction may result from the further loss of a CO ligand from **2** due to the laboratory fluorescent light.

The structure of **2** was characterized by a single-crystal X-ray diffraction study. Four CO ligands and $CpMo(CO)_3PPh_2$ coordinate to the Fe^0 atom to form a

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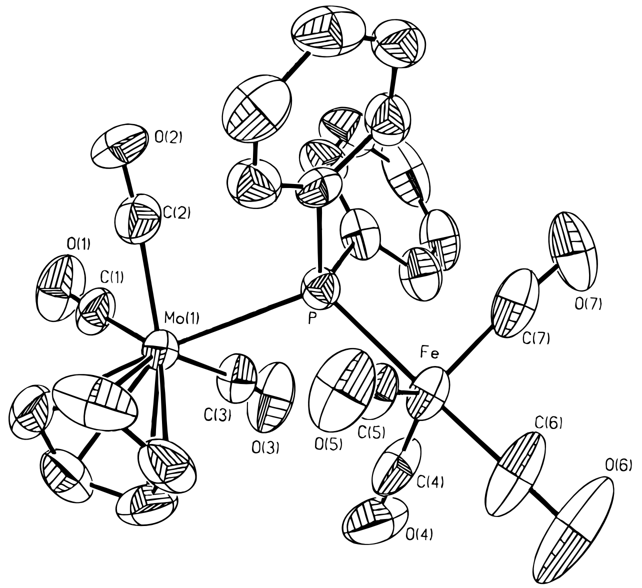


Figure 1. ORTEP drawing of **2**. Hydrogen atoms are omitted.

distorted trigonal bipyramid (Figure 1). A Mo−Fe distance of 4.246(6) Å is consistent with the observed upfield resonance of the phosphido bridge signal in its ^{31}P NMR, which indicates the absence of a metal−metal bond.[8]

Photolysis or thermolysis of **2** removes one CO from the Mo atom to form **1**. The Fe−Mo bond is formed such that both metals fulfill the 18-electron rule. The structure of complex **1** has been reported.[4] Interestingly, unlike its W analogue, which has a semibridging carbonyl ligand,[1b] no bridging carbonyl ligand is observed in its structure.

Similar to the reaction between $CpW(CO)_2(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_3$ (**1-w**) and Lewis bases L (L = $P(OMe)_3$, PPh_2H, PPh_3), reaction of **1** with Lewis bases L in THF at ambient temperature yielded **3** with L regiospecifically coordinated to Fe (Scheme 1).[1b] The structure of $CpMo(CO)_2(\mu\text{-}PPh_2)Fe(CO)_3P(OMe)_3$ (**3a**) was determined by a single-crystal X-ray diffraction study. The $P(OMe)_3$ ligand in **3a** is coordinated to the Fe atom with an Mo−Fe−P(2) angle of 172.55(3)° (Figure 2). The Mo−Fe distance of 2.9295(5) Å, indicative of a Mo−Fe bond, is consistent with the observed downfield resonance of the phosphido bridge signal in its ^{31}P NMR.

Complex **2** did not react with L at room temperature; however, heating **2** with L in THF at refluxing temperature produced **3**. The reaction probably proceeded through the formation of **1**, which further reacted with L to produce **3**. Interestingly, **2-w** did not react with L even at reflux temperature overnight. This is understandable, because **2-w** does not lose CO to form **1-w** under this reaction condition.

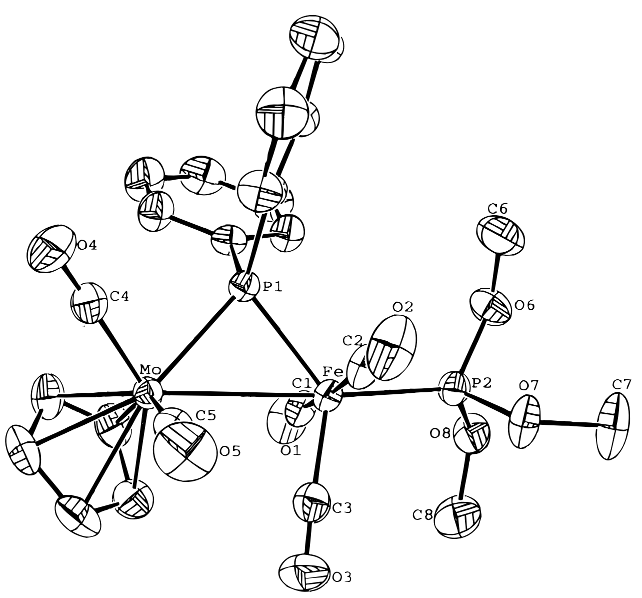
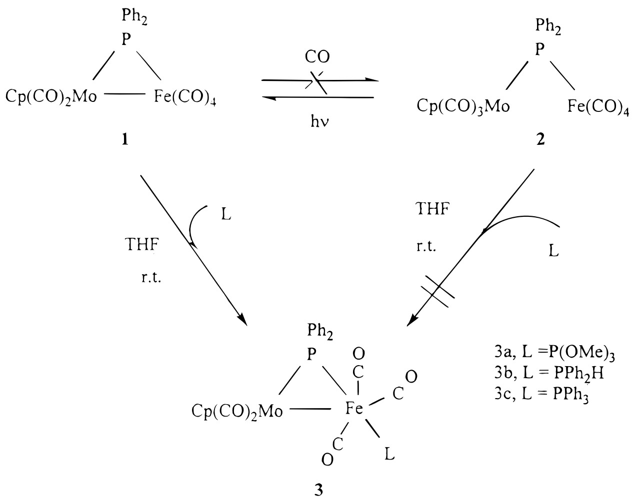


Figure 2. 2. ORTEP drawing of **3a**. Hydrogen atoms are omitted.

Scheme 1



Carbonyl ligands on Fe in **2** were inert toward L (L = $P(OMe)_3$, PPh_2H, PPh_3) when a THF solution of **2** and L was stirred for 1 day. In **1**, substitution of the Fe carbonyl was completed overnight at room temperature. Complexes **1** and **2** have similar frameworks, except that **1** has a metal−metal bond and **2** does not. These observations clearly indicate that CO ligands on Fe in **1** are labilized by the metal−metal bond. In **1**, no semibridging or bridging carbonyl ligand was observed in its solid-state structure. In addition, variable-temperature ^{13}C NMR of ^{13}CO-enriched **1** in d_8-toluene did not show any evidence of semibridging carbonyl ligands or exchange of carbonyl ligands between metals in the solution from 200 K to 340 K. Therefore, complexes **1** and **2** provide a definite example that a semibridging or bridging carbonyl ligand between metals in binuclear phosphido complexes is not an essential factor in the activation of the metal carbonyl ligands by its adjacent metal.

The Fe CO's in **1** are probably activated by the electron donation from Fe to its adjacent Mo through the metal−metal bond. The net result will be a decrease in d(Fe) → π*(CO) bonding of the Fe CO's, as indicated by a increase of stretching frequencies of the carbonyl groups on Fe from 2046 (m), 1966 (s), 1957 (s) cm^{-1} in

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Table 1. Spectroscopic Data for 1, 2, and 3[a]

complex	$^{31}P\{^1H\}$ NMR,[b,c] δ	^1H NMR,[b,d] δ	IR ν(CO),[e] cm^{-1}
1	157.7	5.16 (s, 5H)	2072 m, 2017 m, 1997 s, 1989 s, 1943 s, 1877 m[f]
2	26.0	5.41 (s, 5H)	2046 m, 2029 s, 1966 s, 1957 s, 1943 m, 1910 m[f]
3a	161.4 (d, $^2J_{P-P}$ 21.9, μ-PPh_2), 173.6 (d, $P(OMe)_3$)	5.04 (s, 5H), 3.62 (d, $^3J_{P-H}$ 12.0, 9H)	2034 m, 1961 s, 1919 s, 1845 s
3b	167.3 (d, $^2J_{P-P}$ 19.4, μ-PPh_2), 41.22 (d, J_{P-H} 364.0, PPh_2H)	4.77 (s, 5H)	2024 s, 1956 s, 1913 s, 1841 w
3c	161.6 (d, $^2J_{P-P}$ 12.4, μ-PPh_2), 63.3 (d, PPh_3)	4.78 (s, 5H)	2000 w, 1950 s, 1922 s, 1850 m

[a] At room temperature. [b] *J* values in Hz. [c] In THF solution unless otherwise indicated. [d] In $CDCl_3$ solution unless otherwise indicated: Cp, Me, and H groups only. Abbreviations: s, singlet; d, doublet. [e] In THF solution unless otherwise indicated. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder. [f] In hexane solution.

2 to 2072 (m), 2017 (m), 1998 (s), 1943 (s) cm^{-1} in **1**.[9] This induces weakening of the Fe–CO bond in **1**. The adjacent metal therefore can be considered as an electron sink which can receive or withdraw electrons from the adjacent metal through the formation of the metal–metal bond.

This electron redistribution increases the electron density of the electron-receiving metal, which may further labilize the adjacent carbonyl group through the donation of an electron to the π^* orbital of the adjacent Fe–CO to form the semibridging carbonyl ligand[10] as in **1-w** and other systems reported.[1b,c,3] The amplitude of enhancement should increase as the degree of bridging increases. This is demonstrated by the fact that $CpFe(CO)(\mu\text{-}CO)(\mu\text{-}PPh_2)W(CO)_4$ reacts at a much lower temperature than $CpW(CO)_2(\mu\text{-}PPh_2)W(CO)_5$ because the former has a higher degree of semibridging carbonyl.[1a,d] However, even though both complexes **1-w** and $Cp_2Nb(\mu\text{-}CO)(\mu\text{-}PPh_2)Fe(CO)_3$ (**4**) have semibridging carbonyl ligands, the carbonyl ligand on Fe in **4** is substituted by phosphine at a much higher temperature (reluxing toluene) than for **1-w** (room temperature).[11] For **1**, which has a structure framework similar to that of **1-w** but with a bridging or semibridging carbonyl ligand, substitution of the Fe carbonyl by phosphine proceeds under mild conditions. These observations indicate that the activating metal moiety or the metal–metal bond should also be considered.

Experimental Section

All reactions and manipulations of air-sensitive compounds were carried out at ambient temperatures under an atmosphere of purified N_2 with standard procedures. Infrared (IR) spectra were recorded on a Perkin-Elmer 882 infrared spectrophotometer. ^1H, ^{13}C, and ^{31}P NMR spectra were measured by using Bruker AC-200 and AC-300 spectrometers. ^{31}P NMR shifts are referenced to 85% H_3PO_4. Electron impact (EI) and fast-atom bombardment (FAB) mass spectra were recorded on a VG 70-250S or a JEOL JMS-HX 110 mass spectrometer. Microanalyses were performed in the Microanalytic Laboratory at National Cheng Kung University, Tainan, Taiwan, and at Academia Sinica. Spectroscopic data (^{31}P and ^1H NMR and IR) of all new complexes are listed in Table 1.

Materials. THF was distilled from potassium and benzophenone under an atmosphere of N_2 immediately before use. Metal carbonyls ($Mo(CO)_6$, $Fe_2(CO)_9$), PPh_2Cl, PPh_2H, and PPh_3 were obtained from Strem, $P(OMe)_3$ was purchased from Merck, and ^{13}CO (99 atom % ^{13}C) was obtained from Isotec. Other reagents and solvents were obtained from various commercial sources and used as received. $Na[CpMo(CO)_3]$[12] and $MoCp(CO)_3PPh_2$[5] were prepared by literature procedures.

Synthesis of $CpMo(CO)_2(\mu\text{-}PPh_2)Fe(CO)_4$ (1) and $CpMo(CO)_3(\mu\text{-}PPh_2)Fe(CO)_4$ (2). A yellow solution of $Na[CpMo(CO)_3]$ (4.20 g, 15.56 mmol) in 150 mL of THF was cooled to 0 °C. PPh_2Cl (2.82 mL, 15.56 mmol) was then added slowly into the above solution. After 1 h, the solution turned dark red. $Fe_2(CO)_9$ (5.66 g, 15.56 mmol) was then added into the above solution. After the solution was stirred overnight, the solvent was removed and the residue was chromatographed on grade I Al_2O_3. Elution with CH_2Cl_2/hexane (1:6) afforded two fractions. The red solid **1** was obtained from the first band, which was dark red. It was identified as $CpMo(CO)_2(\mu\text{-}PPh_2)Fe(CO)_4$. Yield: 1.85 g (32.34%). A trace amount of light brown solid was obtained from the second band and was not characterized. The orange solid **2** was obtained from the third band after the solvent was removed. Yield: 2.50 g (41.67%). Anal. Calcd for $C_{24}H_{15}FeO_7PMo$: C, 48.01; H, 2.52. Found: C, 47.60; H, 2.55. MS(FAB): $[M - CO]^+$, *m/z* 572.

Photolysis Reaction of 2. A red solution of **2** (0.24 g, 0.40 mmol) in 30 mL of THF in a Pyrex Schlenk tube was photolyzed with a Hanovia UV lamp for 1.5 h. After the solvent was removed, the residue was chromatographed on grade I Al_2O_3 and eluted with CH_2Cl_2/hexane (1:4). After this solvent was removed, **1** was obtained from the first band. Yield: 0.16 g, 70%. A trace amount of red solid was obtained from the second band and was not identified.

Thermolysis of 2. A red solution of **2** (0.14 g, 0.23 mmol) in 30 mL of THF was heated to reflux for 16 h. After the solvent was removed, the residue was chromatographed on grade I Al_2O_3 and eluted with CH_2Cl_2/hexane (1:4). After this solvent was removed, **1** was obtained from the first band. Yield: 85 mg, 64.7%. A trace amount of red solid was obtained from the second band and was not identified.

Synthesis of $CpMo(CO)_2(\mu\text{-}PPh_2)Fe(CO)_3(PR_3)$ (R = OMe (3a), Ph (3c); PR_3 PPh_2H (3c)). To a red solution of **1** (0.21 g, 0.36 mmol) in 40 mL of THF was added 44 μL of $P(OMe)_3$ (0.36 mmol) under N_2 at ambient temperatures. After the mixture was stirred overnight, the solvent was removed. The residue was chromatographed on grade I Al_2O_3 and eluted with CH_2Cl_2/hexane (1:4) to afford a red band. After this solvent was removed, **3a** was obtained as a red solid. Yield: 0.17 g (67%). Anal. Calcd for $C_{25}H_{24}FeO_8P_2Mo$: C, 45.07; H, 3.63. Found: C, 44.87; H, 3.64. MS (FAB): M^+, *m/z* 667.9.

Reaction conditions similar to those for **3a** were applied to prepare **3b** and **3c**. Complex **3b**: yield 0.15 g (84%). Anal. Calcd for $C_{34}H_{26}FeO_5P_2Mo$: C, 55.89; H, 3.59. Found: C, 55.45; H, 3.75. MS (FAB): M^+, *m/z* 728. Complex **3c:** yield

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[9] The assignments of Fe carbonyl stretching frequencies and the remaining Mo carbonyl stretching frequencies in **1** and **2** are based on their favorable comparison to the Fe carbonyl frequencies of $PPh_3Fe(CO)_4$ (2055, 1978, 1943 cm^{-1}), $CpMo(CO)_3$ (1993 s, 1925 vs, br cm^{-1}), and $CpMo(CO)_2PMe_3$ (1927 s, 1864 vs, br cm^{-1}). Clifford, A. G.; Mukherjee, A. K. *Inorg. Chem.* **1963**, *2*, 141. See also ref 5.

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Table 2. Crystal and Intensity Collection Data for 2 and 3a

	2	**3a**
mol formula	$C_{24}H_{15}FeMoO_7P$	$C_{25}H_{24}FeMoO_8P_2$
mol wt	598.12	667.9
space group	$Pca2_1$	$P2_1$
a (Å)	16.621(3)	10.8113(8)
b (Å)	9.048(2)	11.525(2)
c (Å)	15.941(3)	10.9303(7)
α (deg)	90	90
β (deg)	90	97.243(6)
γ (deg)	90	90
V (Å^3)	2397.3(8)	1351.0(2)
ρ(calcd) (Mg m^{-3})	1.657	1.687
Z	4	2
cryst dimens (mm)	0.36 × 0.32 × 0.30	0.38 × 0.19 × 0.34
temp	room temp	room temp
λ(Mo Kα) (Å)	0.710 69	0.710 69
2θ range (deg)	45	50
scan type	$\omega-2\theta$	$\omega-2\theta$
no. of unique rflns	1639	2497
no. of observed rflns	1366 ($>2.0\sigma(I)$)	2413 ($>2.5\sigma(I)$)
variables	307	334
R	0.0372	0.018
R_w	0.0812	0.022
S	0.913	1.33
ΔF (e/Å^3)	<0.691	<0.17

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) in 2 and 3a

complex **2**		complex **3a**	
Selected Bond Lengths			
Mo⋯Fe	4.246(6)	Mo−Fe	2.9295(5)
Mo−P(1)	2.635(3)	Mo−P(1)	2.3824(9)
Mo−C(1)	1.978(10)	Mo−C(4)	1.953(4)
Mo−C(2)	2.006(13)	Mo−C(5)	1.949(4)
Mo−C(3)	2.015(9)	Fe−P(1)	2.2638(11)
Fe−P(1)	2.327(3)	Fe−P(2)	2.1519(9)
Fe−C(4)	1.72(2)	Fe−C(1)	1.789(4)
Fe−C(5)	1.801(10)	Fe−C(2)	1.793(4)
Fe−C(6)	1.745(11)	Fe−C(3)	1.784(4)
Fe−C(7)	1.82(2)	C(1)−O(1)	1.142(5)
C(1)−O(1)	1.149(11)	C(2)−O(2)	1.137(5)
C(2)−O(2)	1.13(2)	C(3)−O(3)	1.143(5)
C(3)−O(3)	1.117(10)	C(4)−O(4)	1.146(6)
C(4)−O(4)	1.21(2)	C(5)−O(5)	1.155(5)
C(5)−O(5)	1.114(12)		
C(6)−O(6)	1.138(14)		
C(7)−O(7)	1.14(2)		
Selected Bond Angles			
Fe−P(1)−Mo	117.51(12)	Fe−P(1)−Mo	78.13(3)
P(1)−Fe−C(4)	90.3(4)	P(1)−Fe−P(2)	121.95(4)
P(1)−Fe−C(5)	89.8(3)	P(1)−Fe−C(1)	87.36(12)
P(1)−Fe−C(6)	178.1(6)	P(1)−Fe−C(2)	88.48(13)
P(1)−Fe−C(7)	88.1(4)	P(1)−Fe−C(3)	132.76(13)
Mo−C(1)−O(1)	177.7(12)	P(1)−Fe−Mo	52.735(24)
Mo−C(2)−O(2)	175.3(10)	P(2)−Fe−Mo	172.55(3)
Mo−C(3)−O(3)	174.1(13)	Fe−C(1)−O(1)	176.4(3)
Fe−C(4)−O(4)	174.0(14)	Fe−C(2)−O(2)	178.4(3)
Fe−C(5)−O(5)	178.3(8)	Fe−C(3)−O(3)	177.7(4)
Fe−C(6)−O(6)	178(2)	Mo−C(4)−O(4)	178.7(4)
Fe−C(7)−O(7)	175.5(13)	Mo−C(5)−O(5)	175.9(3)

0.16 g (82%). Anal. Calcd for $C_{40}H_{30}FeO_5P_2Mo$: C, 59.55; H, 3.76. Found: C, 59.15; H, 3.81. MS (FAB): M$^+$, *m/z* 806.

Reaction of 2 with PR_3 (R = Ph, OMe) and PPh_2H. To a yellow solution containing 0.18 mg (0.30 mmol) of **2** in 30 mL of THF was added 78 mg (0.30 mmol) of PPh_3. The solution was stirred in the dark at ambient temperature for 22 h. No color change was observed. The ^{31}P NMR spectrum of the reaction mixture indicated the presence of unreacted **2** and PPh_3. The solution was then heated to reflux for 16 h. After the solvent was removed, the residue was chromatographed on grade I Al_2O_3 and eluted with CH_2Cl_2/hexane (1:4) to afford a red band. After the solvent was removed, **3c** was obtained as a red solid. Yield: 0.20 g (82.7%). Similar conditions were used for the reaction between **2** and PPh_2H or $P(OMe)_3$. No complex **3** was observed among the reaction products, according to ^{31}P NMR spectra of the reaction mixtures, when the reaction was carried out at room temperature. After the solution was heated to reflux, complex **3** was obtained.

Reaction between 1 and CO. A solution of **1** (0.19 g, 0.33 mmol) in 20 mL of THF in a 100 mL Schlenk flask was stirred under 1 atm of CO overnight at room temperature. A ^{31}P NMR study of the solution indicated that no reaction took place between **1** and CO.

Structure Determination of $Cp\overline{Mo(CO)_3(\mu\text{-}PPh_2)Fe}(CO)_4$ (2) and $CpMo(CO)_2(\mu\text{-}PPh_2)Fe(CO)_3(POMe_3)$ (3a). Crystals of complexes **2** and **3a** were grown by slow diffusion of hexanes into the saturated CH_2Cl_2 solutions of the relevant complexes at −15 °C in air. Diffraction measurements were made using an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Structures were solved by direct methods and refined by full-matrix least squares using SHELXL-93. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were constrained to geometrically calculated positions.

Crystal data and details of data collection and structure analysis are summarized in Table 2. Selected interatomic distances and bond angles are given in Table 3. The final positional and displacement parameters for all atoms are provided in the Supporting Information.

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Supporting Information Available: Listings of calculated atomic coordinates, anisotropic thermal parameters, and bond distances and angles of compounds **2** and **3a** (15 pages). Ordering information is given on any current masthead page.

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