$[Cp_2(OC)_4Mo_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ as a Useful Building Block toward Heterometallic Clusters Containing a Naked Phosphorus Atom

Adam J. Bridgeman,[†] Martin J. Mays,*[,‡] and Anthony D. Woods[‡]

Department of Chemistry, University of Hull, Hull, U.K., and Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, U.K.

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Summary: The reactivity of the title complex $[Cp_2(OC)_4Mo_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ toward a variety of metal carbonyls has been investigated. In each case heterometallic clusters are formed in which the phosphorus has been dehydrogenated to yield, for example, $[\{Cp(OC)_2Mo\}_2PMn(CO)_4]$, which contains a trigonal planar phosphorus atom.

Introduction

The synthesis of transition metal complexes with encapsulated phosphorus atoms generally requires precursors in which the phosphorus to be encapsulated is bound only to the metal(s) and to hydrogen.[1−3] The synthesis of such precursors almost invariably involves the use of PH_3 gas, which is difficult to handle, and this has limited research in the area. Recently, Johnson et al. have synthesized osmium complexes containing encapsulated phosphorus using the more easily handled reagent PH_4I, which, on reaction with $[Os_3(CO)_{10}(MeCN)_2]$, yields $[Os_3(CO)_{10}(\mu\text{-}PH_2)(\mu\text{-}H)]$,[4] the H atoms of which may then be readily removed.[5−7] Encapsulation of phosphorus atoms may also be achieved by replacement of a P-*SiMe*$_3$ group by a transition metal fragment.[8−10]

We have recently reported a more convenient synthesis of $[Cp_2(OC)_4Mo_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ that does not involve the use of PH_3 gas, and the reaction of this with metal carbonyls has now been studied, since the formation of heterometallic molybdenum-containing clusters with naked phosphorus groups in unusual coordination modes seemed a real possibility.

Results and Discussion

Reaction with $M_3(CO)_{12}$ (M = Fe, Ru). Thermolysis of a toluene solution of $[Cp_2(OC)_4Mo_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ (**1**) with a slight excess of $Fe_3(CO)_{12}$ for 2 h followed by TLC separation gave, in addition to a slight amount of unreacted starting material, two new products, $[Cp(OC)_8MoFe_2\{\mu_3\text{-}PMoCp(CO)_3\}(\mu\text{-}H)]$ (**2**) and $[Cp_2(OC)_7Mo_2Fe\{\mu_3\text{-}PMoCp(CO)_3\}]$ (**3**) (Figure 1). The amount of **3** obtained relative to **2** was increased by longer reflux, although the overall amount of decomposition also increased significantly. Reaction of **1** with $Ru_3(CO)_{12}$ yielded $[Cp(OC)_8MoRu_2\ \{\mu_3\text{-}PMoCp(CO)_3\}(\mu\text{-}H)]$ (**4**) in addition to a large degree of decomposition and several minor bands which could not be fully characterized.

The reaction is assumed to involve insertion of highly reactive $M(CO)_3$ fragments, which are known to be formed from $M_3(CO)_{12}$ (M = Ru, Fe) under forcing conditions, into a P−H bond; similar reactions have been previously reported by Vahrenkamp.[2] Although complexes containing a phosphinidine-capping group are relatively common,[11−13] it is far rarer to find complexes containing a naked μ_4-P atom such as those reported here. Other complexes containing a μ_4-P atom have been formed by the reaction of a μ_3-P tetrahedrane with a 16-electron transition-metal fragment. Such a strategy requires that the phosphorus lone pair is *exo* to the metal triangle, so that it may be used to form a dative bond to a fourth metal center.[14−16] In complexes **2**−**4**, however, the effective atomic number rule requires the phosphorus lone pair to be involved in bonding to the metal triangle and the fourth metal center is then σ-bonded to the phosphorus. There exists one other complex, $[(OC)_9Fe_3(\mu\text{-}H)_2(\mu_3\text{-}PAuPPh_3)]$,[9,17] which has a similar coordination.

Complexes **2**−**4** have been characterized by FABMS, IR, ^{31}P NMR, and ^{1}H NMR spectroscopy. In addition **2** and **3** have been the subjects of single-crystal X-ray diffraction studies, and their molecular structures are shown in Figure 2, relevant bond lengths (Å) and angles (deg) being presented in Table 1.

The Fe_2Mo core in **2** represents a scalene triangle [Mo(1)−Fe(1) 2.8823(5) Å, Mo(1)−Fe(2) 2.9321(5) Å, Fe-

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* Corresponding author. E-mail: mjm14@cus.cam.ac.uk.
† University of Hull.
‡ University of Cambridge.

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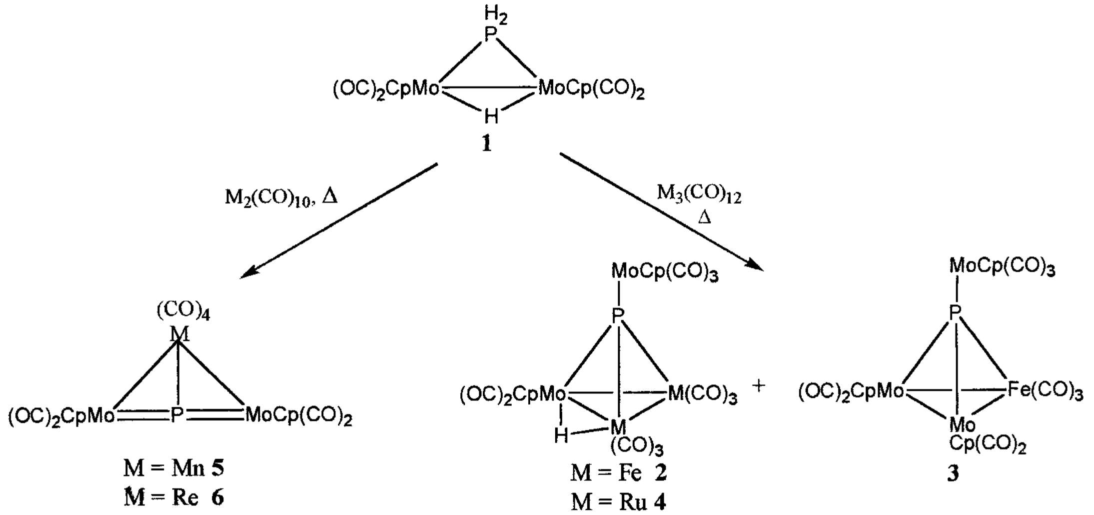

Figure 1. Reaction of [$Cp_2(OC)_4Mo_2(\mu\text{-}PH_2)(\mu\text{-}H)$] with $M_3(CO)_{12}$ (M = Fe, Ru) and $M_2(CO)_{10}$ (M = Mn, Re).

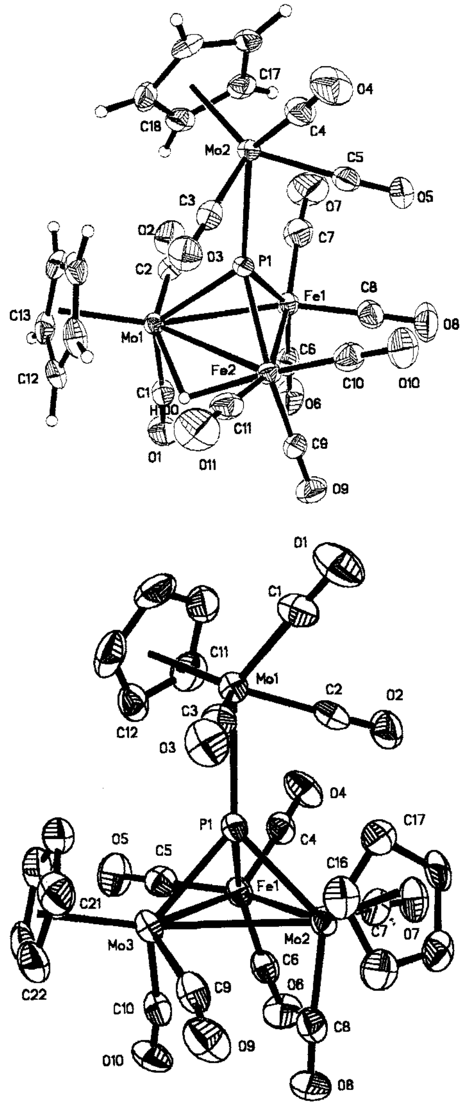

Figure 2. Molecular structure of **2** and **3**. ORTEPs shown at 50% probability.

(1)−Fe(2) 2.6428(6) Å]. These bond lengths are all in accord with other documented Fe−Fe and Mo−Fe single bond lengths.[18] The fact that the Mo(1)−Fe(2) bond length is longer than the Mo(1)−Fe(1) separation provides support for the placement of the bridging hydride on the Mo(1)−Fe(2) edge, despite the fact that this makes the individual metal centers electron-imprecise.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2 and 3

2		**3**	
Mo(1)−Fe(1)	2.8823(5)	Mo(1)−P(1)	2.559(2)
Mo(1)−Fe(2)	2.9321(5)	Mo(2)−P(1)	2.404(2)
Mo(1)−H(100)	1.8491(3)	Mo(2)−Mo(3)	3.1446(8)
Mo(1)−P(1)	2.4374(9)	Mo(2)−Fe(1)	2.8791(9)
Mo(2)−P(1)	2.5481(9)	Mo(3)−P(1)	2.400(2)
Fe(1)−Fe(2)	2.6428(6)	Mo(3)−Fe(1)	2.871(1)
Fe(1)−P(1)	2.196(1)	Fe(1)−P(1)	2.201(2)
Fe(2)−H(100)	1.8552(5)	Mo(1)−P(1)−Mo(2)	132.53(7)
Fe(2)−P(1)	2.2016(9)	Mo(1)−P(1)−Mo(3)	135.40(7)
Mo(1)−Fe(1)−P(1)	55.39(2)	Mo(1)−P(1)−Fe(1)	130.38(7)
Mo(1)−Fe(2)−Fe(1)	62 0.01(2)	Mo(2)−Mo(3)−P(1)	49.17(4)
Mo(1)−Fe(2)−P(1)	54.47(2)	Mo(2)−Fe(1)−P(1)	54.54(4)
Mo(1)−C(2)−O(2)	169.3(3)	Mo(2)−Mo(3)−Fe(1)	56.97(2)
Mo(2)−P(1)−Fe(1)	133.62(4)	Mo(2)−Fe(1)−Mo(3)	66.30(2)
Mo(2)−P(1)−Fe(2)	137.98(4)	Mo(2)−C(7)−O(7)	169.2(5)
Fe(1)−Mo(1)−Fe(2)	54.06(1)	Mo(3)−Mo(2)−Fe(1)	56.73(2)
Fe(1)−Mo(1)−P(1)	47.87(2)	Mo(3)−Mo(2)−P(1)	49.05(4)
Fe(1)−P(1)−Fe(2)	73.87(3)	Mo(3)−Fe(1)−P(1)	54.55(5)
Fe(2)−Mo(1)−P(1)	47.31(2)	Mo(3)−C(9)−O(9)	166.9(6)
Fe(2)−Fe(1)−P(1)	53.16(3)	Mo(3)−C(10)−O(10)	169.1(6)

The phosphorus atom is in a highly distorted tetrahedral environment, with an average internal M−P−M angle of 76.13(3)° and an external M−P−Mo(2) angle of 134.47(4)°, as is typical for a capping phosphinidene group.[11−15] The P−Mo(2) separation of 2.5481(9) Å is markedly longer than that of the P−Mo(1) bond length, but is typical of a σ-bonded Mo−P distance.[19]

The average internal M−P−M bond angle of 78.19(5)° in **3** is somewhat larger than the average of 76.13(3)° found in **2** and is consistent with the replacement of an $HFe(CO)_3$ group by the isolobal, but sterically larger, $MoCp(CO)_2$. All other bond lengths fall within the expected range.

Reactions with $M_2(CO)_{10}$ (M = Mn, Re). Thermolysis of a solution of **1** with $Mn_2(CO)_{10}$ in toluene for 2.5 h yielded a deep red solution. Separation by TLC gave some unreacted **1** and [$\{Cp(OC)_2Mo\}_2PMn(CO)_4$] (**5**) in 40% yield (Figure 1). Complex **5** appears to be somewhat acid sensitive and decomposed to give **1** on prolonged

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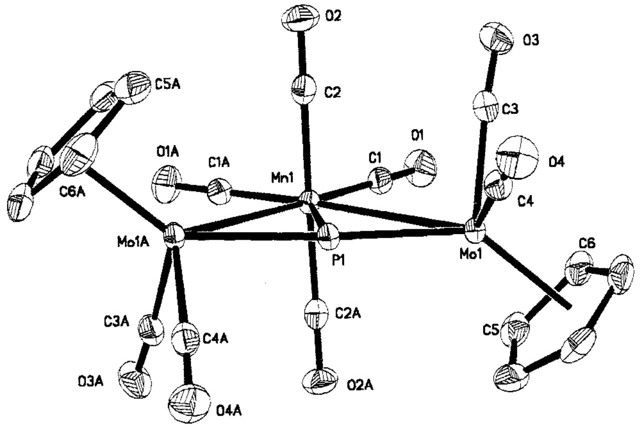

Figure 3. Molecular structure of [$\{Cp(OC)_2Mo\}_2PMn(CO)_4$], **5**. ORTEPs shown at 50% probability.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5[a]

Mo(1)−Mn(1)	3.0714(4)
Mo(1)−P(1)	2.2619(2)
Mo(1)#1−Mn(1)	3.0714(4)
Mo(1)#1−P(1)	2.2619(2)
Mn(1)−P(1)	2.283(1)
Mn(1)−C(1)	1.806(3)
Mn(1)−C(2)	1.861(3)
Mo(1)−P(1)−Mo(1)#1	170.06(4)
Mo(1)−P(1)−Mn(1)	85.03(2)
P(1)−Mo(1)−Mn(1)	47.78(2)
P(1)−Mn(1)−Mo(1)	47.194(7)
C(1)−Mn(1)−C(2)	92.7(1)
C(1)−Mn(1)−C(2)#1	91.3(1)
C(1)−Mn(1)−C(1)#1	97.2(2)
C(2)−Mn(1)−C(2)#1	173.9(2)
Mo(1)−Mn(1)−P(1)	47.194(7)
C(1)−Mn(1)−Mo(1)	84.24(8)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1/2$, $-y + 1/2$, z.

contact with silica plates; thus it was found that separation was more easily effected by chromatography on Florisil or alumina.

Reaction with $Re_2(CO)_{10}$ followed a similar course but required a prolonged 8 h reflux to yield [$\{Cp(OC)_2Mo\}_2PRe(CO)_4$] (**6**) (17%).

Complex **5** has been characterized unambiguously by a combination of ^{31}P and ^{1}H NMR spectroscopy, microanalysis, and a single-crystal X-ray diffraction study. Thus the extremely downfield resonance of 987.79 ppm in the ^{31}P NMR spectrum of **5** is typical of a triply metalated sp-phosphorus, as is the value 975.12 ppm recorded for **6**.[20−26]

The molecular structure of **5** is shown in Figure 3, with relevant bond lengths (Å) and angles (deg) being given in Table 2.

It can clearly be seen that **5** possesses a 2-fold axis of rotation about the Mn−P bond, which results from the totally planar Mo_2PMn core; previous examples of such phosphinidenes have shown minor deviations of up to 0.05 Å from planarity.[20−26]

The Mo−P bond length of 2.2619(2) Å is significantly shorter than known Mo−P single bond lengths, which vary from 2.4 to 2.60 Å,[27,28] and is comparable to the Mo−P bond lengths of 2.297(8) Å found in [$Cp_2(OC)_4Mo_2(\mu\text{-}PMes)$] (Mes = 2,4,6-$Me_3C_6H_2$), which have been formulated as Mo=P double bonds.[29] In contrast, the Mn−P bond length of 2.283(1) Å in **5** is more typical of a P−Mn single bond[30] and is significantly longer than the average Mn−P bond length of 2.10 Å in [$\{Cp(OC)_2Mn\}_2(\mu_3\text{-}P)_2\{Fe_2(CO)_6\}$], which corresponds to a formal Mn−P double bond.[23] The Mo−Mn bond length of 3.0714(4) Å is to the long end but is within the range of known Mo−Mn single bond lengths.

Ignoring the Mn−P bond, the geometry about the Mn atom is slightly distorted from octahedral, although by no more than 5° in any direction. This may be understood if the P−Mn interaction is based on π overlap of the phosphorus p_z orbital with the Mn d_{xz} orbital, this orbital being nonbonding with respect to the remaining octahedrally disposed set of ligands about the Mn atom.[31]

The Mo(1)−P(1)−Mo(1)#1 bond angle of 170.06(4)° and the Mo(1)−P(1)−Mn(1) bond angle of 85.03(2)° highlight the approximately sp-hybridized state of the phosphorus center.

It is very rare to find phosphorus in a trigonal planar μ_3 coordination mode in a trinuclear M_3P cluster.[20−26] In the previously characterized trinuclear complexes two of the metal atoms in the M_3P core may be linked by a metal−metal bond if such a bond is required by the electron count at the metal centers. However, to the authors' knowledge, complex **5** is the first structurally characterized neutral complex with an M_3P core, whether planar or not, in which two metal−metal bonds are present.

Experimental Section

General Procedures. Unless otherwise stated, all reactions were conducted under an atmosphere of dry, oxygen-free nitrogen using solvents freshly distilled from the appropriate drying agent.

Infrared absorption spectra were, unless otherwise stated, recorded in dichloromethane solution in 0.5 mm NaCl solution cells using a Perkin-Elmer 1710 Fourier transform instrument. FAB mass spectra were obtained on a Kratos CONCEPT instrument using 3-nitrobenzyl alcohol as a matrix. NMR spectra were, unless otherwise stated, recorded on a Bruker DRX 400 using TMS (^{1}H, ^{13}C) or H_3PO_4 (^{31}P) as external standards. Microanalysis was performed by the Microanalytical Department, University Chemical Laboratories, Cambridge. Preparative TLC was carried out on 1 mm silica plates prepared at the University of Cambridge. Column chromatography was performed on Kieselgel 60 (70−230 mesh). Products are given in order of decreasing R_f values.

Unless otherwise stated, all reagents were obtained from

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(31) A molecular orbital diagram for **5** is included in the Supporting Information.

Table 3. X-ray Crystallographic Data for the New Complexes[a]

	2	**3**	**5**
empirical formula	$C_{21}H_{11}Fe_2Mo_2O_{11}P$	$C_{26}H_{17}Cl_2FeMo_3O_{10}P$	$C_{18}H_{10}MnMo_2O_8P$
cryst syst	triclinic	triclinic	orthorhombic
cryst size	0.09 × 0.09 × 0.07	0.12 × 0.09 × 0.07	0.23 × 0.16 × 0.14
space group	*P*	*P*	*Pccn*
a (Å), α (deg)	8.4770(3), 91.568(2)	9.7114(7), 82.694(4)	11.2189(3), 90
b (Å), β (deg)	9.4970(4), 97.516(2)	10.5271(8), 73.364(4)	12.0361(5), 90
c (Å), γ (deg)	17.0940(6), 115.304(2)	15.560(1), 82.158(4)	14.9963(6), 90
V (Å^3)	1228.11(8)	1503.3(2)	2025.0(1)
Z	2	2	4
D_c (Mg/m^3)	2.093	2.065	2.073
abs coeff (mm^{-1})	2.279	1.981	1.956
F(000)	752	908	1224
θ range (deg)	3.05 to 27.50	1.37 to 25.03	2.48 to 27.47
index ranges	$0 \le h \le 11$	$-11 \le h \le 9$	$0 \le h \le 14$
	$-12 \le k \le 11$	$-12 \le k \le 12$	$-15 \le k \le 15$
	$-22 \le l \le 21$	$-18 \le l \le 18$	$-19 \le l \le 19$
no. of reflns measd	8780	8250	8276
no. of ind reflns	5544	5272	2310
R_{int}	0.0358	0.0441	0.0427
goodness of fit on F^2	1.073	1.039	1.029
final R indices			
R1	0.0319	0.0450	0.0288
wR2	0.0735	0.0946	0.0723
R indices (all data)			
R1	0.0460	0.0771	0.0406
wR2	0.0904	0.1381	0.0957
largest diff peak and hole (e Å^{-3})	0.773 and −1.082	1.252 and −1.390	0.636 and −1.064

[a] Data in common: Temperature of collection 180(2) K, wavelength 0.71069 Å.

commercial suppliers and used without further purification. $[Cp_2(OC)_4Mo_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ was prepared by the literature method.[32]

X-ray diffraction data were collected using a Nonius-Kappa CCD diffractometer, equipped with an Oxford Cryostream cryostream. Data reduction and cell refinement were performed with the programs DENZO[33] and COLLECT,[34] and multiscan absorption corrections were applied to all intensity data with the program SORTAV.[35] Structures were solved and refined with the programs SHELXS97 and SHELXL97,[36] respectively.

Reaction of $[Cp_2(OC)_4Mo_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ (1) with $M_3(CO)_{12}$ (M = Fe, Ru). A solution of $[Cp_2(OC)_4Mo_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ (**1**) (300 mg, 0.64 mmol) and $Fe_3(CO)_{12}$ (450 mg, 0.96 mmol) in toluene (60 mL) was refluxed for 1 h. The solvent was removed under reduced pressure, the residue redissolved in the minimum CH_2Cl_2, and the reaction mixture applied to the base of TLC plates. Elution with 3:2 hexane/CH_2Cl_2 gave orange **1** (60 mg, 20%), brown $[Cp(OC)_8MoFe_2\{\mu_3\text{-}PMoCp(CO)_3\}(\mu\text{-}H)]$ (**2**) (216 mg, 40%), and $[Cp_2(OC)_7Mo_2Fe\{\mu_3\text{-}PMoCp(CO)_3\}]$ (**3**) (65 mg, 13%) in addition to several other trace bands. The amount of **3** formed was increased on longer reflux.

For 2: IR (νCO) 2056(m), 2027(s), 2009(s), 1996(m), 1980(m), 1962(vs), 1945(w), 1915(w), 1896 (w), 1835(m) cm^{-1}; ^{1}H NMR δ 5.80 (s, 5H, P-MoCp), 5.12 (s, 5H, Fe_2Mo-Cp), −20.90 (d, $^2J_{P-H}$ 24.66 Hz, μ-H); ^{31}P NMR δ 405.98 (s, μ_4-P). Anal. Calcd for $C_{21}Fe_2H_{11}Mo_2O_{11}P$: C 32.64, H 1.30, P 4.01. Found: C 32.46, H 1.46, P 4.11. FABMS: 772 (M$^+$), M$^+$ − nCO (n = 1 to 8).

For 3*:* IR (νCO) 2075(vs), 2043(s), 2031(s), 2004(s), 1982(s), 1909(w), 1850(w), 1830(w) cm^{-1}; ^{1}H NMR δ 5.76 (s, 5H, P-MoCp), 5.13 (s, 10H, FeMo-Cp); ^{31}P NMR δ 387.12 (s, μ_4-P). Anal. Calcd for $C_{25}FeH_{15}Mo_3O_{10}P{\cdot}CH_2Cl_2$: C 33.40, H 1.83, P 3.32. Found: C 33.43, H 2.01, P 3.75. FABMS 850 (M$^+$), M$^+$ − 3CO.

An analogous method was used for $Ru_3(CO)_{12}$, using **1** (100 mg, 0.21 mmol) and $Ru_3(CO)_{12}$ (200 mg, 0.3 mmol). The solution was refluxed for 3 h, and separation in the above manner yielded brown $[Cp(OC)_8MoRu_2\{\mu_3\text{-}PMoCp(CO)_3\}(\mu\text{-}H)]$ (**4**) (43 mg, 23%) as well as several other bands, which were not fully analyzed.

IR (νCO): 2108(m), 2047(vs), 2014(s), 1994(s), 1949(w) cm^{-1}. ^{1}H NMR: δ 5.54 (s, 5H, Cp, P-MoCp), 5.45 (s, 5H, Ru_2Mo-Cp), −17.48 (d, $^3J_{P-H}$ 4.4 Hz, μ-H). ^{31}P NMR: δ 338.65 (s, μ_4-P). Anal. Calcd for $C_{21}Ru_2H_{11}Mo_2O_{11}P$: C 29.18, H 1.28, P 3.58. Found: C 29.47, H 1.45, P 3.56. FABMS 833 (M$^+$), M$^+$ − nCO (n = 1−3, 6−10).

Reaction of $[Cp_2(OC)_4Mo_2(\mu\text{-}PH_2)(\mu\text{-}H)]$ (1) with $M_2(CO)_{10}$ (M = Mn, Re). A solution of **1** (200 mg, 0.43 mmol) and $Mn_2(CO)_{10}$ (386 mg, 1.4 equiv) in toluene (60 mL) was refluxed for 2.5 h. The solvent was removed under reduced pressure, the residue redissolved in the minimum CH_2Cl_2, and the mixture applied to the base of TLC plates. Elution with 9:1 hexane/EtOAc yielded unreacted **1** (28 mg, 14%) and $[\{Cp(OC)_2Mo\}_2PMn(CO)_4]$ (**5**) (103 mg, 38%).

IR (νCO): 2048(m), 1976(vs), 1958(s), 1950(s,sh), 1920(m), 1877(w) cm^{-1}. ^{1}H NMR: δ 5.34 (s, 10H, Cp). ^{31}P NMR: δ 987.79 (s, μ_3-P). Anal. Calcd for $C_{18}H_{10}MnMo_2O_8P$: C 29.76, H 1.38, P 4.25. Found: C 30.01, H 1.67, P 4.47. FABMS 632 (M$^+$), M$^+$ − nCO (n = 1−3, 5).

An analogous procedure was used for $Re_2(CO)_{10}$, but an 8 h reflux was required to yield after separation $[\{Cp(OC)_2Mo\}_2PRe(CO)_4]$ (**6**) (57 mg, 17%).

IR (νCO): 2061(m), 1970(s), 1944(s), 1916(m), 1874(w) cm^{-1}. ^{1}H NMR: δ 5.27 (s, 10H, Cp). ^{31}P NMR: δ 975.32 (s, μ_3-P). FABMS 753 (M$^+$), M$^+$ − nCO (n = 1−3).

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Supporting Information Available: X-ray cif files and results of a DFT study into the bonding of **5** are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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