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Differences in coordination chemistry of alkyne and phosphaalkyne metal carbonyl complexes. Syntheses, crystal and molecular structures of $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(Bu^tCP)Fe(CO)_4]$ and $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(Bu^tCP)W(CO)_5]$

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Abstract

Whereas tetrahedral alkyne complexes of the type [MM'(RCCR)], (M = $Ni(\eta^5\text{-}C_5H_5)$, M' = $Ni(\eta^5\text{-}C_5H_5)$; $Co(CO)_3$; $Mo(CO)_2(\eta^5\text{-}C_5H_5)$) react with $[Fe_2(CO)_9]$ to give cluster-expanded square pyramidal trimetallic complexes of the type $(MM'Fe(CO)_3(RCCR)]$, the tetrahedral phosphaalkyne complex $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2Bu^tCP]$ reacts with $[Fe_2(CO)_9]$ or $[W(CO)_5THF]$ to give $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(Bu^tCP)Fe(CO)_4]$ and $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(Bu^tCP)W(CO)_5]$, respectively, in which the original tetrahedral cluster is intact. Structural features of these complexes and related alkyne and P_2 compounds are discussed.

Introduction

The coordination chemistry of compounds containing phosphorus-carbon multiple bonds is developing rapidly [1-6]. In a series of papers [7-13] we have drawn attention to similarities in the ligating behaviour of phosphaalkynes, RC≡P, and alkynes. Here we discuss some differences in their ligating behaviour.

Results and discussion

Recently McGlinchey and Jaouen and their coworkers [14] have described an attractive approach to synthesis of transition metal clusters involving different metals in which a tetrahedral bimetallic alkyne complex undergoes cluster expansion to a square based pyramidal complex.

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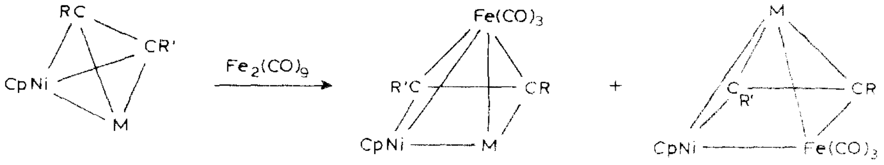


(1) M = NiCp
(2) M = $Co(CO)_3$
(3) M = $MoCp(CO)_2$

(4) M = NiCp
(5) M = $Co(CO)_3$

(6) = $MoCp(CO)_2$

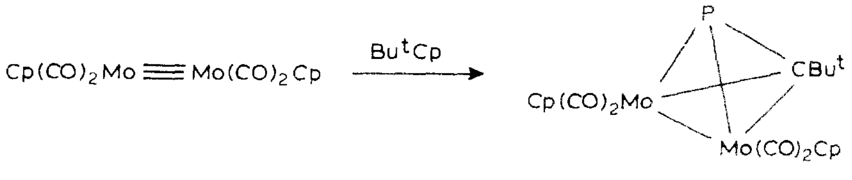
(R = Ph ; R' = CO_2Pr^i)

Scheme 1

Thus treatment of a variety of alkyne complexes of the type $[MNi(\eta^5\text{-}C_5H_5)(RCCR')]$, ($M = Ni(\eta^5\text{-}C_5H_5)$; $Co(CO)_3$; $Mo(\eta^5\text{-}C_5H_5)(CO)_2$) with $[Fe_2(CO)_9]$ readily affords trimetallic compounds of the general type $[MNi(\eta^5\text{-}C_5H_5)Fe(CO)_3(RCCR')]$ (**1**–**6**) (see Scheme 1) in which an $[Fe(CO)_3]$ unit has been incorporated into the original cluster.

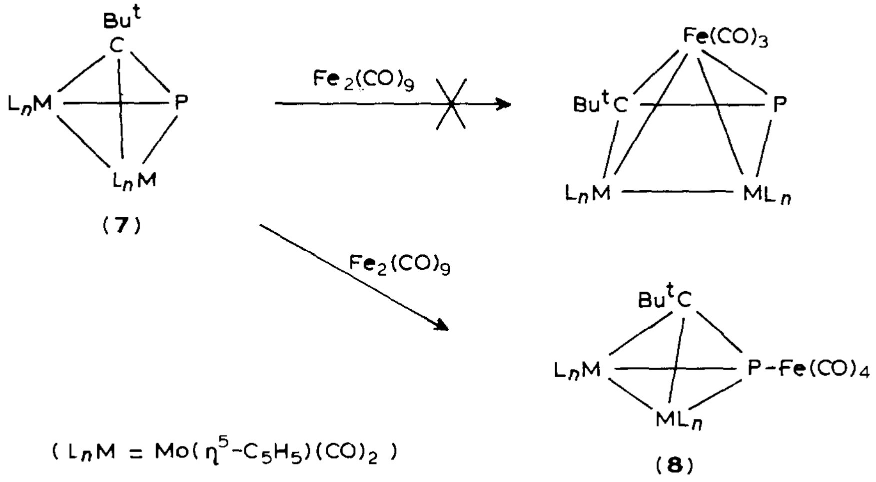
These reactions can be regarded as involving addition of a metal ligand fragment containing 2 skeletal electrons in three frontier orbitals [15], and therefore involve a change from a *nido* trigonal bipyramidal (tetrahedral) structure to a *nido*-octahedron (square based pyramid).

We and others [11,16] previously described the synthesis of the dinuclear phosphaalkyne compound $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(Bu^tCP)]$ (**7**), by addition of Bu^tCP across the molybdenum≡molybdenum triple bond of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$.

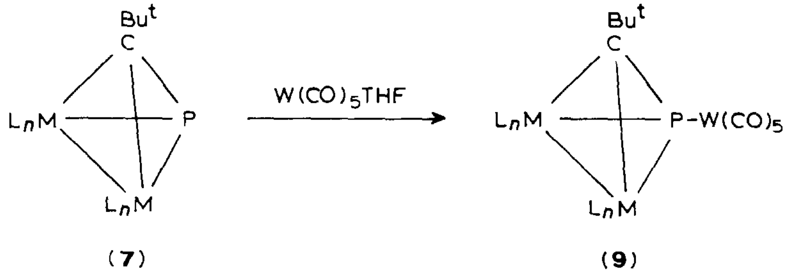


(**7**)

This reaction can be extended to the synthesis of the mixed metal phosphaalkyne complex $[MoW(\eta^5\text{-}C_5H_5)_2(CO)_4(Bu^tCP)]$ [17]. Treatment of **7** with $[Fe_2(CO)_9]$ under mild conditions does not give rise to the expected cluster expansion observed for the corresponding alkyne complex, but instead **7** acts as a 'phosphane' ligand and coordinates an $[Fe(CO)_4]$ fragment via the phosphorus lone pair to form $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(Bu^tCP)Fe(CO)_4]$ (**8**), in which the original tetrahedral cluster remains intact. Interestingly complex **8**, which was characterised by elemental analysis and its structure confirmed by a single crystal X-ray study (vide infra), showed no further reactivity towards $[Fe_2(CO)_9]$. Similarly **7** reacts smoothly at room temperature with $[W(CO)_5(THF)]$ to form $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(Bu^tCP)W(CO)_5]$ (**9**), briefly reported previously [18], whose structure has now been confirmed by single crystal X-ray diffraction study (vide infra).



(L_nM = Mo(η^5-C_5H_5)$(CO)_2$)



(L_nM = Mo(η^5-C_5H_5)$(CO)_2$)

Structural aspects

The molecular structures of **8** and **9** are shown in Fig. 1 and Fig. 2, respectively, with the appropriate atomic numbering schemes. The bond distances and bond angles of complex **8** are listed in Table 2, and those of **9** in Table 4, respectively. Both complexes **8** and **9** show the basic tetrahedrane structure, consisting of two molybdenum atoms, carbon, and phosphorus, with this structural unit linked via phosphorus to Fe and W, respectively.

The IR spectra of **8** and **9** in the carbonyl stretching region show bands between 2075 and 1910 cm^{-1} indicative of only terminal carbonyl ligands. The single crystal X-ray structural data reveal no evidence of any semi-bridging behaviour, whereas such bonding is present in the structurally related alkyne complexes of the type $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(RC_2R)]$ (R = H, Et, Ph) [22].

Coordination of **7** to $[Fe(CO)_4]$ and $[W(CO)_5]$ fragments leads to significant ^{31}P chemical shift changes. For **8** the resonance appears 63 ppm downfield from that for **7**, whereas for **9** the coordination shift is 17 ppm upfield. In the latter complex $^1J(PW)$ is 229 Hz, which is in the range expected for phosphane complexes of the type $[W(CO)_5(PR_3)]$ [24], in spite of the very small MoPC bond angles (ca. 60 °). A

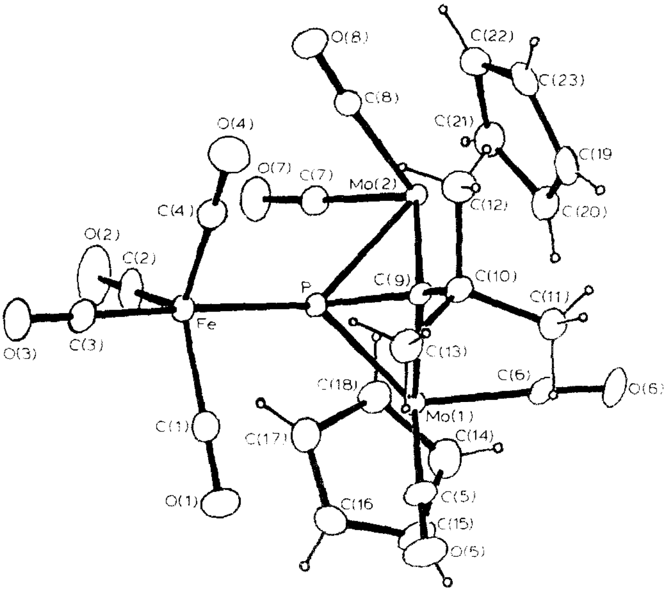


Fig. 1. Molecular structure of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(Bu^tCP)Fe(CO)_4]$ (**8**).

similar value for ${}^1J(PW)$ was observed by Seyferth et al. for $[Co_2(CO)_6(PhCP)W(CO)_5]$ [25], which was synthesised from $PhCCl_2PCl_2$.

Table 5 lists selected bond lengths for the structurally related complexes **7** [16], **8** and **9**, and $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(Bu^tCP)Os_3(CO)_{11}]$ (**10**) [19], $[Mo_2(CO)_4(\eta^5\text{-}$

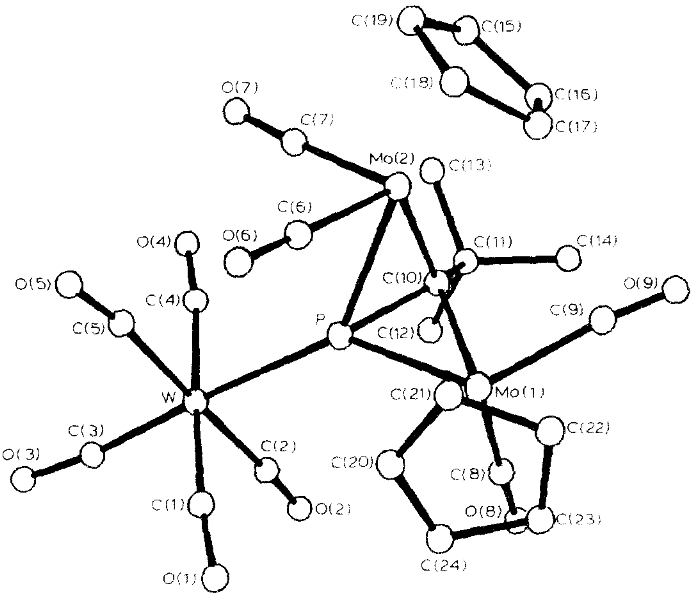


Fig. 2. Molecular structure of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(Bu^tCP)W(CO)_5]$ (**9**).

Table 1

Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses of **8**

	x	y	z		x	y	z
Mo(1)	4029.1(1)	1019.9(4)	3232.6(2)	C(6)	3566(2)	−386(5)	3012(4)
Mo(2)	3389.1(1)	2779.1(4)	3728.1(3)	C(7)	3874(2)	3669(6)	4562(3)
Fe	4202.9(2)	5178.0(7)	2444.2(4)	C(8)	3195(2)	4651(6)	3378(3)
P	3890.7(4)	3356.2(13)	2873.5(7)	C(9)	3458(1)	2320(5)	2438(3)
O(1)	4570(2)	3275(5)	1452(4)	C(10)	3143(2)	2248(5)	1528(3)
O(2)	4708(2)	5876(6)	4202(3)	C(11)	2952(2)	819(6)	1319(4)
O(3)	4584(2)	7443(4)	1765(3)	C(12)	2770(2)	3242(7)	1481(4)
O(4)	3363(1)	6381(5)	1649(3)	C(13)	3354(2)	2659(6)	831(3)
O(5)	4141(2)	245(5)	1438(3)	C(14)	4369(2)	−356(7)	4397(4)
O(6)	3323(1)	−1243(4)	2920(3)	C(15)	4586(2)	−449(6)	3752(4)
O(7)	4142(1)	4226(5)	5063(3)	C(16)	4765(2)	819(6)	3664(4)
O(8)	3073(1)	5735(4)	3237(3)	C(17)	4665(2)	1680(6)	4255(4)
C(1)	4432(2)	4010(6)	1849(4)	C(18)	4424(2)	978(6)	4704(3)
C(2)	4513(2)	5557(6)	3531(4)	C(19)	2824(2)	1192(7)	3613(4)
C(3)	4436(2)	6551(6)	2032(3)	C(20)	3163(2)	814(6)	4330(4)
C(4)	3687(2)	5899(6)	1980(4)	C(21)	3229(2)	1879(6)	4934(3)
C(5)	4083(2)	589(6)	2071(4)	C(22)	2935(2)	2915(6)	4586(4)
				C(23)	2682(2)	2473(7)	3762(4)

$C_5H_5)_2P_2]$ (**11**) [20], and $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(RC_2R)]$ (**12**) [22], all of which are based on the tetrahedrane type structure.

Inspection of the data indicates the following structural features: (a) the P–C bonds in **7**, **8** and **9**, although formally single bonds have lengths in the range normally found for P=C double bonds, whereas the P–C bond in complex **10** is much longer, and its length is comparable with the P–C single bond lengths in phosphanes; (b) the Mo–Mo bond lengths in **7** → **12** lie in the range 2.95–3.02 Å, intermediate between the Mo–Mo single bond length of 3.235(1) Å [23] and double bond length of (2.618(1) Å) [21]; (c) in complexes **7**–**11**, the Mo(1)–P and Mo(2)–P bond lengths are significantly different; and (d) only the alkyne complexes show evidence of semibridging carbonyl behaviour.

Variable temperature NMR studies in solution and solid state studies on complex **7** and $[MoW(CO)_4(\eta^5\text{-}C_5H_5)_2(Bu^tCP)]$ will be the subject of a future paper.

Experimental

Standard Schlenk techniques were used throughout. Solvents were dried and distilled prior to use. ^1H and ^{31}P NMR spectra were recorded with a Bruker WP80 Multinuclear Fourier transform spectrometer. The ^1H and ^{31}P chemical shift data are quoted relative to internal $SiMe_4$ and external $(MeO)_3P$, respectively. Infrared spectra were recorded with a Perkin–Elmer 1430 spectrometer. Elemental analyses were carried out by Ms. A.G. Olney of the School of Chemistry and Molecular Sciences in the University of Sussex.

$[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(Bu^tCP)]$ (**7**) was prepared as described in ref. 11.

Preparation of $[Mo_2(CO)_4(\eta^5\text{-}C_5H_5)_2(Bu^tCP)Fe(CO)_4]$ *(8)*

A suspension of $Fe_2(CO)_9$ (0.365 g, 1 mmol) in toluene (5 cm^3) was treated with

Table 2

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for **8**

(a) Bonds			
Mo(1)–P	2.385(1)	Mo(1)–C(5)	1.982(6)
Mo(1)–C(6)	2.000(6)	Mo(1)–C(9)	2.322(4)
Mo(1)–C(14)	2.330(6)	Mo(1)–C(15)	2.283(6)
Mo(1)–C(16)	2.301(5)	Mo(1)–C(17)	2.345(5)
Mo(1)–C(18)	2.365(5)	Mo(2)–P	2.479(1)
Mo(2)–C(7)	1.967(5)	Mo(2)–C(8)	1.979(6)
Mo(2)–C(9)	2.206(5)	Mo(2)–C(19)	2.375(6)
Mo(2)–C(20)	2.374(7)	Mo(2)–C(21)	2.329(6)
Mo(2)–C(22)	2.294(8)	Mo(2)–C(23)	2.330(7)
Fe–P	2.263(1)	Fe–C(1)	1.789(7)
Fe–C(2)	1.802(5)	Fe–C(3)	1.769(6)
Fe–C(4)	1.778(6)	P–C(9)	1.719(5)
O(1)–C(1)	1.140(9)	O(2)–C(2)	1.137(7)
O(3)–C(3)	1.142(8)	O(4)–C(4)	1.142(7)
O(5)–C(5)	1.143(8)	O(6)–C(6)	1.134(7)
O(7)–C(7)	1.148(6)	O(8)–C(8)	1.139(7)
C(9)–C(10)	1.540(6)	C(10)–C(11)	1.536(8)
C(10)–C(12)	1.540(8)	C(10)–C(13)	1.529(8)
C(14)–C(15)	1.418(10)	C(14)–C(18)	1.398(9)
C(15)–C(16)	1.401(9)	C(16)–C(17)	1.383(9)
C(17)–C(18)	1.392(9)	C(19)–C(20)	1.406(8)
C(19)–C(23)	1.387(10)	C(20)–C(21)	1.408(9)
C(21)–C(22)	1.404(9)	C(22)–C(23)	1.423(8)
Mo–Cen1	2.00	Mo–Cen2	2.01
(b) Angles			
P–Mo(1)–C(5)	92.1(2)	P–Mo(1)–C(6)	123.0(2)
P–Mo(1)–C(9)	42.8(1)	P–Mo(1)–Cen1	118.5
C(5)–Mo(1)–C(6)	86.8(2)	C(5)–Mo(1)–C(9)	82.1(2)
C(5)–Mo(1)–Cen1	111.6	C(6)–Mo(1)–C(9)	80.8(2)
C(6)–Mo(1)–Cen1	114.6	C(9)–Mo–Cen1	159.1
P–Mo(2)–C(7)	75.9(2)	P–Mo(2)–C(8)	80.3(2)
P–Mo(2)–C(9)	42.6(1)	P–Mo(2)–Cen2	164.92
C(7)–Mo(2)–C(8)	84.8(2)	C(7)–Mo(2)–C(9)	117.8(2)
C(7)–Mo(2)–Cen2	114.9	C(8)–Mo(2)–C(9)	91.6(2)
C(8)–Mo(2)–Cen2	110.1	C(9)–Mo(2)–Cen2	124.2
P–Fe–C(1)	86.8(2)	P–Fe–C(2)	92.3(2)
P–Fe–C(3)	175.8(2)	P–Fe–C(4)	89.8(2)
C(1)–Fe–C(2)	117.1(3)	C(1)–Fe–C(3)	90.1(3)
C(1)–Fe–C(4)	120.9(3)	C(2)–Fe–C(3)	91.7(3)
C(2)–Fe–C(4)	122.0(3)	C(3)–Fe–C(4)	89.3(3)
Mo(1)–P–Mo(2)	75.58(4)	Mo(1)–P–Fe	140.35(6)
Mo(1)–P–C(9)	66.6(2)	Mo(2)–P–Fe	140.64(6)
Mo(2)–P–C(9)	60.2(2)	Fe–P–C(9)	136.9(2)
Fe–C(1)–O(1)	178.3(5)	Fe–C(2)–O(2)	175.8(6)
Fe–C(3)–O(3)	179.4(5)	Fe–C(4)–O(4)	176.6(6)
Mo(1)–C(5)–O(5)	173.5(5)	Mo(1)–C(6)–O(6)	175.3(5)
Mo(2)–C(7)–O(7)	176.5(5)	Mo(2)–C(8)–O(8)	174.4(5)
Mo(1)–C(9)–Mo(2)	82.3(1)	Mo(1)–C(9)–P	70.6(1)
Mo(1)–C(9)–C(10)	135.7(3)	Mo(2)–C(9)–P	77.2(2)
Mo(2)–C(9)–C(10)	134.2(4)	P–C(9)–C(10)	131.7(4)
C(9)–C(10)–C(11)	111.8(4)	C(9)–C(10)–C(12)	108.6(4)
C(9)–C(10)–C(13)	112.2(4)	C(11)–C(10)–C(12)	108.1(4)
C(11)–C(10)–C(13)	108.4(5)	C(12)–C(10)–C(13)	107.5(4)

Table 2 (continued)

(b) Angles			
C(15)–C(14)–C(18)	106.3(6)	C(14)–C(15)–C(16)	108.9(6)
C(15)–C(16)–C(17)	107.0(6)	C(16)–C(17)–C(18)	109.4(5)
C(14)–C(18)–C(17)	108.4(6)	C(20)–C(19)–C(23)	108.6(5)
C(19)–C(20)–C(21)	107.9(5)	C(20)–C(21)–C(22)	108.0(5)
C(21)–C(22)–C(23)	107.5(5)	C(19)–C(23)–C(22)	108.0(5)

Cen1 and Cen2 are the centroids of cyclopentadienyl rings C(14) to C(18) and C(19) to C(23) respectively.

7 (0.535 g, 1 mmol) in toluene (5 cm^3). The mixture was stirred at room temperature for 24 h. The resulting deep red solution was filtered and the volatiles removed in vacuo. Crystallisation of the residue from toluene/hexane (10/1) at −40 °C yielded wine-red, air-stable hexagonal crystals of **8** [*] (0.55 g, 78%). Found C, 39.58; H, 2.84.

Table 3

Fractional atomic coordinates ($\times 10^4$) with estimated standard deviations in parentheses for **9**

	x	*y*	*z*		*x*	*y*	*z*
W	1695.0(6)	2245.5(10)	703.8(5)	C(7)	3560(16)	1554(23)	2575(13)
Mo(1)	1889(1)	−1875(2)	1832(1)	C(8)	1853(16)	−2326(23)	683(14)
Mo(2)	3122(1)	−155(2)	2825(1)	C(9)	2778(15)	−3290(23)	2091(14)
P	2288(4)	299(6)	1519(3)	C(10)	3152(13)	−793(22)	1583(11)
O(1)	−162(12)	1036(22)	703(11)	C(11)	3904(14)	−958(32)	1084(13)
O(2)	1839(13)	748(21)	−887(10)	C(12)	3603(16)	−577(28)	239(13)
O(3)	882(13)	4682(17)	−252(11)	C(13)	4672(13)	−108(29)	1397(13)
O(4)	3600(14)	3346(25)	641(12)	C(14)	4253(19)	−2414(25)	1085(15)
O(5)	1529(14)	3894(16)	2238(9)	C(15)	4499(16)	−544(31)	3539(12)
O(6)	1508(11)	1362(18)	3212(10)	C(16)	4121(18)	−1740(27)	3320(14)
O(7)	3858(12)	2573(17)	2468(11)	C(17)	3413(18)	−1939(28)	3714(13)
O(8)	1776(12)	−2654(19)	46(11)	C(18)	3284(16)	−813(25)	4135(13)
O(9)	3211(12)	−4173(17)	2241(12)	C(19)	3977(17)	57(30)	4022(12)
C(1)	550(17)	1585(27)	740(13)	C(20)	558(15)	−1150(27)	2214(16)
C(2)	1804(16)	1246(21)	−307(12)	C(21)	977(14)	−1742(21)	2837(14)
C(3)	1161(16)	3661(27)	102(14)	C(22)	1056(16)	−3091(24)	2609(16)
C(4)	2891(19)	2843(29)	679(14)	C(23)	671(15)	−3196(24)	1832(15)
C(5)	1619(18)	3241(23)	1720(13)	C(24)	364(13)	−1949(22)	1569(14)
C(6)	2090(15)	807(22)	3067(12)				

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[*] **8**. *Crystal data*: $C_{23}H_{19}FeMo_2O_8P$, $M = 702.1$, monoclinic, space group $C2/c$, a 32.432(2), b 9.850(1), c 16.174(1) Å, β 106.30(1)°, U 4959.3 Å, $Z = 8$, D_c 1.88 g cm^{-1}, monochromated Mo-K_α radiation, λ 0.71069 Å, μ 16.6 cm^{-1}.

A crystal ca. 0.15 × 0.1 × 0.08 mm was mounted on an Enraf-Nonius CAD4 diffractometer. Intensities for $-h$ $-k$ $\pm l$ reflections with $2 < \theta < 25°$ were measured by an ω–2θ scan with a maximum scan time of 1 minute. No correction was made for absorption. Out of 4931 measured, 3232 unique reflections with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = \{\sigma^2(I) - (0.04I)^2\}^{1/2}/LP$. The structure was solved by routine heavy atom methods and refined by full matrix least squares with anisotropic temperature factors. Hydrogen atoms were located on a difference map and refined with isotropic temperature factors. The final residuals were $R = 0.034$, $R' = 0.040$ with a weighting scheme of $w = 1/\sigma^2(F)$. All calculations were carried out on a PDP 11/34 computer using the Enraf–Nonius SDP-Plus program package.

Table 4

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for **9**

(a) Bonds			
W–P	2.539(3)	W–C(1)	1.90(2)
W–C(2)	2.038(12)	W–C(3)	1.91(2)
W–C(4)	1.95(2)	W–C(5)	2.035(14)
Mo(1)–P	2.388(3)	Mo(1)–C(8)	2.02(2)
Mo(1)–C(9)	2.01(2)	Mo(1)–C(10)	2.325(11)
Mo(2)–P	2.484(3)	Mo(2)–C(6)	1.958(13)
Mo(2)–C(7)	1.943(15)	Mo(2)–C(10)	2.235(10)
Mo(1)–Cen2	2.01	Mo(2)–Cen1	2.01
P–C(10)	1.733(12)	O(1)–C(1)	1.23(2)
O(2)–C(2)	1.126(13)	O(3)–C(3)	1.26(2)
O(4)–C(4)	1.22(2)	O(5)–C(5)	1.135(14)
O(6)–C(6)	1.116(13)	O(7)–C(7)	1.164(14)
O(8)–C(8)	1.134(14)	O(9)–C(9)	1.134(15)
C(10)–C(11)	1.53(2)	C(11)–C(12)	1.52(2)
C(11)–C(13)	1.51(2)	C(11)–C(14)	1.58(2)
C(15)–C(16)	1.39(2)	C(15–C(19)	1.37(2)
C(16)–C(17)	1.37(2)	C(17)–C(18)	1.39(2)
C(18)–C(19)	1.42(2)	C(20)–C(21)	1.32(2)
C(20)–C(24)	1.38(2)	C(21)–C(22)	1.45(2)
C(22)–C(23)	1.39(2)	C(23)–C(24)	1.42(2)
(b) Angles			
P–W–C(1)	88.5(4)	P–W–C(2)	90.7(3)
P–W–C(3)	175.6(4)	P–W–C(4)	89.0(4)
P–W–C(5)	88.7(4)	C(1)–W–C(2)	91.4(7)
C(1)–W–C(3)	87.0(6)	C(1)–W–C(4)	177.4(6)
C(1)–W–C(5)	89.9(7)	C(2)–W–C(3)	89.8(5)
C(2)–W–C(4)	87.7(6)	C(2)–W–C(5)	178.6(6)
C(3)–W–C(4)	95.4(6)	C(3)–W–C(5)	90.9(5)
C(4)–W–C(5)	90.9(7)	P–Mo(1)–C(8)	88.3(4)
P–Mo(1)–C(9)	122.4(4)	P–Mo(1)–C(10)	43.1(3)
C(8)–Mo(1)–C(9)	89.2(5)	C(8)–Mo(1)–C(10)	81.4(4)
C(9)–Mo(1)–C(10)	79.7(5)	P–Mo(2)–C(6)	75.8(4)
P–Mo(2)–C(7)	77.7(4)	P–Mo(2)–C(10)	42.7(3)
C(6)–Mo(2)–C(7)	84.7(5)	C(6)–Mo(2)–C(10)	117.6(5)
C(7)–Mo(2)–C(10)	90.2(5)	W–P–Mo(1)	140.5(1)
Cen2–Mo(1)–P	120.4	Cen2–Mo(1)–C(8)	110.9
Cen2–Mo(1)–C(9)	114.1	Cen1–Mo(2)–P	164.2
Cen1–Mo(2)–C(6)	116.3	Cen1–Mo(2)–C(7)	112.2
Cen1–Mo(2)–C(10)	122.9	Cen2–Mo(1)–C(10)	160.8
W–P–Mo(2)	138.9(1)	W–P–C(10)	139.7(4)
Mo(1)–P–Mo(2)	75.01(9)	Mo(1)–P–C(10)	66.5(4)
Mo(2)–P–C(10)	61.0(4)	W–C(1)–O(1)	172(2)
P–C(10)–C(11)	131.7(9)	C(10)–C(11)–C(12)	110(1)
C(10)–C(11)–C(13)	111(1)	C(10)–C(11)–C(14)	113(1)
C(12)–C(11)–C(13)	109(1)	C(12)–C(11)–C(14)	108(1)
C(13–C(11)–C(14)	107(1)	C(16)–C(15)–C(19)	108(1)
C(15)–C(16)–C(17)	109(1)	C(16)–C(17)–C(18)	108(1)
C(17)–C(18)–C(19)	107(1)	C(15)–C(19)–C(18)	108(1)
C(21)–C(20)–C(24)	114(1)	C(20)–C(21)–C(22)	106(1)
C(21)–C(22)–C(23)	107(1)	C(22)–C(23)–C(24)	109(1)
C(20)–C(24)–C(23)	104(1)		

Cen1 and Cen2 are the centroids of the cyclopentadiene rings C(15)–C(19) and C(20)–C(24) respectively.

Table 5

Selected bond length data (Å) for complexes **7**–**12**

	7 [a]	**8** [b]	**9** [c]	**10** [d]	**11** [e]	**12** [f]		
P–C	1.719(3)	1.719(5)	1.733(12)	1.86(1)	–		–	
Mo(1)–P	2.497(1)	2.385(1)	2.388(3)	2.397(3)	2.552(1)		–	
Mo(2)–P	2.442(1)	2.479(1)	2.484(3)	2.514(3)	2.463(1)		–	
Mo(1)–C	2.224(4)	2.322(4)	2.325(11)	2.36(2)	–	2.190(3) [g] 2.172(3)	2.251(6) [h] 2.188(6)	2.203(4) [i] 2.192(4)
Mo(2)–C	2.222(4)	2.206(5)	2.335(10)	2.33(1)	–	2.122(3) [g] 2.203(3)	2.153(6) [h] 2.219(6)	2.148(4) [i] 2.185(4)
Mo(1)–Mo(2)	3.014(1)	2.981(1)	2.968(3)	2.949(3)	3.022(1)	2.980(3) [g] 2.977(1) [h] 2.956(1) [i]		

[a] Ref. 16. [b] This work. [c] This work. [d] Ref. 19. [e] Ref. 20. [f] Ref. 22. [g] C_2H_2 complex. [h] C_2Et_2 complex. [i] C_2Ph_2 complex.

$C_{23}H_{19}FeMo_2O_8P$ calcd.: C, 39.82; H, 2.70%. IR ν(CO)(Nujol): 1910m, 1930s, 1955m(br), 1980sh, 2030m, cm^{-1}, ^1H NMR($CDCl_3$): δ 1.26 (s, 9H, Bu^t), 5.26 (s, 10H, $2C_5H_5$) ppm. $^{31}P\{^1H\}$ NMR(toluene): δ(P) – 189.4 ppm.

Preparation of [$Mo_2(CO)_4(\eta^5$-$C_5H_5)_2(Bu^tCP)W(CO)_5$] (9)

A solution of [$Mo_2(CO)_4(\eta^5$-$C_5H_5)_2(Bu^tCP)$] (7) (0.54 g, 1 mmol) in THF (10 cm^3) was treated with a freshly prepared solution of [$W(CO)_5THF$] (1 mmol) in THF (30 cm^3) and the mixture was stirred for 24 h. The volatile components were removed in vacuo and the residue was recrystallised from toluene at $-40\,°C$ to yield deep red crystals of [$Mo_2(CO)_4(\eta^5$-$C_5H_5)_2(Bu^tCP)W(CO)_5$] (**9**) * (0.73 g, 85%). Found: C, 33.86; H. 2.20. $C_{24}H_{19}Mo_2O_9PW$ calcd.: C, 33.56; H, 2.21%. IR ν(CO)(thf): 2075w, 1990sh, 1972s, 1940s, 1920m cm^{-1}. $^{31}P\{^1H\}$NMR(toluene) δ(P): – 269.2 ppm, ^1J(PW) 229 Hz. ^1H NMR($CDCl_3$): δ 1.27 (s, 9H, Bu^t); 5.2 (s, 10H, $2C_5H_5$) ppm.

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* **9**. *Crystal data*: $C_{24}H_{19}Mo_2O_9PW$, $M = 858.1$, monoclinic, a 15.409(2), b 10.243(2), c 17.154(4) Å, β 97.15(2)°. U 2686.4 Å^3, $Z = 4$, $D_c = 2.12$ g cm^{-3}, monochromated Mo-K_α radiation, λ 0.71069 Å, μ 55.14 cm^{-1}.

Details of the data collection and structure solution were as for **8** except for the following. The crystal was ca. 0.4×0.2×0.05 mm sealed in a Lindemann capillary under argon. Intensities were measured for $2 < \theta < 20°$, and 2163 reflections with $|F^2| > \sigma(F^2)$ were used in the refinement. An empirical absorption correction was made based on ψ scan measurements. Hydrogen atoms were fixed at calculated positions with B_{iso} of 6.0 Å. Final residuals were $R = 0.063$, $R' = 0.082$.

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