Bimetallic Systems. Part 22.[1] Molybdenum(O)- and Manganese(I)-Iron(O) Carbonyl Complexes containing One Bridging $Ph_2PCH_2PPh_2$ Ligand, including the Reversible Uptake of Carbon Monoxide: Crystal Structure of $[(OC)_4Fe(\mu\text{-}Ph_2PCH_2PPh_2)Mo(CO)_4]\cdot 0.5\ C_6H_5Cl$†

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Treatment of $[Fe_2(CO)_9]$ with dppm ($Ph_2PCH_2PPh_2$) in tetrahydrofuran gave $[Fe(CO)_4(\text{dppm-}P)]$ and other products. Treatment of $[Fe(CO)_4(\text{dppm-}P)]$ with $[Mn(CO)_5Br]$ gave $[(OC)_4Fe(\mu\text{-dppm})Mn(CO)_3Br]$ in 58% yield. This bimetallic complex reacted reversibly with carbon monoxide, breaking the metal–metal bond to give $[(OC)_4Fe(\mu\text{-dppm})Mn(CO)_4Br]$. Treatment of $[Fe(CO)_4(\text{dppm-}P)]$ with $[Mo(CO)_4(nbd)]$ {nbd = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)} gave $[(OC)_4Fe(\mu\text{-dppm})Mo(CO)_4]$ in 47% yield. This bimetallic complex reacts with carbon monoxide to give a complex, formulated as $[(OC)_4Fe(\mu\text{-dppm})Mo(CO)_5]$, which was not isolated. Analogous reactions with the diphosphine $CH_2{=}C(PPh_2)_2$ are described. Crystals of $[(OC)_4Fe(\mu\text{-dppm})Mo(CO)_4]$ are tetragonal, space group $I4_1cd$ (no. 110), with a = 1 853.1(4), c = 4 106.8(9) pm, and Z = 16; final R = 0.0633 for 3 357 observed reflections. The structure shows that there is a metal–metal bond [Fe–Mo 302.4(5) pm] formulated as a donor→acceptor bond, *viz.* Fe→Mo.

Although there are many examples of heterobimetallic complexes bridged by two dppm ($Ph_2PCH_2PPh_2$) ligands, *i.e.* containing the moiety $M^1(\mu\text{-dppm})_2M^2$, where M^1 and M^2 are different metals, there are relatively few containing a single bridging dppm ligand. The growing number of examples include $[(\eta\text{-}C_5H_5)Ni(\mu\text{-dppm})(\mu\text{-SPh})Mo(CO)_4]$,[2] $[PtW\{\mu\text{-}C(OMe)\text{-}C_6H_4Me\text{-}4\}(\mu\text{-dppm})(CO)_5]$,[3] $[H(\text{dppm-}PP')Ru(\mu\text{-dppm})(\mu\text{-}H)Rh(1,5\text{-}C_8H_{12})]$,[4] $[ReW(\mu\text{-}OCCH_2R)(\mu\text{-dppm})(CO)_6\{P(OMe)_3\}]$,[5] $[(\eta\text{-}C_5H_4Me)Mo(CO)_2(\mu\text{-dppm})Pt(dppm)]_2[Mo_2O_7]$,[6] $[(OC)_4Fe(\mu\text{-dppm})RhCl(CO)]$, and $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)PtBr_2]$.[7] It is likely that complexes containing the moiety $M^1(\mu\text{-dppm})M^2$ might display greater reactivity than those with the moiety $M^1(\mu\text{-dppm})_2M^2$ due to the more open nature of one side of the molecule to attack.

We recently reported the use of the monodentate-phosphine iron complex $[Fe(CO)_4(\text{dppm-}P)]$ in the systematic synthesis of heterobimetallic complexes containing the metals Rh^I or Pt^{II}.[7] In the present paper we report an extension of this method to the synthesis of heterobimetallic complexes of iron(0) carbonyl with the metals Mo^0 and Mn^I and also give details of the preparation of the iron carbonyl phosphine complexes $[Fe(CO)_4(\text{dppm-}P)]$ and $[Fe(CO)_4(\text{vdpp-}P)]$ [vdpp = vinylidenebis(diphenylphosphine)].

Table 1. Hydrogen-1[a] and $^{31}P\text{-}\{^1H\}$[b] n.m.r. data

	$^{31}P\text{-}\{^1H\}$			^1H		
Complex	$\delta(P_A)$	$\delta(P_B)$	$^2J(P_AP_B)$	$\delta(CH_2)$	$^2J(PH)$	$^2J(HH)$
(1a)[c]	65.9	−25.9	80	3.38	9	
(1b)	80.1	−10.6	61			
(2a)	58.3	48.9	78	3.47, 2.93	*d*	14
(2b)[c]	65.5	55.4	127	6.58, 5.90	24, 14 20, 10	
(3)	66.5	40.4	37	4.35	8, 6	
(4)	60.9	35.1	85	3.58	11, 8	
(5)	66.7	31.6	27			

[a] Spectra (100 MHz) measured in CD_2Cl_2 at +20 °C; chemical shifts (δ) in p.p.m. (±0.01) to high frequency of $SiMe_4$ and coupling constants (J) in Hz (±0.1). [b] Spectra (40.5 MHz) measured at +20 °C in CD_2Cl_2; chemical shifts (δ) in p.p.m. (±0.1) to high frequency of 85% H_3PO_4 and coupling constants (J) in Hz (±3). Atom P_A is bonded to iron and P_B is bonded to manganese or molybdenum, or is unco-ordinated. [c] Hydrogen-1 spectrum measured at 400 MHz. [d] Coupling constants $^2J(PH)$ not resolved.

Table 2. Infrared absorption maxima (cm^{-1})*

Complex	ν(C≡O)
(1a)	2 052m, 1 976m, 1 938s br
(2a)	2 042s, 2 000s, 1 956 (sh), 1 940s, 1 928 (sh)
(2b)	2 040s, 1 998s, 1 952 (sh), 1 936s, 1 924 (sh)
(3)	2 095s, 2 055s, 2 027m, 2 009s, 1 977m, 1 945s, 1 935 (sh)
(4)	2 070s, 2 018m, 2 005m, 1 962s, 1 915m, 1 865m
(5)	2 076s, 2 050s, 1 976m, 1 944s

* Measured in CH_2Cl_2 solution (m = medium, s = strong, br = broad, sh = shoulder).

Results and Discussion

The monodentate dppm complex $[Fe(CO)_4(\text{dppm-}P)]$ **(1a)** was prepared previously by substituting $[Fe(CO)_5]$ with dppm photochemically but this method involved a tedious chromatographic separation of various products.[8] We find that on treatment of $[Fe_2(CO)_9]$ with dppm in tetrahydrofuran (thf) the required complex **(1a)** is readily formed and is separated by one crystallisation from methylcyclohexane in *ca.* 35% yield; **(1a)** was characterised by $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectroscopy (Table 1) and i.r. spectroscopy (Table 2). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum was an AX pattern, the low-field doublet being assigned to the phosphorus atom bonded to iron and the high-field doublet, with a chemical shift (−25.9 p.p.m.) similar to that of free dppm (*ca.* −26 p.p.m.), to the unco-ordinated phosphine atom. The ^1H n.m.r. spectral parameters were the same as those previously reported.[8] The product was contaminated with *ca.* 10% of an impurity showing a singlet ^{31}P resonance at δ(P) 62.5 p.p.m. and tentatively formulated as the known bridged

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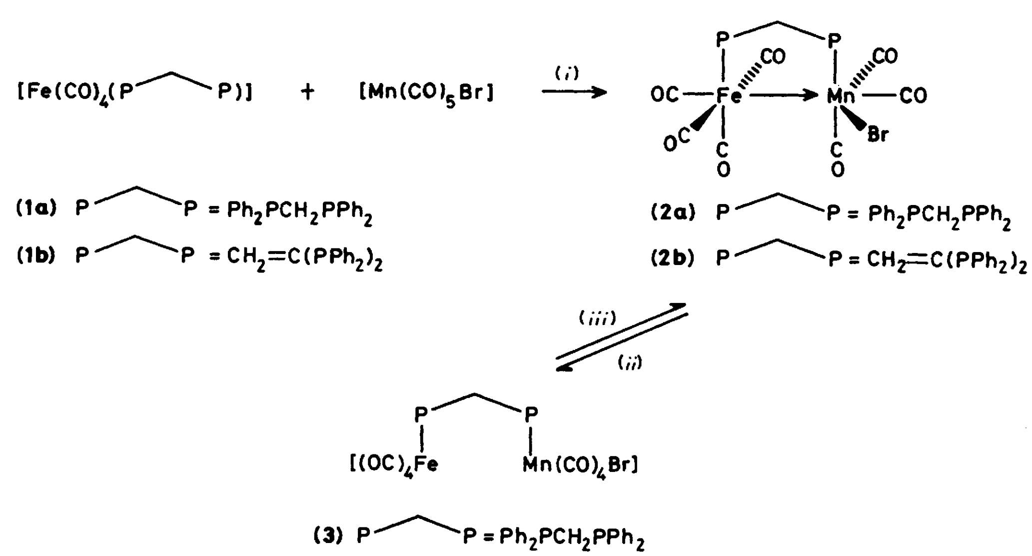
† μ-[Bis(diphenylphosphino)methane]-1,1,1,1,2,2,2,2-octacarbonyl-ironmolybdenum(*Fe–Mo*)–chlorobenzene (2/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.



Scheme 1. (*i*) toluene at +100 °C; (*ii*) CO in CH_2Cl_2 at +20 °C; (*iii*) benzene at +80 °C

Table 3. Colours, yields, and microanalytical data for the bimetallic complexes

Complex	Colour	Yield (%)	Analysis[a] (%) C	H	Br
(**2a**)	Red	58	50.75 (49.85)	2.95 (2.9)	10.4 (10.35)
(**2b**)	Red	*ca.* 50	50.0 (50.6)	2.8 (2.85)	10.45 (10.0)
(3)	Yellow	57	49.2 (49.4)	2.8 (2.75)	10.05 (9.95)
(4)·$0.5C_7H_8$[b]	Orange	47	54.2 (54.35)	3.2 (3.25)	

[a] Calculated values in parentheses. [b] Presence of toluene solvent confirmed by ^1H n.m.r. spectroscopy.

dimer [$(OC)_4Fe(\mu\text{-dppm})Fe(CO)_4$]. The i.r. spectrum of (**1a**) in the ν(CO) region was the same as those reported for both [$Fe(CO)_4$(dppm-*P*)] and [$(OC)_4Fe(\mu\text{-dppm})Fe(CO)_4$].[8]

The vdpp analogue of (**1a**), [$Fe(CO)_4$(vdpp-*P*)] (**1b**) was prepared similarly and the characterisation followed from ^{31}P-{^1H} n.m.r. spectroscopy (Table 1), the spectrum being very like that of (**1a**). The product contained *ca.* 20—30% of an impurity tentatively formulated as [$(OC)_4Fe(\mu\text{-vdpp})Fe(CO)_4$] on the basis of ^{31}P-{^1H} n.m.r. spectroscopy [δ(P) 85.1 p.p.m.]. Although analytically pure samples of (**1a**) and (**1b**) were not obtained, the materials were of sufficient purity to use in the preparations described below.

When we treated the monodentate-dppm iron complex (**1a**) with an equivalent amount of [$Mn(CO)_5Br$] in toluene at +100 °C we obtained the red iron–manganese complex, [$(OC)_4Fe(\mu\text{-dppm})Mn(CO)_3Br$] (**2a**) in 58% yield. The vdpp analogue (**2b**) was made similarly (see Scheme 1); details are given in the Experimental section and n.m.r. and elemental analytical data are given in Tables 1 and 3, respectively.

Treatment of (**1a**) with the labile molybdenum complex [$Mo(CO)_4$(nbd)] {nbd = norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)} in benzene gave the iron–molybdenum complex [$(OC)_4Fe(\mu\text{-dppm})Mo(CO)_4$] (**4**). Attempts to prepare the vdpp analogue of (**4**) gave only decomposition products. The bimetallic complexes (**2a**), (**2b**), and (**4**) are all crystalline solids that do not decompose appreciably after several weeks in air. They are readily soluble in chlorinated hydrocarbons, slightly soluble in benzene, but insoluble in alkanes. The formulation of the complexes as (**2a**), (**2b**), and (**4**) follows from ^{31}P-{^1H} and ^1H n.m.r. spectroscopy (Table 1), elemental analysis (Table 3), and i.r. spectroscopy (Table 2). Furthermore, the structure of complex (**4**) has been determined by *X*-ray crystallography (see below).

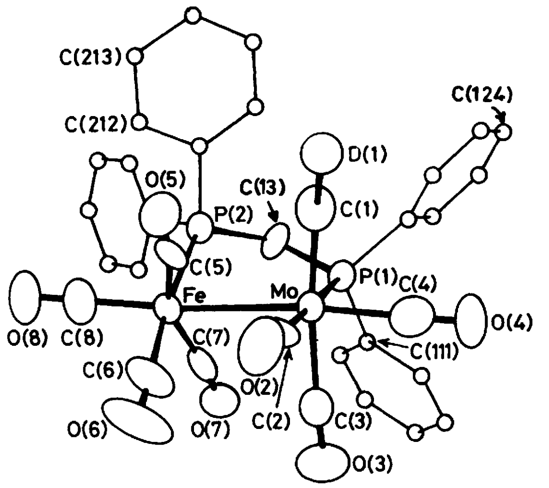
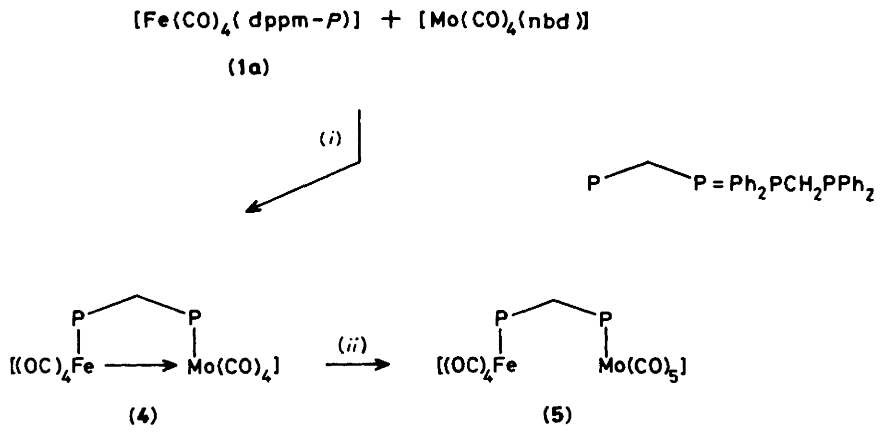


Figure. Molecular structure of [$(OC)_4Fe(\mu\text{-dppm})Mo(CO)_4$] (**4**), showing the principal atomic numbering

The ^{31}P-{^1H} n.m.r. spectra of complexes (**2a**), (**2b**), and (**4**) were similar. They were all AX spin systems, consisting of a low-field doublet (*ca.* 60 p.p.m.), assigned to the phosphorus atom bonded to iron, and a doublet at higher field assigned to the phosphorus atom bonded to manganese or molybdenum. The resonance due to the phosphorus atom on manganese was significantly broadened due to the quadrupolar effect of the ^{55}Mn nucleus (100%, $I = \frac{5}{2}$). The ^1H-{^{31}P} n.m.r. spectrum of (**2a**) showed an AB pattern at +20 °C for the CH_2 protons of the dppm ligand. The CH_2 protons of (**4**) showed a single resonance at +20 °C. This indicates that the Br substituent is *cis* to the iron–manganese bond, as shown in (**2a**); similarly for (**2b**).



Scheme 2. (*i*) benzene at +80 °C; (*ii*) CO in CH_2Cl_2 at +20 °C

Table 4. Selected interatomic distances (pm) and angles (°) for $[(OC)_4Fe(\mu\text{-dppm})Mo(CO)_4]$ (**4**) with estimated standard deviations (e.s.d.s) in parentheses

Fe–Mo	302.4(5)		
Mo–P(1)	252.3(7)	Fe–P(2)	228.5(6)
Mo–C(1)	200(2)	Fe–C(5)	178(2)
Mo–C(2)	202(2)	Fe–C(6)	175(2)
Mo–C(3)	203(2)	Fe–C(7)	181(2)
Mo–C(4)	195(2)	Fe–C(8)	181(2)
C(1)–Mo–C(2)	85.6(6)	C(6)–Fe–C(7)	88.4(8)
C(1)–Mo–C(3)	171.0(6)	C(5)–Fe–C(7)	152.6(6)
P(1)–Mo–C(4)	90.0(5)	P(2)–Fe–C(5)	91.6(6)
P(1)–Mo–C(2)	178.7(4)	P(2)–Fe–C(6)	173.5(5)
Mo–C(1)–O(1)	171(1)	Fe–C(5)–O(5)	167(1)
Mo–C(2)–O(2)	178(1)	Fe–C(6)–O(6)	174(1)
Mo–C(3)–O(3)	174(1)	Fe–C(7)–O(7)	174(1)
Mo–C(4)–O(4)	177(1)	Fe–C(8)–O(8)	178(2)

Crystal Structure of $[(OC)_4Fe(\mu\text{-dppm})Mo(CO)_4]$ (**4**).—Complex (**4**) was crystallised from chlorobenzene–methylcyclohexane (1 : 3). The structure is shown in the Figure and selected intramolecular distances and angles are in Table 4. The Fe and Mo moieties are linked by a single dppm bridge to give a five-membered FeP_2CMo ring. There are no bridging or semi-bridging carbonyls but the Fe–Mo distance [302.4(5) pm] indicates a metal–metal bond. This distance is slightly longer than that found for the average of the Mo–Fe bond lengths in the cluster dianion $[Fe_5MoC(CO)_{17}]^{2-}$ (Mo–Fe 291.5 pm),[9] and is very close to the length [304.7(5) pm] found in the related iron–molybdenum complex $[(OC)_3Fe(\mu\text{-dppm})_2Mo(CO)_3]$.[10] In order to satisfy an 18-electron configuration for each metal centre in (**4**) the metal–metal bond is formulated as donor→acceptor, *viz.* Fe→Mo, *i.e.* the Fe atom can be viewed as occupying the sixth co-ordination site of Mo by electron-pair donation from a filled orbital on Fe to this empty co-ordination position. Consistent with the donor→acceptor bond between the two metals is the easy displacement of the Fe atom from Mo by CO (see below).

Reactions.—Recently Geoffroy and co-workers[11] have reported the preparation of the phosphido-bridged bimetallic complex $[(OC)_5W(\mu\text{-PPh}_2)Re(CO)_5]$, which readily lost CO to give $[(OC)_5W(\mu\text{-PPh}_2)Re(CO)_4]$. The latter complex was formulated with a donor→acceptor bond, *viz.* W→Re and underwent reactions with some donor molecules such as MeCN or $PhMe_2P$ breaking the metal–metal bond. However, no such reaction occurred with CO, even at high pressure. These results prompted us to attempt similar reactions with our bimetallic complexes. Thus, when we treated (**2a**) with CO at +20 °C the complex $[(OC)_4Fe(\mu\text{-dppm})Mn(CO)_4Br]$ (**3**) was formed quantitatively ($^{31}P-\{^1H\}$ evidence). When a solution of (**3**) heated under N_2 this process was reversed and the metal–metal bond reformed, to give back (**2a**) ($^{31}P-\{^1H\}$ evidence). Complex (**3**) was isolated in 57% yield and the formulation follows from $^{31}P-\{^1H\}$ and ^1H n.m.r. spectroscopy (Table 1), elemental analysis (Table 3), and i.r. spectroscopy (Table 2). The $^{31}P-\{^1H\}$ n.m.r. spectrum showed an AX pattern with the two resonances slightly shifted relative to their positions in (**2a**). The i.r. spectrum showed the presence of two strong, high-energy bands assigned to ν(CO) which are characteristic of the presence of both $Fe(CO)_4$ and $Mn(CO)_4Br$ moieties.

A similar experiment with (**4**) gave a pale yellow solution containing the complex $[(OC)_4Fe(\mu\text{-dppm})Mo(CO)_5]$ (**5**), which was not isolated, but characterised on the basis of $^{31}P-\{^1H\}$ n.m.r. spectroscopy and i.r. spectroscopy. In particular, the i.r. spectrum shows two high-energy bands assigned to ν(CO), characteristic of the presence of both $Fe(CO)_4$ and $Mo(CO)_5$ moieties. Attempts to convert (**5**) to (**4**) by heating caused extensive decomposition.

Reactions with other donor molecules were less successful. Treatment of (**2a**) with an excess of MeNC in CH_2Cl_2 gave a major product which was tentatively formulated as $[(OC)_4Fe(\mu\text{-dppm})Mn(CO)_3(CNMe)Br]$ on the basis of the $^{31}P-\{^1H\}$ n.m.r. spectrum [δ(P)(Fe) 73.1, δ(P)(Mn) 43.2 p.p.m., ^2J(PP) 36 Hz]. Attempted isolation, however, caused decomposition. Treatment of (**2a**) with an excess of PPh_2H in CH_2Cl_2 gave cleavage products, one of which was tentatively formulated as $[Fe(CO)_3(dppm\text{-}P)(PPh_2H)]$ on the basis of $^{31}P-\{^1H\}$ n.m.r. spectroscopy [δ(P) 75.9, ^2J(PP) 81 and 32; 55.0, ^2J(PP) 32; −25.4 p.p.m., ^2J(PP) 81 Hz].

Experimental

General methods were as previously described in recent papers from this laboratory.[12] The complexes $[Mn(CO)_5Br]$[13] and $[Mo(CO)_4(nbd)]$[14] were prepared by literature methods.

Preparations.—[$Fe(CO)_4$(dppm-*P*)] (**1a**) *from* [$Fe_2(CO)_9$] *and* $Ph_2PCH_2PPh_2$. [$Fe_2(CO)_9$] (3.90 g, 10.71 mmol) and dppm (3.00 g, 7.82 mmol) were stirred together in thf (80 cm^3) under an atmosphere of dinitrogen in the dark for 18 h. The solvent was removed under reduced pressure and the residue extracted into hot (100 °C) methylcyclohexane (60 cm^3). The extract was filtered and refrigerated (5 °C). After 48 h the product was isolated by filtration (yield 1.68 g). This material contained *ca.* 10% of an impurity, having a singlet resonance in the $^{31}P-\{^1H\}$ n.m.r., probably due to [$(OC)_4Fe(\mu$-dppm)-$Fe(CO)_4$]. However, the product was sufficiently pure for the preparations described below.

[$Fe(CO)_4$(vdpp-*P*)] (**1b**) was prepared similarly. In this case, however, as much as 30% of the product was the bridged species [$(OC)_4Fe(\mu$-vdpp)$Fe(CO)_4$].

[$(OC)_4Fe(\mu$-dppm)$Mn(CO)_3Br$] (**2a**) *from* [$Fe(CO)_4$(dppm-*P*)] (**1a**) *and* [$Mn(CO)_5Br$]. Complex (**1a**) (0.552 g, 1 mmol) was heated with [$Mn(CO)_5Br$] (0.275 g, 1 mmol) in toluene (25 cm^3) solution at 100 °C for 2 h with a constant stream of dinitrogen blowing over the solution. The resultant red solution was cooled to room temperature and filtered. Addition of light petroleum (b.p. 60—80 °C) gave the required product as red prisms (yield 58%).

Complex (**2b**) was prepared similarly.

[$(OC)_4Fe(\mu$-dppm)$Mn(CO)_4Br$] (**3**) *from* [$(OC)_4Fe(\mu$-dppm)$Mn(CO)_3Br$] (**2a**). Carbon monoxide was bubbled through a solution of (**2a**) (0.100 g, 0.130 mmol) in benzene–dichloromethane (1:1, 20 cm^3) for 2 h. The solvent was removed under reduced pressure from the yellow solution and the residue extracted into toluene (3 cm^3). Addition of light petroleum (b.p. 60—80 °C) gave the required product as yellow needles (yield 57%).

In a separate experiment carbon monoxide was bubbled through a solution of (**2a**) (0.030 g, 0.039 mmol) in benzene (0.5 cm^3) for 20 min. $^{31}P-\{^1H\}$ N.m.r. spectroscopy indicated the quantitative formation of the octacarbonyl complex (**3**). This solution was then heated to reflux for 5 min while dinitrogen was bubbled through it. The resulting orange solution was examined by $^{31}P-\{^1H\}$ n.m.r. spectroscopy which showed the quantitative regeneration of (**2a**).

[$(OC)_4Fe(\mu$-dppm)$Mo(CO)_4$] (**4**) *from* [$Fe(CO)_4$(dppm-*P*)] (**1a**) *and* [$Mo(CO)_4$(nbd)]. The complexes (**1a**) (0.552 g, 1 mmol) and [$Mo(CO)_4$(nbd)] (0.300 g, 1 mmol) were refluxed together in benzene (10 cm^3) for 20 min. The solution was cooled to room temperature and the solvent removed under reduced pressure. The residue was extracted into toluene (5 cm^3) and the extract refrigerated (−20 °C) to give the desired product as orange prisms (yield 47%).

[$(OC)_4Fe(\mu$-dppm)$Mo(CO)_5$] (**5**) *from* [$(OC)_4Fe(\mu$-dppm)-$Mo(CO)_4$] (**4**). Carbon monoxide was bubbled through a solution of (**4**) in dichloromethane (20 cm^3) for 5 h. Infrared and $^{31}P-\{^1H\}$ n.m.r. analysis of the resulting pale yellow solution indicated conversion to a single new complex.

Crystallography.—Suitable crystals of [$(OC)_4Fe(\mu$-dppm)-$Mo(CO)_4$]$\cdot 0.5C_6H_5Cl$ were grown from chlorobenzene–methylcyclohexane (1:3).

Intensity data were collected on a Nicolet P3/F diffractometer operating in the ω scan mode, using graphite-monochromated Mo-K_α radiation (λ = 71.069 pm) following a standard procedure.[15] The data set was corrected for absorption empirically once the structure had been determined.[16] The structure was solved *via* standard heavy-atom methods and refined by full-matrix least-squares methods using the SHELX program system.[17] All non-hydrogen atoms were assigned anisotropic thermal parameters except for the carbon atoms on the chlorobenzene solvent molecule (situated on a crystallographic two-fold axis) which were assigned an overall isotropic thermal parameter. All the hydrogen atoms were included in calculated positions (C–H = 108 pm) and were assigned to an overall isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used at the end of refinement in which the parameter g was adjusted so as to give a flat analysis of variance with increasing sinθ and $(F/F_{max.})^{\frac{1}{2}}$.

Table 5. Atom co-ordinates (× 10^4) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Mo(1)	1 344(1)	3 119(1)	0
Fe(1)	1 408(1)	4 036(1)	608(1)
P(1)	2 578(2)	3 621(2)	−125(1)
P(2)	1 626(2)	3 850(2)	628(1)
Cl(1S)	0*	0*	−638(2)
C(111)	2 591(6)	4 394(4)	−409(2)
C(112)	2 280(6)	4 264(4)	−713(2)
C(113)	2 290(6)	4 800(4)	−951(2)
C(114)	2 611(6)	5 466(4)	−886(2)
C(115)	2 922(6)	5 595(4)	−582(2)
C(116)	2 912(6)	5 059(4)	−344(2)
C(121)	3 257(4)	3 028(5)	−318(2)
C(122)	3 183(4)	2 279(5)	−311(2)
C(123)	3 717(4)	1 841(5)	−446(2)
C(124)	4 326(4)	2 153(5)	−589(2)
C(125)	4 400(4)	2 902(5)	−596(2)
C(126)	3 866(4)	3 339(5)	−461(2)
C(13)	3 083(8)	3 970(9)	237(3)
C(211)	2 893(5)	2 984(4)	794(2)
C(212)	2 648(5)	2 815(4)	1 105(2)
C(213)	2 826(5)	2 153(4)	1 246(2)
C(214)	3 250(5)	1 661(4)	1 074(2)
C(215)	3 495(5)	1 830(4)	762(2)
C(216)	3 317(5)	2 492(4)	622(2)
C(221)	3 135(5)	4 484(4)	878(2)
C(222)	3 034(5)	5 221(4)	825(2)
C(223)	3 441(5)	5 723(4)	999(2)
C(224)	3 949(5)	5 488(4)	1 226(2)
C(225)	4 050(5)	4 751(4)	1 279(2)
C(226)	3 643(5)	4 249(4)	1 105(2)
C(1)	1 738(8)	2 195(9)	176(3)
O(1)	1 887(6)	1 620(7)	261(3)
C(2)	366(8)	2 705(8)	109(3)
O(2)	−171(7)	2 469(8)	180(3)
C(3)	855(8)	3 959(10)	−228(3)
O(3)	562(8)	4 392(7)	−377(3)
C(4)	1 317(7)	2 663(10)	−428(4)
O(4)	1 284(6)	2 366(7)	−673(2)
C(5)	1 232(8)	3 112(9)	697(3)
O(5)	1 076(6)	2 547(6)	814(2)
C(6)	483(9)	4 160(8)	546(4)
O(6)	−147(6)	4 190(7)	511(4)
C(7)	1 571(7)	4 775(9)	330(4)
O(7)	1 633(6)	5 277(6)	168(3)
C(8)	1 384(8)	4 446(10)	1 008(4)
O(8)	1 352(7)	4 702(8)	1 257(3)
C(1S)	0*	0*	−217(6)
C(2S)	244(9)	603(9)	−61(4)
C(3S)	238(9)	593(10)	288(4)
C(4S)	0*	0*	452(6)

* Co-ordinate fixed on special position.

Crystal data. $C_{33}H_{22}FeMoO_8P_2 \cdot 0.5C_6H_5Cl$, $M = 816.55$, tetragonal, $a = 1\,853.1(4)$, $c = 4\,106.8(9)$ pm, $U = 14.102$ nm^3, $Z = 16$, space group $I4_1cd$ (no. 110), $D_c = 1.54$ g cm^{-3}, μ(Mo-K_α) = 8.97 cm^{-1}, $F(000) = 6\,432$, $T = 290$ K.

Data collection. Scans running from 0.5° below K_{α_1} to 0.5° above K_{α_2}, scan speeds 2.0—29.3° min^{-1}, $4.0 \leqslant 2\theta \leqslant 45°$. 5 028 Unique data, 3 357 observed [$I > 2.0\sigma(I)$].

Structure refinement. Number of parameters = 372, weighting factor $g = 0.0002$, $R = 0.0633$, $R' = 0.0533$. The final atomic co-ordinates and their standard deviations are listed in Table 5.

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