Bimetallic Systems. Part 19.[1] Chromium(0)-, Molybdenum(0)-, or Tungsten(0)-Iron(0) Carbonyl Complexes containing One or Two Bridging $Ph_2PCH_2PPh_2$ Ligands: Crystal Structure of $[(OC)_3Mo(\mu\text{-}Ph_2PCH_2PPh_2)_2Fe(CO)_3]$ †

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Treatment of *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (M = Cr, Mo, or W) (dppm = $Ph_2PCH_2PPh_2$) or *fac*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P')]$ (M = Mo or W) with $[Fe_2(CO)_9]$ or $[Fe_3(CO)_{12}]$ gave the bimetallics $[(OC)_3M(\mu\text{-}dppm)_2Fe(CO)_3]$ (M = Cr, Mo, or W) in moderate (2—52%) yields. The bimetallics were protonated with $HBF_4{\cdot}Et_2O$ to give the hydrides $[(OC)_3HM(\mu\text{-}dppm)_2Fe(CO)_3]^+BF_4^-$. Proton n.m.r. studies indicated that the hydride ligand was located terminally on the Group 6 metal. In addition, complexes tentatively formulated as *mer*-$[(dppm\text{-}PP')(OC)_3M(\mu\text{-}dppm)Fe(CO)_4]$ (M = Cr, Mo, or W) and *fac*-$[(dppm\text{-}PP')(OC)_3W(\mu\text{-}dppm)Fe(CO)_4]$ are also formed in the above reactions and have been characterised by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. These complexes appear not to be the simple precursors to the bimetallics containing two bridging dppm ligands. Crystals of $[(OC)_3Mo(\mu\text{-}dppm)Fe(CO)_3]$ are triclinic, space group $P\bar{1}$, with a = 1 219.1(3) b = 1 225.2(2), c = 2 142.4(4) pm, α = 92.97(2), β = 95.42(2), γ = 100.58(2)°, and Z = 4; final R factor 0.0791 for 6 771 observed reflections. The structure shows that there is a metal–metal bond [304.7(5) pm], probably best considered as a weak donor→acceptor bond, *viz.* Fe→Mo. Both metal centres show distortions from idealised geometries.

We have shown in previous papers that the monodentate-chelate bis(dppm) Group 6 metal complexes *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (M = Cr, Mo, or W) and *fac*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (M = Mo or W, dppm = $Ph_2PCH_2PPh_2$) readily form heterobimetallic complexes with the metals rhodium(I), iridium(I), platinum(II), copper(I), silver(I), gold(I), or mercury(II).[2–4] In the present paper we report methods for the synthesis of heterobimetallic complexes of iron(0) carbonyls with the d^6 metals, chromium(0), molybdenum(0), and tungsten(0).

Results and Discussion

One of our most successful methods for making heterobimetallic complexes of the Group 6 metals containing bridging dppm ligands has been by treatment of the complexes (**1a**)—(**1c**) or (**2b**),(**2c**) with a substitition-labile complex of the second metal; thus when we treated the molybdenum complex (**1b**) with an equimolar amount of $[Fe_2(CO)_9]$ in tetrahydrofuran we obtained the molybdenum–iron complex (**3b**) in 25% yield, as orange crystals. The chromium (**3a**) and tungsten (**3c**) analogues were made similarly (see Scheme). The same products, (**3b**), (**3c**), were formed when the *fac* isomer (**2b**) or (**2c**) was used. We also prepared the bimetallic complexes (**3b**) and (**3c**) using $[Fe_3(CO)_{12}]$ as the source of iron carbonyl, resulting in slightly improved yields; details are given in the Experimental section and characterising data in Tables 1—4.

The iron–Group 6 complexes (**3a**)—(**3c**) are highly coloured crystalline solids (Table 1) which do not decompose appreciably after several weeks in air. They are readily soluble in chlorinated hydrocarbons or benzene, but insoluble in alkanes. Crystals of the iron–molybdenum complex could readily be grown from dichloromethane–light petroleum, however, these rapidly lost solvent of crystallisation on removal of the mother-liquor. This problem was overcome by growing the crystals from chlorobenzene–methylcyclohexane mixtures and these crystals had a much higher stability with respect to solvent loss. The formulation of the complexes as (**3a**)—(**3c**) follows from elemental analysis (Table 1), $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectroscopy (Table 2), and i.r. spectroscopy (Table 4). Furthermore, the structure of complex (**3b**) has been determined by X-ray crystallography (see below).

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of complexes (**3a**)—(**3c**) are very characteristic,[5] that for (**3a**) being an AA′BB′ spin system and those for (**3b**) and (**3c**) being AA′XX′ spin systems. Data are given in Table 2. The value of $^1J(WP_B)$ is consistent with the *trans* configuration of phosphines around tungsten(0). The $^1H\text{-}\{^{31}P\}$ n.m.r. spectra all show a single PCH_2P resonance at +20 °C. Previously, we have observed fluxionality in many of our binuclear complexes, giving rise to a single PCH_2P resonance at ambient temperatures, and have associated this with rapid flipping of the $M(\mu\text{-}dppm)_2M'$ ring.[6,7]

Along with the bimetallics (**3a**)—(**3c**), complexes containing one bridging dppm ligand, tentatively formulated as *mer*-$[(dppm\text{-}PP')(OC)_3M(\mu\text{-}dppm)Fe(CO)_4]$ (M = Cr, Mo, or W) (**4a**)—(**4c**) and *fac*-$[(dppm\text{-}PP')(OC)_3W(\mu\text{-}dppm)Fe(CO)_4]$ (**5c**), were formed in the above described reactions with both $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$. They were the only phosphorus-containing products present in the mother-liquors after the crystallisation of complexes (**3a**)—(**3c**), as evidenced by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. However, in the case of molybdenum, the complex *fac*-$[(dppm\text{-}PP')(OC)_3Mo(\mu\text{-}dppm)Fe(CO)_4]$ was not observed. Instead, decomposition products (presumably phosphine complexes of Mo and Fe) were formed. The complexes (**4a**)—(**4c**) and (**5c**) were not isolated and were formulated only on the basis of their $^{31}P\text{-}\{^1H\}$ n.m.r. spectra (Table 3). These spectra were very similar to those of the corresponding starting materials (**1a**)—(**1c**) and (**2c**).[3,8,9] In each case the high-field doublet around −25 p.p.m., characteristic of the unco-ordinated phosphorus atom of dppm, has been shifted markedly downfield to *ca.* 62—65 p.p.m., suggesting co-ordination to the $Fe(CO)_4$ moiety. The remaining resonances due to the phosphorus atoms bonded to the Group 6 metals are not significantly changed in chemical shifts. Thus, the

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† Bis[μ-bis(diphenylphosphino)methane-*PP′*]-1,1,1,2,2,2-hexacarbonylironmolybdenum.

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

Table 1. Colours, yields, and microanalytical data[a] for complexes of type (**3**)

Complex	Colour	Yields[b]/%		Analysis/%			
		$[Fe_2(CO)_9]$	$[Fe_3(CO)_{12}]$	C	H	Cl	P
$[(OC)_3Cr(\mu\text{-dppm})_2Fe(CO)_3]\cdot 2CH_2Cl_2$	Red-brown	2		57.05 (57.35)	4.15 (4.0)	11.55 (11.65)	n.d.
$[(OC)_3Mo(\mu\text{-dppm})_2Fe(CO)_3]\cdot 2CH_2Cl_2$	Orange	25	52	55.15 (55.25)	3.75 (3.85)	11.0 (11.25)	9.6 (9.95)
$[(OC)_3W(\mu\text{-dppm})_2Fe(CO)_3]\cdot 2CH_2Cl_2$	Red	14	26	51.7 (51.7)	3.5 (3.6)	10.75 (10.5)	n.d.

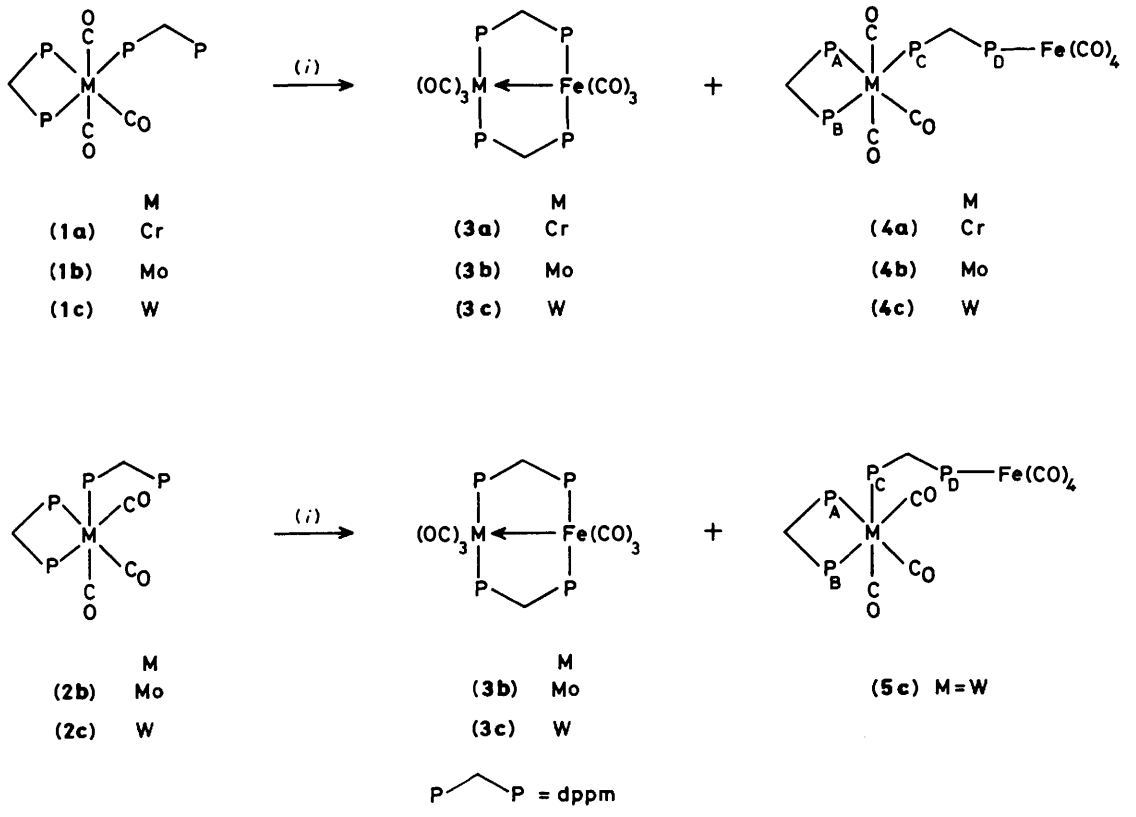
n.d. = Not determined.

[a] Calculated values in parentheses. [b] See Experimental section.

Table 2. $^{31}P\text{-}\{^1H\}$[a] and ^1H n.m.r. data[b] for complexes of types (**3**) and (**6**)

Complex	$^{31}P\text{-}\{^1H\}$				^1H			
	$\delta(P_A)$	$\delta(P_B)$	N[c]	$^1J(WP_B)$	$\delta(CH_2)$	$\delta(H)$	$^2J(PH)$	$^1J(WH)$
(**3a**)[d]	64.6	66.7	97		3.59			
(**3b**)[d]	65.0	43.7	96		3.67			
(**3c**)[d]	65.1	22.9	102	300	3.74			
(**6a**)					3.80	−6.52	42	
(**6b**)[e]	57.7	37.0	85		3.96	−6.19	35	
(**6c**)[e]	58.9	18.0	83	*f*	4.27	−5.72	41	20

[a] Spectra 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). P_A is bonded to iron and P_B to chromium, molybdenum, or tungsten. [b] Spectra (100 MHz) measured in CD_2Cl_2; chemical shifts (δ) p.p.m. (±0.01) to high frequency of $SiMe_4$ and coupling constants (J) in Hz (±0.1). [c] $N = {}^2J(P_AP_B) + {}^4J(P_AP_{B'})$. [d] $^{31}P\text{-}\{^1H\}$ spectra measured at 162 MHz. [e] $^{31}P\text{-}\{^1H\}$ spectra measured at 40.5 MHz. [f] Coupling to ^{183}W not resolved.



Scheme. (*i*) $[Fe_2(CO)_9]$ in thf at +20 °C or $[Fe_3(CO)_{12}]$ in thf at +67 °C

spectra of (**4a**)—(**4c**) and (**5c**) have been assigned with some confidence.

Attempts to convert the singly bridged complex (**4a**) into the doubly bridged complex (**3a**) by heating in tetrahydrofuran (thf) resulted only in decomposition. Thus, it appears that the type (**4**) complexes may not be the simple precursors to the doubly bridged bimetallics (**3**). This suggests that the latter may result from direct attack on the four-membered chelate ring by the reactive $Fe(CO)_4(thf)$ moiety. However, we have no definite evidence for a mechanism of this type.

Table 3. ^{31}P-{^{1}H} N.m.r.[a] data for complexes of the type *fac*- or *mer*-[(dppm-*PP′*)(OC)$_3$M(μ-dppm)Fe(CO)$_4$]

Complex	δ(P)[b]	Assignment[c]	*J*(W–P)	^{2}*J*(P–P)
(4a)[d]	74.3 (ddd)	C		33(C–D), 17, 27
	62.0 (d)	D		33
	47.5 (dd)	A(B)		27, 3(A–B)
	24.1 (dd)	B(A)		17, 3
(4b)[e]	52.9 (ddd)	C		29(C–D), 24(A–C), 73(B–C)
	64.6 (d)	D		29
	20.7 (dd)	B		19(A–B), 73
	1.4 (dd)	A		24, 19
(4c)[e]	29.0 (ddd)	C	306	30(C–D), 35(A–C), 71(B–C)
	65.3 (d)	D	40	30
	−11.1 (dd)	B	244	30(A–B), 71
	−23.0 (dd)	A	180	35, 30
(5c)[e]	62.9 (d)	D	n.o.[f]	34(C–D)
	20.5 (dt)	C	222	34, 22(A–C)
	−21.6	A	200	22

[a] Spectra measured at 20 °C in CD$_2$Cl$_2$; chemical shifts (δ) in p.p.m. (±0.1) to high frequency of 85% H$_3$PO$_4$ and coupling constants (*J*) in Hz (±3). [b] d = Doublet, t = triplet, dd = doublet of doublets, ddd = double doublet of doublets, dt = doublet of triplets. [c] For assignments see Scheme. [d] Measured at 162 MHz. [e] Measured at 40.5 MHz. [f] Not observed.

Table 4. I.r. absorption maxima (cm^{-1}) for bimetallics of type (**3**), measured in CH$_2$Cl$_2$ solutions (s = strong, m = medium, w = weak)

Complex	ν(C≡O)
(**3a**)	1 980w, 1 935s, 1 910s, 1 830s
(**3b**)	1 990w, 1 952s, 1 904s, 1 850m, 1 815m
(**3c**)	1 990w, 1 948s, 1 912s, 1 840m, 1 810m

Table 5. Selected interatomic distances (pm) and angles (°) for complex (**3b**) with estimated standard deviations (e.s.d.s) in parentheses

Mo ··· Fe	304.7(5)	Fe–P(2)	223.2(5)
Mo–P(1)	243.8(4)	Fe–P(4)	225.9(5)
Mo–P(3)	244.9(4)	Fe–C(4)	176(1)
Mo–C(1)	202(1)	Fe–C(5)	179(1)
Mo–C(2)	192(1)	Fe–C(6)	175(1)
Mo–C(3)	204(1)	C–O	115(2)— 120(1)
Mo ··· C(4)	285(1)		
Fe–Mo–C(2)	177.3(3)	Mo–Fe–C(6)	166.5(3)
C(1)–Mo–C(2)	88.7(5)	C(4)–Fe–C(6)	100.1(6)
C(1)–Mo–C(3)	173.0(4)	C(4)–Fe–C(5)	147.3(5)
Mo–C(1)–O(1)	174.6(10)	Fe–C(4)–O(4)	162.7(9)
Mo–C(2)–O(2)	178.6(8)	Fe–C(5)–O(5)	172.2(10)
Mo–C(3)–O(3)	175.2(9)	Fe–C(6)–O(6)	173.7(10)
P(1)–C(131)–P(2)	113.2(5)	P(3)–C(131)–P(4)	116.3(6)

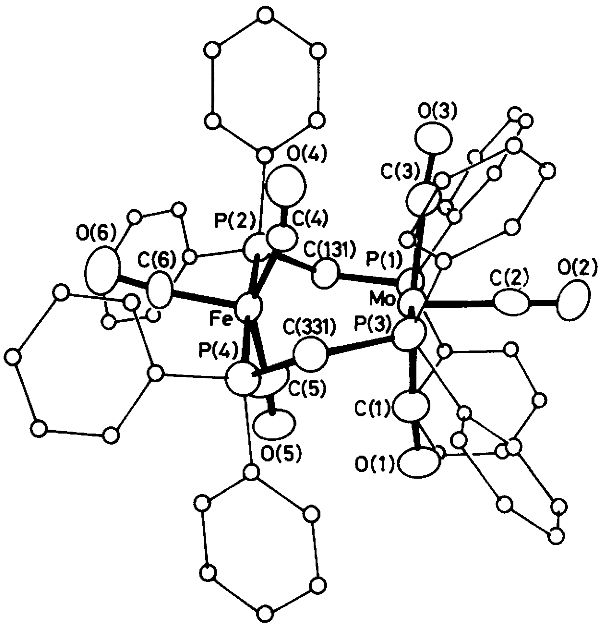


Figure. Molecular structure of [(OC)$_3$Mo(μ-dppm)$_2$Fe(CO)$_3$] (**3b**), showing the principal atomic numbering

Crystal Structure of [(OC)$_3$Mo(μ-dppm)$_2$Fe(CO)$_3$] (**3b**).—The complex (**3b**) was crystallised from chlorobenzene–methylcyclohexane (1:3). The structure is shown in the Figure and selected intramolecular distances and angles are in Table 5. The molybdenum and iron moieties are linked by two dppm bridges to give an eight-membered MoP$_4$C$_2$Fe ring. The Mo ··· Fe distance [304.7(5) pm] is slightly longer than that found for the average of the Mo–Fe bond lengths in the cluster dianion [Fe$_5$MoC(CO)$_{17}$]$^{2-}$ (Mo–Fe 291.5 pm).[10] We thus formulate the metal–metal interaction in our compound as being of the weak donor→acceptor, type *viz*. Fe→Mo, giving each metal centre an 18-electron configuration. Support for this formulation comes from the structure of the related iron–molybdenum bimetallic [(OC)$_4$Mo(μ-dppm)Fe(CO)$_4$] which contains a single bridging dppm ligand and an Fe–Me bond,[11] [302.4(5) pm].

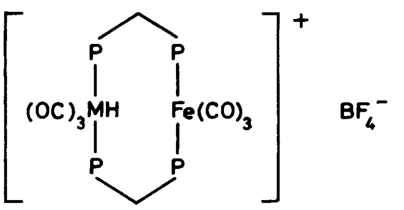
Both metal centres in complex (**3b**) show some distortions from idealised geometries. The Fe(CO)$_3$P$_2$ unit has a distorted trigonal-bipyramidal geometry, whilst the Mo(CO)$_3$P unit has a distorted octahedral geometry (assuming a bond on the Fe–Mo vector). The major source of the distortion is likely to be the close proximity of those carbonyl groups which are required to point towards each other. Thus, for example, the expected angle of 120° between the carbonyl groups CO(4) and CO(5) on the iron atom is increased to 147.3(5)°. None of the CO groups on iron appears to have any significant interaction with the molybdenum centre. The structure is very similar to that reported recently for the related complex [(OC)$_3$Cr(μ-dmpm)$_2$-Fe(CO)$_3$](dmpm = Me$_2$PCH$_2$PMe$_2$).[12]

Protonation Studies.—It seemed likely that these mixed iron–Group 6 bimetallics of type (**3**) might be protonated and indeed treatment of [(OC)$_3$W(μ-dppm)$_2$Fe(CO)$_3$] (**3c**) with HBF$_4$·Et$_2$O in CD$_2$Cl$_2$ solution gave a single product, which was not isolated but formulated as the hydride (**6c**) on the basis of ^{31}P-{^{1}H}, ^{1}H, and ^{1}H-{^{31}P} n.m.r. spectroscopy. Similar experiments were carried out for the chromium and molybdenum analogues (**3a**) and (**3b**), producing similar results. Characteristing data are given in Table 2.

The ^{31}P-{^{1}H} n.m.r. spectra of the complexes (**6b**) and (**6c**) show the characteristic AA′XX′ spin systems. The ^{1}H n.m.r. spectra of (**6a**)—(**6c**) all show single PCH$_2$P resonances of relative area four and a high-field resonance of relative area one, assigned to the metal hydride. In each case the hydride resonance is a triplet, indicating coupling to only two of the

Table 6. Atom co-ordinates (× 10^4)

Atom	x	y	z
Mo	1 160(1)	−936(1)	2 800.1(3)
Fe	3 367(1)	20(1)	2 299(1)
P(1)	809(2)	948(2)	2 962(1)
P(2)	2 667(2)	1 529(2)	2 071(1)
P(3)	1 626(2)	−2 793(2)	2 690(1)
P(4)	4 064(2)	−1 485(2)	2 590(1)
C(1)	1 943(9)	−743(7)	3 684(5)
O(1)	2 308(7)	−655(6)	4 205(4)
C(2)	−223(9)	−1 472(7)	3 139(4)
O(2)	−1 064(7)	−1 814(6)	3 334(4)
C(3)	194(9)	−1 191(8)	1 958(5)
O(3)	−399(7)	−1 389(7)	1 503(3)
C(4)	2 420(8)	−876(8)	1 744(5)
O(4)	1 994(6)	−1 401(6)	1 267(3)
C(5)	3 665(10)	628(7)	3 090(5)
O(5)	3 961(7)	1 089(6)	3 573(3)
C(6)	4 464(9)	436(8)	1 841(5)
O(6)	5 108(7)	720(7)	1 497(4)
C(111)	−504(5)	1 342(5)	2 652(3)
C(112)	−614(5)	2 456(5)	2 707(3)
C(113)	−1 594(5)	2 770(5)	2 450(3)
C(114)	−2 465(5)	1 972(5)	2 139(3)
C(115)	−2 355(5)	858(5)	2 084(3)
C(116)	−1 375(5)	544(5)	2 341(3)
C(121)	803(6)	1 396(5)	3 796(2)
C(122)	1 784(6)	1 868(5)	4 178(2)
C(123)	1 751(6)	2 084(5)	4 821(2)
C(124)	737(6)	1 828(5)	5 082(2)
C(125)	−244(6)	1 355(5)	4 700(2)
C(126)	−211(6)	1 139(5)	4 057(2)
C(131)	1 854(9)	2 059(7)	2 673(4)
C(211)	3 704(5)	2 819(4)	2 036(3)
C(212)	4 737(5)	2 984(4)	2 402(3)
C(213)	5 483(5)	3 996(4)	2 414(3)
C(214)	5 197(5)	4 844(4)	2 058(3)
C(215)	4 164(5)	4 679(4)	1 692(3)
C(216)	3 418(5)	3 667(4)	1 680(3)
C(221)	1 812(6)	1 460(6)	1 314(2)
C(222)	2 303(6)	1 202(6)	777(2)
C(223)	1 715(6)	1 180(6)	184(2)
C(224)	635(6)	1 416(6)	128(2)
C(225)	143(6)	1 674(6)	666(2)
C(226)	732(6)	1 696(6)	1 259(2)
C(311)	1 564(7)	−3 683(4)	3 364(2)
C(312)	1 954(7)	−4 684(4)	3 330(2)
C(313)	1 895(7)	−5 358(4)	3 835(2)
C(314)	1 447(7)	−5 031(4)	4 375(2)
C(315)	1 058(7)	−4 030(4)	4 409(2)
C(316)	1 116(7)	−3 356(4)	3 903(2)
C(321)	734(5)	−3 822(5)	2 110(3)
C(322)	1 153(5)	−4 512(5)	1 692(3)
C(323)	416(5)	−5 280(5)	1 274(3)
C(324)	−740(5)	−5 360(5)	1 274(3)
C(325)	−1 159(5)	−4 670(5)	1 693(3)
C(326)	−422(5)	−3 902(5)	2 111(3)
C(331)	3 047(8)	−2 807(7)	2 452(4)
C(411)	4 711(6)	−1 390(6)	3 396(2)



	M
(6a)	Cr
(6b)	Mo
(6c)	W

phosphorus nuclei of the bridging dppm ligands. For (**6c**), selective ^{1}H-{^{1}P} irradiation experiments confirmed that this coupling arose from the phosphorus bonded to the tungsten atom. Therefore, although not definite, the n.m.r. data strongly support placement of the hydride ligand terminally on the Group 6 metal.

Experimental

General methods were as previously described in recent papers from this laboratory.[13] The complex *fac*-[Mo(CO)$_3$(dppm-*PP′*)(dppm-*P*)] was prepared by the method of Isaacs and Graham.[8] The complexes *mer*-[M(CO)$_3$(dppm-*PP′*)(dppm-*P*)] (M = Cr, Mo, or W) and *fac*-[W(CO)$_3$(dppm-*PP′*)(dppm-*P*)] were prepared as described in recent publications.[3,9]

Preparations.—[(OC)$_3$Mo(μ-dppm)$_2$Fe(CO)$_3$] (**3b**) *from mer*-[Mo(CO)$_3$(dppm-*PP′*)(dppm-*P*)] (**1b**) *and* [Fe$_2$(CO)$_9$]. The complex *mer*-[Mo(CO)$_3$(dppm-*PP′*)(dppm-*P*)] (0.184 g, 0.194 mmol) was dissolved in tetrahydrofuran (20 cm^3) under dinitrogen, [Fe$_2$(CO)$_9$] (0.073 g, 0.2 mmol) was added, and the mixture stirred for 2 h. The solvent was evaporated from the red solution under reduced pressure and the residue extracted into dichloromethane (10 cm^3). Light petroleum (b.p. 40—60 °C) was added to give the required product. Yield 25%. Complexes (**3a**) and (**3c**) were made similarly.

In each of these syntheses, examination of the mother-liquors by ^{31}P-{^{1}H} n.m.r. spectroscopy indicated the presence of a single phosphorus-containing species which was not isolated but tentatively formulated as *mer*-[(dppm-*PP′*)(OC)$_3$M(μ-dppm)Fe(CO)$_4$] (**4**) (M = Cr, Mo, or W). Characterising data are given in Tables 1—4.

[(OC)$_3$Mo(μ-dppm)$_2$Fe(CO)$_3$] (**3b**) *from mer*-[Mo(CO)$_3$(dppm-*PP′*)(dppm-*P*] (**1b**) *and* [Fe$_3$(CO)$_{12}$]. The complex [Mo(CO)$_3$(dppm-*PP′*)(dppm-*P*)] (0.095 g, 0.1 mmol) was refluxed with [Fe$_3$(CO)$_{12}$] (0.05 g, 0.1 mmol) in tetrahydrofuran (20 cm^3) solution. After 0.5 h the colour of the solution had changed from dark green to red. The product was isolated in a similar fashion to that described in the [Fe$_2$(CO)$_9$] preparation. Complex (**3c**) was prepared similarly.

Species formulated as (**4b**) and (**4c**) were present, as the only phosphorus-containing species, in the mother-liquors of these reactions.

Complex (**3b**) or (**3c**) was similarly prepared from *fac*-[M(CO)$_3$(dppm-*PP′*)(dppm-*P*)] (M = Mo or W) with [Fe$_2$(CO)$_9$] or [Fe$_3$(CO)$_{12}$]. However, only in the case of tungsten was a species formulated as *fac*-[(dppm-*PP′*)(OC)$_3$W(μ-dppm)Fe(CO)$_4$] (**5c**) present in the mother-liquor.

Protonation Studies.—The complex (**3b**) (0.02 g, 0.0184 mmol) was dissolved in CD$_2$Cl$_2$ (0.5 cm^3). An excess of HBF$_4$·Et$_2$O (*ca.* 0.05 g) was added to give a yellow solution. This was examined by ^{1}H, ^{1}H-{^{31}P}, and ^{31}P-{^{1}H} n.m.r. spectroscopy. Similar experiments were carried out on (**3a**) and (**3b**). Characterising data are given in Table 2.

Crystallography.—Suitable crystals of $[(OC)_3Mo(\mu\text{-dppm})_2Fe(CO)_3]\cdot 2C_6H_5Cl$ were grown from chlorobenzene–methylcyclohexane (1:3). All crystallographic measurements were made on a Syntex $P2_1$ diffractometer operating in ω—2θ scan mode and using graphite-monochromated Mo-K_α radiation (λ = 71.069 pm) as described in detail elsewhere.[14] The data set was corrected for absorption empirically once the structure had been solved.[15]

Crystal data. $C_{68}H_{54}Cl_2FeMoP_4$, M = 1 217.76, triclinic, a = 1 219.1(3), b = 1 225.2(2), c = 2 142.4(4) pm, α = 92.97(2), β = 95.42(2), γ = 100.58(2)°, U = 3.124 nm^3, space group $P\bar{1}$, Z = 4, D_c = 1.29 g cm^{-3}, μ(Mo-K_α) = 5.58 cm^{-1}, $F(000)$ = 1 286.

Data collection parameters. Scans ranging from 1° below K_{α_1} to 1° above K_{α_2}, scan speeds 2.0—29.3° min^{-1}, $4.0 \leqslant 2\theta \leqslant 45.0°$. 8 388 Data were collected, 6 771 being considered observed $[I > 2.0\sigma(I)]$.

Refinement. Number of variables = 574, weighting factor g = 0.0002, final R and R' = 0.0791 and 0.0818 respectively.

The structure was determined *via* standard heavy-atom procedures and refined by blocked full-matrix least squares using the SHELX program system.[16] All non-hydrogen atoms were refined anisotropically apart from those on a second solvent molecule. This was found to be disordered over two positions and so to each part molecule was assigned an overall isotropic thermal parameter. All phenyl groups were treated as rigid bodies and were included in refinement as regular hexagons (C–C 139.5 pm). All hydrogen atoms were included in calculated positions and an overall isotropic thermal parameter was assigned for each ligand. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used at the end of refinement with the parameter g varied in the refinement so as to obtain a flat analysis of variance with increasing sin θ and$(F/F_{max.})^{\frac{1}{2}}$. The final atomic co-ordinates and their standard deviations are listed in Table 6.

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