Bimetallic Systems. Part 20.[1] Synthesis of Group 6 Metal(0)–Iridium(I) or –Rhodium(I) Complexes bridged by $Ph_2PCH_2PPh_2$

Adrian Blagg, Paul G. Pringle, and Bernard L. Shaw *
School of Chemistry, The University of Leeds, Leeds LS2 9JT

Complexes of the type [(OC)$_3$M′(μ-dppm)$_2$M(CO)X] (M′ = Cr, Mo, or W; M = Rh or Ir; dppm = Ph$_2$PCH$_2$PPh$_2$) were synthesised by two independent routes. When M′ = Mo, M = Ir, treatment of [Ir(CO)(dppm-*PP′*)$_2$]X (X = Cl, Br, or I) with [Mo(CO)$_3$(cht)] (cht = η^6-cyclohepta-1,3,5-triene) or ring opening of *fac*- or *mer*-[Mo(CO)$_3$(dppm-*PP′*)(dppm-*P*)] with [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-*p*)] gave moderate yields. The complex [(OC)$_3$W(μ-dppm)$_2$Ir(CO)Cl] was made similarly but could not be isolated pure by either method. Treatment of [Rh(CO)(dppm-*PP′*)$_2$]Cl with [Mo(CO)$_3$(cht)] did not give the corresponding molybdenum–rhodium complex. However, [(OC)$_3$Mo(μ-dppm)$_2$Rh(CO)Cl] was obtained on transmetallation of [ClAg(μ-dppm)$_2$Rh(CO)Cl] with [Mo(CO)$_3$(cht)], and more readily and in superior yield from *fac*- or *mer*-[Mo(CO)$_3$(dppm-*PP′*)(dppm-*P*)] and [Rh$_2$Cl$_2$(CO)$_4$]. The corresponding chromium and tungsten complexes were prepared similarly in high yield. Spectroscopic evidence suggests that [(OC)$_3$W(μ-dppm)$_2$Rh(CO)X] (X = Cl, Br, or I) occur in two isomeric forms. Treatment of [(OC)$_3$M′(μ-dppm)$_2$Rh(CO)Cl] with carbon monoxide and NH$_4$PF$_6$, in polar solvents, gave [(OC)$_3$M′(μ-dppm)$_2$Rh(CO)$_2$]PF$_6$ (M′ = Cr, Mo, or W). These cationic species were readily prepared in one step from *fac*- or *mer*-[M′(CO)$_3$(dppm-*PP′*)(dppm-*P*)]. Similarly, treatment of *fac*- or *mer*-[M′(CO)$_3$(dppm-*PP′*)(dppm-*P*)] with [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-*p*)], in the presence of CO and NH$_4$PF$_6$, gave the analogous iridium cationic complexes. The cationic species [(OC)$_3$M′(μ-dppm)$_2$M(CO)$_2$]PF$_6$ (M′ = Cr, Mo, or W; M = Rh or Ir) were found to react with Cl$^-$ to give the corresponding neutral species [(OC)$_3$M′(μ-dppm)$_2$M(CO)Cl]; thus [(OC)$_3$W(μ-dppm)$_2$Ir(CO)Cl] was obtained analytically pure by this method.

We have previously shown that the five-co-ordinate Ph$_2$PCH$_2$PPh$_2$ (dppm) complexes [M(CO)(dppm-*PP′*)$_2$]Cl (M = Rh or Ir) ring-open when treated with labile compounds of Rh^I, Cu^I, Ag^I, or Au^I to give heterobimetallic species containing *trans,trans*-M(μ-dppm)$_2$M′ moieties.[2] In the present paper we report the synthesis of mixed iridium– or rhodium–Group 6 metal complexes from [M(CO)(dppm-*PP′*)$_2$]Cl. We also describe an alternative and superior route to these complexes starting from *fac*- or *mer*-[M′(CO)$_3$(dppm-*PP′*)(dppm-*P*)] (M = Cr, Mo, or W). A preliminary account of some of this work has been published.[3]

Results and Discussion

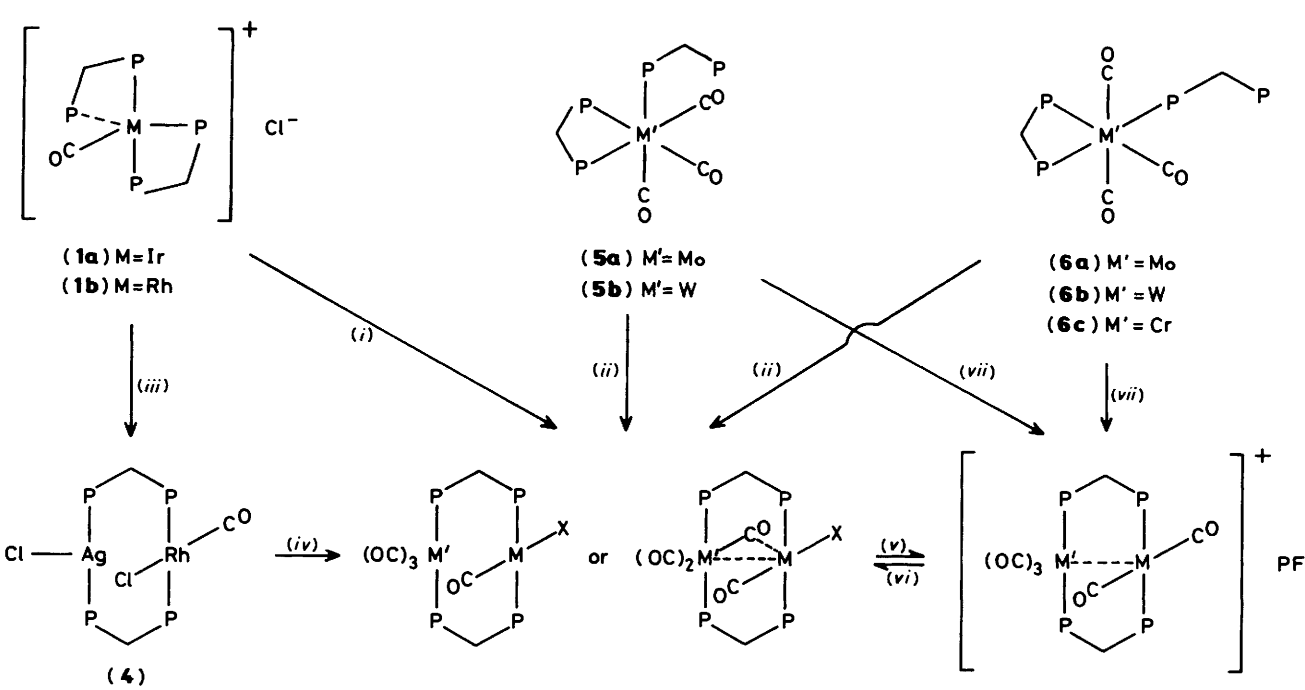
We have shown in a previous paper that [Ir(CO)(dppm-*PP′*)$_2$]Cl reacts with copper(I), silver(I), gold(I), or rhodium(I) derivatives to give heterobimetallic complexes bridged by dppm, and [Rh(CO)(dppm-*PP′*)$_2$]Cl gives a mixed rhodium–silver complex.[2] We have also reported that complexes of the type *fac*- or *mer*-[M′(CO)$_3$(dppm-*PP′*)(dppm-*P*)] (M = Cr, Mo, or W) undergo ring-opening reactions with labile compounds of Cu^I, Ag^I, Au^I, or Pt^{II} to give heterobimetallic species containing M(μ-dppm)$_2$M′ moieties.[4,5] In the present paper we describe the synthesis of complexes of the type [(OC)$_3$M′(μ-dppm)$_2$M(CO)X] or [(OC)$_3$M′(μ-dppm)$_2$M(CO)$_2$]PF$_6$, either from [M(CO)(dppm-*PP′*)$_2$]X or from *fac*- or *mer*-[M′(CO)$_3$(dppm-*PP′*)(dppm-*P*)].

When [Ir(CO)(dppm-*PP′*)$_2$]Cl (**1a**) is treated with [Mo(CO)$_3$(cht)] (cht = η^6-cyclohepta-1,3,5-triene), in boiling benzene for 35 min, an orange complex is formed in 51% yield. This complex is formulated as [(OC)$_3$Mo(μ-dppm)$_2$Ir(CO)Cl] (**2a**) on the basis of microanalysis (Table 1), ^{31}P-{^{1}H} n.m.r. spectroscopy (Table 2), and ^{1}H-{^{31}P} n.m.r. and i.r. spectroscopy (Table 3). The ^{31}P-{^{1}H} n.m.r. spectrum of (**2a**) shows a deceptively simple AA′MM′ splitting pattern typical of a *trans,trans*-Mo(μ-dppm)$_2$Ir moiety. Its ^{1}H-{^{31}P} n.m.r. spectrum is temperature dependent: at +20 °C a singlet resonance is observed for the methylene (PCH$_2$P) protons, whereas at −60 °C this has separated into two broad resonances. The i.r. spectrum shows no low-frequency (< 1 800 cm^{-1}) carbonyl band, suggesting that this complex has terminal carbonyls in the solid state. A band due to ν(Ir–Cl) is not observed in the far-i.r. region, presumably because of lack of intensity; metal–halogen stretching vibrations are commonly found to be of low intensity in heterobimetallic systems containing dppm.[6] A bridging chloride is thought unlikely as this is expected to render the PCH$_2$P protons inequivalent at ambient or moderately low temperatures (see above).

Treatment of [Ir(CO)(dppm-*PP′*)$_2$]X (X = Br or I) with [Mo(CO)$_3$(cht)] gave the corresponding bromide or iodide complexes, [(OC)$_3$Mo(μ-dppm)$_2$Ir(CO)X]. These complexes are assigned the structures (**3a**) (X = Br) or (**3b**) (X = I) on the basis of ^{31}P-{^{1}H} n.m.r. (Table 2) and i.r. data (Table 3). The i.r. spectra of both (**3a**) and (**3b**) show a low-frequency ν(C≡O) band (< 1 770 cm^{-1}), indicative of a semibridging carbonyl group.

Treatment of [Ir(CO)(dppm-*PP′*)$_2$]Cl with [W(CO)$_3$(cht)] in boiling benzene gave a mixture of the analogous [(OC)$_3$W(μ-dppm)$_2$Ir(CO)Cl] (**2b**) (^{31}P-{^{1}H} n.m.r. spectroscopic evidence) and an unidentified species. The desired heterobimetallic species (**2b**) was not isolated pure despite repeated attempts. No heterobimetallic product was observed (by ^{31}P-{^{1}H} n.m.r. spectroscopy) in a similar reaction between [Ir(CO)(dppm-*PP′*)$_2$]Cl and [Cr(CO)$_4$(nbd)] (nbd = norbornadiene).

We have found that the metal–iridium species (M′ = Mo, W, or Cr) (**2a**)–(**2c**) are formed on treatment of *fac*- or *mer*-[M′(CO)$_3$(dppm-*PP′*)(dppm-*P*)] with [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$-



	M'	M	X
(2a)	Mo	Ir	Cl
(2b)	W	Ir	Cl
(2c)	Cr	Ir	Cl
(2d)	Mo	Rh	Cl
(2e)	W	Rh	Cl
(2f)	W	Rh	Br
(2g)	W	Rh	I

	M'	M	X
(3a)	Mo	Ir	Br
(3b)	Mo	Ir	I
(3c)	Cr	Rh	Cl
(3d)	W	Rh	Cl
(3e)	W	Rh	Br
(3f)	W	Rh	I

	M'	M
(7a)	Mo	Rh
(7b)	W	Rh
(7c)	Cr	Rh
(7d)	Mo	Ir
(7e)	W	Ir
(7f)	Cr	Ir

Scheme. (*i*) [M'(CO)$_3$(cht)], M' = Mo, M = Ir, X = Cl, Br, or I; M' = W, M = Ir, X = Cl; (*ii*) [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-*p*)] or [Rh$_2$Cl$_2$(CO)$_4$]; (*iii*) [Ag$_4$Cl$_4$(PPh$_3$)$_4$]; (*iv*) [Mo(CO)$_3$(cht)]; (*v*) CO and PF$_6^-$; (*vi*) NR$_4$Cl, R = alkyl; (*vii*) [Rh$_2$Cl$_2$(CO)$_4$] or [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-*p*)] + CO and PF$_6$

Table 1. Colours, yields, microanalytical, and solution conductivity[a] data

Complex						Analyses[b]/%			Λ
M'	M	X		Colour	Yield/%	C	H	Halogen	Ω^{-1} cm^2 mol^{-1}
Mo	Ir	Cl	(2a)	Red-orange	51 or 44[c]	53.65 (53.85)	3.75 (3.7)	Cl 3.2 (3.0)	
W	Ir	Cl	(2b)	Red	64	49.9 (50.2)	3.5 (3.4)	Cl 3.2 (2.8)	
Mo	Rh	Cl	(2d)·C$_6$H$_6$[d]	Orange	71 or 91[c]	60.65 (60.4)	4.45 (4.2)	Cl 3.1 (2.95)	2
W	Rh	Cl	(2e)/(3d)	Olive-brown	86	53.75 (53.9)	3.65 (3.7)	Cl 3.05 (2.95)	1
W	Rh	Br	(2f)/(3e)	Olive-brown	88	51.8 (52.0)	3.4 (3.55)	Br 6.3 (6.4)	
W	Rh	I	(2g)/(3f)	Olive-brown	96	49.9 (50.1)	3.3 (3.45)	I 9.55 (9.8)	
Cr	Rh	Cl	(3c)	Olive-green	71	60.7 (60.55)	4.25 (4.15)	Cl 3.45 (3.3)	1[e]
Mo	Rh		(7a)·C$_6$H$_6$[d]	Brown	95	54.25 (54.4)	3.75 (3.75)	F 8.4 (8.45)	27
W	Rh		(7b)·0.75C$_6$H$_6$[d]	Brown	86	51.05 (51.05)	3.45 (3.5)	F 7.8 (8.15)	24
Cr	Rh		(7c)·0.25C$_6$H$_6$[d]	Olive-green	89	55.1 (55.25)	3.9 (3.75)	F 9.2 (9.3)	25
Mo	Ir		(7d)·C$_6$H$_6$[d]	Brown	73	51.65 (51.6)	3.45 (3.55)	F 7.8 (8.0)	27
W	Ir		(7e)·C$_6$H$_6$[d]	Brown	72	48.3 (48.6)	3.35 (3.35)	F 7.3 (7.6)	25

[a] Conductivity measurements performed in nitrobenzene at 20 °C, unless otherwise stated. [b] Calculated values in parentheses. [c] See Experimental section. [d] Presence of solvent confirmed by ^{1}H n.m.r. spectroscopy. [e] In acetone.

Me-*p*)]. For example, treatment of the *fac*-molybdenum complex (**5a**) with [IrCl(CO)$_2$(H$_2$NC$_6$H$_4$Me-*p*)] in benzene gave [(OC)$_3$Mo(μ-dppm)$_2$Ir(CO)Cl] (**2a**) in 44% yield. The corresponding tungsten (**2b**) and chromium complexes (**2c**) are also formed by this method (^{31}P-{^{1}H} n.m.r. evidence) but could not be isolated pure despite repeated attempts. Complexes (**2a**)—(**2c**) all decompose in solution to give [Ir(CO)(dppm-*PP'*)$_2$]$^+$ and other, unidentified products (^{31}P-{^{1}H} n.m.r. evidence), the chromium complex (**2c**) decomposing the most readily.

Treatment of the rhodium complex [Rh(CO)(dppm-*PP'*)$_2$]Cl (**1b**) with [Mo(CO)$_3$(cht)] in CH$_2$Cl$_2$ did not give [(OC)$_3$Mo(μ-dppm)$_2$Rh(CO)Cl] (**2d**), instead a dirhodium complex and a Mo(dppm) species were formed (^{31}P-{^{1}H} n.m.r. evidence). However, treatment of the complex [ClAg(μ-dppm)$_2$-

Table 2. ^{31}P-{^{1}H} N.m.r. data[a]

Complex[b]				$\delta(P_B)$	$\delta(P_A)$	J(Rh–P_B)	J(W–P_A)	N[c]	
M′	M	X		p.p.m.		Hz			Solvent
Mo	Ir	Cl	**(2a)**	34.2	9.3			66	$CDCl_3$
W	Ir	Cl	**(2b)**	13.9	8.5		n.o.	56	CD_2Cl_2
Cr	Ir	Cl	**(2c)**	56.7	10.5			62	$(CD_3)_2CO$[d]
Mo	Rh	Cl	**(2d)**	36.9	24.3	118		73	$CDCl_3$
W	Rh	Cl	**(2e)**/**(3d)**[e]	16.8	26.1	113	283	143	$CDCl_3$
W	Rh	Br	**(2f)**/**(3e)**[e]	15.2	22.9	112	282	142	CD_2Cl_2
W	Rh	I	**(2g)**/**(3f)**[f]	7.9	22.4	106	n.o.	101	CD_2Cl_2
				14.2	19.7	113	n.o.	141	
Mo	Ir	Br	**(3a)**	33.6	4.4			93	$CDCl_3$
Mo	Ir	I	**(3b)**	31.4	−1.0			110	$CDCl_3$
Cr	Rh	Cl	**(3c)**	72.7	25.7	114		149	$CDCl_3$
Mo	Rh		**(7a)**	38.1	23.8	103		137	CD_2Cl_2
W	Rh		**(7b)**	13.6	25.4	104	n.o.	134	CD_2Cl_2
Cr	Rh		**(7c)**	64.1	24.9	105		137	CD_2Cl_2
Mo	Ir		**(7d)**	40.6	16.7			134	CD_2Cl_2
W	Ir		**(7e)**	17.6	17.6				CD_2Cl_2
Cr	Ir		**(7f)**	68.5	18.5			140	$(CD_3)_2CO$[d]

[a] Spectra recorded at 40.25 MHz and +20 °C, unless otherwise stated; 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 bound to the Group 6 metal, P_B to iridium or rhodium. n.o. = Not observed. [b] See Scheme. [c] $N = |^2J(P_AP_B) + {}^4J(P_AP_{B'})|$. [d] External reference. [e] Spectrum recorded at 162 MHz and −50 °C. [f] Spectrum recorded at 162 MHz.

Table 3. ^{1}H-{^{31}P} N.m.r.[a] and i.r.[b] data

Complex							$\tilde{\nu}(C{\equiv}O)/cm^{-1}$
M′	M	X		θ/°C	$\delta(CH_2)$	Solvent	
Mo	Ir	Cl	**(2a)**	+20	3.41	$CDCl_3$	1 974s, 1 946s,br, 1 833s,br, 1 804s,br
				−60	3.75, 3.14, ^2J(HH) n.r.		
W	Ir	Cl	**(2b)**	+20	3.49	$CDCl_3$	1 969s, 1 942s,br, 1 839s,br, 1 794s,br
Mo	Rh	Cl	**(2d)**	[c] +20	3.47	$CDCl_3$	[d] 1 975 (sh), 1 948s,br, 1 840s,br, 1 800s,br
				−50	3.89, 3.10, ^2J(HH) = 13	CD_2Cl_2	
W	Rh	Cl	**(2e)**/**(3d)**	+20	2.96	$CDCl_3$	[d] 1 973vs,br, 1 942 (sh), 1 915s,br, 1 832s,br, 1 800s,br, 1 750s,br
				−80	2.81	CD_2Cl_2	
W	Rh	Br	**(2f)**/**(3e)**				1 964s,br, 1 939s, 1 917s,br, 1 835m,br, 1 769s,vbr
W	Rh	I	**(2g)**/**(3f)**				1 966s, 1 940s, 1 919s, 1 854m,br, 1 775s,br
Mo	Ir	Br	**(3a)**				1 966 (sh), 1 945s,br, 1 860s, 1 765s,br
Mo	Ir	I	**(3b)**				1 969 (sh), 1 944s,br, 1 874s, 1 762s,br
Cr	Rh	Cl	**(3c)**	−95	2.58	CD_2Cl_2	[d] 1 960vs,br, 1 914s,br, 1 782 (sh), 1 753s,br
Mo	Rh		**(7a)**	+20	3.28	CD_2Cl_2	2 032m, 2 012s, 1 989s,br, 1 859s,br, 1 840s,br
W	Rh		**(7b)**	+20	3.46	CD_2Cl_2	2 026m, 2 012s, 1 981s,br, 1 854s,br, 1 836s,br
Cr	Rh		**(7c)**	+20	3.28	$CDCl_3$	2 022s, 2 000s, 1 973s,br, 1 844s,br, 1 818s,br
Mo	Ir		**(7d)**	+20	3.23	$CDCl_3$	2 028m, 2 000s, 1 976s,br, 1 929w, 1 843 (sh), 1 822s,br
W	Ir		**(7e)**	+20	3.33	$CDCl_3$	2 022m, 1 999s, 1 972s,br, 1 835 (sh), 1 823s,br

[a] Spectra recorded at 100 MHz, unless otherwise stated; chemical shifts (δ) in p.p.m. (±0.01) to high frequency of internal $SiMe_4$, coupling constants (J) in Hz (±0.3). n.r. = Not resolved. [b] Spectra recorded as Nujol mulls, unless otherwise stated. v = Very, s = strong, m = medium, br = broad, and sh = shoulder. [c] Spectrum recorded at 360 MHz. [d] Spectrum recorded in CH_2Cl_2 solution.

Rh(CO)Cl] (4) {prepared from **(1b)** and $[Ag_4Cl_4(PPh_3)_4]$} with $[Mo(CO)_3(cht)]$ gave complex **(2d)** quantitatively (by ^{31}P-{^{1}H} n.m.r. spectroscopy). It was isolated in high yield (71%) and fully characterised (see Tables 1—3). The ^{31}P-{^{1}H} n.m.r. spectrum shows a deceptively simple AA′MM′ splitting pattern with coupling of the low-frequency resonance P_B to ^{103}Rh ($I = \frac{1}{2}$, 100% natural abundance). The ^{1}H-{^{31}P} n.m.r. spectrum, like that of the molybdenum–iridium analogue **(2a)**, is temperature dependent, the CH_2 protons being equivalent at +20 °C and inequivalent below −50 °C. The i.r. spectrum suggests that all the carbonyls are terminal in the static structure. Again no metal–chlorine stretch is observed in the far-i.r., presumably due to lack of intensity, as before.

We find that [(OC)$_3$Mo(μ-dppm)$_2$Rh(CO)Cl] is more readily prepared and in higher yield (91%) by treatment of *fac*-[Mo(CO)$_3$(dppm-*PP*′)(dppm-*P*)] **(5a)** with $[Rh_2Cl_2(CO)_4]$. The product obtained by this route is identical to that described above. The complex *mer*-[Mo(CO)$_3$(dppm-*PP*′)(dppm-*P*)] **(6a)** reacts with $[Rh_2Cl_2(CO)_4]$ under similar conditions to give the same complex **(2d)**. The analogous *fac*- or *mer*-tungsten complexes **(5b)** or **(6b)** and the *mer*-chromium complex **(6c)** react with $[Rh_2Cl_2(CO)_4]$ similarly to give heterobimetallic species of formula [(OC)$_3$M′(μ-dppm)$_2$Rh(CO)Cl] (M′ = W or Cr), see Table 1 for analytical data. In the reaction of *fac*- or *mer*-[W(CO)$_3$(dppm-*PP*′)(dppm-*P*)] with $[Rh_2Cl_2(CO)_4]$ a red-brown tungsten-rhodium complex is formed on mixing. Later identified as [(OC)$_3$W(μ-dppm)$_2$Rh(CO)$_2$]Cl by ^{31}P-{^{1}H} n.mr. spectroscopy, this species becomes the olive-brown [(OC)$_3$W(μ-dppm)$_2$Rh(CO)Cl] over a period of several minutes (see later).

The complex [(OC)$_3$Cr(μ-dppm)$_2$Rh(CO)Cl] is assigned the structure **(3c)** on the basis of its spectroscopic data (Tables 2 and

3); its intense colour suggests some metal–metal interaction. Its i.r. spectrum shows a low-frequency carbonyl band characteristic of a semibridging CO.[7]

Assignment of a structure to $[(OC)_3W(\mu\text{-dppm})_2Rh(CO)Cl]$ is less straightforward. The 40.25-MHz $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum (+20 °C) (Table 2) could not be interpreted because of broadening and poor separation of the resonances. At high-field (162 MHz) the resonance assigned to the phosphorus atoms bound to tungsten, P_A, appears as a slightly broad half of a simplified AA′MM′ pattern with ^{183}W satellites. In contrast, the resonance assigned to the phosphorus atoms co-ordinated to rhodium, P_B, appears as a broad hump. At −50 °C the 162-MHz $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows a well defined simplified AA′MM′ splitting pattern with coupling of P_B to ^{103}Rh, and coupling of P_A to ^{183}W. Only one species is observed at −50 °C. As the sample is warmed from −50 to +20 °C the P_A resonance gradually broadens, while the P_B resonance decreases in intensity and collapses. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of $[(OC)_3W(\mu\text{-dppm})_2Rh(CO)Cl]$ at +20 °C suggests that there are two species in dynamic equilibrium in solution which are interconverting rapidly on the n.m.r. time-scale. At −50 °C the position of this equilibrium is such that only one species is present in a detectable amount. We propose that as the temperature is raised from −50 °C the proportion of the minor species gradually increases and rapid interconversion leads to the observed broadening of the resonances.

The i.r. spectrum of $[(OC)_3W(\mu\text{-dppm})_2Rh(CO)Cl]$ in solution (CH_2Cl_2) shows six carbonyl stretching bands. The lowest-frequency band [ν(CO) 1 750 cm^{-1}] is indicative of a semibridging carbonyl group; the other ν(CO) absorbances are assigned to terminal CO groups on tungsten and rhodium. Six CO bands are also observed in the solid-state i.r. spectrum [Nujol mull: ν(CO) 1 973s,br, 1942s,br, 1 924s,br, 1 838s,br, 1 797(sh), and 1 774s,vbr cm^{-1}]. Thus the spectroscopic data suggest that $[(OC)_3W(\mu\text{-dppm})_2Rh(CO)Cl]$ is present in two isomeric forms in solid and solution. These two species are thought to have the structures (**2e**) and (**3d**) by analogy with the molybdenum (**2d**) and chromium (**3c**) complexes. Spectroscopic evidence suggests that the bromide and iodide analogues of $[(OC)_3W(\mu\text{-dppm})_2Rh(CO)Cl]$ both exist in two isomeric forms (see Tables 1—3 for characterising data). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of $[(OC)_3W(\mu\text{-dppm})_2Rh(CO)Br]$ varies with temperature in a similar manner to that of the chloro complex; again only one species is detected at low temperature. Thus it is thought that a rapid dynamic equilibrium exists in solution between the forms (**2f**) and (**3e**), similar to that proposed for $[(OC)_3W(\mu\text{-dppm})_2Rh(CO)Cl]$. In contrast to the above, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of $[(OC)_3W(\mu\text{-dppm})_2Rh(CO)I]$ (162 MHz) shows two heterobimetallic species at 20 °C in the ratio of *ca.* 4:1. An identical mixture is obtained on preparing $[(OC)_3W(\mu\text{-dppm})_2Rh(CO)I]$ from *mer*-$[W(CO)_3$(dppm-*PP*′)(dppm-*P*)] and $[Rh_2I_2(CO)_4]$. It seems likely that an equilibrium exists between these two species and that interconversion is slow on the n.m.r. time-scale. The $^{31}P\text{-}\{^1H\}$ n.m.r. data suggest that the major species: [$\delta(P_A)$ 14.2, $\delta(P_B)$ 19.7 p.p.m., $^1J(Rh\text{-}P_B)$ 113, *N* 141 Hz] has a structure similar to those of the chloro- and bromo-complexes at low temperature (see Table 2). The major species is tentatively assigned the semibridging carbonyl structure (**3f**) on the basis of the i.r. data. We believe that the minor species may have the structure (**2g**) by analogy with $[(OC)_3Mo(\mu\text{-dppm})_2Rh(CO)Cl]$ (**2d**).

The $^1H\text{-}\{^{31}P\}$ n.m.r. spectra of complexes (**2a**)—(**2g**) and (**3a**)—(**3f**) all show single PCH_2P resonances at +20 °C (see Table 3). We have previously 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.[8,9] However, this process alone cannot render the methylene protons equivalent in our complexes. A second process, which operates in conjunction with 'ring flipping,' is also required. We propose that the PCH_2 protons in our complexes are rendered equivalent at ambient temperatures by rapid CO exchange between the two metals accompanied by flipping of the $M(\mu\text{-dppm})_2M'$ ring. Carbonyl scrambling is well known in bimetallic and cluster complexes even at low temperatures.[10]

Treatment of the neutral complexes $[(OC)_3M'(\mu\text{-dppm})_2Rh(CO)Cl]$ (M′ = Mo, W, or Cr) with CO in polar solvents gave dark cationic heterobimetallic species $[(OC)_3M'(\mu\text{-dppm})_2Rh(CO)_2]^+$. These cationic species could not be isolated as their Cl^- salts, reverting to the corresponding neutral species on evaporation of the reacting mixture to dryness or on attempted precipitation from solution. However, addition of a large counter ion, such as BPh_4^- or PF_6^-, stabilised the ionic species. The cationic species were isolated and characterised as their PF_6^- salts $[(OC)_3M'(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ [M′ = Mo (**7a**), W (**7b**), or Cr (**7c**)], see Tables 1—3. The i.r. spectroscopic data suggest the absence of bridging or semibridging carbonyls, while the intense dark colour suggests some metal–metal interaction.

The 40.25-MHz $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of $[(OC)_3W(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ is well defined at +20 °C, in contrast to that of $[(OC)_3W(\mu\text{-dppm})_2Rh(CO)Cl]$. The $^{31}P\text{-}\{^1H\}$ n.m.r. parameters of the cationic species (**7b**) are identical to those of the red-brown species observed on mixing of *fac*- or *mer*-$[W(CO)_3$(dppm-*PP*′)(dppm-*P*)] and $[Rh_2Cl_2(CO)_4]$. Thus $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy shows that $[(OC)_3W(\mu\text{-dppm})_2Rh(CO)_2]Cl$ is formed first in the reaction between $[W(CO)_3$(dppm-*PP*′)(dppm-*P*)] and $[Rh_2Cl_2(CO)_4]$, and that subsequent attack of the chloride anion on the rhodium centre leads to elimination of CO and formation of the neutral species $[(OC)_3W(\mu\text{-dppm})_2Rh(CO)Cl]$. We find that the neutral species $[(OC)_3M'(\mu\text{-dppm})_2Rh(CO)Cl]$ (M′ = Mo, W, or Cr) can be generated in quantitative yield ($^{31}P\text{-}\{^1H\}$ n.m.r. evidence) by treating the cationic complexes $[(OC)_3M'(\mu\text{-dppm})_2Rh(CO)_2]PF_6$ with an excess of $NBu^n{}_4Cl$.

The cationic complexes (**7a**)—(**7c**) are readily prepared in one step from *fac*- or *mer*-$[M'(CO)_3$(dppm-*PP*′)(dppm-*P*)] by the method shown in the Scheme. Similarly, treatment of *fac*- or *mer*-$[M'(CO)_3$(dppm-*PP*′)(dppm-*P*)] with $[IrCl(CO)_2(H_2NC_6H_4Me\text{-}p)]$, in the presence of CO and NH_4PF_6, gave the analogous iridium cationic complexes $[(OC)_3M'(\mu\text{-dppm})_2Ir(CO)_2]PF_6$ (M′ = Mo, W, or Cr). The molybdenum (**7d**) and tungsten (**7e**) cationic complexes are readily isolated and characterised, see Tables 1—3. They are more stable in solution than the corresponding neutral species (**2a**) and (**2b**), *e.g.* they are stable for days in CH_2Cl_2 ($^{31}P\text{-}\{^1H\}$ n.m.r. evidence) whereas the neutral species tend to decompose slowly. The chromium cationic complex (**7f**), like the corresponding neutral species (**2c**), is unstable in solution and could not be isolated pure despite repeated attempts.

The complexes (**7d**)—(**7f**) react with an excess of Cl^- in polar solvents to give the corresponding neutral species (**2a**)—(**2c**). For example, treatment of $[(OC)_3W(\mu\text{-dppm})_2Ir(CO)_2]PF_6$ with an excess of NEt_4Cl in acetone gave $[(OC)_3W(\mu\text{-dppm})_2Ir(CO)Cl]$ (**2b**) in 64% isolated yield; we had previously been unable to isolate this species pure, see above.

Experimental

General methods were as previously described in recent papers from this laboratory.[11]

Preparations.—$[(OC)_3Mo(\mu\text{-dppm})_2Ir(CO)Cl]$ (**2a**) *from* $[Ir(CO)$(dppm-*PP*′)$_2]Cl$. A mixture of $[Ir(CO)$(dppm-*PP*′)$_2]Cl$ (0.300 g, 0.29 mmol) and $[Mo(CO)_3(cht)]$ (0.080 g, 0.29 mmol) in benzene (10 cm^3) was refluxed under dinitrogen for 35 min.

The mixture was then filtered and methanol (*ca.* 100 $\mathrm{cm^3}$) added to the filtrate. The desired product was precipitated as an orange solid on standing at -20 °C for 1 h. Yield 0.180 g (51%). The corresponding bromide (**3a**) and iodide (**3b**) complexes were prepared similarly in 73 and 50% yield, respectively.

Alternatively, $[\mathrm{IrCl(CO)_2(H_2NC_6H_4Me}\text{-}p)]$ (0.080 g, 0.20 mmol) was added to a stirred solution of *fac*-$[\mathrm{Mo(CO)_3(dppm}\text{-}PP')(\mathrm{dppm}\text{-}P)]$ (0.200 g, 0.21 mmol) in benzene (10 $\mathrm{cm^3}$). The mixture was stirred for 30 min, then filtered. Methanol was added to precipitate the required product as orange microcrystals. Yield 0.106 g (44%).

$[\mathrm{(OC)_3Mo(\mu\text{-}dppm)_2Rh(CO)Cl}]$ (**2d**). A mixture of $[\mathrm{ClAg(\mu\text{-}dppm)_2Rh(CO)Cl}]$ (**4**) (0.020 g, 0.02 mmol) and $[\mathrm{Mo(CO)_3(cht)}]$ (0.010 g, 0.04 mmol) in benzene (0.4 $\mathrm{cm^3}$) was warmed in a hot (*ca.* 60 °C) water-bath for 30 s, then set aside for 1 h. The orange solution was filtered and the filtrate evaporated to dryness under reduced pressure. Trituration of the residue with light petroleum (b.p. 40—60 °C) gave the desired product as a red-orange solid. Yield 0.015 g (71%).

Alternatively, $[\mathrm{Rh_2Cl_2(CO)_4}]$ (0.041 g, 0.11 mmol) was added to a stirred solution of *fac*-$[\mathrm{Mo(CO)_3(dppm}\text{-}PP')(\mathrm{dppm}\text{-}P)]$ (0.200 g, 0.21 mmol) in benzene (10 $\mathrm{cm^3}$). The solution became red immediately and was stirred for a further 10 min. Light petroleum (b.p. 60—80 °C) was then added and the required product was deposited as orange microcrystals. Yield 0.215 g (91%). The complexes $[\mathrm{(OC)_3Cr(\mu\text{-}dppm)_2Rh(CO)Cl}]$ and $[\mathrm{(OC)_3W(\mu\text{-}dppm)_2Rh(CO)Cl}]$ were prepared similarly in 71 and 86% yields, respectively.

$[\mathrm{(OC)_3W(\mu\text{-}dppm)_2Rh(CO)Br}]$(**2f**)/(**3e**). Carbon monoxide was passed into a suspension of $[\mathrm{(OC)_3W(\mu\text{-}dppm)_2Rh(CO)Cl}]$ (0.150 g, 0.125 mmol) in acetone–methanol (1:1, 14 $\mathrm{cm^3}$) until the reaction mixture was clear. This solution was then rapidly added to a solution of $\mathrm{NBu^n{}_4Br}$ (0.600 g, 1.86 mmol) in methanol (7 $\mathrm{cm^3}$). The required product was deposited as green microcrystals. Yield 0.138 g (88%). The complex $[\mathrm{(OC)_3W(\mu\text{-}dppm)_2Rh(CO)I}]$ was prepared similarly.

$[\mathrm{(OC)_3Mo(\mu\text{-}dppm)_2Rh(CO)_2}]\mathrm{PF_6}$ (**7a**). Carbon monoxide was bubbled into a mixture of $[\mathrm{(OC)_3Mo(\mu\text{-}dppm)_2Rh(CO)Cl}]$ (0.600 g, 0.54 mmol) in $\mathrm{CH_2Cl_2}$ (25 $\mathrm{cm^3}$), $\mathrm{NEt_4Cl}$ (0.020 g, 0.13 mmol), and $\mathrm{NH_4PF_6}$ (0.500 g, 3.07 mmol) in water (25 $\mathrm{cm^3}$) for 45 min. The dark brown dichloromethane layer was separated from the aqueous layer and washed with water. The dichloromethane layer was again separated and reduced in volume to *ca.* 20 $\mathrm{cm^3}$ under pressure. Benzene (30 $\mathrm{cm^3}$) was then added to precipitate the required product as brown crystals. Yield 0.670 g (95%). The complexes $[\mathrm{(OC)_3M'(\mu\text{-}dppm)_2Rh(CO)_2}]\mathrm{PF_6}$ [M′ = W (**7b**) or Cr (**7c**)] were prepared similarly.

$[\mathrm{(OC)_3Mo(\mu\text{-}dppm)_2Ir(CO)_2}]\mathrm{PF_6}$ (**7d**). Carbon monoxide was bubbled into a mixture of *mer*-$[\mathrm{Mo(CO)_3(dppm}\text{-}PP')(\mathrm{dppm}\text{-}P)]$ (0.200 g, 0.21 mmol) dissolved in $\mathrm{CH_2Cl_2}$ (10 $\mathrm{cm^3}$) and $\mathrm{NH_4PF_6}$ (0.020 g, 1.2 mmol) in MeOH (10 $\mathrm{cm^3}$) for a few minutes, then $[\mathrm{IrCl(CO)_2(H_2NC_6H_4Me}\text{-}p)]$ (0.083 g, 0.21 mmol) was added. The mixture was stirred for 50 min while CO was bubbled into the solution. The brown reaction mixture was evaporated to dryness under reduced pressure and the product redissolved in $\mathrm{CH_2Cl_2}$. The solution was filtered and benzene added to precipitate the required product as brown crystals. Yield 0.219 g (73%). The complex $[\mathrm{(OC)_3W(\mu\text{-}dppm)_2Ir(CO)_2}]\mathrm{PF_6}$ (**7e**) was prepared similarly.

$[\mathrm{(OC)_3W(\mu\text{-}dppm)_2Ir(CO)Cl}]$ (**2b**) *from* $[\mathrm{(OC)_3W(\mu\text{-}dppm)_2Ir(CO)_2}]\mathrm{PF_6}$. A solution of $\mathrm{NEt_4Cl}$ (0.055 g, 0.32 mmol) in acetone (5 $\mathrm{cm^3}$) was added to a solution of $[\mathrm{(OC)_3W(\mu\text{-}dppm)_2Ir(CO)_2}]\mathrm{PF_6}$ (0.100 g, 0.066 mmol) in acetone with stirring. Dinitrogen was bubbled into the mixture to aid elimination of CO. The required product was precipitated as red microcrystals. Yield 0.055 g (64%).

Acknowledgements

We thank Johnson Matthey PLC for the generous loan of heavy-metal salts and the S.E.R.C. for support.

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Received 28*th July* 1986; *Paper* 6/1527