Bimetallic Systems. Part 17.[1] Synthesis of Group 6 Metal(0)–Copper(I) –Silver(I), or –Gold(I) Complexes with two $Ph_2PCH_2PPh_2$ (dppm) Bridging Ligands: Crystal Structure of $[(OC)_2W(\mu\text{-}CO)(\mu\text{-}dppm)_2(\mu\text{-}Cl)Cu]\cdot CH_2Cl_2$†

Adrian Blagg, Bernard L. Shaw,* and Mark Thornton-Pett
School of Chemistry, The University of Leeds, Leeds LS2 9JT

Treatment of *fac*- or *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (M = Cr, Mo, or W; dppm = $Ph_2PCH_2PPh_2$) with Cu^I, Ag^I, or Au^I compounds sometimes induced ring-opening to give heterobimetallic complexes, but in other cases rapid redox reactions, or more complicated processes, occurred. Treatment of *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (M = Cr, Mo, or W) with CuX (X = Cl or I) gave $[(OC)_2M(\mu\text{-}CO)(\mu\text{-}dppm)_2(\mu\text{-}X)Cu]$ in moderate yields, whereas treatment of *fac*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (M = Mo or W) with CuX gave only Cu^I–dppm species. *fac*- or *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ were oxidised by $AgNO_3$, but in general reacted with $[Ag_4Cl_4(PPh_3)_4]$ to give M–Ag complexes with one bridging dppm. However, treatment of *mer*-$[Mo(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ with $[Ag_4Cl_4(PPh_3)_4]$ gave an unstable complex $[(OC)_3Mo(\mu\text{-}dppm)_2AgCl]$, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of which varied with temperature. Treatment of *fac*-or *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ with $[Ag(PPh_3)(CN)]$ gave stable, heterobimetallic, complexes of the type $[(OC)_3M(\mu\text{-}dppm)_2Ag(CN)]$ (M = Cr, Mo, or W). Reaction between *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (M = Mo or W) and $[Au(PPh_3)Cl]$ gave $[(OC)_3M(\mu\text{-}dppm)_2AuCl]$, whereas a complex mixture of unidentified products was formed on treating *fac*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ with $[Au(PPh_3)Cl]$. The molecular structure of $[(OC)_2W(\mu\text{-}CO)(\mu\text{-}dppm)_2(\mu\text{-}Cl)Cu]\cdot CH_2Cl_2$ was determined from a monoclinic crystal of space group $P2_1/c$, with a = 1 076.0(2), b = 2 513.2(4), c = 2 067.5(3) pm, β = 112.62(1)°, and Z = 4; final R factor 0.0359 for 6 138 observed reflections. The structure shows that the two metal centres [W–Cu 275.9(4) pm] are almost symmetrically bridged by chlorine [W–Cl 259.2(5), Cu–Cl 255.3(5) pm] and semibridged by CO.

We have shown in previous papers that $Ph_2PCH_2PPh_2$ (dppm) complexes of the types *fac*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ [M = Mo (**1a**) or W (**1b**)] or *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ [M = Cr (**2a**), Mo (**2b**), or W (**2c**)] ring-open when treated with labile Rh^I, Ir^I, or Pt^{II} compounds to give heterobimetallic species containing *trans,trans*-$M(\mu\text{-}dppm)_2M'$ moieties.[1,2] We have also described the oxidation of *fac*- or *mer*-$[Mo(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ by Hg^{II} compounds.[3,4] The present paper reports the reaction of *fac*- or *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ on treatment with Cu^I, Ag^I, or Au^I compounds. A preliminary account of some of this work has appeared.[3]

Results and Discussion

It has previously been shown that *fac*- or *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ can react with substitution-labile compounds of Ru^I, Ir^I, or Pt^{II} to give heterobimetallic complexes, in high yield; or undergo redox reactions with Hg^{II}.[1,3,4] We now report that similar treatment of *fac*- or *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ with Cu^I, Ag^I, or Au^I compounds sometimes induces ring-opening to give heterobimetallic complexes, but in other cases rapid redox reactions, or more complicated processes, occur.

When *mer*-$[Cr(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (**2a**) is treated with CuCl or CuI in dichloromethane, heterobimetallics of composition $[CrCu(CO)_3X(dppm)_2]$ (X = Cl or I) are formed in good yield; preparative details are given in the Experimental section. *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ [M = Mo (**2b**) or W (**2c**)] reacts with CuCl or CuI under similar conditions to give the analogous molybdenum– or tungsten–copper complexes $[MCu(CO)_3X(dppm)_2]$ (M = Mo or W, X = Cl or I). In contrast, decomposition occurs on treatment of the *fac* isomers (**1a**) or (**1b**) with CuCl or CuI in CH_2Cl_2 at 20 °C; Cu^I–dppm species are the only observable products by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy.

The above heterobinuclear complexes are formulated as $[(OC)_2M(\mu\text{-}CO)(\mu\text{-}dppm)_2(\mu\text{-}X)Cu]$ (**3a**)—(**3f**) on the basis of microanalysis (Table 1), $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy (Table 2), and $^1H\text{-}\{^{31}P\}$ n.m.r. and i.r. spectroscopy (Table 3). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra are all temperature dependent. At 20 °C the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra all show an AA′XX′ pattern for the phosphorus atoms bound to M (P_A), with all ten possible lines being observed in the case of $[(OC)_2Cr(\mu\text{-}CO)(\mu\text{-}dppm)_2(\mu\text{-}I)Cu]$ (**3b**).[5] In contrast, a broad resonance, P_B, is observed for the phosphorus atoms bound to Cu; this resonance sharpens as the temperature is lowered to give an AA′XX′ type pattern below −60 °C. This AA′XX′ splitting pattern is indicative of a *trans,trans*-$M(\mu\text{-}dppm)_2Cu$ moiety. We attribute the broadening of P_B to quadrupolar effects (both copper isotopes have $I = \frac{3}{2}$, ^{63}Cu natural abundance 69%; ^{65}Cu natural abundance 31%) and not chemical exchange; the sharpening of the P_B resonance on cooling arising from faster quadrupolar relaxation at lower temperatures. The $^1H\text{-}\{^{31}P\}$ n.m.r. spectra all show an AB pattern for the PCH_2P protons (at 21 °C) suggesting a rigid ring system with the MPCPCuPCP ring in the pseudo-boat conformation. A typical $^1H\text{-}\{^{31}P\}$ n.m.r. spectrum, that of

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† Di-μ-[bis(diphenylphosphino)methane-*PP*′]-μ-carbonyl-2,2-dicarbonyl-μ-chloro-coppertungsten–dichloromethane (1/1).

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 for complexes of formula $[MM'(CO)_3X(dppm)_2]$

Complex						Analysis (%)[a]		
M	M′	X		Colour	Yield (%)	C	H	Other(s)
Cr	Cu	Cl	**(3a)**	Dark red	49	63.2 (63.4)	4.4 (4.4)	Cl: 3.7 (3.55)
Cr	Cu	I	**(3b)**	Dark red	63	58.35 (58.1)	4.1 (4.05)	I: 11.35 (11.6)
Mo	Cu	Cl	**(3c)**	Orange	71	60.45 (60.75)	4.25 (4.25)	Cl: 3.3 (3.4)
Mo	Cu	I	**(3d)**·0.5CH_2Cl_2[b]	Orange	56	54.25 (54.4)	3.7 (3.85)	I: 10.75 (10.75) Cl: 3.0 (3.0)
W	Cu	Cl	**(3e)**	Orange	60	55.9 (56.05)	3.85 (3.9)	Cl: 3.2 (3.15)
W	Cu	I	**(3f)**·0.5CH_2Cl_2[b]	Orange	65	50.35 (50.6)	3.5 (3.6)	I: 9.9 (10.0) Cl: 3.0 (2.8)
Cr	Ag	Cl	**(4)**·0.25CH_2Cl_2[b]	Golden yellow	40	59.9 (59.8)	4.1 (4.2)	Cl: 5.0 (4.95)
Cr	Ag	CN	**(6a)**·0.5C_6H_6[b]	Yellow	78	63.55 (63.5)	4.45 (4.4)	N: 1.25 (1.3)
Mo	Ag	CN	**(6b)**	Yellow	89	60.2 (59.9)	4.15 (4.1)	N: 1.05 (1.3)
W	Ag	CN	**(6c)**·0.75C_6H_6[b]	Yellow	56	57.0 (57.15)	4.0 (4.0)	N: 1.2 (1.15)
Mo	Au	Cl	**(7a)** or **(7b)**	Orange	64	53.95 (53.9)	3.9 (3.75)	Cl: 3.0 (3.0)
W	Au	Cl	**(7c)** or **(7d)**	Orange	78	52.25 (52.0)	3.7 (3.7)	Cl: 2.5 (2.7)

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

Table 2. ^{31}P-$\{^1H\}$ N.m.r. data[a] for complexes of formula $[MM'(CO)_3X(dppm)_2]$

Complex[b]						$^1J(W-P_A)$	$^1J(^{107}Ag-P_B)$	$^1J(^{109}Ag-P_B)$	L[c]	M[c]	N[c]	
M	M′	X		$\delta(P_A)$	$\delta(P_B)$					Hz		$\lvert J(P_AP_B), J(P_AP_{B'})\rvert$[d]
Cr	Cu	Cl	**(3a)**	64.3	−1.2				73	61	93	83,10
Cr	Cu	I	**(3b)**	60.8	5.4				73	56	92	82,10
Mo	Cu	Cl	**(3c)**	44.0	−0.1				76	34	93	84,8
Mo	Cu	I	**(3d)**	39.9	6.2				74	40	90	82,8
W	Cu	Cl	**(3e)**	26.2	0.7	301			70	34	88	79,9
W	Cu	I	**(3f)**	18.4	8.1	298			68	39	90	79,11
Mo	Ag	Cl	**(5)**[e]	39.7	4.2		487	562	n.r.	n.r.	71	
Cr	Ag	CN	**(6a)**	68.6	3.7		474	547	n.r.	n.r.	73	
Mo	Ag	CN	**(6b)**	45.2	5.8		459	527	68	35	81	74,6
W	Ag	CN	**(6c)**	19.8	8.2	291	457	527	57	31	73	65,8
Mo	Au	Cl	**(7a)** or **(7b)**	40.1	29.7				n.r.	n.r.	61	
W	Au	Cl	**(7c)** or **(7d)**	21.0	29.9	308			n.r.	n.r.	57	

[a] Spectra (40.25 MHz) measured at +20 °C in CD_2Cl_2 unless otherwise stated; chemical shifts (δ) in p.p.m. ($\pm$0.1) to high frequency of 85% H_3PO_4 and coupling constants (J) in Hz ($\pm$3). P_A is bound to the Group 6 metal, P_B is bonded to copper, silver, or gold. [b] See Scheme. [c] $L = |^2J(P_AP_B) - {}^4J(P_AP_{B'})|, M = |^2J(P_AP_{A'}) - {}^2J(P_BP_{B'})|, N = |^2J(P_AP_B) + {}^4J(P_AP_{B'})|$. [d] It is not possible to distinguish between $^2J(P_{AB})$ and $^4J(P_{AB'})$. [e] Spectrum recorded at −50 °C; n.r. = not resolved.

Table 3. ^1H-$\{^{31}P\}$ N.m.r.[a] and i.r. data[b] for complexes of formula $[MM'(CO)_3X(dppm)_2]$

Complex				Methylene protons				
M	M′	X		$\delta(H_a)$	$\delta(H_e)$	$J(H_aH_e)$	$J(AgH_e)$	$\tilde{\nu}(C\equiv O)/cm^{-1}$
Cr	Cu	Cl	**(3a)**	3.41	3.20	14		1 949s br, 1 851s br, 1 775 (sh), 1 766s br
Cr	Cu	I	**(3b)**	3.59	3.32	14[c]		[d]1 956s br, 1 844s br, 1 784s br
Mo	Cu	Cl	**(3c)**	3.52	3.09	14[c]		[d]1 965s br, 1 856s br, 1 794s br
Mo	Cu	I	**(3d)**	3.68	3.30	14[c]		[d]1 970s br, 1 852s br, 1 802s br
W	Cu	Cl	**(3e)**	3.62	3.11	14[c]		[d]1 952s br, 1 838s br, 1 784s br
W	Cu	I	**(3f)**	3.74	3.38	14[c]		[d]1 958s br, 1 844s br, 1 794s br
Cr	Ag	Cl	**(4)**	$\delta(CH_2)$ 4.47 and 3.05				1 951m, 1 854s br, 1 840 (sh)
Mo	Ag	Cl	**(5)**[e]					1 961s, 1 862s, 1 835s, 1 777s
Cr	Ag	CN	**(6a)**	3.82	3.47	13	4	2 042w [ν(CN)], 1 953br, 1 861s, br, 1 847s br, 1 795 (sh), 1 786s br
Mo	Ag	CN	**(6b)**	3.80	3.47	13	4	2 044w [ν(CN)], 1 968 (sh), 1 957s, 1 867s br, 1 813s br
W	Ag	CN	**(6c)**	3.89	3.59	13	5	2 046w [δ(CN)], 1 954s br, 1 860 (sh), 1 850s, 1 804 (sh), 1 796s br
Mo	Au	Cl	**(7a)** or **(7b)**	$\delta(CH_2)$ 3.69 4.02	3.40	13[f]		1 955s br, 1 835s br, 1 783s br, 1 751 (sh)
W	Au	Cl	**(7c)** or **(7d)**	4.06	3.46	13[f]		1 944s br, 1 830s br, 1 777s, br

[a] Spectra (100 MHz) measured in CD_2Cl_2 at 20 °C unless otherwise stated; chemical shifts (δ) in p.p.m. ($\pm$0.01) to high frequency of $SiMe_4$ and coupling constants (J) in Hz ($\pm$0.3). H_a and H_e are defined in the text and cannot be distinguished except for **(6a)**—**(6c)**. [b] Spectra recorded as Nujol mulls unless otherwise stated. [c] In $CDCl_3$. [d] In CH_2Cl_2 solution. [e] ^1H-$\{^{31}P\}$ spectrum not recorded. [f] Measured at −30 °C.

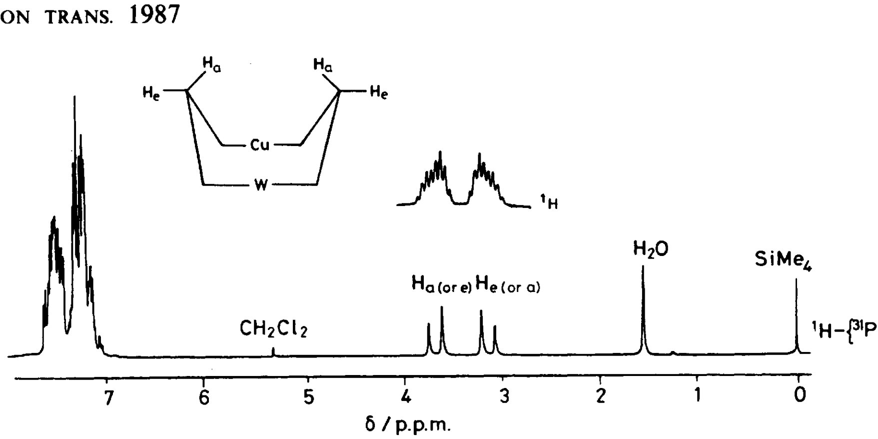


Figure 1. ^1H-{^{31}P} and ^1H n.m.r. spectra of [$(OC)_2W(\mu\text{-}CO)(\mu\text{-}dppm)_2(\mu\text{-}Cl)Cu$] (**3e**) at 20 °C

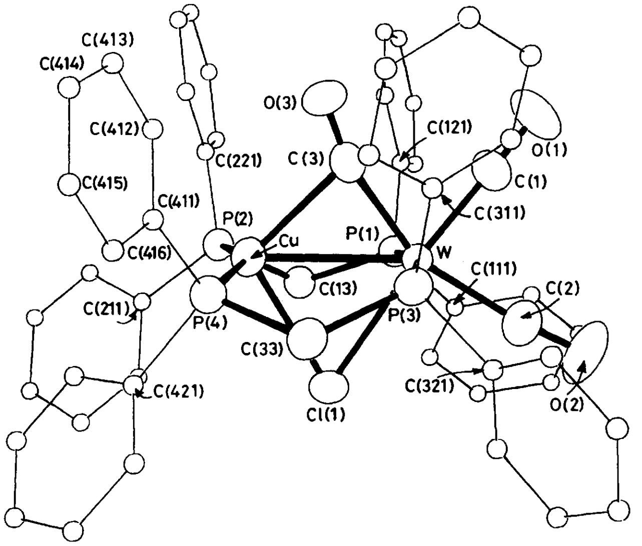


Figure 2. Molecular structure of [$(OC)_2W(\mu\text{-}CO)(\mu\text{-}dppm)_2(\mu\text{-}Cl)Cu]\cdot CH_2Cl_2$ (**3e**), showing the principal atomic numbering

[$(OC)_2W(\mu\text{-}CO)(\mu\text{-}dppm)_2(\mu\text{-}Cl)Cu$] (**3e**), is shown in Figure 1. The i.r. spectra all show a low-frequency band (< 1 810 cm^{-1}) in the carbonyl region suggesting the presence of a semibridging carbonyl group. No band attributable to terminal ν(Cu–Cl) is observed in the far-i.r. spectra of (**3a**), (**3c**), or (**3e**). The crystal structure of complex (**3e**) has been determined and is shown in Figure 2.

Crystal Structure of [$(OC)_2W(\mu\text{-}CO)(\mu\text{-}dppm)_2(\mu\text{-}Cl)Cu]\cdot CH_2Cl_2$ (**3e**).—Complex (**3e**) crystallised from dichloromethane–methanol (*ca.* 1:1) as orange plates and was found to crystallise in two distinct forms. Initially, a solvent dependent triclinic crystal of space group $P\bar{1}$ was selected for structural study. However, this crystal lost solvent in the *X*-ray beam before a sufficiently large data set was obtained in order to allow an accurate structure determination.

A monoclinic crystal of space group $P2_1/c$ was obtained on crystallisation of a second sample of (**3e**), for which the structure was accurately determined. Table 4 lists the relevant bond lengths and angles. It can be clearly seen from Figure 2 that there is a strong interaction between tungsten(0) and the chloride ligand. Indeed if the larger covalent radius of tungsten(0) over copper(I) is taken into account the chloride ligand is almost symmetrically bound to both metals. There is also a semibridging interaction between one of the carbonyl ligands and the copper nucleus. Two interesting isomeric forms of [$(\eta^5\text{-}C_5H_5)W(CO)_3Cu(PPh_3)_2$] have been described, one of which has two semibridging carbonyls (to copper) and a W–Cu bond with similar internuclear distances (Cu–CO 220 and 226 pm, W–Cu 277 pm) to (**3e**).[6]

Table 4. Selected bond lengths (pm) and angles (°) for [$(OC)_2W(\mu\text{-}CO)(\mu\text{-}dppm)_2(\mu\text{-}Cl)Cu]\cdot CH_2Cl_2$ (**3e**)

W–Cu	275.9(4)	P(1)–W–P(3) (internal)	167.3(1)
W–P	246.9(4)*	P(2)–Cu–P(4) (internal)	211.5(1)
Cu–P	222.6(4)*	W–C(3)–Cu	80.2(3)
W–Cl	259.2(5)	W–Cl–Cu	64.8(0.5)
Cu–Cl	255.3(5)	W–C(3)–O(3)	164.4(6)
W–C(3)	200.4(11)		
Cu–C(3)	226.7(8)		

* Averaged value.

An interesting feature of the structure is the remarkably high P(2)–Cu–P(4) internal angle [211.5(1)°] compared with P(1)–W–P(3) [167.3(1)°]. Many crystal structures containing $M(\mu\text{-}dppm)_2M'$ moieties have been determined and usually the internal angle P–M–P is less than 190°. The $W(\mu\text{-}dppm)_2Cu$ ring is in a pseudo-boat conformation as in most other bis(μ-dppm) complexes.

Although the crystal structure of the triclinic form could not be accurately determined, a crude molecular structure was obtained (R = 0.090). This shows the structure of the triclinic form to be very similar to that of the monoclinic, with the exception that the $W(\mu\text{-}dppm)_2Cu$ ring is in a pseudo-chair conformation. Bis(μ-dppm) complexes where the $M(\mu\text{-}dppm)_2M'$ ring adopts a pseudo-chair conformation are rare; [$Pt_2Me_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$ is one such complex.[7] Whether or not the triclinic crystal selected from the first crystallised sample of (**3e**) was truly representative of the bulk of the solid is uncertain.

We propose that complexes (**3a**)—(**3d**) and (**3f**) all have a similar structure to (**3e**); the semibridging interaction between the carbonyl and copper is weak in complex (**3d**).

Redox reactions occur on treatment of *fac*- or *mer*-[$M(CO)_3$(dppm-*PP′*)(dppm-*P*)] (M = Cr, Mo, or W) with some silver(I) compounds. For example, treatment of *fac*- or *mer*-[$M(CO)_3$(dppm-*PP′*)(dppm-*P*)] with $AgNO_3$ at 20 °C in CH_2Cl_2 gives metallic silver and oxidised Group 6 metal species. In contrast, treatment of *fac*- or *mer*-[$M(CO)_3$(dppm-*PP′*)(dppm-*P*)] with 0.25 mol equivalents of [$Ag_4Cl_4(PPh_3)_4$] gives no oxidation products. *mer*-[$Cr(CO)_3$(dppm-*PP′*)(dppm-*P*)] (**2a**) and [$Ag_4Cl_4(PPh_3)_4$] react to give a golden yellow solid, formulated as *mer*-[$(OC)_3$(dppm-*PP′*)$Cr(\mu\text{-}dppm)AgCl$] (**4**) on the basis of microanalysis, ^{31}P-{^1H} and ^1H-{^{31}P} n.m.r.

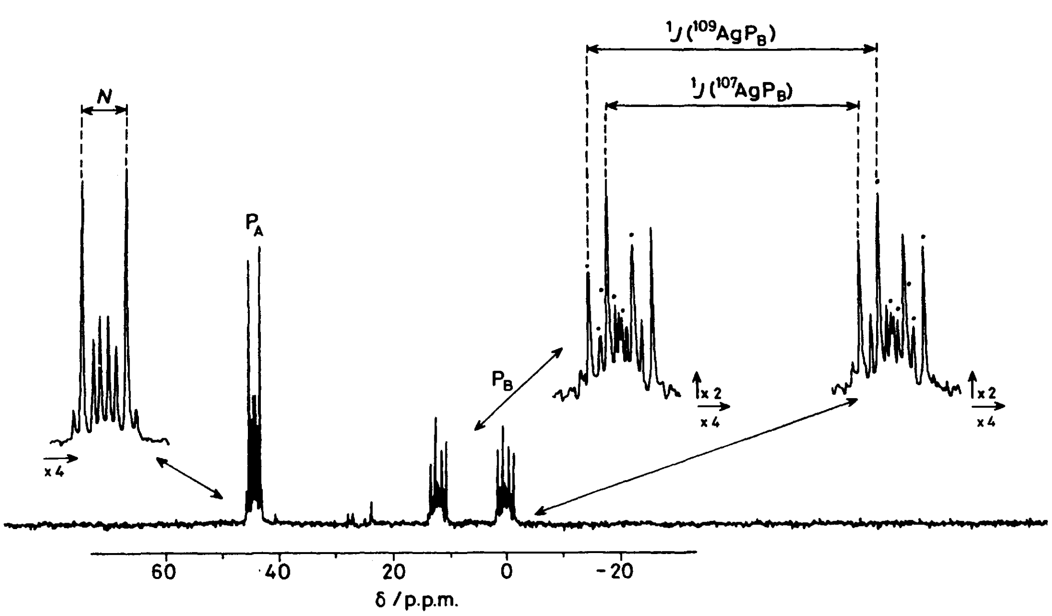


Figure 3. $^{31}P-\{^1H\}$ N.m.r. spectrum of $[(OC)_3Mo(\mu\text{-dppm})_2Ag(CN)]$ (**6b**) at +20 °C. The resonances due to the complex containing ^{109}Ag are marked with •

spectroscopy, and i.r. spectroscopy. Its $^{31}P-\{^1H\}$ n.m.r. spectrum at 21 °C shows a splitting pattern typical of complex (**2a**), with the resonance at −25.9 p.p.m. (due to the phosphorus atom unco-ordinated to Cr, P_D)[8] shifted to high frequency (−5.6 p.p.m.) and broadened, indicating that P_D is co-ordinated to silver. No coupling of P_D to ^{107}Ag or ^{109}Ag is observed, probably due to rapid phosphine exchange at silver, common in silver(I) phosphine complexes.[9] Treatment of *fac*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (M = Mo or W) or *mer*-$[W(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ with $[Ag_4Cl_4(PPh_3)_4]$ gave the analogous *fac*- or *mer*-$[(OC)_3(dppm\text{-}PP')M(\mu\text{-dppm})AgCl]$ complexes ($^{31}P-\{^1H\}$ n.m.r. spectroscopic evidence). However, treatment of *mer*-$[Mo(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (**2b**) with $[Ag_4Cl_4(PPh_3)_4]$, under similar conditions, gave an unstable golden yellow species, to which we assign the structure $[(OC)_3Mo(\mu\text{-dppm})_2AgCl]$ (**5**) on the basis of $^{31}P-\{^1H\}$ n.m.r. and i.r. spectroscopy (see Tables 2 and 3). The $^{31}P-\{^1H\}$ n.m.r. spectrum of (**5**) is broad at ambient temperature, whereas an AA′XX′ type pattern is clearly resolved at −50 °C: coupling of P_B (phosphorus atoms bound to Ag) to ^{107}Ag and ^{109}Ag is not observed at 20 °C but well defined at −50 °C. Similar behaviour has been observed for other bis(μ-dppm) complexes of silver,[10,11] where the broadening of the P_{Ag} resonance is attributed to rapid phosphine exchange at silver.

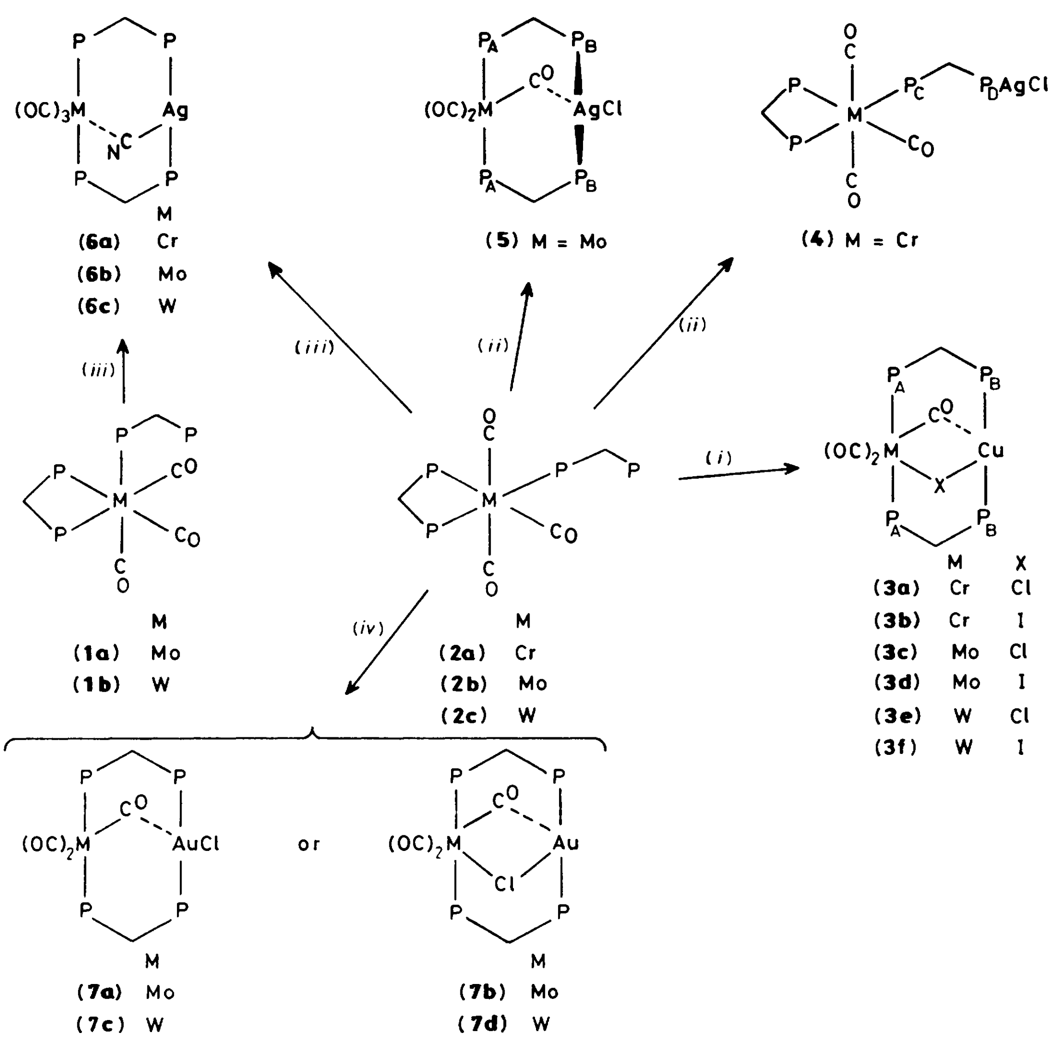
Treatment of *fac*- or *mer*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ with $[Ag(PPh_3)(CN)]$ gave stable, yellow heterobimetallic complexes of the type $[(OC)_3M(\mu\text{-dppm})_2Ag(CN)]$ [M = Cr (**6a**), Mo (**6b**), or W (**6c**)] (see Experimental section for experimental details and Tables 1—3 for characterising data). In contrast to above, the $^{31}P-\{^1H\}$ n.m.r. spectra of the cyano complexes (**6a**)—(**6c**) all show well defined AA′XX′ splitting patterns at 20 °C, with well resolved coupling to ^{107}Ag, ^{109}Ag, and ^{183}W. The spectrum of $[(OC)_3Mo(\mu\text{-dppm})_2Ag(CN)]$ (**6b**) is shown in Figure 3. The ratios $^1J(^{109}AgP)/^1J(^{107}AgP)$ are all *ca.* 1.15 : 1, the same as the ratio of the gyromagnetic ratios of the respective isotopes.

The $^1H-\{^{31}P\}$ n.m.r. spectra show resonances due to both pseudo-axial (H_a) and pseudo-equatorial (H_e) PCH_2P hydrogens at 20 °C, suggesting that the $\overline{MPCPAgPCP}$ rings are rigid and in the pseudo-boat conformation. Coupling of the H_e resonance to silver is observed but no $^3J(Ag\text{-}H_a)$ coupling is seen: this feature has been noted previously[10] and is associated with Karplus-type behaviour of the $^3J(AgH)$ couplings. All three complexes show a single sharp band due to ν(CN) in their i.r. spectrum, at 2 042 (Cr), 2 044 (Mo), or 2 046 (W) cm^{-1}: these frequencies are low for ν(CN) (usually >2 100 cm^{-1}) and suggest a semibridging interaction, which would explain the presence of non-equivalent methylene protons in the $^1H-\{^{31}P\}$ n.m.r. spectrum.

We find that, on treatment with $[Au(PPh_3)Cl]$ at 20 °C in CH_2Cl_2, *mer*-$[Cr(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (**2a**) co-ordinates to Au^I *via* the free phosphorus atom P_D ($^{31}P-\{^1H\}$ n.m.r. spectroscopic evidence). Its $^{31}P-\{^1H\}$ n.m.r. spectrum shows four resonances typical of a *mer* isomer, with broadening of the P_D resonance due to ligand exchange at gold {rapid ligand exchange is known to occur at 20 °C on treatment of $[Au(PR_3)Cl]$ (R = alkyl or aryl) with additional phosphine[12,13]}. The mono(μ-dppm) species did not ring open on warming the solution.

On the other hand, treatment of *mer*-$[Mo(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (**2b**) with $[Au(PPh_3)Cl]$ under the same conditions gave a bis(μ-dppm) species as the only dppm-containing product ($^{31}P-\{^1H\}$ n.m.r. evidence). This bis(μ-dppm) species is unstable in solution, but was successfully isolated as an orange powder from benzene (see Experimental section). Treatment of *mer*-$[W(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (**2c**) with $[Au(PPh_3)Cl]$ similarly gave the analogous W–Au complex. In contrast, treatment of *fac*-$[M(CO)_3(dppm\text{-}PP')(dppm\text{-}P)]$ (M = Mo or W) with $[Au(PPh_3)Cl]$ gave a complex mixture of unidentified products ($^{31}P-\{^1H\}$ n.m.r. evidence).

These bis(μ-dppm) species are assigned the formula $[(OC)_3M(\mu\text{-dppm})_2AuCl]$ on the basis of $^{31}P-\{^1H\}$ and $^1H-\{^{31}P\}$ n.m.r. spectroscopy, microanalysis, and i.r. spectroscopy (Tables 1—3). The $^1H-\{^{31}P\}$ n.m.r. spectra of both complexes show a very broad resonance for the CH_2 protons at 20 °C which sharpens to an AB pattern on cooling to −30 °C. The i.r. spectra (Nujol mull) both indicate that a semibridging carbonyl is present in the solid-state structure. No band attributable to ν(Au–Cl) is observed in the far-i.r. spectrum of either complex: the absence of ν(Au–Cl) is common for three-co-ordinate gold(I) chloro complexes.[14,15] The conductivity of the more



Scheme. (*i*) CuX (X = Cl or I) in CH_2Cl_2, (*ii*) $[Ag_4(PPh_3)_4Cl_4]$ in CH_2Cl_2, (*iii*) $[Ag(PPh_3)(CN)]$ in CH_2Cl_2, (*iv*) $[Au(PPh_3)Cl]$ in benzene

stable W–Au complex was found to be typical of a non-electrolyte (Λ_M 4 Ω^{-1} cm^2 mol^{-1}). Thus we suggest that [(OC)$_3$Mo(μ-dppm)$_2$AuCl] has the structure (**7a**) or (**7b**), with the W–Au complex having an analogous structure [(**7c**) or (**7d**)]. We slightly favour the bridging chloride structure [(**7b**) or (**7d**)] because the PCH$_2$P protons are inequivalent at moderately low temperatures (see above), consistent with a bridging structure (see above).

Reactions are summarised in the Scheme.

Experimental

General methods were as previously described in recent papers from this laboratory.[16]

Preparations.—[(OC)$_2$Cr(μ-CO)(μ-dppm)$_2$(μ-Cl)Cu] (**3a**). CuCl (0.023 g, 0.23 mmol) was added to a stirred solution of *mer*-[Cr(CO)$_3$(dppm-*PP'*)(dppm-*P*)] (**2a**) (0.200 g, 0.22 mmol) in CH$_2$Cl$_2$ (5 cm^3). The reaction mixture was stirred for 10 min and then filtered. Et$_2$O (7 cm^3) was added and the solution cooled to +5 °C. The required product was precipitated as dark red crystals, which were isolated by decanting off the pale orange mother-liquors and washing with Et$_2$O. Yield: 0.109 g (49%).

[(OC)$_2$Cr(μ-CO)(μ-dppm)$_2$(μ-I)Cu] (**3b**). CuI (0.041 g, 0.22 mmol) was added to a solution of *mer*-[Cr(CO)$_3$(dppm-*PP'*)(dppm-*P*)] (**2a**) (0.200 g, 0.22 mmol) in CH$_2$Cl$_2$ (6 cm^3). The mixture was stirred for 30 min, and then filtered. MeOH (10 cm^3) was added to precipitate out the required product as a dark red solid. Yield: 0.153 g (63%).

The complexes [(OC)$_2$M(μ-CO)(μ-dppm)$_2$(μ-X)Cu] [M = Mo, X = Cl (**3c**) or I (**3d**); M = W, X = Cl (**3e**) or I (**3f**)] were prepared similarly; colours and yields are given in Table 1.

mer-[(OC)$_3$(dppm-*PP'*)Cr(μ-dppm)AgCl] (**4**). [Ag$_4$Cl$_4$(PPh$_3$)$_4$] (0.100 g, 0.06 mmol) was added to a stirred solution of *mer*-[Cr(CO)$_3$(dppm-*PP'*)(dppm-*P*)] (**2a**) (0.200 g, 0.22 mmol) in CH$_2$Cl$_2$ (10 cm^3). The solution was stirred for 10 min, and then filtered. Et$_2$O (10 cm^3) was added and the orange solution reduced in volume under reduced pressure until the golden yellow product was deposited. Yield: 0.091 g (40%).

[(OC)$_3$Mo(μ-dppm)$_2$Ag(CN)] (**6b**). [Ag(PPh$_3$)(CN)] (0.167 g, 0.42 mmol) was added to a stirred solution of *mer*-[Mo(CO)$_3$(dppm-*PP'*)(dppm-*P*)] (**2b**) (0.300 g, 0.32 mmol) in CH$_2$Cl$_2$ (10 cm^3). The mixture was stirred for 5 min and light petroleum (b.p. 60—80 °C, *ca.* 15 cm^3) then added. The solution was reduced in volume under reduced pressure until the required product was precipitated as yellow microcrystals. Yield: 0.304 g (89%).

[(OC)$_3$Cr(μ-dppm)$_2$Ag(CN)] (**6a**) was prepared similarly, the crude product being isolated in 78% yield as a yellow

Table 5. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for $[(OC)_2W(\mu\text{-}CO)(\mu\text{-dppm})_2(\mu\text{-}Cl)Cu]\cdot CH_2Cl_2$ (**3e**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	1 490.1(3)	983.4(1)	2 176.1(1)	C(312)	941(5)	2 747(2)	2 796(3)
Cu	1 132(1)	841.5(3)	3 416.3(4)	C(313)	−7(5)	3 150(2)	2 513(3)
P(1)	753(2)	46(1)	1 959(1)	C(314)	−618(5)	3 214(2)	1 788(3)
P(2)	352(2)	16(1)	3 363(1)	C(315)	−281(5)	2 875(2)	1 346(3)
P(3)	2 439(2)	1 856(1)	2 666(1)	C(316)	667(5)	2 473(2)	1 629(3)
P(4)	2 116(2)	1 544(1)	4 066(1)	C(321)	3 950(4)	2 095(2)	2 543(3)
Cl(1)	3 333(2)	594(1)	3 295(1)	C(322)	4 060(4)	2 606(2)	2 306(3)
C(111)	1 651(5)	−367(2)	1 551(2)	C(323)	5 233(4)	2 757(2)	2 219(3)
C(112)	2 326(5)	−837(2)	1 838(2)	C(324)	6 297(4)	2 398(2)	2 370(3)
C(113)	2 987(5)	−1 123(2)	1 487(2)	C(325)	6 187(4)	1 888(2)	2 608(3)
C(114)	2 973(5)	−938(2)	848(2)	C(326)	5 014(4)	1 736(2)	2 695(3)
C(115)	2 298(5)	−468(2)	560(2)	C(33)	3 119(7)	1 886(3)	3 641(4)
C(116)	1 637(5)	−182(2)	912(2)	C(411)	1 209(5)	2 076(2)	4 294(3)
C(121)	−1 003(3)	−117(2)	1 395(2)	C(412)	−188(5)	2 099(2)	3 953(3)
C(122)	−2 031(3)	239(2)	1 347(2)	C(413)	−904(5)	2 518(2)	4 087(3)
C(123)	−3 372(3)	99(2)	971(2)	C(414)	−222(5)	2 916(2)	4 562(3)
C(124)	−3 684(3)	−397(2)	643(2)	C(415)	1 176(5)	2 894(2)	4 902(3)
C(125)	−2 655(3)	−752(2)	692(2)	C(416)	1 891(5)	2 474(2)	4 769(3)
C(126)	−1 315(3)	−612(2)	1 068(2)	C(421)	3 329(5)	1 327(2)	4 909(2)
C(13)	953(7)	−338(3)	2 761(3)	C(422)	2 904(5)	913(2)	5 226(2)
C(211)	1 029(5)	−391(2)	4 151(2)	C(423)	3 771(5)	710(2)	5 869(2)
C(212)	224(5)	−711(2)	4 382(2)	C(424)	5 063(5)	920(2)	6 196(2)
C(213)	805(5)	−1 008(2)	4 995(2)	C(425)	5 488(5)	1 334(2)	5 880(2)
C(214)	2 192(5)	−985(2)	5 377(2)	C(426)	4 621(5)	1 537(2)	5 236(2)
C(215)	2 997(5)	−665(2)	5 146(2)	C(1)	210(8)	1 197(3)	1 281(4)
C(216)	2 416(5)	−367(2)	4 533(2)	O(1)	−604(6)	1 320(3)	734(3)
C(221)	−1 459(3)	−91(2)	3 008(2)	C(2)	2 705(8)	947(3)	1 635(4)
C(222)	−2 052(3)	−571(2)	2 707(2)	O(2)	3 309(7)	966(3)	1 284(4)
C(223)	−3 451(3)	−619(2)	2 416(2)	C(3)	−75(8)	1 246(3)	2 385(4)
C(224)	−4 257(3)	−187(2)	2 427(2)	O(3)	−1 049(5)	1 447(2)	2 356(3)
C(225)	−3 663(3)	293(2)	2 729(2)	Cl(1S)	5 364(5)	3 390(2)	5 639(3)
C(226)	−2 264(3)	341(2)	3 019(2)	Cl(2S)	6 386(7)	2 702(2)	4 841(4)
C(311)	1 278(5)	2 409(2)	2 354(3)	C(1S)	6 638(16)	3 007(9)	5 597(11)

powder. Yellow needles were obtained on recrystallisation from benzene–light petroleum (b.p. 60—80 °C). The complex $[(OC)_3W(\mu\text{-dppm})_2Ag(CN)]$ (**6c**) was prepared in a similar manner from *mer*-$[W(CO)_3(\text{dppm-}PP')(\text{dppm-}P)]$ (**2c**) and $[Ag(PPh_3)(CN)]$. The impure product was precipitated from the reaction mixture with diethyl ether. Pure (**6c**) was obtained as yellow needles on recrystallisation from benzene–light petroleum (b.p. 60—80 °C). Yield: 56%.

$[(OC)_3Mo(\mu\text{-dppm})_2AuCl]$. The compound $[Au(PPh_3)Cl]$ (0.110 g, 0.22 mmol) was added to a stirred solution of *mer*-$[Mo(CO)_3(\text{dppm-}PP')(\text{dppm-}P)]$ (**2b**) (0.200 g, 0.21 mmol) in benzene (10 cm^3). The solution immediately became orange and $[Au(PPh_3)Cl]$ rapidly went into a solution; after a few min the solution became cloudy. Et_2O (10 cm^3) was then added to precipitate out the required product as a deep orange powder. Yield: 0.160 g (64%).

$[(OC)_3W(\mu\text{-dppm})_2AuCl]$ was prepared similarly, under N_2, in 78% yield.

Single Crystal X-*Ray Diffraction Analysis*.—Crystals suitable for this work were grown by diffusion of methanol into a solution of $[(OC)_2W(\mu\text{-}CO)(\mu\text{-dppm})_2(\mu\text{-}Cl)Cu]$ in CH_2Cl_2 at room temperature.*

Crystal data. $C_{54}H_{46}Cl_3CuO_3P_4W$, M = 1 220.7 monoclinic, a = 1 076.0(2), b = 2 513.2(4), c = 2 067.5(3) pm, β = 112.62(1)°, U = 5.161 nm^3, Z = 4, space group $P2_1/c$ (no. 14), D_c = 1.57 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 27.7 cm^{-1}, $F(000)$ = 2 404.

Data collection. Scans running from 0.9° below K_{α_1} to 0.9° above K_{α_2}, scan speeds 2.0—29.3° min^{-1}, $4.0 < 2\theta < 45.0°$. 6 554 Unique data, 6 138 observed $[I > 2.0\sigma(I)]$, T = 290 K.

Structure refinement. Number of parameters = 520, R = 0.0359 (unit weights).

Data collection and structure solution. Unit cell and intensity data were recorded on a Syntex $P2_1$ diffractometer operating in the ω–2θ scan mode using graphite monochromated Mo-K_α radiation (λ = 71.069 pm) and following a procedure described elsewhere in detail.[17] The data were corrected for absorption empirically.[18]

The structure was solved *via* standard heavy-atom methods and refined by blocked full-matrix least squares using the SHELX program system.[19] All non-hydrogen atoms were assigned anisotropic thermal parameters with the phenyl rings treated as rigid bodies and included in the refinement with idealised hexagonal symmetry (C–C = 139.5 pm). All hydrogen atoms were included in calculated positions (C–H = 108 pm) and were assigned an overall isotropic thermal parameter for each dppm ligand. The final R value was 0.0359 (unit weights). Non-hydrogen and atomic co-ordinates are given in Table 5.

Acknowledgements

We thank the S.E.R.C. for support.

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* A second crystalline form was also obtained using this method. The crystals were triclinic, a = 1 314.0(3), b = 1 427.2(4), c = 1 518.0(4) pm, α = 87.24(2), β = 110.90(2), γ = 106.21(2)°, U = 2.549 nm^3. However, a complete data set for this form was not obtained due to the highly solvent dependent nature of the crystals.

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Received 8*th June* 1986; *Paper* 6/1141