Bimetallic Systems. Part 6.[1] Chromium(0)–, Molybdenum(0)–, or Tungsten(0)–Platinum(II) Acetylide Complexes containing Bridging $Ph_2PCH_2PPh_2$, including their Efficient Formation from Platinum–Silver Complexes by Transmetallation. Crystal Structure of [(*p*-$MeC_6H_4C{\equiv}C$)-Pt(μ-$C{\equiv}CC_6H_4Me$-*p*)(μ-$Ph_2PCH_2PPh_2$)$_2$W(CO)$_3$] †

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Treatment of *trans*-[Pt(C≡CR)$_2$(dppm-*P*)$_2$] (dppm = $Ph_2PCH_2PPh_2$) with [W(CO)$_3$(NCMe)$_3$] gave [(RC≡C)Pt(μ-C≡CR)(μ-dppm)$_2$W(CO)$_3$] (R = Ph, *p*-tolyl, or Me) accompanied by [Pt$_2$(C≡CR)$_4$-(μ-dppm)$_2$] and other products. Treatment of *trans*-[Pt(C≡CPh)$_2$(dppm-*P*)$_2$] with [Mo(CO)$_4$-(1,5-cod)] (1,5-cod = cyclo-octa-1,5-diene) or with [Mo(CO)$_3$(cht)] (cht = cyclohepta-1,3,5-triene) gave [(PhC≡C)Pt(μ-C≡CPh)(μ-dppm)$_2$Mo(CO)$_3$], in 20—25% yield, but the corresponding chromium compound could not be made in this way. However, treatment of the readily available complexes [(RC≡C)$_2$Pt(μ-dppm)$_2$AgX] (X = Cl or I) with [W(CO)$_3$(NCMe)$_3$] or [Mo(CO)$_3$(cht)] gave the above mentioned platinum–tungsten or –molybdenum complexes with displacement of silver halide (transmetallation), usually in good yield and without formation of the diplatinum complexes. Purple [(PhC≡C)Pt(μ-C≡CPh)(μ-dppm)$_2$Cr(CO)$_3$] was made similarly but not isolated. ^1H-{^{31}P} N.m.r. studies at different temperatures showed the complexes to be fluxional, corresponding to rapid terminal–bridging C≡CR interchange with inversion of the Pt(μ-dppm)$_2$M boat-shaped eight-membered rings. The complexes [(RC≡C)Pt(μ-C≡CR)(μ-dppm)$_2$W(CO)$_3$] (R = Me or Ph) were rapidly and reversibly protonated by CF_3CO_2H to give [(RC≡C)Pt(μ-C=CHR)(μ-dppm)$_2$W(CO)$_3$]$^+$, isolated as the PF_6^- salts; preliminary studies suggested that the molybdenum complexes could also be protonated. Phosphorus-31 and ^1H n.m.r. data are given and discussed. With the Pt(μ-$Ph_2PCH_2PPh_2$)$_2$M moieties, platinum-195 was observed to be quite strongly (magnetically) coupled to one of the methylene hydrogens, that which was pseudo-equatorial, but coupling to the pseudo-axial hydrogen was not observed. Crystals of the title compound are monoclinic, space group $P2_1$, with a = 11.847(3), b = 16.023(4), c = 18.351(4) Å, β = 116.23(1)°, and Z = 2; final R factor 0.026 for 4 043 observed reflections. The structure shows that the two metal centres [Pt · · · W 3.037(1) Å] are asymmetrically bridged by one of the *p*-tolylacetylide groups such that the Pt–C and W · · · C distances are 2.094(9) and 2.398(9) Å, respectively, with the C≡C vector perpendicular to the PtP_4W plane.

We have shown in previous papers that the unidentate-dppm species *trans*-[Pt(C≡CR)$_2$(dppm-*P*)$_2$] (1a)—(1c)[2,3] (dppm = $Ph_2PCH_2PPh_2$) readily form heterobimetallic complexes with the d^{10} metals copper(I), silver(I), gold(I), cadmium(II), or mercury(II).[3–5] For example, the platinum–silver complexes (2a)—(2d) are made from (1a)—(1c) and [{AgX(PPh$_3$)}$_4$] (X = Cl or I)[4,5] or, more conveniently, from the salt [Pt(dppm-*PP*′)$_2$]X$_2$ and Ag(O$_2$CMe)–RC≡CH.[5,6] In the present paper we report methods for the systematic synthesis and some reactions of heterobimetallic complexes of platinum(II) acetylides with the d^6 metals chromium(0), molybdenum(0), and tungsten(0). We have published preliminary accounts of some of this work.[7,8]

Results and Discussion

One of our most successful methods for making heterobimetallic complexes containing bridging dppm ligands has been by treatment of the unidentate-dppm platinum species, *e.g.* (1a)—(1c), with a substitution-labile complex of the second metal; thus when we treated the platinum complex (1a) with the labile tungsten(0) complex [W(CO)$_3$(NCMe)$_3$] in boiling benzene we obtained the platinum–tungsten complex (3a) in 40% yield, as maroon crystals. The *p*-tolylacetylide (3b) and methylacetylide (3c) analogues were made similarly (see Scheme 1). In each case considerable amounts of the corresponding diplatinum complexes (4a)—(4c) were also formed, along with (presumably) tungsten(0)–dppm species; details are given in the Experimental section and characterising data in the Tables. We then attempted to make a corresponding platinum–molybdenum complex from *trans*-[Pt(C≡CPh)$_2$-(dppm-*P*)$_2$] (1a) and [Mo(CO)$_4$(1,5-cod)] (1,5-cod = cyclo-octa-1,5-diene) or [Mo(CO)$_3$(cht)] (cht = cyclohepta-1,3,5-triene) under similar conditions. The yields of the desired platinum–molybdenum complex (3d) were low (20—25%) and the product was difficult to obtain free from the diplatinum complex (4a). The other platinum–molybdenum complexes (3e) and (3f) were made similarly. Attempts to make the platinum–chromium complex (3g) from the unidentate-dppm species (1a) and [Cr(CO)$_4$(nbd)] (nbd = norborna-2,5-diene) or [Cr(CO)$_3$(NCMe)$_3$] were completely unsuccessful, only the diplatinum complex (4a) and chromium–dppm species being detected (by ^{31}P-{^1H} n.m.r. spectroscopy).

We then studied the possibility of making the heterobimetallic complexes of types (3a)—(3g) by displacing silver from the readily available platinum–silver complexes (2a)—(2d)[4,6] using a labile Group 6 metal carbonyl derivative (transmetallation, see Scheme 2). It was anticipated that the transmetallation reaction would be thermodynamically favour-

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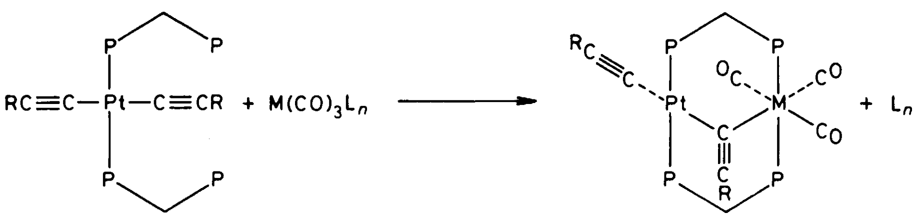
† Bis-μ-[bis(diphenylphosphino)methane-*PP*′]-2,2,2-tricarbonyl-μ-*p*-tolylethynyl-1-*p*-tolylethynylplatinumtungsten.

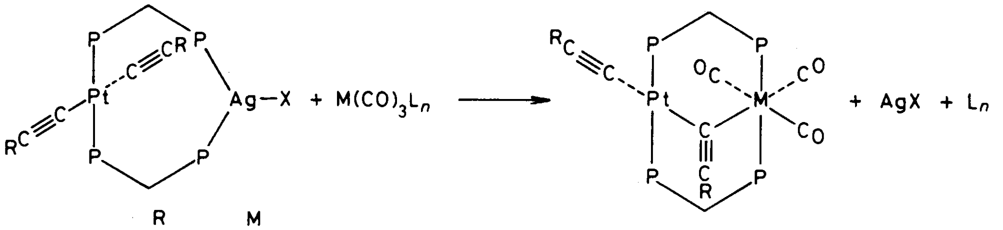
Supplementary data available (No. SUP 23932, 32 pp.): thermal parameters, complete bond lengths and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



(1a) R = Ph
(1b) R = C_6H_4Me-*p*
(1c) R = Me

	R	M
(3a)	Ph	W
(3b)	C_6H_4Me-*p*	W
(3c)	Me	W
(3d)	Ph	Mo
(3e)	C_6H_4Me-*p*	Mo
(3f)	Me	Mo

Scheme 1. $\widehat{P\,P}$ = $Ph_2PCH_2PPh_2$; L_n = $(NCMe)_3$, M = W; L_n = cycloheptatriene, M = Mo

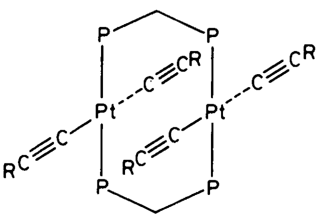


	R	M
(2a)	Ph	Cl
(2b)	C_6H_4Me-*p*	Cl
(2c)	Me	Cl
(2d)	Ph	I

(3a)-(3g)

Scheme 2. $\widehat{P\,P}$ = $Ph_2PCH_2PPh_2$; L_n = $(NCMe)_3$, M = W; L_n = cycloheptatriene, M = Mo; for (3g), M = Cr, R = Ph

able because (*i*) the d^6 metal(0) centre would have a greater affinity for P-donor ligands than silver(I) and (*ii*) silver halide would be precipitated. Thus we treated the platinum-silver chloride complex (2a) with substitution-labile tungsten(0) or molybdenum(0) complexes in boiling benzene and obtained very good yields (see Table 1) of the required products; none of the diplatinum species (4a)—(4c) was formed. Thus, treatment of the platinum-silver chloride complex (2a) with $[Mo(CO)_3(cht)]$ in boiling benzene gave a red solution and a precipitate of silver chloride. From the red solution, the desired orange-red crystalline complex (3d) was obtained in 72% yield which was in contrast to the *ca.* 20% yield obtained directly from the unidentate-dppm complex (1a) (Scheme 1). With one exception, the platinum-tungsten or -molybdenum complexes were made in higher yields by the transmetallation route (Scheme 2) than by the direct route (Scheme 1): Table 1 shows a comparison of the yields. In one experiment we treated the platinum-silver iodide complex (2d) with $[W(CO)_3(NCMe)_3]$ in boiling C_6D_6 and followed the progress of the reaction by $^{31}P-\{^1H\}$ n.m.r. spectroscopy. We found that the platinum-tungsten species (3a) was the *only* phosphorus-containing product.



(4a) R = Ph
(4b) R = C_6H_4Me-*p*
(4c) R = Me

As mentioned above, the platinum-chromium complex (3g) was not observed by the direct route (Scheme 1) but treatment of the platinum-silver chloride complex (2a) with $[Cr(CO)_4(nbd)]$ in boiling benzene gave a deep purple solution, shown by $^{31}P-\{^1H\}$ n.m.r. spectroscopy to contain some starting platinum-silver complex (2a) and one other species, to which we assign the structure (3g) on the basis of its $^{31}P-\{^1H\}$ n.m.r. spectrum, which was of the AA'BB' type (see Table 2). Unfortunately, the prolonged boiling required to drive the reaction to completion also led to substantial decomposition of the platinum-chromium complex (3g) and the yield estimated by ^{31}P n.m.r. spectroscopy was *ca.* 35%. Thus far, we have been unable to prepare a pure sample of complex (3g).

The platinum-tungsten (3a)—(3c) and platinum-molybdenum (3d)—(3f) complexes are highly coloured crystalline solids (Table 1) which decompose over several weeks on standing in air. They are readily soluble in most organic solvents but decompose slowly in the presence of alcohols; the rate of decomposition at *ca.* 20 °C in the presence of alcohols is in the order Pt–Cr (10 min) > Pt–Mo (a few hours) > Pt–W (a few days). It was thus possible to grow crystals of the platinum-molybdenum or -tungsten complexes from benzene-methanol (see below). The formulation of the complexes as (3a)—(3g) follows from elemental analysis (Table 1), $^{31}P-\{^1H\}$ (Table 2) and $^1H-\{^{31}P\}$ (Table 3) n.m.r.,

Table 1. Colours, yields, melting points, and microanalytical data

Complex	Colour	Yields (%)		M.p./°C [d]	Analysis (%) [a]		
		Direct [b]	Transmetallation [c]		C	H	F
(3a)	Maroon	40	61	>155	57.65 (57.8)	4.0 (4.8)	
(3b)	Maroon	34	—	192—194	58.1 (58.35)	4.05 (4.0)	
(3c)	Orange	51	—	166—168	52.6 (52.85)	3.85 (3.95)	
(3d)·C_6H_6 [e]	Red	23	72	>125	63.15 (63.25)	4.4 (4.25)	
(3e)	Red	—	42	>134	62.05 (62.05)	4.45 (4.25)	
(3f)	Golden yellow	46	37	152—154	58.2 (58.0)	4.3 (4.1)	
(5a) or (5b)·$0.5C_6H_{14}$ [e]	Yellow-green	60		198—202	49.55 (49.7)	3.8 (3.85)	7.8 (7.6)
(5c) or (5d)	Golden yellow	72		168—172	52.2 (52.45)	3.6 (3.5)	7.0 (7.2)

[a] Calculated values in parentheses. [b] See Scheme 1 and text. [c] See Scheme 2 and text. [d] All complexes melted with decomposition. [e] Presence of solvent confirmed by ^1H n.m.r. spectroscopy.

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

Complex	Solvent	$\delta(P_A)$	$^1J(PtP_A)$	$\delta(P_B)$	$^3J(PtP_B)$	$^1J(WP_B)$	N [b]
(3a)	$CDCl_3$	+3.4	2 546	+14.0	19	298	71
(3b) [c]	$CDCl_3$	+3.2	2 556	+14.3	20	300	71
(3c)	CD_2Cl_2	−3.5	2 717	+12.9	28	308	39
(3d)	$CDCl_3$	+2.3	2 596	+36.4	24		61
(3e)	CD_2Cl_2	+2.0	2 593	+35.4	*d*		59
(3f)	CD_2Cl_2	−1.5	2 700	+34.8	26		46
(3g)	C_6H_6	+5.5	2 568	+60.8	25		71
(5a) or (5b)	$CDCl_3$	+15.8	2 292	+4.7	*d*	274	86
(5c) or (5d)	$CDCl_3$	+14.9	2 253	+5.1	*d*	267	87
(5e) or (5f)	$CDCl_3$	+13.5	2 263	+28.3	*d*		88

[a] Spectra (40.25 MHz) measured at +21 °C; 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 platinum and P_B is bonded to tungsten, molybdenum, or chromium. [b] $N = |^2J(P_AP_B) + {}^4J(P_AP_B')|$. [c] δ(Pt) +122 p.p.m. to high frequency of Ξ(Pt) = 21.4 MHz, $^1J(PtP)$ 2 544, $^3J(PtP)$ 16, and $J(PtW)$ 0 Hz (measured in CD_2Cl_2). [d] Coupling to ^{195}Pt not resolved.

Table 3. $^1H-\{^{31}P\}$ N.m.r. data [a]

							Measured at +21 °C		
Complex	θ_c/°C	$\delta(H_a)$	$\delta(H_e)$	$J(H_aH_e)$	$^3J(PtPCH_e)$	Other resonances	$\delta(CH_2)$	$^3J(PtPCH_2)$	Other resonances
(3a)	−60	3.98	3.61	11.7	*b*		3.80	35.2	
(3b)	−60	3.99	3.62	13.0	*ca.* 66	$\delta(CH_3)$ 2.32, 2.19	3.80	32.0	$\delta(CH_3)$ 2.21
(3c)	−60	4.03	*c*	12.2	*c*	$\delta(CH_3)$ 1.70, 1.59	3.70	36.0	$\delta(CH_3)$ 1.88, $^4J(PtH)$ 12.6
(3d) [d]	−70	3.98	3.51	11.0	*ca.* 70		3.76	37.1	
(3e) [d]	−60	3.91	3.48	10.4	*ca.* 56	$\delta(CH_3)$ 2.25, 2.18	3.77	36.7	$\delta(CH_3)$ 2.20
(3f) [d]	−80	4.38	3.85	11.7	*b*	$\delta(CH_3)$ 1.55, 1.50	3.65	38.1	$\delta(CH_3)$ 1.58, $^4J(PtH)$ 14.2
(5a) or (5b)	+21	4.16	3.71	13.2	61	$\delta(HCMe{=}C)$ 5.12, q, $J(HH)$ 7.2, $J(PtH)$ 28.0 $\delta(HCMe{=}C)$ 1.97, d, $J(HH)$ 7.2, $J(PtH)$ 6.2 $\delta(MeC{\equiv}C)$ 1.33, $J(PtH)$ 16.0			
(5c) or (5d) [e]	+21	4.13	3.81	13.7	61	$\delta(HCPh{=}C)$ 5.55, $J(PtH)$ 27			

[a] Spectra (100 MHz) measured in $CDCl_3$ unless otherwise stated; chemical shifts (δ) in p.p.m. (±0.01) to high frequency of $SiMe_4$ and coupling constants (J) in Hz (±0.1). H_a and H_e are defined in the text. [b] Not resolved. [c] Obscured by peaks due to solvent impurities. [d] Measured in CD_2Cl_2. [e] Data in accord with spectrum measured at 360 MHz.

and i.r. spectroscopy (Table 4). Furthermore, the structure of complex (3b) has been determined by *X*-ray crystallography (see below).

The $^{31}P-\{^1H\}$ n.m.r. spectra of complexes (3a)—(3g) are very characteristic since they are all AA′BB′ spin systems, giving deceptively simple triplet patterns, with additional couplings to ^{195}Pt and ^{183}W. A typical $^{31}P-\{^1H\}$ n.m.r. spectrum is shown in Figure 1 and the data are given in Table 2. The values of $^1J(PtP_A)$ are consistent with a *trans* configuration of phosphines around the platinum(II) and the $^1J(WP_B)$ values are consistent with the *trans* configuration of phosphines around tungsten(0).[9] $^3J(PtP_B)$ couplings were observed in most cases but not $^3J(WP_A)$ couplings. The $^{31}P-\{^1H\}$ n.m.r. spectra were sharp over the temperature range −60 to +60 °C.

The $^1H-\{^{31}P\}$ n.m.r. spectra for complexes (3a)—(3f) all show a single PCH_2P resonance with ^{195}Pt satellites at +21 °C but at lower temperatures (−60 °C) this was resolved into an AB pattern with one of these resonances coupled to ^{195}Pt (assigned to the pseudo-equatorial hydrogen, H_e) and the other one not observably coupled (assigned to the pseudo-axial hydrogen, H_a): this is a feature we have noted previously[7] and associated with Karplus-type behaviour of the $^3J(PtH)$ couplings. Furthermore, at ambient temperature the methyl resonances for the *p*-tolylacetylides in (3b) and (3e) and methylacetylides in (3c) and (3f) are singlets but at low temperatures (−60 °C) they are resolved into two signals (see Figure 2). Previously, we have observed fluxionality in many of our binuclear complexes, giving rise to a single

Table 4. I.r. absorption maxima (cm^{-1}) [a]

Complex	ν(C≡C)	ν(C≡O) or ν(μ-C≡C)
(3a)	2 110	1 959, 1 848, 1 820
(3b)	2 108	1 973, 1 940(sh), 1 847, 1 785
(3c)	2 140	2 010, 1 940, 1 902, 1 845, 1 820(sh)
(3d) [b]	2 120	1 968, 1 852, 1 815
(3e)	2 120	1 980, 1 950, 1 855, 1 815, 1 790
(3f)	2 145	1 950, 1 850, 1 815
(5a) or (5b) [c]	2 140	2 025, 1 950br
(5c) or (5d) [b]	2 120w	2 021, 1 937br, 1 908

[a] Measured as KBr discs unless otherwise stated (sh = shoulder, br = broad, w = weak). [b] Measured as Nujol mull. [c] 1 610 cm^{-1} tentatively assigned to ν(μ-C≡C).

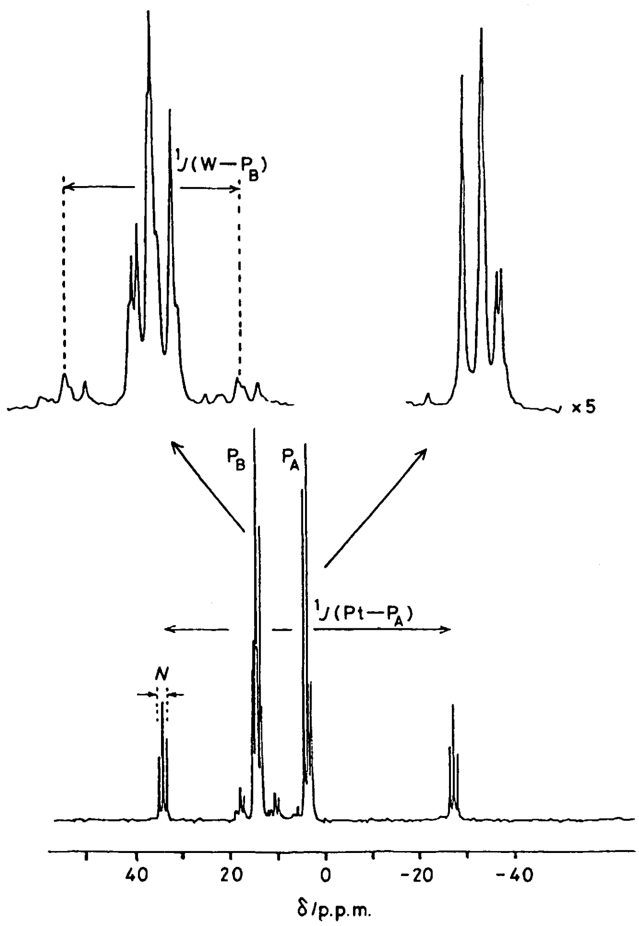


Figure 1. ^{31}P-{^{1}H} N.m.r. spectrum (40.25 MHz) of [(PhC≡C)Pt(μ-C≡CPh)(μ-dppm)$_2$W(CO)$_3$] (3a) in CDCl$_3$ at +21 °C. P$_A$ is bonded to Pt and P$_B$ to W

PC*H*$_2$P resonance at ambient temperatures, and have associated the fluxionality with ring flipping of the M(μ-dppm)$_2$M′ ring or phosphine exchange at one of the metals.[5] The sharp ^{31}P-{^{1}H} n.m.r. spectra, *e.g.* for complex (3b), even at +60 °C indicate that phosphine exchange is very slow on the n.m.r. time-scale. The cause of the fluxionality was suggested by the *X*-ray crystal structure of (3b) (see below) which shows that one of the acetylide ligands is bridging the two metals. We suggest that at low temperatures, in solution, the platinum–tungsten (3a)—(3c) or -molybdenum (3d)—(3f) complexes have the same structure as in the solid state, *i.e.* that one acetylide group is bridging and the other is terminal. At higher temperatures an unusual fluxional process takes place: interconversion of bridging and terminal acetylide ligands as shown in Scheme 3. This process would cause interchange in the environments of the pseudo-axial and pseudo-equatorial hydrogens of the CH$_2$ groups and also interchange the environments of the *p*-tolylacetylide or methylacetylide ligands. The bridging acetylide ligand is important in stopping the methylene-hydrogen interchange at low temperatures (*e.g.* −60 °C); we [3,5] and others [10] have found that a M(μ-dppm)$_2$M′ ring, without another bridging group, undergoes rapid ring flipping even at −80 °C.

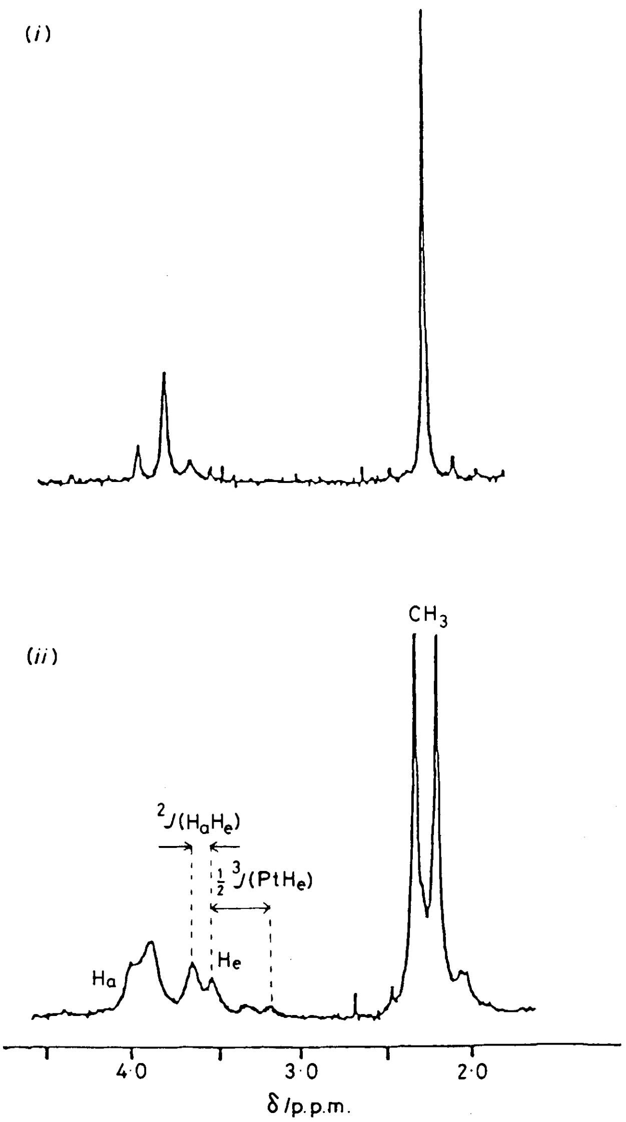
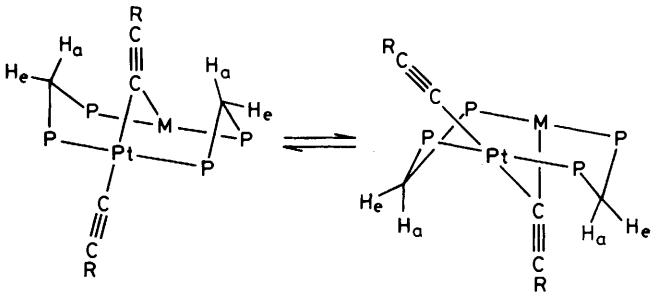


Figure 2. ^{1}H-{^{31}P} N.m.r. spectrum (100 MHz) of [(*p*-MeC$_6$H$_4$C≡C)-Pt(μ-C≡CC$_6$H$_4$Me-*p*)(μ-dppm)$_2$W(CO)$_3$] (3b) in CDCl$_3$ at (*i*) +21 °C and (*ii*) −50 °C

Crystal Structure of [(*p*-MeC$_6$H$_4$C≡C)Pt(μ-C≡CC$_6$H$_4$Me-*p*)(μ-dppm)$_2$W(CO)$_3$] (3b).—The complex (3b) crystallised from benzene–methanol (1 : 3) as maroon plates. The structure is shown in Figure 3 and selected intramolecular distances and angles are in Table 5. The Pt and W moieties are linked by two dppm bridges to give an eight-membered PtP$_4$C$_2$W ring in the 'boat' conformation; the Pt···W distance [3.037(1) Å] is substantially longer than that generally accepted for at Pt–W

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

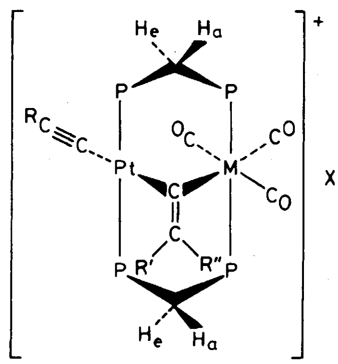
Pt–C(3)	2.000(8)	C(3)–C(4)	1.19(1)	P(1)–Pt–P(3)	171.4(1)	Pt–C(3)–C(4)	176.5(9)
Pt–C(5)	2.094(9)	C(5)–C(6)	1.19(1)	P(1)–Pt–C(5)	87.3(2)	Pt–C(5)–W	84.8(3)
Pt–P(1)	2.307(3)	C(4)–C(11)	1.45(1)	P(3)–Pt–C(5)	90.3(3)	Pt–C(5)–C(6)	136.8(8)
Pt–P(3)	2.302(2)	C(6)–C(21)	1.46(1)	C(3)–Pt–C(5)	166.7(4)	W–C(5)–C(6)	138.4(8)
W–P(2)	2.454(3)	C(14)–Me(1)	1.56(2)	P(2)–W–P(4)	168.9(1)	W–C(7)–O(7)	174(1)
W–P(4)	2.442(2)	C(24)–Me(2)	1.53(2)	P(2)–W–C(5)	85.9(2)	W–C(8)–O(8)	172.4(8)
W–C(7)	2.05(1)	P–CH_2	1.824(9)—1.851(9)	P(4)–W–C(5)	84.1(2)	W–C(9)–O(9)	179.4(9)
W–C(8)	2.04(1)	P–C_6H_5	1.807(5)—1.840(5)	C(5)–W–C(7)	81.6(4)	P(1)–C(1)–P(2)	113.6(5)
W–C(9)	1.92(1)	W ··· C(5)	2.398(9)	C(5)–W–C(8)	109.5(3)	P(3)–C(2)–P(4)	112.2(5)
C(7)–O(7)	1.14(1)	Pt ··· C(8)	2.89(1)	C(7)–W–C(8)	168.7(4)	M–P–CH_2	112.2(3)—113.1(3)
C(8)–O(8)	1.14(1)	Pt ··· W	3.037(1)	C(5)–W–C(9)	166.6(4)		
C(9)–O(9)	1.18(1)						



Scheme 3. Proposed interconversion of bridging and terminal acetylide ligands with ring flipping to account for room-temperature magnetic equivalence of the pseudo-axial (H_a) and pseudo-equatorial (H_e) methylene protons in complexes (3a)—(3f). This also accounts for the equivalence of the Me protons when R = *p*-tolyl or Me. The Ph and CO groups are omitted for clarity

bond (*ca.* 2.8 Å).[11] The two metal centres are asymmetrically bridged by one of the *p*-tolylacetylide groups such that W ··· C(5) is 2.398(9) Å and Pt–C(5) is 2.094(9) Å. The latter distance is in the middle of the range 1.99—2.15 Å generally observed for platinum-carbon σ bonds.[11] The W–C(5) separation is somewhat longer than that (2.1—2.3 Å) found for W–C(alkyl) σ bonds,[11] but does constitute a strong interaction which completes the octahedral co-ordination about the tungsten atom. The positions of the mutually *trans* μ-dppm ligands and the μ-acetylide ligand confine the three carbonyl ligands to the less common *mer* rather than the more usual *fac* arrangement. We note that the W–CO distance *trans* to C(5) is significantly shorter than the two *cis* (Table 5). Uncharacteristically for a semi-bridging acetylide, there is no π interaction of the C≡C acetylenic linkage with the tungsten atom. Indeed, the Pt–C(5)≡C(6) and W–C(5)≡C(6) angles are virtually the same [136.8(8) and 138.4(8)°, respectively], while the C(5)≡C(6)–C(tolyl) angle remains nearly linear [175(1)°] and perpendicular to the PtP_4W plane. Interestingly, the C≡C bond lengths in the bridging and terminal acetylide groups are identical [1.19(1) Å]. There are no unusual bond lengths (Table 5) and there are no significant intermolecular contacts.

Protonation Studies.—It seemed likely that these mixed platinum-tungsten or -molybdenum complexes of type (3) might be protonated and a preliminary $^{31}P-\{^1H\}$ n.m.r. study, in which [(MeC≡C)Pt(μ-C≡CMe)(μ-dppm)$_2$W(CO)$_3$] (3c) in $CDCl_3$ solution was treated with an excess of CF_3CO_2H, gave essentially one phosphorus-containing product showing an AA′BB′ pattern with satellites due to platinum-195 or tungsten-183 coupling. A trifluoroacetate salt was not isolated in a pure form but a hexafluorophosphate salt was prepared by addition of NH_4PF_6 (see Experimental section). The $^{31}P-\{^1H\}$ n.m.r. spectrum of the PF_6^- salt was virtually identical to that of the $CF_3CO_2^-$ salt except for the resonance due to PF_6^-; integration established that the ratio of dppm : PF_6^- in the protonated complex was 2 : 1, as did elemental analysis (C, H, and F) (Table 1). The $^1H-\{^{31}P\}$ n.m.r. spectrum (Table 3) showed that the added proton had become attached to one of the acetylide carbons. In particular, a methyl 1 : 1 doublet at δ 1.97 p.p.m. and a 1 : 3 : 3 : 1 quartet at δ 5.12 p.p.m. due to one proton, both with *J*(HH) = 7.2 Hz, are consistent with the presence of a propylidene [HC(CH_3)=C] group and exclude a co-ordinated propyne group: the *J*(HH) coupling of 7.2 Hz is typical of $^3J(HCCH_3)$ and is too large for a $^4J(cis\text{-}HC{=}CCH_3)$ coupling (typically 0—3 Hz). Thus we suggest that the protonated complex has a bridging propylidene structure (5a) or (5b). We slightly favour (5b) with the added proton *cis* to platinum, rather than (5a), because of the small value of $^3J(PtC{=}CH)$ of 28 Hz (Table 3). For non-bridging alkenyl groups attached to platinum(II), *viz.* of type *trans*-[PtCl(alkenyl)(PPh$_3$)$_2$], the *trans*-$^3J(PtC{=}CH)$ couplings are *ca.* 140 Hz whilst the corresponding values for *cis*-$^3J(PtC{=}CH)$ couplings are *ca.* 70 Hz.[12] A medium-intensity i.r. absorption at 1 610 cm^{-1} (Table 4) may be due to ν(C=C) of the μ-propylidene group. Treatment of the platinum-tungsten phenylacetylide complex (3a) with CF_3CO_2H gave a protonated species which was isolated as the PF_6^- salt and formulated as either (5c) or (5d) (see Experimental section and Tables 1—4 for characterising data). Figure 4 shows the



(5a) R = R′ = Me, R″ = H, M = W, X = PF_6
(5b) R = R″ = Me, R′ = H, M = W, X = PF_6
(5c) R = R′ = Ph, R″ = H, M = W, X = PF_6
(5d) R = R″ = Ph, R′ = H, M = W, X = PF_6
(5e) R = R′ = Ph, R″ = H, M = Mo, X = CF_3CO_2
(5f) R = R″ = Ph, R′ = H, M = Mo, X = CF_3CO_2

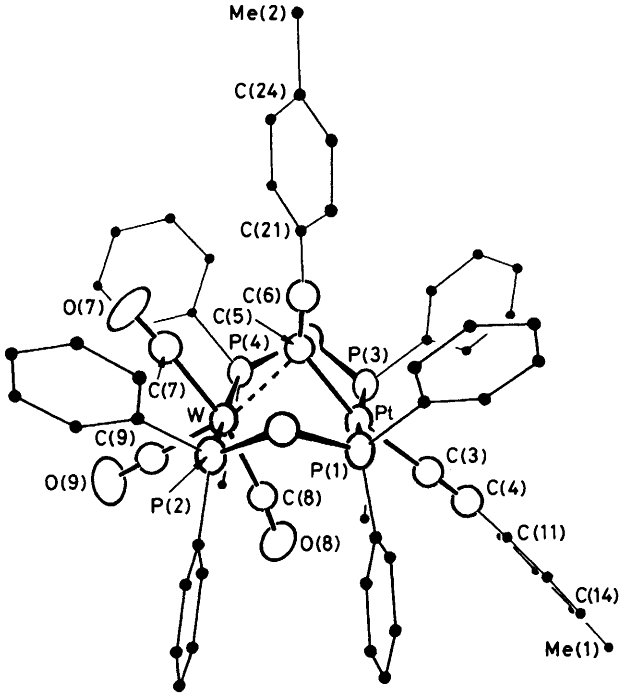


Figure 3. Molecular structure of [(p-MeC$_6$H$_4$C≡C)Pt(μ-C≡CC$_6$H$_4$Me-p)(μ-dppm)$_2$W(CO)$_3$] (3b), showing the principal atomic numbering

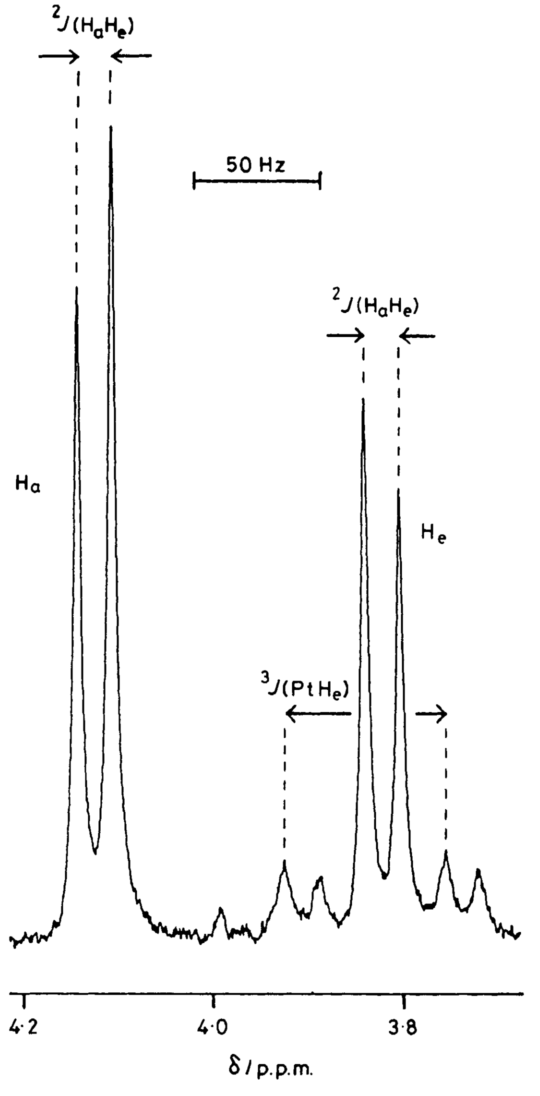


Figure 4. ^{1}H-{^{31}P} N.m.r. pattern (360 MHz) for the PCH$_2$P protons of [(PhC≡C)Pt(μ-C=CHPh)(μ-dppm)$_2$W(CO)$_3$][PF$_6$] (5c) or (5d) at 20 °C in CDCl$_3$ showing the resonances due to H$_e$ and H$_a$: only H$_e$ is coupled to platinum-195 (see Discussion section)

high-field ^{1}H-{^{31}P} n.m.r. pattern of the PCH$_2$P protons of (5c) or (5d): as can be seen, the platinum-195 nucleus is coupled to only one of the methylene hydrogens, there being no detectable coupling to the other. The proton showing coupling to platinum-195 is almost certainly H$_e$, which will have a transoid arrangement (torsion angle *ca.* 180°) with respect to platinum, as depicted in (5c) or (5d) whereas the Pt–P–C–H$_a$ torsion angle will be *ca.* 60°, *i.e.* there is a Karplus-type behaviour for these three-bond coupling constants. These protonated species of type (5) were readily deprotonated by weak bases. Thus treatment of a CDCl$_3$ solution of the protonated methylacetylide complex (5a) or (5b) with an excess of diethylamine gave back the neutral platinum–tungsten complex (3c), characterised by its ^{31}P-{^{1}H} n.m.r. spectrum. Similarly the protonated phenylacetylide complex (5c) or (5d) was deprotonated by methylamine to give back (3a) (as shown in a ^{31}P-{^{1}H} n.m.r. experiment). A preliminary ^{31}P-{^{1}H} n.m.r. experiment showed that treatment of the platinum–molybdenum phenylacetylide complex (3d) with CF$_3$CO$_2$H in CDCl$_3$ gave essentially one product which was not isolated, but is tentatively assigned structure (5e) or (5f): the ^{31}P-{^{1}H} n.m.r. data for this protonated species are given in Table 2.

Experimental

General methods were as previously described in recent papers from this laboratory.[13] The previously unreported complex [(MeC≡C)$_2$Pt(μ-dppm)$_2$AgCl] (2c) was made from *trans*-[Pt(C≡CMe)$_2$(dppm-*P*)$_2$] and [{AgCl(PPh$_3$)}$_4$] in 91% yield in a similar manner to the reported synthesis of the phenylacetylide analogue (2a).[5]

Preparations.—[(PhC≡C)Pt(μ-C≡CPh)(μ-dppm)$_2$W(CO)$_3$] (3a) *from trans*-[Pt(C≡CPh)$_2$(dppm-*P*)$_2$] (1a). The complex *trans*-[Pt(C≡CPh)$_2$(dppm-*P*)$_2$] (0.30 g, 0.26 mmol) was added to a solution of [W(CO)$_3$(NCMe)$_3$] (0.110 g, 0.28 mmol) in benzene (20 cm^3) under dinitrogen. The mixture was boiled under reflux for 1 h and then allowed to cool slowly. After 14 h a yellow solid had separated and this was collected and shown to be [Pt$_2$(C≡CPh)$_4$(μ-dppm)$_2$] (4a) by ^{31}P-{^{1}H} n.m.r. spectroscopy; the yield was 0.087 g (43%). The deep red filtrate was concentrated to *ca.* 5 cm^3, methanol (20 cm^3) added, and the resulting solution refrigerated (−30 °C) for 3 h to give the maroon, crystalline product which was filtered off, washed with methanol, and dried *in vacuo*.

The complex [(p-MeC$_6$H$_4$C≡C)Pt(μ-C≡CC$_6$H$_4$Me-p)(μ-dppm)$_2$W(CO)$_3$] (3b) was made similarly except that the more soluble diplatinum complex (4b) did not crystallise from the cooled reaction mixture; however, by cautious addition of methanol the required mixed platinum–tungsten complex (3b) crystallised out first. The platinum–tungsten methylacetylide complex (3c) was made similarly. The platinum–molybdenum complexes (3d) and (3f) were similarly made from *trans*-[Pt(C≡CR)$_2$(dppm-*P*)$_2$] [(1a) or (1c)] and [Mo(CO)$_3$(cht)] or [Mo(CO)$_4$(1,5-cod)]. Yields and other characterising data are given in Tables 1—4.

Table 6. Fractional atomic co-ordinates for complex (3b) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Pt	0.278 24(3)	$\frac{1}{4}$ *	0.222 05(2)
W	0.495 21(3)	0.342 95(3)	0.354 75(2)
P(1)	0.270 9(2)	0.150 1(2)	0.310 4(1)
P(2)	0.483 1(2)	0.241 8(2)	0.451 4(1)
P(3)	0.288 2(2)	0.333 1(2)	0.122 7(1)
P(4)	0.521 5(2)	0.420 7(1)	0.248 8(1)
C(1)	0.418 8(7)	0.141 0(6)	0.403 4(6)
C(2)	0.448 1(7)	0.367 8(6)	0.148 9(4)
C(3)	0.091 2(7)	0.255 2(6)	0.157 5(4)
C(4)	−0.019 0(8)	0.261 5(6)	0.116 7(6)
C(5)	0.471 1(7)	0.225 0(4)	0.268 7(4)
C(6)	0.535 7(8)	0.173 9(6)	0.258 5(6)
Me(1)	−0.540 2(12)	0.364 0(9)	−0.062 6(8)
Me(2)	0.881 3(14)	−0.066 8(11)	0.235 1(9)
C(11)	−0.150 0(4)	0.284 4(3)	0.068 6(3)
C(12)	−0.245 3(4)	0.239 1(3)	0.075 6(3)
C(13)	−0.370 3(4)	0.264 5(3)	0.033 3(3)
C(14)	−0.400 1(4)	0.335 2(3)	−0.016 2(3)
C(15)	−0.304 8(4)	0.380 4(3)	−0.023 2(3)
C(16)	−0.179 8(4)	0.355 0(3)	0.019 1(3)
C(21)	0.621 9(6)	0.112 4(3)	0.252 9(4)
C(22)	0.724 0(6)	0.139 1(3)	0.240 3(4)
C(23)	0.807 0(6)	0.080 7(3)	0.234 3(4)
C(24)	0.787 8(6)	−0.004 3(3)	0.241 0(4)
C(25)	0.685 7(6)	−0.030 9(3)	0.253 6(4)
C(26)	0.602 7(6)	0.027 4(3)	0.259 5(4)
C(31)	0.154 4(6)	0.154 8(3)	0.348 8(3)
C(32)	0.137 0(6)	0.085 7(3)	0.389 0(3)
C(33)	0.058 9(6)	0.091 7(3)	0.427 6(3)
C(34)	−0.001 9(6)	0.166 8(3)	0.425 9(3)
C(35)	0.015 5(6)	0.235 8(3)	0.385 6(3)
C(36)	0.093 6(6)	0.229 8(3)	0.347 1(3)
C(41)	0.249 3(6)	0.047 1(2)	0.263 6(3)
C(42)	0.321 7(6)	−0.021 6(2)	0.304 6(3)
C(43)	0.300 7(6)	−0.099 1(2)	0.266 1(3)
C(44)	0.207 4(6)	−0.107 7(2)	0.186 5(3)
C(45)	0.135 0(6)	−0.039 0(2)	0.145 5(3)
C(46)	0.156 0(6)	0.038 5(2)	0.184 0(3)
C(51)	0.398 5(6)	−0.265 7(3)	−0.512 2(3)
C(52)	0.374 1(6)	0.202 7(3)	0.555 7(3)
C(53)	0.308 5(6)	0.220 9(3)	0.600 9(3)
C(54)	0.267 5(6)	0.302 2(3)	0.602 6(3)
C(55)	0.292 0(6)	0.365 2(3)	0.559 1(3)
C(56)	0.357 5(6)	0.346 9(3)	0.513 9(3)
C(61)	0.636 1(4)	0.210 7(3)	0.532 4(3)
C(62)	0.713 6(4)	0.274 4(3)	0.580 4(3)
C(63)	0.833 4(4)	0.255 6(3)	0.641 0(3)
C(64)	0.875 7(4)	0.173 2(3)	0.653 6(3)
C(65)	0.798 1(4)	0.109 5(3)	0.605 5(3)
C(66)	0.678 3(4)	0.128 3(3)	0.544 9(3)
C(71)	0.197 0(6)	0.428 5(3)	0.091 8(3)
C(72)	0.209 6(6)	0.480 0(3)	0.034 6(3)
C(73)	0.145 9(6)	0.556 1(3)	0.013 6(3)
C(74)	0.069 6(6)	0.580 6(3)	0.049 9(3)
C(75)	0.057 0(6)	0.529 0(3)	0.107 1(3)
C(76)	0.120 7(6)	0.453 0(3)	0.128 1(3)
C(81)	0.247 3(6)	0.270 1(3)	0.031 0(2)
C(82)	0.318 6(6)	0.198 7(3)	0.037 8(2)
C(83)	0.290 9(6)	0.148 4(3)	−0.030 0(2)
C(84)	0.192 0(6)	0.169 6(3)	−0.104 7(2)
C(85)	0.120 7(6)	0.241 1(3)	−0.111 5(2)
C(86)	0.148 4(6)	0.291 3(3)	−0.043 6(2)
C(91)	0.470 9(6)	0.529 6(2)	0.223 7(3)
C(92)	0.507 1(6)	0.573 4(2)	0.171 7(3)
C(93)	0.473 1(6)	0.657 0(2)	0.153 8(3)
C(94)	0.402 9(6)	0.696 7(2)	0.187 8(3)
C(95)	0.366 7(6)	0.652 9(2)	0.239 7(3)
C(96)	0.400 7(6)	0.569 3(2)	0.257 7(3)
C(101)	0.685 5(4)	0.433 8(3)	0.265 5(3)
C(102)	0.734 8(4)	0.398 7(3)	0.216 2(3)
C(103)	0.860 5(4)	0.412 1(3)	0.233 6(3)
C(104)	0.937 0(4)	0.460 6(3)	0.300 4(3)
C(105)	0.887 7(4)	0.495 8(3)	0.349 8(3)
C(106)	0.761 9(4)	0.482 4(3)	0.332 3(3)
C(7)	0.680 8(9)	0.310 4(6)	0.398 7(6)
O(7)	0.785 7(6)	0.297 3(6)	0.427 9(4)
C(8)	0.322 5(8)	0.390 6(6)	0.330 3(6)
O(8)	0.232 6(6)	0.422 6(4)	0.324 1(4)
C(9)	−0.555 6(8)	0.432 2(6)	0.432 4(6)
O(9)	0.593 6(7)	0.486 6(4)	0.480 8(4)

* Co-ordinate fixed.

$[(PhC{\equiv}C)Pt(\mu\text{-}C{\equiv}CPh)(\mu\text{-dppm})_2Mo(CO)_3]$ (3d) *from* $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2AgCl]$ (2a). A mixture of the platinum–silver complex (2a) (0.20 g, 0.15 mmol) and $[Mo(CO)_3(cht)]$ (0.044 g, 0.16 mmol) in benzene (5 cm^3) was heated under reflux for 1.5 h to give a red solution and a grey precipitate. The mixture was filtered under gravity and the filtrate treated with methanol (20 cm^3) and then put aside at room temperature for 30 min. The orange-red crystals were then filtered off, washed with methanol, and dried *in vacuo*.

The platinum–molybdenum complexes (3e) and (3f) were made similarly. The platinum–tungsten complex (3a) was also made in this way from the platinum–silver complex (2a) and $[W(CO)_3(NCMe)_3]$. Yields and other characterising data are given in Tables 1—4.

$[(MeC{\equiv}C)Pt(\mu\text{-}C{=}CHMe)(\mu\text{-dppm})_2W(CO)_3][PF_6]$ (5a) *or* (5b). Trifluoroacetic acid (35 μl, 0.31 mmol) was added to a solution of $[(MeC{\equiv}C)Pt(\mu\text{-}C{\equiv}CMe)(\mu\text{-dppm})_2W(CO)_3]$ (3c) (0.20 g, 0.15 mmol) in chloroform (3 cm^3) to give a dark green solution which was filtered and then evaporated to dryness under reduced pressure. The green residue was dissolved in acetone (10 cm^3) and the resultant solution treated with NH_4PF_6 (0.1 g). The mixture was then warmed (*ca.* 40 °C), filtered, and evaporated to dryness under reduced pressure. Water (10 cm^3) was added to the residue and the resulting yellow-brown solid filtered off and then dried *in vacuo*. The solid was recrystallised from chloroform–hexane.

The complex $[(PhC{\equiv}C)Pt(\mu\text{-}C{=}CHPh)(\mu\text{-dppm})_2W(CO)_3][PF_6]$ (5c) or (5d) was made similarly. Yields and other characterising data are given in Tables 1—4.

Crystallography.—*Crystal data.* $C_{71}H_{58}O_3P_4PtW$, M = 1 462.1, monoclinic, a = 11.847(3), b = 16.023(4), c = 18.351(4) Å, β = 116.23(1)°, U = 3 125(1) Å^3, space group $P2_1$, Z = 2, D_c = 1.55 g cm^{-3}, $F(000)$ = 1 440, graphite-monochromated Mo-K_α radiation, λ = 0.710 69 Å, and μ(Mo-K_α) = 42.8 cm^{-1}.

Structure determination. Measurements were made on a crystal of dimensions 0.09 × 0.25 × 0.34 mm, using a Syntex $P2_1$ diffractometer. Cell dimensions and their standard deviations were obtained by least-squares treatment of the setting angles for 15 reflections having $35 < 2\theta < 40°$. Intensities of all independent reflections with $4 < 2\theta < 45°$ were measured in the ω—2θ scan mode using a scan speed, according to a pre-scan intensity, between 2 and 29° min^{-1}, and with the scans running from 1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$. The structure analysis used the 4 043 reflections having

$I > 2\sigma(I)$, leaving 134 reflections as 'unobserved.' Corrections were applied for Lorentz, polarisation, and transmission factors ($A^* = 1.46$—2.62 for the full data set).

Solution by Patterson and difference syntheses was followed by full-matrix least-squares refinement with anisotropic thermal parameters for Pt, W, P, and O atoms using the SHELX program system.[14] All aromatic rings were refined as rigid groups with idealised D_{6h} geometry, the C atoms having individual isotropic thermal parameters and C–C distances of 1.395 Å. All H atoms, many of which were found in difference maps, were included in the calculation at idealised positions with C–H fixed at 1.08 Å; their isotropic thermal parameters were treated as three single parameters (for aromatic, methyl, or methylene H). The refinement for 248 parameters converged to $R = 0.026$ and $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o| = 0.026$, employing the weighting scheme $w = 1/(\sigma^2 F_o + 0.0002\ F_o^2)$. Refinement of the alternative enantiomorphic specification gave significantly larger R factors. A final difference map was featureless. Complex neutral-atom scattering factors were calculated from the analytical approximation and coefficients given in ref. 15. The final atomic coordinates and their standard deviations are listed in Table 6.

Acknowledgements

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