Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 12.[1] Reaction of the Complexes $[PtW(\mu\text{-}CC_6H_4\text{-}Me\text{-}4)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ with Carbon Monoxide. Crystal Structure of $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)]$ †

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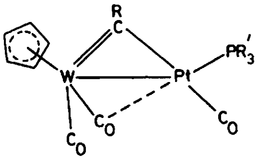
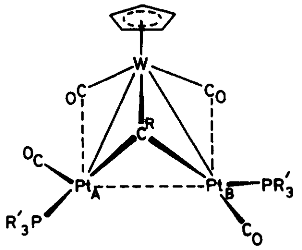
Di- and tri-metal complexes $[PtW(\mu\text{-}CR)(CO)_3(PR'_3)(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4; PR'_3 = PMe_3, PMe_2Ph, or PPh_3) and $[Pt_2W(\mu_3\text{-}CR)(CO)_4(PR'_3)_2(\eta\text{-}C_5H_5)]$ (PR'_3 = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, or PEt_3) have been isolated by treating toluene solutions of the compounds $[PtW(\mu\text{-}CR)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)]$ with CO gas at 1 bar and room temperature. N.m.r. data (^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$, and $^{195}Pt\text{-}\{^1H\}$) for the new compounds are reported and a single-crystal *X*-ray diffraction study has been carried out on the complex $[Pt_2W(\mu_3\text{-}CR)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)]$. The crystals are monoclinic, space group $P2_1/c$ (no. 14), $Z = 4$, in a unit cell with $a = 14.932(13)$, $b = 11.438(11)$, $c = 26.394(24)$ Å, $\beta = 97.42(7)°$. Poor crystal quality resulted in refinement to R 0.075 (R' 0.080) for 2 488 reflections to $2\theta \leqslant 40°$ collected at ambient temperature. The study established that the molecular structure is based on a Pt_2W metal triangle, having a long Pt ··· Pt distance [2.989(3) Å], and capped by a CC_6H_4Me-4 group with the ligated carbon atom equidistant from all three metals. The terminal phosphine and carbonyl ligands on each Pt atom are unsymmetrically *transoid* with respect to the Pt ··· Pt vector, and the two carbonyl ligands on the W atom are semi-bridging to the Pt atoms, again unsymmetrically. The molecule possesses no symmetry. The nature of the Pt ··· Pt interaction, and the relationship between the complexes $[Pt_2W(\mu_3\text{-}CR)(CO)_4(PR'_3)_2(\eta\text{-}C_5H_5)]$ and previously reported di- and tri-platinum complexes with bridging alkyne ligands, are discussed.

We have previously shown[2] that the dimetallacyclopropene rings present in the metal complexes $[PtW(\mu\text{-}CR)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me$-4; PR'_3 = PMe_3, PMe_2Ph, $PMePh_2$, or PEt_3) readily react with $[Fe_2(CO)_9]$ to afford trimetallic compounds containing ' tetrahedrane ' core structures $FeWPt(\mu_3\text{-}CR)$ in good yield. However, in the reaction between $[PtW(\mu\text{-}CR)(CO)_2(PEt_3)_2(\eta\text{-}C_5H_5)]$ and $[Fe_2(CO)_9]$ which gave $[FePtW(\mu\text{-}CR)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$, a minor product was formed which did not contain iron. Moreover, a related species with a similar i.r. spectrum was observed as one of three products of a complex reaction between the dimetal compound $[PtW(\mu\text{-}CR)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ and $[Co_2(CO)_8]$, a further product being the dicobalt-tungsten compound $[Co_2W(\mu\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$.[3] Since $[Co_2(CO)_8]$ and $[Fe_2(CO)_9]$ were producing variable amounts of structurally similar compounds in reactions with some of the complexes $[PtW(\mu\text{-}CR)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)]$ and, moreover, since these unidentified products did not contain cobalt or iron, it seemed likely that they were formed by reaction of the platinum-tungsten complexes with free carbon monoxide released from the iron and cobalt carbonyls. These observations prompted a study of the effect of CO on the species $[PtW(\mu\text{-}CR)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)]$.

RESULTS AND DISCUSSION

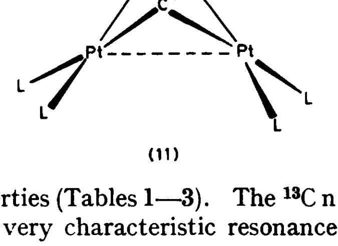
A stream of carbon monoxide gas reacts at room temperature with a toluene solution of $[(\eta\text{-}C_5H_5)(OC)_2\overline{W(\mu\text{-}CC_6H_4Me\text{-}4)Pt}(PMe_3)_2]$ to give a chromatographically (alumina) separable mixture of three products. The first species to be eluted from the column was formulated as $[(\eta\text{-}C_5H_5)(OC)_2\overline{W(\mu\text{-}CR)Pt}(CO)(PMe_3)]$ (1), on the basis of microanalysis and spectroscopic properties (Tables 1—3). The ^{13}C n.m.r. spectrum showed the very characteristic resonance for the μ-CR group at δ 330 p.p.m. with the expected $^{195}Pt\text{-}^{13}C$ coupling (728 Hz).[4] It was also evident from this





R = C_6H_4Me-4

	PR'_3		PR'_3
(1)	PMe_3	(6)	PMe_3
(2)	PMe_2Ph	(7)	PMe_2Ph
(3)	$PMePh_2$	(8)	$PMePh_2$
(4)	PPh_3	(9)	PPh_3
(5)	PEt_3	(10)	PEt_3



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† μ-[Dicarbonyl(η-cyclopentadienyl)tungstenio]-μ_3-*p*-tolylmethylidyne-bis[carbonyl(methyldiphenylphosphine)platinum]-(2 *Pt–W*).

TABLE 1

Analytical [a] and physical data for the platinum–tungsten complexes

Complex	M.p.[b] (θ_c/°C)	Colour	Yield [c] (%)	ν(CO) [d]/cm^{-1}	Analysis (%)	
					C	H
(1) $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)(\eta\text{-}C_5H_5)]$	110—112	Pink	18	2 033vs, 1 939s, 1 865m (sh), 1 845m	32.3 (32.2)	3.0 (3.2)
(2) $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_2Ph)(\eta\text{-}C_5H_5)]$		Red	10	2 016s, 1 939m, 1 843m, br	37.6 (37.5)	3.2 (3.0)
(4) $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PPh_3)(\eta\text{-}C_5H_5)]$ [e]		Red	40	2 027s, 1 938s, 1 857m, br		
(6) $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_3)_2(\eta\text{-}C_5H_5)]$	128—134	Orange	40	2 003s, 1 989s, 1 857m, br, 1 763m, br	26.9 (27.4)	3.4 (3.0)
(7) $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ [f]	136—140	Orange	41	1 993s, 1 980s, 1 729m	34.3 (34.3)	3.2 (3.0)
(8) $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)]$ [f]	141—145	Dark orange	43	[g] 1 999vs, 1 839s, br, 1 746m, br	40.5 (40.3)	3.2 (3.0)
(9) $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PPh_3)_2(\eta\text{-}C_5H_5)]$ [h]	112—115	Red	27	2 003s, 1 983s, 1 967s, 1 923s, 1 864m, br, 1 784m, br	48.2 (47.6)	3.6 (3.2)
(10) $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PEt_3)_2(\eta\text{-}C_5H_5)]$	160—169	Red	10	1 990s, 1 829m, 1 732m	32.1 (31.9)	3.6 (3.2)

[a] Calculated values are given in parentheses. [b] With decomposition. [c] Based on tungsten. [d] In methylcyclohexane, unless otherwise stated. [e] Compound not obtained analytically pure due to contamination with PPh_3. [f] Crystallised with 0.2 molecule CH_2Cl_2. [g] In dichloromethane. [h] Crystallised with ½ molecule PhMe.

TABLE 2

Phosphorus-31 and platinum-195 n.m.r. data [a] for the platinum–tungsten complexes

Compound		^{31}P [b] (δ)		^{195}Pt [c] (δ)
(1) [d]		−17.1 [s, J(PtP) 3 471, J(WP) 44]		219.3 [d, J(PPt) 3 467, J(WPt) 112]
(2) [e]		−6.1 [s, J(PtP) 3 506]		
(4) [d]		27.5 [s, J(PtP) 3 576]		161.2 [d, J(PPt) 3 579]
(6) [d]	B	−16.3 [s, J(PtP) 3 061, 36]	B	−2.7 [d of d, J(PPt) 3 061, 29; J(PtPt) 786, J(WPt) 72]
	A	−24.5 [s, J(PtP) 3 354, 27]	A	−59.7 [d of d, J(PPt) 3 353, 37; J(WPt) 78]
(7) [d]	B	−7.6 [s, J(PtP) 3 084, 36]	[e] B	19.5 [d of d, J(PPt) 3 045, 25; J(PtPt) 772]
	A	−15.9 [s, J(PtP) 3 342, 29]	A	−77.6 [d of d, J(PPt) 3 362, 32; J(PtPt) 772]
(8) [e]	B	9.7 [s, J(PtP) 3 110, 32]	B	26.5 [d, J(PPt) 3 110, J(PtPt) 795]
	A	0.3 [s, J(PtP) 3 369, 25]	A	−105.5 [d of d, J(PPt) 3 368, 36; J(PtPt) 795]
(9) [d]	B	29.5 [s, J(PtP) 3 129, 37]		
	A	16.1 [s, J(PtP) 3 282, 15]		
(10) [d]		−7.0 [d, J(PP) 2, J(PtP) 3 347, 34]		−63.8 [d, J(PPt) 3 078, 32; J(PtPt) 696, J(WP) 82]
		−18.8 [d, J(PP) 2, J(PtP) 3 075, 28]		134.2 [d, J(PPt) 3 346, 29; J(PtPt) 696, J(WP) 80]

[a] Hydrogen-1-decoupled, chemical shifts in p.p.m., coupling constants in Hz. In the diplatinum complexes the letters A and B refer to particular platinum nuclei (see text, and the structural formula). [b] Chemical shifts to high frequency of 85% H_3PO_4 (external). [c] Chemical shifts are to high frequency of $\Xi(^{195}Pt)$ 21.4 MHz. [d] Measured in $[^2H_1]$chloroform. [e] Measured in $[^2H_2]$-dichloromethane–dichloromethane.

spectrum that a Pt(CO) group [δ 198 p.p.m., J(PtC) 1 798 Hz] was present.[5] The ^{31}P and ^{195}Pt n.m.r. spectra (Table 2) confirmed the presence of a $Pt(PMe_3)$ group. Moreover, the magnitude of the observed ^{31}P–^{195}Pt coupling (3 467 Hz) and the observation of W satellite peaks on the singlet resonance in the ^{31}P spectrum is in accord with a structure in which the PMe_3 ligand is *transoid* to the metal–metal bond. Thus in the reaction of $[(\eta\text{-}C_5H_5)(OC)_2W(\mu\text{-}CR)Pt(PMe_3)_2]$ with CO it is the phosphine ligand *transoid* to the bridging alkylidyne group which is replaced. A similar substitution pattern has been observed [6] in reactions of complexes containing bridging alkylidene groups. For example, $[(OC)_5Cr\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ reacts with $CNBu^t$ with replacement of the trimethylphosphine group *transoid* to the bridging carbon atom by t-butyl isocyanide. Evidently in these dimetalla-cyclopropene and -cyclopropane ring complexes the bridging carbon atoms have a very strong *trans*-directing influence.

The second product which was eluted from the chromatography column was the diplatinumtungsten compound (6), discussed with related species below, while the third product was the η^2-ketenyl complex $[W\{\eta^2\text{-}C(C_6H_4Me\text{-}4)=C=O\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$.[7] The latter species is evidently formed in a side-reaction between liberated PMe_3 and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$.

The compounds $[PtW(\mu\text{-}CR)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)]$ ($PR'_3 = PMe_2Ph$ or PPh_3) reacted with CO in a similar manner to $[PtW(\mu\text{-}CR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ giving the dimetal species (2) and (4), and the trimetal complexes (7) and (9), respectively. In contrast, only the trimetal compound (8) was isolated in the reaction of CO with $[PtW(\mu\text{-}CR)(CO)_2(PMePh_2)_2(\eta\text{-}C_5H_5)]$, there being no evidence for complex (3).

As a consequence of these experiments, it was established that compounds (2) and (7) were the hitherto unidentified products of the reaction between $[PtW(\mu\text{-}CR)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ and $[Co_2(CO)_8]$, referred to earlier. It was also shown that (10) was the non-iron-containing product of the reaction of $[Fe_2(CO)_9]$ with $[PtW(\mu\text{-}CR)(CO)_2(PEt_3)_2(\eta\text{-}C_5H_5)]$. The dimetal species (5), which might have been an expected product, was not isolated. Interestingly, the triphenylphosphine-containing complex (9) has also been observed [8] as a product of the reaction of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and the anion $[Fe_2Pt_2(\mu\text{-}H)(CO)_8(PPh_3)_2]^-$. Evidently the trimetal complexes (6)—(10) are thermodynamically relatively stable, and form as side-products in a number of reactions.

The i.r. spectra of (1), (2), and (4) all show CO stretching frequencies at *ca.* 1 850 cm^{-1}, indicative of the presence of semi-bridging carbonyl ligands.[4] The trimetal complexes (6)—(10) all show in their i.r. spectra (Table 1) a band near 1 750 cm^{-1} in the bridging CO region. Low solubility, particularly for the PPh_3 derivative, high molecular weight, and complex splitting patterns make ^{13}C n.m.r. data difficult to obtain for complexes (6)—(9). However, four carbonyl signals are observed (Table 3), which are distinguishable in favourable cases by ^{195}Pt and ^{183}W satellites. A signal at *ca.* 230 p.p.m. may be assigned [2,9] to a triply metal-bridging CC_6H_4Me group, with coupling observed to one ^{31}P and one ^{195}Pt only.

The structures of the trimetal compounds were not established until an *X*-ray diffraction study was carried out on one member of this class. Fortunately, single crystals of (8) were obtained; the results of the *X*-ray work are summarised in Tables 4 and 5, and the molecular structure is shown in the Figure.

The molecule is strangely asymmetric, despite the fact that the triply bridging C(1) atom is equidistant from

TABLE 3

Hydrogen-1 and carbon-13 n.m.r. data [a] for the platinum–tungsten complexes

Complex	^1H (δ)	^{13}C [b] (δ)
(1) $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_3)(\eta\text{-}C_5H_5)]$ [c]	1.34 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 35], 2.40 (s, 3 H, Me-4), 5.46 (s, 5 H, C_5H_5), 6.68—7.04 (m, 4 H, C_6H_4)	330.3 [μ-C, *J*(PtC) 728], 223.0 [WCO, *J*(PtC) 30], 222.7 [WCO, *J*(PtC) 34], 198.2 [PtCO, *J*(PtC) 1 798], 161.6 [d, C^1 (C_6H_4), *J*(PC) 5, *J*(PtC) 58, *J*(WC) 20], 134.1, 127.4, 121.1 (C_6H_4), 91.3 (C_5H_5), 21.0 (Me-4), 17.5 [d, MeP, *J*(PC) 32, *J*(PtC) 44]
(2) $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PMe_2Ph)(\eta\text{-}C_5H_5)]$ [d,e]	1.57 [d, 6 H, MeP, *J*(PH) 10, *J*(PtH) 35], 2.35 (s, 3 H, Me-4), 5.45 (s, 5 H, C_5H_5), 6.42—6.84 (m, 4 H, C_6H_4)	330.5 (μ-C), 223.3 [WCO, *J*(PtC) 37], 199.9 (CO), 161.8 [C^1 (C_6H_4), *J*(PtC) 24], 134—122 (C_6H_4, Ph), 92.3 (C_5H_5), 21.2 (Me-4), 16.5 [d, MeP, *J*(PC) 32, *J*(PtC) 44]
(4) $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PPh_3)(\eta\text{-}C_5H_5)]$ [f,g]	2.06 (s, 3 H, Me-4), 5.31 (s, 5 H, C_5H_5), 6.02—6.32 (m, 4 H, C_6H_4), 6.6—8.0 (m, 30 H, Ph)	326.5 (μ-C), 222.5 (WCO), 198.2 [PtCO, *J*(PtC) 1 611], 159.7 [C^1 (C_6H_4)], 142—121 (C_6H_4, Ph), 91.8 (C_5H_5), 20.9 (Me-4)
(6) $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_3)_2(\eta\text{-}C_5H_5)]$ [c]	1.37 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 32], 1.51 [d, 9 H, MeP, *J*(PH) 11, *J*(PtH) 26], 2.30 (s, 3 H, Me-4), 5.04 (s, 5 H, C_5H_5), 6.88—7.06 (m, 4 H, C_6H_4)	240.8 [WCO, *J*(WC) 170], 235.7 [WCO, *J*(WC) 153], 233.6 [d, μ_3-C, *J*(PC) 42], 197.3 [PtCO, *J*(PtC) 1 456], 181.9 [PtCO, *J*(PtC) 1 697], 161.0 [C^1 (C_6H_4)], 132.6, 127.8, 127.1 (C_6H_4), 91.3 (C_5H_5), 20.9 (Me-4), 17.4 [d, MeP, *J*(PC) 27, *J*(PtC) 34], 14.7 [d, MeP, *J*(PC) 32, *J*(PtC) 34]
(7) $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ [d,g]	1.20—1.92 (m, 12 H, MeP), 2 32 (s, 3 H, Me-4), 4.99 (s, 5 H, C_5H_5), 6.92—7.12 (m, 4 H, C_6H_4), 7.2—7.8 (m, 10 H, Ph)	238.4 [WCO, *J*(WC) 146], 235.0 [d, WCO, *J*(PC) 7, *J*(PtC) 356], 234.2 [d, μ_3-C, *J*(PC) 41, *J*(PtC) 570], 197.6 [PtCO, *J*(PtC) 1 465], 181.8 [PtCO, *J*(PtC) 1 718], 161.1 [C^1 (C_6H_4)], 141—125 (C_6H_4, Ph), 91.3 (C_5H_5); 20.9 (Me-4), 16.4 [d, MeP, *J*(PC) 29, *J*(PtC) 40], 15.6 [d, MeP, *J*(PC) 29, *J*(PtC) 27], 14.3 [d, MeP, *J*(PC) 27, *J*(PtC) 31], 12.8 [d, MeP, *J*(PC) 32, *J*(PtC) 29]
(8) $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)]$ [d,g]	1.56 [d, 3 H, MeP, *J*(PH), 9, *J*(PtH) 31], 2.13 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 27], 2.28 (s, 3 H, Me-4), 4.96 (s, 5 H, C_5H_5), 6.8—7.0 (m, 4 H, C_6H_4), 7.2—7.5 (m, 20 H, Ph)	239.7 [WCO, *J*(WC) 143], 237.3 [d, μ_3-C, *J*(PC) 42, *J*(PtC) 580], 236.5 [d, WCO, *J*(PC) 7], 200.4 [PtCO, *J*(PtC) 1 479], 184.6 [PtCO, *J*(PtC) 1 735], 163.8 [C^1 (C_6H_4)], 140—125 (C_6H_4, Ph), 91.4 (C_5H_5), 21.0 (Me-4), 14.3 [d, MeP, *J*(PC) 29, *J*(PtC) 30], 13.8 [d, MeP, *J*(PC) 26, *J*(PtC) 48]
(9) $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PPh_3)_2(\eta\text{-}C_5H_5)]$ [f,g]	2.37 (s, 3 H, Me-4), 4.92 (s, 5 H, C_5H_5), 6.55—6.72 (m, 4 H, C_6H_4), 6.8—8.0 (m, 30 H, Ph)	231.5 (br, WCO, μ_3-C), 197.9 [d, PtCO, *J*(PC) 8, *J*(PtC) 1 508], 182.4 [PtCO, *J*(PtC) 1 746], 159.5 [C^1 (C_6H_4)], 141—126 (C_6H_4, Ph), 90.5 (C_5H_5), 20.9 (Me-4)
(10) $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PEt_3)_2(\eta\text{-}C_5H_5)]$ [c]	0.75—1.20 (m, 18 H, MeP), 1.50—2.12 (m, 12 H, CH_2), 2.28 (s, 3 H, Me-4), 4.95 (s, 5 H, C_5H_5), 6.88—7.04 (m, 4 H, C_6H_4)	

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Hydrogen-1 decoupled to high frequency of $SiMe_4$. [c] In $[^2H_1]$-chloroform. [d] Hydrogen-1 spectrum measured in $[^2H_2]$dichloromethane. [e] Carbon-13 spectrum measured in $[^2H_6]$acetone. [f] Hydrogen-1 spectrum measured in $[^2H_1]$chloroform. [g] Carbon-13 spectrum measured in $[^2H_2]$dichloromethane–CH_2Cl_2.

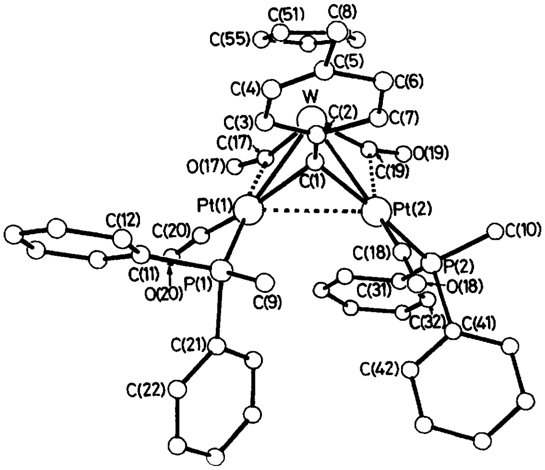
the three metal atoms, and that the bond to the tolyl ligand lies perpendicular to the metal-atom plane. Unfortunately, because of crystal problems, the structure was not very accurately determined, but among the essential features which were established with certainty the following are noteworthy. (*i*) The two Pt atoms each carry one terminal carbonyl ligand, and these are in a *transoid*, but inequivalent, relationship to the Pt–Pt vector (Table 5). (*ii*) The other two carbonyl groups are attached to the W atom but are semi-bridging to the Pt atoms, again not equivalently, and, even more remarkably, the interplanar angles between the metal-atom plane and the bridging carbonyl planes are different [for C(17) the angle is 120°, for C(19), 137°]. (*iii*) The phosphine ligands likewise adopt a *transoid*, but inequivalent, relationship to the Pt–Pt vector, and the phosphines have no symmetry relationship to one another either in the mode of attachment of the methyl and phenyl ligands to the phosphorus atom or in the twist of the rings relative to the P–C bond directions.

TABLE 4

Atomic positional parameters (fractional co-ordinates) for $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)]$ (8), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt(1)	0.185 88(11)	0.546 77(14)	0.193 76(6)
Pt(2)	0.190 26(11)	0.806 94(14)	0.183 83(6)
W	0.040 21(11)	0.687 71(15)	0.210 03(7)
P(2)	0.189 7(8)	0.920 8(10)	0.110 3(5)
P(1)	0.334 4(8)	0.493 3(10)	0.219 0(5)
C(1)	0.173(3)	0.688(4)	0.240 4(14)
C(2)	0.215(3)	0.695(4)	0.297 4(15)
C(3)	0.232(3)	0.599(4)	0.326 0(15)
C(4)	0.267(4)	0.619(5)	0.381(2)
C(5)	0.270(4)	0.715(4)	0.399(2)
C(6)	0.254(4)	0.821(5)	0.374(2)
C(7)	0.226(3)	0.813(4)	0.319(2)
C(8)	0.309(4)	0.740(6)	0.458(2)
C(11)	0.343(3)	0.346(2)	0.251 1(12)
C(12)	0.386(2)	0.327(2)	0.300 4(12)
C(13)	0.392(2)	0.214(2)	0.320 8(12)
C(14)	0.354(2)	0.120(2)	0.291 8(12)
C(15)	0.310(2)	0.139(2)	0.242 5(12)
C(16)	0.305(2)	0.252(2)	0.222 1(12)
C(21)	0.393(2)	0.471(3)	0.162 8(11)
C(22)	0.465(2)	0.393(3)	0.163 4(11)
C(23)	0.510(2)	0.382(3)	0.120 5(11)
C(24)	0.483(2)	0.448(3)	0.076 9(11)
C(25)	0.411(2)	0.526(3)	0.076 3(11)
C(26)	0.366(2)	0.538(3)	0.119 2(11)
C(9)	0.415(4)	0.581(5)	0.257(2)
C(31)	0.140(2)	0.858(3)	0.052 0(10)
C(32)	0.120(2)	0.924(3)	0.007 5(10)
C(33)	0.083(2)	0.870(3)	−0.037 8(10)
C(34)	0.065(2)	0.750(3)	−0.038 5(10)
C(35)	0.084(2)	0.684(3)	0.006 0(10)
C(36)	0.122(2)	0.738(3)	0.051 3(10)
C(41)	0.304(2)	0.952(3)	0.095 2(11)
C(42)	0.357(2)	0.857(3)	0.084 6(11)
C(43)	0.445(2)	0.875(3)	0.074 0(11)
C(44)	0.480(2)	0.988(3)	0.073 9(11)
C(45)	0.427(2)	1.083(3)	0.084 5(11)
C(46)	0.339(2)	1.065(3)	0.095 1(11)
C(10)	0.138(4)	1.064(5)	0.113(2)
C(17)	0.017(3)	0.582(4)	0.152(2)
O(17)	−0.019(3)	0.510(3)	0.121 2(13)
C(18)	0.306(4)	0.847(4)	0.209(2)
O(18)	0.381(3)	0.867(3)	0.220 0(13)
C(51)	−0.011(2)	0.636(3)	0.288 6(11)
C(52)	−0.010(2)	0.760(3)	0.284 6(10)
C(53)	−0.071(2)	0.793(3)	0.241 6(10)
C(54)	−0.111(2)	0.690(3)	0.218 9(10)
C(55)	−0.074(2)	0.593(3)	0.247 9(10)
C(19)	0.028(4)	0.806(5)	0.161(2)
O(19)	−0.004(2)	0.883(3)	0.132 5(12)
C(20)	0.155(3)	0.439(5)	0.144(2)
O(20)	0.150(3)	0.369(4)	0.114(2)
C(8) *	0.814(12)	0.722(15)	0.053(7)
Cl(81) *	0.752(7)	0.730(10)	0.089(5)
Cl(82) *	0.811(7)	0.672(9)	0.006(4)
Cl(83) *	0.756(9)	0.811(11)	0.067(5)

* Solvent molecule. The final electron-density difference synthesis showed residual peaks corresponding to *ca.* 0.2 molecule of CH_2Cl_2 per molecule of complex, disordered between two positions but with one chlorine position common to both.



Molecular structure of $[Pt_2W(\mu_3\text{-}CC_8H_4Me\text{-}4)(CO)_4(PMePh_2)_2\text{-}(\eta\text{-}C_5H_5)]$ (8), showing the atom numbering

(*iv*) In viewing the structure along the Pt(1)–Pt(2) direction, the torsion angles between the *transoid* pairs of ligands are not equal [C(20)–Pt(1)–Pt(2)–C(18), −123°; P(1)–Pt(1)–Pt(2)–P(2), 100°], neither are the *cisoid* pairs of ligands truly eclipsed [C(20)–Pt(1)–Pt(2)–P(2), −16°; P(1)–Pt(1)–Pt(2)–C(18), −7°]. Indeed, the projection of the angle C(20)–Pt(1)–P(1) overlaps that of the angle P(2)–Pt(2)–C(18) by 100°. Furthermore, if the plane defined by the atoms W, C(1), C(2), C(5), and C(8) were regarded as a pseudo-symmetry plane for the central skeleton of the molecule, corresponding pairs of atoms show very considerable differences in their distances from this plane: Pt(1) −1.40, Pt(2) 1.59; C(20) −2.49, C(18) 2.08; O(20) −3.19, O(18) 2.35; P(1) −1.94, P(2) 3.12; C(17) −1.03, C(19) 1.48; O(17) −1.78, O(19) 2.42 Å.

The interatomic distances in the structure call for no comment except in the case of Pt(1)–Pt(2) which, at 2.989(3) Å, coupled with the observation that each of these Pt atoms has a 16-electron configuration in the absence of any direct metal–metal bond, strongly suggests that there is little or no direct metal–metal interaction. We have observed earlier,[10] in our study of the compound $[Pt_3(\mu\text{-}PhC_2Ph)_2(PEt_3)_4]$ which contains an open arrangement of Pt atoms (Pt · · · Pt 2.904 Å) with the acetylenic moieties transversely bridging pairs of atoms, that a Pt–Pt distance of *ca.* 2.9 Å will occur inevitably if two metal atoms are bonded to an alkyne using orthogonal π orbitals of the alkyne as electron donors. Further evidence of similar interaction is given in structural studies[11] of $[Pt_2(\mu\text{-}PhC_2SiMe_3)(cod)_2]$ (cod = cyclo-octa-1,5-diene) in which a Pt $\cdots$ Pt separation of 2.914 Å was found, and again in $[Pt_2(\mu\text{-}PhC_2Ph)(PhC_2Ph)(PMe_3)_2]$ for which[12] a Pt $\cdots$ Pt distance of 2.890 Å has been reported. In the title compound, if the tungsten–carbyne moiety is regarded as a transverse bridge holding the two Pt atoms in position by interaction with orthogonal π orbitals, the very long Pt $\cdots$ Pt distance is rationalised. The bridge is, of necessity, asymmetric in that it comprises one C and one W atom, but as the angle subtended by the two Pt atoms at C(1) is 93° and at the W atom is 65°, it is clear that the π orbitals of the W≡C bond can readily interact with the two Pt atoms.

TABLE 5

Selected interatomic distances (Å) and angles (°) for $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMePh_2)_2(\eta\text{-}C_5H_5)]$ (8)

(*a*) Distances			
W–Pt(1)	2.785(3)	W–Pt(2)	2.785(3)
Pt(1)–Pt(2)	2.989(3)	C(1)–C(2)	1.56(5)
Pt(1)–C(1)	2.05(4)	Pt(2)–C(1)	2.06(4)
W–C(1)	2.04(4)		
W–C(17)	1.94(5)	W–C(19)	1.85(5)
Pt(1)–C(17)	2.64(5)	Pt(2)–C(19)	2.42(5)
C(17)–O(17)	1.23(6)	C(19)–O(19)	1.23(6)
Pt(1)–C(20)	1.83(5)	Pt(2)–C(18)	1.83(5)
C(20)–O(20)	1.11(7)	C(18)–O(18)	1.14(6)
Pt(1)–P(1)	2.314(11)	Pt(2)–P(2)	2.337(12)
P(1)–C(9)	1.78(5)	P(2)–C(10)	1.81(5)
P(1)–C(11)	1.89(3)	P(2)–C(31)	1.77(3)
P(1)–C(21)	1.84(4)	P(2)–C(41)	1.83(3)
(*b*) Angles			
W–Pt(1)–Pt(2)	57.6(1)	W–Pt(2)–Pt(1)	57.5(1)
W–C(1)–Pt(1)	85.6(13)	W–C(1)–Pt(2)	85.5(13)
W–C(1)–C(2)	129(3)	Pt(1)–W–Pt(2)	64.9(1)
Pt(1)–C(1)–C(2)	124(3)	Pt(2)–C(1)–C(2)	126(3)
Pt(1)–C(1)–Pt(2)	93.2(15)		
W–C(17)–O(17)	162(4)	W–C(19)–O(19)	162(5)
W–C(17)–Pt(1)	73(1)	W–C(19)–Pt(2)	80(2)
W–Pt(1)–C(20)	111.8(14)	W–Pt(2)–C(18)	141.9(14)
Pt(1)–C(20)–O(20)	169(5)	Pt(2)–C(18)–O(18)	173(4)
Pt(2)–Pt(1)–C(20)	128.0(14)	Pt(1)–Pt(2)–C(18)	104.4(13)
P(1)–Pt(1)–C(20)	100(1)	P(2)–Pt(2)–C(18)	94(1)
W–Pt(1)–P(1)	147.9(3)	W–Pt(2)–P(2)	124.2(3)
Pt(2)–Pt(1)–P(1)	104.9(3)	Pt(1)–Pt(2)–P(2)	129.1(3)
Pt(1)–P(1)–C(9)	125(2)	Pt(2)–P(2)–C(10)	115(2)
Pt(1)–P(1)–C(11)	112(1)	Pt(2)–P(2)–C(31)	117(1)
Pt(1)–P(1)–C(21)	110(1)	Pt(2)–P(2)–C(41)	113(1)
C(9)–P(1)–C(11)	104(2)	C(10)–P(2)–C(31)	106(2)
C(9)–P(1)–C(21)	100(2)	C(10)–P(2)–C(41)	104(2)
C(11)–P(1)–C(21)	103(1)	C(31)–P(2)–C(41)	101(1)
P(1)–C(11)–C(12)	124(1)	P(2)–C(31)–C(32)	122(1)
P(1)–C(21)–C(22)	122(1)	P(2)–C(41)–C(42)	117(1)

Having established the molecular structure of compound (8) it was possible to give a satisfactory assignment to the n.m.r. data of complexes (6)—(10). Thus in the ^{13}C spectra (Table 3) the pattern observed for the μ_3-C group arises as a result of ^{31}P coupling to the *transoid* PR'_3 ligand, while the ^{195}Pt satellites are probably due to Pt_A, since the satellites due to Pt_B will be broadened by chemical-shift anisotropy. The latter effect is evident from the ^{195}Pt spectra (Table 2), where the higher frequency signals are considerably broadened. The values of J(PtC) [570 Hz for (7), and 580 Hz for (8)] are comparable with values observed previously for μ_3-C ligated groups.[2,9]

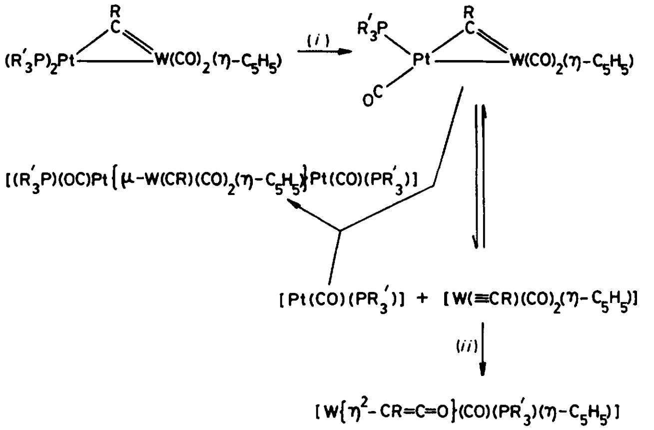
The ^{31}P and ^{195}Pt n.m.r. data (Table 2) for (6)—(10) are completely consistent with the structure established for (8) (Figure 1) by *X*-ray diffraction. In each spectrum both phosphorus signals show satellites due to each platinum, but ^{31}P–^{31}P coupling is generally too small to be resolved. One of the ^1J(PPt) values is consistently higher, and the associated ^{195}Pt shift is lower for (6)—(8). This signal is assigned to Pt_A, having the phosphine ligand *transoid* to the tungsten. The other platinum resonance (Pt_B) is noticeably broader, due presumably to chemical-shift anisotropy. The ^{195}Pt spectra were of sufficiently high signal-to-noise ratio to allow J(PtPt) to be measured (Table 2) directly from the second-order spectrum (ABMX) of the isotopomer with two ^{195}Pt nuclei.

Complexes (6)—(10) are 48-electron species, and as is typical for platinum-containing clusters,[13,14] the number of skeletal pairs (five) is one less than expected for *closo*-tetrahedrane-type structures on the basis of electron-counting rules.[15] Thus the tricobalt complexes $[Co_3(\mu_3\text{-}CX)(CO)_9]$ and the cluster $[Co_2W(\mu_3\text{-}CR)(CO)_8(\eta\text{-}C_5H_5)]$ have six skeletal bond pairs and 50 cluster valence electrons. However, as discussed above for (8), the structures of (6)—(10) are more correctly viewed as being of the 'butterfly' variety in view of the long Pt $\cdots$ Pt separation, and are related to those of complexes of type (11),[10-12] by the isolobal similarity which exists between $W(CO)_2(\eta\text{-}C_5H_5)$ and CR groups. Hence all the molecules (6)—(11) can be regarded as being of the *arachno* type based on octahedra with two vertices missing.[15]

An interesting feature concerning the existence of the trimetal complexes $[Pt_2W(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PR'_3)_2(\eta\text{-}C_5H_5)]$ (6)—(10) is that the related cluster compounds $[Pt_2W(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR'_3)_4(\eta\text{-}C_5H_5)]$ have not been isolated. They are not formed when the species $[Pt(C_2H_4)(PR'_3)_2]$ are added to the dimetal complexes $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)]$, nor when $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ is treated with excess of $[Pt(C_2H_4)(PR'_3)_2]$. The apparent non-existence of the compounds $[Pt_2W(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR'_3)_4(\eta\text{-}C_5H_5)]$ and the existence of (6)—(10) may be due to relative differences in the cluster building properties of $Pt(PR'_3)_2$ and $Pt(CO)(PR'_3)$ groups. Although both formally contribute an electron pair for skeletal bonding, the latter, by virtue of the strong π bonding characteristics of the CO group, might increase the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital of the cluster and thus lead to stabilization.

A plausible pathway for the formation of the compounds (1), (2), (4), and (6)—(10) is shown in the accompanying Scheme, which is based on analogy with the formation of the diplatinum μ-alkyne complexes (11) from the monoplatinum compounds $[Pt(alkyne)L_2]$ and the species PtL_2.[10,11] Replacement of a PR'_3 ligand of a $[PtW(\mu\text{-}CR)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)]$ complex by CO affords the dimetal species $[PtW(\mu\text{-}CR)(CO)_3(PR'_3)(\eta\text{-}C_5H_5)]$. However, the presence of the stronger π-acceptor CO ligand on platinum could lead to dissociation into [W-

($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)] and Pt(CO)(PR$'_3$) fragments. The latter could then combine with the compounds [PtW(μ-CR)(CO)$_3$(PR$'_3$)(η-C$_5$H$_5$)] to give the trimetal complexes. In support of this mechanism it was observed that the tricarbonyldimetal compounds (1), (2), and (4) converted slowly (*ca.* 60 h in solution) into the trimetal compounds (6), (7), and (9), respectively. Moreover, [W($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)] produced by dissociation of the tricarbonyldimetal compounds could combine with PR$'_3$ displaced by CO in the first step to give the ketenyl complexes [W(η^2-CR=C=O)(CO)(PR$'_3$)(η-C$_5$H$_5$)].[7] Indeed, as mentioned above, such a compound was identified in the reaction which gave (6). Similar ketenyl–tungsten complexes were observed on chromatography but were not characterised in the reactions which produced (7)—(9).



SCHEME (*i*) +CO, −PR$'_3$; (*ii*) +PR$'_3$

EXPERIMENTAL

The techniques employed and the instrumentation used are described in earlier Parts of this series.[1,3] Analytical and other data for the new compounds are given in Table 1, and n.m.r. data in Tables 2 and 3. The two compounds [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PR$'_3$)$_2$(η-C$_5$H$_5$)] (PR$'_3$ = PMe$_3$ or PMe$_2$Ph) were prepared as previously described.[4] Two related compounds required for the study were synthesized for the first time as described below.

Preparation of [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PR$'_3$)$_2$(η-C$_5$H$_5$)] (PR$'_3$ = PMePh$_2$ *and* PPh$_3$).—(*a*) An ethylene-saturated light petroleum (20 cm^3) solution of [Pt(cod)$_2$][16] (0.41 g, 1 mmol) at 0 °C was treated with PMePh$_2$ (8 cm^3 of a 0.25 mol dm^{-3} solution in pentane, 2 mmol). To this *in situ* preparation of [Pt(C$_2$H$_4$)(PMePh$_2$)$_2$] was added [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.41 g, 1 mmol), and the red solution obtained was stirred (1 h) while warming to room temperature. Cooling to −20 °C for several hours produced red *microcrystals* (washed, 4 × 20 cm^3, with light petroleum) of [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMePh$_2$)$_2$(η-C$_5$H$_5$)] (0.88 g, 88%), m.p. 162—165 °C (decomp.) [Found: C, 48.8; H, 3.9; *M* (mass spectrum, field desorption) 1 004. C$_{41}$H$_{38}$O$_2$P$_2$PtW requires C, 49.1; H, 3.9%; *M* 1 004]; $\nu_{max.}$(CO) (Nujol), 1 885vs and 1 815vs, br cm^{-1}. N.m.r.: ^{1}H ([^{2}H$_1$]chloroform), δ 1.32 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 35], 2.20 (s, 3 H, Me-4), 2.28 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 26 Hz], 5.33 (s, 5 H, C$_5$H$_5$), 6.39 (m, 4 H, C$_6$H$_4$), 6.95—7.70 (m, 20 H, Ph); ^{31}P-{^{1}H} ([^{2}H$_1$]chloroform), δ −12.2 [d, *J*(PP) 6, *J*(PtP) 4 100] and −7.5 p.p.m. [d, *J*(PP) 6, *J*(PtP) 2 936 Hz]; ^{13}C-{^{1}H} ([^{2}H$_2$]dichloromethane), δ 338.2 [d, μ-C, *J*(PC) 59, *J*(PtC) 746, *J*(WC) 142], 223.4 [WCO, *J*(PtC) 22, *J*(WC) 178], 162.3 [C^1 (C$_6$H$_4$), *J*(PtC) 54], 138—119 (Ph, C$_6$H$_4$), 91.4 (C$_5$H$_5$), 21.0 (Me-4), and 16.0 p.p.m. [d, MeP, *J*(PC) 27, *J*(PtC) 25 Hz].

(*b*) A sample of [Pt(cod)$_2$] (0.41 g, 1 mmol) in ethylene-saturated light petroleum (20 cm^3) at 0 °C was treated with PPh$_3$ (0.57 g, 2.2 mmol) in toluene (10 cm^3). The resulting solution was stirred (5 min) under an ethylene purge, then [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.41 g, 1 mmol) in toluene (40 cm^3) was added, and the ethylene atmosphere replaced by nitrogen. After 0.5 h, all solvent was removed *in vacuo* and the residue was treated with toluene (5 cm^3) and chromatographed (alumina column, 3 × 20 cm^3). Elution with toluene afforded, after removal of solvent, pale orange *microcrystals* of [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PPh$_3$)$_2$(η-C$_5$H$_5$)] (1.06 g, 89%), m.p. 185—188 °C (decomp.) (Found: C, 54.1; H, 4.1. C$_{51}$H$_{42}$O$_2$P$_2$PtW requires C, 54.3; H, 3.7%); $\nu_{max.}$(CO) (CH$_2$Cl$_2$), 1 898s and 1 797s, br cm^{-1}. N.m.r.: ^{1}H ([^{2}H$_1$]chloroform), δ 2.10 (s, 3 H, Me-4), 5.21 (s, 5 H, C$_5$H$_5$), 6.23 (m, 4 H, C$_6$H$_4$), 6.6—7.8 (m, 30 H, Ph); ^{31}P-{^{1}H} ([^{2}H$_2$]dichloromethane–CH$_2$Cl$_2$, −30 °C), δ 32.5 p.p.m. [s, *J*(PP) 14, *J*(PtP) 4 064 and 3 128, *J*(WP) 28 Hz]; ^{195}Pt-{^{1}H} ([^{2}H$_2$]dichloromethane–CH$_2$Cl$_2$, −30 °C), 331.7 p.p.m. [d of d, *J*(PtP) 4 060 and 3 127 Hz]; ^{13}C-{^{1}H} ([^{2}H$_2$]dichloromethane–CH$_2$Cl$_2$), δ 341.5 [d, μ-C, *J*(PC) 56], 227.2 [CO, *J*(PtC) 17, *J*(WC) 186 Hz], 160.7 [C^1 (C$_6$H$_4$)], 135—121 (Ph, C$_6$H$_4$), 92.1 (C$_5$H$_5$), 21.0 p.p.m. (Me-4).

Reactions of the Complexes [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PR$'_3$)$_2$(η-C$_5$H$_5$)] *with* CO.—A typical reaction was as follows. Carbon monoxide was slowly bubbled through a toluene (60 cm^3) solution of [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)] at room temperature for 24 h. The reaction mixture was treated with alumina (*ca.* 5 g) and solvent removed *in vacuo*. The dry residue was added to the top of an alumina chromatography column (4 × 30 cm) charged with light petroleum. The column was then gradient eluted with CH$_2$Cl$_2$–light petroleum (2 : 3), increasing to 100% CH$_2$Cl$_2$, and finally with CH$_2$Cl$_2$–tetrahydrofuran (9 : 1). The first band from the column afforded, after removal of solvent, pink *microcrystals* of [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(PMe$_3$)(η-C$_5$H$_5$)] (1) (0.13 g). The second band gave orange *microcrystals* of [Pt$_2$W(μ_3-CC$_6$H$_4$Me-4)(CO)$_4$(PMe$_3$)$_2$(η-C$_5$H$_5$)] (6) (0.38 g), while the third band yielded purple *microcrystals* of the known[7] compound [W{η^2-C(C$_6$H$_4$Me-4)=C=O}(CO)(PMe$_3$)(η-C$_5$H$_5$)] (0.15 g).

The other compounds (Table 1) were similarly prepared.

Crystal Structure Determination of Complex (8).—Crystals of (8) grow as ill formed dark orange prisms, and contain included solvent when grown from dichloromethane. Intensities were collected at ambient temperature from a crystal of dimensions *ca.* 0.2 × 0.2 × 0.2 mm in the range $2.9 \leqslant 2\theta \leqslant 40°$. Of the 4 103 independent intensities measured on a Nicolet *P*3*m* four-circle diffractometer, 2 488 for which $|F_o| > 2.5\sigma(F_o)$ were used for the solution and refinement of the structure. Two check reflections were remeasured every 50 reflections and showed no significant decay over the 43 h of data collection. Correction was made for Lorentz and polarisation effects, but not for the effects of *X*-ray absorption (despite the relatively high value of μ) because of difficulty in defining the crystal boundaries; a very small crystal was used. The poor crystal quality and limited data range have resulted in a structure of only moderate accuracy but which nevertheless gives valuable stereochemical information.

Crystal data. $C_{41}H_{38}O_4P_2Pt_2W\cdot0.2CH_2Cl_2$, $M = 1\,216.4$, Monoclinic, $a = 14.932(13)$, $b = 11.438(11)$, $c = 26.394(24)$ Å, $\beta = 97.42(7)°$, $U = 4\,470(7)$ Å^3, $Z = 4$, $D_c = 1.81$ g cm^{-3}, $F(000) = 2\,365$. Space group $P2_1/c$ (no. 14), Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 90.7 cm^{-1}.

A Patterson synthesis gave clear indications of the presence of three ' equally ' heavy atoms (initially assumed to be Pt) in a triangular array. Location of the other non-hydrogen atoms by successive electron-density difference syntheses revealed the overall stereochemistry of the molecule and hence which atom was tungsten. Confirmation of this ascription was afforded by the realism of the thermal parameters in the least-squares refinement. Because of the generally poor quality of the data, anisotropic thermal parameters were used only for Pt, W, and P; all other atoms were given isotropic thermal parameters. Hydrogen atoms were incorporated at calculated positions and were not refined. An electron-density difference synthesis at this stage revealed residual peaks characteristic of partial occupation by disordered solvent molecules of voids in the molecular packing. An overall population parameter for the atoms of a CH_2Cl_2 unit refined to 0.2. The cyclopentadienyl ring and the phenyl ligands were constrained geometrically to their idealised configurations during refinement. Convergence of the blocked-cascade least-squares refinement was obtained at R 0.075 (R' 0.080), with individual weights ascribed according to the scheme $w = [\sigma^2(F_o) + 0.003|F_o|^2]^{-1}$. Scattering factors were from refs. 17—19 and were corrected for the effects of anomalous dispersion. All computations were carried out within the laboratory on an Eclipse (Data General) Minicomputer with the SHELXTL system of programs.[20] Results are summarised in Tables 4 and 5. Observed and calculated structure factors, hydrogen atom co-ordinates, all thermal parameters, and a complete Table of bond lengths and angles are given in Supplementary Publication No. SUP 23317 (23 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.