Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 1. Synthesis of Platinum–Chromium, –Molybdenum, and –Tungsten Compounds; Crystal Structure of $[(OC)_5\overline{W\{\mu\text{-}C(OMe)Ph\}Pt}(PMe_3)_2]$ †

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The compounds $[M\{C(OMe)Ph\}(CO)_5]$ (M = Cr or W) react with $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) to give metal—metal-bonded complexes $[(OC)_5\overline{M\{\mu\text{-}C(OMe)Ph\}Pt}(cod)]$. Ethylene-saturated light petroleum solutions of $[Pt(cod)_2]$, treated with 2 mol of tertiary phosphine, react with the mononuclear metal compounds $[M\{C(OMe)Ph\}(CO)_5]$ (M = Cr, Mo, or W) and $[W\{C(OMe)Me\}(CO)_5]$ to afford the carbene-bridged dimetal complexes $[(OC)_5\overline{M\{\mu\text{-}C(OMe)Ph\}Pt}(PR_3)_2]$ (M = Cr or Mo, PR_3 = PMe_3 or PMe_2Ph; M = W, PR_3 = PMe_3) and $[(OC)_5\overline{W\{\mu\text{-}C(OMe)Me\}Pt}(PMe_3)_2]$. Phosphorus-31, ^1H, and ^{13}C n.m.r. studies support the structures proposed, and for $[(OC)_5\overline{W\{\mu\text{-}C(OMe)Ph\}Pt}(PMe_3)_2]$ the structure has been confirmed by a single-crystal *X*-ray diffraction study. Crystals are triclinic, with space group $P\bar{1}$ and $Z = 2$ in a unit cell of dimensions a = 9.728(5), b = 16.002(13), c = 9.611(6) Å, α = 109.86(6), β = 116.34(4), and γ = 83.77(6)°. The structure has been determined by heavy-atom methods from automated diffractometer data for $2.9 \leqslant 2\theta \leqslant 50°$ and refined to R 0.049 (R' 0.048) for 3 735 independent reflections. A tungsten–platinum bond [2.861(1) Å] is asymmetrically bridged by a C(OMe)Ph group [C–Pt 2.04(1), C–W 2.48(1) Å]. Reaction of the compounds $[(OC)_5\overline{M\{\mu\text{-}C(OMe)Ph\}Pt}(PMe_3)_2]$ (M = Cr or W) with trimethylphosphine gives the complexes $[(Me_3P)(OC)_4\overline{M\{\mu\text{-}C(OMe)Ph\}Pt}(PMe_3)_2]$, while the chromium compound with Bu^{t}NC yields $[(Bu^tNC)_2(OC)_3\overline{Cr\{\mu\text{-}C(OMe)Ph\}Pt}(CNBu^t)(PMe_3)]$. The n.m.r. data for these products are discussed.

In 1964 Fischer and Maasböl[1] reported the first successful synthesis of carbene complexes of metals of the chromium sub-group. Subsequently many other carbene–metal complexes have been characterised and their chemistry explored. The properties of Fischer's[2] carbene–metal compounds are such that they are more correctly formulated as transition-metal ylides;[3,4] the presence of heteroatoms (*e.g.* O or N) as substituents on the metal-bonded carbene-carbon atoms cause these species to behave as dipolar reagents having electrophilic carbon centres. In 1968 we initiated an investigation[5] of reactions of complexes of zerovalent platinum with a variety of electrophilic fluorocarbon compounds. From these studies it was concluded[6] that the reactions proceed *via* attack of the electron-rich metal on the substrate such that a dipolar intermediate collapses to give the observed adducts [Scheme (*a*)]. This idea receives support from the more recent observations[7] that the complex $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) reacts with hexafluoroacetone and with tetrafluoroethylene to give diplatinum compounds $[(cod)\overline{Pt\text{–}C(CF_3)_2\text{–}O\text{–}Pt}(cod)]$ and $[Pt_2(\mu\text{-}CF_2\text{–}CF_2)_2(cod)_2]$ respectively. The former could arise *via* attack of a $[Pt(cod)_2]$ molecule on the platinum centre of a 1,3-dipolar intermediate $[(cod)\overset{+}{Pt}\text{–}C(CF_3)_2\text{–}\overset{-}{O}]$, followed by ring closure, and the latter by dimerisation of an intermediate $[(cod)\overset{+}{Pt}\text{–}CF_2\text{–}\overset{-}{C}F_2]$. These results prompted the idea that low-valent metal compounds, particularly Pt^0 (d^{10}) and related species, would react with transition-metal ylide complexes according to Scheme (*b*). The resultant products would contain *heteronuclear* metal–metal bonds, representing a novel method of synthesis for these relatively rare complexes. The recent observation[7b] that $[Pt(cod)_2]$ reacts with perfluoropropene to afford the binuclear platinum compound $[Pt_2\{\mu\text{-}C(CF_3)_2\}(cod)_2]$, possibly *via* an ylide $[Pt\{C(CF_2)_3\}(cod)]$, lent support to these ideas. A preliminary account of this work has been given.[8]

RESULTS AND DISCUSSION

The carbene complex $[Cr\{C(OMe)Ph\}(CO)_5]$[9] reacted rapidly with an ethylene-saturated light petroleum solution of $[Pt(cod)_2]$ at 0 °C to afford a dark brown, air-stable, crystalline complex (1). Analytical (Table 1) and other data revealed that this product was a 1 : 1 adduct of the chromium–carbene complex and a Pt(cod) group. Similar compounds (2) and (3) were obtained by treating the mononuclear chromium–carbene complex with $[Pt(C_2H_4)_3]$ to which had been added 2 mol of PMe_3 or PMe_2Ph, respectively. The molybdenum carbene complex $[Mo\{C(OMe)Ph\}(CO)_5]$ behaved similarly to give compounds (4) and (5), but these compounds decompose at room temperature especially in solution. In contrast, the products (6)—(8) obtained from the tungsten complexes $[W\{C(OMe)R\}(CO)_5]$ (R = Ph or Me) are stable in air and in solution at room temperature, and are

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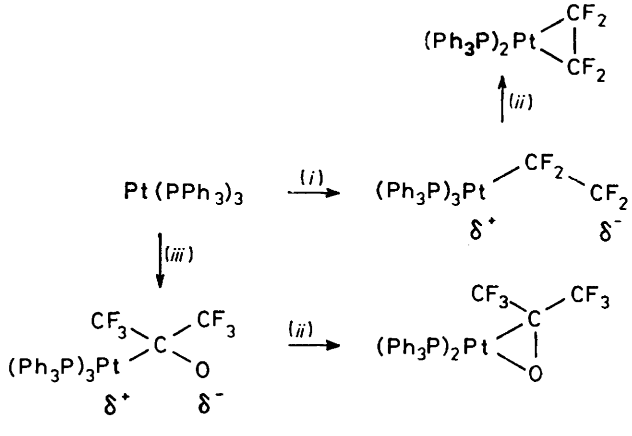
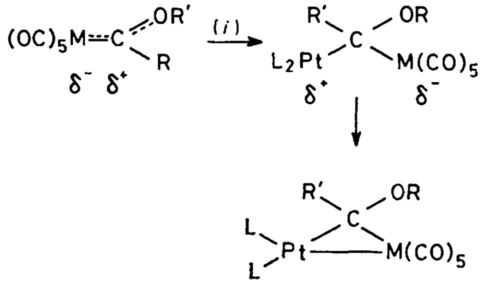
† μ-Methoxy(phenyl)carbene-[bis(trimethylphosphine)-platinum][pentacarbonyltungsten] (*Pt–W*).

particularly suitable for characterisation *via* n.m.r. studies. It was possible to measure a mass spectrum for (8) which showed a parent ion at *m/e* 728 followed by ions corresponding to loss of five CO ligands. The other compounds failed to give interpretable mass spectra but (2) showed an ion corresponding to the molecular ion minus a carbonyl ligand. Cryoscopic measurements of the molecular weight of several of the compounds (Table 1) were in accord with the formulation of the compounds as dimetal species.

In the ^{1}H n.m.r. spectra of (1) and (6) there are four resonances for the CH groups of the cod ligands (Table 2). This is to be expected for the asymmetric dimetallacyclopropane ring structures proposed in which the Ph and OMe groups are above and below the M–C–Pt planes.



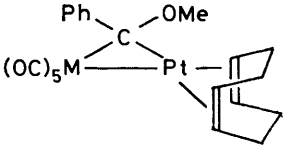
(*a*) (*i*)C_2F_4, (*ii*) $-PPh_3$, (*iii*)$(CF_3)_2CO$



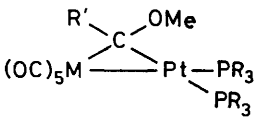
(*b*) (*i*) PtL_2 = Pt(cod) or $Pt(PR_3)_2$, M = Cr, Mo, or W

SCHEME

It was possible to examine the ^{13}C n.m.r. spectrum of complex (6) in detail. A resonance at 197 p.p.m. showed coupling to platinum [*J*(PtC) 1 367 Hz] and to tungsten [*J*(WC) 41 Hz], and therefore may be assigned to the dimetal-bridging carbon atom. This signal is shifted 125 p.p.m. upfield from that observed in the mononuclear tungsten–carbene complex [W{C(OMe)Ph}(CO)$_5$].[10] In the ^{13}C n.m.r. spectra of (7) and (8) the bridging carbene–carbon atoms resonate at 203 [*J*(PtC) 880] and 214 p.p.m. [*J*(PtC) 983 Hz], respectively. For (8) the spectrum was of sufficient quality to detect two ^{31}P–^{13}C couplings arising from *trans*- and *cis*-C–Pt–P arrangements so that the resonance pattern appeared as a doublet of doublets [*J*(PC) 83 and 17 Hz] with the platinum satellites. The ^{13}C spectrum of (6) also showed eight distinct resonances for the carbon atoms of the cod ligand, each with ^{195}Pt–^{13}C coupling. The four CH signals at 112, 107, 96, and 94 p.p.m. had ^{195}Pt–^{13}C couplings of 61, 64, 145, and 157 Hz, respectively. The relative magnitudes of these couplings accord with the resonances at 96 and 94 p.p.m. being due to the pair of CH groups *trans* to the tungsten atom, with the other pair *trans* to the bridging carbene ligand.



	M
(1)	Cr
(6)	W



	M	PR_3	R′
(2)	Cr	PMe_3	Ph
(3)	Cr	PMe_2Ph	Ph
(4)	Mo	PMe_3	Ph
(5)	Mo	PMe_2Ph	Ph
(7)	W	PMe_3	Ph
(8)	W	PMe_3	Me

The ^{31}P n.m.r. spectra of complexes (2)—(5), (7), and (8) were also informative (Table 2). Each spectrum revealed two resonances with similar ^{31}P–^{31}P and ^{195}Pt–^{31}P coupling patterns, but for the high-field doublets *J*(PtP) was *ca.* 4 500 Hz while for the lower-field doublets it was *ca.* 2 500 Hz. The former signals may be ascribed to the phosphorus nuclei of the *transoid*-R_3P–Pt–W arrangement and the latter to the phosphorus atoms of the *cisoid*-R_3P–Pt–W group. Indeed, in the spectra of complexes (7) and (8), the resonances at 22.0 and 17.8 p.p.m. also showed ^{183}W–^{31}P couplings.

The ^{1}H spectra of (1)—(8) (Table 2) are in accord with the formulations shown. The spectra of the molybdenum compounds were measured at −40 °C to inhibit the decomposition of these complexes mentioned above. The i.r. spectrum of each of the compounds (1)—(8) showed five carbonyl-stretching bands (see Experimental section). For the molybdenum and tungsten compounds none of these bands appeared below 1 896 cm^{-1} but for the chromium compounds one band was observed at a somewhat lower frequency and may reflect a carbonyl ligand semi-bridging to the platinum as found in the complex $[(Me_3P)(OC)_4Cr\{\mu\text{-}C(CO_2Me)Ph\}Pt(PMe_3)_2]$.[11]

Although the spectroscopic properties of the compounds (1)—(8) confirmed the dimetallacyclopropane type structures it was important to establish firmly the molecular configuration of a member of this new class of compound. Accordingly, a single-crystal *X*-ray dif-

TABLE 1

Analytical[a] and physical data for the dimetal complexes

	Compound[b]	M.p. (θ_c/°C)	Colour	Yield (%)	Analysis (%)	
					C	H
(1)	$[(\mathrm{OC})_5\mathrm{Cr}\{\mu\text{-}\mathrm{C(OMe)Ph}\}\mathrm{Pt(cod)}]$	95—97 (decomp.)	Dark brown	20	40.9 (41.0)	3.1 (3.3)
(2)	$[(\mathrm{OC})_5\mathrm{Cr}\{\mu\text{-}\mathrm{C(OMe)Ph}\}\mathrm{Pt(PMe_3)_2}]$	122—124	Orange	87	34.4 (34.6)	4.0 (4.0)
(3)	$[(\mathrm{OC})_5\mathrm{Cr}\{\mu\text{-}\mathrm{C(OMe)Ph}\}\mathrm{Pt(PMe_2Ph)_2}]$	126—127	Orange	40	44.2 (44.5)	4.0 (3.9)
(4)	$[(\mathrm{OC})_5\mathrm{Mo}\{\mu\text{-}\mathrm{C(OMe)Ph}\}\mathrm{Pt(PMe_3)_2}]$	80—82 (decomp.)	Orange	58	29.2 (32.4)	3.8 (3.7)
(5)	$[(\mathrm{OC})_5\mathrm{Mo}\{\mu\text{-}\mathrm{C(OMe)Ph}\}\mathrm{Pt((PMe_2Ph)_2}]$	104—106 (decomp.)	Orange-brown	25	41.7 (42.1)	3.9 (3.7)
(6)	$[(\mathrm{OC})_5\mathrm{W}\{\mu\text{-}\mathrm{C(OMe)Ph}\}\mathrm{Pt(cod)}]$	110 (decomp.)	Orange-brown	75	34.0 (33.8)	3.0 (2.7)
(7)	$[(\mathrm{OC})_5\mathrm{W}\{\mu\text{-}\mathrm{C(OMe)Ph}\}\mathrm{Pt(PMe_3)_2}]$	168—174 (decomp.)	Orange	76	28.6 (28.9)	3.4 (3.3)
(8)	$[(\mathrm{OC})_5\mathrm{W}\{\mu\text{-}\mathrm{C(OMe)Me}\}\mathrm{Pt(PMe_3)_2}]$	123—125	Pale orange	72	22.8 (23.1)	3.2 (3.3)
(9)	$[(\mathrm{Me_3P})(\mathrm{OC})_4\mathrm{Cr}\{\mu\text{-}\mathrm{C(OMe)Ph}\}\mathrm{Pt(PMe_3)_2}]$	119—121	Orange	55	35.8 (35.7)	4.9 (5.0)
(10)	$[(\mathrm{Me_3P})(\mathrm{OC})_4\mathrm{W}\{\mu\text{-}\mathrm{C(OMe)Ph}\}\mathrm{Pt(PMe_3)_2}]$	130—132	Brown	60	30.2 (30.1)	4.2 (4.2)
(11)	$[(\mathrm{Bu^tNC})_2(\mathrm{OC})_3\mathrm{Cr}\{\mu\text{-}\mathrm{C(OMe)Ph}\}\mathrm{Pt(CNBu^t)(PMe_3)}]$ [c]	101—103	Orange	32	43.1 (44.8)	6.0 (5.7)

[a] Calculated values are given in parentheses. [b] Molecular weights, measured in benzene, were as follows [Found (Calc.)]: (2), 645 (659); (3), 774 (784); (6), 728 (747); (9), 700 (706). [c] N, 5.1 (5.4%).

TABLE 2

Phosphorus-31 and ^{1}H n.m.r. data[a]

Complex	^{31}P (δ/p.p.m.)[b]	^{1}H (τ)
(1)[c]		2.4—3.2 (m, 5 H, Ph), 4.44, 4.80, 5.52, and 6.0 (m, 1 H, CH, cod), 6.39 (s, 3 H, OMe), 8.2—8.8 (m, 8 H, CH_2)
(2)[d]	14.4 [d, *J*(PP) 4, *J*(PtP) 2 441] 22.0 [d, *J*(PP) 4, *J*(PtP) 4 513]	2.6—3.2 (m, 5 H, Ph), 6.29 (s, 3 H, OMe), 8.38 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 20], 8.67 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 42]
(3)	[c] 5.9 [d, *J*(PP) 4, *J*(PtP) 2 463] 12.6 [d, *J*(PP) 4, *J*(PtP) 4 545]	[d] 2.5—3.2 (m, 15 H, Ph), 6.10 (s, 3 H, OMe), 8.50 and 8.58 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 20], 8.92 and 9.02 [d, 3 H, MeP, *J*(PH) 4, *J*(PtH) 46]
(4)[d,e]	14.0 [d, *J*(PP) 9, *J*(PtP) 2 607] 22.8 [d, *J*(PP) 9, *J*(PtP) 4 423]	2.4—3.1 (m, 5 H, Ph), 6.29 (s, 3 H, OMe), 8.34 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 23], 8.65 [d, 9 H, MeP, *J*(PH) 11, *J*(PtH) 44]
(5)[d–f]	4.4 [d, *J*(PP) 8, *J*(PtP) 2 526] 13.5 [d, *J*(PP) 8, *J*(PtP) 4 457]	2.2—3.2 (m, 15 H, Ph), 6.08 (s, 3 H, OMe), 8.50 [d, 3 H, MeP, *J*(PH) 3], 8.72 [d, 3 H, MeP, *J*(PH) 3], 8.99 [d, 3 H, MeP, *J*(PH) 7], 9.10 [d, 3 H, MeP, *J*(PH) 7]
(6)[d,g]		2.3—3.1 (m, 5 H, Ph), 4.16, 4.60, 5.20, and 5.84 (m, 1 H, CH, cod), 6.20 (s, 3 H, OMe), 7.2—8.2 (m, 8 H, CH_2)
(7)	[g] 15.0 [d, *J*(PP) 10, *J*(PtP) 2 510] 22.0 [d, *J*(PP) 10, *J*(WP) 8, *J*(PtP) 4 485]	[h] 2.1—3.6 (m, 5 H, Ph), 6.40 (s, 3 H, OMe), 8.84 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 25], 9.23 [d, 9 H, MeP, *J*(PH) 11, *J*(PtH) 44]
(8)[d]	[d] 15.8 [d, *J*(PP) 27, *J*(PtP) 2 377] 17.8 [d, *J*(PP) 27, *J*(WP) 12, *J*(PtP) 4 465]	6.44 (s, 3 H, OMe), 6.94 [d of d, 3 H, CCH_3, *J*(PH) 6 and 12, *J*(PtH) 8], 8.44 [d, 9 H, MeP, *J*(PH) 10, *J*(PH) 10, *J*(PtH) 43], 8.46 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 20]
(9)[c]	15.4 [d, *J*(PP) 5, *J*(PtP) 2 392] 21.6 [br, *J*(PtP) 4 564], −5.3 (br)	2.4—3.2 (m, 5 H, Ph), 6.33 (s, 3 H, OMe), 8.70 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 20], 8.89 [d, 9 H, MeP, *J*(PH) 10], 9.10 [d 9 H, MeP, *J*(PH) 10, *J*(PtH) 38]
(10)[c]	16.3 [d, *J*(PP) 6, *J*(PtP) 2 455] 21.6 [d of d, *J*(PP) 6 and 12, *J*(PtP) 4 753] 44.6 [d, *J*(PP) 12, *J*(WP) 202]	2.2—3.2 (m, 5 H, Ph), 6.44 (s, 3 H, OMe), 8.69 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 20], 8.92 [d, 9 H, MeP, *J*(PH) 9], 9.16 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 46]
(11)[d]	20.3 [s, *J*(PtP) 4 365]	[c] 2.3—3.3 (m, 5 H, Ph), 6.06 (s, 3 H, OMe), 8.82, 8.86, and 9.10 (s, 9 H, Bu^t), 8.92 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 42]

[a] Measured at room temperature unless otherwise stated. Coupling constants in Hz. [b] Hydrogen-1 decoupled, chemical shifts in p.p.m. to low frequency of 85% H_3PO_4 (external). [c] Measured in [^{2}H$_6$]benzene. [d] Measured in [^{2}H$_1$]chloroform. [e] Measured at −40 °C. [f] Platinum-195 satellites observed for ^{1}H signals of MeP groups but *J*(PtH) values not measurable. [g] Measured at −30 °C. [h] Measured in [^{2}H$_8$]toluene.

TABLE 3

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for complex (7)

Atom	x	y	z
Pt	0.308 67(5)	0.228 35(3)	0.061 50(5)
W	−0.003 93(5)	0.173 61(3)	−0.167 13(5)
C(6)	0.215 5(14)	0.239 2(9)	−0.167 9(14)
O(6)	0.273 9(9)	0.189 7(6)	−0.278 8(9)
C(06)	0.331 0(14)	0.105 2(9)	−0.265 7(15)
C(61)	0.176 9(13)	0.326 8(8)	−0.195 6(15)
C(62)	0.142 2(15)	0.333 6(9)	−0.349 4(14)
C(63)	0.102 5(18)	0.415 6(10)	−0.373 5(18)
C(64)	0.098 4(18)	0.489 0(10)	−0.253 1(18)
C(65)	0.135 4(17)	0.481 9(9)	−0.096 3(18)
C(66)	0.170 7(16)	0.401 1(9)	−0.071 8(16)
Carbonyl groups			
C(1)	0.014 9(13)	0.248 8(10)	0.058 4(15)
O(1)	0.013 2(12)	0.295 0(7)	0.179 6(12)
C(2)	−0.203 6(16)	0.120 7(10)	−0.218 0(19)
O(2)	−0.315 8(11)	0.088 1(8)	−0.245 8(16)
C(3)	−0.034 7(16)	0.119 2(9)	−0.404 6(16)
O(3)	−0.052 9(12)	0.094 8(7)	−0.538 1(11)
C(4)	−0.119 5(15)	0.279 5(10)	−0.236 6(15)
O(4)	−0.191 7(12)	0.334 0(8)	−0.278 9(13)
C(5)	0.097 7(15)	0.062 4(10)	−0.109 0(14)
O(5)	0.147 9(12)	−0.000 1(6)	−0.081 7(12)
P(1)	0.534 8(4)	0.298 8(3)	0.148 6(4)
C(11)	0.573 2(19)	0.315 4(12)	−0.012 0(20)
C(12)	0.551 3(22)	0.411 6(14)	0.286 2(25)
C(13)	0.713 0(19)	0.251 6(17)	0.260 3(26)
P(2)	0.360 6(4)	0.188 8(2)	0.291 9(4)
C(21)	0.433 9(19)	0.279 5(13)	0.488 3(18)
C(22)	0.506 6(9)	0.107 6(14)	0.324 1(23)
C(23)	0.210 6(15)	0.135 3(11)	0.303 9(15)

fraction study was carried out on complex (7) for which a suitable crystal was obtained. The results of this study are summarised in Tables 3 and 4, and two views of the molecule are shown in Figures 1 and 2 which also indicate the atomic numbering system. The contents of the triclinic unit cell are shown in Figure 3.

The Pt–W bond [2.861(1) Å] is asymmetrically bridged by the C(OMe)Ph group such that W–C(6) is 2.48(1) Å and Pt–C(6) is 2.04(1) Å. The latter is at the short end of the range 1.99(3)—2.15(2) Å generally observed for platinum–carbon σ bonds.[12] The W–C(6) separation is significantly longer than that (2.1—2.3 Å) found by other workers[13] for σ bonds between tungsten and sp^3-carbon atoms. The asymmetric bridging of the hetero-nuclear metal–metal bond by the carbene ligand is reminiscent of the many examples of asymmetric bridging by carbonyl groups in bi- and tri-nuclear metal carbonyl complexes.[14] It is possible that the asymmetry of the bridge in (7) reflects a need to equalize charge distribution between the two adjacent metal atoms. A similar asymmetry (2.33 and 2.08 Å) has recently been found in the structure of $[(OC)_4\overline{W(\mu\text{-}CO)\{\mu\text{-}C(PMe_3)Ph\}Re}\text{-}(CO)_4]$ although it was not possible from the X-ray diffraction study of this complex to distinguish between the rhenium and the tungsten atoms.[15]

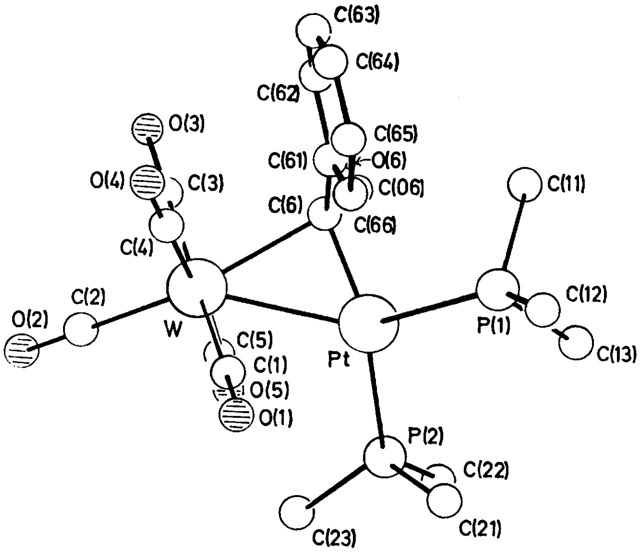


FIGURE 1 Molecular structure of the complex $[(OC)_5\overline{W\{\mu\text{-}C(OMe)Ph\}Pt}(PMe_3)_2]$ (7) projected onto the plane of the W(μ-C)Pt ring

TABLE 4

Bond lengths (Å) and angles (°) for the complex $[(OC)_5\overline{W\{\mu\text{-}C(OMe)Ph\}Pt}(PMe_3)_2]$ (7)

(a) Distances

Pt–W	2.861(1)	C(61)–C(62)	1.40(1)
Pt–C(6)	2.04(1)	C(62)–C(63)	1.39(2)
W–C(6)	2.48(1)	C(63)–C(64)	1.35(2)
C(6)–O(6)	1.40(1)	C(64)–C(65)	1.43(2)
O(6)–C(06)	1.43(1)	C(65)–C(66)	1.37(2)
C(6)–C(61)	1.49(2)	C(66)–C(61)	1.39(2)
Pt–P(1)	2.253(3)	Pt–P(2)	2.335(3)
P(1)–C(11)	1.84(1)	P(2)–C(21)	1.83(2)
P(1)–C(12)	1.81(2)	P(2)–C(22)	1.81(2)
P(1)–C(13)	1.83(2)	P(2)–C(23)	1.83(2)
W–C(1)	2.03(1)	C(1)–O(1)	1.15(2)
W–C(2)	1.99(1)	C(2)–O(2)	1.14(2)
W–C(3)	2.04(1)	C(3)–O(3)	1.14(2)
W–C(4)	2.07(2)	C(4)–O(4)	1.13(2)
W–C(5)	2.06(1)	C(5)–O(5)	1.13(2)

(b) Angles

W–Pt–C(6)	58.0(3)	Pt–W–C(6)	44.2(3)
W–C(6)–Pt	77.8(3)	O(6)–C(6)–C(61)	106.6(9)
W–C(6)–O(6)	118.6(8)	Pt–C(6)–O(6)	119.1(8)
W–C(6)–C(61)	110.5(7)	Pt–C(6)–C(61)	122.0(9)
C(6)–Pt–P(1)	95.4(4)	W–Pt–P(2)	107.6(1)
C(6)–Pt–P(2)	164.8(4)	W–Pt–P(1)	152.8(1)
C(6)–O(6)–C(06)	116.6(9)	P(1)–Pt–P(2)	99.3(1)
C(6)–C(61)–C(62)	120(1)	C(6)–C(61)–C(66)	120(1)
C(61)–C(62)–C(63)	119(1)	C(62)–C(63)–C(64)	122(1)
C(63)–C(64)–C(65)	119(1)	C(64)–C(65)–C(66)	120(1)
C(65)–C(66)–C(61)	121(1)	C(66)–C(61)–C(62)	120(1)
Pt–P(1)–C(11)	116.0(5)	C(11)–P(1)–C(12)	102.2(9)
Pt–P(1)–C(12)	112.7(6)	C(11)–P(1)–C(13)	101.5(8)
Pt–P(1)–C(13)	119.1(6)	C(12)–P(1)–C(13)	103.1(11)
Pt–P(2)–C(21)	115.5(6)	C(21)–P(2)–C(22)	103.5(9)
Pt–P(2)–C(22)	112.7(6)	C(21)–P(2)–C(23)	101.8(6)
Pt–P(2)–C(23)	120.8(4)	C(22)–P(2)–C(23)	100.1(8)
Pt–W–C(1)	68.3(3)	W–C(1)–O(1)	174(1)
Pt–W–C(2)	148.5(4)	W–C(2)–O(2)	178(1)
Pt–W–C(3)	113.3(4)	W–C(3)–O(3)	175(1)
Pt–W–C(4)	110.0(4)	W–C(4)–O(4)	175(1)
Pt–W–C(5)	74.0(4)	W–C(5)–O(5)	177(1)
C(6)–W–C(1)	100.1(4)	C(1)–W–C(2)	89.6(6)
C(6)–W–C(2)	167.3(5)	C(1)–W–C(3)	169.3(5)
C(6)–W–C(3)	76.3(5)	C(1)–W–C(4)	84.0(5)
C(6)–W–C(4)	84.2(5)	C(1)–W–C(5)	97.8(5)
C(6)–W–C(5)	98.9(5)	C(2)–W–C(3)	92.7(6)
		C(2)–W–C(4)	88.7(6)
		C(2)–W–C(5)	87.8(6)
		C(3)–W–C(4)	85.6(5)
		C(3)–W–C(5)	92.7(5)
		C(4)–W–C(5)	176.0(5)

The semi-bridging character of C(6) is accompanied by four non-tetrahedral angles at this atom (Table 4), only the angles O(6)C(6)C(61) [106.6(9)°] and W–C(6)–C(61) [110.5(7)°] conforming to that expected for an sp^3-hybridised carbon atom. The plane of the carbene ligand [O(6),C(6),C(61)] is at an angle of 79.8° to the plane comprising Pt, W, and C(6) (Table 5). The platinum atom is in an essentially planar environment since the angle between the planes P(1)PtP(2) and Pt, W, C(6) is only 7.2°. The five carbonyl groups on the tungsten are disposed in octahedral positions and the four radial CO ligands are staggered with respect to the Pt–C(6) axis (Figure 2). Indeed, C(4)WC(5) is inclined at 64.5° to the plane defined by W–Pt–C(6). The W–C–O groups are essentially linear and there is no evidence for semi-bridging to the platinum.

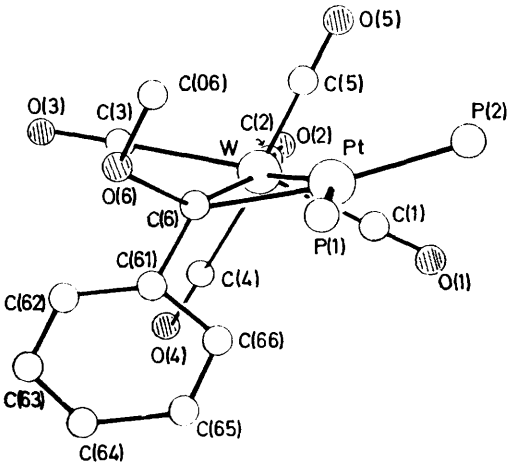


FIGURE 2 Molecular structure of complex (7) projected onto the plane of the C_6H_5 ring. Methyl groups on P(1) and P(2) are omitted for clarity

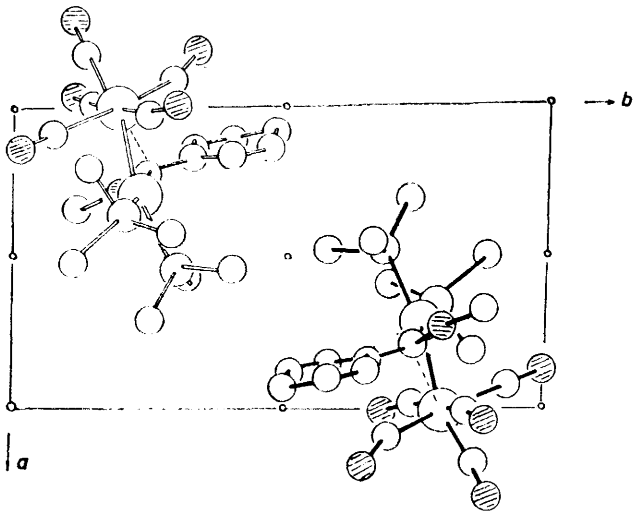


FIGURE 3 Contents of the triclinic unit cell seen in projection viewed down c^* towards the origin

The Pt–P distances fall in the range previously observed,[12a] although Pt–P(2) is somewhat longer than Pt–P(1), perhaps reflecting the *trans* influence of the carbene moiety. The phosphine ligands tend towards being either *trans* to the tungsten atom or to C(6), with P(1)PtW 152.8(1)° and P(2)PtC(6) 164.8(4)°. The substantial difference between the two *J*(PPt) values related to the *transoid* or *cisoid* P–Pt–W arrangement was mentioned above in connection with the n.m.r. studies (Table 2), and this accords with angle P(2)PtW [107.6(1)°] being much smaller than P(1)PtW.

The semi-bridging nature of the carbene ligand in (7) suggests a formulation (7a) in which an electron-rich d^{10} platinum atom donates an electron pair to the 16-electron d^6 tungsten atom which relieves itself of excess of charge by transfer of electron density to the π^* orbital of the carbene. If such a situation exists it is analogous to that proposed by Cotton [14b] to account for the semi-bridging carbonyl group in the anion $[(OC)_4Fe{-}Co(CO)_4]^-$.

TABLE 5

Least-squares planes for $[(OC)_5W\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ (7) in the form $Ax + By + Cz = D$, where x, y, z are fractional co-ordinates. Distances (Å) of relevant atoms from the planes are given in square brackets

Plane (i): Pt, W, C(6)
$-3.823x + 12.823y + 2.157z = 1.880$

Plane (ii): Pt, P(1), P(2)
$-4.788x + 11.548y + 3.060z = 1.350$

Plane (iii): O(6), C(6), C(61)
$6.989x + 3.721y + 2.016z = 2.058$

Plane (iv): W, C(1), O(1), C(3), O(3), C(4), O(4), C(5), O(5)
$8.792x + 7.154y - 2.852z = 1.652$

[W 0.03, C(1) 0.09, O(1) 0.06, C(3) 0.05, O(3) 0.09, C(4) −0.03, O(4) −0.15, C(5) −0.03, O(5) −0.12]

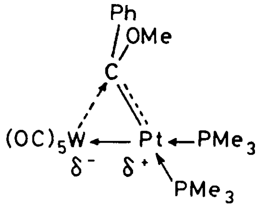
Plane (v): C(6), C(61), C(62), C(63), C(64), C(65), C(66)
$9.181x + 3.664y - 1.899z = 3.182$

[C(6) −0.008, C(61) 0.011, C(62) 0.009, C(63) −0.008, C(64) −0.006, C(65) 0.010, C(66) −0.009]

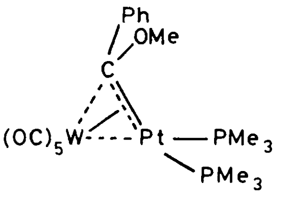
Dihedral angles (°):
(i)—(ii) 7.2; (i)—(iii) 79.8; (i)—(iv) 88.3; (i)—(v) 98.9

However, it is surprising that the five carbonyl ligands on the tungsten cannot dissipate the negative charge from the platinum without the need for an interaction between the tungsten atom and C(6). Nevertheless, without support from a bridging ligand, a platinum–tungsten bond by itself may not be sufficient to hold the dimetal structure together. The bonding in (7) can be represented as (7b) to emphasize an analogy between C=C and C=M co-ordination to a 16-electron pentacarbonylmetal group.

Since the C(OMe)Ph group in (7) originated from the mononuclear compound $[W\{C(OMe)Ph\}(CO)_5]$ we are in effect observing partial transfer, *via* the asymmetric bridge, of the carbene from one metal centre to another. The extent of semi-bridging of the carbene ligand across a metal–metal bond will depend on the particular metals which afford this type of structure and on the nature of the other ligands present. The properties of the latter, in particular, must effect the three-centre $[\overline{M(\mu\text{-}CR^1R^2)M'}]$ bonding pattern. Evidently complete transfer of the carbene group is often accompanied by rupture of the heteronuclear metal–metal bond at least in dimetal species. Thus $[(OC)_5\overline{Cr\{\mu\text{-}C(OMe)Ph\}Pt}(PMe_3)_2]$ in toluene solution at 80 °C decomposes to $[Cr(CO)_5(PMe_3)]$, $[Pt_3\{\mu\text{-}C(OMe)Ph\}_2(\mu\text{-}CO)(PMe_3)_3]$, and $[Pt_3\{\mu\text{-}C(OMe)Ph\}_3(PMe_3)_3]$.[16] Interestingly, Fischer and Beck [17] found that the mononuclear carbene complex $[Mo\{C(OMe)Ph\}(\eta\text{-}C_5H_5)(CO)(NO)]$ reacted $[Ni(CO)_4]$ to give $[Mo(\eta\text{-}C_5H_5)(CO)_2(NO)]$ and $[Ni_3\{\mu\text{-}C(OMe)Ph\}_3(CO)_3]$. It seems likely from our studies that this reaction proceeds *via* a molybdenum–nickel-bonded species containing a $\overline{Mo\{\mu\text{-}C(OMe)Ph\}Ni}$ group, and that the intermediate dimetal complex decomposes *via* concomitant transfer of CO from nickel to molybdenum and the carbene ligand to the nickel.

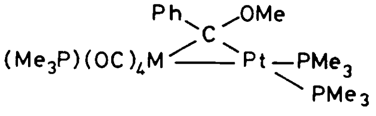


(7a)



(7b)

As an initial step in investigating the chemical reactivity of the dimetal compounds reported in this paper, we have studied the reactions of (2) and (7) with trimethylphosphine, and complex (2) also with t-butyl isocyanide. Reaction with trimethylphosphine occurred at room temperature to give complex (9), and with u.v. irradiation to yield (10). These compounds were characterised by analysis and by their spectroscopic properties (Tables 1 and 2). The ^{13}P n.m.r. spectra of (9) and (10) showed three resonances corresponding to three non-equivalent PMe_3 ligands. Two of the signals in each spectrum showed platinum satellites as in the precursors (2) and (7), and must correspond to the $Pt(PMe_3)_2$ groups. The third signal had no detectable ^{31}P–^{195}Pt coupling, but in the case of (10) this resonance showed ^{31}P–^{185}W coupling (202 Hz). It seems likely that the absence of any platinum satellites on the resonances at −5.3 and 44.6 p.p.m. in the spectra of (9) and (10) indicates that these PMe_3 ligands on chromium or tungsten are not *trans* to the platinum atoms. The relative simplicity of both the ^{31}P and ^{1}H spectra of (9) and (10) establishes the presence of only one isomer. Thus the ^{1}H spectra show only three methyl-group environments, only two with ^{195}Pt–^{1}H coupling.



M
(9) Cr
(10) W

The reaction of compound (2) with t-butyl isocyanide proceeded at room temperature to afford the complex $[(Bu^tNC)_2(OC)_3\overline{Cr\{C(OMe)Ph\}Pt}(CNBu^t)(PMe_3)]$ (11), two CO and one PMe_3 ligands being substituted by $CNBu^t$ groups. From the ^{31}P n.m.r. spectrum it may be concluded that the PMe_3 group is *trans* to the Pt–Cr bond on account of the large ^{31}P–^{195}Pt coupling. Hence it is the PMe_3 group *trans* to the bridging carbene which has been replaced by Bu^tNC in accord with the *trans* influence of the carbene. The stereochemistry is confirmed from the ^{1}H n.m.r. spectrum where the CH_3P signal appears as a doublet with a ^{195}Pt–^{1}H coupling (42 Hz) of the same magnitude as that measured for the *trans*-Me_3P–Pt–Cr group in (2).

It was thought possible that the reaction of (2) with Bu^tNC might have yielded a complex in which the t-butyl isocyanide group had inserted into one or other of the metal–carbon bonds involving the μ-C(OMe)Ph group. This process evidently did not occur with this reagent, but nevertheless the reactions with PMe_3 and Bu^tNC revealed that the dimetallacyclopropane rings in (2) and (7) were sufficiently robust to allow replacement of substituent ligands.

EXPERIMENTAL

N.m.r. studies were made with JEOL PFT and PS 100 spectrometers at 100 (^{1}H), 40.48 (^{31}P), and 25.15 (^{13}C) MHz. Carbon-13 shifts are relative to $SiMe_4$, and data from ^{31}P and ^{1}H spectra are summarised in Table 2. Infrared spectra were measured on Perkin-Elmer 257 and 457 spectrophotometers. The former was used to record carbonyl-stretching frequencies measured in cyclohexane, and the latter for other bands recorded from Nujol mulls. Mass spectra were measured on an A.E.I. MS 902 instrument at 70 eV.*

All experiments were carried out under nitrogen using Schlenk-tube techniques, and dry oxygen-free solvents. Light petroleum refers to that fraction of b.p. 40—60 °C. The mononuclear carbene complexes $[M\{C(OMe)R\}(CO)_5]$ (M = Cr, Mo, or W; R = Ph or Me) were prepared as described in the literature,[9,18] as was $[Pt(cod)_2]$.[19] Analytical data and yields for the new compounds are given in Table 1.

Reactions of the Mononuclear Carbene–Metal Complexes of Chromium, Molybdenum, and Tungsten with the Zerovalent Platinum Compounds.—The following representative preparations are described for compounds listed in Table 1.

(*a*) The complex $[Pt(cod)_2]$ (0.41 g, 1 mmol) was added portionwise to ethylene-saturated light petroleum (20 cm^3). Trimethylphosphine (2 mmol) in light petroleum (2 cm^3) was then added to this mixture, followed by $[Cr\{C(OMe)Ph\}(CO)_5]$ (0.31 g, 1 mmol) in light petroleum (10 cm^3). After stirring for 1 h, solvent was removed from the orange precipitate with a syringe, and the residue was washed with light petroleum (2 × 5 cm^3). Recrystallisation from diethyl ether–light petroleum gave orange *crystals* of $[(OC)_5\overline{Cr\{\mu\text{-}C(OMe)Ph\}Pt}(PMe_3)_2]$ (2) (Table 1).

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* 1 eV ≈ 1.60×10^{-19} J.

(*b*) The complex [Pt(cod)$_2$] (0.41 g, 1 mmol) was added portionwise to a stirred ethylene-saturated solution of light petroleum (20 cm^3) at 0 °C. The tungsten compound [W{C(OMe)Ph}(CO)$_5$] (0.44 g, 1 mmol) in light petroleum (20 cm^3) at 0 °C was then added, the ethylene atmosphere was replaced by nitrogen, and the mixture was stirred (1 h) at 0 °C. If precipitation does not commence within 5 min it is necessary to scratch the glass in contact with the solution. After allowing the precipitate to settle, the solvent was decanted, and the residue washed with light petroleum (3 × 1 cm^3). Drying *in vacuo* afforded orange brown *needles* of $[(OC)_5W\{\mu\text{-}C(OMe)Ph\}Pt(cod)]$ (6).

(*c*) A solution of [W{C(OMe)Me}(CO)$_5$] (0.38 g, 1 mmol) in light petroleum (10 cm^3) was added to a cold (0 °C) vigorously stirred suspension of [Pt(C$_2$H$_4$)(PMe$_3$)$_2$] (1 mmol), generated by treating [Pt(cod)$_2$] (1 mmol) in light petroleum (20 cm^3) with ethylene followed by PMe$_3$ (2 mmol). Within 2 min a pale orange precipitate began to form. Reaction was continued with stirring for 0.5 h, after which the mixture was filtered and the solid product washed with pentane (4 × 3 cm^3) at 0 °C to give pale orange microcrystals of $[(OC)_5W\{\mu\text{-}C(OMe)Me\}Pt(PMe_3)_2]$ (8).

Reaction of the Complexes $[(OC)_5M\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ (M = Cr *or* W) *with Trimethylphosphine.*—To a solution of compound (2) (0.66 g, 1 mmol) in diethyl ether (40 cm^3) was added PMe$_3$ (1.1 mmol) at room temperature. After stirring for 48 h an i.r. spectrum showed consumption of starting material. The volume of solvent was reduced (*ca.* 20 cm^3) *in vacuo*, and the black mixture filtered through an alumina column (2 × 5 cm). The resulting solution was further reduced in volume to *ca.* 10 cm^3 giving an orange solid. The solvent was removed with a syringe, and the residue washed with light petroleum (3 × 3 cm^3), dried *in vacuo*, and recrystallised from diethyl ether–light petroleum to give orange *crystals* of $[(Me_3P)(OC)_4Cr\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ (9).

Complex (10) was prepared by irradiating with u.v. light a diethyl ether solution (40 cm^3) of (7) (0.79 g, 1 mmol) and PMe$_3$ (1.1 mmol) for 48 h, after which all the starting tungsten–platinum complex had been consumed. Solvent was removed *in vacuo* and the residue recrystallised from diethyl ether–light petroleum to give orange-brown *crystals* of $[(Me_3P)(OC)_4W\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ (10), washed with light petroleum (2 × 3 cm^3).

Reaction of the Complex $[(OC)_5Cr\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ *with t-Butyl Isocyanide.*—To a solution of compound (2) (0.66 g, 1 mmol) in diethyl ether (40 cm^3) was added excess of Bu^{t}NC (4 mmol). After 1 h at room temperature the orange-red solution was reduced to dryness *in vacuo*. The residue was redissolved in diethyl ether (10 cm^3), and hexane (20 cm^3) added. The volume was then reduced to *ca.* 10 cm^3 giving an orange solid, solvent was removed with a syringe, and the solid residue recrystallised from diethyl ether–light petroleum and dried *in vacuo* to give orange *crystals* of $[(Bu^tNC)_2(OC)_3Cr\{\mu\text{-}C(OMe)Ph\}Pt(CNBu^t)(PMe_3)]$ (11), washed with light petroleum (2 × 2 cm^3).

Infrared Spectral Bands [$\nu_{max.}$/cm^{-1}] *for Compounds* (1)—(11).—(1) 2 035vs, 1 977m, 1 960vs, 1 923s, and 1 852w,br (CO); 1 585w, 1 566w, 1 465m, 1 447m, 1 435m, 1 361m, 1 338w, 1 311w, 1 302w, 1 190w, 1 162m, 1 156m, 1 099s, 1 076m, 1 027w, 985w, 957m, 875w, 857w, 819w, 780w, 765m, 702s, 670s, 653vs, 647(sh), 632s, 622m, 610m, 548w, 531w, 510w, 502(sh), 459w, 411w, and 402w.

(2) 2 027vs, 1 972m, 1 909vs, 1 890w, and 1 851vs (CO); 1 583w, 1 440m, 1 419m, 1 307w, 1 300w, 1 284m, 1 217m, 1 173m, 1 162m, 1 093m, 1 072m, 960(sh), 953vs,br, 891w, 853w, 761w, 728w, 720w, 697m, 665(sh), 653vs, 615w, 580s, 521w, 494w, 478w, 469, and 440w.

(3) 2 028vs, 1 972m, 1 936vs, 1 893m, and 1 878m (CO); 1 582w, 1 565w, 1 435m, 1 430s, 1 422(sh), 1 295m, 1 270m, 1 210w, 1 168w, 1 158m, 1 087s, 1 070m, 1 027w, 955(sh), 948m, 940(sh), 918vs, 909vs, 887w, 841w, 831m, 761m, 740s, 712w, 705m, 696s, 690s, 665(sh), 658w, 650vs, 635m, 618w, 584s, 522w, 500w, 485s, 465m, 428m, and 400m.

(4) 2 042vs, 1 977s, 1 938vs, and 1 903vs, br (CO); 1 585w, 1 440m, 1 431m, 1 427m, 1 307w, 1 300w, 1 284m, 1 172w, 1 160w, 1 092m, 1 072w, 952w, br, 890w, 855w, 847w, 760w, 737m, 718w, 697m, 667w, and 646m.

(5) 2 041vs, 1 977s, 1 939vs and 1 906vs,br (CO); 1 582w, 1 566w, 1 430m, 1 297w, 1 270w, 1 169w, 1 158w, 1 086m, 1 070w, 958w, 949m, 919s, 909s, 832w, 760w, 742m, 713w, 702w, 697m, 691m, 675w, 642w, 605w, 591s,br, 570m, 487m, and 429m.

(6) 2 050s, 1 976m, 1 954s, 1 926s, and 1 918(sh) (CO); 1 586w, 1 440w, 1 424w, 1 334w, 1 302w, 1 222w, 1 172w, 1 164w, 1 096w, 1 074w, 996w, 960w, 694w, 646w, 622w, 586m, 578(sh), and 564w.

(7) 2 040s, 1 972m, 1 934s, 1 908(sh), and 1 896s (CO); 1 580w, 1 310w, 1 300w, 1 284w, 1 172w, 1 161w, 1 150w, 1 091m, 1 072w, 964(sh), 952s, 890w, 852w, 845w, 760w, 725m, 719(sh), 695m, 661w, 665w, 642m, 614w, 592(sh), 580s, and 563m.

(8) 2 036s, 1 956m, 1 926s, 1 908(sh), and 1 900s (CO); 1 344w, 1 306w, 1 282w, 1 185w, 1 110w, 1 092w, 1 002w, 945s, 865w, 855w, 835(sh), 720m, 672w, 664w, 590m, and 574s.

(9) 1 997s, 1 967s, 1 899(sh), 1 894vs, 1 842s, and 1 828s (CO); 1 578w, 1 557w, 1 475m, 1 419m, 1 305(sh), 1 300m, 1 289m, 1 270m, 1 203w, 1 158m, 1 086s, 1 075(sh), 1 022w, 990w, 940vs,br, 875w, 860(sh), 855m, 848(sh), 842m, 836m, 755w, 734m, 727s, 719s, 696s, 668s, 660s, 640vs, 622w, 585s, 572m, 550w, 510m, 492w, 472m, 460w, 452w, 435w, and 419w.

(10) 1 992m, br, 1 904(sh), 1 902vs, 1 861s, and 1 848s (CO); 1 582m, 1 559w, 1 478w, 1 418w, 1 302w, 1 298w, 1 287m, 1 160w, 1 099m, 990w, 952vs,br, 850w, 766w, 730w, 720w, 705m, 681w, 668w, 640w, 600m, 584m, 487w, 460w, and 440w.

(11) 2 110s, 2 070m,br, 1 917vs, 1 856s, and 1 836s (NC and CO); 1 580m, 1 558w, 1 476s, 1 414m, 1 302w, 1 288m, 1 278m, 1 229m, 1 211vs,br, 1 175w, 1 163m, 1 095s, 1 025w, 992w, 961vs, 947s, 885w, 856w, 844w, 761w, 739w, 731m, 699s, 666s, 648vs, and 642vs.

Carbon-13 (*^{1}H-decoupled*) *N.M.R. Data for Compounds* (2) *and* (6)—(8) (δ p.p.m., *Coupling Constants in* Hz).—(2) (in [^{2}H$_1$]chloroform–CH$_2$Cl$_2$), δ 223, 229 (CO), 209 [d of d, μ-*C*(OMe)Ph, *J*(PC) 83 and 13], 158 (C^1, Ph), 127.7, 124.5, 120.4 (Ph), 59.0 [OMe, *J* (PtC) 56], 16.96 [d, MeP, *J*(PC) 33], and 16.72 [d, MeP, *J*(PC) 21].

(6) (in [^{2}H$_1$]chloroform–CH$_2$Cl$_2$ at −30 °C), δ 206 [CO, *J*(PtC) 24], 200 [CO, *J*(PtC) 21, *J*(WC) 122], 197 [μ-*C*(OMe)-Ph, *J*(PtC) 1 367, *J*(WC) 41], 156 [C^1 (Ph), *J*(PtC) 81], 126, 125.3, 124.8 (Ph), 112 [CH(cod), *J*(PtC) 61], 107 [CH(cod), *J*(PtC) 64], 96 [CH(cod), *J*(PtC) 145], 94 [CH(cod), *J*(PtC) 157], 61 [OMe, *J*(PtC) 49], 33 [CH$_2$(cod), *J*(PtC) 27], 32.6 [CH$_2$(cod), *J*(PtC) *ca.* 15], 25.6 [CH$_2$(cod), *J*(PtC) 21], and 24.9 [CH$_2$(cod), *J*(PtC) *ca.* 5].

(7) (in [$^2H_1$]chloroform), δ 207, 203.1 (CO), 203 [μ-*C*(OMe)-Ph, *J*(PtC) 880], 160, 128, 127, 124 (Ph), 60 [OMe, *J*(PtC) 56], 18 and 17 (m, MeP).

(8) (in [$^2H_1$]chloroform–CH_2Cl_2), δ 214 [d of d, μ-*C*(OMe), *J*(PC) 83 and 17, *J*(PtC) 983], 207 (CO), 204 [CO, *J*(PtC) 24, *J*(WC) 120], 60 [OMe, *J*(PtC) 59], 44 [C–*C*H_3, *J*(PtC) 117], 18 and 17 (m, MeP).

Crystal-structure Determination of $[\overline{(OC)_5W\{\mu\text{-}C(OMe)Ph\}Pt}(PMe_3)_2]$ (7).—Crystals of (7) grow as orange thin plates; that for data collection was of dimensions 0.20 × 0.25 × 0.05 mm, and diffracted intensities were recorded at 200 K for $2.9 \leqslant 2\theta \leqslant 50°$ on a Syntex $P2_1$ four-circle diffractometer.[20] Of the total 4 726 recorded intensities, 3 735 had $|F| \geqslant 2\sigma(F)$ where $\sigma(F)$ is the standard deviation based on counting statistics, and only these were used in the final refinement of the structure. Corrections were applied for Lorentz and polarisation effects and for the effects of *X*-ray absorption. Computations were carried out with the SHELX system of programs.[21]

Crystal data. $C_{19}H_{26}O_6P_2PtW$, $M = 791.4$, Triclinic, $a = 9.728(5)$, $b = 16.002(13)$, $c = 9.611(6)$ Å, $\alpha = 109.86(6)$, $\beta = 116.34(4)$, $\gamma = 83.77(6)°$, $U = 1\,259.5$ Å^3, $D_m = 2.05$ (flotation), $Z = 2$, $D_c = 2.09$ g cm^{-3}, $F(000) = 740$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 108.2 cm^{-1}, space group $P\bar{1}$.

Structure solution and refinements. The structure was solved by the heavy-atom method and all atoms (except H) were located by successive electron-density difference syntheses. The structure was refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were included at positions calculated for rigid-group atoms and only common temperatures factors for chemically equivalent hydrogen atoms were refined. Refinement for the structure converged at *R* 0.049 (*R′* 0.048), with the mean shift-to-error ratio in the final four cycles of refinement being 0.05 : 1 with a maximum of 0.2 : 1. A weighting scheme of the form $w = 1.387/(\sigma^2F + 0.002F^2)$, where $\sigma(F)$ is the estimated error in the observed structure factor based on counting statistics only, gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >1.2 e Å^{-3} except in the region of the metal atoms (max. 2.6 e Å^{-3}). Scattering factors were from ref. 22 for C, O, and P, ref. 23 for hydrogen, and ref. 24 for Pt and W, including corrections for the effects of anomalous dispersion for Pt ($\Delta f'$ −2.352, $\Delta f''$ 8.388), W ($\Delta f'$ −1.421, $\Delta f''$ 6.872), and P ($\Delta f'$ 0.090, $\Delta f''$ 0.095). Atomic positional parameters are in Table 3, interatomic distances and angles in Table 4, and some least-squares planes in Table 5. Observed and calculated structure factors, all thermal parameters, and positional parameters for hydrogen atoms are listed in Supplementary Publication No. SUP 22757 (21 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.