Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 6.[1] Synthesis of Platinum–Chromium and –Tungsten Compounds. *X*-Ray Crystal Structure of $[(Me_3P)(OC)_4W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$ †

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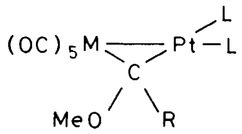
Addition of light petroleum solutions of $[M\{C(OMe)C_6H_4R\text{-}4\}(CO)_5]$ (M = Cr or W, R = Me or CF_3) to ethylene-saturated solutions of $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene), to which two molar equivalents of tertiary phosphine had been added, afforded the heteronuclear dimetal complexes $[(OC)_5Cr\{\mu\text{-}C(OMe)C_6H_4R\text{-}4\}Pt(PR_3)_2]$ (R = Me, PR_3 = PMe_3 or PMe_2Ph; R = CF_3, PR_3 = PMe_3) and $[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4R\text{-}4\}Pt(PR_3)_2]$ (R = Me or CF_3, PR_3 = PMe_3 or PMe_2Ph), characterised by ^{31}P and ^1H n.m.r. spectroscopy. The compounds $[(OC)_5W\{\mu\text{-}C(OMe)Me\}Pt(PMe_2Ph)_2]$, $[(OC)_5Cr(\mu\text{-}COCH_2CH_2CH_2)Pt(PMe_2Ph)_2]$, and $[(OC)_5W(\mu\text{-}CPh_2)Pt(PMe_3)_2]$ were similarly obtained from $[W\{C(OMe)Me\}(CO)_5]$, $[Cr(COCH_2CH_2CH_2)(CO)_5]$, and $[W(CPh_2)(CO)_5]$, respectively. Although $[PtW(\mu\text{-}CPh_2)(CO)_5(PMe_3)_2]$ is a relatively unstable complex, reaction with trimethylphosphine affords air-stable $[(Me_3P)(OC)_4W(\mu\text{-}CPh_2)Pt(PMe_3)_2]$ as a single isomer. A similar enhanced thermal and oxidative stability relative to the pentacarbonyl species is also observed with the compounds $[(Me_3P)(OC)_4Cr\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$ and $[(R_3P)(OC)_4W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PR_3)_2]$ (PR_3 = PMe_3 or PMe_2Ph). A single-crystal *X*-ray diffraction study on the complex $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_4(PMe_3)_3]$ shows that the tungsten–platinum bond [2.825(1) Å] is asymmetrically bridged by a $C(OMe)C_6H_4Me\text{-}4$ group [C–W 2.37(1) Å; C–Pt 2.03(1) Å], that the co-ordination of the W atom is close to octahedral, and that the Pt atom is in a near-planar environment. The crystals are orthorhombic, space group $Pna2_1$ (no. 33), with $Z = 4$ in a unit cell of dimensions a = 18.180(6), b = 10.720(3), c = 14.697(4) Å. The structure has been elucidated by heavy-atom methods from 3 882 independent intensities measured to 2θ = 60° at 200 K, and refined to R 0.044.

EARLIER[2] we reported that complexes containing a dimetallacyclopropane ring $[(OC)_5M\{\mu\text{-}C(OMe)Ph\}PtL_2]$ (M = Cr or W; L = PMe_3 or PMe_2Ph; L_2 = cod = cyclo-octa-1,5-diene) could be prepared by treating the mononuclear metal carbene compounds $[M\{C(OMe)Ph\}(CO)_5]$ with zerovalent platinum compounds $[Pt(C_2H_4)L_2]$ and $[Pt(cod)_2]$. The studies reported in this paper were designed to extend the range of known compounds of the type $[(OC)_5M(\mu\text{-}CR^1R^2)PtL_2]$, prior to investigating the chemistry of the dimetallacyclopropane ring systems in these molecules.[3] Moreover, a single crystal *X*-ray diffraction study of the complex $[(OC)_5W\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ revealed[2] a carbon–tungsten bond significantly longer than other known σ bonds between these two elements, whereas the carbon–platinum separation was within the range previously found for such bonds. Thus, in this molecule the alkylidene ligand asymmetrically bridges the two metal atoms. In these circumstances it was thought important to carry out an *X*-ray diffraction study on another dimetal complex of this class, in order to establish to what degree the asymmetric bridging by the alkylidene ligand is affected by varying the nature of the ligands on the metal atoms.

RESULTS AND DISCUSSION

The chromium–platinum complexes (1)—(3) were prepared by adding light petroleum solutions of $[Cr\{C(OMe)C_6H_4R\text{-}4\}(CO)_5]$ (R = Me or CF_3) at 0 °C to ethylene-saturated light petroleum solutions of $[Pt(cod)_2]$ which had been treated with 2 molar equivalents of the respective tertiary phosphine. The tungsten–platinum complexes (4)—(8) were similarly synthesized by treating $[W\{C(OMe)C_6H_4R\text{-}4\}(CO)_5]$ (R = Me or CF_3) or $[W\{C(OMe)Me\}(CO)_5]$ with $[Pt(C_2H_4)(PR_3)_2]$ (PR_3 = PMe_3 or PMe_2Ph); the latter species being generated *in situ*. Compounds (1)—(8) were character-



	M	R	L
(1)	Cr	$C_6H_4Me\text{-}4$	PMe_3
(2)	Cr	$C_6H_4Me\text{-}4$	PMe_2Ph
(3)	Cr	$C_6H_4CF_3\text{-}4$	PMe_3
(4)	W	$C_6H_4Me\text{-}4$	PMe_3
(5)	W	$C_6H_4Me\text{-}4$	PMe_2Ph
(6)	W	$C_6H_4CF_3\text{-}4$	PMe_3
(7)	W	$C_6H_4CF_3\text{-}4$	PMe_2Ph
(8)	W	Me	PMe_2Ph

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† *defg*-Tetracarbonyl-*c*-μ-(methoxo-*p*-tolylmethylidene)-*abh*-tris(trimethylphosphine)platinumtungsten (*Pt*—*W*).

TABLE 1

Analytical [a] and physical data for the dimetal complexes

	Compound	M.p. (θ_c/°C)	Colour	Yield (%)	Analysis (%)	
					C	H
(1)	$[(OC)_5Cr\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$	128—130 (decomp.)	Yellow-orange	80	35.2 (35.7)	4.2 (4.2)
(2)	$[(OC)_5Cr\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_2Ph)_2]$	108—110	Orange	17	44.8 (45.1)	4.4 (4.0)
(3)	$[(OC)_5Cr\{\mu\text{-}C(OMe)C_6H_4CF_3\text{-}4\}Pt(PMe_3)_2]$	122—124	Yellow-orange	57	33.2 (33.8)	3.6 (3.5)
(4)	$[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$	126—128	Orange	74	30.3 (29.8)	3.9 (3.5)
(5)	$[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_2Ph)_2]$	110—112	Orange	66	38.8 (38.8)	3.7 (3.5)
(6)	$[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4CF_3\text{-}4\}Pt(PMe_3)_2]$	128	Orange	61	28.0 (28.0)	3.2 (2.9)
(7)	$[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4CF_3\text{-}4\}Pt(PMe_2Ph)_2]$	128	Orange	75	37.0 (36.7)	3.1 (3.0)
(8)	$[(OC)_5W\{\mu\text{-}C(OMe)Me\}Pt(PMe_2Ph)_2]$	106—108	Yellow	27	34.3 (33.8)	3.6 (3.3)
(9)	$[(OC)_5Cr(\mu\text{-}COCH_2CH_2CH_2)Pt(PMe_2Ph)_2]$ [b]		Orange	32	40.9 (40.9)	4.0 (3.9)
(11)	$[(Me_3P)(OC)_4W(\mu\text{-}CPh_2)Pt(PMe_3)_2]$	140—146 (decomp.)	Dark red	28	35.1 (35.3)	4.6 (4.2)
(12)	$[(Me_3P)(OC)_4Cr\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$	118	Orange	40	36.6 (36.7)	5.3 (5.2)
(13)	$[(Me_3P)(OC)_4W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$	106	Orange-brown	59	31.2 (31.0)	4.4 (4.4)
(14)	$[(PhMe_2P)(OC)_4W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_2Ph)_2]$	104—106	Brown	42	43.6 (42.7)	4.7 (4.2)

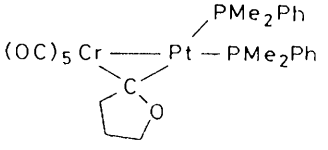
[a] Calculated values are given in parentheses. [b] Unstable, see text.

ised by microanalysis (Table 1), and by their ^{31}P and ^{1}H n.m.r. spectra (Table 2).

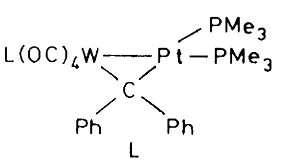
The ^{31}P n.m.r. spectra of compounds (1) and (4)—(8) show two doublet signals with ^{195}Pt satellites, as expected for structures with *cis*-$Pt(PR_3)_2$ groups, and as confirmed earlier by *X*-ray crystallography for the related compound $[(OC)_5W\{C(OMe)Ph\}Pt(PMe_3)_2]$.[2] The ^{31}P n.m.r. spectrum of (3) showed two singlets, corresponding to non-equivalent phosphine ligands, with ^{195}Pt satellites. Evidently for this compound *J*(PP) is very small. For compounds (1) and (3)—(8) the higher-field resonance showed couplings $J(^{195}Pt\text{–}^{31}P)$ *ca.* 4 500 Hz, while for the signal at lower field this coupling was much less, *ca.* 2 500 Hz. The former signals may be assigned to the tertiary phosphine ligands *transoid* to the metal–metal bond, and the latter resonance pattern to the tertiary phosphine ligands *trans* to the bridging carbene group.[2] The ^{1}H n.m.r. spectra are also in accord with the proposed formulations of the compounds, and call for no comment.

The ^{13}C n.m.r. spectra of several of the complexes (1)—(8) were examined, but due to weak signals the resonances of the bridging carbon atom could only be detected for compounds (3)—(5). For these three species the carbene-carbon atom resonance was a doublet of doublets due to coupling with *trans* and *cis* phosphorus nuclei, and appeared for (3) at 203 p.p.m. [*J*(PC) 81, 10 Hz], for (4) at 204 p.p.m. [*J*(PC) 56, 15 Hz], and for (5) at 207 p.p.m. [*J*(PC) 83, 19 Hz]. These chemical shifts for the bridge-carbon atoms are *ca.* 100 p.p.m. upfield from those observed for the carbene-carbon atoms of the mononuclear chromium and tungsten precursors.[4]

Reaction of the 2-oxacyclopentylidenechromium complex $[Cr(COCH_2CH_2CH_2)(CO)_5]$ [5] with a light petroleum solution containing $[Pt(cod)_2]$ saturated with ethylene and to which 2 molar equivalents of PMe_2Ph had been added, afforded orange crystals of compound (9) (Table 1). Unfortunately this complex proved very unstable, particularly in solution when it appears to revert to $[Cr(COCH_2CH_2CH_2)(CO)_5]$ within a few minutes. Formation of (9) is in contrast to the reaction of $[Pt(C_2H_4)(PMe_3)_2]$ with $[MnI(COCH_2CH_2CH_2)(CO)_4]$, which affords $[(OC)_4Mn\{\mu\text{-}(1\text{-}\sigma,1\text{—}2\text{-}\eta\text{-}C{=}CHCH_2CH_2O)\}Pt(PMe_3)_2]$ *via* loss of hydrogen from the oxacyclopentylidene group.[1]



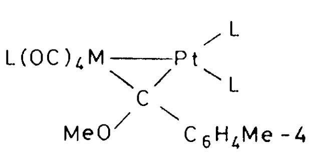
(9)



L

(10) CO

(11) PMe_3



M	L
(12) Cr	PMe_3
(13) W	PMe_3
(14) W	PMe_2Ph

Complexes (1)—(8), and the similar compounds described previously,[2] were all derived from carbene-chromium and -tungsten complexes in which the carbene-carbon atom carries an OMe substituent group.

TABLE 2

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

	Complex	$^{31}P(\delta/\text{p.p.m.})$ [b]	$^1H(\tau)$
(1)	$[(OC)_5Cr\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$	14.4 [d, *J*(PP) 6, *J*(PtP) 2 451] 22.3 [d, *J*(PP) 6, *J*(PtP) 4 511]	2.66—2.98 (m, 4 H, C_6H_4), 6.26 (s, 3 H, OMe), 7.67 (s, 3 H, Me-4), 8.38 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 19], 8.66 [d, 9 H, MeP, *J*(PH) 11, *J*(PtH) 45]
(2)	$[(OC)_5Cr\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_2Ph)_2]$ [c]		2.60—3.00 (m, 14 H, C_6H_4, Ph), 6.10 (s, 3 H, OMe), 7.69 (s, 3 H, Me-4), 8.52 and 8.72 [d, 3 H, MeP, *J*(PH) 9], 8.92 and 9.06 [d, 6 H, MeP, *J*(PH) 6]
(3)	$[(OC)_5Cr\{\mu\text{-}C(OMe)C_6H_4CF_3\text{-}4\}Pt(PMe_3)_2]$	14.1 [s, *J*(PP) <2, *J*(PtP) 2 444] 21.4 [s, *J*(PP) <2, *J*(PtP) 4 527]	2.54 (m, 4 H, C_6H_4), 6.27 (s, 3 H, OMe), 8.33 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 20], 8.61 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 45]
(4)	$[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$	15.1 [d, *J*(PP) 11, *J*(PtP) 2 514] 22.3 [d, *J*(PP) 11, *J*(PtP) 4 469]	2.60—2.98 (m, 4 H, C_6H_4), 6.32 (s, 3 H, OMe), 7.66 (s, 3 H, Me-4), 8.37 [d, 9 H, MeP, *J*(PH), 8, *J*(PtH) 20], 8.74 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 45]
(5)	$[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_2Ph)_2]$	5.6 [d, *J*(PP) 11, *J*(PtP) 2 540] 12.3 [d, *J*(PP) 11, *J*(PtP) 4 487]	2.36—2.92 (m, 14 H, C_6H_4, Ph), 6.10 (s, 3 H, OMe), 7.62 (s, 3 H Me-4), 8.46 and 8.57 [d, 6 H, MeP, *J*(PH) 8, *J*(PtH) 23], 8.94 and 9.06 [d, 6 H, MeP, *J*(PH) 6, *J*(PtH) 44]
(6)	$[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4CF_3\text{-}4\}Pt(PMe_3)_2]$	14.9 [d, *J*(PP) 5, *J*(PtP) 2 508] 21.8 [d, *J*(PP) 5, *J*(PtP) 4 494]	2.42 (m, 4 H, C_6H_4), 6.15 (s, 3 H, OMe), 8.17 [d of d, 9 H, MeP, *J*(PH) 8 and 2, *J*(PtH) 20], 8.63 [d of d, 9 H, MeP, *J*(PH) 10 and 2, *J*(PtH) 48]
(7)	$[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4CF_3\text{-}4\}Pt(PMe_2Ph)_2]$	5.6 [d, *J*(PP) 5, *J*(PtP) 2 539] 12.0 [d, *J*(PP) 5, *J*(PtP) 4 534]	2.15—3.10 (m, 14 H, C_6H_4, Ph), 6.16 (s, 3 H, OMe), 8.46 and 8.56 [d, 6 H, MeP, *J*(PH) 8, *J*(PtH) 21], 8.93 and 9.03 [d, 9 H, MeP, *J*(PH) 5, *J*(PtH) 48]
(8)	$[(OC)_5W\{\mu\text{-}C(OMe)Me\}Pt(PMe_2Ph)_2]$	5.8 [d, *J*(PP) 14, *J*(PtP) 2 434] 6.7 [d, *J*(PP) 14, *J*(PtP) 4 530]	2.68 (m, 10 H, Ph), 6.32 (s, 3 H, OMe), 6.97 [d of d, 3 H, Me, *J*(PH) 12 and 6], 8.43 and 8.54 [d, 6 H, MeP, *J*(PH) 7, *J*(PtH) 21], 8.55 and 8.73 [d, 6 H, MeP, *J*(PH) 10, *J*(PtH) 42]
(10)	$[(OC)_5W(\mu\text{-}CPh_2)Pt(PMe_3)_2]$	16.9 [d, *J*(PP) 16, *J*(PtP) 4 620] 18.9 [d, *J*(PP) 16, *J*(PtP) 2 393]	
(11)	$[(Me_3P)(OC)_4W(\mu\text{-}CPh_2)Pt(PMe_3)_2]$	17.0 [d of d, *J*(PP) 13 and 15, *J*(PtP) 4 643] 18.0 [d, *J*(PP) 15, *J*(PtP) 2 358] 41.8 [d, *J*(PP) 13, *J*(WP) 233]	2.15—3.25 (m, 10 H, Ph), 8.36 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 19], 8.65 [d, 9 H, MeP, *J*(PH) 8], 8.89 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 40]
(12)	$[(Me_3P)(OC)_4Cr\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$	−6.5 (s,br) 14.7 [d, *J*(PP) 6, *J*(PtP) 2 391] 21.1 [d, *J*(PP) 6, *J*(PtP) 4 686]	2.76—3.15 (m, 4 H, C_6H_4), 6.50 (s, 3 H, OMe), 7.74 (s, 3 H, Me-4), 8.43 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 20], 8.73 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 40], 8.74 [d, 9 H, MeP, *J*(PH) 8]
(13)	$[(Me_3P)(OC)_4W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$	15.4 [d, *J*(PP) 8, *J*(PtP) 2 446] 20.8 [d of d, *J*(PP) 8 and 9, *J*(PtP) 4 797] 43.6 [d, *J*(PP) 9. *J*(WP) 229]	2.72—3.12 (m, 4 H, C_6H_4), 6.55 (s, 3 H, OMe), 7.74 (s, 3 H, Me-4), 8.45 [d, 9 H, MeP, *J*(PH) 7, *J*(PtH) 20], 8.70 [d, 9 H, MeP, *J*(PH) 9], 8.80 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 42]
(14)	$[(PhMe_2P)(OC)_4W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_2Ph)_2]$	6.4 [d, *J*(PP) 6, *J*(PtP) 2 448] 11.6 [d of d, *J*(PP) 6 and 11, *J*(PtP) 4 855] 28.8 [d, *J*(PP) 11, *J*(WP) 227]	2.40—3.10 (m, 14 H, C_6H_4, Ph), 6.56 (s, 3 H, OMe), 7.72 (s, 3 H, Me-4), 8.30 [d, 6 H, MeP, *J*(PH) 9], 8.34 [d, 6 H, MeP, *J*(PH) 8, *J*(PtH) 16], 8.54 and 8.72 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 19]

[a] Measured in $CDCl_3$ at room temperature. Coupling constants in Hz. [b] Hydrogen-1 decoupled, chemical shifts in p.p.m. to low frequency of 85% H_3PO_4 (external). [c] Phosphorus-31 n.m.r. spectrum not measured due to insufficient sample available.

It was of some interest, therefore, to establish whether the compound $[W(CPh_2)(CO)_5]$,[6] which does not have a heteroatom attached to the carbene-carbon atom, would yield a stable dimetallacyclopropane structure on reaction with a platinum(0) species. Addition of $[W(CPh_2)(CO)_5]$ in light petroleum to a solution of $[Pt(C_2H_4)(PMe_3)_2]$ in the same solvent at −60 °C led rapidly to formation of a red compound (10), the ^{31}P n.m.r. spectrum of which (Table 2) strongly supported the proposed formulation as a species containing the

$\overline{\mathrm{W}(\mu\text{-CPh}_2)\mathrm{Pt}}$ ring system. However, it was not possible to obtain good microanalytical data on (10) and it proved to be much less stable in air and decomposed thermally more readily than compounds (1)—(8); the latter species generally remaining unchanged in air at room temperature after several weeks. It thus seems that the heteronuclear dimetallacyclopropane rings in the platinum–chromium and –tungsten complexes are stabilised to some degree by the presence of an electronegative OMe group on the bridging carbon atom. We have previously drawn attention to the stability of the complex $[\mathrm{Pt_2\{\mu\text{-}C(CF_3)_2\}(cod)_2}]$,[7] containing the very electronegative perfluoromethyl groups.

During the course of our work it was observed that a second factor stabilised the dimetallacyclopropane ring structures, namely replacement of one of the five CO ligands on chromium or tungsten by a tertiary phosphine group. This effect is seen very clearly in the preparation of the air-stable compound (11) by reaction of (10), generated ***in situ***, with trimethylphosphine. Complex (11) was characterised by microanalysis, and by its ^{31}P and ^{1}H n.m.r. spectra. In the ^{31}P n.m.r. spectrum three signals were observed; that at 41.8 p.p.m. occurred as a doublet with ^{183}W satellites and is thus due to a $\mathrm{PMe_3}$ ligand attached to tungsten. The other two resonances had ^{195}Pt satellites as expected for $\mathrm{PMe_3}$ groups bonded to platinum. Moreover, whereas the signal at 18.0 p.p.m. was a doublet, that at 17.0 p.p.m. was a double-doublet, reflecting coupling both with the $\mathrm{PMe_3}$ ligand attached to the tungsten atom and the other $\mathrm{PMe_3}$ bound to platinum. The ^{1}H n.m.r. spectrum (Table 2) of (11) also showed bands corresponding to three distinct $\mathrm{PMe_3}$ ligands, two of these doublet resonances showing ^{195}Pt satellites. The relative simplicity of the ^{31}P and ^{1}H spectra established that (11) was formed as a single isomer.

TABLE 3

Atomic positional (fractional co-ordinates) parameters for complex (13) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt	0.370 52(3)	0.112 22(4)	0.000 00
W	0.434 03(3)	0.283 76(4)	0.122 93(5)
C(6)	0.395 7(7)	0.291 7(12)	−0.031 3(7)
O(6)	0.447 6(5)	0.317 3(8)	−0.101 4(6)
C(06)	0.507 0(8)	0.236 2(14)	−0.107 5(9)
C(61)	0.333 8(7)	0.382 6(11)	−0.048 1(8)
C(62)	0.263 5(9)	0.358 7(12)	−0.008 8(10)
C(63)	0.205 5(9)	0.437 1(14)	−0.017 9(8)
C(64)	0.211 2(3)	0.546 9(12)	−0.071 6(10)
C(65)	0.279 8(11)	0.568 9(13)	−0.111 3(10)
C(66)	0.340 1(9)	0.490 7(14)	−0.098 8(9)
C(67)	0.148 9(9)	0.633 9(15)	−0.082 9(12)
Carbonyl groups			
C(1)	0.344 9(10)	0.202 6(14)	0.169 4(9)
O(1)	0.289 9(6)	0.165 0(12)	0.204 2(7)
C(2)	0.468 3(8)	0.287 0(11)	0.248 8(10)
O(2)	0.492 2(7)	0.288 6(11)	0.322 9(7)
C(3)	0.377 7(8)	0.445 9(15)	0.135 3(10)
O(3)	0.346 1(7)	0.538 3(10)	0.143 7(7)
C(4)	0.498 9(8)	0.131 1(15)	0.114 4(12)
O(4)	0.539 6(6)	0.046 9(11)	0.111 2(9)
Phosphine ligands			
P(1)	0.320 4(2)	0.070 3(3)	−0.135 5(2)
C(11)	0.341 0(11)	0.171 1(16)	−0.230 3(9)
C(12)	0.339 7(12)	−0.078 1(16)	−0.190 2(13)
C(13)	0.220 2(10)	0.073 5(23)	−0.133 5(13)
P(2)	0.360 6(2)	−0.082 9(3)	0.068 1(2)
C(21)	0.272 3(10)	−0.165 3(14)	0.057 1(11)
C(22)	0.425 9(9)	−0.192 8(13)	0.024 3(13)
C(23)	0.378 1(12)	−0.100 9(17)	0.191 0(11)
P(3)	0.539 1(2)	0.430 1(3)	0.094 5(3)
C(31)	0.543 5(11)	0.555 6(14)	0.176 7(11)
C(32)	0.629 3(8)	0.362 4(15)	0.106 3(15)
C(33)	0.545 4(9)	0.520 4(13)	−0.010 4(11)

TABLE 4

Bond lengths (Å) and angles (°) for complex (13)

$[\overline{\mathrm{(Me_3P)(OC)_4W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt}}\mathrm{(PMe_3)_2}]$

(*a*) Distances			
Pt–W	2.825(1)	C(61–C(62)	1.43(2)
Pt–C(6)	2.03(1)	C(62)–C(63)	1.36(2)
W–C(6)	2.37(1)	C(63)–C(64)	1.42(2)
C(6)–O(6)	1.42(1)	C(64)–C(65)	1.40(2)
O(6)–C(06)	1.39(2)	C(65)–C(66)	1.39(2)
C(6)–C(61)	1.51(2)	C(66)–C(61)	1.38(2)
		C(64)–C(67)	1.48(2)
Pt–P(1)	2.236(4)	Pt–P(2)	2.326(3)
P(1)–C(11)	1.80(2)	P(2)–C(21)	1.84(2)
P(1)–C(12)	1.82(2)	P(2)–C(22)	1.79(2)
P(1)–C(13)	1.82(2)	P(2)–C(23)	1.84(2)
W–P(3)	2.507(4)	P(3)–C(31)	1.81(2)
P(3)–C(32)	1.80(2)	P(3)–C(33)	1.82(2)
W–C(1)	1.96(2)	C(1)–O(1)	1.19(2)
W–C(2)	1.95(1)	C(2)–O(2)	1.17(2)
W–C(3)	2.03(2)	C(3)–O(3)	1.15(2)
W–C(4)	2.02(2)	C(4)–O(4)	1.17(2)
(*b*) Angles			
W–Pt–C(6)	55.7(3)	Pt–W–C(6)	45.0(3)
W–C(6)–Pt	79.4(4)	O(6)–C(6)–C(61)	104.6(9)
W–C(6)–O(6)	120.2(8)	Pt–C(6)–O(6)	119.7(9)
W–C(6)–C(61)	113.5(7)	Pt–C(6)–C(61)	118.7(8)
C(6)–Pt–P(1)	94.6(3)	W–Pt–P(1)	150.1(1)
C(6)–Pt–P(2)	165.3(3)	W–Pt–P(2)	110.0(1)
C(6)–O(6)–C(06)	116(1)	P(1)–Pt–P(2)	99.9(1)
C(6)–C(61)–C(62)	119(1)	C(6)–C(61)–C(66)	125(1)
C(61)–C(62)–C(63)	123(1)	C(62)–C(63)–C(64)	121(1)
C(63)–C(64)–C(65)	116(1)	C(64)–C(65)–C(66)	123(1)
C(65)–C(66)–C(61)	121(1)	C(66)–C(61)–C(62)	116(1)
C(63)–C(64)–C(67)	122(1)	C(67)–C(64)–C(65)	122(1)
Pt–P(1)–C(11)	118 9(5)	C(11)–P(1)–C(12)	98.2(8)
Pt–P(1)–C(12)	119.4(7)	C(11)–P(1)–C(13)	102.1(10)
Pt–P(1)–C(13)	112.9(6)	C(12)–P(1)–C(13)	102.5(10)
Pt–P(2)–C(21)	117.5(5)	C(21)–P(2)–C(22)	103.3(8)
Pt–P(2)–C(22)	112.6(5)	C(21)–P(2)–C(23)	100.8(9)
Pt–P(2)–C(23)	120.1(6)	C(22)–P(2)–C(23)	99.7(9)
W–P(3)–C(31)	112.8(6)	C(31)–P(3)–C(32)	101.2(9)
W–P(3)–C(32)	115.2(5)	C(31)–P(3)–C(33)	99.6(7)
W–P(3)–C(33)	121.4(5)	C(32)–P(3)–C(33)	103.8(9)
Pt–W–C(1)	66.2(4)	W–C(1)–O(1)	172(1)
Pt–W–C(2)	138.4(4)	W–C(2)–O(2)	177(1)
Pt–W–C(3)	114.2(4)	W–C(3)–O(3)	179(1)
Pt–W–C(4)	70.8(4)	W–C(4)–O(4)	176(1)
Pt–W–P(3)	127.7(1)	C(1)–W–C(2)	86.7(6)
C(6)–W–C(1)	96.1(5)	C(1)–W–C(3)	86.1(6)
C(6)–W–C(2)	176.6(5)	C(1)–W–C(4)	98.3(6)
C(6)–W–C(3)	84.6(5)	C(1)–W–P(3)	164.8(4)
C(6)–W–C(4)	98.1(6)	C(2)–W–C(3)	93.5(6)
C(6)–W–P(3)	92.4(3)	C(2)–W–C(4)	83.5(6)
C(3)–W–C(4)	174.5(6)	C(2)–W–P(3)	84.5(4)
C(3)–W–P(3)	82.2(4)	C(4)–W–P(3)	93.0(4)

Earlier it had been observed[8] that the complex $[\overline{\mathrm{(OC)_5Cr\{\mu\text{-}C(OMe)Ph\}Pt}}\mathrm{(PMe_3)_2}]$ in organic solvents above 80 °C readily decomposes into $[\mathrm{Cr(CO)_5(PMe_3)}]$, $[\mathrm{Pt_3\{\mu\text{-}C(OMe)Ph\}_2(\mu\text{-}CO)(PMe_3)_3}]$, and $[\mathrm{Pt_3\{\mu\text{-}C(OMe)\text{-}Ph\}_3(PMe_3)_3}]$. The enhanced stability of (11) relative to

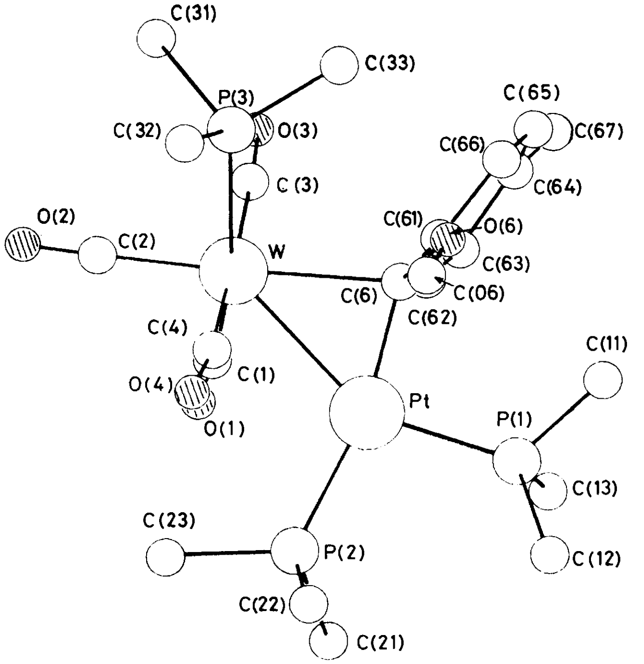


FIGURE 1 Molecular structure of the complex $[(Me_3P)(OC)_4W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$ (13), projected onto the plane of the $W(\mu\text{-}C)Pt$ ring, and showing the crystallographic numbering sequence

(10) led us to prepare complexes (12)—(14) by u.v. irradiation of compounds (1) and (4) with PMe_3, and compound (5) with PMe_2Ph. Each of (12)—(14) was produced as a single isomer, as revealed by the relative simplicity of the ^{31}P and ^{1}H n.m.r. spectra. The ^{31}P n.m.r. spectrum of complexes (13) and (14) showed three resonances, one with ^{183}W satellites and two with ^{195}Pt satellites, in accord with replacement of one CO ligand on tungsten by a tertiary phosphine group.

The species (12)—(14) were observed qualitatively to be thermally more stable than their pentacarbonyl analogues, particularly with respect to decomposition to triplatinum compounds.[8] It was important, therefore, to establish quantitatively *via* *X*-ray crystallography what effect trimethylphosphine substitution on the chromium or tungsten atoms had on the geometry of the dimetallacyclopropane rings. Since the earlier structural study involved $[(OC)_5W\{C(OMe)Ph\}Pt(PMe_3)_2]$, for comparison purposes a crystal of complex (13) was selected for *X*-ray diffraction work. The results of the *X*-ray study on $[(Me_3P)(OC)_4W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$ are summarised in Tables 3 and 4 and in Figures 1—3.

The W–Pt bond [2.825(1) Å] is asymmetrically bridged by the $C(OMe)C_6H_4Me$-4 group [C–W 2.37(1); C–Pt 2.03(1) Å]. Here the W–C(6) distance is significantly longer than those found (2.1—2.3 Å) for σ bonds between tungsten and sp^3-carbon atoms in other compounds,[9] but is not significantly different from the W–C distance in the anion $[(OC)_5W\text{-}CH(OMe)Ph]^-$, 2.34(1) Å.[6] It is, however, significantly shorter than the corresponding W–C distance [2.48(1) Å] found in the pentacarbonyl complex $[(OC)_5W\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$.[2] As the Pt–W distance in the title compound [2.825(1) Å] is also considerably shorter than that in the pentacarbonyl species [2.861(1) Å],[2] the enhanced stability of the title compound is manifest in terms of tighter bonding in the dimetallacyclopropane ring. A summary of these differences is given in Table 5. The Pt–C(6) distance lies at the lower end of the range [1.99(3)—2.15(2) Å] generally observed for platinum–carbon σ bonds.[10] The co-ordination geometry of the platinum atom is essentially planar, the angle between the planes Pt, W, C(6) and Pt, P(1), P(2) being only 4.4°. Of the two phosphine ligands on the Pt atom, one is *trans* to the bridging C atom and the other is *trans* to the tungsten atom, with an interbond angle P(1)–Pt–P(2) of 99.9°. The methyl groups of the phosphines are positioned to minimise steric interactions. The two Pt–P distances, however,

TABLE 5

Comparison of internuclear distances (Å) and angles (°) in the complexes $[(OC)_5W\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ and $[(Me_3P)(OC)_4W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$

	$[PtW\{\mu\text{-}C(OMe)Ph\}\text{-}(CO)_5(PMe_3)_2]$	$[PtW\{\mu\text{-}C(OMe)\text{-}C_6H_4Me\text{-}4\}(CO)_4\text{-}(PMe_3)_3]$
Pt–W	2.861(1)	2.825(1)
Pt–μ-C	2.04(1)	2.03(1)
W–μ-C	2.48(1)	2.37(1)
Pt–μ-C–W	77.8(3)	79.4(4)
Pt–W–μ-C	44.2(3)	45.0(3)
W–Pt–μ-C	58.0(3)	55.7(3)

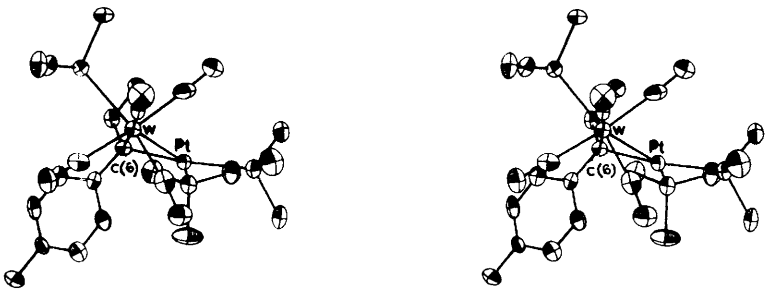


FIGURE 2 Stereoscopic view of the structure of complex (13)

though lying within the range commonly observed, are significantly different from one another, the one *trans* to the bridging carbon atom [Pt–P(2), 2.326(3) Å] being longer than the one *trans* to the tungsten atom [Pt–P(1), 2.236(4) Å].

Around the tungsten atom the co-ordination is octahedral if the W–Pt bond is excluded, though the distortions are primarily due to this W–Pt interaction. The largest deviations from orthogonality are seen (Table 4) in the angles C(6)–W–C(1), 96°; C(6)–W–C(4), 98°; and C(1)–W–C(4), 98°. If the bridging carbon atom, C(6), the tungsten atom, and the carbonyl group *trans* to C(6) are taken to define an 'axial' direction of the octahedron, then the phosphine ligand on the tungsten atom occupies one equatorial site. The plane of the dimetallacyclopropane ring, when viewed looking along this 'axial' direction of the tungsten octahedron, bisects the angles between the equatorial ligands, and, as might be expected, the phosphine ligand is on the opposite side of this plane to the *p*-tolyl ligand on the bridging carbon atom. Both ligands point away from the platinum atom and its two phosphine ligands. This is clearly seen in the stereoscopic view of the molecule (Figure 2). The W–P bond length [2.507(4) Å] is in the range previously recorded for tungsten–phosphorus bonds, *viz.* 2.427(1)—2.614(5) Å,[11] but the tungsten–carbonyl distances show significant variations, the two carbonyls *trans* to one another having longer W–C distances (*ca.* 2.03 Å) than those *trans* to the phosphine or to the bridging carbon atom (*ca.* 1.96 Å). The carbonyl groups themselves are essentially linear with the metal except perhaps C(1)–O(1). Here the W–C(1)–O(1) angle of 172(1)° combined with a Pt–W–C(1) angle of 66.2(4)° suggests some incipient semi-bridging of the Pt–W bond [Pt–C(1), 2.71 Å].

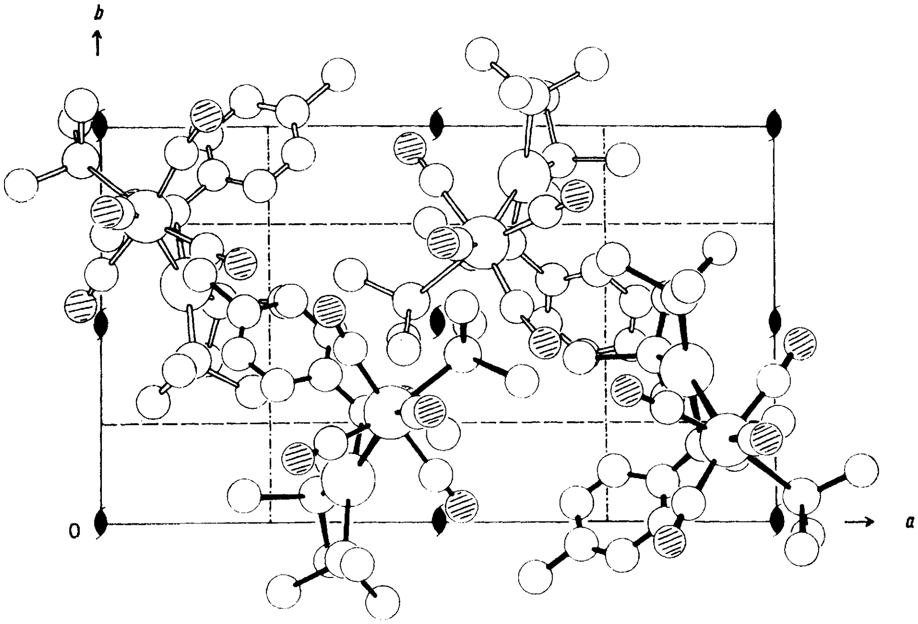


FIGURE 3 Contents of the orthorhombic unit cell ($Pna2_1$) seen in projection down *c* looking towards the origin

The bridging carbon atom is, of course, constrained in its geometry by the bond lengths in the dimetallacyclopropane ring, giving a ring angle of 79.4(4)°, and hence severe deviation from ideal tetrahedral geometry. Of the six interbond angles, only two [W–C(6)–C(61), 113.5(7)° and O(6)–C(6)–C(61), 104.6(9)°] are close to the tetrahedral angle. The plane defined by the carbene ligand O(6) • • • C(6) • • • C(61), is almost perpendicular (87°) to the dimetallacyclopropane ring.

The packing of the molecules in the orthorhombic unit cell is illustrated in Figure 3.

EXPERIMENTAL

The instrumentation used was as described in earlier work.[2] Light petroleum refers to that fraction of b.p. 40—60 °C, unless otherwise stated. Hydrogen-1 and ^{31}P and ^{13}C (^{1}H-decoupled) n.m.r. spectra were measured at 100, 40.48, and 25.15 MHz, respectively. Data from the ^{1}H and ^{31}P spectra are summarized in Table 2. For ^{13}C, chemical shifts are in p.p.m., relative to $\mathrm{SiMe_4}$, with positive values to high frequency. Literature methods were used to prepare the compounds $[\mathrm{Pt(cod)_2}]$,[12] $[\mathrm{M\{C(OMe)C_6H_4R\text{-}4\}(CO)_5}]$ (M = Cr or W; R = Me or $\mathrm{CF_3}$), $[\mathrm{W\{C(OMe)Me\}(CO)_5}]$,[13] $[\mathrm{W(CPh_2)(CO)_5}]$,[6] and $[\mathrm{Cr(\overline{COCH_2CH_2CH_2})(CO)_5}]$ [5] employed in the various syntheses. All reactions were carried out under an atmosphere of nitrogen using Schlenk-tube techniques, and dry oxygen-free solvents. Analytical data for new compounds are given in Table 1. Carbonyl bands in the i.r. spectra of the complexes were measured in cyclohexane solution; all other bands are recorded from Nujol mulls.

Synthesis of the Dimetal Compounds (1)—(10).—(*a*). A solution of $[\mathrm{Cr\{C(OMe)C_6H_4Me\text{-}4\}(CO)_5}]$ (0.49 g, 1.5 mmol) in light petroleum (50 cm^3) was added to a cold (0 °C) vigorously stirred solution of $[\mathrm{Pt(C_2H_4)(PMe_3)_2}]$ {1.5 mmol, generated from $[Pt(cod)_2]$ (0.62 g, 1.5 mmol), C_2H_4, and PMe_3 (3 mmol)} in light petroleum (40 cm^3). The reaction mixture was stirred for 40 min at 0 °C, the volume of solvent reduced *in vacuo* to *ca.* 30 cm^3, and the remaining liquid removed with a syringe. The yellow-orange solid obtained was washed (2 × 5 cm^3) with light petroleum and dried *in vacuo* to afford *microcrystals* of $[CrPt\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_5(PMe_3)_2]$ (1); $\nu_{max.}$ at 2 025s, 1 969m, 1 933s, 1 891m, and 1 878 (CO); 1 290m, 1 219w, 1 180w, 1 167m, 1 098s, 958s, 946(sh), 822w, 798w, 732w, 720w, 661s, 651s, 592s, and 569s cm^{-1}.

(*b*). A solution of $[Cr\{C(OMe)C_6H_4Me\text{-}4\}(CO)_5]$ (0.26 g, 0.8 mmol) in light petroleum (15 cm^3) was added to a vigorously stirred solution of $[Pt(C_2H_4)(PMe_2Ph)_2]$ {0.8 mmol, prepared in the usual way from $[Pt(cod)_2]$, PMe_2Ph, and C_2H_4} in light petroleum (25 cm^3) at 0 °C. Stirring was continued overnight at room temperature. The resulting mixture was filtered, and solvent removed *in vacuo* to give a red oil. The latter was dissolved in diethyl ether (20 cm^3), and the mixture filtered through a short alumina column (6 cm). Light petroleum (15 cm^3) was added to the solution, and solvent was then reduced in volume *in vacuo* to *ca.* 2 cm^3. Dropwise addition of diethyl ether afforded orange *microcrystals* of $[CrPt\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_5(PMe_2Ph)_2]$ (2); $\nu_{max.}$ at 2 026s, 1 972m, 1 937s, 1 894m, and 1 878m (CO); 1 259s, 1 166m, 1 095s, 1 019s, 938w, 928w, 908m, 800s, 740m, 716w, 691w, 666w, 650s, 588m, 571w, and 489w cm^{-1}.

(*c*). The complex $[CrPt\{\mu\text{-}C(OMe)C_6H_4CF_3\text{-}4\}(CO)_5(PMe_3)_2]$ (3) was prepared in a similar manner to (1) from $[Cr\{C(OMe)C_6H_4CF_3\text{-}4\}(CO)_5]$ (0.29 g, 0.75 mmol) in light petroleum (40 cm^3) and an ethylene-saturated light petroleum (30 cm^3) solution of $[Pt(cod)_2]$ (0.31 g, 0.75 mmol) treated with PMe_3 (1.5 mmol). Compound (3) had $\nu_{max.}$ at 2 029s, 1 982m, 1 939s, 1 901m, and 1 880m (CO); 1 326s, 1 298s, 1 259w, 1 169s, 1 158s, 1 120s, 1 096s, 1 066s, 1 010w, 979w, 953s, 942(sh), 842s, 736w, 721w, 666s, 655(sh), 649s, 606s, and 568s cm^{-1}. Carbon-13 n.m.r. (in $CDCl_3$), δ(p.p.m.) 228, 222 (CO), 203 [d of d, μ-C, *J*(PC) 81 and 10], 161 [C^1 of C_6H_4, *J*(PtC) 85], 126—120 (C_6H_4), 59 [OMe, *J*(PtC) 51 Hz], and 19—15 (MeP).

(*d*). A solution of $[W\{C(OMe)C_6H_4Me\text{-}4\}(CO)_5]$ (0.46 g, 1 mmol) in light petroleum (30 cm^3) was added to a cold (0 °C) vigorously stirred solution of $[Pt(C_2H_4)(PMe_3)_2]$ {1 mmol, generated from $[Pt(cod)_2]$ (0.41 g, 1 mmol) and PMe_3 (2 mmol)}. After 40 min, solvent was removed, and the orange solid washed with light petroleum (2 × 5 cm^3) to afford *microcrystals* of $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_5(PMe_3)_2]$ (4); $\nu_{max.}$ at 2 044s, 1 973m, 1 936s, 1 908(sh), and 1 900s (CO); 1 291m, 1 260w, 1 220w, 1 181w, 1 178m, 1 097s, 960(sh), 952s, 947(sh), 860w, 851w, 824m, 736w, 725(sh), 722m, 591s, 569m, and 460m cm^{-1}. Carbon-13 n.m.r. (in $CDCl_3$), δ (p.p.m.) 207 (CO), 204 [d, of d, μ-C, *J*(PC) 56 and 15], 203 (CO), 157 [d, C^1 (C_6H_4), *J*(PC) 5, *J*(PtC) 79], 134, 127 (C_6H_4), 60 [OMe, *J*(PtC) 58 Hz], 30 (Me-4), and 20—15 (MeP).

(*e*). The complex $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_5(PMe_2Ph)_2]$ (5) was similarly prepared as orange *crystals* from $[W\{C(OMe)C_6H_4Me\text{-}4\}(CO)_5]$ (1 mmol) and $[Pt(C_2H_4)(PMe_2Ph)_2]$ (1 mmol); $\nu_{max.}$ at 2 044s, 1 973m, 1 938s, 1 905s, and 1 901(sh) (CO); 1 261s, 1 165m, 1 093s, 1 020m, 965w, 944(sh), 940w, 920m, 911s, 868w, 824m, 801s, 742s, 715m, 704w, 695s, 677w, and 640w cm^{-1}. Carbon-13 n.m.r. (in $CDCl_3$), δ (p.p.m.) 207 (CO), 207 [d of d, μ-C, *J*(PC) 83 and 19], 203 (CO), 157 [d, C^1 (C_6H_4), *J*(PC) 5, *J*(PtC) 84], 134—127 (aromatic C), 60 [OMe, *J*(PtC) 56 Hz], 21 (Me-4), and 15—11 (MeP).

(*f*). Similarly orange *crystals* of $[PtW\{\mu\text{-}C(OMe)C_6H_4CF_3\text{-}4\}(CO)_5(PMe_3)_2]$ (6) were prepared from $[W\{C(OMe)C_6H_4\text{-}CF_3\text{-}4\}(CO)_5]$ (0.75 mmol) and $[Pt(C_2H_4)(PMe_3)_2]$ (0.75 mmol); $\nu_{max.}$ at 2 045s, 1 978m, 1 945s, 1 916(sh), and 1 907s (CO); 1 333s, 1 302s, 1 288m, 1 168m, 1 153m, 1 120m, 1 109w, 1 092m, 1 063m, 1 009w, 972w, 950s, 942(sh), 843m, 800w, 745w, 739w, 721m, 670m, 612s, 589s, and 575s cm^{-1}.

(*g*). The compound $[PtW\{\mu\text{-}C(OMe)C_6H_4CF_3\text{-}4\}(CO)_5(PMe_2Ph)_2]$ (7) was obtained in a 0.5 h reaction between $[W\{\mu\text{-}C(OMe)C_6H_4CF_3\text{-}4\}(CO)_5]$ (0.75 mmol) and $[Pt(C_2H_4)(PMe_2Ph)_2]$ (0.75 mmol) in light petroleum (60 cm^3) at 0 °C. For (7), $\nu_{max.}$ at 2 046s, 1 977m, 1 944s, 1 910s, and 1 903(sh) (CO); 1 322m, 1 261w, 1 154w, 1 093m, 1 064w, 940w, 920w, 911m, 800w, 752m, 693m, and 610m cm^{-1}.

(*h*). From $[W\{C(OMe)Me\}(CO)_5]$ (1 mmol) and $[Pt(C_2H_4)(PMe_2Ph)_2]$ (1 mmol), yellow *crystals* of the complex $[PtW\{\mu\text{-}C(OMe)Me\}(CO)_5(PMe_2Ph)_2]$ (8) were obtained, with $\nu_{max.}$ at 2 040s, 1 963m, 1 934s, 1 915(sh), and 1 907s (CO); 1 348w, 1 310w, 1 286m, 1 260w, 1 190w, 1 110(sh), 1 095s, 1 003m, 960(sh), 948s, 868m, 813m, 722m, 678w, and 670w cm^{-1}.

(*i*). A solution of $[Cr(\overline{COCH_2CH_2CH_2})(CO)_5]$ (0.21 g, 0.8 mmol) in light petroleum (40 cm^3) was added to a cold (0 °C) vigorously stirred solution prepared from $[Pt(cod)_2]$ (0.33 g, 0.8 mmol) and PMe_2Ph (1.6 mmol) in light petroleum saturated with ethylene. The reaction mixture was stirred for 90 min at 0—10 °C, and then for 30 min at room temperature. Solvent was removed *in vacuo* and the solid washed with light petroleum (3 × 10 cm^3) to give orange *microcrystals* of $[CrPt(\mu\text{-}\overline{COCH_2CH_2CH_2})(CO)_5(PMe_2Ph)_2]$ (9); $\nu_{max.}$ (CO) at 2 026s, 1 955s, 1 930s, and 1 905m cm^{-1}. Complex (9) is very unstable in solution; after *ca.* 10 min in cyclohexane the i.r. spectrum shows only bands in the CO region due to $[Cr(\overline{COCH_2CH_2CH_2})(CO)_5]$.

(*j*). A solution of $[Pt(C_2H_4)(PMe_3)_2]$ (0.25 mmol) in light petroleum (30—40 °C) (10 cm^3) was prepared *in situ* from $[Pt(cod)_2]$ and PMe_3, and cooled to −60 °C. A solution of $[W(CPh_2)(CO)_5]$ (0.12 g, 0.25 mmol) in 10 cm^3 of light petroleum (30—40 °C) was added dropwise with stirring, affording a red precipitate. The mixture was stirred at −60 °C (10 min) and allowed to warm to −10 °C (45 min). The supernatant liquid was removed, and the precipitate washed with light petroleum (2 × 5 cm^3) at −10 °C and dried to give red *microcrystals* of $[PtW(\mu\text{-}CPh_2)(CO)_5(PMe_3)_2]$ (10), m.p. 94—96 °C (decomp.), $\nu_{max.}$ (CO) at 2 049s, 1 980m, 1 943vs, 1 908(sh), and 1 893s cm^{-1}. The ^{31}P n.m.r. spectrum (Table 2) was in agreement with the proposed formulation, but satisfactory microanalytical data were not obtained for (10) in spite of recrystallisation and chromatography, both of which led to decomposition. However, reaction with PMe_3 gave compound (11), also prepared as described below.

Synthesis of the Tertiary Phosphine Derivatives (11)—(14).—(*a*). A solution of $[Pt(C_2H_4)(PMe_3)_2]$ (0.5 mmol) in light petroleum (30—40 °C) (15 cm^3) was added to a suspension of $[W(CPh_2)(CO)_5]$ (0.5 mmol) in the same solvent (10 cm^3) at −70 °C. After warming to room temperature, the supernatant liquid was removed, and the solid dissolved in diethyl ether (10 cm^3). A solution of PMe_3 (0.50 mmol) in light petroleum (1 cm^3) was then added, and the mixture stirred for 19 h. Solvent was removed *in vacuo* and the red oil treated with diethyl ether at −20 °C to give dark red *prisms* of the compound $[PtW(\mu\text{-}CPh_2)(CO)_4(PMe_3)_3]$ (11); $\nu_{max.}$ (CO) 2 004s, 1 910vs, 1 863s, and 1 846s cm^{-1}.

(*b*). Complex (1) (0.67 g, 1 mmol) in diethyl ether (80 cm^3) was treated with PMe_3 (1.1 mmol) in light petroleum (5 cm^3). The mixture was irradiated with u.v. light and stirred for 48 h at room temperature. After removal of solvent *in vacuo*, the resulting orange-brown oil was dissolved in diethyl ether (30 cm^3) and filtered through a column (3 cm) of alumina. After reduction of the volume to *ca.* 10 cm^3, light petroleum (30 cm^3) was added. Reduction in volume to *ca.* 5 cm^3 gave, after drying *in vacuo*, orange *microcrystals* of $[CrPt\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_4(PMe_3)_3]$ (12); $\nu_{max.}$ at 1 979s, 1 971s, 1 900vs, 1 850s, and 1 829s (CO); 1 493w, 1 421m, 1 303w, 1 284m, 1 261w, 1 165m, 1 093s, 968m, 947s, 850w, 832w, 800w, 720s, 681s, 641s, and 632s cm^{-1}.

(*c*). The complex $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_4(PMe_3)_3]$ (13) was prepared as brown-orange *crystals* in a similar manner to (12) by u.v. irradiation of (4) (0.60 g, 0.75 mmol) with PMe_3 (0.8 mmol); $\nu_{max.}$ 1 998m, 1 990(sh), 1 908s, 1 903(sh), 1 863s, and 1 850s (CO); 1 283s, 1 259w, 1 161m, 1 090s, 966s, 947vs, 855w, 846w, 819w, 730m, 719m, 677w, 669w, 640w, and 611s cm^{-1}.

(*d*). The compound $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_4(PMe_2Ph)_3]$ (14) was obtained similarly as brown *microcrystals* from (5) (1 mmol) and PMe_2Ph (1.1 mmol); $\nu_{max.}$ at 1 996m, 1 989(sh), 1 908s, 1 870s, and 1 850s (CO); 1 280w, 1 262m, 1 158m, 1 090s, 1 015m, 941w, 905m, 800m, 735s, 722s, 704w, 693w, 673w, and 640w cm^{-1}.

Crystal-structure Determination of $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_4(PMe_3)_3]$ (13).—Crystals of (13) grow as brown-orange prisms. Diffracted intensities were recorded at 200 K for a crystal of dimensions 0.31 × 0.31 × 0.27 mm. Of the 4 893 reflections measured for $2\theta \leqslant 60°$ on a Syntex *P*3 four-circle diffractometer, 3 882 had $I \geqslant 3\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation based on counting statistics, and only these were used in the refinement of the structure. Corrections were applied for Lorentz, polarisation, and *X*-ray absorption effects. Computations were carried out with the ' SHELX ' system of programs.[14]

Crystal data. $C_{22}H_{37}O_5P_3PtW$, $M = 853.4$, Orthorhombic, $a = 18.180(6)$, $b = 10.720(3)$, $c = 14.697(4)$ Å, $U = 2\,864.3(15)$ Å^3, $D_m = 1.84$ g cm^{-3}, $Z = 4$, $D_c = 1.98$ g cm^{-3}, $F(000) = 1\,624$, space group $Pna2_1$ (no. 33), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 87.1$ cm^{-1}.

Structure solution and refinement. The metal atoms were located from a Patterson synthesis and the *z* co-ordinate of the Pt atom was arbitrarily fixed at zero to define the origin. All other non-hydrogen atoms were located by successive electron-density difference syntheses. Hydrogen atoms were generated at calculated positions (C–H = 1.08 Å), those for methyl groups with rigid geometry pivoting around the C_3 axis. Isotropic thermal parameters for H atoms were constrained to be equivalent when attached to chemically equivalent C atoms; the final values were $U_{iso.} = 0.07(3)$ for aromatic hydrogen atoms and $U_{iso.} = 0.06(1)$ for all others. Refinement converged at R 0.043 7 (R' 0.040 9), and the final electron-density difference synthesis showed no peaks > 1.5 or < -1.5 e Å^{-3} except in the region of the metal atoms where values of 2.4 occurred. Scattering factors were from ref. 15 for C, O, and P, ref. 16 for hydrogen, and ref. 17 for Pt and W, including corrections for the effects of anomalous dispersion: 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). A check was made that the co-ordinates of Table 3 do in fact correspond with the enantiomer contained in the original crystal; inversion of x, y, z to $\bar{x}, \bar{y}, \bar{z}$ gave a significantly less good refinement. Observed and calculated structure factors, anisotropic thermal parameters for all non-hydrogen atoms, and hydrogen-atom positional parameters are listed in Supplementary Publication No. SUP 22952 (23 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.