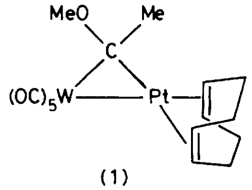
Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 22.[1] Synthesis and Some Reactions of [Bis(diphenylphosphino)methane]pentacarbonyl-μ-[methoxy(methyl)-methylene]-platinumtungsten and the Crystal Structure of $[PtW(\mu\text{-}C{=}CH_2)(Ph_2PCH_2PPh_2)(CO)_5]$ *

M. Rasol Awang, John C. Jeffery, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Treatment of the compound $[PtW\{\mu\text{-}C(OMe)Me\}(CO)_5(cod)]$ (cod = cyclo-octa-1,5-diene) with dppm ($Ph_2PCH_2PPh_2$) affords the complex $[PtW\{\mu\text{-}C(OMe)Me\}(dppm)(CO)_5]$. Solutions of the latter in toluene on standing afford the isomeric species $[PtW\{\mu\text{-}C(OMe)Me\}(\mu\text{-}dppm)(CO)_5]$ and side-products, whereas chromatography on basic alumina yields the vinylidene-bridged compound $[PtW(\mu\text{-}C{=}CH_2)(dppm)(CO)_5]$. The structure of the latter was established by a single-crystal *X*-ray diffraction study. Crystals are monoclinic, space group $P2_1/c$ (no. 14), with $Z = 4$ in a unit cell of dimensions $a = 9.325(2)$, $b = 17.837(3)$, $c = 19.451(3)$ Å, and $\beta = 105.74(1)°$. Intensities were measured at room temperature to $2\theta \leqslant 50°$, and the structure has been refined to R 0.036 (R' 0.038) for 4 032 reflections. The metal–metal bond [2.774(1) Å] is asymmetrically spanned by the vinylidene ligand [C–Pt 2.012(9), C–W 2.198(8), and C=C 1.363(13) Å]. The tungsten atom carries five terminal CO groups, one of which semi-bridges [W–C–O 167.8(9)°] to the platinum atom, the latter being chelated by the dppm ligand [Pt–P 2.250(2) and 2.335(2) Å]. Protonation of the compound $[PtW\{\mu\text{-}C(OMe)Me\}(\mu\text{-}dppm)(CO)_5]$ with $HBF_4{\cdot}OEt_2$ affords the salt $[PtW(\mu\text{-}CMe)(\mu\text{-}dppm)(CO)_5][BF_4]$. This reaction is only partially reversed by treatment of the latter with sodium methoxide in methanol, the main product being the bridged vinylidene complex $[PtW(\mu\text{-}C{=}CH_2)(\mu\text{-}dppm)(CO)_5]$. The latter is also formed by treating $[PtW(\mu\text{-}CMe)(\mu\text{-}dppm)(CO)_5][BF_4]$ with the reagent $K[BH(CHMeEt)_3]$ in tetrahydrofuran. The n.m.r. data (^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{H\}$, and $^{195}Pt\text{-}\{^1H\}$) for the new compounds are reported and discussed in relation to their structures.

In the preceding paper [1] we described the synthesis of the compound $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(\mu\text{-}dppm)(CO)_5]$ (dppm = $Ph_2PCH_2PPh_2$), its conversion into the salt $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}dppm)(CO)_5][BF_4]$, and some reactions of the latter with nucleophilic reagents to give bridged alkylidene bimetal complexes $[PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)R\}(\mu\text{-}dppm)(CO)_5]$ (R = Me, H, C≡CBu^t, and SC_6H_4Me-4). In this paper we report some aspects of the chemistry of $[PtW\{\mu\text{-}C(OMe)Me\}(\mu\text{-}dppm)(CO)_5]$ which although closely related to its analogue with a μ-C(OMe)C_6H_4Me-4 ligand was expected to show a modified reactivity pattern. It is known that with mononuclear metal compounds $[M\{=C(OMe)R\}(CO)_5]$ (M = Cr or W, R = Me or aryl), the methyl(methoxy)methylene species undergo certain reactions associated with deprotonation of the methyl group.[2] For example, treatment of $[W\{=C(OMe)Me\}(CO)_5]$ with butyl-lithium followed by $MeSO_3F$ affords $[W\{=C(OMe)Et\}(CO)_5]$.[3] Hence one reason for preparing $[PtW\{\mu\text{-}C(OMe)Me\}(\mu\text{-}dppm)(CO)_5]$ and the salt $[PtW(\mu\text{-}CMe)(\mu\text{-}dppm)(CO)_5][BF_4]$ was to establish whether the Me groups in the bridging ligands deprotonated. Moreover, in the synthesis of $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(\mu\text{-}dppm)(CO)_5]$ from $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_5(cod)]$ (cod = cyclo-octa-1,5-diene) and dppm, the unstable species $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(dppm)(CO)_5]$ was detected spectroscopically, but it readily isomerised to the μ-dppm complex in solution.[1] It was, therefore, of interest to follow the course of the reaction of dppm with $[PtW\{\mu\text{-}C(OMe)Me\}(CO)_5(cod)]$ to see whether the initially formed non-bridged dppm complex $[PtW\{\mu\text{-}C(OMe)Me\}(dppm)(CO)_5]$ was more or less kinetically stable than the μ-C(OMe)C_6H_4Me-4 analogue.



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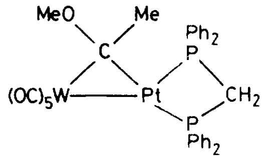

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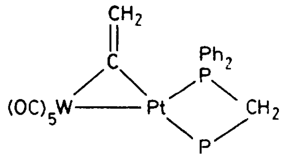

(3)

Results and Discussion

Treatment of $[W\{=C(OMe)Me\}(CO)_5]$ [4] with a solution of $[Pt(cod)_2]$ [5] in light petroleum (b.p. 40—60 °C) afforded the complex (1). We have previously prepared several other platinum–tungsten compounds analogous to (1), but in general the bridging groups C(OMe)R have had aryl substituents (R = Ph or C_6H_4Me-4); only two species have been characterised with methoxy(methyl)methylene ligands, *viz.* $[PtW\{\mu\text{-}C(OMe)Me\}(CO)_5(PR_3)_2]$ (PR_3 = PMe_3 or PMe_2Ph).[6] Analytical and spectroscopic data for (1) are given in Tables 1 and 2, and are in accord with the structure proposed. Thus the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum showed a resonance for the

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* 1-[Bis(diphenylphosphino)methane-*PP'*]-2,2,2,2,2-pentacarbonyl-μ-vinylidene-platinumtungsten (*Pt–W*).

Supplementary data available (No. SUP 23667, 31 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Analytical [a] and physical data for the platinum–tungsten complexes

Compound	M.p. (θ_c/°C) [b]	Colour	Yield (%)	$\tilde{\nu}_{max.}$(CO) [c]/cm^{-1}	Analysis (%) C	Analysis (%) H
(1) [PtW{μ-C(OMe)Me}$(CO)_5$(cod)]	80	Brown-black	77	2 055s, 1 980m, 1 958s, 1 934s, 1 923m	27.5 (28.0)	2.6 (2.6)
(2) [PtW{μ-C(OMe)Me}(dppm)$(CO)_5$]	108	Yellow	96	2 045m, 1 965w, 1 939m, 1 921s	42.5 (42.6)	3.1 (3.0)
(3) [PtW(μ-C=CH_2)(dppm)$(CO)_5$]	138	Yellow	78	2 056vs, 1 988m, 1 955vs, 1 945s, 1 901w	41.6 (41.3)	2.7 (2.6)
(4) [PtW{μ-C(OMe)Me}(μ-dppm)$(CO)_5$]	99	Yellow	35	2 027w, 2 006s, 1 936m, 1 898m	43.1 (42.6)	3.8 (3.0)
(5) [PtW{μ-C(OMe)Me}(μ-dppm)$(CO)_4$(dppm)]	130	Yellow	15	2 009s, 1 920m, 1 892m, 1 883s	51.7 (51.9)	4.1 (3.8)
(6) [PtW(μ-CMe)(μ-dppm)$(CO)_5$][BF_4]	148	Orange	70	[d] 2 036m, 2 010s, 1 944vs, 1 917s	37.4 (37.8)	2.6 (2.5)
(7) [PtW(μ-C=CH_2)(μ-dppm)$(CO)_5$]	70	Yellow	100 [e]	2 041s, 2 017vs, 1 957s, 1 920s, 1 581w [f]	42.3 (41.3)	3.0 (2.6)

[a] Calculated values are given in parentheses. [b] With decomposition. [c] In pentane, unless otherwise stated. [d] In tetrahydrofuran. [e] Formed quantitatively on chromatographing compound (4) on basic alumina (see text). [f] $\nu_{max.}$(C=C).

ligated μ-C group at δ 201.6 p.p.m. with strong ^{195}Pt–^{13}C coupling (1 306 Hz). Moreover, the non-chemically equivalent carbon nuclei of the cod ligand give rise to eight signals, in accord with the structure proposed.

Treatment of (1) in cold toluene (−78 °C) with dppm afforded, after column chromatography on deactivated alumina, compound (2) in essentially quantitative yield. The n.m.r. data for (2) establish firmly that it has the structure shown, with both phosphorus groups of the dppm ligand attached to the platinum atom. The ^{31}P-{^{1}H} spectrum (Table 3) shows peaks due to two non-equivalent ^{31}P sites, and both resonances exhibit strong ^{195}Pt–^{31}P coupling of the magnitude expected for direct phosphorus–platinum bonding. The ^{195}Pt n.m.r. spectrum has the doublet of doublets pattern expected. The ^{13}C-{^{1}H} spectrum (Table 2) has no resonance corresponding to a carbonyl ligand bonded to platinum, in contrast with the spectra of other species discussed below. The bridging alkylidene carbon signal is at δ 211.9 p.p.m., and is a doublet of doublets through coupling with non-equivalent phosphorus nuclei.

The ready isolation of compound (2), as a relatively stable crystalline complex in the solid state, is in distinct contrast with the transient nature of its analogue [PtW{μ-C(OMe)-C_6H_4Me-4}(dppm)$(CO)_5$].[1] In solution the latter is rapidly converted into the bridged isomer [PtW{μ-C(OMe)C_6H_4Me-4}(μ-dppm)$(CO)_5$].

If the mixture obtained by treating (1) with dppm is chromatographed on basic alumina the yellow microcrystalline compound (3) is obtained in good yield (Table 1). The gross features of the structure of (3) were established by the n.m.r. data (Tables 2 and 3). Both the ^{1}H and ^{13}C-{^{1}H} spectra of compound (3) show the absence of peaks due to Me or OMe groups, resonances for these substituents being readily seen in the spectra of (2). The ^{13}C-{^{1}H} spectrum of (3) shows a signal for the μ-C ligand at 241.3 p.p.m., and a resonance at δ 125.9 p.p.m. tentatively attributed to the CH_2 group of the vinylidene moiety. In the ^{13}C-{^{1}H} spectrum of [Ru_2(μ-C=CH_2)(μ-CO)$(CO)_2$(η-C_5H_5)$_2$] the peaks for the μ-C=CH_2 group occur at δ 249.1 and 122.7 p.p.m., respectively.[7] The ^{31}P-{^{1}H} n.m.r. data for compound (3) are similar to those for (2), the two ^{195}Pt–^{31}P couplings corresponding to a Pt($PPh_2CH_2PPh_2$) group being present in both species.

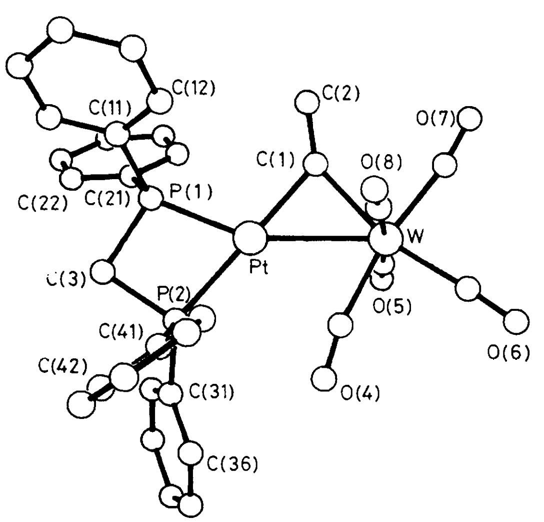


Figure. Molecular structure of the complex [PtW(μ-C=CH_2)(dppm)$(CO)_5$] (3), showing the atom-numbering scheme

Several compounds are known in which a C=CH_2 group bridges two metal atoms in a complex, but none appears to have been described where this ligand spans a heteronuclear metal–metal bond in a bimetal species.[8] However, the compounds [MnRe(μ-C=CHPh)$(CO)_4$(η-C_5H_5)$_2$][9] and [FeMn{μ-C=CH(CO_2Me)}$(CO)_6$(η-C_5H_5)][10] with substituted vinylidene groups have been described, and one isomer of the latter studied by *X*-ray diffraction methods. Because of the need to establish the structure of (3) an *X*-ray crystallographic study was made, and the results are summarised in Table 4.

It will be seen from the Figure that the dppm ligand is coordinated to the platinum atom, the tungsten atom carries five terminal CO ligands, and the metal–metal bond is asymmetrically bridged by the vinylidene group [μ-C–P.

Table 2. Hydrogen-1 and carbon-13 n.m.r. data [a] for the platinum–tungsten complexes

Complex	^{1}H (δ)	^{13}C [b] (δ)
(1) [PtW{μ-C(OMe)Me}(CO)$_5$(cod)]	[c] 2.20 (m, 8 H, CH$_2$), 3.08 [s, 3 H, CMe, *J*(PtH) 10], 3.37 [s, 3 H, OMe, *J*(PtH) 4], 4.76 (s br, 1 H, CH), 5.89 (s br, 1 H, CH), 6.07 (s br, 1 H, CH), 6.25 (s br, 1 H, CH)	[d] 207.1 [1 × CO, *J*(WC) 140], 202.7 [4 × CO, *J*(WC) 120], 201.6 [μ-C, *J*(PtC) 1 306], 110.8 [CH, *J*(PtC) 44], 108.3 [CH, *J*(PtC) 56], 95.5 [CH, *J*(PtC) 160], 93.8 [CH, *J*(PtC) 165], 60.9 [OMe, *J*(PtC) 43], 42.8 [Me, *J*(PtC) 82], 33.0, 31.8, 26.9, 25.8 (CH$_2$)
(2) [PtW{μ-C(OMe)Me}(dppm)(CO)$_5$]	[e] 3.21 [d of d, 3 H, Me, *J*(PH) 13 and 8], 3.33 (s, 3 H, OMe), 4.29 [(ABMX), 1 H, CH$_2$, *J*(HH) 15, *J*(PH) 10 and 10], 4.63 [(ABMX), 1 H, CH$_2$, *J*(HH) 15, *J*(PH) 10 and 8], 7.30—7.75 (m, 20 H, Ph)	[e] 211.9 [d of d, μ-C, *J*(PC) 86 and 19, *J*(PtC) 1 106], 208.4 [1 × CO, *J*(WC) 151], 205.8 [4 × CO, *J*(PtC) 24, *J*(WC) 122], 134—128 (Ph), 60.9 [OMe, *J*(PtC) 61, *J*(WC) 29], 47.7 [t, CH$_2$, *J*(PC) 28], 43.6 [Me, *J*(PtC) 125]
(3) [PtW(μ-C=CH$_2$)(dppm)(CO)$_5$]	[c] 4.01 [d of d, 2 H, CH$_2$ (dppm), *J*(PH) 11 and 9, *J*(PtH) 46], 7.50—7.60 (m, 22 H, CH$_2$ and Ph)	[c] 241.3 [d, μ-C, *J*(PC) 68, *J*(PtC) 1 875], 208.0 [1 × CO, *J*(WC) 140], 203.6 [4 × CO, *J*(WC) 123], 133—127 (Ph), 125.9 [s, μ-C=*C*H$_2$, *J*(PtC) 190], 50.2 [t, CH$_2$, *J*(PC) 27]
(4) [PtW{μ-C(OMe)Me}(μ-dppm)(CO)$_5$]	[f] 3.62 (s br, 3 H, Me), 3.80 (s, 3 H, OMe), 4.29 (s br, CH$_2$, dppm), 7.08—7.44 (m, 20 H, Ph)	[f] 228.7 [d, μ-C, *J*(PC) 67, *J*(PtC) 1 070], 211.2 [d, WCO, *J*(PC) 14], 210.2, 204.1, 203.1 (WCO), 186.8 [d, PtCO, *J*(PC) 14, *J*(PtC) 1 718], 135.7—128.3 (Ph), 61.2 [OMe, *J*(PtC) 57], 45.5 [Me, *J*(PtC) 104] [g]
(5) [PtW{μ-C(OMe)Me}(μ-dppm)(CO)$_4$(dppm)]	[h] 2.65 (m, 2 H, CH$_2$), 3.15 [d of d, 3 H, Me, *J*(PH) 11 and 5], 3.20 (s, 3 H, OMe), 4.15 [d of d of d, 1 H, CH$_2$, *J*(HH) 14, *J*(PH) 10 and 6], 5.42 [d of t, 1 H, CH$_2$, *J*(HH) 14, *J*(PH) 9, *J*(PtH) 48], 6.70—7.70 (m, 40 H, Ph)	[h] 230.8 [d of d of d, μ-C, *J*(PC) 74, 18, and 5, *J*(PtC) 1 178], 214.0 [d of d, CO, *J*(PC) 17 and 5, *J*(PtC) 28], 211.4 [d, CO, *J*(PC) 7, *J*(WC) 141], 206.2 [d, 2 × CO, *J*(PC) 7, *J*(PtC) 36, *J*(WC) 127], 139—127 (Ph), 60.9 [OMe, *J*(PtC) 60], 45.6 [Me, *J*(PtC) 114], 29.1 (CH$_2$) [g]
(6) [PtW(μ-CMe)(μ-dppm)(CO)$_5$][BF$_4$]	[i] 4.15 [d of d, 3 H, Me, *J*(PH) 9 and 2], 5.32 [t, 2 H, CH$_2$, *J*(PH) 10], 7.20—7.60 (m, 20 H, Ph)	[i] 405.0 [d, μ-C, *J*(PC) 49, *J*(PtC) 1 003], 194.5 (2 × WCO), 194.0, 191.8 (WCO), 191.3 [d, PtCO, *J*(PC) 11, *J*(PtC) 1 939], 134—129 (Ph), 57.7 [Me, *J*(PtC) 87], 38.4 [t, CH$_2$, *J*(PC) 29, *J*(PtC) 25]
(7) [PtW(μ-C=CH$_2$)(μ-dppm)(CO)$_5$]	[h] 5.07 [d of d, 2 H, CH$_2$, *J*(PH) 10 and 9, *J*(PtH) 43], 7.1—7.4 (m, 22 H, CH$_2$ and Ph)	[h] 254.4 [d of d, μ-C, *J*(PC) 57 and 6, *J*(PtC) 1 082], 210.9 [d, WCO, *J*(PC) 11, *J*(WC) 113], 206.7 [d, WCO, *J*(PC) 9], 200.3 [d, 2 × WCO, *J*(PC) 5, *J*(PtC) 28, *J*(WC) 122], 189.7 [d, PtCO, *J*(PC) 13], 137—127 (Ph), 123.9 [C=*C*H$_2$, *J*(PtC) 139], 49.1 [d of d, CH$_2$, *J*(PC) 30 and 26, *J*(PtC) 86]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Hydrogen-1 decoupled, to high frequency of SiMe$_4$. [c] Measured in [^{2}H$_6$]benzene. [d] Measured in [^{2}H$_8$]toluene at −70 °C. [e] Measured in [^{2}H$_2$]dichloromethane at −20 °C. [f] Measured in [^{2}H$_1$]chloroform. [g] Signal due to CH$_2$ group of μ-dppm ligand obscured by solvent. [h] Measured in [^{2}H$_2$]dichloromethane at 25 °C. [i] Measured in [^{2}H$_2$]dichloromethane at −50 °C.

2.012(9) and μ-C−W 2.198(8) Å]. Perhaps to compensate for the asymmetry of the μ-C=CH$_2$ ligand, one of the CO ligands semi-bridges the metal–metal bond [W−C(4)−O(4) 167.8(9)°]. The tungsten atom is in an essentially octahedral environment with respect to the five CO groups and the midpoint of the C(1)−Pt bond. Since the Pt(dppm) and W(CO)$_5$ groups have similar frontier orbitals to CH$_2$, in the context of isolobal relationships,[11] compound (3) is analogous to one or other of the allene complexes [W(η-CH$_2$=C=CH$_2$)(CO)$_5$] and [Pt(η-CH$_2$=C=CH$_2$)(PR$_3$)$_2$]. The distance C(1)−C(2) [1.363(13) Å] in (3) is slightly longer than the corresponding distance [1.30(2) Å] in [FeMn{μ-C=CH(CO$_2$Me)}(CO)$_6$(η-C$_5$H$_5$)],[10] and is also at the long end of the range found (1.30—1.38 Å) for C=C in several homonuclear dimetal compounds containing a variety of μ-C=CR^{1}R^2 ligands.[8]

The dimensions of the μ-$\overline{\mathrm{CPtW}}$ ring in compound (3) are of particular interest and the data are summarised in Table 5, together with those for related compounds. It is apparent from the internuclear separations that the bonding of the ring system in (3) is stronger than that in the two compounds containing a μ-C(OMe)C$_6$H$_4$Me-4 ligand,[1,6] or the species having both μ-C(H)C$_6$H$_4$Me-4 and μ-H groups.[12] Indeed, the μ-C−W separation in (3) is close to that found in the dimetallacyclopropene compound [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)] which is formulated with a carbon–tungsten double bond.[13] The μ-C−Pt and μ-C−W distances in (3) thus suggest an analogy with [Pt(η-CH$_2$=C=CH$_2$)(PPh$_3$)$_2$][14,15] rather than with [W(η-CH$_2$=C=CH$_2$)(CO)$_5$] (see above).

Table 3. Phosphorus-31 and platinum-195 n.m.r. data ^{a}

Complex	^{31}P (δ/p.p.m.) ^{b}	^{195}Pt (δ/p.p.m.) ^{c}
(2) ^{d}	−5.4 [s, *J*(PtP) 1 914], −7.5 [s, *J*(PtP) 3 750]	137 [d of d, *J*(PPt) 3 750, 1 914]
(3) ^{e}	−2.5 [d, *J*(PP) 7, *J*(PtP) 3 308], −8.6 [d, *J*(PP) 7, *J*(PtP) 2 864]	
(4)	8.6 [d, PPt, *J*(PP) 142, *J*(PtP) 2 495], −2.8 [d, PW, *J*(PP) 142, *J*(PtP) 112]	^{f} 430 [d of d, *J*(PPt) 2 495, 112]
(5) ^{f}	24.9 [d of d of d, P$^{\alpha}$, *J*(P$^{\beta}$P$^{\alpha}$) 10, *J*(P$^{\gamma}$P$^{\alpha}$) 39, *J*(P$^{\delta}$P$^{\alpha}$) 24, *J*(PtP$^{\alpha}$) 3 636], 7.9 [d of d, P$^{\beta}$, *J*(P$^{\alpha}$P$^{\beta}$) 10, *J*(P$^{\gamma}$P$^{\beta}$) 129, *J*(PtP$^{\beta}$) 2 575], −0.8 [d of d, P$^{\gamma}$, *J*(P$^{\alpha}$P$^{\gamma}$) 39, *J*(P$^{\beta}$P$^{\gamma}$) 129, *J*(PtP$^{\gamma}$) 157], −22.3 [d, P$^{\delta}$, *J*(P$^{\alpha}$P$^{\delta}$) 24, *J*(PtP$^{\delta}$) 76]	
(6) ^{g}	1.4 [d, PW, *J*(PP) 95, *J*(PtP) 83], −3.5 [d, PPt, *J*(PP) 95, *J*(PtP) 2 417]	1 071 [d of d, *J*(PPt) 2 417, 83]
(7)	5.5 [d, PPt, *J*(PP) 122, *J*(PtP) 2 676], −4.2 [d, PW, *J*(PP) 122, *J*(PtP) 88]	357 [d of d, *J*(PPt) 2 676, 88]

^{a} Spectra measured in [^{2}H$_{2}$]dichloromethane at room temperature, unless otherwise stated; coupling constants are in Hz. ^{b} Hydrogen-1 decoupled, chemical shifts in p.p.m., positive to high frequency of 85% H$_3$PO$_4$ (external). ^{c} Hydrogen-1 decoupled, chemical shifts to high frequency of Ξ(^{195}Pt) 21.4 MHz. ^{d} Spectra measured at −20 °C. ^{e} Measured in [^{2}H$_{6}$]benzene. ^{f} Measured in [^{2}H$_{1}$]chloroform. ^{g} Measured in [^{2}H$_{6}$]acetone.

Table 4. Internuclear distances (Å) and angles (°) for [PtW(μ-C=CH$_2$)(dppm)(CO)$_5$] (3), with estimated standard deviations in parentheses

Pt–W	2.774(1)	C(11)–C(16)	1.393(12)	Pt–P(1)	2.250(2)	C(12)–C(13)	1.380(13)
Pt–P(2)	2.335(2)	C(13)–C(14)	1.349(14)	Pt–C(1)	2.012(9)	C(14)–C(15)	1.40(2)
Pt–C(4)	2.614(10)	C(16)–C(15)	1.377(14)	W–C(1)	2.198(8)	C(21)–C(22)	1.399(13)
W–C(4)	2.035(12)	C(21)–C(26)	1.370(15)	W–C(5)	2.042(10)	C(22)–C(23)	1.37(2)
W–C(6)	2.009(9)	C(23)–C(24)	1.39(2)	W–C(7)	2.026(12)	C(24)–C(25)	1.346(15)
W–C(8)	2.034(11)	C(26)–C(25)	1.405(15)	P(1)–C(3)	1.842(9)	C(31)–C(32)	1.391(14)
P(1)–C(11)	1.809(8)	C(31)–C(36)	1.382(13)	P(1)–C(21)	1.830(9)	C(32)–C(33)	1.370(15)
P(2)–C(3)	1.859(8)	C(33)–C(34)	1.36(2)	P(2)–C(31)	1.819(9)	C(34)–C(35)	1.38(2)
P(2)–C(41)	1.814(10)	C(36)–C(35)	1.38(2)	C(1)–C(2)	1.363(13)	C(41)–C(42)	1.38(2)
C(4)–O(4)	1.158(14)	C(41)–C(46)	1.376(14)	C(5)–O(5)	1.151(13)	C(42)–C(43)	1.36(2)
C(6)–O(6)	1.134(12)	C(43)–C(44)	1.37(2)	C(7)–O(7)	1.164(15)	C(44)–C(45)	1.36(2)
C(8)–O(8)	1.143(15)	C(46)–C(45)	1.41(2)	C(11)–C(12)	1.396(13)		

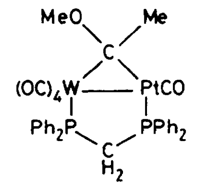
W–Pt–P(1)	158.4(1)	C(1)–Pt–C(4)	96.0(3)	C(22)–C(23)–C(24)	121.6(10)
P(1)–Pt–P(2)	73.3(1)	Pt–W–C(4)	63.7(3)	C(24)–C(25)–C(26)	121.6(11)
P(1)–Pt–C(1)	106.8(2)	Pt–W–C(5)	87.8(3)	P(2)–C(31)–C(32)	119.4(7)
W–Pt–C(4)	44.3(3)	C(4)–W–C(5)	89.3(4)	C(32)–O(31)–C(36)	119.3(9)
P(2)–Pt–C(4)	83.7(3)	C(1)–W–C(6)	167.0(4)	C(32)–C(33)–C(34)	121.2(12)
Pt–W–C(1)	46.0(2)	C(5)–W–C(6)	93.7(4)	C(34)–C(35)–C(36)	119.3(11)
C(1)–W–C(4)	109.7(4)	C(1)–W–C(7)	77.4(4)	P(2)–C(41)–C(42)	122.6(8)
C(1)–W–C(5)	88.9(3)	C(5)–W–C(7)	89.3(4)	C(42)–C(41)–C(46)	117.9(10)
Pt–W–C(6)	146.8(3)	Pt–W–C(8)	87.1(3)	C(42)–C(43)–C(44)	120.3(12)
C(4)–W–C(6)	83.1(4)	C(4)–W–C(8)	90.8(4)	C(44)–C(45)–C(46)	119.8(11)
Pt–W–C(7)	123.3(3)	C(6)–W–C(8)	92.0(4)	W–C(6)–O(6)	179.7(9)
C(4)–W–C(7)	172.7(4)	Pt–P(1)–C(3)	97.2(3)	W–C(8)–O(8)	177.7(8)
C(6)–W–C(7)	89.9(4)	C(3)–P(1)–C(11)	105.6(4)	P(1)–C(11)–C(16)	122.1(7)
C(1)–W–C(8)	85.7(3)	C(3)–P(1)–C(21)	106.8(4)	C(11)–C(12)–C(13)	120.8(8)
C(5)–W–C(8)	174.3(4)	Pt–P(2)–C(3)	93.9(3)	C(13)–C(14)–C(15)	118.9(10)
C(7)–W–C(8)	91.3(4)	C(3)–P(2)–C(31)	106.5(4)	C(11)–C(16)–C(15)	120.1(9)
Pt–P(1)–C(11)	117.5(3)	C(3)–P(2)–C(41)	104.4(4)	P(1)–C(21)–C(26)	118.9(7)
Pt–P(1)–C(21)	120.7(3)	Pt–C(1)–W	82.3(3)	C(21)–C(22)–C(23)	119.3(11)
C(11)–P(1)–C(21)	107.0(4)	W–C(1)–C(2)	142.2(7)	C(23)–C(24)–C(25)	118.4(11)
Pt–P(2)–C(31)	126.1(3)	Pt–C(4)–W	72.0(3)	C(21)–C(26)–C(25)	119.7(9)
Pt–P(2)–C(41)	117.3(3)	W–C(4)–O(4)	167.8(9)	P(2)–C(31)–C(36)	121.1(8)
C(31)–P(2)–C(41)	105.2(4)	W–C(5)–O(5)	175.6(9)	C(31)–C(32)–C(33)	119.5(10)
Pt–C(1)–C(2)	135.3(7)	W–C(7)–O(7)	176.4(9)	C(33)–C(34)–C(35)	120.3(11)
P(1)–C(3)–P(2)	95.5(4)	P(1)–C(11)–C(12)	119.8(6)	C(31)–C(36)–C(35)	120.3(10)
Pt–C(4)–O(4)	120.0(8)	C(12)–C(11)–C(16)	118.1(8)	P(2)–C(41)–C(46)	119.3(8)
W–Pt–P(2)	127.8(1)	C(12)–C(13)–C(14)	121.3(10)	C(41)–C(42)–C(43)	121.8(10)
W–Pt–C(1)	51.7(2)	C(14)–C(15)–C(16)	120.8(9)	C(43)–C(44)–C(45)	119.8(12)
P(2)–Pt–C(1)	174.8(3)	P(1)–C(21)–C(22)	121.6(8)	C(41)–C(46)–C(45)	120.3(10)
P(1)–Pt–C(4)	157.1(3)	C(22)–C(21)–C(26)	119.5(9)		

The two P–Pt distances in compound (3) differ, P(2)–Pt being significantly longer than P(1)–Pt. The longer separation is *trans* to μ-C, and a similar asymmetry of PtP$_2$ bonding is shown in the other compounds listed in Table 5, and is presumably due to the strong *trans* influence of the bridging carbon atoms. Reflecting this property, the PR$_3$ groups in the compounds [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PR$_3$)$_2$(η-C$_5$H$_5$)] which are *transoid* to the *p*-tolylmethylidyne ligand are readily dis-

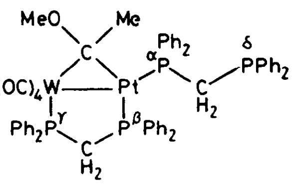
Table 5. Dimensions of three-membered rings in platinum–tungsten complexes [a]

Compound [b]	Pt–W	μ-C–Pt	μ-C–W	P–Pt [c]	Pt–μ-C–W
[PtW(μ-C=CH$_2$)(dppm)(CO)$_5$] (3)	2.774(1)	2.012(9)	2.198(8)	2.250(2) 2.335(2)	82.3(3)
[PtW(μ-CR)(CO)$_2$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)]	2.751(1)	1.997(9)	1.967(6)	2.258(2) 2.325(2)	87.9(3)
[PtW{μ-C(OMe)Ph}(CO)$_5$(PMe$_3$)$_2$]	2.861(1)	2.04(1)	2.48(1)	2.253(3) 2.335(3)	77.8(3)
[PtW{μ-C(OMe)R}(CO)$_4$(PMe$_3$)$_3$]	2.825(1)	2.03(1)	2.37(1)	2.236(4) 2.326(3)	79.4(4)
[PtW{μ-C(OMe)R}(μ-dppm)(CO)$_5$]	2.818(3)	1.97(3)	2.49(3)	2.335(6)	77.3(9)
[PtW(μ-H)(μ-CHR)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)]	2.895(1)	2.109(9)	2.259(9)	2.265(3) 2.305(3)	83.0(3)

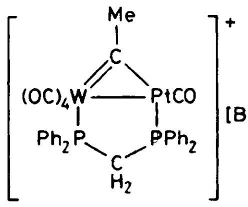
[a] Distances in Å, angles in °. [b] R = C$_6$H$_4$Me-4. [c] Longer P–Pt distances correspond to bond *trans* to μ-C atom.



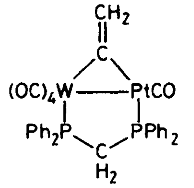
(4)



(5)



(6)



(7)

placed by CO.[16] The platinum atom in (3) is in an essentially planar environment, the dihedral angle between the $\overline{\mathrm{P(1)PtP(2)}}$ and $\overline{\mathrm{C(1)PtW}}$ planes being 5°. It is of interest that the dihedral angle between the planes P$_2$Pt and η-C$_2$Pt in [Pt(η-CH$_2$=C=CH$_2$)(PPh$_3$)$_2$] is 9°.[14]

It was mentioned earlier that the compound [PtW{μ-C(OMe)C$_6$H$_4$Me-4}(dppm)(CO)$_5$] could not be isolated because it is readily converted in solution into its isomer [PtW{μ-C(OMe)C$_6$H$_4$Me-4}(μ-dppm)(CO)$_5$].[1] We were therefore interested to determine whether compound (2) could be transformed into its isomer (4). This was successfully accomplished, albeit in relatively low yield (Table 1), by dissolving (2) in toluene, stirring the solution for *ca.* 15 h, and chromatographing the mixture on deactivated alumina. The conversion of (2) into (4) is accompanied by formation of the bis(dppm) compound (5) and a species presumed to be [Pt$_3${μ-C(OMe)Me}$_3$(CO)$_3$] on the basis that its i.r. spectrum is very similar to that of the complex [Pt$_3${μ-C(OMe)C$_6$H$_4$Me-4}$_3$(CO)$_3$].[17]

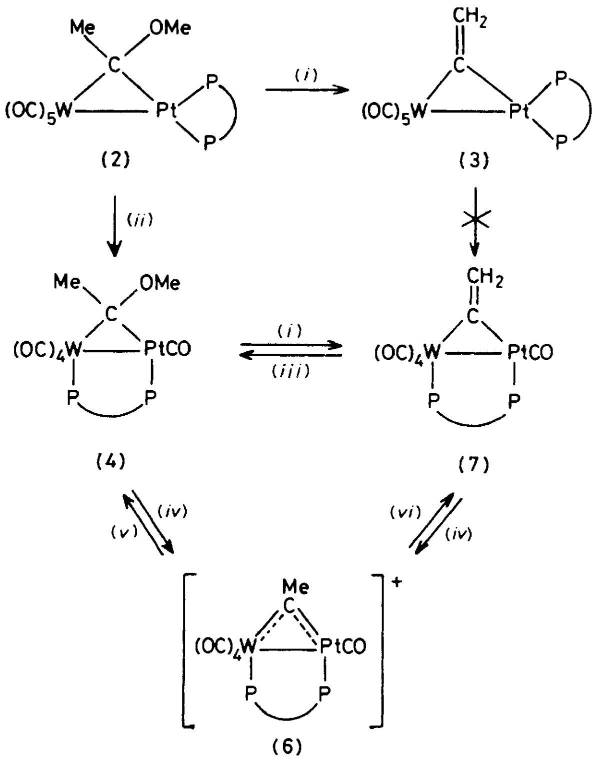
Compound (4) is well characterised by the n.m.r. data (Tables 2 and 3). The ^{13}C-{^{1}H} spectrum, in addition to showing a doublet resonance [δ 228.7 p.p.m., *J*(PC) 67, *J*(PtC) 1 070 Hz] for the μ-C nucleus, also shows a characteristic signal [17,18] for a PtCO group [δ 186.8 p.p.m., doublet, *J*(PC) 14, *J*(PtC) 1 718 Hz]. The ^{31}P-{^{1}H} and ^{195}Pt-{^{1}H} spectra show clearly that in (4) the dppm ligand is bridging the metal–metal bond since one *J*(PtP) value is relatively small (112 Hz) with the other large (2 495 Hz). For *cis*-PtP$_2$ groups such couplings are typically 1 900—4 800 Hz.[6]

Compound (5) has spectroscopic properties (Tables 1—3) very similar to those of its analogue [PtW{μ-C(OMe)C$_6$H$_4$Me-4}(μ-dppm)(CO)$_4$(dppm)], formed in the isomerisation of [PtW{μ-C(OMe)C$_6$H$_4$Me-4}(μ-dppm)(CO)$_5$].[1] The ^{31}P-{^{1}H} n.m.r. spectrum of (5) with four resonances, and appropriate ^{31}P–^{31}P and ^{195}Pt–^{31}P couplings, was particularly informative in assigning the structure, as was the pattern of the μ-C resonance in the ^{13}C-{^{1}H} spectrum, appearing with three distinct ^{31}P-^{13}C couplings. Moreover, the ^{13}C-{^{1}H} spectrum showed the absence of any PtCO group.

The formation of compound (4) from (2) is evidently not a simple process involving transfer of a CO group from tungsten to platinum with concomitant change of the dppm ligand from a terminal to a bridging position. Formation of (5) and [Pt$_3${μ-C(OMe)Me}$_3$(CO)$_3$] implies release of dppm from (2), and at least some degree of metal–metal bond cleavage.

Treatment of (4) with a small excess of HBF$_4$·OEt$_2$ affords in good yield the salt (6) (Table 1), an analogue of [PtW(μ-CC$_6$H$_4$Me-4)(μ-dppm)(CO)$_5$][BF$_4$].[1] The spectroscopic data for (6) are similar to those of the latter; in particular the ^{13}C-{^{1}H} n.m.r. spectrum shows characteristic resonances due to the μ-C (δ 405.0 p.p.m.) and PtCO (191.3 p.p.m.) groups (Table 2). Treatment of (6) in dichloromethane with a methanol solution of sodium methoxide regenerates complex (4) as expected, but a second product was the vinylidene platinum–tungsten compound (7). It is interesting to compare the ^{31}P-{^{1}H} n.m.r. spectrum of (7) with that of (3). Both spectra show the expected two resonances, as required for the structures proposed, but the peak at δ −4.2 p.p.m. in the spectrum of compound (7) has a small ^{195}Pt–^{31}P coupling (88 Hz) indicating that the signal is due to a PW group. In the spectrum of (3) the *J*(PtP) values correspond to the presence of two PPt sites. The ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra of (7) confirm the presence of the bridging C=CH$_2$ ligand. The latter in the ^{13}C-{^{1}H} spectrum gives rise to resonances at δ 254.4 (μ-C) and 123.9 p.p.m. (CH$_2$). In the ^{1}H spectrum the resonance for the vinylidene CH$_2$ group appears with those for the phenyl groups. However, the spectrum shows no Me group peak, a signal for which is present in the spectrum of the precursor (6).

Compound (7) is also formed when the salt (6) is treated with K[BH(CHMeEt)$_3$] in tetrahydrofuran. Evidently the hydrido-group derived from the borohydride reagent is sufficiently basic to deprotonate (6). Also of interest was the observation that (7) could not be obtained by heating its isomer (3) in toluene, in contrast with the conversion of (2) into (4). Protonation (HBF$_4$·OEt$_2$) of compound (7) readily produces (6), while reaction with methanol leads to (4).



Scheme. $\widehat{P\quad P}$ = dppm. (*i*) Basic alumina; (*ii*) toluene, 25 °C; (*iii*) MeOH; (*iv*) HBF$_4$·OEt$_2$; (*v*) OMe$^-$; (*vi*) H$^-$ or OMe$^-$

However, the latter process could be reversed. Chromatography of a toluene solution of (4) on basic alumina gives (7).

The results described in this paper provide an interesting contrast with those described in the preceding paper, and demonstrate the different reactivity patterns of the μ-C(OMe)-C$_6$H$_4$Me-4 *versus* μ-C(OMe)Me, and μ-CC$_6$H$_4$Me-4 *versus* μ-CMe, groups in these bimetal species. Most notable is the ready formation of the vinylidene species (3) and (7), reflecting the ease with which the methyl groups in $\overline{\text{Pt}\{\mu\text{-C(OMe)Me}\}\text{W}}$ and $\overline{\text{Pt}(\mu\text{-CMe})\text{W}}$ deprotonate. The principal transformations observed are shown in the accompanying Scheme.

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere. Basic alumina, used to separate mixtures by column chromatography, was Merck basic aluminium oxide (Brockman Activity I). Deactivated alumina used in chromatography was obtained by exposing BDH aluminium oxide (Brockman Activity II) to air for 2 d. Aldrich tetrafluoroboric acid–diethyl ether complex was used for the protonation studies. The n.m.r. measurements (Tables 2 and 3) were made with JEOL FX90Q and FX200 instruments, and i.r. spectra were recorded with a Nicolet MX-1 FT spectrophotometer. The compounds [Pt(cod)$_2$][19] and [W{=C(OMe)Me}(CO)$_5$][20] were made by methods previously described. Analytical and other data for the new compounds are given in Table 1.

Preparation of the Complexes [PtW{μ-C(OMe)Me}(CO)$_5$L$_2$] (L$_2$ = *cod or dppm*).—An ethylene-saturated light petroleum (20 cm^3) solution of [Pd(cod)$_2$] (0.41 g, 1.0 mmol) at 0 °C was treated with [W{=C(OMe)Me}(CO)$_5$] (0.38 g, 1.0 mmol), the mixture being stirred (15 min). After warming to room temperature, solvent was removed *in vacuo*, the residue washed (5 cm^3) with cold light petroleum and dried to give brown-black *microcrystals* of [PtW{μ-C(OMe)Me}(CO)$_5$-(cod)] (1) (0.54 g).

Complex (1) (0.69 g, 1.0 mmol) was dissolved in toluene (15 cm^3) at −78 °C, and the solution stirred and treated with dppm (0.38 g, 1.0 mmol) in the same solvent (5 cm^3). After 30 min the mixture was chromatographed on deactivated alumina with the column (8 × 2 cm) being cooled to *ca.* 4 °C. Elution with toluene afforded a yellow eluate. Solvent was removed *in vacuo* and the oily product obtained was treated with diethyl ether (5 cm^3) and light petroleum (5 cm^3) to give a yellow precipitate. Removal of solvent (syringe) and drying *in vacuo* yielded yellow *microcrystals* of [PtW{μ-C(OMe)Me}(dppm)(CO)$_5$] (2) (0.92 g).

Synthesis of the Compound [PtW(μ-C=CH$_2$)(dppm)-(CO)$_5$].—A toluene solution of compound (2), prepared from (1) (1 mmol) and dppm (1 mmol), as described above, was chromatographed on a basic alumina column (8 × 2 cm), eluting with the same solvent. After removal of the latter *in vacuo*, the oily residue was treated with diethyl ether (5 cm^3) and then with light petroleum (5 cm^3) giving a yellow precipitate. Solvent was decanted (syringe), and the product dried *in vacuo* to obtain yellow *microcrystals* of [PtW(μ-C=CH$_2$)(dppm)(CO)$_5$] (3) (0.73 g).

Isomerisation of the Complex [PtW{μ-C(OMe)Me}(dppm)-(CO)$_5$].—Compound (2) (0.96 g, 1.0 mmol) in toluene (20 cm^3) was stirred for *ca.* 15 h at room temperature. The solution was chromatographed on a deactivated alumina column (15 × 3 cm), whereupon three bands developed. Elution with toluene–light petroleum (1 : 1) afforded a yellow oil after solvent evaporation *in vacuo*. Treatment of the oil with diethyl ether (5 cm^3) followed by light petroleum (5 cm^3) gave a yellow precipitate. Removal of solvent *in vacuo* afforded yellow *microcrystals* of [PtW{μ-C(OMe)Me}(μ-dppm)(CO)$_5$] (4) (0.34 g).

Elution of the column with toluene–light petroleum (3 : 2) led to the isolation of yellow *microcrystals* of [PtW{μ-C(OMe)Me}(μ-dppm)(CO)$_4$(dppm)] (5) (0.20 g). The third band was collected by eluting with diethyl ether. Evaporation of solvent *in vacuo* gave a purple residue (0.12 g) assumed to be [Pt$_3${μ-C(OMe)Me}$_3$(CO)$_3$] on the basis of comparison of its i.r. spectrum with that of [Pt$_3${μ-C(OMe)C$_6$H$_4$Me-4}$_3$(CO)$_3$].[17]

Synthesis of the Salt [PtW(μ-CMe)(μ-dppm)(CO)$_5$][BF$_4$].—Compound (4) (0.96 g, 1.0 mmol) was dissolved in diethyl ether (20 cm^3) and the solution cooled to −78 °C. Dropwise addition of HBF$_4$·OEt$_2$ (0.15 cm^3) afforded a yellow precipitate. The mixture was stirred (15 min), and then the precipitate allowed to settle. The mother-liquor was removed with a syringe, and the residue washed with diethyl ether (10 cm^3 at −78 °C). Drying *in vacuo* afforded orange *microcrystals* of [PtW(μ-CMe)(μ-dppm)(CO)$_5$][BF$_4$] (6) (0.71 g).

Synthesis of the Compound [PtW(μ-C=CH$_2$)(μ-dppm)-(CO)$_5$].—The salt (6) (0.51 g, 0.5 mmol) was dissolved at −78 °C in tetrahydrofuran (10 cm^3) and K[BH(CHMeEt)$_3$] (0.5 cm^3, 1 mol dm^{-3} solution in tetrahydrofuran) was added with stirring. Gas evolution, presumably hydrogen, was observed. After 30 min the solvent was removed *in vacuo*, and the residue extracted with toluene (20 cm^3). The extracts were passed through a deactivated alumina pad. After removal

Table 6. Atomic positional parameters (fractional co-ordinates), with estimated standard deviations in parentheses, for complex (3)

Atom	*x*	*y*	*z*
Pt	0.772 19(4)	0.729 75(2)	0.077 85(2)
W	0.562 11(4)	0.842 58(2)	0.035 09(2)
P(1)	0.956 3(3)	0.662 83(12)	0.150 67(11)
P(2)	0.853 0(3)	0.643 75(12)	0.005 90(11)
C(1)	0.715 9(10)	0.810 5(5)	0.137 9(5)
C(2)	0.765 0(12)	0.832 3(6)	0.207 5(6)
C(3)	0.990 6(11)	0.599 1(6)	0.082 3(4)
C(4)	0.588 4(12)	0.772 0(7)	−0.042 8(6)
O(4)	0.586 2(12)	0.740 6(6)	−0.095 2(5)
C(5)	0.408 2(11)	0.770 6(5)	0.055 3(5)
O(5)	0.321 9(9)	0.727 4(5)	0.062 8(4)
C(6)	0.414 2(11)	0.892 6(6)	−0.046 7(6)
O(6)	0.330 3(10)	0.920 8(5)	−0.092 7(5)
C(7)	0.512 1(12)	0.917 3(6)	0.103 6(6)
O(7)	0.483 0(11)	0.957 1(5)	0.145 2(5)
C(8)	0.731 0(12)	0.908 6(6)	0.022 4(6)
O(8)	0.823 8(10)	0.945 5(6)	0.012 8(5)
C(11)	1.131 7(10)	0.710 0(5)	0.188 8(4)
C(12)	1.140 2(11)	0.787 9(6)	0.184 1(5)
C(13)	1.273 2(12)	0.824 9(6)	0.212 0(6)
C(14)	1.399 6(12)	0.787 1(7)	0.242 8(6)
C(15)	1.393 8(12)	0.708 7(7)	0.247 2(6)
C(16)	1.261 1(11)	0.670 9(6)	0.222 4(5)
C(21)	0.919 6(10)	0.603 9(5)	0.221 0(5)
C(22)	1.003 4(13)	0.539 4(6)	0.245 2(6)
C(23)	0.979 2(13)	0.500 2(7)	0.301 9(6)
C(24)	0.871 3(13)	0.522 7(7)	0.335 3(6)
C(25)	0.790 9(12)	0.584 6(7)	0.311 0(6)
C(26)	0.813 1(11)	0.626 1(6)	0.253 4(5)
C(31)	0.743 0(10)	0.568 1(5)	−0.045 3(5)
C(32)	0.698 7(12)	0.508 7(6)	−0.009 5(6)
C(33)	0.605 7(14)	0.454 9(7)	−0.047 8(8)
C(34)	0.559 0(14)	0.457 4(7)	−0.120 1(8)
C(35)	0.602 1(15)	0.515 6(7)	−0.156 8(7)
C(36)	0.692 3(14)	0.571 7(7)	−0.118 9(6)
C(41)	0.964 3(10)	0.679 7(6)	−0.058 1(5)
C(42)	1.047 0(14)	0.633 7(6)	−0.081 8(6)
C(43)	1.135 9(15)	0.661 8(8)	−0.120 6(7)
C(44)	1.150 2(12)	0.737 7(7)	−0.127 0(6)
C(45)	1.071 6(12)	0.785 2(7)	−0.096 0(7)
C(46)	0.977 5(12)	0.756 0(6)	−0.057 0(6)

of solvent *in vacuo* the yellow oil produced was treated in succession with diethyl ether (5 cm^3) and light petroleum (5 cm^3). A yellow precipitate was formed and solvent was removed *in vacuo* giving yellow *microcrystals* of [PtW(μ-C=CH$_2$)(μ-dppm)(CO)$_5$] (7) (0.09 g, 20%). Compound (7) was also prepared quantitatively by passing a solution of (4) in dichloromethane through a basic alumina column.

Crystal Structure Determination of [PtW(μ-C=CH$_2$)(dppm)(CO)$_5$] (3).—Crystals of (3) grow from tetrahydrofuran–light petroleum mixtures as yellow prisms. Diffracted intensities were collected at room temperature from a crystal of dimensions *ca.* 0.3 × 0.4 × 0.4 mm with well developed faces of the type $\langle 010 \rangle$, $\langle 011 \rangle$, and $\langle 101 \rangle$. Data were collected on a Nicolet *P*3*m* four-circle diffractometer according to methods described earlier.[21] Of the total of 5 857 independent intensities, recorded to $2\theta \leqslant 50°$, 4 032 had $|F_o| \geqslant 5\sigma(F_o)$ where $\sigma(F_o)$ is the standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure, after correction for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal data. $C_{32}H_{24}O_5P_2PtW$, $M = 928.9$, Monoclinic, $a = 9.325(2)$, $b = 17.837(3)$, $c = 19.451(3)$ Å, $\beta = 105.74(1)°$, $Z = 4$, $D_c = 1.98$ g cm^{-3}, $U = 3\,114.0(8)$ Å^3, $F(000) = 1\,752$, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 82.30 cm^{-1}.

Structure Solution and Refinement.—The structure was solved and all non-hydrogen atoms were located by conventional heavy-atom and difference-Fourier methods. All except the μ-C=CH$_2$ hydrogen atoms were included in calculated positions (C–H 0.960 Å) and were given isotropic thermal parameters *ca.* 1.1 times those of the equivalent isotropic thermal parameters of the parent carbon atoms. Unfortunately the important μ-C=CH$_2$ hydrogen atoms could not be located with certainty in the final difference maps. Refinement by blocked-cascade least squares, with anisotropic thermal parameters for all non-hydrogen atoms, led to *R* 0.036 (*R'* 0.038), and a weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + 0.001|F_o|^2]$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >0.5 e Å^{-3} except in the immediate neighbourhood of the W atom where a peak of *ca.* 1.7 e Å^{-3} occurred. Scattering factors were from ref. 22. All computations were carried out on an 'Eclipse' (Data General) minicomputer with the SHELXTL system of programs.[23] Atom co-ordinates for compound (3) are listed in Table 6.

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