Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 21.[1] Reactivity of μ-(Methoxy-*p*-tolylmethylene) and μ-(*p*-Tolylmethylidyne) Groups at a Platinum–Tungsten Centre. *X*-Ray Crystal Structure of $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_5]$ *

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Treatment of $[PtW\{\mu\text{-}C(OMe)R\}(CO)_5(cod)]$ (R = C_6H_4Me-4, cod = cyclo-octa-1,5-diene) with dppm ($Ph_2PCH_2PPh_2$) affords $[PtW\{\mu\text{-}C(OMe)R\}(\mu\text{-}dppm)(CO)_5]$ (1), the structure of which has been established by *X*-ray crystallography. As expected, the platinum–tungsten bond [2.818(3) Å] is spanned by the dppm and C(OMe)R ligands. The five-membered ring involving the chelating phosphine and the two metal atoms adopts an envelope conformation with one of the P atoms lying out of the plane. The $Pt\{\mu\text{-}C(OMe)R\}W$ ring is asymmetric [Pt–C 1.97(3), W–C 2.49(3) Å]. The platinum atom carries one terminal carbonyl ligand and the tungsten atom four, making the co-ordination at these two metal centres essentially square planar and octahedral, respectively. Compound (1) reacts with $HBF_4{\cdot}OEt_2$ to yield the salt $[PtW(\mu\text{-}CR)(\mu\text{-}dppm)(CO)_5][BF_4]$, and with BBr_3 to give $[PtWBr(\mu\text{-}CR)(\mu\text{-}dppm)(CO)_4]$, but the latter is better prepared by treating the salt with NEt_4Br. Reactions of the complex $[PtW(\mu\text{-}CR)(\mu\text{-}dppm)(CO)_5][BF_4]$ with several nucleophilic reagents have been investigated leading to the synthesis of the compounds $[PtW(\mu\text{-}CRR')(\mu\text{-}dppm)(CO)_5]$ (R' = Me, H, $C{\equiv}CBu^t$, or SC_6H_4Me-4) and $[PtW\{\mu\text{-}C(\eta^2\text{-}C_5H_5)R\}(\mu\text{-}dppm)(CO)_4]$. The n.m.r. data ($^1H$, $^{31}P\text{-}\{^1H\}$, $^{13}C\text{-}\{^1H\}$, and $^{195}Pt\text{-}\{^1H\}$) for the new compounds are reported and discussed.

The reactivity of organic species bonded simultaneously to two metal centres is a topic of considerable current interest.[2] In particular, the behaviour of alkylidene or alkylidyne groups bridging metal–metal bonds is relevant to contemporary ideas on the mechanisms of Fischer–Tropsch reactions.[3] We have developed [1,4–7] versatile methods of synthesising di- and tri-metal complexes having bridging CRR' and CR ligands, thus providing a range of model compounds for study. In most of the species we have prepared the alkylidene and alkylidyne groups bridge heteronuclear metal–metal bonds. Hence the presence in the complexes of different metallic elements with their associated ligands might be expected to influence the chemistry observed.

We have reported previously some reactions of μ-CRR' and μ-CR groups at bimetal centres. For example, the compound $[MnPt\{\mu\text{-}C(OMe)R\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) reacts with $[OMe_3][BF_4]$ to afford the salt $[(\eta\text{-}C_5H_5)(OC)_2Mn(\mu\text{-}CR)Pt(PMe_3)_2][BF_4]$, which reverts quantitatively to its precursor on treatment with sodium methoxide.[8] In contrast, studies with the salts $[(OC)_4LM(\mu\text{-}CR)Pt(PMe_3)_2][BF_4]$ (M = Cr or W, L = CO or PMe_3, R = Ph or C_6H_4Me-4) were less clear cut. Treatment with nucleophilic reagents [$Li(C_6H_4Me$-4), NaOMe, or NaOEt] either afforded complexes with bridging alkylidene ligands in very poor yield, or unexpected reaction products were obtained. For example, treatment of $[CrPt\{\mu\text{-}C(OMe)Ph\}(CO)_4(PMe_3)_3]$ with $[OMe_3][BF_4]$ in dichloromethane followed by sodium methoxide in methanol gave the compound $[CrPt\{\mu\text{-}C(CO_2Me)Ph\}(CO)_4(PMe_3)_3]$ [8] rather than the original μ-[methoxy(phenyl)-methylene]-chromiumplatinum complex.

Low yields of product in some of the syntheses are probably due to cleavage of the metal–metal bonds when reactions at the μ-CRR' groups are attempted. We have observed rupture of the metal–metal bonds and transfer of the alkylidene groups to platinum. Thus, in toluene at 80 °C, $[(OC)_5Cr\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ gives a mixture of the triplatinum compounds $[Pt_3\{\mu\text{-}C(OMe)Ph\}_2(\mu\text{-}CO)(PMe_3)_3]$ and $[Pt_3\{\mu\text{-}C(OMe)Ph\}_3(PMe_3)_3]$,[9] and treatment of $[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(cod)]$ (cod = cyclo-octa-1,5-diene) with CO affords $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_3(CO)_3]$ and $[W(CO)_6]$.[10] In order to stabilise the metal–metal bond in a bimetal complex with a bridging alkylidene group, we have employed the ligand dppm ($Ph_2PCH_2PPh_2$) to hold the metal atoms together. It was anticipated that this would allow studies at the carbon bridge to be conducted more effectively.

Results and Discussion

The cyclo-octa-1,5-diene ligand in $[(OC)_5W\{\mu\text{-}C(OMe)R\}Pt(cod)]$ (R = C_6H_4Me-4) is readily substituted by $Ph_2PCH_2CH_2PPh_2$ (dppe) to give $[(OC)_5W\{\mu\text{-}C(OMe)R\}Pt(dppe)]$.[10] The corresponding reaction with dppm in toluene afforded a mixture of the platinum–tungsten compounds (1)—(3), which were separated by chromatography on an alumina column. It was subsequently found possible to obtain spectroscopic evidence for the intermediacy of the complex (4) in the formation of (1) by conducting the reaction with dppm at −78 °C and separating the products on alumina, which had been vacuum dried, using toluene as eluant. Compound (4) readily isomerises to (1), and hence the n.m.r. data discussed below have to be acquired rapidly.

Compound (3) has been previously characterised.[10] It is

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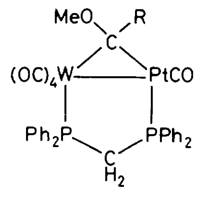
* μ-[Bis(diphenylphosphino)methane-*PP'*]-1,2,2,2,2-pentacarbonyl-μ-[methoxy(*p*-tolyl)methylene]-platinumtungsten (*Pt–W*).

Supplementary data available (No. SUP 23662, 29 pp.): observed and calculated structure factors, H-atom co-ordinates, thermal parameters, complete listing of internuclear separations and angles. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

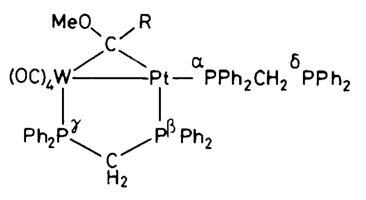
Table 1. Analytical [a] and physical data for the platinum–tungsten complexes

Compound [b]	M.p. (θ_c/°C) [c]	Colour	Yield (%)	$\nu_{max.}$(CO) [d]/cm^{-1}	Analysis (%) C	Analysis (%) H
(1) [PtW{μ-C(OMe)R}(μ-dppm)(CO)$_5$]	132—135	Orange	64	2 010s, 1 939s, 1 931s (sh), 1 899s (br)	45.8 (45.8)	3.8 (3.5)
(2) [PtW{μ-C(OMe)R}(μ-dppm)(CO)$_4$(dppm)]	80—84	Orange	8	2 010s, 1 932s (br), 1 895m (sh), 1 883s	54.4 (54.3)	4.1 (3.9)
(5) [PtW(μ-CR)(μ-dppm)(CO)$_5$][BF$_4$]	190—200	Orange-brown	60	[e] 2 088m, 2 048m, 2 037m, 1 987m (sh), 1 974s	41.7 (41.7)	3.3 (2.7)
(6) [PtWBr(μ-CR)(μ-dppm)(CO)$_4$]	176—180	Yellow	60 [f]	2 049m, 1 997vs, 1 961s	[g] 42.7 (42.0)	3.6 (2.7)
(7) [PtW{μ-C(Me)R}(μ-dppm)(CO)$_5$]	130—133	Orange	30	2 030m, 2 009s, 1 943s, 1 907s	43.6 (43.4)	3.2 (3.1)
(8) [PtW(μ-CHR)(μ-dppm)(CO)$_5$]	174—178	Yellow	68	2 032m, 2 014s, 1 942s (br), 1 908s	45.5 (45.3)	3.2 (3.0)
(9) [PtW{μ-C(C$_2$Bu^t)R}(μ-dppm)(CO)$_5$]	140—144	Orange	25	2 035m, 1 996s, 1 976m, 1 955s	48.1 (48.6)	3.9 (3.5)
(10) [PtW{μ-C(SR)R}(μ-dppm)(CO)$_5$]	138—144	Orange	20	[e] 2 044s, 2 023s, 1 970m, 1 952s, 1 925s	[h] 48.1 (47.8)	3.4 (3.2)
(12) [PtW{μ-C(C$_5$H$_5$)R}(μ-dppm)(CO)$_4$]	150—153	Orange	87	2 009s, 1 980vs, 1 914s, 1 875s	47.7 (47.1)	3.9 (3.2)

[a] Calculated values are given in parentheses. [b] R = C_6H_4Me-4. [c] With decomposition. [d] In methylcyclohexane, unless otherwise stated. [e] In dichloromethane. [f] From NEt_4Br and (5), see text. [g] Br 6.3 (7.2%). [h] S 2.8 (2.8%).



(1)



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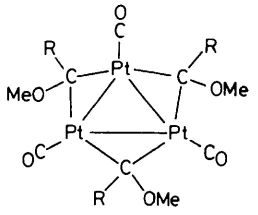

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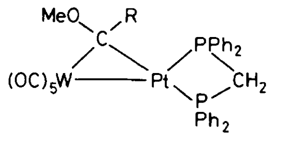

(4)

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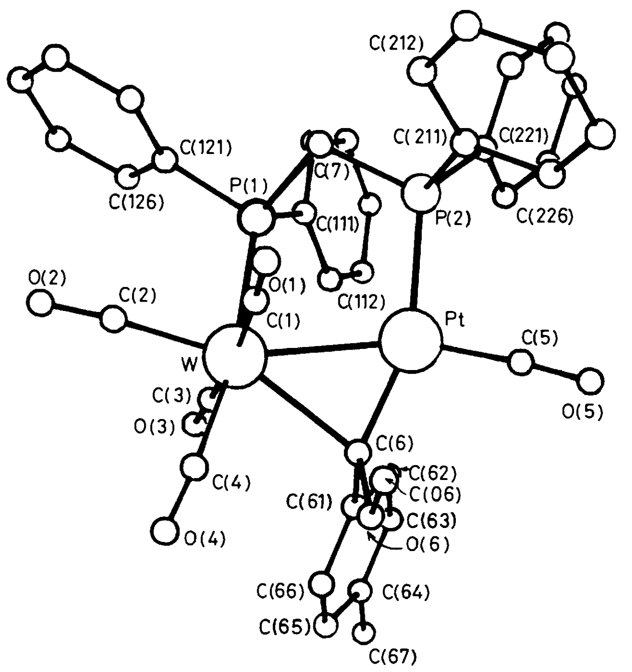


Figure 1. The molecular structure of [PtW{μ-C(OMe)C_6H_4Me-4}-(μ-dppm)(CO)$_5$] (1), showing the crystallographic numbering scheme

known to be readily produced by the action of CO on [(OC)$_5$W{μ-C(OMe)R}Pt(cod)]. Hence its isolation simultaneously with (2) is not surprising, since formation of the latter releases CO. Compounds (1) and (2) were characterised by microanalysis (Table 1) and by their n.m.r. spectra, data from which are given in Tables 2 and 3.

The ^{13}C-{^{1}H} n.m.r. spectrum of (1) (Table 2) shows peaks corresponding to the presence of CO ligands in five different environments, including a resonance (δ 185.0 p.p.m.) with strong ^{195}Pt–^{13}C coupling (1 672 Hz), characteristic of a PtCO group.[11,12] Also informative is the resonance at δ 226.3 p.p.m. due to the bridging *C*(OMe)R carbon, appearing as a doublet of doublets due to coupling with the non-equivalent phosphorus nuclei of the dppm ligand. As expected, the latter gives rise to two signals in the ^{31}P-{^{1}H} n.m.r. spectrum (Table 3). The relative size of the ^{195}Pt–^{31}P coupling constants, 2 532 and 120 Hz, allows a ready distinction to be made between the resonances due to the PPt and PW groups. Moreover, the signal at δ −0.6 p.p.m. also has ^{183}W–^{31}P satellite peaks [*J*(WP) 124 Hz].

The ^{31}P-{^{1}H} n.m.r. spectrum of (2) (Table 3), with four distinct resonances, is in accord with the structure proposed. The PPt groups may be identified by the large ^{195}Pt–^{31}P couplings of 3 600 and 2 658 Hz. In the ^{13}C-{^{1}H} spectrum the μ-C resonance has the pattern (d of d of d) expected for coupling with three non-equivalent phosphorus nuclei (Table 2).

Although compound (4) readily isomerises to (1), it was possible to measure the ^{31}P-{^{1}H} spectrum (Table 3). The latter is very similar to that of the compound [PtW{μ-C(OMe)R}(CO)$_5$(dppe)],[10] the *J*(PP) and *J*(PtP) data for the two species being essentially the same.

Since (1) was a key compound for further investigations it was decided to establish its structure by a single-crystal *X*-ray diffraction study. The results are summarised in Table 4, and the molecular structure with the atom numbering scheme is shown in Figure 1. A stereoscopic view of the molecular structure is shown in Figure 2.

As expected, (1) contains the $\overline{\mathrm{Pt\{\mu\text{-}C(OMe)R\}W}}$ dimetallacyclopropane ring system previously characterised by *X*-ray diffraction methods in the compounds

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

Complex [b]	^{1}H (δ)	^{13}C [c] (δ)
(1) [PtW{μ-C(OMe)R}(μ-dppm)(CO)$_5$]	2.40 (s, 3 H, Me-4), 3.90 (s, 3 H, OMe), 4.22 [d of d of d, 1 H, CH$_2$, *J*(HH) 14, *J*(PH) 10 and 7], 5.50 [d of t, 1 H, CH$_2$, *J*(HH) 14, *J*(PH) 10], 6.6—8.1 (m, 24 H, C$_6$H$_4$ and Ph)	226.3 [d of d, μ-C, *J*(PC) 69 and 11], 210.1 [d, WCO, *J*(PC) 12], 210.0 [d, WCO, *J*(PC) 9], 203.9 [d, WCO, *J*(PC) 6], 200.0 [d, WCO, *J*(PC) 7, *J*(PtC) 135], 185.0 [d, PtCO, *J*(PC) 13, *J*(PtC) 1 672], 157.1 [C^1(C$_6$H$_4$), *J*(PtC) 82], 142—123 (C$_6$H$_4$ and Ph), 60.9 [OMe, *J*(PtC) 60], 44.4 [d of d, CH$_2$, *J*(PC) 27 and 22, *J*(PtC) 96], 22.0 (Me-4)
(2) [PtW{μ-C(OMe)R}(μ-dppm)(CO)$_4$(dppm)]	2.40 (s, 3 H, Me-4), 2.86 (m, 2 H, CH$_2$), 3.88 (s, 3 H, OMe), 4.37 [d of d of d, 1 H, CH$_2$, *J*(HH) 14, *J*(PH) 10 and 7], 5.29 [d of t, 1 H, CH$_2$, *J*(HH) 14, *J*(PH) 5], 6.2—8.0 (m, 44 H, C$_6$H$_4$ and Ph)	[d] 224.7 [d of d of d, μ-C, *J*(PC) 79, 16, and 8], 212.6 [d of d, CO, *J*(PC) 16 and 6], 211.8 [d, CO, *J*(PC) 9, *J*(WC) 144], 206.2 [t, CO, *J*(PC) 6, *J*(PtC) 46], 203.6 [d, CO, *J*(PC) 7, *J*(WC) 132], 151.0 [d, C^1(C$_6$H$_4$), *J*(PC) 4, *J*(PtC) 92], 143—123 (C$_6$H$_4$ and Ph), 60.8 [OMe, *J*(PtC) 62], 25.3 [d of d of d, CH$_2$, *J*(PC) 33, 25, and 8],[e] 21.3 (Me-4)
(4) [PtW{μ-C(OMe)R}(CO)$_5$(dppm)]	2.11 (s, 3 H, Me-4), 3.59 (s, 3 H, OMe), 4.39 [t, 2 H, CH$_2$, *J*(PH) 16, *J*(PtH) 10], 6.8—8.0 (m, 24 H, C$_6$H$_4$ and Ph)	
(5) [PtW(μ-CR)(μ-dppm)(CO)$_5$][BF$_4$]	[f] 2.33 (s, 3 H, Me-4), 5.18 [t, 2 H, CH$_2$, *J*(PC) 10], 6.4—8.0 (m, 24 H, C$_6$H$_4$ and Ph)	[g] 387.0 [d, μ-C, *J*(PC) 51, *J*(PtC) 806], 197.4 [WCO, *J*(PtC) 26], 195.8 [d, 2 × WCO, *J*(PC) 9], 193.0 [d, WCO, *J*(PC) 9], 190.1 [d, PtCO, *J*(PC) 12, *J*(PtC) 1 887], 152.9 [C^1(C$_6$H$_4$), *J*(PtC) 88], 142—127 (C$_6$H$_4$ and Ph), 36.9 [t, CH$_2$, *J*(PtC) 30], 23.0 (Me-4)
(6) [PtWBr(μ-CR)(μ-dppm)(CO)$_4$]	[h] 1.99 (s, 3 H, Me-4), 4.50 [t, 2 H, CH$_2$, *J*(PH) 9, *J*(PtH) 13], 6.7—8.4 (m, 24 H, C$_6$H$_4$ and Ph)	[h] 324.6 [d, μ-C, *J*(PC) 46], 200.6 [d, 2 × WCO, *J*(PC) 7, *J*(PtC) 49], 198.0 [d, WCO, *J*(PC) 35], 196.5 [d, PtCO, *J*(PC) 10, *J*(PtC) 1 785], 153.3 [C^1(C$_6$H$_4$), *J*(PtC) 49], 140—120 (C$_6$H$_4$ and Ph), 37.3 [t, CH$_2$, *J*(PC) 28], 21.5 (Me-4)
(7) [PtW{μ-C(Me)R}(μ-dppm)(CO)$_5$]	2.37 (s, 3 H, Me-4), 3.58 [d of d, 3 H, μ-CMe, *J*(PH) 9 and 6], 4.61 [d of d of d, 1 H, CH$_2$, *J*(HH) 14, *J*(PH) 11 and 8], 5.49 [d of t, 1 H, CH$_2$, *J*(HH) 14, *J*(PH) 10], 6.6—7.7 (m, 24 H, C$_6$H$_4$ and Ph)	212.3 [d, 2 × WCO, *J*(PC) 12], 202.3 [d, WCO, *J*(PC) 7], 201.4 [d, WCO, *J*(PC) 7], 186.0 [d, PtCO, *J*(PC) 16, *J*(PtC) 1 686], 177.3 [d of d, μ-C, *J*(PC) 58 and 10], 159.6 [C^1(C$_6$H$_4$), *J*(PtC) 36], 140—125 (C$_6$H$_4$ and Ph), 50.6 [d of d, CH$_2$, *J*(PC) 29 and 24, *J*(PtC) 104], 40.7 [μ-C*Me*, *J*(PtC) 32], 21.0 (Me-4)
(8) [PtW(μ-CHR)(μ-dppm)(CO)$_5$]	2.36 (s, 3 H, Me-4), 5.11 [m, (ABXY), 1 H, CH$_2$, *J*(HH) 14, *J*(PH) 10 and 9], 5.33 [m, (ABXY), 1 H, CH$_2$, *J*(HH) 14, *J*(PH) 11 and 9], 7.1—7.5 (m, 24 H, C$_6$H$_4$ and Ph), 9.02 [d of d, 1 H, μ-CH, *J*(PH) 7 and 4]	[g] 213.2 [d, WCO, *J*(PC) 12, *J*(WC) 125], 210.0 [d, WCO, *J*(PC) 8, *J*(WC) 130], 204.3 [d, WCO, *J*(PC) 6, *J*(WC) 126, *J*(PtC) 24], 201.8 [d, WCO, *J*(PC) 6, *J*(WC) 124, *J*(PtC) 37], 186.7 [d, PtCO, *J*(PC) 13, *J*(PtC) 1 666], 154.2 [d, C^1(C$_6$H$_4$), *J*(PC) 3], 149.5 [d of d, μ-C, *J*(PC) 55 and 8, *J*(PtC) 973, *J*(WC) 36], 138—128 (C$_6$H$_4$ and Ph), [i] 53.9 [d of d, CH$_2$, *J*(PC) 30 and 25, *J*(PtC) 110], 21.6 (Me-4)
(9) [PtW{μ-C(C$_2$Bu^t)R}(μ-dppm)(CO)$_5$]	1.19 (s, 9 H, Bu^t), 2.39 (s, 3 H, Me-4), 5.05 (m, 2 H, CH$_2$), 6.8—8.1 (m, 24 H, C$_6$H$_4$ and Ph)	[d] 255.6 [d of d, μ-C, *J*(PC) 12 and 6], 205.2 [d, WCO, *J*(PC) 19], 203.7 [d, 2 × CO, *J*(PC) 9, *J*(PtC) 40], 196.2 [d, CO, *J*(PC) 5], 195.4 [d, CO, *J*(PC) 9], 153.7 [C^1(C$_6$H$_4$), *J*(PtC) 69], 139.5 [C^4(C$_6$H$_4$)], 135—127 (C$_6$H$_4$ and Ph), 105.5 (*C*≡C), 90.2 (C≡*C*), 39.1 [t, CH$_2$, *J*(PC) 30], 29.5 (C*Me*$_3$), 27.0 (*C*Me$_3$), 20.7 (Me-4)

Table 2 (*continued*)

Complex [b]	^{1}H (δ)	^{13}C [c] (δ)
(10) [PtW{μ-C(SR)R}(μ-dppm)(CO)$_5$]	[g] 2.31 (s, 3 H, Me-4), 2.41 (s, 3 H, Me-4), 4.59 [d of d of d, 1 H, CH_2, *J*(PH) 11 and 8, *J*(HH) 14], 5.87 [d of t, 1 H, CH_2, *J*(PH) 11, *J*(HH) 14, *J*(PtH) 40], 6.9—7.8 (m, 28 H, C_6H_4 and Ph)	[d] 209.5 [d, WCO, *J*(PC) 14], 204.7 [d, WCO, *J*(PC) 3], 198.2 [d, WCO, *J*(PC) 8], 196.9 [d, WCO, *J*(PC) 5], 179.4 [d of d, PtCO, *J*(PC) 12 and 8, *J*(PtC) 1 698], 174.6 [d of d, μ-C, *J*(PC) 55 and 13], 149.3 [C^{1}(C_6H_4), *J*(PtC) 18], 141.4, 140.3, 140—125 (C_6H_4 and Ph), 48.0 [t, CH_2, *J*(PC) 29, *J*(PtC) 39], 20.6, 20.2 (Me-4)
(12) [PtW{μ-C(C_5H_5)R}(μ-dppm)(CO)$_4$]	2.39 (s, 3 H, Me-4), 2.99 [d of d, 1 H, CH_2 (C_5H_5), *J*(HH) 23 and 2], 3.67 [d of d of d, 1 H, CH (C_5H_5), *J*(PH) 7, *J*(HH) 7 and 2], 4.15 [d of d of d, 1 H, CH_2 (C_5H_5), *J*(HH) 23, 5 and 2], 4.44 [d of d of d, 1 H, PCH_2P, *J*(PH) 12 and 9, *J*(HH) 15], 6.06 [m, 1 H, CH (C_5H_5)], 6.21 [m, 1 H, CH (C_5H_5)], 6.23 [d of d of d, 1 H, PCH_2P, *J*(PH) 11 and 8, *J*(HH) 15], 6.9—7.7 (m, 24 H, C_6H_4 and Ph)	[d] 223.7 [d, WCO, *J*(PC) 15], 223.2 [d, WCO, *J*(PC) 10], 220.8 [WCO, *J*(WC) 131], 187.9 [d, PtCO, *J*(PC) 9, *J*(PtC) 1 526], 183.2 [d of d, μ-C, *J*(PC) 63 and 3, *J*(PtC) 940], 148.3 [C^{1}(C_6H_4)], 139—120 (m, C_6H_4, Ph, C_5H_5), 75.7 [CH (C_5H_5), *J*(PtC) 36], [i] 55.4 [d of d, PCH_2P, *J*(PC) 31 and 23, *J*(PtC) 138], [j] 44.2 [CH_2 (C_5H_5), *J*(PtC) 52], 21.1 (Me-4)

[a] Measured in [$^{2}H_1$]chloroform, unless otherwise indicated; chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] R = C_6H_4Me-4. [c] Hydrogen-1 decoupled, to high frequency of $SiMe_4$. [d] Measured in [$^{2}H_2$]dichloromethane–CH_2Cl_2. [e] Signal for WP*C*H_2PPt obscured by resonances due to solvent mixture. [f] Measured in [$^{2}H_3$]acetonitrile. [g] Measured in [$^{2}H_2$]dichloromethane. [h] Measured in [$^{2}H_6$]benzene. [i] From spectrum in [$^{2}H_1$]chloroform, signal obscured in [$^{2}H_2$]dichloromethane. [j] Triplet signal in un-decoupled spectrum.

Table 3. Phosphorus-31 and platinum-195 n.m.r. data [a]

	^{31}P (δ/p.p.m.) [b]	^{195}Pt (δ/p.p.m.) [c]
(1)	7.4 [d, PPt, *J*(PP) 134, *J*(PtP) 2 532], −0.6 [d, PW, *J*(PP) 134, *J*(PtP) 120, *J*(WP) 124]	395 [d of d, *J*(PPt) 2 532, 120, *J*(WPt) 44]
(2)	14.0 [d of d of d, P^{α}, *J*($P^{\beta}P^{\alpha}$) 9, *J*($P^{\gamma}P^{\alpha}$) 41, *J*($P^{\alpha}P^{\delta}$) 21, *J*(PtP^{α}) 3 600], 7.7 [d of t, P^{β}, *J*($P^{\alpha}P^{\beta}$) 9, *J*($P^{\gamma}P^{\beta}$) 120, *J*($P^{\delta}P^{\beta}$) 9, *J*(PtP^{β}) 2 658], −1.8 [d of d, P^{γ}, *J*($P^{\alpha}P^{\gamma}$) 41, *J*($P^{\beta}P^{\gamma}$) 120, *J*(PtP^{γ}) 115], −27.6 [d of d, P^{δ}, *J*($P^{\alpha}P^{\delta}$) 21, *J*($P^{\beta}P^{\delta}$) 9, *J*(PtP^{δ}) 118]	
(4)	−6.5 [d, PPt, *cis*-PPtW, *J*(PP) 17, *J*(PtP) 2 004], −10.0 [d, PPt, *trans*-PPtW, *J*(PP) 17, *J*(PtP) 3 636]	
(5)	[d] −0.2 [d, PW, *J*(PP) 88, *J*(PtP) 83], −6.0 [d, PPt, *J*(PP) 88, *J*(PtP) 2 340]	[d] 980 [d of d, *J*(PPt) 2 340, 83]
(6)	10.1 [d, PW, *J*(PP) 108, *J*(PtP) 121, *J*(WP) 180], −5.3 [d, PPt, *J*(PP) 108, *J*(PtP) 2 495]	764 [d of d, *J*(PPt) 2 495, 121]
(7)	[d] 7.1 [d, PPt, *J*(PP) 113, *J*(PtP) 2 482], −6.3 [d, PW, *J*(PP) 113, *J*(PtP) 140, *J*(WP) 169]	375 [d of d, *J*(PPt) 2 482, 140]
(8)	[d] 8.3 [d, PPt, *J*(PP) 103, *J*(PPt) 2 639], −9.8 [d, PW, *J*(PP) 103, *J*(PPt) 130, *J*(WP) 174]	312 [d of d, *J*(PPt) 2 639, 130]
(9)	11.0 [d, PW, *J*(PP) 110, *J*(PtP) 106, *J*(WP) 190], −2.6 [d, PPt, *J*(PP) 110, *J*(PtP) 2 528]	835 [d of d, *J*(PPt) 2 528, 106]
(10)	[d] −2.1 [d, PPt, *J*(PP) 77, *J*(PtP) 2 588], −8.3 [d, PW, *J*(PP) 77, *J*(PtP) 128, *J*(WP) 177]	[d] 191 [d of d, *J*(PPt) 2 588, 128]
(11)	4.3 [d, PW, *J*(PP) 103, *J*(PtP) 105], 1.7 [d, PPt, *J*(PP) 103, *J*(PtP) 2 577]	
(12)	4.6 [d, PPt, *J*(PP) 76, *J*(PtP) 2 843], −1.8 [d, PW, *J*(PP) 76, *J*(PtP) 115, *J*(WP) 186]	147 [d of d, *J*(PPt) 2 843, 115]

[a] Spectra measured in [$^{2}H_1$]chloroform, unless otherwise stated; coupling constants in Hz. [b] Hydrogen-1 decoupled, chemical shifts in p.p.m. positive to high frequency of 85% H_3PO_4 (external). [c] Hydrogen decoupled, chemical shifts to high frequency of Ξ(^{195}Pt) 21.4 MHz. [d] Measured in [$^{2}H_2$]dichloromethane–CH_2Cl_2.

[(OC)$_5$W{μ-C(OMe)Ph}Pt(PMe$_3$)$_2$][4] and [(Me$_3$P)(OC)$_4$W{μ-C(OMe)C$_6$H$_4$Me-4}Pt(PMe$_3$)$_2$].[5] The Pt–W bond in (1) is spanned by the dppm ligand forming a five-membered ring which is in an envelope conformation, with P(1) out of the Pt,W,C(7),P(2) plane by 1.07 Å. The P(1)–W separation [2.544(7) Å] is close to that found [2.507(4) Å] in [(Me$_3$P)(OC)$_4$W{μ-C(OMe)C$_6$H$_4$Me-4}Pt(PMe$_3$)$_2$][5] and within the range 2.427(1)—2.614(5) Å typical for P–W bonds.[13] The P(2)–Pt distance [2.335(6) Å] is similar to the corresponding distance [2.326(3) Å] in [(Me$_3$P)(OC)$_4$W{μ-C(OMe)C$_6$H$_4$Me-4}Pt(PMe$_3$)$_2$] in which a PMe$_3$ group is *transoid* to the bridging alkylidene ligand. Both separations are at the long end of the range [2.267(9)—2.331(5) Å] found for P–Pt bonds,[14] and this probably reflects the strong *trans* influence of the μ-C(OMe)R group.

In (1) the platinum atom is in an essentially planar environment, with the angle between the planes defined by W,Pt,C(6) and P(2),Pt,C(5) being only 5.7°. The CO group on platinum lies *transoid* to the Pt–W bond. The tungsten atom is essentially octahedrally co-ordinated by four CO ligands, P(1), and the midpoint of the C(6)–Pt bond, with the equatorial ligands in a staggered conformation with respect to the Pt–C(6) vector.

Interest focuses on the Pt–C(6)–W ring in compound (1). The Pt–W distance [2.818(3) Å] is discernibly shorter than that in [PtW{μ-C(OMe)Ph}(CO)$_5$(PMe$_3$)$_2$] [2.861(1) Å],[4] a consequence probably of the presence of the chelating dppm ligand. As in the two previously studied compounds, the μ-C(OMe)R ligand is asymmetrically bridging the metal–metal bond, with C(6)–W [2.49(3) Å] being appreciably longer than C(6)–Pt [1.97(3) Å]. We have discussed this phenomenon previously [4,5] in the context of the isolobal mapping shown below, so that in all three species the W(CO)$_5$ or W(CO)$_4$(PMe$_3$) groups can be formally regarded as co-ordinated by a R(OMe)C=Pt(PMe$_3$)$_2$ moiety. In spite of the asymmetry of the μ-C(OMe)R ligand, a number of reactions occur at this centre without cleavage of the C(6)–W bond, as will now be described.

$$\mathrm{WL_5} \xleftrightarrow[\circ]{} \mathrm{CH_2} \xleftrightarrow[\circ]{} \mathrm{PtL_2}$$

Treatment of a diethyl ether solution of (1) with HBF$_4$·OEt$_2$

Table 4. Internuclear distances (Å) and angles (°) for [PtW{μ-C(OMe)C_6H_4Me-4}(μ-dppm)$(CO)_5$] (1), with estimated standard deviations in parentheses

Pt–W	2.818(3)	W–C(1)	2.07(3)
W–C(2)	2.02(3)	W–C(3)	1.97(3)
W–C(4)	2.05(4)	Pt–C(5)	1.83(4)
W–C(6)	2.49(3)	Pt–C(6)	1.97(3)
C(6)–C(61)	1.55(4)	C(6)–O(6)	1.43(4)
O(6)–C(06)	1.43(4)	C(64)–C(67)	1.55(4)
W–P(1)	2.544(7)	Pt–P(2)	2.335(6)
P(1)–C(7)	1.83(3)	P(2)–C(7)	1.81(3)
P(1)–C(111)	1.77(2)	P(1)–C(121)	1.82(3)
P(2)–C(211)	1.84(3)	P(2)–C(221)	1.81(2)
C(1)–O(1)	1.11(4)	C(2)–O(2)	1.16(4)
C(3)–O(3)	1.20(4)	C(4)–O(4)	1.11(4)
C(5)–O(5)	1.18(4)	C–C (phenyl)	1.395
C(1A)–Cl(1)	1.53(6)	C(1A)–Cl(2)	1.79(7)
W–Pt–C(6)	59.6(8)	Pt–W–C(6)	43.1(5)
Pt–C(6)–W	77.3(9)	W–C(1)–O(1)	175(3)
W–C(2)–O(2)	170(3)	W–C(3)–O(3)	177(3)
W–C(4)–O(4)	171(4)	Pt–C(5)–O(5)	174(3)
C(61)–C(6)–O(6)	102(2)	C(6)–O(6)–C(06)	114(2)
W–P(1)–C(7)	111.0(9)	P(1)–C(7)–P(2)	108.4(11)
Pt–P(2)–C(7)	111.7(7)	P(2)–Pt–C(5)	97.4(9)
P(2)–Pt–W	98.7(2)	P(2)–Pt–C(6)	157.9(8)
C(5)–Pt–W	163.8(9)	C(5)–Pt–C(6)	104.4(12)
C(1)–W–P(1)	90.0(7)	C(1)–W–C(2)	90.1(11)
C(1)–W–C(3)	175.7(11)	C(1)–W–C(4)	87.6(12)
C(1)–W–C(6)	96.1(10)	C(2)–W–P(1)	83.2(7)
C(2)–W–C(3)	85.6(12)	C(2)–W–C(4)	86.6(11)
C(2)–W–C(6)	158.8(8)	C(3)–W–P(1)	88.9(8)
C(3)–W–C(4)	92.9(12)	C(3)–W–C(6)	88.1(11)
C(4)–W–P(1)	169.4(9)	C(4)–W–C(6)	73.6(10)
P(1)–W–C(6)	116.9(5)	Cl(1)–C(1A)–Cl(2)	114(4)

afforded in 60% yield the salt (5), characterised by the data presented in Tables 1—3. The ^{13}C-{^1H} n.m.r. spectrum showed the characteristic resonance for a bridging tolylmethylidyne group at δ 387.0 p.p.m., this signal appearing as a doublet [*J*(PC) 51 Hz] with ^{195}Pt satellite peaks [*J*(PtC) 806 Hz]. The corresponding data for the neutral complex [PtW(μ-CR)$(CO)_2(PMe_3)_2$(η-C_5H_5)] are δ 338 p.p.m., doublet with *J*(PC) 61 and *J*(PtC) 732 Hz.[15] The ^{31}P-{^1H} and ^{195}Pt-{^1H} spectra (Table 3) are also consistent with the structure proposed for (5). Two sets of signals are seen in the ^{31}P-{^1H} spectrum, assignable to PPt and PW groups on the basis of the observed ^{195}Pt and ^{183}W satellite peaks. The ^{195}Pt-{^1H} spectrum is a doublet of doublets, in accord with the presence of PPt and PWPt groups, the ^{195}Pt–^{31}P couplings being consistent with those observed in the ^{31}P-{^1H} spectrum.

Compound (1) reacts with BBr_3 to give the bromotungsten complex (6), but the latter is produced in better yield by treating (5) with NEt_4Br. The presence of the μ-CR group in (6) is established by the ^{13}C-{^1H} n.m.r. spectrum which shows a doublet signal for the ligated carbon atom at δ 324.6 p.p.m., with *J*(PC) 46 Hz. It is interesting that in the spectra of (5) and (6) the μ-CR signals appear as doublets, indicating coupling to only one ^{31}P nucleus, whereas in the spectra of all but one of the complexes containing μ-CRR′ groups described herein the alkylidene carbon resonance is a doublet of doublets, as expected for coupling to two non-equivalent ^{31}P ligands. Formation of compound (6) from (1) with BBr_3 probably involves co-ordination of the boron trihalide to the OMe group of (1), followed by transfer of Br to tungsten with loss of BBr_2(OMe) and CO. The reaction is reminiscent of the syntheses of bromo(alkylidyne)tetracarbonyltungsten complexes from the monotungsten compound [W{=C(OMe)R}-

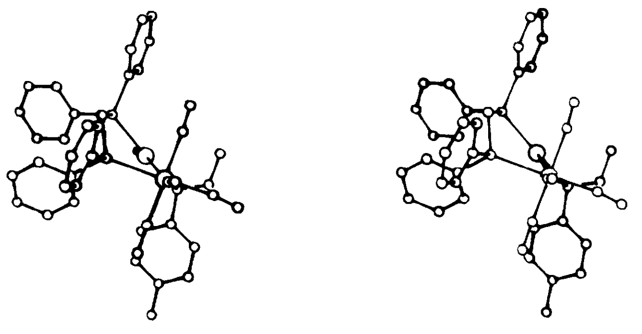
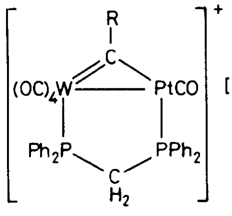
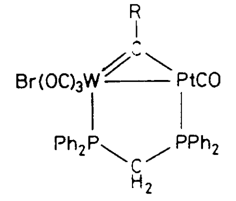


Figure 2. A stereoscopic view of complex (1)



(5)



(6)

R = C_6H_4Me-4

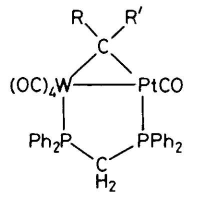
$(CO)_5$] and BBr_3.[16] The synthesis of (6) from (5) presumably involves direct displacement of CO on tungsten with Br^-.

The salt (5) reacts with sodium methoxide in methanol to regenerate (1), and with the reagents LiMe, K[BH(CHMeEt)$_3$], LiC≡CBu^t, and NaSC_6H_4Me-4 in tetrahydrofuran (thf) to afford complexes (7)—(10), respectively, data for which are given in Tables 1—3. All the spectroscopic properties are in accord with the structures proposed. Thus the resonance in the ^{13}C-{^1H} n.m.r. spectrum of (5) due to the μ-CR ligand (δ 387 p.p.m.) is replaced in the spectra of (7)—(10) by signals due to the μ-*C*(Me)R (δ 177.3), μ-*C*HR (δ 149.5), μ-*C*(C_2Bu^t)R (δ 255.6), and μ-*C*(SC_6H_4Me-4)R (δ 174.6 p.p.m.) groups. These resonances are less deshielded than those for a bridging alkylidyne group μ-CR, a feature we have commented upon previously.[8] The ^{31}P-{^1H} n.m.r. data for compounds (7)—(10) are similar to those of (1). There are two signals in each spectrum corresponding to the PPt and PW groups present in these complexes. The resonances due to the tungsten-ligated phosphorus nuclei show both ^{183}W and ^{195}Pt couplings.

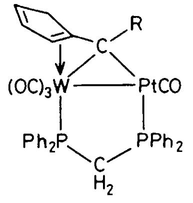
In the ^1H spectrum of (8) a resonance at δ 9.02 p.p.m. [*J*(PH) 7 and 4 Hz] is characteristic for the μ-C*H*R proton. The stability of (8), and its formation in good yield (*ca.* 70%), contrasts with the fragile nature of the species [$(OC)_5$W(μ-CPh_2)Pt$(PMe_3)_2$] which could only be studied in solution and identified by its ^{31}P-{^1H} n.m.r. spectrum.[5] The effect of the dppm ligand in stabilising the bridging CRR′ groups is also apparent in the isolation of (7).

Treatment of a thf solution of (5) with bis(cyclopentadienyl)-magnesium at room temperature afforded a mixture of two products, (11) and (12). However, the former species could not be isolated, since in solution it was converted into (12). The ^{31}P-{^1H} n.m.r. spectrum of compound (11) (Table 3) was similar to those of (7)—(10), and it is, therefore, assigned the structure shown with the bridging μ-C(C_5H_5)R group. Complex (12), which forms in high yield (*ca.* 90%), could be characterised by microanalysis, and by data from the n.m.r. spectra (Tables 2 and 3).

Analysis of the latter supports the proposed structure with

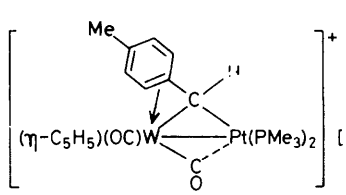


R'
(7) Me
(8) H
(9) C≡CBu^t
(10) SC$_6$H$_4$Me-4
(11) C$_5$H$_5$



(12)

R = C$_6$H$_4$Me-4



(13)

the C$_5$H$_5$ ring η^2-bonded to the tungsten. The ^{13}C-{^{1}H} n.m.r. spectrum of (12) reveals four resonances (relative intensity 1 : 1 : 1 : 1) for CO ligands, as expected, and contrasts with the five signals for these groups seen in the spectra of the pentacarbonyl derivatives (1) or (8). Although the species (7) and (9) show only four CO peaks, one in each spectrum is twice the intensity of the others, and thus corresponds to two ligands. The μ-CPtW group in (12) reveals itself by a resonance at δ 183.2 p.p.m., coupled to non-equivalent phosphine nuclei and with ^{195}Pt satellite peaks [J(PtC) 940 Hz]. The CH$_2$ group of the C$_5$H$_5$ ring gives rise to a signal at δ 44.2 p.p.m., which is a triplet in the non-decoupled spectrum. In the ^{1}H spectrum of (12) the C$_5$H$_5$ group gives five resonances, as expected for the asymmetric structure. The bridge system in compound (12) is thus similar to that found in (13), and established by an X-ray diffraction study.[17]

Experimental

The techniques used have been previously described.[4,7] Light petroleum refers to that fraction of b.p. 40—60 °C. A Nicolet MX-1 FT i.r. spectrometer was used to record i.r. spectra (Table 1). The n.m.r. measurements (Tables 2 and 3) were made with JEOL FX-90Q and FX 200 spectrometers. Analytical data and yields for the new compounds are given in Table 1. Alumina used in chromatography was BDH aluminium oxide (Brockman Activity II).

Reaction of [PtW{μ-C(OMe)R}(CO)$_5$(cod)] *with dppm*.—A toluene (80 cm^3) solution of [PtW{μ-C(OMe)R}(CO)$_5$(cod)] (1.95 g, 2.56 mmol) was treated with dppm (1.00 g, 2.58 mmol) in the same solvent (50 cm^3) and the mixture was stirred (18 h). Alumina (*ca.* 5 g) was added, and all volatile material removed *in vacuo*. The residue of products adsorbed on alumina was transferred to the top of an alumina chromatography column (30 × 4 cm) charged with light petroleum. The column was then gradient eluted with CH$_2$Cl$_2$–light petroleum (1 : 3, increasing to 2.5 : 1). The first band eluted from the column afforded, after removal of solvent *in vacuo*, red microcrystals of the known[10] species [Pt$_3${μ-C(OMe)R}$_3$(CO)$_3$] (0.12 g). The second eluted band yielded orange *microcrystals* of [PtW{μ-C(OMe)C$_6$H$_4$Me-4}(μ-dppm)(CO)$_5$] (1) (1.70 g). The third fraction from chromatography was an unidentified red oil, previously observed to form from [PtW{μ-C(OMe)C$_6$H$_4$Me-4}(CO)$_5$(cod)] and carbon monoxide. The final product was identified as orange *microcrystals* of [PtW{μ-C(OMe)C$_6$H$_4$Me-4}(μ-dppm)(CO)$_4$(dppm)] (2) (0.28 g).

Formation of the Salt (5).—A rapidly stirred diethyl ether (40 cm^3) solution of compound (1) (0.52 g, 0.50 mmol) was treated dropwise with HBF$_4$·OEt$_2$. The orange-brown precipitate was allowed to settle, the mother-liquor was decanted, and the precipitate washed with diethyl ether (4 × 20 cm^3). This treatment afforded, after drying *in vacuo*, orange-brown *microcrystals* of [PtW(μ-CC$_6$H$_4$Me-4)(μ-dppm)(CO)$_5$][BF$_4$] (5) (0.33 g).

Synthesis of the Complex [PtWBr(μ-CC$_6$H$_4$Me-4)(μ-dppm)(CO)$_4$].—A vigorously stirred diethyl ether (50 cm^3) solution of compound (1) (0.52 g, 0.50 mmol) was treated with a 0.21 mol dm^{-3} solution (1 cm^3) of BBr$_3$ in light petroleum. After stirring (10 min), the precipitate was allowed to settle. The mother-liquor was decanted, and the residue washed with portions of diethyl ether (100 cm^3). The mother-liquor and washings were filtered through an alumina pad. Volatile material was removed *in vacuo* and the residue dissolved in dichloromethane–light petroleum (1 : 1). The solution was then chromatographed on an alumina column (20 × 2 cm) initially using CH$_2$Cl$_2$–light petroleum (1 : 1), increasing to 100% CH$_2$Cl$_2$. The first band to be eluted afforded, after removal of solvent, yellow *microcrystals* of [PtWBr(μ-CC$_6$H$_4$Me-4)(μ-dppm)(CO)$_4$] (6) (0.18 g, 35%).

Alternatively, a thf (20 cm^3) solution of compound (5) (0.20 g, 0.18 mmol) was treated with excess of NEt$_4$Br and stirred for 2 h. Solvent was removed *in vacuo*, and the residue applied to the top of an alumina column (10 × 1 cm) charged with light petroleum. Elution with CH$_2$Cl$_2$–light petroleum (2 : 3) increasing to 100% CH$_2$Cl$_2$ gave compound (6) (0.12 g, 60%).

Reactions of the Salt (5).—(*a*) The syntheses of the complexes (7)—(10) were carried out similarly; that for (8) is described in detail.

A thf (10 cm^3) solution of compound (5) (0.25 g, 0.25 mmol) was treated with one equivalent of K[BH(CHMeEt)$_3$] (as a 1 mol dm^{-3} solution in thf). After stirring for 2 h, solvent was removed *in vacuo*. The residue was dissolved in CH$_2$Cl$_2$, filtered through an alumina pad (3 × 1 cm), and dried *in vacuo*. The material was redissolved in CH$_2$Cl$_2$–light petroleum (1 : 4, 3 cm^3) and chromatographed on an alumina column (20 × 2 cm) charged with light petroleum. Gradient elution with CH$_2$Cl$_2$–light petroleum (1 : 4, increasing to 3 : 1) gave, after evaporation of solvent, yellow *microcrystals* of [PtW{μ-C(H)C$_6$H$_4$Me-4}(μ-dppm)(CO)$_5$] (8) (0.17 g).

(*b*) A thf (10 cm^3) solution of compound (5) (0.25 g, 0.25 mmol) was treated with one equivalent of a solution of [Mg(C$_5$H$_5$)$_2$] (1 mol dm^{-3} in thf) and the reactants stirred for 2 h. The mixture was filtered through an alumina pad (5 × 1 cm). At this stage, i.r. and ^{1}H and ^{31}P-{^{1}H} n.m.r. studies on the solution revealed the presence of both compounds (11) [$\nu_{max.}$(CO) 2 025w, 2 007s, 1 973m, 1 935s, and 1 901s cm^{-1} (CH$_2$Cl$_2$)] and (12) (Table 1). Conversion into (12) was completed after the solution had been stirred for 48 h. Solvent was then removed *in vacuo*, and the residue applied to the top of an alumina column (15 × 1 cm). Gradient elution with CH$_2$Cl$_2$–light petroleum (1 : 4, increasing to 3 : 1) gave, after removal of solvent, orange *microcrystals* of [PtW{μ-C(C$_5$H$_5$)C$_6$H$_4$Me-4}(μ-dppm)(CO)$_4$] (12) (0.24 g).

Table 5. Atomic positional parameters (fractional co-ordinates), with estimated standard deviations in parentheses, for complex (1)

Atom	x	y	z	Atom	x	y	z
C(1)	0.261(3)	0.196 1(8)	0.251(2)	C(222)	−0.185 4(15)	0.166 4(5)	−0.169 0(13)
C(2)	0.220(2)	0.200 8(12)	0.469(2)	C(223)	−0.288 5(15)	0.149 4(5)	−0.243 8(13)
C(3)	0.163(3)	0.106 6(11)	0.455(2)	C(224)	−0.322 6(15)	0.103 3(5)	−0.227 9(13)
C(4)	0.376(3)	0.136 1(12)	0.448(3)	C(225)	−0.253 6(15)	0.074 1(5)	−0.137 3(13)
C(5)	0.125(3)	0.058 4(13)	0.012(3)	C(226)	−0.150 5(15)	0.091 2(5)	−0.062 5(13)
C(6)	0.262(3)	0.074 1(10)	0.269(3)	C(221)	−0.116 4(15)	0.137 3(5)	−0.078 3(13)
C(7)	−0.011(2)	0.204 3(8)	0.110(2)	C(62)	0.146 6(13)	0.005 4(7)	0.294 2(13)
C(06)	0.405(3)	0.105 8(11)	0.209(3)	C(63)	0.131 8(13)	−0.037 4(7)	0.346 2(13)
C(112)	−0.088 6(12)	0.089 6(6)	0.246 0(14)	C(64)	0.219 6(13)	−0.057 2(7)	0.440 0(13)
C(113)	−0.180 5(12)	0.059 4(6)	0.217 5(14)	C(65)	0.322 3(13)	−0.034 2(7)	0.481 8(13)
C(114)	−0.286 9(12)	0.078 1(6)	0.161 9(14)	C(66)	0.337 2(13)	0.008 5(7)	0.429 8(13)
C(115)	−0.301 4(12)	0.126 9(6)	0.134 9(14)	C(61)	0.249 3(13)	0.028 3(7)	0.336 0(13)
C(116)	−0.209 5(12)	0.157 1(6)	0.163 4(14)	C(67)	0.202(4)	−0.105 0(11)	0.496(3)
C(111)	−0.103 1(12)	0.138 5(6)	0.219 0(14)	Cl(1)	0.522 4(14)	−0.019 6(7)	0.212(2)
C(122)	−0.010(2)	0.273 5(8)	0.313(2)	Cl(2)	0.682(2)	−0.068 9(7)	0.153(3)
C(123)	−0.036(2)	0.309 3(8)	0.379(2)	C(1A)	0.624(5)	−0.052(2)	0.261(5)
C(124)	−0.077(2)	0.296 8(8)	0.466(2)	O(1)	0.280(2)	0.223 5(6)	0.196 1(2)
C(125)	−0.093(2)	0.248 5(8)	0.486(2)	O(2)	0.241(2)	0.232 0(8)	0.538(2)
C(126)	−0.067(2)	0.212 8(8)	0.420(2)	O(3)	0.137(2)	0.082 0(7)	0.522(2)
C(121)	−0.026(2)	0.225 3(8)	0.333(2)	O(4)	0.460(2)	0.128 0(10)	0.512(3)
C(212)	0.070 1(15)	0.244 6(6)	−0.084 6(15)	O(5)	0.113(3)	0.027 3(8)	−0.058(2)
C(213)	0.104 0(15)	0.267 7(6)	−0.167 1(15)	O(6)	0.373 5(14)	0.069 3(7)	0.272 7(15)
C(214)	0.134 2(15)	0.240 9(6)	−0.247 0(15)	P(1)	0.012 6(6)	0.177 5(3)	0.254 2(5)
C(215)	0.130 7(15)	0.190 8(6)	−0.244 5(15)	P(2)	0.018 4(6)	0.159 4(3)	0.017 7(5)
C(216)	0.096 8(15)	0.167 6(6)	−0.162 0(15)	Pt	0.143 78(8)	0.101 84(4)	0.130 69(8)
C(211)	0.066 5(15)	0.194 5(6)	−0.082 1(15)	W	0.211 26(8)	0.148 21(4)	0.351 98(8)

Crystal Structure Determination of [PtW{μ-C(OMe)-C_6H_4Me-4}(μ-dppm)$(CO)_5$] (1).—Crystals of (1) grow as mauve prisms. Diffracted intensities were recorded at room temperature in the range $2.9 \leqslant 2\theta \leqslant 52°$ for a crystal of dimensions 0.25 × 0.35 × 0.25 mm mounted in a Lindemann capillary tube. Of the 7 678 independent reflections measured on a Nicolet $P2_1$ diffractometer, 2 750 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. Check reflections (1 4 1 and $\bar{1}\ \bar{7}\ \bar{2}$) were remeasured every 50 reflections throughout the 215 h of data collection and indicated crystal decay of *ca.* 43%. Corrections were applied for Lorentz, polarisation, crystal-decay, and *X*-ray absorption effects, the last by a semiempirical method based on azimuthal scan data.[18] All computations were carried out in the laboratory with an Eclipse (Data General) computer and the SHELXTL system of programs.[18]

Crystal data. $C_{39}H_{32}O_6P_2PtW\cdot0.5CH_2Cl_2$, $M = 1\,080.0$, Monoclinic, $a = 12.998(15)$, $b = 27.832(19)$, $c = 12.176(7)$ Å, $\beta = 111.74(6)°$, $U = 4\,092(6)$ Å^3, $Z = 4$, $D_c = 1.75$ g cm^{-3}, $F(000) = 2\,064$, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 61.7 cm^{-1}.

The structure was solved by heavy-atom methods and was refined using blocked-cascade least squares. Because the quality of the intensity data was not high (only 2 750 'observed' reflections from a total of 7 678 measured), attempts to introduce anisotropic thermal parameters for all non-hydrogen atoms gave difficulty. In the final refinement atom C(06) was restrained to isotropic motion, and the ring hydrogen atoms were incorporated at calculated riding positions (C−H 0.96 Å).[19] The methyl groups were constrained to tetrahedral geometry and the six-membered rings to regular hexagonal geometry. Chemically equivalent hydrogen atoms were given a common isotropic thermal parameter, which was allowed to refine. Electron-density difference syntheses revealed the presence of half a molecule of CH_2Cl_2 per asymmetric unit, and this was incorporated into the model with the carbon atom C(1A) being refined isotropically. Individual weights were assigned according to the scheme $w = [\sigma^2(F_o) + 0.0008|F_o|^2]^{-1}$ and refinement converged at R 0.056 (R' 0.052). The final electron-density difference synthesis showed no features >1.4 or < -1.2 e Å^{-3}, the largest peaks lying close to the metal atoms. Scattering factors including corrections for the effects of anomalous dispersion for all atoms were taken from ref. 20. Atomic positional parameters are given in Table 5.

Acknowledgements

We thank the S.E.R.C. for research studentships (to K. A. M. and I. M.).

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Received 7th February 1983; *Paper* 3/188