Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 39.[1] Interconversion of Ethylidyne, Ethylidene, Vinyl, and Ethylene Groups at a Platinum–Tungsten Centre; *X*-Ray Crystal Structure of $[PtW(\mu\text{-}CO)_2(PEt_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$ *

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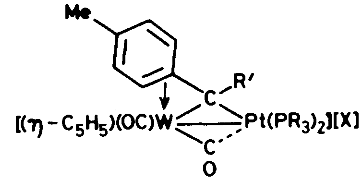
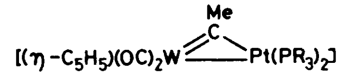
Treatment of the bridged ethylidyne complexes $[PtW(\mu\text{-}CMe)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ ($PR_3 = PMe_3$, PEt_3, PMe_2Ph, or $PMePh_2$) with the reagent $HBF_4{\cdot}Et_2O$ affords the salts $[PtW(\mu\text{-}CO)_2(PR_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$. The product with $PR_3 = PEt_3$ has been structurally characterised by an *X*-ray diffraction study. The tungsten atom is ligated by a cyclopentadienyl group, the ethylene molecule, and two carbonyl ligands. The latter semi-bridge an unusually short Pt–W bond [2.602(1) Å]. The two PEt_3 groups are co-ordinated to the platinum in a *cis* arrangement with the PtP_2 plane being at 90° to that defined by the two carbons of the μ-CO groups and the W atom. In contrast with protonation using $HBF_4{\cdot}Et_2O$, addition of CF_3CO_2H to $[PtW(\mu\text{-}CMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ affords the ethylidene-bridged complex $[PtW(O_2CCF_3)(\mu\text{-}CHMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$, while methylation gives the vinyl- and hydrido-bridged compound $[PtW(\mu\text{-}H)\{\mu\text{-}C(Me){=}CH_2\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][CF_3SO_3]$. Treatment of $[PtW(\mu\text{-}CO)_2(PMe_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$ with $NaBH_4$ yields $[PtW(\mu\text{-}H)(\mu\text{-}CHMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$, while PMe_3 deprotonates the salt to give $[PtW(\mu\text{-}CH{=}CH_2)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$. The ^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$, and $^{195}Pt\{^1H\}$ n.m.r. spectra of the new complexes are reported and discussed.

We have previously reported[2] that the salts (**1**) are formed by protonating or methylating the tolylmethylidyne-bridged complexes $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$. In these products the tolylmethylidene group adopts an η^3-bonding mode to tungsten, while being linked to platinum by a σ bond. If the two carbon atoms of the aryl ring were not η^2-co-ordinated, the tungsten atom would have a 16- rather than an 18-electron shell. Tertiary phosphine ligands add to the tungsten centres in these salts, affording complexes $[PtW\{\mu\text{-}C(C_6H_4Me\text{-}4)R'\}(CO)_2(PR_3)_3(\eta\text{-}C_5H_5)]^+$ ($R' = H$ or Me)[3] in which the C_6H_4Me-4 group is no longer bonded to a metal centre. These reactions further reflect the tendency of tungsten to become electronically saturated, and pose an interesting problem concerning analogous chemistry of ethylidyne-bridged platinum–tungsten compounds such as (**2a**). Protonation or methylation of the latter with the reagents $HBF_4{\cdot}Et_2O$ or CF_3SO_3Me, respectively, should yield the salts (**3**). However, since in these species the tungsten atom has a 16-electron shell it was anticipated that the bridging ethylidene groups would be activated in some manner, so as to produce new complexes in which the tungsten is electronically saturated. It was with these ideas in mind that the studies herein reported were carried out.[4]

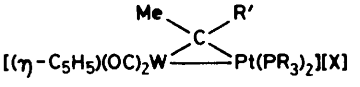


	PR_3	R′	X
(**1a**)	PMe_3	H	BF_4
(**1b**)	PMe_2Ph	H	BF_4
(**1c**)	$PMePh_2$	H	BF_4
(**1d**)	PMe_3	Me	SO_3CF_3



$[(\eta\text{-}C_5H_5)(OC)_2W(\mu\text{-}CMe)Pt(PR_3)_2]$

	PR_3
(**2a**)	PMe_3
(**2b**)	PEt_3
(**2c**)	PMe_2Ph
(**2d**)	$PMePh_2$

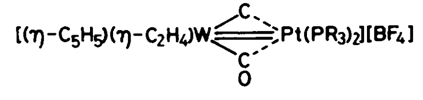


$[(\eta\text{-}C_5H_5)(OC)_2W\{\mu\text{-}C(Me)R'\}Pt(PR_3)_2][X]$

	R′	X
(**3a**)	H	BF_4
(**3b**)	Me	SO_3CF_3

Results and Discussion

The new compounds (**2**) were prepared in high yield by adding $[W({\equiv}CMe)(CO)_2(\eta\text{-}C_5H_5)]$ to light petroleum solutions of the complexes $[Pt(C_2H_4)(PR_3)_2]$ ($PR_3 = PMe_3$, PEt_3, PMe_2Ph, or $PMePh_2$). Data for these species are given in Tables 1—3. The spectroscopic properties are in accord with the structures proposed and are similar to those previously reported for



$[(\eta\text{-}C_5H_5)(\eta\text{-}C_2H_4)W(\mu\text{-}CO)_2Pt(PR_3)_2][BF_4]$

	PR_3
(**4a**)	PMe_3
(**4b**)	PEt_3
(**4c**)	PMe_2Ph
(**4d**)	$PMePh_2$

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* Di-μ-carbonyl-2-(η-cyclopentadienyl)-2-(η-ethylene)-1,1-bis(triethylphosphine)platinumtungsten (*Pt–W*).

Supplementary data available (No. SUP 56355, 5 pp.): full bond distances and angles, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

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

Complex	M.p.[b] (θ_c/°C)	Colour	Yield (%)	ν(CO)[c]/cm^{-1}	Analysis (%)	
					C	H
(2a) $[PtW(\mu\text{-}CMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$	177	Orange	95	1 887vs, 1 797s	26.7 (26.5)	4.0 (3.8)
(2b) $[PtW(\mu\text{-}CMe)(CO)_2(PEt_3)_2(\eta\text{-}C_5H_5)]$	120	Red	97	1 885vs, 1 801s	32.6 (33.0)	5.0 (4.9)
(2c) $[PtW(\mu\text{-}CMe)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$	138	Orange	87	1 886vs, 1 798s	37.0 (37.4)	3.9 (3.7)
(2d) $[PtW(\mu\text{-}CMe)(CO)_2(PMePh_2)_2(\eta\text{-}C_5H_5)]$	160	Pale orange	79	1 891vs, 1 803s	45.2 (45.3)	3.7 (3.7)
(4a) $[PtW(\mu\text{-}CO)_2(PMe_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$	158	Dark red	93	1 831vs	23.8 (23.5)	3.7 (3.5)
(4b) $[PtW(\mu\text{-}CO)_2(PEt_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$	104	Pale orange	42	1 830vs	29.7 (29.6)	4.8 (4.6)
(4c) $[PtW(\mu\text{-}CO)_2(PMe_2Ph)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$	78	Pale orange	91	1 831vs	33.4 (33.7)	3.7 (3.4)
(4d) $[PtW(\mu\text{-}CO)_2(PMePh_2)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$	78	Orange	97	1 831vs	40.5 (41.3)	3.7 (3.4)
(5) $[PtW(O_2CCF_3)(\mu\text{-}CHMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$	94	Yellow	76	1 956s, 1 783m[d]	26.1 (25.7)	3.5 (3.5)
(6) $[PtW(\mu\text{-}H)\{\mu\text{-}C(Me){=}CH_2\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]\text{-}[CF_3SO_3]$	66	Pale brown	77	1 992vs, 1 925s	24.3 (24.2)	3.7 (3.4)
(7) $[PtW(\mu\text{-}H)(\mu\text{-}CHMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$	110	Yellow	88	1 891vs, 1 794s	25.7 (26.4)	4.3 (4.1)
(8a) $[PtW(\mu\text{-}CH{=}CH_2)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$	180	Yellow	30	1 864vs, 1 737w	26.3 (26.5)	4.1 (3.8)
(8b) $[PtW\{\mu\text{-}C(Me){=}CH_2\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$	120	Yellow	5	1 886vs, 1 735w	28.1 (27.7)	4.2 (4.0)

[a] Calculated values are given in parentheses. [b] With decomposition. [c] In CH_2Cl_2. [d] $\nu_{max.}(CF_3CO_2)$ 1 691m cm^{-1}.

related platinum–tungsten complexes with bridging CC_6H_4Me-4 groups.[5] In particular, the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the compounds (**2**) all show (Table 2) characteristic resonances for μ-*C*Me ligands at *ca.* 345 p.p.m., appearing as doublets [$J(P_{trans}C)$ 56—59 Hz], with strong ^{195}Pt coupling [J(PtC) *ca.* 735 Hz]. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra (Table 3) are also characteristic, with each complex showing two doublet signals, corresponding to the presence of *cis*-$Pt(PR_3)_2$ groups, but with non-equivalent PR_3 ligands. Both ^{31}P nuclei show ^{195}Pt coupling. In each spectrum the resonance with the higher J(PtP) value may be ascribed to the *transoid*-$WPt(PR_3)$ arrangement. Two CO stretching bands are observed in the i.r. spectra of the complexes (Table 1), the absorption near 1 800 cm^{-1} being due to a semi-bridging carbonyl ligand.[5]

Treatment of (**2a**) with $HBF_4{\cdot}Et_2O$ afforded a microcrystalline red salt. The spectroscopic properties of the latter did not accord with it being the complex (**3a**), the species expected to be formed initially on protonation, based on earlier work.[2] In the ^1H n.m.r. spectrum of the red salt there were no resonances which could be attributed to a μ-CHMe group. Moreover, in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum there was no signal in the region 100—200 p.p.m. characteristic of an alkylidene group *C*HMe bridging two metal centres.[6] A further spectroscopic property, inexplicable if the product had structure (**3a**), was the observation of a single CO stretching absorption (1 831 cm^{-1}) in the i.r. spectrum, rather than two such bands. The salt (**1a**)[2] has $\nu_{max.}$(CO) at 1 957 and 1 785 cm^{-1}. Since the red salt could not be structurally characterised from the spectroscopic data, attempts were made to undertake an *X*-ray diffraction study. Unfortunately, suitable single crystals could not be obtained. Hence protonation studies on the compounds (**2b**)—(**2d**) were carried out in order to obtain analogous species, and in the hope of obtaining suitable single crystals of one or other of the products. Fortunately, the product from (**2b**) formed good quality crystals.

The results of the *X*-ray diffraction study are summarised in Table 4, and the cation is shown in the Figure. Interestingly, although as expected, the salt (**4b**) is a dimetal compound, the tungsten atom is ligated by an ethylene molecule [C(1)–C(2) 1.43(2) Å]. The metal–metal bond [2.602(1) Å] is significantly shorter (*ca.* 0.2 Å) than those found in several other platinum–tungsten species.[3] For example, the Pt–W separation in (**1a**) is 2.795(1) Å,[2] and in the bridged alkylidene complex $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_4(PMe_3)_3]$ it is 2.825(1) Å.[7] The Pt–W bond in (**4b**) is strongly semi-bridged by two CO ligands [W–C(3)–O(3) 167(1), W–C(4)–O(4) 162(1)°] with the angle between the two planes defined by WC(3)C(4) and P(1)PtP(2) being 90°. Hence the observation of only a single CO stretching band in the i.r. spectra of the salts (**4**) is understandable.

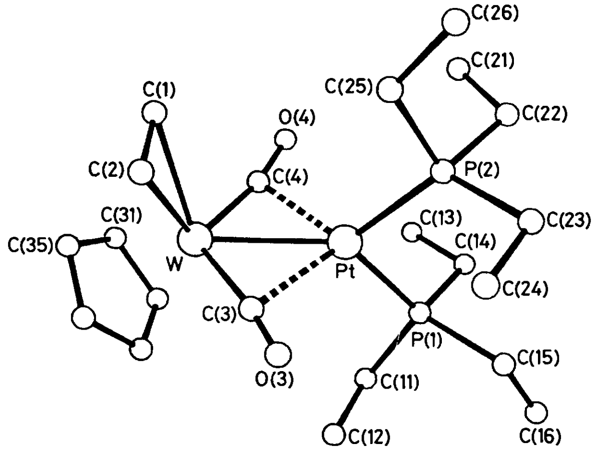


Figure. Molecular structure of the cation of $[PtW(\mu\text{-}CO)_2(PEt_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$ (**4b**)

In addition to being bonded to the ethylene group, and to the two carbonyl ligands, the tungsten atom is as expected ligated by the η-C_5H_5 ring. The presence of the *cis*-$Pt(PEt_3)_2$ group is also unremarkable. However, the valence electron count at the two metal centres in the cation is of interest. A single bond between the tungsten and the platinum would imply 17- and 15-electron configurations at these centres, respectively. However, the presence of a W=Pt bond, as suggested by the short internuclear separation mentioned above, would give the more normal situation of 18- and 16-valence-electron shells, respectively, for these two metals.

Having established the nature of (**4b**), it is possible to interpret the n.m.r. data for this complex, as well as the data for the salts (**4a**), (**4c**), and (**4d**). These last three species must have structures like that of (**4b**) since their various spectroscopic properties (Tables 1—3) are similar. In the ^1H n.m.r. spectrum of (**4a**) characteristic peaks for the C_2H_4 ligand are observed at δ 0.96 and 1.80 p.p.m., with appropriate ^1H and ^{31}P couplings.

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

Complex	^{1}H (δ)[b]	^{13}C (δ)[c]
(2a)	1.62 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 20], 1.63 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 36], 3.20 [d of d, 3 H, μ-CMe, *J*(PH) 11 and 4, *J*(PtH) 5], 5.45 [s, 5 H, C_5H_5, *J*(PtH) 5]	345.3 [d, μ-C, *J*(PC) 59, *J*(PtC) 735, *J*(WC) 142], 222.4 [CO, *J*(PtC) 20, *J*(WC) 179], 90.7 (C_5H_5), 47.8 [μ-C*Me*, *J*(PtC) 66], 20.5 [d, MeP, *J*(PC) 30, *J*(PtC) 53], 18.0 [d, MeP, *J*(PC) 25, *J*(PtC) 24]
(2b)	1.01 [d of t, 9 H, *Me*CH$_2$P, *J*(HH) 8, *J*(PH) 16], 1.05 [d of t, 9 H, *Me*CH$_2$P, *J*(HH) 8, *J*(PH) 16], 1.88 [d of q, 6 H, Me*CH$_2$*P, *J*(HH) 8, *J*(PH) 8], 2.00 [d of q, 6 H, Me*CH$_2$*P, *J*(HH) 8, *J*(PH) 8], 3.15 [d of d, 3 H, μ-CMe, *J*(PH) 9 and 4, *J*(PtH) 6], 5.45 [s, 5 H, C_5H_5, *J*(PtH) 4]	345.9 [d, μ-C, *J*(PC) 59, *J*(PtC) 745], 222.2 [CO, *J*(PtC) 22, *J*(WC) 181], 90.9 (C_5H_5), 47.3 [μ-C*Me*, *J*(PtC) 66], 18.8 [d, C^1(Et), *J*(PC) 25, *J*(PtC) 44], 18.0 [d, C^1(Et), *J*(PC) 22, *J*(PtC) 20], 8.7 [C^2(Et), *J*(PtC) 25], 8.5 [C^2(Et), *J*(PtC) 15]
(2c)	1.45 [d, 6 H, MeP, *J*(PH) 11, *J*(PtH) 36], 1.90 [d, 6 H, MeP, *J*(PH) 8, *J*(PtH) 20], 2.80 [d of d, 3 H, μ-CMe, *J*(PH) 10 and 5, *J*(PtH) 4], 5.49 [s, 5 H, C_5H_5, *J*(PtH) 5], 7.28—7.60 (m, 10 H, Ph)	343.1 [d, μ-C, *J*(PC) 59, *J*(PtC) 729], 221.4 [CO, *J*(PtC) 25, *J*(WC) 179], 141.1 [d, C^1(Ph), *J*(PC) 37, *J*(PtC) 15], 138.6 [d, C^1(Ph), *J*(PC) 44, *J*(PtC) 44], 131.2 [C^2(Ph), *J*(PtC) 25], 131.0 [d, C^2(Ph), *J*(PC) 7, *J*(PtC) 25], 129.6—128.2 (Ph), 90.8 (C_5H_5), 46.5 [μ-C*Me*, *J*(PtC) 61], 18.4 [d, MeP, *J*(PC) 27, *J*(PtC) 44], 16.1 [d, MeP, *J*(PC) 25, *J*(PtC) 20]
(2d)	1.54 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 34], 2.31 [d, 3 H, MeP, *J*(PH) 7, *J*(PtH) 22], 2.55 [d of d, 3 H, μ-CMe, *J*(PH) 10 and 5, *J*(PtH) 5], 5.46 [s, 5 H, C_5H_5, *J*(PtH) 4], 7.20—7.60 (m, 20 H, Ph)	344.1 [d, μ-C, *J*(PC) 56, *J*(PtC) 730], 233.7 [CO, *J*(WC) 181], 137.4 [d, C^1(Ph), *J*(PC) 39, *J*(PtC) 19], 136.6 [d, C^1(Ph), *J*(PC) 42, *J*(PtC) 42], 133.2—128.3 (Ph), 91.0 (C_5H_5), 46.2 [d, μ-C*Me*, *J*(PC) 5, *J*(PtC) 54], 18.1 [d, MeP, *J*(PC) 29, *J*(PtC) 30], 16.1 [d, MeP, *J*(PC) 25, *J*(PtC) 25]
(4a)	0.96 [d of d of d of d, 2 H, C_2H_4, *J*(HH) 11 and 4, *J*(PH) 6 and 6], 1.42 [d of d, 9 H, MeP, *J*(PH) 12 and 1, *J*(PtH) 29], 1.70 [d of d, 9 H, MeP, *J*(PH) 12 and 1, *J*(PtH) 31], 1.80 [d of d, 2 H, C_2H_4, *J*(HH) 11 and 4], 5.27 (s, 5 H, C_5H_5)	235.3 [CO, *J*(PtC) 281, *J*(WC) 175], 90.7 (C_5H_5), 22.2 (C_2H_4), 19.8 [d, MeP, *J*(PC) 34, *J*(PtC) 31], 16.9 [d, MeP, *J*(PC) 34, *J*(PtC) 31]
(4b)[d]	1.03 [d of t, 9 H, *Me*CH$_2$P, *J*(HH) 8, *J*(PH) 18], 1.16 [d, of t, 9 H, *Me*CH$_2$P, *J*(HH) 8, *J*(PH) 18], 1.56 [d of q, 6 H, Me*CH$_2$*P, *J*(HH) 8, *J*(PH) 10], 1.81 [d of q, 6 H, Me*CH$_2$*P, *J*(HH) 8, *J*(PH) 10], 5.27 (s, C_5H_5)	237.5 [CO, *J*(PtC) 279, *J*(WC) 162], 91.0 (C_5H_5), 22.8 (C_2H_4), 20.8 [d, C^1(Et), *J*(PC) 29, *J*(PtC) 29], 18.2 [d, C^1(Et), *J*(PC) 29, *J*(PtC) 29], 8.1 [C^2(Et)], 7.6 [C^2(Et)]
(4c)[d]	0.66 [d of d of d of d, 2 H, C_2H_4, *J*(HH) 13 and 5, *J*(PH) 5 and 5], 1.45 [d, 6 H, MeP, *J*(PH) 12, *J*(PtH) 28], 1.72 (m, 2 H, C_2H_4), 1.77 [d, 6 H, MeP, *J*(PH) 12, *J*(PtH) 31], 5.16 (s, 5 H, C_5H_5), 7.19—7.52 (m, 10 H, Ph)	235.7 [d, CO, *J*(PC) 6, *J*(PtC) 277, *J*(WC) 163], 131.8—129.5 (Ph), 90.9 (C_5H_5), 23.3 (C_2H_4), 18.1 [d, MeP, *J*(PC) 32, *J*(PtC) 34], 15.2 [d, MeP, *J*(PC) 32, *J*(PtC) 29]
(4d)	0.23 (m, 2 H, C_2H_4), 1.60 (m, 2 H, C_2H_4), 1.83 [d, 3 H, MeP, *J*(PH) 8], 1.96 [d, 3 H, MeP, *J*(PH) 11], 4.92 (s, 5 H, C_5H_5), 7.18—7.50 (m, 20 H, Ph)	235.9 [CO, *J*(PtC) 284, *J*(WC) 162], 131.4—128.5 (Ph), 89.9 (C_5H_5), 23.8 (C_2H_4), 15.3—12.9 (MeP)
(5)[e]	1.52 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 35], 1.58 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 22], 2.29 [d of d of d, 3 H, μ-CMe, *J*(HH) 8, *J*(PH) 9 and 5, *J*(PtH) 6], 4.75 [d of d of q, 1 H, μ-CH, *J*(HH) 8, *J*(PH) 5 and 4, *J*(PtH) 24], 5.27 [d, 5 H, C_5H_5, *J*(PH) 1, *J*(PtH) 7]	239.1 [d, CO, *J*(PC) 12, *J*(PtC) 89], 225.3 [d, CO, *J*(PC) 9, *J*(PtC) 44], 160.1 [q, *C*O$_2$CF$_3$, *J*(FC) 36], 114.1 [q, CF$_3$, *J*(FC) 290], 111.9 [d, μ-C, *J*(PC) 55, *J*(PtC) 494, *J*(WC) 53], 91.5 (C_5H_5), 32.1 (μ-CH*Me*), 18.2 [d, MeP, *J*(PC) 32, *J*(PtC) 49], 17.3 [d, MeP, *J*(PC) 30, *J*(PtC) 25]
(6)[f]	−13.2 [(ABX), 1 H, μ-H, *J*(PH) ± 69, *J*(P′H) ± 14, *J*(AB) 3, *J*(PtH) 521], 1.66 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 37], 1.77 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 40], 3.29 (br m, 3 H, CMe), 4.17 (br m, 1 H, CH$_2$), 4.20 [d, 1 H, CH$_2$, *J*(PH) 14, *J*(PtH) 96], 5.63 (s, 5 H, C_5H_5)	224.0 [CO, *J*(WC) 157], 219.8 [CO, *J*(WC) 167], 175.8 [d, μ-*C*Me, *J*(PC) 81, *J*(PtC) 534], 120.9 [q, CF$_3$, *J*(FC) 322], 87.5 (C_5H_5), 40.1 (μ-CH$_2$), 34.9 [μ-C*Me*, *J*(PtC) 37], 18.7 [d of d, MeP, *J*(PC) 17 and 17, *J*(PtC) 25], 17.1 [d of d, MeP, *J*(PC) 29 and 12, *J*(PtC) 26]
(7)[g]	(**a**)[h] −7.77 [d of d, 1 H, μ-H, *J*(PH) 82 and 16, *J*(PtH) 505, *J*(WH) 53], 1.53—1.91 (m, 18 H, MeP), 2.21 [d of d, 3 H, μ-CMe, *J*(HH) 8, *J*(PH) 13], 5.17 (s, 5 H, C_5H_5), 6.11 [d of q, 1 H, μ-CH, *J*(HH) 8, *J*(PH) 4]	242.7 [CO, *J*(WC) 147], 234.1 [CO, *J*(WC) 184], 103.0 [d, μ-C, *J*(PC) 55, *J*(PtC) 471], 89.0 (C_5H_5), 34.5 (μ-C*Me*), 19.5 [d, MeP, *J*(PC) 25, *J*(PtC) 28], 17.6 [d, MeP, *J*(PC) 34, *J*(PtC) 49]
	(**b**)[h] −8.29 [d of d, 1 H, μ-H, *J*(PH) 80 and 18, *J*(PtH) 525, *J*(WH) 56], 1.53—1.91 (m, 18 H, MeP), 2.36 [d of d, 3 H, μ-CMe, *J*(HH) 8, *J*(PH) 14], 5.28 (s, 5 H, C_5H_5), 5.80 [d of q, 1 H, μ-CH, *J*(HH) 8, *J*(PH) 4]	238.4 (CO), 236.0 (CO), 114.0 [d, μ-C, *J*(PC) 58, *J*(PtC) 560], 89.0 (C_5H_5), 35.2 (μ-C*Me*), 20.1—16.8 (MeP)
(8a)	1.49 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 22], 1.66 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 34], 2.54 [d of d of d, 1 H, CH$_2$, *J*(HH) 9 and 1, *J*(PH) 8, *J*(PtH) 25], 3.25 [d of d of d of d, 1 H, CH$_2$, *J*(HH) 10 and 1, *J*(PH) 12 and 2, *J*(PtH) 110], 5.18 (s, 5 H, C_5H_5), 6.55 [d of d of d of d, 1 H, CH, *J*(HH) 10 and 9, *J*(PH) 7 and 3, *J*(PtH) 6]	235.0 [d of d, CO, *J*(PC) 7 and 6], 230.6 [CO, *J*(WC) 169], 129.4 [d, μ-CH, *J*(PC) 81, *J*(PtC) 581], 87.8 (C_5H_5), 37.2 (CH$_2$), 20.5 [d, MeP, *J*(PC) 31, *J*(PtC) 44], 17.7 [d, MeP, *J*(PC) 29, *J*(PtC) 26]
(8b)	1.50 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 34], 1.60 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 21], 2.41 [d, 1 H, CH$_2$, *J*(PH) 8, *J*(PtH) 12], 2.55 [d of d, 3 H, CMe, *J*(PH) 5 and 5, *J*(PtH) 35], 3.23 [d, 1 H, CH$_2$, *J*(PH) 11, *J*(PtH) 60], 5.17 (s, 5 H, C_5H_5)	233.3 [CO, *J*(WC) 144], 230.4 [CO, *J*(WC) 144], 147.8 [d, μ-C, *J*(PC) 83, *J*(PtC) 635, *J*(WC) 43], 89.4 (C_5H_5), 42.2 (CH$_2$), 35.2 [μ-C*Me*, *J*(PtC) 49], 19.2 [d, MeP, *J*(PC) 28, *J*(PtC) 138], 17.9 [d, MeP, *J*(PC) 28, *J*(PtC) 25]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at room temperature unless otherwise stated. [b] Measured in CD_2Cl_2. [c] Hydrogen-1 decoupled, chemical shifts to high frequency of $SiMe_4$, measured in CD_2Cl_2–CH_2Cl_2. [d] Signals for C_2H_4 ligand in ^{1}H spectrum obscured or partially obscured by those for Et (**4b**) or Me (**4c**) groups. [e] Carbon-13 spectrum measured at −50 °C. [f] Spectra measured at −50 °C. [g] Spectra measured at −30 °C. [h] Mixture of isomers (see text), with (**a**):(**b**) ≃ 3:1.

Table 3. Phosphorus-31 and platinum-195 n.m.r. data[a] for the platinum–tungsten complexes

Compound	^{31}P[b] (δ)	^{195}Pt[c] (δ)
(2a)	−13.2 [d, *J*(PP) 15, *J*(PtP) 4 104], −23.3 [d, *J*(PP) 15, *J*(PtP) 2 527]	391 [d of d, *J*(PPt) 4 104 and 2 527]
(2b)	23.9 [d, *J*(PP) 10, *J*(PtP) 4 083], 3.8 [d, *J*(PP) 10, *J*(PtP) 2 629]	350 [d of d, *J*(PPt) 4 083 and 2 629]
(2c)	2.1 [d, *J*(PP) 17, *J*(PtP) 4 225], −8.4 [d, *J*(PP) 17, *J*(PtP) 2 611]	325 [d of d, *J*(PPt) 4 225 and 2 611]
(2d)	16.3 [d, *J*(PP) 16, *J*(PtP) 4 174], 10.9 [d, *J*(PP) 16, *J*(PtP) 2 780]	276 [d of d, *J*(PPt) 4 174 and 2 780]
(4a)	−7.5 [d, *J*(PP) 42, *J*(PtP) 3 145, *J*(WP) 37], −17.0 [d, *J*(PP) 42, *J*(PtP) 2 993]	2 267 [d of d, *J*(PPt) 3 145 and 2 993]
(4b)	30.3 [d, *J*(PP) 39, *J*(PtP) 3 091, *J*(WP) 34], 18.4 [d, *J*(PP) 39, *J*(PtP) 2 935]	2 150 [d of d, *J*(PPt) 3 091 and 2 935]
(4c)	0.2 [d, *J*(PP) 41, *J*(PtP) 3 152, *J*(WP) 37], −6.4 [d, *J*(PP) 41, *J*(PtP) 2 976]	2 101 [d of d, *J*(PPt) 3 152 and 2 976, *J*(WPt) 287]
(4d)	10.1 [s, *J*(PP) 41, *J*(PtP) 3 223 and 2 981, *J*(WP) 86]	2 224 [d of d, *J*(PPt) 3 223 and 2 981, *J*(WPt) 273]
(5)[d]	−8.3 [s, *J*(PtP) 3 782, *J*(WP) 29], −12.2 [s, *J*(PtP) 2 527]	−115 [d of d, *J*(PPt) 3 782 and 2 527]
(6)[d]	−27.0 [s, *J*(PP) 22, *J*(PtP) 3 721 and 1 963]	−947 [d of d *J*(PPt) 3 721 and 1 963]
(7)[e,f]	(**a**) −20.2 [s, *J*(PtP) 4 040], −25.6 [s, *J*(PtP) 2 090]	−996 [d of d, *J*(PPt) 4 040 and 2 090]
	(**b**) −22.4 [d, *J*(PP) 7, *J*(PtP) 4 026], −26.4 [d, *J*(PP) 7, *J*(PtP) 2 075]	−1 024 [d of d, *J*(PPt) 4 026 and 2 075]
(8a)	−14.2 [d, *J*(PP) 5, *J*(PtP) 2 737, *J*(WP) 20], −21.9 [d, *J*(PP) 5, *J*(PtP) 3 489, *J*(WP) 20]	−386 [d of d, *J*(PPt) 3 489 and 2 737, *J*(WPt) 30]
(8b)	−16.7 [s, *J*(PtP) 2 586], −23.5 [s, *J*(PtP) 3 625, *J*(WP) 15]	−267 [d of d, *J*(PPt) 3 625 and 2 586]

[a] Hydrogen-1 decoupled, spectra measured in CD_2Cl_2 at room temperature, unless otherwise stated; chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Chemical shifts to high frequency of 85% H_3PO_4 (external) taken as positive. [c] Chemical shifts to high frequency of $\Xi(^{195}Pt) = 21.4$ MHz. [d] Measured at −50 °C. [e] Isomers (see text), with (**a**):(**b**) $\simeq$ 3:1. [f] Measured at −30 °C.

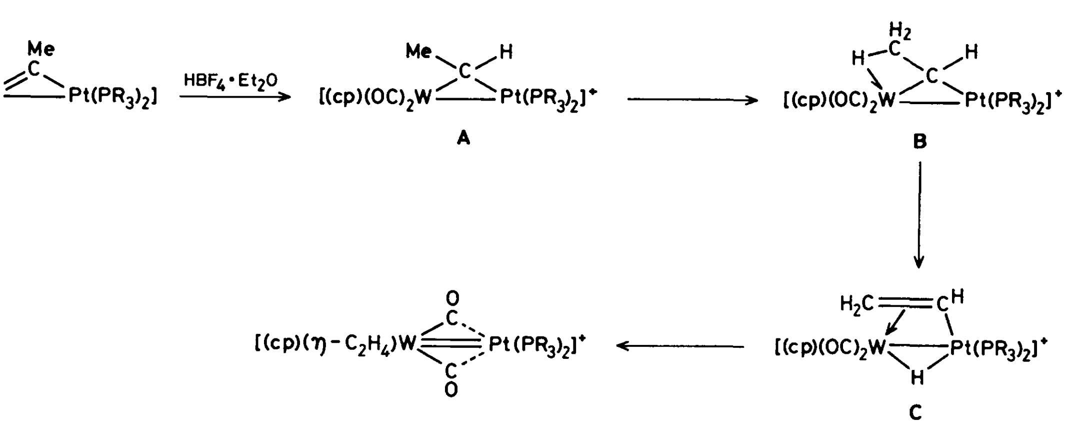
Table 4. Selected interbond lengths (Å) and angles (°) for $[PtW(\mu\text{-}CO)_2(PEt_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$ (**4b**)

W–Pt	2.602(1)	W–C(1)	2.28(2)	W–C(2)	2.26(2)	W–C(3)	1.96(2)
W–C(4)	2.01(2)	Pt–P(1)	2.306(4)	Pt–P(2)	2.299(4)	Pt–C(3)	2.25(2)
Pt–C(4)	2.21(2)	C(1)–C(2)	1.43(2)	C(3)–O(3)	1.19(2)	C(4)–O(4)	1.15(2)
Pt–W–C(1)	105.3(5)	Pt–W–C(2)	105.7(5)	C(1)–W–C(2)	36.7(6)	Pt–W–C(3)	57.1(5)
C(1)–W–C(3)	113.0(6)	C(2)–W–C(3)	82.2(6)	Pt–W–C(4)	55.4(4)	C(1)–W–C(4)	78.8(6)
C(2)–W–C(4)	109.0(6)	C(3)–W–C(4)	112.1(6)	W–Pt–P(1)	129.1(1)	W–Pt–P(2)	132.1(1)
P(1)–Pt–P(2)	98.8(1)	W–Pt–C(3)	47.0(4)	P(1)–Pt–C(3)	118.0(4)	P(2)–Pt–C(3)	114.8(4)
W–Pt–C(4)	48.4(4)	P(1)–Pt–C(4)	117.3(4)	P(2)–Pt–C(4)	113.9(4)	C(3)–Pt–C(4)	95.2(5)
W–C(1)–C(2)	70.7(9)	W–C(2)–C(1)	72.6(9)	W–C(3)–Pt	75.8(5)	W–C(3)–O(3)	167(1)
Pt–C(3)–O(3)	117(1)	W–C(4)–Pt	76.2(5)	W–C(4)–O(4)	162(1)	Pt–C(4)–O(4)	121(1)

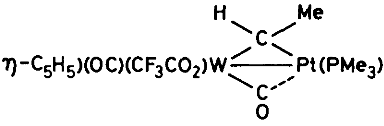
Bands for the two groups of non-equivalent protons present in the ethylene ligand are also observed in the spectrum of (**4d**). However, the corresponding resonances in the spectrum of (**4b**) are obscured by those for the ethyl groups in the PEt_3 ligand. Moreover, in the spectrum of (**4c**), although the signal at δ 0.66 is clearly seen, that at 1.72 p.p.m. is partially overlapped by that due to one of the MeP bands. The observation of two proton resonances for the ethylene ligand in the spectra of (**4a**), (**4c**), and (**4d**) implies that in these complexes this ligand is not rotating on the n.m.r. time-scale at room temperature. In contrast, the co-ordinated C_2H_4 group in $[Ru_2(\mu\text{-}CO)_2(CO)(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)_2]$ shows dynamic behaviour at ambient temperatures, with only a singlet ethylene resonance at δ 1.92 p.p.m.[8] The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of all four salts (**4**) show a single resonance for the ethylene ligand near 23 p.p.m. (Table 2). All four $^{13}C\text{-}\{^1H\}$ spectra also show only one resonance for the CO ligands. For each salt this resonance has ^{195}Pt and ^{183}W satellite peaks in accord with the semi-bridging character of the carbonyl groups.

It seems reasonable to propose that the salts (**4**) form from the complexes (**2**) *via* the pathway shown in the Scheme. It was mentioned earlier that protonation of (**2a**) would be expected to afford (**3a**) in the first step (intermediate **A**), but since the tungsten centre would be electronically unsaturated this species might well undergo further transformation. We have demonstrated that there is nothing inherently unstable about the $\overline{Pt(\mu\text{-}CHMe)W}$ system, provided the tungsten atom has an 18-electron shell. Thus we have prepared the stable complex (**5**), characterised by the data summarised in Tables 1—3. This complex was obtained by treating (**2a**) with CF_3CO_2H. The trifluoroacetate ligand, in contrast to BF_4^-, is able to co-ordinate to tungsten and satisfy the electron deficiency at this metal centre. The presence of the μ-CHMe ligand in (**5**) is clearly established by the ^{1}H and $^{13}C\text{-}\{^1H\}$ spectra (Table 2). The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum in particular shows a characteristic[6] resonance for the μ-*C*HMe group at δ 111.9 p.p.m., appearing as a doublet [*J*(PC) 55 Hz] with ^{195}Pt and ^{183}W satellite peaks.

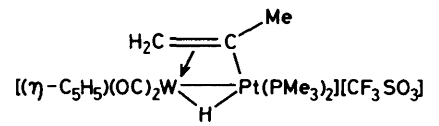
Intermediate **B** (Scheme) would provide a pathway for conversion of **A** into **C**; the latter in turn, *via* hydride migration, could yield the final product (**4**). The agostic[9] C(μ-H)W inter-



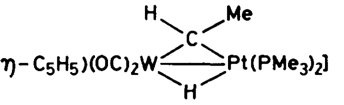
Scheme. cp = η-C_5H_5



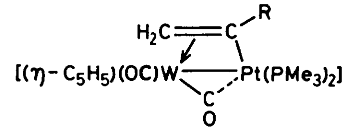
(5)



(6)



(7)



R
(8a) H
(8b) Me

action postulated in **B** has precedent in the stable alkyl-bridged compound $[ReW(\mu\text{-}CH_2C_6H_4Me\text{-}4)(\mu\text{-}Me_2PCH_2PMe_2)(CO)_7]$ described in a preliminary communication[10a] and in the following paper.[10b] The bridged-hydrido and -vinyl intermediate **C** is modelled by compound (**6**), described below. Formation of the complexes (**4**) and (**2**) is of interest in demonstrating that a μ-CMe ligand under protonic conditions can transform into a metal-bound C_2H_4 group. This reaction pathway may be relevant to Fischer–Tropsch type chemistry. The 'carbide' mechanism[11] for reduction of CO on a metal surface could yield μ-CMe groups, *via* a combination of active surface carbon with nearby methylmetal centres. The alkylidynemetal fragments so produced might then be attacked by protons from surface activated water molecules to form μ-CHMe. The latter could then afford metal-bound ethylene centres which are an intrinsic part of the currently favoured mechanism.[11]

In view of the synthesis of the salt (**4a**), and the earlier preparation of compound (**1d**),[2] it was of interest to study the methylation of (**2a**). Treatment of the latter with methyl trifluoromethanesulphonate in dichloromethane at −50 °C afforded pale brown microcrystals of compound (**6**) (Table 1). In solution this species is unstable, and hence the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra were measured at −50 °C (Table 2). It was immediately apparent from the n.m.r. data that (**6**) did not contain a μ-CMe_2 group, as would be present in (**3b**), the initially expected product of the methylation of (**2a**). There was no resonance in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (**6**) corresponding to a μ-$\mathit{C}Me_2$ group. Moreover, the ^1H spectrum showed a characteristic resonance for a μ-H ligand at δ −13.2 p.p.m. with ^{31}P coupling and ^{195}Pt satellite peaks [*J*(PtH) 521 Hz]. Other signals in the ^1H spectrum at δ 3.29, 4.17, and 4.20 p.p.m. were as expected for a $\mu\text{-}C(Me)\text{=}CH_2$ ligand. This was substantiated by the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum with signals at δ 175.8 [d, μ-*C*Me, *J*(PC) 81, *J*(PtC) 534 Hz], 40.1 (μ-CH_2), and 34.9 p.p.m. [μ-C*Me*, *J*(PtC) 37 Hz]. It is interesting to compare these $^{13}C\text{-}\{^1H\}$ data with those for the structurally related compound $[Ru_2\{\mu\text{-}C(Me)\text{=}CH_2\}(\mu\text{-}H)(CO)_2(\eta\text{-}C_5H_5)_2]$ [δ, 175.8 (μ-*C*Me), 52.0 (μ-CH_2), and 44.6 p.p.m. (μ-C*Me*)].[12]

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**6**) was unusual in displaying fortuitously identical chemical shifts for the non-equivalent PMe_3 groups (Table 3). However, the ^{195}Pt spectrum showed the expected doublet of doublets pattern. We have observed coincidence of the ^{31}P shifts for non-equivalent PR_3 groups in a *cis*-$Pt(PR_3)_2$ complex previously in the spectrum of $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2(\eta\text{-}C_5H_5)]$.[5]

It seems likely that complex (**6**) is formed *via* (**3b**), which undergoes a β-hydride shift to tungsten, thereby generating the $Pt(\mu\text{-}H)\{\mu\text{-}C(Me)\text{=}CH_2\}W$ bridged system. It is perhaps surprising that (**6**) does not rearrange to a propylene analogue of (**4a**), but its isolation lends credence to the intermediacy of **C** shown in the Scheme.

Treatment of the salt (**4a**) in tetrahydrofuran (thf) at *ca.* −20 °C with $NaBH_4$ gave the neutral complex (**7**), characterised by the data given in Tables 1—3. Although stable under nitrogen in the solid state, it decomposes slowly in dichloromethane solutions. Compound (**7**) is the analogue of the species $[PtW(\mu\text{-}H)\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$, prepared by treating (**1a**) with $K[BH(CHMeEt)_3]$.[3] Examination of the ^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$, and $^{195}Pt\text{-}\{^1H\}$ n.m.r. data for (**7**) (Tables 2 and 3) reveal that it exists as a mixture of two diastereoisomers in a ratio of *ca.* 3:1, based on peak heights in the spectra. The isomers would be related by the relative orientations of the η-C_5H_5 and μ-CHMe ligands with respect to the plane of the $Pt(\mu\text{-}C)W$ ring, as previously observed with $[PtW(\mu\text{-}H)\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$.[3]

The two isomers undergo dynamic behaviour in solution. At room temperature, the ^{1}H n.m.r. spectrum of (7) shows only one broad hydrido-ligand resonance at δ −7.80 p.p.m. Correspondingly the ^{31}P-{^{1}H} spectrum shows only two resonances for the PMe_3 ligands at δ −25.9 and −21.2 p.p.m., rather than the four expected if two isomers were present. However, when the ^{1}H n.m.r. spectrum of (7) is measured at −30 °C, two hydrido-resonances are observed at δ −7.77 and −8.29 p.p.m. Both signals occur as doublets of doublets, due to ^{31}P–^{1}H coupling with the *transoid* and *cisoid* PMe_3 groups. Also, ^{195}Pt and ^{183}W satellite peaks are observed with couplings of the magnitude expected for a $Pt(\mu\text{-}H)W$ bridge system. When measured at −30 °C, the ^{31}P-{^{1}H} and ^{195}Pt-{^{1}H} n.m.r. spectra (Table 3) show four and two resonances, respectively, in accord with the low-temperature limiting spectra for the isomeric mixture. In the ^{13}C-{^{1}H} spectrum, resonances for the ligated alkylidene carbon nuclei are observed at δ 103.0 p.p.m. [isomer (**a**)] and 114.0 p.p.m. [isomer (**b**)], in the range expected.[6]

Complexes similar to (7), with alkylidene and hydride ligands simultaneously bridging a metal–metal bond are rare. The tolylmethylidene analogue of (7) has been mentioned above. In addition, the dirhodium salt $[Rh_2(\mu\text{-}H)(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2][BF_4]$ has been prepared, and also shown to exist as an equilibrium mixture of two diastereoisomers.[13]

In order to elucidate the pathway by which (**4a**) is converted to (7), the former was treated with $NaBD_4$ and the ^{1}H and ^{2}H n.m.r. spectra of the product examined. The low-temperature ^{2}H spectrum showed deuterium to be present in all three of the bridging positions but with a $\mu\text{-}CH_2D:\mu\text{-}CD:\mu\text{-}D$ distribution ratio 3:1:0.35. This observation suggests that initial attack of D^- on the co-ordinated ethylene of (**4a**) affords a $W\text{–}CH_2CH_2D$ group which rapidly scrambles deuterium *via* reversible β-elimination and tungsten hydride to ethylene addition steps. Subsequent rate-determining α-H or α-D migration, with a significant kinetic deuterium isotope effect, could then produce the deuteriated version of (7) with an appropriate distribution of the deuterium label.

Treatment of the salt (**1a**) with PMe_3 affords a tris(trimethylphosphine) complex $[PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)][BF_4]$, in which the $\mu\text{-}CH(C_6H_4Me\text{-}4)$ ligand no longer adopts a $\sigma{:}\eta^3$-bonding mode.[3] In contrast, the reaction between PMe_3 and (**4a**) leads to deprotonation of the latter, and formation of the vinyl-bridged complex (**8a**). Compound (**8a**) was characterised in the usual manner (Tables 1—3). The ^{1}H n.m.r. spectrum of (**8a**) showed the characteristic three signals, with appropriate J(HH) couplings, for the $\mu\text{-}CH{=}CH_2$ group bridging a dimetal centre.[14,15] In the ^{13}C-{^{1}H} n.m.r. spectrum, characteristic resonances for the vinyl group are seen at δ 129.4 [d, μ-CH, J(PC) 81, J(PtC) 581 Hz] and 37.2 p.p.m. ($\mu\text{-}CH_2$).

An attempt to deprotonate (**4a**) with the reagent $K[BH(CHMeEt)_3]$ gave a mixture of (7) and (**8a**), as well as another complex, possibly $[PtW(\mu\text{-}CH{=}CH_2)(CO)_3(PMe_3)(\eta\text{-}C_5H_5)]$. The i.r. spectrum of the latter showed carbonyl stretching bands at 2 030s, 1 879s, and 1 777m (br) cm^{-1}. These frequencies are similar to those reported[3] for the related compound $[PtW\{\mu\text{-}C(C_6H_4Me\text{-}4){=}CH_2\}(CO)_3(PMe_3)(\eta\text{-}C_5H_5)]$ [$\nu_{max.}$(CO) at 2 034s, 1 882s, and 1 774m cm^{-1}]. With $K[BH(CHMeEt)_3]$, evidently the deprotonation reaction which affords (**8a**) is in competition with hydride addition which yields (7).

When the salt (6) is treated with PMe_3, in dichloromethane at −78 °C, it affords $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ and a new compound (**8b**) in low yield (*ca.* 5%). Complex (**8b**) proved to be the platinum–tungsten complex shown, containing a bridging $\mu\text{-}C(Me){=}CH_2$ ligand. It was fully characterised in the usual manner (Tables 1—3). During the course of our work, it was discovered that (**8b**) could be prepared in high yield by an alternative method, *viz.* from the reaction between compound (**2a**) and the titanium reagent $[\overline{Ti{\cdot}Cl{\cdot}AlMe_2{\cdot}CH_2}(\eta\text{-}C_5H_5)_2]$.[16] The latter functions as a source of CH_2 which adds across the C=W bond in (**2a**). The n.m.r. data (Tables 2 and 3) confirm the structure proposed for (**8b**). Moreover, an *X*-ray crystallographic study[16] has established the structure of an analogue of (**8b**) containing a $\mu\text{-}\sigma{:}\eta^2\text{-}C(C_6H_4Me\text{-}4){=}CH_2$ bridging ligand.

Some other reactions of the salt (6) were investigated. Treatment with $NaBH_4$ at −78 °C gave a very unstable species believed to be $[PtW(\mu\text{-}H)(\mu\text{-}CMe_2)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (9), a compound similar to (7). Complex (9) could not be fully characterised, due to it decomposing even at *ca.* −30 °C. The i.r. spectrum showed CO bands at 1 899 and 1 811 cm^{-1}; the ^{1}H n.m.r. spectrum revealed a resonance at δ −7.96 p.p.m. [J(PH) 24 Hz] for a hydrido-ligand. In a poor quality ^{13}C-{^{1}H} n.m.r. spectrum, a signal at δ 102.5 p.p.m. may be due to the $\mu\text{-}CMe_2$ nucleus.

Compound (6), like (**4a**), reacts with $K[BH(CHMeEt)_3]$ to give a mixture of products. Among those identified were (**8b**), and the unstable species (9). Although the compounds (**4a**) and (6) are structurally very different, nevertheless the reaction of either complex with $K[BH(CHMeEt)_3]$ gives very similar products: (7) and (**8a**), and (9) and (**8b**), respectively.

The results described in this paper, and those reported earlier,[2,3] demonstrate differences in the nature of the products obtained when dimetal complexes with μ-CMe or $\mu\text{-}CC_6H_4\text{-}Me\text{-}4$ ligands are treated with similar reagents. Differences in reactivity patterns have also been observed when these same groups triply bridge trimetal compounds.[17] Moreover, the work reported herein demonstrates the interesting sequence of transformations shown below.

$$\overline{Pt(\mu\text{-}CMe)W} \longrightarrow \overline{Pt(\mu\text{-}CHMe)W} \longrightarrow Pt\text{–}W(\eta\text{-}C_2H_4) \longrightarrow \overline{Pt(\mu\text{-}H)(\mu\text{-}CHMe)W}$$

Experimental

All experiments were carried out under an atmosphere of oxygen-free nitrogen, using Schlenk-tube techniques. All solvents were dried and deoxygenated before use. Infrared spectra were measured on Nicolet FT 10-MX or 5-MX spectrometers. All n.m.r. spectra were recorded on JEOL FX 90Q or FX 200 instruments. Light petroleum refers to that fraction of b.p. 40—60 °C. The reagent $HBF_4{\cdot}Et_2O$ consisted of a 54% solution of HBF_4 in diethyl ether. The complexes $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$[18] and $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene)[19] were prepared by published methods. The compounds $[Pt(C_2H_4)(PR_3)_2]$ (PR_3 = PMe_3, PEt_3, PMe_2Ph, or $PMePh_2$) were prepared *in situ* from $[Pt(cod)_2]$. The latter (0.41 g, 1 mmol) was added portionwise to light petroleum (20 cm^3) which was rapidly stirred and which had been saturated with ethylene at 0 °C. The resultant pale yellow solution, under ethylene, was treated with 2 mmol of the appropriate tertiary phosphine in light petroleum (*ca.* 10 cm^3). The ethylene atmosphere was then replaced by nitrogen, and the resulting suspension of $[Pt(C_2H_4)(PR_3)_2]$ (1 mmol) used as required. Microanalytical and other data for the new compounds are given in Table 1.

Synthesis of the Complexes $[PtW(\mu\text{-}CMe)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ (2).—The compound $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.33 g, 1 mmol) was added to a suspension of $[Pt(C_2H_4)(PMe_3)_2]$ (1 mmol) in light petroleum (*ca.* 30 cm^3) at 0 °C, and the mixture stirred (*ca.* 20 min). The solvent was decanted, and the orange residue washed with light petroleum (2 × 10 cm^3) and dried *in vacuo* to give bright orange *microcrystals* of $[PtW(\mu\text{-}CMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (**2a**) (0.64 g). The related complexes

Table 5. Atomic positional parameters (fractional co-ordinates) (× 10^4) for complex (**4b**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	1 294(1)	7 320(1)	7 370(1)	C(1)	−611(19)	6 209(11)	7 474(8)
Pt	2 688(1)	7 500(1)	8 376(1)	C(2)	772(19)	5 772(11)	7 269(8)
P(1)	4 154(4)	8 741(3)	8 745(2)	C(3)	3 434(17)	6 849(11)	7 557(7)
P(2)	2 857(4)	6 522(3)	9 155(2)	O(3)	4 726(12)	6 529(8)	7 559(5)
C(11)	4 524(20)	9 557(11)	8 171(8)	C(4)	246(17)	7 798(10)	8 060(7)
C(12)	5 637(21)	9 114(13)	7 732(8)	O(4)	−652(12)	8 133(11)	8 352(6)
C(13)	1 547(20)	9 813(14)	9 096(9)	C(31)	−388(27)	8 227(21)	6 744(10)
C(14)	3 193(17)	9 448(11)	9 290(9)	C(32)	1 127(37)	8 735(13)	6 910(10)
C(15)	6 091(17)	8 465(11)	9 109(6)	C(33)	2 351(25)	8 234(16)	6 658(7)
C(16)	7 155(18)	9 338(13)	9 222(8)	C(34)	1 733(25)	7 428(15)	6 371(7)
C(21)	288(26)	7 218(16)	9 741(10)	C(35)	99(23)	7 468(14)	6 442(8)
C(22)	2 015(21)	6 973(12)	9 828(7)	B	5 840(22)	7 784(15)	809(10)
C(23)	4 824(19)	6 086(12)	9 420(8)	F(1)	7 088(14)	7 803(11)	501(7)
C(24)	5 731(23)	5 617(16)	8 921(9)	F(2)	4 607(12)	8 330(9)	636(7)
C(25)	1 686(21)	5 445(11)	8 947(7)	F(3)	6 276(16)	8 090(13)	1 348(5)
C(26)	1 622(23)	4 692(13)	9 425(9)	F(4)	5 338(17)	6 874(9)	849(8)

(**2b**) (0.74 g), (**2c**) (0.81 g), and (**2d**) (0.66 g) were similarly prepared.

Protonation of the Complexes $[PtW(\mu\text{-}CMe)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ (**2**).—Complex (**2a**) (0.38 g, 0.56 mmol) was dissolved in thf (20 cm^3), and the reagent $HBF_4{\cdot}Et_2O$ was then added slowly and dropwise until no further precipitate formed. The mother-liquor was decanted, and the residue washed with thf (2 × 5 cm^3), and then dried *in vacuo* to give dark red *microcrystals* of $[PtW(\mu\text{-}CO)_2(PMe_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$ (**4a**) (0.40 g).

The complex (**2b**) (0.12 g, 0.16 mmol) in diethyl ether (20 cm^3) was cooled to −78 °C and treated dropwise with $HBF_4{\cdot}Et_2O$. The mixture was warmed to *ca.* −50 °C and stirred for 3 h, during which time a pale orange precipitate formed. The mother-liquor was decanted, and the precipitate washed with cold (*ca.* −50 °C) diethyl ether (2 × 10 cm^3), and dried *in vacuo* affording pale orange *microcrystals* of $[PtW(\mu\text{-}CO)_2(PEt_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$ (**4b**) (0.06 g).

The complex (**2c**) (0.23 g, 0.28 mmol) was suspended in diethyl ether (20 cm^3) at −25 °C, and $HBF_4{\cdot}Et_2O$ added dropwise. The mixture was stirred for 30 min, after which the solvent was decanted. The residue thereby obtained was washed with diethyl ether (3 × 10 cm^3 at −25 °C) and dried *in vacuo* to give pale orange *microcrystals* of $[PtW(\mu\text{-}CO)_2(PMe_2Ph)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$ (**4c**) (0.23 g). The compound $[PtW(\mu\text{-}CO)_2(PMePh_2)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$ (**4d**) (0.13 g) was similarly prepared as orange *microcrystals* from (**2d**) (0.13 g, 0.13 mmol).

Reaction of the Complex $[PtW(\mu\text{-}CMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (**2a**) *with Trifluoroacetic Acid.*—Complex (**2a**) (0.36 g, 0.53 mmol), suspended in diethyl ether (20 cm^3) at −20 °C, was treated dropwise with CF_3CO_2H, and the mixture was rapidly stirred until a yellow solution formed. The latter was filtered through a jacket-cooled (−20 °C) Celite column into a previously cooled Schlenk tube. Light petroleum (20 cm^3 at *ca.* −20 °C) was added, and the volume of solvent reduced *in vacuo* to *ca.* 5 cm^3 causing precipitation. Solvent was decanted, and the residue washed with diethyl ether (5 cm^3) and dried *in vacuo* to give yellow *microcrystals* of $[PtW(O_2CCF_3)(\mu\text{-}CHMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (**5**) (0.32 g).

Preparation of $[PtW(\mu\text{-}H)\{\mu\text{-}C(Me){=}CH_2\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][CF_3SO_3]$ (**6**).—Compound (**2a**) (0.70 g, 1 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and the solution cooled to −50 °C. Methyl trifluoromethanesulphonate (1.32 mmol) was added dropwise, and the mixture stirred for 30 min. Removal of solvent *in vacuo* gave a residue which was washed with cold diethyl ether (3 × 20 cm^3). The product was dried *in vacuo* to give pale brown *microcrystals* of $[PtW(\mu\text{-}H)\{\mu\text{-}C(Me){=}CH_2\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][CF_3SO_3]$ (**6**) (0.67 g).

Preparation of $[PtW(\mu\text{-}H)(\mu\text{-}CHMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (**7**).—The salt (**4a**) (0.50 g, 0.65 mmol) was suspended in thf (20 cm^3) at −20 °C, and solid $NaBH_4$ (0.10 g, 2.6 mmol) was added. The slightly soluble (**4a**) dissolved immediately to form a yellow solution. The latter was passed through a jacket-cooled (*ca.* −20 °C) Celite column (2 × 5 cm) into a chilled Schlenk tube. Solvent was removed *in vacuo* give a greenish yellow oil. The latter was washed with light petroleum (2 × 20 cm^3, at −20 °C) to yield greenish yellow *microcrystals* of $[PtW(\mu\text{-}H)(\mu\text{-}CHMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (**7**) (0.39 g).

Preparation of $[PtW(\mu\text{-}CH{=}CH_2)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (**8a**).—A slight excess of PMe_3 was condensed, using liquid nitrogen, directly into an evacuated Schlenk tube attached to a vacuum line, and containing (**4a**) (0.64 g, 0.84 mmol). The reaction vessel was filled with nitrogen and CH_2Cl_2 (20 cm^3) added with a syringe. After stirring (30 min), solvent was removed *in vacuo* affording a dark yellow oil. The latter was dissolved in toluene (10 cm^3) and chromatographed on a short alumina column (2 × 15 cm). Elution, initially with toluene and subsequently with a diethyl ether–toluene mixture (1:9), gave a yellow solution. Removal of solvent *in vacuo*, and treatment of the oily residue with diethyl ether (5 cm^3) followed by light petroleum (5 cm^3), and subsequent concentration of the solution gave yellow *microcrystals* of $[PtW(\mu\text{-}CH{=}CH_2)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (**8a**) (0.17 g).

The compound $[PtW\{\mu\text{-}C(Me){=}CH_2\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (**8b**) was prepared in low yield by addition of PMe_3 to (**6**). A more satisfactory synthesis is described elsewhere.[16]

Crystal Structure Determination of Compound (**4b**).—Crystals of (**4b**) were grown from dichloromethane–light petroleum. Diffracted intensities were collected at 200 K on a Nicolet *P*2_1 four-circle diffractometer using a crystal of dimensions *ca.* 0.45 × 0.25 × 0.10 mm with well developed faces of the type ⟨1 0 0⟩, ⟨0 1 0⟩, and ⟨0 0 1⟩. Of the total 4 984 reflections, measured to $2\theta \leqslant 50°$ (ω scans), 3 465 had $I \geqslant 2.5\sigma(I)$, and only these were used in the refinement of the structure, after the data had been corrected for Lorentz, polarisation, and *X*-ray absorption effects, the latter by an analytical procedure.[20]

Crystal data. $C_{21}H_{39}BF_4O_2P_2PtW$, $M = 851.3$, monoclinic, $a = 8.481(2)$, $b = 14.246(3)$, $c = 23.488(7)$ Å, $\beta = 92.76(2)°$, $U = 2\,835(1)$ Å^3, space group $P2_1/c$ (no. 14), $Z = 4$, $D_c = 2.00$ g cm^{-3}, $F(000) = 1\,616$, $\mu(\text{Mo-}K_\alpha) = 90.4$ cm^{-1}, Mo-K_α *X*-radiation (graphite monochromator, $\bar{\lambda} = 0.710\,69$ Å).

The structure was solved by conventional heavy-atom and electron-density difference methods, and was refined by blocked-cascade least squares. All non-hydrogen atoms were given anisotropic thermal parameters and hydrogen atoms were not included in the refinement. Refinement converged at R 0.051 (R' 0.055) with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.001|F_o|^2]^{-1}$ giving a satisfactory weight analysis. A final electron-density difference synthesis showed no peaks > 1.2 e Å^{-3}, except in the region of the tungsten and platinum atoms where peaks of *ca.* 2 e Å^{-3} were observed. The latter presumably reflect our inability to correct completely for absorption effects for this crystal. All computations were carried out on an Eclipse S230 (Data General) computer with the SHELXTL system of programs.[20] Atomic scattering factors, anomalous dispersion corrections, and mass absorption coefficients were taken from ref. 21. Atom co-ordinates are given in Table 5.

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