Interconversion of Ethylidyne, Ethylidene, Vinyl, and Ethylene Groups at a Dimetal 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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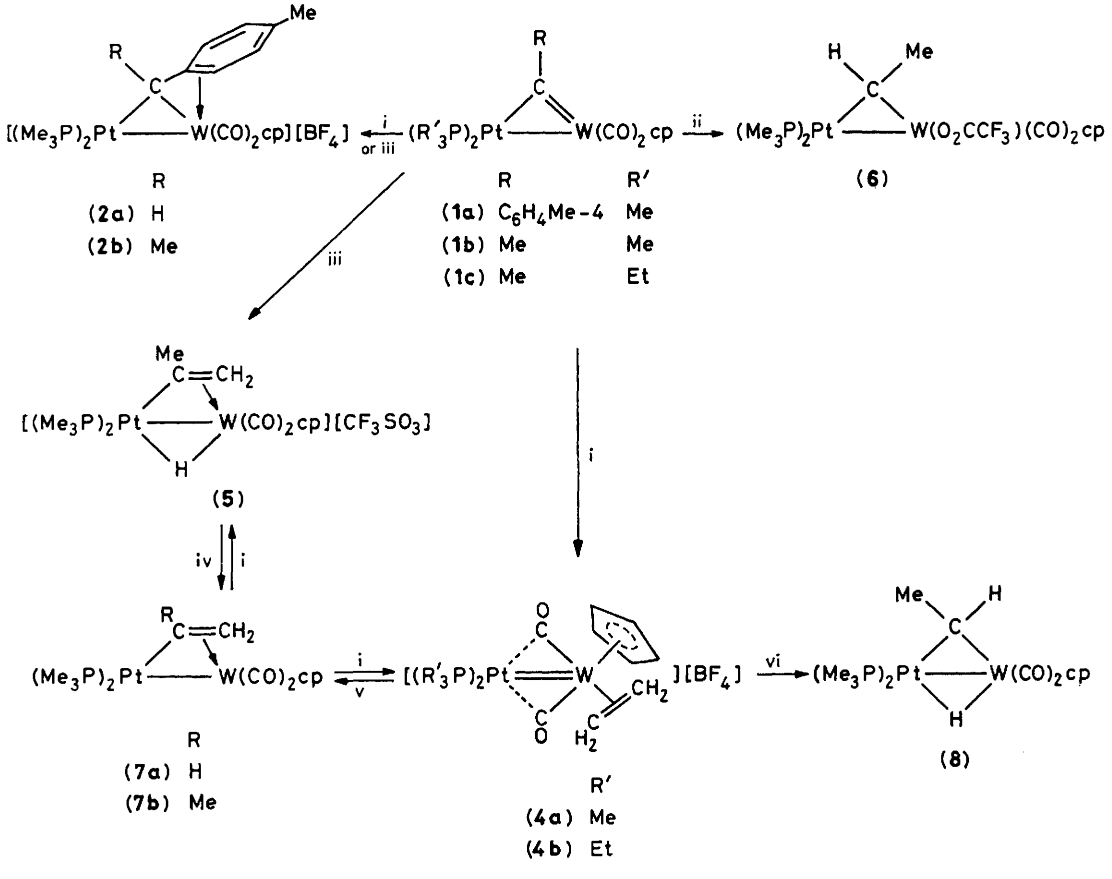
Treatment of the ethylidyne complex $[PtW(\mu\text{-}CMe)(CO)_2(PEt_3)_2(\eta\text{-}C_5H_5)]$ with $HBF_4{\cdot}Et_2O$ affords the salt $[PtW(\mu\text{-}CO)_2(PEt_3)_2(\eta\text{-}C_2H_4)(\eta\text{-}C_5H_5)][BF_4]$, structurally characterised by *X*-ray crystallography; other complexes are described, derived from $[PtW(\mu\text{-}CMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$, with platinum–tungsten bonds bridged by CHMe or $C(R){=}CH_2$ (R = H or Me) groups.

In seeking to understand mechanisms involved in the transition metal catalysed reduction of CO, alkene metathesis, alkyne polymerisation, and methylene transfer reactions, considerable interest has developed in the reactivity of compounds with metal–metal bonds bridged by alkylidene or alkylidyne groups.[1–4] Attention has focused on dimetal compounds having either neutral $[\overline{M(\mu\text{-}CRR')M}]$ or cationic $[\overline{M(\mu\text{-}CR)M}]^+$ (R = R′ = H or Me) core structures. In contrast, the reactivity of carbyne groups bridging metal–metal bonds in neutral complexes has not been explored, except for studies on bimetal compounds with $\mu\text{-}CC_6H_4Me\text{-}4$ ligands.[5]

Herein we describe for the first time some reactions of the μ-CMe group when spanning a heteronuclear metal–metal bond in a neutral complex. These studies were prompted by the knowledge that protonation ($HBF_4{\cdot}Et_2O$) and methylation ($MeSO_3CF_3$) of (**1a**) (Scheme 1) affords the compounds (**2**) in which electron deficiency at the tungsten centre is relieved by η^2-co-ordination with the tolyl ring.[6] Protonation or methylation of (**1b**) should initially give the salts (**3**). However, these species have formally unsaturated tungsten centres, and might be expected to be unstable unless there were agostic interactions between C–H groups of the μ-CMe ligands and the metal.[7]

$$[(Me_3P)_2\overline{Pt\{\mu\text{-}C(R)Me\}W}(CO)_2(\eta\text{-}C_5H_5)][X]$$

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



Scheme 1. cp = $\eta\text{-}C_5H_5$. i, $HBF_4{\cdot}Et_2O$; ii, CF_3CO_2H; iii, CF_3SO_3Me in CH_2Cl_2; iv, $K[BH(CHMeEt)_3]$ in tetrahydrofuran (THF); v, Me_3P in CH_2Cl_2; vi, $NaBH_4$ in THF at −20 °C.

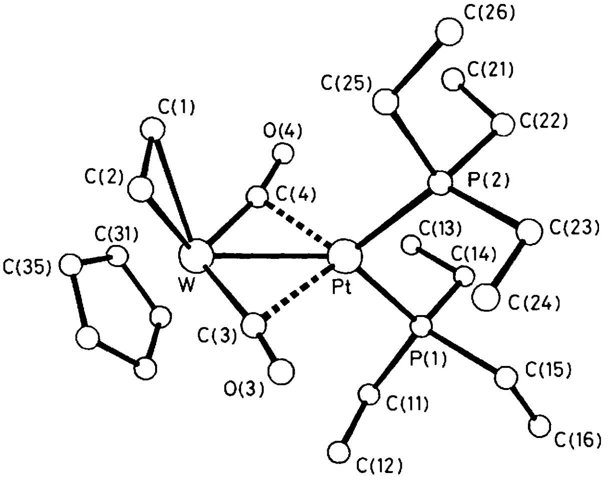


Figure 1. Molecular structure of the cation of $[\mathrm{WPt}(\mu\text{-CO})_2(\mathrm{PEt}_3)_2(\eta\text{-C}_2\mathrm{H}_4)(\eta\text{-C}_5\mathrm{H}_5)][\mathrm{BF}_4]$ (**4b**). W–Pt 2.602(1), W–C(1) 2.283(16), W–C(2) 2.259(15), C(1)–C(2) 1.431(24), W–C(3) 1.964(14), Pt–C(3) 2.253(16), W–C(4) 2.005(16), Pt–C(4) 2.206(14), Pt–P(1) 2.306(4), Pt–P(2) 2.299(4) Å; W–C(3)–O(3) 167.2(14), W–C(4)–O(4) 162.3(13)°.

Protonation of (**1b**) afforded a stable product (**4a**), the spectroscopic properties† of which showed that it could not be (**3a**). Thus the i.r. spectrum had only one CO stretching band in contrast with that of (**2a**) which has two such absorptions. Moreover, the ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra of (**4a**) did not possess the characteristic resonances[1] for a species with a μ-CHMe group. Crystals of (**4a**) were of poor quality, and hence an *X*-ray diffraction study was not possible. However, treatment of (**1c**) with $\mathrm{HBF_4{\cdot}Et_2O}$ yielded (**4b**) which afforded good crystals for *X*-ray diffraction.‡

The molecular structure (Figure 1) reveals that in (**4b**) an ethylene molecule is co-ordinated to tungsten, and the Pt–W bond [2.602(1) Å] is *ca.* 0.2 Å shorter than that found in a range of platinum–tungsten species previously studied.[8] The metal–metal bond in (**4b**) is strongly semi-bridged by the two CO ligands, with a coplanar WC(4)PtC(3) system forming an interplanar angle of 90° with the P(1)PtP(2) plane. The structure of (**4b**) is similar to that of the complex $[\mathrm{MoRh}(\mu\text{-CO})_2(\mathrm{CO})(\mathrm{PPh}_3)_2(\eta\text{-C}_5\mathrm{H}_5)]$ for which multiple metal–metal bonding has also been invoked.[9] This is not surprising since both compounds are composed of fragments which are isolobally related: $\mathrm{W(CO)_2}(\eta\text{-C}_2\mathrm{H}_4)(\eta\text{-C}_5\mathrm{H}_5)$ *vs.* $\mathrm{Mo(CO)_3}(\eta\text{-C}_5\mathrm{H}_5)$, and $\mathrm{Pt(PEt_3)_2}^+$ *vs.* $\mathrm{Rh(PPh_3)_2}$. However, in (**4b**) the positive charge in the cation may well be delocalised.

Treatment of (**1b**) with $\mathrm{MeSO_3CF_3}$ does not yield (**3b**), nor is a propylene analogue of (**4**) formed. The product (**5**) has spectroscopic properties† consistent with it containing μ-H and μ-C(Me):CH$_2$ groups. Addition of $\mathrm{CF_3CO_2H}$ to (**1b**) affords (**6**), the n.m.r. spectra† of which clearly establish the presence of the μ-CHMe ligand. In view of the synthesis of (**6**) it is probable that protonation of (**1b**) with $\mathrm{HBF_4{\cdot}Et_2O}$ gives (**3a**) initially which then undergoes a μ-H transfer step to yield a species analogous to (**5**). However, unlike the latter, and for reasons not yet apparent, this intermediate rearranges to produce the thermodynamically stable species (**4a**). Compounds (**4a**) and (**5**) are readily deprotonated giving the bridged vinyl complexes (**7a**) and (**7b**), respectively, but these reactions are reversed with $\mathrm{HBF_4{\cdot}Et_2O}$ (Scheme 1).

The reaction between (**4a**) and $\mathrm{K[BH(CHMeEt)_3]}$ affords a mixture of (**7a**) and (**8**). The latter is cleanly prepared, however, by treating (**4a**) with $\mathrm{NaBH_4}$. Compound (**8**) exists as a mixture of diastereoisomers.† From the relative intensity of the n.m.r. peaks measured from ^{31}P-{^{1}H} and ^{195}Pt-{^{1}H} spectra at −30 °C the isomers are present in a *ca.* 3:1 ratio. If $\mathrm{NaBD_4}$ is used to prepare (**8**), the product has the deuterium label (^{2}H and ^{1}H n.m.r. studies) in all three bridge positions but with $\mathrm{CH_2D}$:μ-CD:μ-D in the ratio 3:1:0.35. This suggests that initial attack of deuteride at ethylene affords a $\mathrm{W{-}CH_2CH_2D}$ 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 would produce (**8**) with an appropriate distribution of the deuterium label.

The various reactions summarised in Scheme 1 show that a heteronuclear dimetal system $\overline{\mathrm{M}(\mu\text{-CMe})\mathrm{M}'}$ can readily afford species containing the groups $\mathrm{M{-}M'}(\eta\text{-C}_2\mathrm{H}_4)$,

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† Selected spectroscopic data [i.r. measured in $\mathrm{CH_2Cl_2}$, n.m.r. measured in $\mathrm{CD_2Cl_2}$ (^{1}H, ^{31}P-{^{1}H}, ^{195}Pt-{^{1}H}) or $\mathrm{CD_2Cl_2}$–$\mathrm{CH_2Cl_2}$ (^{13}C-{^{1}H}), coupling constants in Hz, chemical shifts are to high frequency and relative to 85% $\mathrm{H_3PO_4}$ (external) for ^{31}P-{^{1}H}, and $\Xi(^{195}\mathrm{Pt})$ 21.4 MHz for ^{195}Pt-{^{1}H}]: Compound (**4a**), dark red microcrystals, ν_{CO} (max) at 1 831 cm^{-1}. N.m.r.: ^{1}H, δ 0.96 [dddd, 2 H, $\mathrm{C_2H_4}$, *J*(HH) (*trans* vicinal) 11, *J*(HH) (geminal) 4, *J*(PH) 6 and 6] and 1.80 [dd, 2 H, $\mathrm{C_2H_4}$, *J*(HH) (*trans* vicinal) 11, *J*(HH) (geminal) 4]; ^{13}C-{^{1}H}, δ 235.3 [CO, *J*(PtC) 281, *J*(WC) 175] and 22.2 p.p.m. ($\mathrm{C_2H_4}$); ^{31}P-{^{1}H}, δ −7.5 [d, *J*(PP) 42, *J*(PtP) 3 145, *J*(WP) 37] and −17.0 p.p.m. [d, *J*(PP) 42, *J*(PtP) 2 993]; ^{195}Pt-{^{1}H}, δ 2 267 p.p.m. [dd, *J*(PPt) 3 145 and 2 993]. Compound (**5**), brown microcrystals, ν_{CO} (max) at 1 992vs and 1 925s cm^{-1}. N.m.r. (−50 °C): ^{1}H, δ −13.20 [(ABX), 1 H, μ-H, *J*(PH) ± 69, *J*(P′H) ± 14, *J*(PtH) 521, Δ_{AB} 3], 3.29 [m(br.), 3 H, μ-CMe], 4.17 [m(br.), 1 H, $\mathrm{CH_2}$], 4.20 [d(br.), 1 H, $\mathrm{CH_2}$, *J*(PH) 14, *J*(PtH) 96], and 5.63 (s, 5 H, $\mathrm{C_5H_5}$); ^{13}C-{^{1}H}, δ 224.0 [CO, *J*(WC) 157], 219.8 [CO, *J*(WC) 167], 175.8 [d, μ-*C*Me, *J*(PC) 81, *J*(PtC) 534], 40.1 ($\mathrm{CH_2}$), and 34.9 p.p.m. [C*Me*, *J*(PtC) 37]. Compound (**6**), yellow crystals, ν_{CO} (max) at 1 956s and 1 783m cm^{-1}. N.m.r.: ^{1}H, δ 2.29 [ddd, 3 H, μ-CH*Me*, *J*(HH) 8, *J*(PH) 9 and 5, *J*(PtH) 6] and 4.75 [ddq, 1 H, μ-C*H*Me, *J*(HH) 8, *J*(PH) 5 and 4, *J*(PtH) 24]; ^{13}C-{^{1}H}, (at −50 °C), δ 239.1 [d, CO, *J*(PC) 12, *J*(PtC) 89], 225.3 [d, CO, *J*(PC) 9, *J*(PtC) 44], 111.9 [d, μ-C, *J*(PC) 55, *J*(PtC) 494, *J*(WC) 53], and 32.1 p.p.m. (μ-C*Me*). Compound (**7a**), yellow crystals, ν_{CO} (max) at 1 864s and 1 737w cm^{-1}. N.m.r.: ^{1}H, δ 2.54 [ddd, 1 H, $\mathrm{CH_2}$, *J*(HH) 9 and 1, *J*(PH) 8, *J*(PtH) 25], 3.25 [dddd, 1 H, $\mathrm{CH_2}$, *J*(HH) 10 and 1, *J*(PH) 12 and 2, *J*(PtH) 110], and 6.55 [dddd, 1 H, μ-CH, *J*(HH) 10 and 9, *J*(PH) 7 and 3, *J*(PtH) 6]. Compound (**8**), greenish-yellow crystals, ν_{CO} (max) at 1 891vs and 1 794s cm^{-1}. N.m.r. (−30 °C), isomer (i): ^{1}H, δ −7.77 [dd, 1 H, μ-H, *J*(PH) 82 and 16, *J*(PtH) 505, *J*(WH) 53], 2.21 [dd, 3 H, μ-CMe, *J*(HH) 8, *J*(PH) 13], and 6.11 [dq, 1 H, μ-CH, *J*(HH) 8, *J*(PH) 4]; ^{13}C-{^{1}H}, δ 242.7 [CO, *J*(WC) 147], 234.1 [CO, *J*(WC) 184], 103.0 [d, μ-C, *J*(PC) 55, *J*(PtC) 471], and 34.5 p.p.m. (μ-C*Me*); ^{31}P-{^{1}H}, δ −20.2 [s, *J*(PtP) 4 040] and −25.6 p.p.m. [s, *J*(PtP) 2 090]; ^{195}Pt-{^{1}H}, δ −996 p.p.m. [dd, *J*(PPt) 4 040, 2 090]. Isomer (ii): ^{1}H, δ −8.29 [dd, μ-H, *J*(PH) 80 and 18, *J*(PtH) 525, *J*(WH) 56], 2.36 [dd, 3 H, μ-CMe, *J*(HH) 8, *J*(PH) 14], and 5.80 [dq, 1 H, μ-CH, *J*(HH) 8, *J*(PH) 4]; ^{13}C-{^{1}H}, δ 238.4 (CO), 236.0 (CO), 114.0 [d, μ-C, *J*(PC) 58, *J*(PtC) 560], and 35.2 p.p.m. (μ-C*Me*); ^{31}P-{^{1}H}, δ −22.4 [d, *J*(PP) 7, *J*(PtP) 4 026] and −26.4 p.p.m. [d, *J*(PP) 7, *J*(PtP) 2 075]; ^{195}Pt-{^{1}H}, δ −1 024 p.p.m. [dd, *J*(PPt) 4 026, 2 075].

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Crystal data for (**4b**): $\mathrm{C_{21}H_{39}BF_4O_2P_2PtW}$, $M = 851.3$, monoclinic, space group $P2_1/c$ (no. 14), $a = 8.481(2)$, $b = 14.246(3)$, $c = 23.488(7)$ Å, $\beta = 92.76(2)°$, $U = 2\,835(1)$ Å^3, $Z = 4$, $D_c = 2.00$ g cm^{-3}, $F(000) = 1\,616$, $\mu(\text{Mo-}K_\alpha) = 90.4$ cm^{-1}. Current R 0.051 (R_w 0.052) for 3 465, absorption-corrected reflections [293 K, ω-scans, $2\theta \leqslant 50°$, $I \geqslant 2.5\sigma(I)$, Nicolet *P*3m diffractometer, Mo-K_α ($\bar{\lambda} = 0.710\,69$ Å)].

$\text{M}(\mu\text{-CHMe})\text{M}'$, $\text{M}\{\mu\text{-C(R)}:\text{CH}_2\}\text{M}'$ (R = H or Me), $\overline{\text{M}\{\eta\text{-C(Me)}:\text{CH}_2\}(\mu\text{-H})\text{M}'}$, and $\overline{\text{M}(\mu\text{-CHMe})(\mu\text{-H})\text{M}'}$.

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