Protonation of Tolylidyne Ligands bridging Tungsten–Cobalt and –Platinum Bonds; Reactivity of the Cationic Dimetal μ-Carbene Complexes Produced, and *X*-Ray Crystal Structures of $[PtW\{\mu\text{-}\eta^1,\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$, $[PtW(\mu\text{-}H)\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$, and $[CoW\{\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)H\}(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)][BF_4]$

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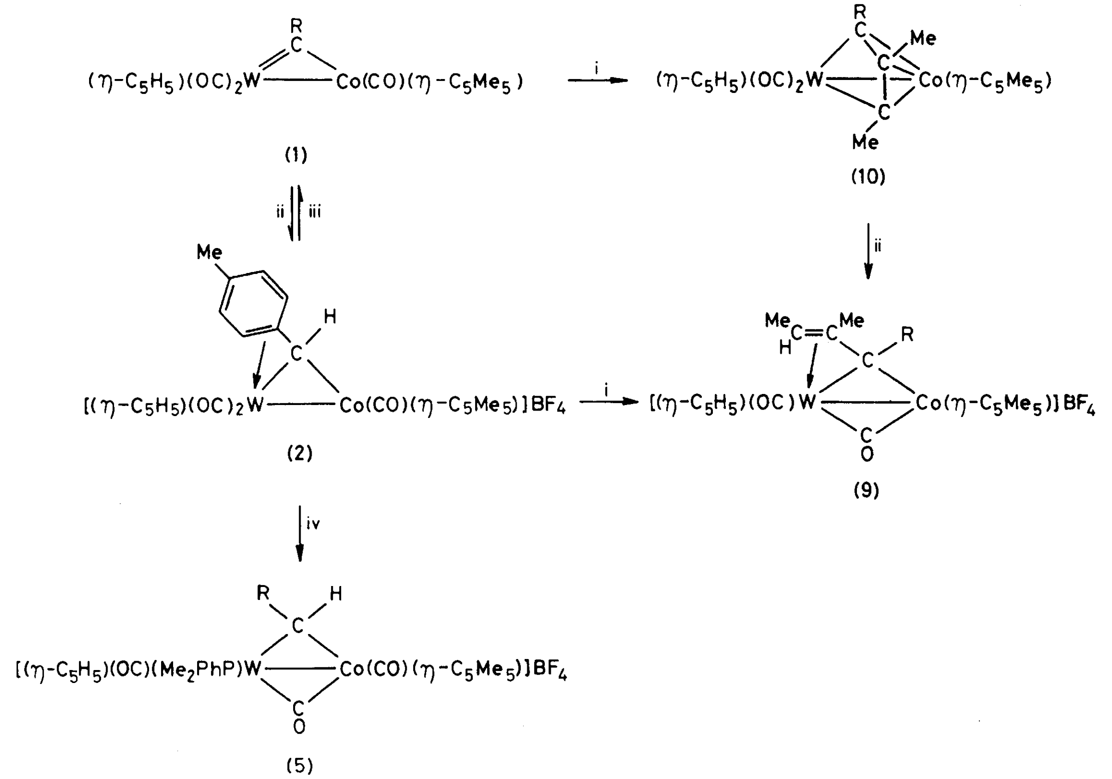
Summary The synthesis and reactions of the complex salts $[MW\{\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_4Me\text{-}4)H\}(CO)_2L_n(\eta\text{-}C_5H_5)][BF_4]$ $[ML_n = Co(CO)(\eta\text{-}C_5Me_5)$ and $Pt(PMe_3)_2]$ are described; the structures of the platinum–tungsten species, and the compounds $[PtW(\mu\text{-}H)\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ and $[CoW\{\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)H\}$-

(μ-CO)(CO)(η-C_5H_5)(η-C_5Me_5)][BF_4] being established by *X*-ray diffraction.

Herein we report the first examples of conversion of μ-carbyne groups in heteronuclear dimetal compounds into reactive cationic species with bridging carbene ligands. The reactivity of carbene and carbyne groups when bridging metal–metal bonds in discrete metal complexes may be relevant to processes which occur in various catalytic syntheses.[1–4]

The cobalt–tungsten compound (**1**)[5] (Scheme 1) treated with $HBF_4{\cdot}Et_2O$ affords, quantitatively, dark green crystals of the salt (**2**).† Similar protonation of the platinum–tungsten complex (**3**)[6] (Scheme 2) yields (90%) yellow crystals of (**4**).‡ In order to identify the carbon-bridge systems in (**2**) and (**4**), a single crystal *X*-ray diffraction study was undertaken on the latter.§

Crystal data: $C_{21}H_{31}BF_4O_2P_2PtW$, $M = 843{\cdot}2$, monoclinic, space group $P2_1/c$, $a = 13{\cdot}903(3)$, $b = 16{\cdot}213(3)$, $c = 11{\cdot}859(2)$ Å, $\beta = 96{\cdot}89(2)°$, $U = 2\,654(1)$ Å^3, $Z = 4$,



Scheme 1. R = C_6H_4Me-4, i, MeC_2Me in PhMe, ii, $HBF_4{\cdot}Et_2O$, iii, K[BH(CHMeEt)$_3$] in tetrahydrofuran (thf), iv, PMe_2Ph.

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† Selected spectroscopic data for the cobalt–tungsten compounds (i.r. measured in CH_2Cl_2, ^1H n.m.r. in CD_2Cl_2, $^{13}C\{^1H\}$-decoupled in CD_2Cl_2–CH_2Cl_2, coupling constants in Hz): (**2**), ν_{CO} 2 001vs, 1 953, and 1 825s cm^{-1}; n.m.r.: ^1H, δ (25 °C) 1·9 (s, 15 H, C_5Me_5), 2·4 (s, 3 H, 4-Me), 5·3 (s, 5 H, C_5H_5), 7·2 (br. m, 4 H, C_6H_4), and 10·0 (s 1 H, μ-CH): δ(-70 °C) 1·9 (s, 15 H, C_5Me_5), 2·4 (s, 3 H, 4-Me), 5·3 (s, 5 H, C_5H_5), 4·8 [d, 1 H, η^2-CH=C of C_6H_4, *J*(HH) 6], 7·1 [d, 1 H, C_6H_4, *J*(HH) 6], 7·3 [d, 1 H, C_3H_4, *J*(HH) 8], 7·8 [d, 1 H, C_6H_4, *J*(HH) 8 Hz], and 10·1 (s, 1 H, μ-CH). (**5**), ν_{CO} 2 001vs, 1 933vs, and 1 795vs cm^{-1}; n.m.r. (-50 °C): isomer A, ^{13}C, δ 244·5 (μ-CO), 229·5 [d, WCO, *J*(PC) 21], 222·4 (μ-C), and 200 p.p.m. (CoCO); $^{31}P\{^1H\}$ (to high frequency of H_3PO_4), δ $-12{\cdot}3$ p.p.m. [*J*(WP) 115]; isomer B, ^{13}C, δ 243 (μ-CO), 228·5 [d, WCO, *J*(PC) 27], 221·7 (μ-C), and 199·0 p.p.m. (CoCO); $^{31}P\{^1H\}$, δ $-3{\cdot}8$ p.p.m. [*J*(WP) 134]. (**9**), ν_{CO} 1 969vs and 1 767s cm^{-1}; n.m.r.: ^1H, δ 1·0 (s, 15 H, C_5Me_5), 2·1 [d, 3 H, CH*Me*, *J*(HH) 6], 2·3 (s 3 H, :CMe), 2·6 (s, 3 H, 4-Me), 3·0 [q, 1 H, C*H*Me, *J*(HH) 6], 5·3 (s, 5 H, C_5H_5), 4·6 (m, 1 H, C_6H_4), 7·0 (m, 1 H, C_6H_4), 7·5 (m, 1 H, C_6H_4), and 8·2 (m, 1 H, C_6H_4); ^{13}C, δ 253·7 [μ-CO, *J*(WC) 129], 206 [CO, *J*(WC) 167], and 192·3 p.p.m. (μ-C).

‡ Selected spectroscopic data for the platinum–tungsten complexes: (**4**), ν_{CO} 1 957s and 1 785br.m cm^{-1}; n.m.r. (25 °C): ^1H, δ 1·64 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 24], 1·67 [d, 9 H, MeP, *J*(PH) 10·5, *J*(PtH) 36], 2·35 (s, 3 H, 4-Me), 4·75 [d, 5 H, C_5H_5, *J*(PH) 1, *J*(PtH) 4], 6·03 [d, 1 H, C_6H_4, *J*(HH) 6], 6·71 [d, 1 H, μ-CH, *J*(PH) 7], 7·09 [d of d, 1 H, C_6H_4, *J*(HH) 6 and 1], 7·17 (m, 1 H, C_6H_4), and 7·24 (m, 1 H, C_6H_4); ^{13}C, δ 224·1 [μ-CO, *J*(PC) 22, *J*(PtC) 139], 219·4 [WCO, *J*(WC) 163, *J*(PtC) 30], and 116·3 p.p.m. [d of d, μ-C, *J*(PC) 75 and 5, *J*(PtC) 554, *J*(WC) 30]; $^{31}P\{^1H\}$ (to high frequency of H_3PO_4), δ $-10{\cdot}2$ [d, *J*(PP) 15, *J*(PtP) 3 408, *J*(WP) 40] and $-14{\cdot}2$ p.p.m. [d, *J*(PP) 15, *J*(PtP) 2 663, *J*(WP) 14]. (**7**), ν_{CO} 2 026s, 1 978 s, and 1 861br. m cm^{-1}; n.m.r.: ^1H, δ 1·52 [d, 9 H, MeP, *J*(PH) 11, *J*(PtH) 45], 1·70 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 22], 2·29 (s, 3 H, 4-Me), 5·32 (s, 5 H, C_5H_5), 5·78 [d of d, μ-CH, *J*(PH) 4 and 1], and 7·10 (m, 4 H, C_6H_4); $^{31}P\{^1H\}$, δ $-10{\cdot}5$ [d, *J*(PP) 10, *J*(PtP) 4 324, *J*(WP) 40] and $-13{\cdot}5$ p.p.m. [d, *J*(PP) 10, *J*(PtP) 2 510]. (**8**), ν_{CO} 1 897s and 1 802s cm^{-1}; n.m.r.: isomer A, ^1H (-30 °C), δ $-7{\cdot}92$ [d of d, 1 H, μ-H, *J*(PH) 15 and 82, *J*(PtH) 509], 1·29 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 37], 1·67 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 24], 2·18 (s, 3 H, 4-Me), 5·25 (s, 5 H, C_5H_5), and 6·10—6·93 (br. m, 5 H, C_6H_4 and μ-CH); isomer B, ^1H (-30 °C), δ $-8{\cdot}57$ [d of d, 1 H, μ-H, *J*(PH) 15 and 83, *J*(PtH) 473], 1·43 [d, 9 H, MeP, *J*(PH) 12], 1·67 (m, 9 H, MeP), 2·18 (s, 3 H, 4-Me), (4·92 s, 5 H, C_5H_5), and 6·10—6·93 (br. m, 5 H, C_6H_4 and μ-CH).

§ 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.

$D_c = 2{\cdot}11$ g cm^{-3}, $F(000) = 1\,584$, μ(Mo-K_α) = 99·1 cm^{-1}. Current R 0·054 (R' 0·054) for 3 430, absorption-corrected reflections [293 K, $2\theta \leqslant 50°$, $I \geqslant 3\sigma(I)$, Nicolet $P3m$ diffractometer, Mo-K_α ($\bar{\lambda}$ = 0·710 69 Å)].

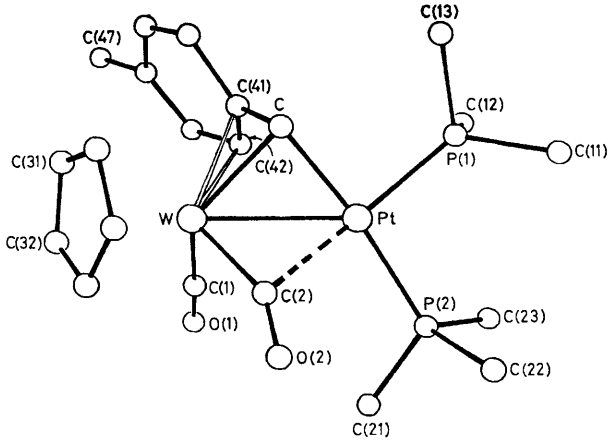


FIGURE 1. Molecular structure of the cation [PtW{μ-η^1,η^3-CH(C_6H_4Me-4)}$(CO)_2(PMe_3)_2(\eta$-$C_5H_5)]^+$ (4). W–Pt 2·795(1), W–C 2·166(14), W–C(41) 2·406(14), W–C(42) 2·602(13), Pt–C 2·053(14), Pt–P(1) 2·281(4), Pt–P(2) 2·314(4), W–C(2) 1·956(15), Pt–C(2) 2·27(2) Å; ∠W·C(2)·O(2) 155·1(14), W·C·Pt 83·0(5)°.

The molecular structure of the cation (Figure 1) reveals a bridge system in which two carbon atoms [C(41) and C(42)] of the aryl ring form an η^2-attachment to the tungsten, so that the μ-C(H)C_6H_4Me group as a whole adopts an η^3-bonding mode to the metal, as previously established[7] for this ligand in [Mo_2{μ-C(C_6H_4Me-4)$_2$}$(CO)_4(\eta$-$C_5H_5)_2$]. There is n.m.r. evidence[8] for similar bonding of a μ-C·C_6H_5 group in [$Ru_2(\mu$-$CPh_2)(\mu$-CO)(CO)$(\eta$-$C_5H_5)_2$]. The n.m.r. data‡ for (4) at 25 °C reveal that in solution the tolyl group does not rotate about the μ-C–C(41) bond on the n.m.r. time scale. In contrast, the data† for (2) show dynamic behaviour for the tolyl group at 25 °C, which ceases at −70 °C. Reaction of (2) and (4) with tertiary phosphines affords compounds (5) and (6), respectively, in which the bonding of the tolyl ring to tungsten has been displaced. Reaction of (4) with CO (1 bar) affords (7), but this compound‡ reverts slowly to (4) in solution. Complex (5) exists as a mixture of two diastereoisomers, exchange between which (n.m.r. studies†) is fast at room temperature but ceases at −50 °C.

Whereas (2) is readily deprotonated by K[BH(CHMeEt)$_3$], compound (4) gives the stable hydrido-bridged complex (8), which undergoes dynamic behaviour in solution. The ^{1}H n.m.r. spectrum shows a broad resonance for the μ-H ligand at room temperature, but two signals are seen at −30 °C corresponding to isomers in 70:30 ratio.‡ Two isomers of (8) are possible, depending on the relative orientation of the C_5H_5 and H ligands with respect to the plane

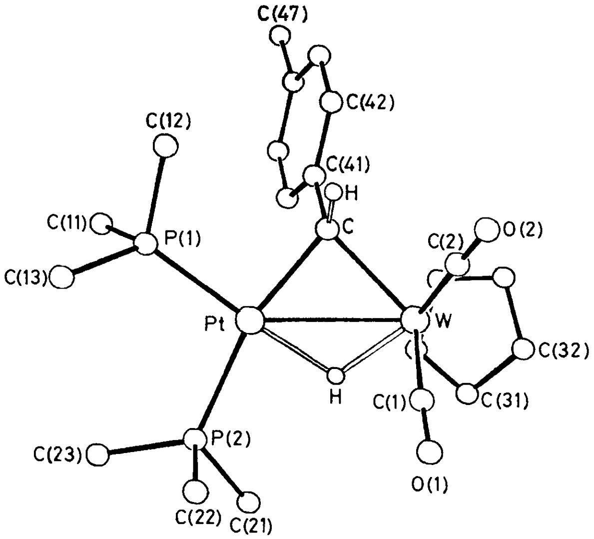
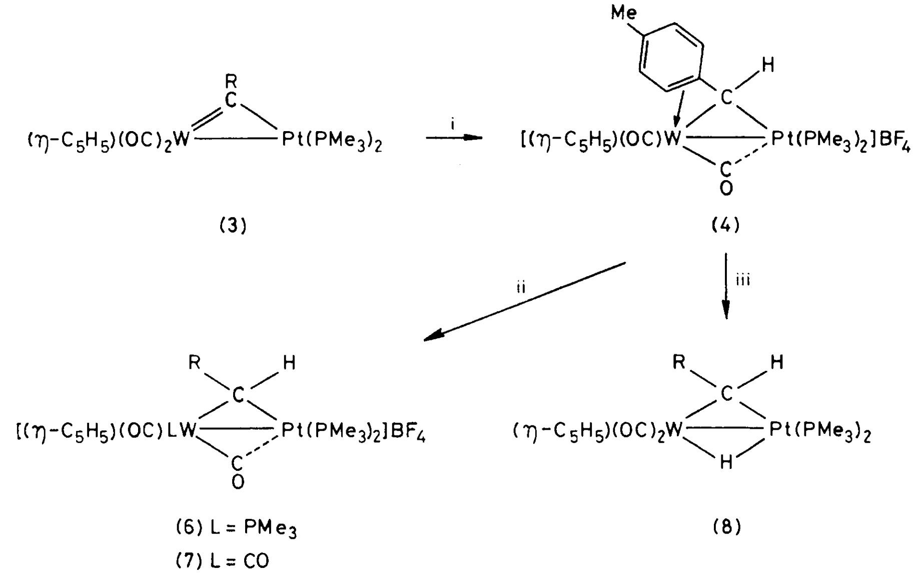


FIGURE 2. Molecular structure of [PtW(μ-H){μ-CH(C_6H_4Me-4)}$(CO)_2(PMe_3)_2(\eta$-$C_5H_5)$] (8). Reasonable positions for the μ-H and μ-CH hydrogen atoms were obtained from a final difference Fourier synthesis, but could not be refined. W–Pt 2·895(1), W–C 2·259(9), Pt–C 2·109(9), Pt–P(1) 2·265(3), Pt–P(2) 2·305(3) Å; ∠Pt·C·W 83·0(3)°.



SCHEME 2. R = C_6H_4Me-4, L = PMe_3 or CO, i, $HBF_4{\cdot}Et_2O$, ii, CO or PMe_3, iii, K[BH(CHMeEt)$_3$] in thf.

defined by $\overline{\text{Pt}(\mu\text{-C})\text{W}}$. An equilibrium between diastereoisomers has recently been reported[9] for the cation $[\text{Rh}_2(\mu\text{-H})(\mu\text{-CH}_2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]^+$ which also has a metal–metal bond doubly-bridged by hydrido- and carbene ligands. The molecular structure of (**8**), established from an *X*-ray diffraction study,§ is shown in Figure 2.

Crystal data: $\text{C}_{21}\text{H}_{32}\text{O}_2\text{P}_2\text{PtW}$, M = 757·4, monoclinic, space group $P2_1/c$, a = 10·554(4), b = 11·624(3), c = 19·393(7) Å, β = 97·64(3)°, U = 2 358(1) Å^3, Z = 4, D_c = 2·13 g cm^{-3}, $F(000)$ = 1 424, $\mu(\text{Mo-}K_\alpha)$ = 111·2 cm^{-1}. Current R 0·039 (R' 0·041) for 3 083, absorption-corrected reflections [220 K, $2\theta \leqslant 50°$, $I \geqslant 3\sigma(I)$]. The Pt–W distance [2·895(1) Å] is *ca.* 0·1 Å longer than in complexes of type (**3**),[6] as expected for the presence of a bridging hydrido-ligand,[10,11] clearly revealed by the ^{195}Pt satellites in the ^{1}H n.m.r. spectrum.‡

Compound (**2**) reacts rapidly with but-2-yne to give, quantitatively, the bright green complex (**9**),† the structure of which was established by *X*-ray diffraction.§

Crystal data: $\text{C}_{29}\text{H}_{34}\text{BCoF}_4\text{O}_2\text{W}$, M = 744·2, monoclinic, space group $P2_1/c$, a = 10·793(9), b = 16·503(13), c = 15·957(5) Å, β = 93·52(5)°, U = 2 837(4) Å^3, Z = 4, D_c = 1·74 g cm^{-3}, $F(000)$ = 1 464, $\mu(\text{Mo-}K_\alpha)$ = 45·2 cm^{-1}. Current R 0·037 (R' 0·038) for 3 678, absorption-corrected reflections [293 K, $2\theta \leqslant 50°$, $I \geqslant 3\sigma(I)$]. The cation (Figure 3) has an η^3-allylic attachment of C(1), C(2), and C(3) to the tungsten, and η^1-bonding of C(1) to cobalt. However, (**9**) can also be formulated as involving a 'vinylcarbene' bridge system; similar alternative representations have been discussed for related di-iron and -ruthenium compounds.[12]

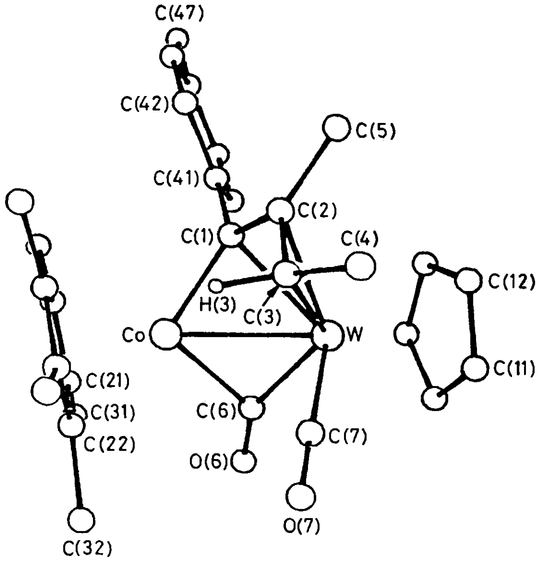


FIGURE 3. Molecular structure of the cation $[\text{CoW}\{\mu\text{-}\eta^1,\eta^3\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{Me})\text{C}(\text{Me})\text{H}\}(\mu\text{-CO})(\text{CO})(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]^+$ (**9**). W–Co 2·552(1), W–C(1) 2·225(7), W–C(2) 2·352(7), W–C(3) 2·377(8), W–C(6) 2·014(7), Co–C(1) 1·939(6), Co–C(6) 1·991(8) Å; ∠W·C(6)·Co 79·2(3), W·C(1)·Co 75·2(2)°.

Complex (**9**) can also be prepared by protonation of (**10**). Whereas formation of (**10**) from (**1**) requires elevated temperatures,[5] reaction of alkynes with (**2**) proceeds at or below 25 °C. The high reactivity of (**2**) is presumably due to the easy transformation of the μ-C(H)C$_6$H$_4$Me-4 group from an η^3- to an η^1-bonding mode, thereby providing a vacant site on tungsten for alkyne co-ordination, as a preliminary step for C–C bond formation and hydrogen migration.

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