Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 27.[1] Studies on the Compounds $[\mathrm{MW}\{\mu\text{-}\sigma{:}\eta^3\text{-CH}(\mathrm{C_6H_4Me}\text{-}4)\}(\mathrm{CO})_2\mathrm{L}_n(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$ $[\mathrm{ML}_n = \mathrm{Pt(PR_3)_2}$ or $\mathrm{Co(CO)}(\eta\text{-}\mathrm{C_5Me_5})]$; *X*-Ray Crystal Structures of $[\mathrm{CoW}\{\mu\text{-}\sigma{:}\eta^3\text{-C}(\mathrm{C_6H_4Me}\text{-}4)\mathrm{C(Me)C(Me)H}\}(\mu\text{-CO})(\mathrm{CO})(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$ and $[\mathrm{PtW}\{\mu\text{-CH}(\mathrm{C_6H_4Me}\text{-}4)\}(\mu\text{-CO})(\mathrm{PMe_3})_2(\eta\text{-MeC_2Me})(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$ †

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The compound $[\mathrm{CoW}\{\mu\text{-}\sigma{:}\eta^3\text{-CH}(\mathrm{C_6H_4Me}\text{-}4)\}(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$ reacts with $\mathrm{PMe_2Ph}$ to form $[\mathrm{CoW}\{\mu\text{-CH}(\mathrm{C_6H_4Me}\text{-}4)\}(\mathrm{CO})_3(\mathrm{PMe_2Ph})(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, as a mixture of diastereoisomers, and with MeC≡CMe to give the complex $[\mathrm{CoW}\{\mu\text{-}\sigma{:}\eta^3\text{-C}(\mathrm{C_6H_4Me}\text{-}4)\mathrm{C(Me)C(Me)H}\}(\mu\text{-CO})(\mathrm{CO})(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$. The structure of the latter has been established by an *X*-ray diffraction study. The Co–W bond [2.552(1) Å] is asymmetrically bridged by a CO ligand [W–C–O 150.7(6), Co–C–O 130.1(6)°] and is also spanned by the $\mathrm{C(C_6H_4Me\text{-}4)C(Me)C(Me)H}$ group *via* what may be regarded as an η^3-allylic attachment to the tungsten and a σ bond of the $\mathrm{C(C_6H_4Me\text{-}4)}$ end of the chain to the cobalt. The tungsten atom carries a terminal CO ligand and the $\eta\text{-}\mathrm{C_5H_5}$ group, and the cobalt atom the $\eta\text{-}\mathrm{C_5Me_5}$ ring. Crystals are monoclinic ($P2_1/c$); the structure has been refined to $R = 0.037$ for 3 678 reflections measured to $2\theta = 50°$ at 298 K. In contrast with the facile reaction at 0—25 °C between $[\mathrm{CoW}\{\mu\text{-}\sigma{:}\eta^3\text{-CH}(\mathrm{C_6H_4Me}\text{-}4)\}(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})(\eta\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$ and MeC≡CMe, the alkyne only slowly reacts with the platinum–tungsten salt $[\mathrm{PtW}\{\mu\text{-}\sigma{:}\eta^3\text{-CH}(\mathrm{C_6H_4Me}\text{-}4)\}(\mathrm{CO})_2(\mathrm{PMe_3})_2(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$ to give $[\mathrm{PtW}\{\mu\text{-CH}(\mathrm{C_6H_4Me}\text{-}4)\}(\mu\text{-CO})(\mathrm{PMe_3})_2(\eta\text{-MeC_2Me})(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$, a compound in which the but-2-yne molecule is η^2-co-ordinated to the tungsten centre. This was confirmed by an *X*-ray diffraction study. The Pt–W bond [2.771(1) Å] is asymmetrically bridged by the CO ligand [W–C–O 151.9(15), Pt–C–O 124.3(13)°] and symmetrically bridged by the tolylmethylene group [μ-C–W 2.101(18), μ-C–Pt 2.110(15) Å]. In addition to the $\mathrm{MeC_2Me}$ ligand, the tungsten atom is bonded to the $\eta\text{-}\mathrm{C_5H_5}$ ring, while the platinum atom is in an essentially planar environment ligated by the two $\mathrm{PMe_3}$ groups, the tungsten, the asymmetrically bridging CO, and the carbon atom of the tolylmethylene ligand. Crystals are monoclinic ($P2_1/n$); the structure has been refined to $R = 0.063$ for 3 798 reflections measured to $2\theta = 50°$ at 298 K. The alkyne complexes $[\mathrm{PtW}\{\mu\text{-CH}(\mathrm{C_6H_4Me}\text{-}4)\}(\mu\text{-CO})(\mathrm{PR_3})_2(\eta\text{-R'C_2R'})(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$ ($\mathrm{PR_3} = \mathrm{PMe_2Ph}$, R′ = Me; $\mathrm{PR_3} = \mathrm{PMe_2Ph}$ or $\mathrm{PMePh_2}$, R′ = Ph) have also been prepared. The n.m.r. spectra of the new tungsten–cobalt and –platinum compounds are reported and discussed in relation to their structures, and the dynamic behaviour of some of the species in solution.

We have reported[2] the synthesis of the salts (1) by protonation ($\mathrm{HBF_4{\cdot}Et_2O}$) of the neutral bimetal compounds $[\mathrm{MW}(\mu\text{-CC_6H_4Me\text{-}4})(\mathrm{CO})_2\mathrm{L}_n(\eta\text{-}\mathrm{C_5H_5})]$ $[\mathrm{ML}_n = \mathrm{Pt(PR_3)_2}$ ($\mathrm{PR_3} = \mathrm{PMe_3}$, $\mathrm{PMe_2Ph}$, or $\mathrm{PMePh_2}$) or $\mathrm{Co(CO)}(\eta\text{-}\mathrm{C_5Me_5})]$.[3] In the preceding paper[1] we have described reactions of the platinum–tungsten salts with a variety of nucleophilic reagents. In this paper we report on the reactivity of the cobalt-tungsten compound (1a),[4] and give an account of some further chemistry of the species (1b)—(1d).

Results and Discussion

Treatment of compound (1a) with $\mathrm{PMe_2Ph}$ in dichloromethane affords complex (2), some physical data for which are given in Table 1. In the formation of (2) then η^2 bonding of the $\mathrm{C_6H_4}$ group to tungsten in (1a) has been displaced. Similar reactions occur between the salts (1b)—(1d) and tertiary phosphines.[1] However, compound (2) differs from its platinum–tungsten analogues in being formed as a mixture of two diastereoisomers, exchange between which is fast at room temperature but ceases at −50 °C. This was established from the n.m.r. spectra (^{1}H, ^{13}C-{^{1}H}, and ^{31}P-{^{1}H}).

The ^{31}P-{^{1}H} n.m.r. spectrum measured at room temperature consists of a very broad signal at δ −9.4 p.p.m. [relative to 85% $\mathrm{H_3PO_4}$ (external)]. At −50 °C, however, two resonances are observed of relative intensity 2 : 3 at δ −12.3 [*J*(WP) 115 Hz] and −3.8 p.p.m. [*J*(WP) 134 Hz], respectively. The appearance of ^{183}W–^{31}P coupling in these signals confirms that the $\mathrm{PMe_2Ph}$ group is bonded to tungsten.

The ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra of (2) also vary with temperature. Thus at 25 °C the ^{1}H spectrum shows only broad signals for the $\eta\text{-}\mathrm{C_5H_5}$ and μ-CH groups. In contrast, at −50 °C two resonances for both these groups are seen, the two sets of peaks being of relative intensity 2 : 3, (A) : (B) (Table 2). The resonances for the μ-C*H* groups in the two isomers appear as doublets, due to ^{31}P–^{1}H coupling, and are characteristic.[1] Signals due to the μ-*C*H groups of two species are also clearly seen in the ^{13}C-{^{1}H} spectrum measured at −50 °C. Each isomer also gives rise to three CO ligand signals, which may be assigned (Table 2) on the basis of their chemical shifts.[3,5]

The dynamic process occurring within (2) in solution could be explained either by rotation of the $\mathrm{W(CO)(PMe_2Ph)}$-

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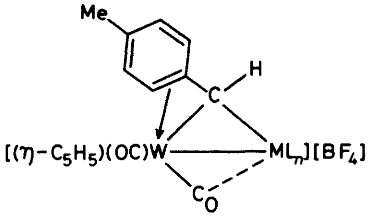
† μ-Carbonyl-2′-carbonyl-2′-η-cyclopentadienyl-μ-[σ : 1—3-η-2-methyl-1-*p*-tolylbut-2-enylidene-C^1(Co)C^{1-3}(W)]-1′-(η-pentamethylcyclopentadienyl)cobalt-tungsten(*Co–W*) tetrafluoroborate and 2′-2—3-η-but-2-yne-μ-carbonyl-2′-η-cyclopentadienyl-μ-*p*-tolylmethylene-1′,1′-bis(trimethylphosphine)platinumtungsten-(*Pt–W*) tetrafluoroborate.

Supplementary data available (No. SUP 23915, 55 pp.): H-atom co-ordinates, thermal parameters, structure factors, full bond length and angle data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

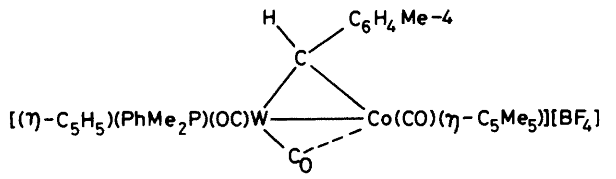
Table 1. Analytical [a] and physical data for the tungsten–cobalt and –platinum complexes

	Complex	M.p. [b] (θ_c/°C)	Colour	Yield (%)	ν(CO)[c]/cm^{-1}	Analysis (%)	
						C	H
(2)	$[CoW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_3(PMe_2Ph)(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)][BF_4]$		Green	86	2 001vs, 1 933vs, 1 795vs	44.9 (44.7)	4.6 (4.3)
(4)	$[CoW\{\mu\text{-}\sigma:\eta^3\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)H\}(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)][BF_4]$		Green	90	1 969vs, 1 797s	[d] 45.4 (45.0)	4.3 (4.5)
(5a)	$[PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)(PMe_3)_2(\eta\text{-}MeC_2Me)(\eta\text{-}C_5H_5)][BF_4]$	138—140	Yellow	50	1 766s	33.4 (33.1)	4.5 (4.3)
(5b)	$[PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)(PMe_2Ph)_2(\eta\text{-}MeC_2Me)(\eta\text{-}C_5H_5)][BF_4]$	72—76	Orange	80	1 777s	40.7 (41.1)	4.6 (4.0)
(5c)	$[PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)(PMe_2Ph)_2(\eta\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)][BF_4]$	106—110	Orange	85	1 777s	47.4 (47.3)	4.1 (4.0)
(5d)	$[PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)(PMePh_2)_2(\eta\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)][BF_4]$	118—122	Orange-brown	90	1 781s	52.6 (52.2)	4.1 (3.9)

[a] Calculated values are given in parentheses. [b] With decomposition. [c] In CH_2Cl_2. [d] Crystallises with half a molecule of CH_2Cl_2.



	ML_n
(1a)	$Co(CO)(\eta\text{-}C_5Me_5)$
(1b)	$Pt(PMe_3)_2$
(1c)	$Pt(PMe_2Ph)_2$
(1d)	$Pt(PMePh_2)_2$



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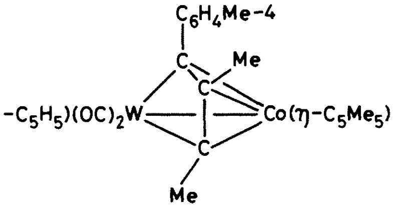

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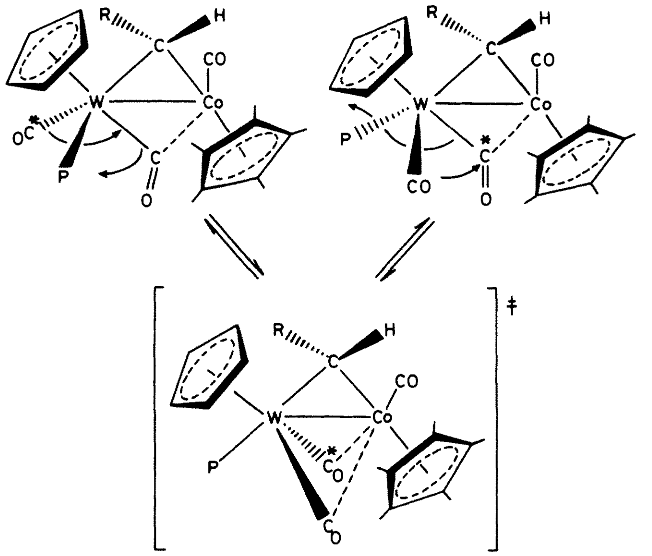


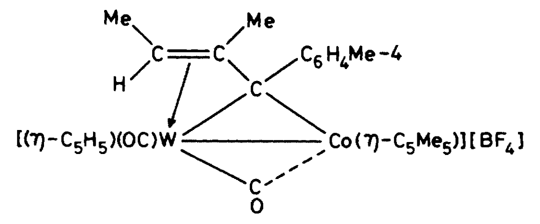
Scheme 1.

(η-C_5H_5) fragment, similar to that invoked to explain the fluxionality of the diastereoisomers of $[PtW(\mu\text{-}H)\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$,[1] or alternatively by a pair-wise carbonyl exchange mechanism as shown in Scheme 1.

Interestingly, the i.r. spectrum of (2) (Table 1) shows only three absorptions for the CO groups instead of the six which might have been expected for the two diastereoisomers. However, due to the insolubility of (2) in hydrocarbons, the spectrum was measured in dichloromethane, in which peaks are broad. Moreover, in both diastereoisomers the CO ligands are *transoid* to similar groups so that the absorptions may be very similar. The band at lowest frequency (1 795 cm^{-1}) is due to the strongly semi-bridging carbonyl ligand.

The platinum–tungsten compounds (1b) and (1c) react with $K[BH(CHMeEt)_3]$ to afford hydrido-bridged complexes $[PtW(\mu\text{-}H)\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ (PR_3 = PMe_3 or PMe_2Ph).[1] In contrast, treatment of (1a) with $K[BH(CHMeEt)_3]$ results in facile deprotonation to give $[CoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$. The cobalt compound (1a) also differs from the platinum complex (1b) in its reactivity pattern with but-2-yne, in the manner now described.

We have previously reported [6] that the compound $[CoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$, the precursor of (1a), reacts with but-2-yne in toluene to give complex (3). Formation of (3) in this manner, however, requires heating the reactants at *ca.* 100 °C for several hours. In contrast, (1a) in dichloromethane reacts rapidly with MeC≡CMe at 0—25 °C. The bright green crystalline product (4) was characterised by microanalysis and spectroscopy, but discussion of the



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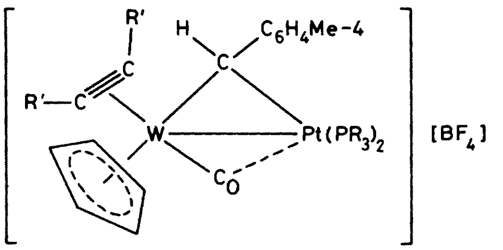


	PR_3	R'
(5a)	PMe_3	Me
(5b)	PMe_2Ph	Me
(5c)	PMe_2Ph	Ph
(5d)	$PMePh_2$	Ph

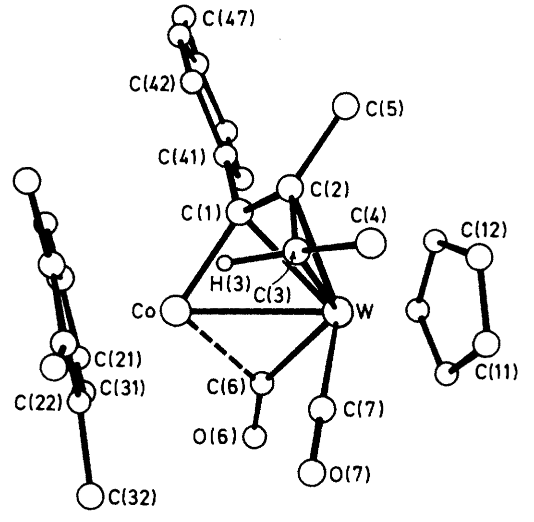
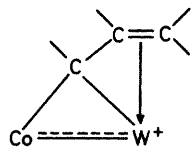
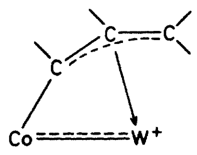


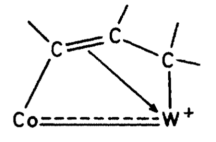
Figure 1. Structure of the cation of [CoW{μ-σ:η^3-C(C$_6$H$_4$Me-4)C(Me)C(Me)H}(μ-CO)(CO)(η-C$_5$H$_5$)(η-C$_5$Me$_5$)][BF$_4$] (4), showing the crystallographic numbering



(i)



(ii)



(iii)

spectral properties is deferred until the results of an *X*-ray diffraction study are described.

The structure of the cation of (4) is shown in Figure 1, and the salient parameters for the species are given in Table 3. The cobalt–tungsten bond is bridged by the C(C$_6$H$_4$Me-4)–C(Me)=C(Me)H group such that the three carbon atoms of the chain are η^3-attached to tungsten whilst C(1) is σ-bound to cobalt. The Co–W bond is also asymmetrically bridged by a carbonyl ligand, C(6)O(6) [W–C(6) 2.014(7), Co–C(6) 1.991(8) Å, and W–C(6)–O(6) 150.7(6)°], and the existence of a ν(CO) band at 1 797 cm^{-1} in the i.r. (Table 1) confirms that this bridging carbonyl is also present in solution. In addition, the tungsten atom carries a terminal carbonyl ligand [W–C(7)–O(7) 179.0(8)°] and a cyclopentadienyl ring, whilst the cobalt atom is co-ordinated to the pentamethylcyclopentadienyl ligand. The two methyl groups C(4) and C(5) are mutually *cis*.

Interest centres on the bonding associated with the C(1)-C(2)C(3) chain which is similar to that found in the C$_3$-bridging ligands in the homonuclear di-iron and diruthenium complexes [Fe$_2${μ-σ:η^3-C(CO$_2$Me)C(CO$_2$Me)C(Me)H}(μ-CO)(CO)(η-C$_5$H$_5$)$_2$] and [Ru$_2${μ-σ:η^3-C(Me)C(Me)CH$_2$}(μ-CO)(CO)(η-C$_5$H$_5$)$_2$].[7] In these species, as in (4), there are equally satisfactory alternative representations for the bridge bonding: for (4), structures (i)—(iii). The *X*-ray data can be interpreted as supporting all three representations. The C(1)–W separation [2.225(7) Å] is at the shorter end of the range [2.198(8)—2.49(3) Å] found for μ-C–W bonds in dimetallacyclopropane ring systems.[8,9] The C(1)–Co distance [1.939(6) Å] is as expected for a single bond, and is identical with that found [1.939(8) Å] in [CoW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)].[3] The C(2)–W [2.352(7) Å] and C(3)–W [2.377(8) Å] separations are significantly longer than C(1)–W, suggesting an η^2-C(2)–C(3) interaction with tungsten. Thus these data support the 'vinylcarbene' formulation (i). Alternatively, the near equivalence of C(1)–C(2) [1.436(9) Å] and C(2)–C(3) [1.410(10) Å], which are between carbon–carbon single and double bonds, might be taken to indicate allylic delocalisation within the C$_3$ chain [see (ii)]. Such delocalisation is evident in the bridge system of [FeW{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(CO)$_5$(η-C$_5$H$_5$)].[6] However, unlike the latter the substituent carbon atoms attached to the C$_3$ chain in (4) are not coplanar. The plane defined by C(2),C(3),C(4),H(3) is at an angle of 23.5° to that defined by C(1),C(2),C(5),C(3), and the latter plane is at an angle of 10° to that defined by C(41),C(1),C(2),C(5). Thus in (4), as in [Ru$_2${μ-σ:η^3-C(Me)C(Me)CH$_2$}(μ-CO)(CO)(η-C$_5$H$_5$)$_2$],[7] there is more 'twist' about the C(2)–C(3) bond than C(1)–C(2), and this suggests a possible bonding contribution from structure (iii).

Complex (4) has 32 valence electrons and is, therefore, electronically unsaturated. If the cation had a fully bridging CO group and a Co–W double bond, both metal atoms could achieve 18-electron configurations. Although few data are available for comparison, the metal–metal distance [2.552(1) Å] (Table 3) is substantially shorter than that observed in [CoW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] [2.758(1) Å],[3] or in the trimetal cluster compound [Co$_2$W(μ$_3$-CC$_6$H$_4$Me-4)(CO)$_8$(η-C$_5$H$_5$)] [2.672(1) Å],[10] and this is consistent with some degree of multiple metal–metal bonding in (4). Evidently there is considerable electron delocalisation within the bridging systems in this compound.

Elucidation of the structure of (4) in the solid state allows the various ^{1}H and ^{13}C-{^{1}H} n.m.r. signals to be assigned (Table 2). An interesting feature of the spectra is the non-equivalence of the ^{1}H and ^{13}C nuclei in the C$_6$H$_4$ ring, sug-

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

Complex	^1H (δ)	^{13}C (δ) [b]
(2) [c,d] (A)[e]	1.60 (s, 15 H, C_5Me_5), 2.18 (m, 6 H, MeP), 2.40 (s, 3 H, Me-4), 4.90 (s, 5 H, C_5H_5), 6.75—7.85 (m, 9 H, C_6H_4, Ph), 9.91 [d, 1 H, μ-CH, *J*(PH) 17]	244.5 (μ-CO), 229.5 [d, WCO, *J*(PC) 21], 222.4 (μ-C), 200.3 (CoCO), 153.6—129.4 (C_6H_4, Ph), 103.4 (C_5Me_5), 102.3 (C_5H_5), 21.3 (Me-4), 18.6—14.0 (MeP), 9.3 ($C_5\mathit{Me}_5$)
(B)[e]	1.65 (s, 15 H, C_5Me_5), 2.18 (m, 6 H, MeP), 2.40 (s, 3 H, Me-4), 5.50 (s, 5 H, C_5H_5), 6.75—7.85 (m, 9 H, C_6H_4, Ph), 9.15 [d, 1 H, μ-CH, *J*(PH) 9]	243.0 (μ-CO), 228.5 [d, WCO, *J*(PC) 27], 221.7 (μ-C), 199.0 (CoCO), 153.6—129.4 (C_6H_4, Ph), 103.1 (C_5Me_5), 98.9 (C_5H_5), 21.3 (Me-4), 18.6—14.0 (MeP), 9.3 ($C_5\mathit{Me}_5$)
(4) [c]	0.97 (s, 15 H, C_5Me_5), 2.09 [d, 3 H, μ-CH*Me*, *J*(HH) 6], 2.32 (s, 3 H, =CMe), 2.56 (s, 3 H, Me-4), 3.02 [q, 1 H, C*H*Me, *J*(HH) 6], 4.62 (m, 1 H, C_6H_4), 5.32 (s, 5 H, C_5H_5), 6.97 (m, 1 H, C_6H_4), 7.45 (m, 1 H, C_6H_4), 8.20 (m, 1 H, C_6H_4)	253.7 [μ-CO, *J*(WC) 129], 206.1 [CO, *J*(WC) 167], 192.3 (μ-C), 145.2 [$C^1(C_6H_4)$], 140.6, 138.0, 130.3, 128.8, 125.2 (C_6H_4), 109.0 (*C*Me), 95.8 (C_5Me_5), 95.7 (C_5H_5), 58.5 (*C*HMe), 21.9 (Me-4), 21.4, 17.3 (C*Me*), 8.6 ($C_5\mathit{Me}_5$)
(5a) [f,g]	1.30 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 32], 1.85 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 29], 2.31 (s, 3 H, Me-4), 2.80 (s, 6 H, MeC_2Me), 4.75 [d of d, 1 H, μ-CH, *J*(PH) 11, 3], 5.38 (s, 5 H, C_5H_5), 6.47 [d, 1 H, C_6H_4, *J*(HH) 8], 6.81 [d, 1 H, C_6H_4, *J*(HH) 8], 6.99 [d, 1 H, C_6H_4, *J*(HH) 8], 7.07 [d, 1 H, C_6H_4, *J*(HH) 8]	266.0 [d, CO, *J*(PC) 44], 193.4 ($\mathit{C}{\equiv}C$), 188.3 [$C{\equiv}\mathit{C}$, *J*(WC) 52], 153.2 [$C^1(C_6H_4)$], 133.5 [$C^4(C_6H_4)$], 133.3 [d, μ-CH, *J*(PC) 48, *J*(PtC) 364], 127.6, 127.3, 125.3 (C_6H_4), 97.9 (C_5H_5), 21.1 (Me-4), 19.9, 18.8 ($\mathit{Me}C_2\mathit{Me}$), 15.2 [d, MeP, *J*(PC) 33, *J*(PtC) 41], 14.2 [d, MeP, *J*(PC) 31, *J*(PtC) 34]
(5b) [h,i]	0.95 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 30], 1.16 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 32], 1.60 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 29], 1.86 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 29], 2.37 (s, 3 H, Me-4), 2.70 (s, 3 H, MeC_2Me), 3.15 (s, 3 H, MeC_2Me), 4.66 [d of d, 1 H, μ-CH, *J*(PH) 10, 3], 5.36 (s, 5 H, C_5H_5), 6.61 [d, 1 H, C_6H_4, *J*(HH) 8], 6.66 [d, 1 H, C_6H_4, *J*(HH) 8], 7.05 [d, 1 H, C_6H_4, *J*(HH) 8], 7.15 [d, 1 H, C_6H_4, *J*(HH) 8], 7.2—7.6 (m, 10 H, Ph)	262.2 [d, CO, *J*(PC) 34], 193.4 ($\mathit{C}{\equiv}C$), 189.7 ($C{\equiv}\mathit{C}$), 153.5 [$C^1(C_6H_4)$], 140—126 (C_6H_4, Ph), 98.8 (C_5H_5), 22.0 ($\mathit{Me}C_2Me$), 20.9 (Me-4), 19.8 ($MeC_2\mathit{Me}$), 15.6 [d, MeP, *J*(PC) 31], 15.3 [d, MeP, *J*(PC) 32], 12.8 [d, MeP, *J*(PC) 36, *J*(PtC) 30], 12.1 [d, MeP, *J*(PC) 32, *J*(PtC) 34]
(5c) [f,j]	0.91 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 31], 0.99 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 32], 1.60 [d, 3 H, MeP, *J*(PH) 10], 1.89 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 30], 2.39 (s, 3 H, Me-4), 5.15 [d of d, 1 H, μ-CH, *J*(PH) 11, 3], 5.45 (s, 5 H, C_5H_5), 6.5—7.7 (m, 24 H, C_6H_4, Ph)	266.0 [d, CO, *J*(PC) 46], 195.3 [$\mathit{C}{\equiv}C$, *J*(WC) 31], 192.1 [$C{\equiv}\mathit{C}$, *J*(WC) 56], 153.7 [$C^1(C_6H_4)$], 138.5 [d, μ-CH, *J*(PC) 48, *J*(PtC) 369], 138—123 (C_6H_4, Ph), 99.6 (C_5H_5), 21.1 (Me-4), 15.8 [d, MeP, *J*(PC) 24, *J*(PtC) 24], 15.5 [d, MeP, *J*(PC) 20], 12.5 [d, MeP, *J*(PC) 34], 12.3 [d, MeP, *J*(PC) 31, *J*(PtC) 30]
(5d) [c,k]	0.91 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 31], 2.18 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 30], 2.42 (s, 3 H, Me-4), 4.49 [d of d, 1 H, μ-CH, *J*(PH) 13, 3, *J*(PtH) 23], 5.38 (s, 5 H, C_5H_5), 5.8—7.8 (m, 34 H, C_6H_4, Ph)	192.9 $\mathit{C}{\equiv}C$, 190.4 ($C{\equiv}\mathit{C}$), 151.9 [$C^1(C_6H_4)$], 137.3 [d, μ-CH, *J*(PC) 59, *J*(PtC) 516], 137—122 (C_6H_4, Ph), 99.8 (C_5H_5), 21.4 (Me-4), 7.8 [d, MeP, *J*(PC) 29], 6.5 [d, MeP, *J*(PC) 32]

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements at ambient temperature unless otherwise stated. [b] Hydrogen-1 decoupled, to high frequency of $SiMe_4$. [c] Hydrogen-1 spectrum in CD_2Cl_2, ^{13}C spectrum in CD_2Cl_2–CH_2Cl_2. [d] Spectra measured at −50 °C. [e] (A) and (B) refer to isomers, see text. [f] Hydrogen-1 spectrum in $CDCl_3$, ^{13}C spectrum in CD_2Cl_2–CH_2Cl_2. [g] Hydrogen-1 spectrum measured at 55 °C, ^{13}C spectrum at −60 °C. [h] Spectra measured in $CDCl_3$. [i] Hydrogen-1 spectrum measured at −35 °C, ^{13}C spectrum at −45 °C. [j] Carbon-13 spectrum measured at −50 °C. [k] Carbon-13 spectrum measured at −80 °C.

gesting that rotation of the tolyl group about the C(1)–C(41) bond is restricted. Consideration of a space-filling diagram suggests that free rotation about the μ-C–C_6H_4Me-4 bond would be severely hindered by the proximity of the bulky η-C_5Me_5 ligand. In the solid state the nearly parallel orientation of these rings minimises contact, but as a consequence of this arrangement the Me groups of the C_5Me_5 group are constrained to rotate in the face of the C_6H_4 ring while concomitantly H(42) lies towards the face of the pentamethylcyclopentadienyl ring. In agreement with these constraints, the ^1H n.m.r. spectrum of (4) reveals an unusual up-field shift both for the protons of the η-C_5Me_5 ligand (δ 0.97) and for one of the protons of the C_6H_4 group (δ 4.62). A somewhat similar situation applies in the chemistry of the cluster compound [$MoRh_3(\mu_3\text{-}CO)_3(CO)_3(PPh_3)_3(\eta\text{-}C_5H_5)$] [11] where *X*-ray diffraction results reveal a situation in which the protons of the η-C_5H_5 group are directed into C_6H_5 rings, while in the ^1H n.m.r. spectrum they resonate at δ 3.80, significantly upfield from their usual position (δ *ca.* 5).

During the course of studies on compound (4) it was found that it could be prepared in high yield by protonation of (3). The high reactivity of (1a) towards $MeC{\equiv}CMe$, compared with [$CoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)$], is presumably due to the easy transformation of the μ-$CH(C_6H_4$-Me-4) group in (1a) from an η^3- to a σ-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. These processes are discussed more fully below after some results on the related platinum–tungsten system have been described.

In contrast with the ready formation of (4) from (1a), the salt (1b) does not readily react with MeC_2Me. Initial experiments revealed that reaction proceeded over a period of several hours to afford a mixture of products as well as unreacted starting material. One product proved to be the tricarbonyl species [$PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_3(PMe_3)_2(\eta\text{-}C_5H_5)$][$BF_4$], described previously,[1] and which can only have been generated by release of CO in the reaction of (1b) with MeC_2Me. Subsequent reactions were, therefore, carried out with a nitrogen purge to remove liberated CO, however, minor amounts of [$PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_3(PMe_3)_2(\eta\text{-}C_5H_5)$][$BF_4$] were still present in the reaction mixture, as well as some unreacted (1b). These two species could be removed from a major product (5a) by treating the mixture with NEt_4Br, thus generating [$PtWBr\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)$].[1] The latter could be extracted with diethyl ether, and excess NEt_4Br with water. Remarkably the new salt (5a) survived this treatment and could be isolated in good yield (Table 1). The compounds (5b)—(5d) were similarly prepared from (1c) or (1d) using MeC_2Me or PhC_2Ph.

Table 3. Selected internuclear distances (Å) and angles (°), with estimated standard deviations in parentheses, for (4)

(*a*) Distances

W–Co	2.552(1)	W–C(1)	2.225(7)	Co–C(22)	2.087(5)	Co–C(23)	2.114(5)
W–C(2)	2.352(7)	W–C(3)	2.377(8)	Co–C(24)	2.113(5)	Co–C(25)	2.084(5)
W–C(6)	2.014(7)	W–C(7)	1.981(8)	C(1)–C(2)	1.436(9)	C(1)–C(41)	1.500(7)
W–C(11)	2.327(6)	W–C(12)	2.356(7)	C(2)–C(3)	1.410(10)	C(2)–C(5)	1.534(10)
W–C(13)	2.364(7)	W–C(14)	2.341(7)	C(3)–C(4)	1.520(11)	C(3)–H(3)	0.896(64)
W–C(15)	2.317(7)	Co–C(1)	1.939(6)	C(6)–O(6)	1.195(9)	C(7)–O(7)	1.158(11)
Co–C(6)	1.991(8)	Co–C(21)	2.068(5)	B–F (mean)	1.332(16)		

(*b*) Angles

Co–W–C(1)	47.3(2)	Co–W–C(2)	74.9(2)	Co–C(1)–C(2)	123.8(5)	W–C(1)–C(41)	114.0(4)
C(1)–W–C(2)	36.4(2)	Co–W–C(3)	80.7(2)	C(2)–C(1)–C(41)	121.1(5)	W–C(2)–C(1)	66.9(4)
C(1)–W–C(3)	63.8(2)	C(2)–W–C(3)	34.7(2)	W–C(2)–C(3)	73.6(4)	C(1)–C(2)–C(3)	117.7(6)
Co–W–C(6)	50.0(2)	C(1)–W–C(6)	92.2(3)	W–C(2)–C(5)	124.2(5)	C(1)–C(2)–C(5)	122.2(6)
C(2)–W–C(6)	124.7(3)	C(3)–W–C(6)	123.4(3)	C(3)–C(2)–C(5)	119.7(6)	W–C(3)–C(2)	71.7(4)
Co–W–C(7)	86.2(2)	C(1)–W–C(7)	117.9(3)	W–C(3)–C(4)	122.2(6)	C(2)–C(3)–C(4)	124.2(7)
C(2)–W–C(7)	105.0(3)	C(3)–W–C(7)	71.3(3)	W–C(3)–H(3)	106.9(42)	C(2)–C(3)–H(3)	117.3(39)
C(6)–W–C(7)	78.5(3)	W–Co–C(1)	57.5(2)	C(4)–C(3)–H(3)	109.2(40)	W–C(6)–Co	79.2(3)
W–Co–C(6)	50.8(2)	C(1)–Co–C(6)	102.2(3)	W–C(6)–O(6)	150.7(6)	Co–C(6)–O(6)	130.1(6)
W–C(1)–Co	75.2(2)	W–C(1)–C(2)	76.6(4)	W–C(7)–O(7)	179.0(8)	F–B–F (mean)	109.3

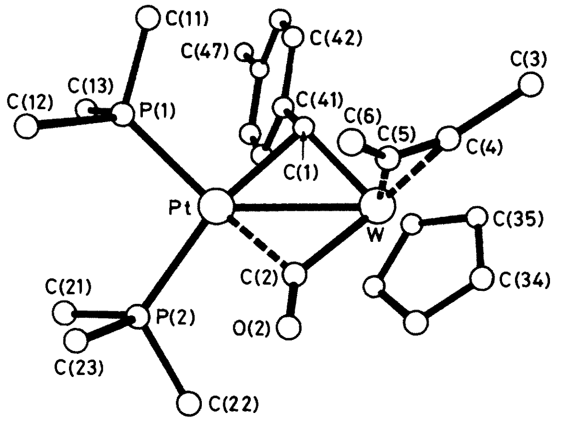


Figure 2. Structure of the cation of [PtW{μ-CH(C_6H_4Me-4)}(μ-CO)-(PMe_3)$_2$(η-MeC_2Me)(η-C_5H_5)][BF_4] (5a), showing the crystallographic numbering

In order to characterise these compounds, an *X*-ray diffraction study was carried out on (5a). The cation is shown in Figure 2, and the results are summarised in Table 4. The MeC_2Me ligand is co-ordinated to the tungsten atom having displaced both a CO group and the η^2-bonded C_6H_4 ring from (1b). The W–C(4) [2.045(22)] and W–C(5) [2.021(22) Å] distances are similar to those between molybdenum and the η^2-MeC_2Me ligand in the compounds [Mo(NCMe)(η-MeC_2Me)$_2$(η-C_5H_5)][BF_4] [mean 2.064(4) Å][12] and [Mo(CO)-(PEt_3)(η-MeC_2Me)(η-C_9H_7)][BF_4] [2.063(4) and 2.030(4) Å].[13]

The geometry of the $\overline{\mathrm{Pt}(\mu\text{-C})\mathrm{W}}$ ring in (5a) is slightly different from that in (1b).[2] The Pt–W bond length [2.771(1) Å] is somewhat shorter, and there is essentially no asymmetry in the position of the alkylidene carbon across the two metals [C(1)–W 2.101(18), C(1)–Pt 2.110(15) Å]. The hydrogen atom bonded to C(1) was not located in the electron-density map but its presence is indicated by the disposition of the tolyl group with respect to the C(1)PtW ring. Moreover, this hydrogen atom is clearly revealed in the ^{1}H n.m.r. spectrum (Table 2) by a resonance at δ 4.75, appearing as a doublet of doublets as a result of coupling with the two non-equivalent ^{31}P nuclei. The semi-bridging CO in (5a) has similar associated angles [W–C(2)–O(2) 152, Pt–C(2)–O(2) 124°] to those found in (1b) (155 and 122°, respectively), but is closer to the platinum atom in (5a) [2.17(2) Å] than in (1b) [2.27(2) Å]. However, in (5a) the asymmetrically bridging carbonyl lies within the plane of co-ordination about the platinum atom, whereas this is not so in (1b). The in-plane bonding of C(2)O(2) is reflected in the similarity of the two P–Pt distances [2.309(6) and 2.316(5) Å], as both PMe_3 ligands lie *trans* to rather similar groups. In related structures the P_2Pt group has measurably different P–Pt lengths, the longer distance being associated with the PR_3 ligand *transoid* to the alkylidene or alkylidyne carbon.[9]

The spectroscopic data for (5a) are in accord with the structure established in the solid state, and the data for (5b)—(5d) are similar. The i.r. spectra of the four compounds show a CO absorption in the semi-bridging region (Table 1). The n.m.r. spectra reveal that (5a)—(5d) undergo dynamic behaviour in solution involving rotation of the alkyne groups. The ^{1}H n.m.r. spectrum of (5a) measured at *ca.* 55 °C showed only one resonance for the ligated MeC_2Me group, but at *ca.* −50 °C two signals were observed [δ 2.45 and 3.12]. The ^{13}C-{^{1}H} n.m.r. spectrum (Table 2) at −60 °C showed two resonances for the non-chemically equivalent contact carbon nuclei of the MeC_2Me ligand (δ 193.4 and 188.3), as well as separate peaks for the methyl groups (δ 19.9 and 18.8). The spectra of (5b)—(5d) were broadly similar, and from coalescence temperatures, $\Delta G_{T_c}^{\ddagger}$ for alkyne rotation is estimated at *ca.* 60 kJ mol^{-1}. Interestingly, in the spectra of (5) only the signals due to the alkyne ligands vary significantly with temperature. The chemical shift for the CO ligand (*ca.* 265 p.p.m.) is relatively deshielded, as expected for a semi-bridging carbonyl.

From the structure established for (5a) (Figure 2) it would appear that there is a 16-electron count at tungsten, if the but-2-yne ligand is considered to be a two-electron donor. However, the chemical shifts of the ligated carbon nuclei in the ^{13}C-{^{1}H} spectra of (5) (Table 2) fall in the range of those found in alkyne complexes where the alkyne is believed to function as a four-electron donor,[14] and it is reasonable to assume that this is the situation with the platinum–tungsten salts. The ^{31}P-{^{1}H} and ^{195}Pt-{^{1}H} spectra (Table 5) are as expected for complexes containing *cis*-Pt(PR_3)$_2$ groups. However, an interesting feature is the comparability in size of *J*(PtP), which is presumably due to the PR_3 ligands being *transoid* to groups with a similar *trans* influence. This contrasts

Table 4. Selected internuclear distances (Å) and angles (°), with estimated standard deviations in parentheses, for (5a)

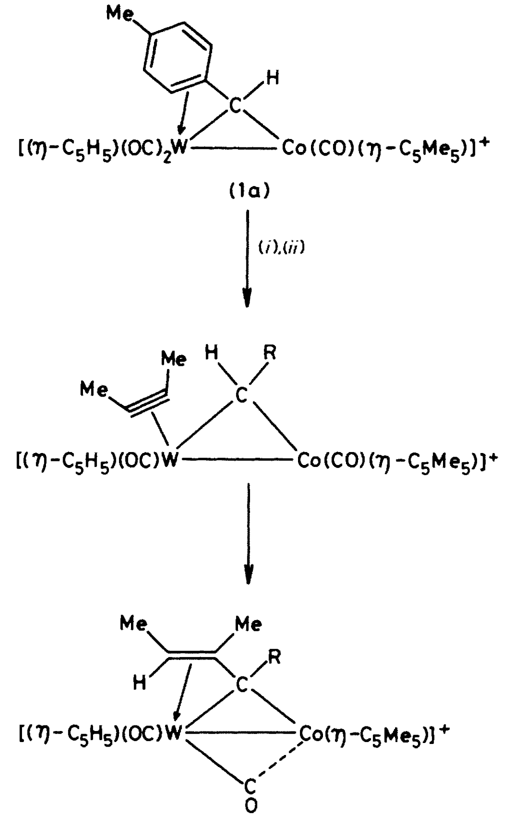
(*a*) Distances

W–Pt	2.771(1)	W–C(1)	2.101(18)	P(1)–C(11)	1.817(24)	P(1)–C(12)	1.860(21)
W–C(2)	1.997(17)	W–C(4)	2.045(22)	P(1)–C(13)	1.853(25)	P(2)–C(21)	1.845(26)
W–C(5)	2.021(22)	W–C(31)	2.388(16)	P(2)–C(22)	1.824(22)	P(2)–C(23)	1.870(22)
W–C(32)	2.395(17)	W–C(33)	2.361(15)	C(1)–C(41)	1.502(22)	C(2)–O(2)	1.208(21)
W–C(34)	2.333(16)	W–C(35)	2.349(15)	C(3)–C(4)	1.626(31)	C(4)–C(5)	1.273(29)
Pt–P(1)	2.309(6)	Pt–P(2)	2.316(5)	C(5)–C(6)	1.500(37)	C(47)–C(44)	1.549(27)
Pt–C(1)	2.110(15)	Pt–C(2)	2.173(19)	B–F *	1.341(29)		

(*b*) Angles

Pt–W–C(1)	49.0(4)	Pt–W–C(2)	51.1(5)	W–Pt–C(2)	45.7(4)	P(1)–Pt–C(2)	153.1(5)
C(1)–W–C(2)	99.2(7)	Pt–W–C(4)	124.8(7)	P(2)–Pt–C(2)	86.3(5)	C(1)–Pt–C(2)	93.6(7)
C(1)–W–C(4)	103.1(8)	C(2)–W–C(4)	111.3(9)	W–C(1)–Pt	82.3(6)	W–C(1)–C(41)	132.4(11)
Pt–W–C(5)	94.5(6)	C(1)–W–C(5)	99.0(8)	Pt–C(1)–C(41)	114.4(11)	W–C(2)–Pt	83.2(7)
C(2)–W–C(5)	76.4(8)	C(4)–W–C(5)	36.5(8)	W–C(2)–O(2)	151.9(15)	Pt–C(2)–O(2)	124.3(13)
W–Pt–P(1)	134.9(1)	W–Pt–P(2)	125.5(1)	W–C(4)–C(5)	70.7(14)	C(3)–C(4)–C(5)	150.5(23)
P(1)–Pt–P(2)	99.5(2)	W–Pt–C(1)	48.7(5)	W–C(5)–C(4)	72.8(14)	W–C(5)–C(6)	148.8(16)
P(1)–Pt–C(1)	89.0(5)	P(2)–Pt–C(1)	161.5(5)	C(4)–C(5)–C(6)	138.4(22)	F–B–F *	109.5

* Rigid group with B–F fixed at 1.340(1) Å and F–B–F at 109.5°.



Scheme 2. R = C_6H_4Me-4; (*i*) + MeC≡CMe, (*ii*) –CO

with the situation in related platinum–tungsten compounds.[1,8]

Complex (1b) did not react with $CF_3C_2CF_3$ or $Me_3SiC_2SiMe_3$, alkynes with electron-withdrawing substituents, nor did any reaction occur with ethylene. Reaction of (1b) with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$, isolobal with PhC_2Ph, afforded in the absence of a nitrogen purge the tricarbonyl complex $[PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_3(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$[1] and the bridged alkyne complex $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$. Evidently, the latter is formed by dimerisation of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$; a process which does not occur by heating the tolylmethylidyne tungsten compound alone, but is catalysed by metal co-ordination.[15]

It is interesting to contrast the structure of (4) with that of (5), which suggests that the former complex may be produced *via* an intermediate with a structure similar to (5a) (Scheme 2). Subsequent carbon–carbon bond formation between the tolylmethylene group and the η^2-co-ordinated but-2-yne with concomitant or subsequent hydrogen migration could then give the observed product (4) by a mechanism similar to that proposed by Knox and co-workers [7,16] to account for the photoinduced insertion of alkynes into di-iron– or diruthenium–μ-carbene complexes.

Experimental

The techniques and instrumentation employed in this work have been described earlier, as have the preparations of the salts (1).[2] Light petroleum refers to that fraction of b.p. 40—60 °C. Analytical data for the new compounds are given in Table 1.

Reactions of $[CoW\{\mu\text{-}\sigma\text{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)][BF_4]$.—(*a*) *With* PMe_2Ph. Compound (1a) (0.50 g, 0.70 mmol) in dichloromethane (20 cm^3) at 0 °C was treated with PMe_2Ph (0.097 g, 0.70 mmol). Solvent was evaporated *in vacuo* to afford, after washing with light petroleum, green *microcrystals* of $[CoW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_3(PMe_2Ph)(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)][BF_4]$ (2) (0.51 g).

(*b*) *With* MeC≡CMe. A dichloromethane (20 cm^3) solution of (1a) (0.29 g, 0.41 mmol) at 0 °C was treated with but-2-yne (0.41 mmol) at room temperature. After 20 min, the solvent was removed *in vacuo*, and the residue crystallised from dichloromethane–light petroleum to give green *crystals* of $[CoW\{\mu\text{-}\sigma\text{:}\eta^3\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)H\}(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)][BF_4]$ (4) (0.27 g, 90%).

Reactions of the Compounds $[PtW\{\mu\text{-}\sigma\text{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)][BF_4]$ *with Alkynes*.—A vigorously nitrogen purged dichloromethane (100 cm^3) solution of (1b) (0.42 g, 0.50 mmol) was treated with an excess of but-2-yne (2.0 cm^3, 26.0 mmol). The volatile nature of the alkyne and the solvent necessitated attaching a reflux condenser maintained at *ca.* –25 °C to the top of the Schlenk tube. After 18 h, NEt_4Br (0.11 g, 0.50 mmol) was added, solvent was removed *in vacuo*, and the residue exhaustively washed with diethyl ether (25 × 20

Table 5. Phosphorus-31 and platinum-195 n.m.r. data [a] for the platinum–tungsten complexes

Compound	^{31}P [b] (δ)	^{195}Pt [c] (δ)
(5a) [d]	−10.8 [d, *J*(PP) 8, *J*(PtP) 3 144, *J*(WP) 10]	−706 [d of d, *J*(PPt) 3 258, 3 144]
	−17.4 [d, *J*(PP) 8, *J*(PtP) 3 258, *J*(WP) 10]	
(5b)	−1.2 [d, *J*(PP) 8, *J*(PtP) 3 209]	−671 [d of d, *J*(PPt) 3 363, 3 209]
	−5.5 [d, *J*(PP) 8, *J*(PtP) 3 363]	
(5c)	−2.4 [d, *J*(PP) 10, *J*(PtP) 3 258, *J*(WP) 27]	−634 [d, of d, *J*(PPt) 3 320, 3 258]
	−7.2 [d, *J*(PP) 10, *J*(PtP) 3 320, *J*(WP) 24]	
(5d)	11.2 [d, *J*(PP) 4, *J*(PtP) 3 379]	−603 [d of d, *J*(PPt) 3 392, 3 379]
	4.5 [d, *J*(PP) 4, *J*(PtP) 3 392, *J*(WP) 27]	

[a] Hydrogen-1 decoupled, chemical shifts in p.p.m., coupling constants in Hz; spectra measured in $CDCl_3$ unless otherwise stated. [b] Chemical shifts to high frequency of 85% H_3PO_4 (external). [c] Chemical shifts to high frequency of $\Xi(^{195}Pt) = 21.4$ MHz. [d] Measured in CD_2Cl_2.

Table 6. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) for (4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	2 274(1)	1 594(1)	954(1)	C(24)	5 313	3 531	1 338
Co	4 200(1)	2 483(1)	1 117(1)	C(25)	5 603	3 102	604
C(1)	2 872(6)	2 728(4)	342(4)	C(31)	6 502(8)	1 669(5)	296(5)
C(2)	2 521(7)	2 209(4)	−355(4)	C(32)	6 398(9)	1 537(5)	2 273(6)
C(3)	3 098(8)	1 444(4)	−385(5)	C(33)	5 407(9)	3 231(5)	2 941(5)
C(4)	2 683(9)	771(5)	−989(6)	C(34)	4 963(8)	4 410(4)	1 401(6)
C(5)	1 445(8)	2 416(5)	−992(5)	C(35)	5 575(8)	3 453(5)	−284(5)
C(6)	3 326(7)	1 833(4)	2 011(5)	C(41) *	2 396(4)	3 580(2)	381(3)
O(6)	3 571(6)	1 732(4)	2 744(3)	C(42)	2 477	4 091	−310
C(7)	3 435(8)	663(5)	996(6)	C(43)	2 063	4 890	−270
O(7)	4 098(7)	111(4)	1 020(5)	C(44)	1 568	5 178	460
C(11) *	708(6)	629(3)	1 008(5)	C(45)	1 487	4 667	1 151
C(12)	245	1 245	451	C(46)	1 901	3 868	1 112
C(13)	159	1 973	918	C(47)	1 081(9)	6 060(6)	495(10)
C(14)	567	1 808	1 763	B	1 238(11)	8 708(8)	2 233(9)
C(15)	907	977	1 819	F(1)	2 052(6)	9 249(4)	2 573(5)
C(21) *	6 006(5)	2 314(3)	850(3)	F(2)	55(6)	8 974(4)	2 228(5)
C(22)	5 965	2 255	1 735	F(3)	1 497(8)	8 665(7)	1 409(6)
C(23)	5 536	3 008	2 037	F(4)	1 408(8)	7 995(6)	2 517(10)

* Pivot atom of a rigid group; other atoms in the group have identical errors on their positional parameters.

Table 7. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) for (5a)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	5 818(1)	8 762(1)	1 125(1)	C(44)	2 495	7 583	2 382
Pt	3 715(1)	7 281(1)	796(1)	C(45)	2 129	8 300	2 017
P(1)	2 861(6)	5 317(5)	969(2)	C(46)	2 862	8 250	1 698
P(2)	2 289(6)	7 787(5)	201(2)	C(47)	1 703(23)	7 624(26)	2 742(7)
C(11)	4 029(27)	4 243(20)	1 267(8)	C(31) *	5 127(17)	10 317(15)	1 590(5)
C(12)	2 358(31)	4 293(21)	498(6)	C(32)	4 448	10 587	1 186
C(13)	1 456(22)	5 323(24)	1 240(7)	C(33)	5 342	10 953	926
C(21)	599(23)	7 483(26)	233(8)	C(34)	6 575	10 909	1 170
C(22)	2 258(21)	9 515(21)	59(6)	C(35)	6 442	10 517	1 580
C(23)	2 587(26)	6 962(22)	−288(6)	B	667(17)	1 208(17)	1 082(5)
C(1)	4 761(19)	7 377(16)	1 404(5)	F(1)	−149(28)	2 147(26)	924(9)
C(2)	5 084(18)	8 453(17)	528(5)	F(2)	333(32)	69(20)	890(6)
O(2)	5 133(12)	8 513(14)	160(3)	F(3)	639(34)	1 084(29)	1 492(4)
C(3)	8 891(22)	8 261(32)	1 612(8)	F(4)	1 847(21)	1 532(32)	1 024(13)
C(4)	7 636(20)	8 062(23)	1 260(7)	C(51) *	7 264(50)	4 403(68)	2 277(16)
C(5)	7 084(21)	7 543(21)	923(6)	C(52)	8 426	5 110	2 317
C(6)	7 374(26)	6 554(31)	610(8)	C(53)	9 169	4 568	2 033
C(41) *	3 959(11)	7 483(12)	1 743(3)	C(54)	8 467	3 525	1 817
C(42)	4 325	6 766	2 108	C(55)	7 290	3 423	1 968
C(43)	3 592	6 817	2 428				

* Pivot atom of a rigid group; other atoms in the group have identical errors on their positional parameters.

cm³). The residue was then dissolved in dichloromethane (20 cm³) and distilled water (5 cm³) added. The mixture was vigorously stirred (10 min) and then allowed to separate. The aqueous layer was decanted, and the dichloromethane solution was passed through an anhydrous Na_2SO_4 plug (5 × 2 cm) to dry it. Removal of solvent *in vacuo*, followed by washing with diethyl ether (5 × 10 cm³) yielded yellow *microcrystals* of $[PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}CO)(PMe_3)_2(\eta\text{-}MeC_2Me)(\eta\text{-}C_5H_5)][BF_4]$ (5a) (0.30 g). The compounds (5b)—(5d) were similarly prepared.

Crystal Structure Determinations.—(*a*) [$CoW\{\mu\text{-}\sigma\text{:}\eta^3\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)H\}(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)$][$BF_4$] (4). Crystals of (4) grow from dichloromethane–diethyl ether as deep green needles. Diffracted intensities were collected at room temperature from a crystal of dimensions *ca.* 0.50 × 0.20 × 0.15 mm with well developed faces of the type <1 0 0>, <0 1 0>, and <0 0 1>. Data were collected on a Nicolet *P*3*m* four-circle diffractometer according to methods described earlier.[17] Of the total 5 920 independent intensities, recorded to $2\theta \leqslant 50°$, 3 678 had $I \geqslant 3\sigma(I)$ where $\sigma(I)$ is the standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure, after correction for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal data for (4). $C_{29}H_{34}BCoF_4O_2W$, $M = 744.2$, monoclinic, $a = 10.793(9)$, $b = 16.503(13)$, $c = 15.957(5)$ Å, $\beta = 93.52(5)°$, $U = 2\,837(4)$ Å^3, $Z = 4$, $D_c = 1.74$ g cm^{-3}, $F(000) = 1\,464$, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 45.2$ cm^{-1}.

(*b*) [$PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}CO)(PMe_3)_2(\eta\text{-}MeC_2Me)(\eta\text{-}C_5H_5)$][$BF_4$]$\cdot C_4H_8O$ (5a). Crystals of (5a) grow from tetrahydrofuran–diethyl ether mixtures as red prisms. Diffracted intensities were collected at room temperature from a crystal of dimensions *ca.* 0.48 × 0.24 × 0.32 mm with well developed faces of the type <1 0 0 >, <0 1 0>, and <0 0 1>. Data were collected as for (4). Of the total 6 346 independent intensities, recorded to $2\theta \leqslant 50°$, 3 798 had $I \geqslant 2.5\sigma(I)$ where $\sigma(I)$ is the standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure, after correction for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal data for (5a). $C_{24}H_{37}BF_4OP_2PtW\cdot C_4H_8O$, $M = 941.4$, monoclinic, $a = 10.647(6)$, $b = 10.214(7)$, $c = 32.494(16)$ Å, $\beta = 99.21(4)$ °, $U = 3\,488(3)$ Å^3, $Z = 4$, $D_c = 1.79$ g cm^{-3}, $F(000) = 1\,808$, space group $P2_1/n$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 73.57$ cm^{-1}.

Structure solutions and refinements for (4) *and* (5a). The structures were solved and all non-hydrogen atoms were located by conventional heavy-atom and difference-Fourier methods. The cyclopentadienyl and aryl ring systems were treated as rigid groups [C–C (C_5H_5) 1.420, C–C (C_6H_4) 1.395 Å]. The allylic hydrogen atom H(3) in (4) was located from an electron-density difference synthesis, and was refined with an isotropic temperature factor. All other hydrogen atoms in (4) were included in calculated positions [C–H 0.96 Å], and chemically related hydrogen atoms were given common refined isotropic temperature factors. For (5a) hydrogen atoms were not included in the refinement. All non-hydrogen atoms were refined with anisotropic temperature factors.

For (4a) no peaks > *ca.* 0.5 e Å^{-3} nor < *ca.* −0.5 e Å^{-3} were observed in the final electron-density difference map, and refinement with the weighting scheme $w = [\sigma^2(F_o) + 0.001|F_o|^2]^{-1}$ led to $R = 0.037$ ($R' = 0.038$). Atom co-ordinates for (4) are listed in Table 6.

In (5a) the BF_4^- anion showed evidence of disorder, but was reasonably approximated by a rigid tetrahedral model, with correspondingly large anisotropic temperature factors for the constituent atoms. The asymmetric unit also contained a severely disordered molecule of tetrahydrofuran (C_4H_8O) (or possibly diethyl ether) for which no geometrically meaningful model could be established. Accordingly the electron density in this region has been approximated by a rigid five-membered tetrahydrofuran ring with correspondingly large isotropic temperature factors for the constituent atoms.

Refinement by blocked-cascade least squares, with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.001|F_o|^2]^{-1}$, gave a satisfactory weight analysis and led to $R = 0.063$ ($R' = 0.065$). The final electron-density difference synthesis showed no peaks > *ca.* 1 e Å^{-3} nor < *ca.* −1 e Å^{-3} except in the region of the metal atoms where peaks of *ca.* 2 e Å^{-3} were observed. Atom co-ordinates are in Table 7. For both compounds, scattering factors were from ref. 18. All computations were carried out on an 'Eclipse' Data General computer with the SHELXTL system of programs.[19]

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