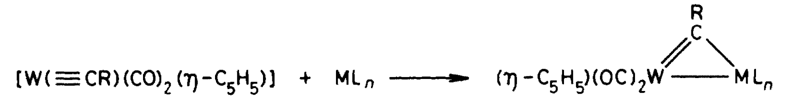
Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 25.[1] Protonation of Tolylmethylidyne Ligands bridging Tungsten–Chromium, –Cobalt, and –Platinum Bonds and the *X*-Ray Crystal Structure of $[PtW\{\mu\text{-}\sigma{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$ *

John C. Jeffery, Jill C. V. Laurie, Iain Moore, Hayat Razay, and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The complex $[Cr(thf)(CO)(NO)(\eta\text{-}C_5H_5)]$ (thf = tetrahydrofuran), generated *in situ* from $[Cr(CO)_2(NO)(\eta\text{-}C_5H_5)]$ by u.v. irradiation, reacts with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ to afford the dimetal compound $[CrW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(NO)(\eta\text{-}C_5H_5)_2]$. Protonation of the latter, and the complexes $[CoW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)]$ and $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ (PR_3 = PMe_3, PMe_2Ph, or $PMePh_2$), with $HBF_4{\cdot}Et_2O$ affords the salts $[MW\{\mu\text{-}\sigma{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(L_n)(\eta\text{-}C_5H_5)][BF_4]$ [ML_n = $Cr(CO)(NO)(\eta\text{-}C_5H_5)$, $Co(CO)(\eta\text{-}C_5Me_5)$, or $Pt(PR_3)_2$]. N.m.r. data (^1H, $^{13}C\text{-}\{^1H\}$, $^{31}P\text{-}\{^1H\}$, and $^{195}Pt\text{-}\{^1H\}$) for the new compounds are reported and discussed. A single-crystal *X*-ray diffraction study was made on the compound $[PtW\{\mu\text{-}\sigma{:}\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$. In this salt the Pt–W bond [2.795(1) Å] is bridged by the $CH(C_6H_4Me\text{-}4)$ group in such a manner that two carbons of the aryl ring form an η^2 attachment to the tungsten so that the $\mu\text{-}CH(C_6H_4Me\text{-}4)$ group as a whole adopts an η^3-bonding mode to the tungsten and σ to the platinum [W–C 2.166(14), 2.406(14), and 2.602(13) Å; Pt–μ-C 2.053(14) Å]. The tungsten atom carries a cyclopentadienyl ligand and a terminally bound CO group, while the remaining carbonyl semi-bridges the metal–metal bond [W–C–O 155.1(14)°]. The platinum atom is in an essentially planar environment, ligated by the two PMe_3 groups, the tungsten atom, and the bridging carbon atom. Crystals are monoclinic (space group $P2_1/c$); the structure has been refined to *R* 0.054 for 3 430 reflections measured to 2θ = 50° at room temperature.

A range of dimetal compounds in which tungsten is bonded to another transition element have been prepared *via* reaction (i) with R = $C_6H_4Me\text{-}4$ and ML_n = $Pt(PR'_3)_2$ (PR'_3 = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, or PEt_3),[2] $M(CO)(\eta\text{-}C_5Me_5)$ (M = Co or Rh),[3,4] $M(CO)(\eta\text{-}C_9H_7)$ (M = Rh or Ir, C_9H_7 = indenyl),[3] M(CO)(acac) (M = Rh or Ir, acac = acetylacetonate),[3,5] $Fe(CO)_4$,[6] $M(CO)_2(\eta\text{-}C_5H_4R')$ (M = Mn, R' = Me; M = Re, R' = H),[3] $Cr(CO)_2(\eta\text{-}C_6Me_6)$,[3] and $M(\eta\text{-}C_5H_5)_2$ (M = Ti, Zr, or V).[7,8] The dimetallacyclopropene ring systems in these complexes are reactive, and the compounds are proving to be useful precursors to other organometallic species. For example, we have recently reviewed [9] their use in the synthesis of trimetal compounds with capping μ_3-CR ligands.

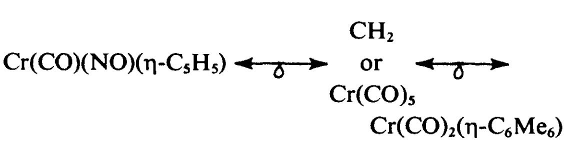


(i)

Reactions occurring at the bridging carbon atoms of the dimetal compounds are potentially interesting, and in this paper we describe the protonation of some of the tolylmethylidyne-bridged species. The resulting products contain the ligand $\mu\text{-}CH(C_6H_4Me\text{-}4)$, which adopts an η^3 bonding mode to tungsten. A preliminary account of some of the results described herein has been given.[10]

Results and Discussion

The compounds investigated involved those with bonds between tungsten and chromium, cobalt, and platinum. The chromium complex chosen for study was $[CrW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(NO)(\eta\text{-}C_5H_5)_2]$ (1), prepared by addition of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ [11] to a tetrahydrofuran (thf) solution of $[Cr(thf)(CO)(NO)(\eta\text{-}C_5H_5)]$. The latter was generated *in situ* by irradiation of $[Cr(CO)_2(NO)(\eta\text{-}C_5H_5)]$ in thf.[12] Compound (1) is related to the previously prepared complex $[CrW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(\eta\text{-}C_5H_5)(\eta\text{-}C_6Me_6)]$,[3] *via* the isolobal [13] mapping shown in (ii).



$$Cr(CO)(NO)(\eta\text{-}C_5H_5) \overset{}{\underset{\circ}{\longleftrightarrow}} \begin{matrix} CH_2 \\ \text{or} \\ Cr(CO)_5 \end{matrix} \underset{\circ}{\longleftrightarrow} Cr(CO)_2(\eta\text{-}C_6Me_6) \quad \text{(ii)}$$

Characterisation of compound (1) was accomplished by microanalysis (Table 1), mass spectrometry, and by i.r. and n.m.r. spectroscopy. The mass spectrum, measured by the fast-atom-bombardment technique, showed a molecular ion at *m/e* 584. The i.r. spectrum when measured in Nujol showed the expected number of peaks [$\nu_{max.}$(CO) at 1 987s, 1 923vs, and 1 904s cm^{-1}; $\nu_{max.}$(NO) at 1 620s cm^{-1}]. However, in solution (Et_2O) six CO bands were observed and the NO absorption was broad (Experimental section), suggesting that compound (1) exists as an equilibrium mixture of two isomers, presumably the *cis* and *trans* species (1a) and (1b). The exchange between the *cis* and *trans* forms must be rapid on

---

* μ-Carbonyl-2-carbonyl-2-η-cyclopentadienyl-μ-[σ:η³-*p*-tolylmethylene-C^{α}(Pt,W)$C^{1,2}$(W)]-1,1-bis(trimethylphosphine)platinumtungsten(1+)(*Pt–W*) tetrafluoroborate.

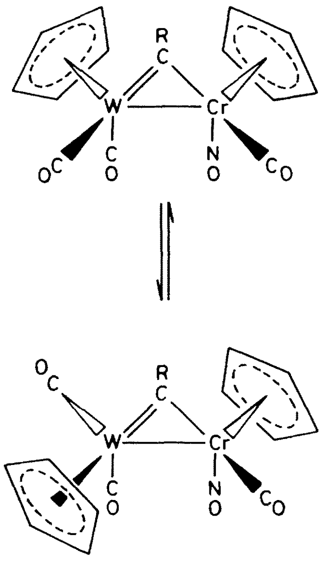
Supplementary data available (No. SUP 23918, 28 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Analytical [a] and physical data for the dimetal complexes

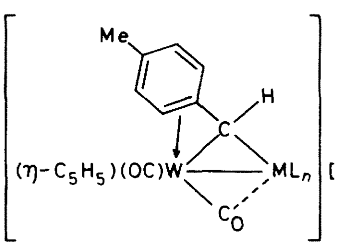
Complex	M.p. (θ_c/°C) [b]	Colour	Yield (%)	ν(CO) [c]/cm^{-1}	Analysis (%) C	Analysis (%) H
(1) [CrW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(NO)(η-C$_5$H$_5$)$_2$]	130—131	Red	72 [d]	[e] 1 987s, 1 923vs, 1 904s	[f] 43.1 (43.3)	2.8 (2.9)
(2) [CrW{μ-σ:η^3-CH(C$_6$H$_4$Me-4)}(CO)$_3$(NO)(η-C$_5$H$_5$)$_2$][BF$_4$]	125	Red	40	[g] 2 050s, 1 988s, 1 876s	[h] 37.4 (37.6)	2.6 (2.7)
(3) [CoW{μ-σ:η^3-CH(C$_6$H$_4$Me-4)}(CO)$_3$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)][BF$_4$]		Green	92	2 001vs, 1 953vs, 1 825s	[i] 39.5 (40.4)	4.1(3.7)
(4a) [PtW{μ-σ:η^3-CH(C$_6$H$_4$Me-4)}(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$]	180—184	Yellow	90	1 957s, 1 785m(br)	29.6 (29.9)	3.5 (3.7)
(4b) [PtW{μ-σ:η^3-CH(C$_6$H$_4$Me-4)}(CO)$_2$(PMe$_2$Ph)$_2$(η-C$_5$H$_5$)][BF$_4$]	83—87	Yellow	81	1 957s, 1 795m(br)	38.6 (38.5)	3.9 (3.6)
(4c) [PtW{μ-σ:η^3-CH(C$_6$H$_4$Me-4)}(CO)$_2$(PMePh$_2$)$_2$(η-C$_5$H$_5$)][BF$_4$]	135—137	Yellow	87	1 961s, 1 801m(br)	45.1 (45.1)	3.8 (3.6)
(5) [PtW{μ-σ:η^3-C(Me)C$_6$H$_4$Me-4}(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)][SO$_3$CF$_3$]	160—164	Yellow	83	1 953s, 1 812m(br)	29.6 (30.0)	3.8 (3.6)

[a] Calculated values are given in parentheses. [b] With decomposition. [c] In dichloromethane, unless otherwise stated. [d] Based on [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] consumed. [e] Measured in Nujol; ν$_{max.}$(NO) at 1 620s cm^{-1}. [f] N, 2.4 (2.4%). [g] Measured in Nujol; ν$_{max.}$(NO) at 1 695m cm^{-1}. [h] N, 1.9 (2.1%). [i] With one molecule of CH$_2$Cl$_2$ of crystallisation.

(1a)



(1b)



ML$_n$

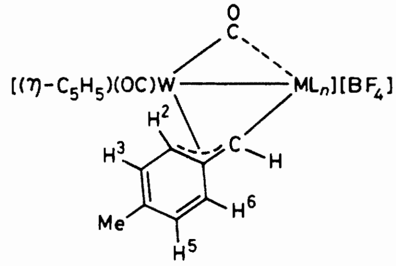
(2) Cr(CO)(NO)(η-C$_5$H$_5$)
(3) Co(CO)(η-C$_5$Me$_5$)
(4a) Pt(PMe$_3$)$_2$
(4b) Pt(PMe$_2$Ph)$_2$
(4c) Pt(PMePh$_2$)$_2$

the n.m.r. time-scale, since even at −90 °C the ^{1}H n.m.r. spectrum of (1) shows resonances corresponding to the presence of only one species. The ^{13}C-{^{1}H} n.m.r. spectrum had a characteristic [3] signal for the μ-*C*C$_6$H$_4$Me-4 group at δ 363.5 p.p.m. Peaks were also observed for a CO group bonded to chromium (δ 252.7 p.p.m.) and for two CO ligands attached to tungsten [δ 217.6 and 214.6 p.p.m., with *J*(^{183}W^{13}C) 99 Hz for both signals].

Treatment of (1) in dichloromethane with HBF$_4$·Et$_2$O afforded a deep red crystalline compound (2). In diethyl ether the complex [CoW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)] similarly gave a dark green salt (3). Reaction of the species [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PR$_3$)$_2$(η-C$_5$H$_5$)] (PR$_3$ = PMe$_3$, PMe$_2$Ph, or PMePh$_2$) with HBF$_4$·Et$_2$O produced the complexes (4a)—(4c). Analytical and other data for (2)—(4c) are given in Table 1. The salts vary markedly in stability. The cobalt–tungsten species (3) readily decomposes in solution above −20 °C, while the chromium–tungsten complex (2) slowly decomposes above −10 °C. In contrast, the platinum–tungsten compounds (4) are very stable in solution or in the solid state. It seemed likely from the ^{1}H n.m.r. spectra of compounds (2)—(4) (Table 2) that the C$_6$H$_4$ group was non-innocent, being involved in bonding with one of the metal centres. Normally, if a C$_6$H$_4$ group is part of a bridging ligand system as in μ-CC$_6$H$_4$Me-4 or in μ-C(C$_6$H$_4$Me-4)-(OMe),[3,14] the C$_6$H$_4$ protons appear as an (AB)$_2$ pattern or as an unresolved multiplet. In contrast, the spectrum of compound (4a) (Table 2) shows four resonances for the C$_6$H$_4$ group (δ 6.03, 7.09, 7.17, and 7.24 p.p.m.), corresponding to four different proton environments. A similar pattern is shown in the ^{1}H n.m.r. spectrum of the cobalt–tungsten compound (3), when measured at −70 °C. However, at room temperature the peaks for the C$_6$H$_4$ group appear as two broad multiplets, indicating that a fluxional process is occurring. Analysis of the signals due to the C$_6$H$_4$ group in the ^{1}H n.m.r. spectra of compounds (4b) and (4c) is inhibited by the presence of resonances due to the Ph groups. However, both spectra show a doublet signal for one of the C$_6$H$_4$ protons at *ca.* δ 6.15 p.p.m., the relatively high field implying proximity of a metal centre.

The ^{31}P-{^{1}H} and ^{195}Pt-{^{1}H} n.m.r. spectra of (4a)—(4c) (Table 3) were as expected for the presence of *cis*-Pt(PR$_3$)$_2$ groups in these three complexes. The ^{13}C-{^{1}H} spectra (Table 2) showed resonances due to two CO ligands, one signal having appreciable ^{195}Pt–^{13}C coupling (*ca.* 107—139 Hz), implying that this peak is due to a carbonyl group which is bridging or semi-bridging the tungsten–platinum bond. In accord with this, the i.r. spectra of compounds (4a)—(4c) (Table 1) each show one CO-stretching band at relatively low frequency, *viz.* 1 785, 1 795, and 1 801 cm^{-1}, respectively. The corresponding ^{13}C-{^{1}H} n.m.r. spectra also show the absence of any resonance due to a bridging *C*C$_6$H$_4$Me-4 group. In the precursors to (4a)—(4c), the ligated μ-C groups

Table 2. Hydrogen-1 and carbon-13 n.m.r. data [a] for the dimetal compounds with the μ-σ:η^3-CH(C_6H_4Me-4) ligands



Compound	^{1}H (δ) [b]	^{13}C (δ) [c]
(2)	[d] 2.49 (s, 3 H, Me-4), 5.65 [s, 5 H, Cr(η-C_5H_5)], 5.66 [s, 5 H, W(η-C_5H_5)], 7.03 [d, 1 H, H^2, $J(H^3H^2)$ 8], 7.26 (m, 2 H, H^5 and H^6), 7.61 [d, 1 H, H^3, $J(H^2H^3)$ 8], 10.94 (s, 1 H, μ-CH)	[d] 224 (3 CO), 181.3 (μ-C), 150.2 (C^4), 143.0 (C^3), 131.7 (C^5), 121.1 (C^6), 115.6 (C^2), 98.8 [W(η-C_5H_5) and C^1], 94.0 [Cr(η-C_5H_5)], 22.7 (Me-4)
(3)	[e] 1.94 (s, 15 H, C_5Me_5), 2.44 (s, 3 H, Me-4), 4.80 [d, 1 H, H^2, $J(H^3H^2)$ 6], 5.30 (s, 5 H, C_5H_5), 7.05 [d, 1 H, H^3, $J(H^2H^3)$ 6], 7.28 [d, 1 H, H^5, $J(H^6H^5)$ 8], 7.81 [d, 1 H, H^6, $J(H^5H^6)$ 8], 10.09 (s, 1 H, μ-CH)	[f] 230.0, 229.6 (WCO), 202.8 (CoCO), 158.2 (C^6), 146.4 (μ-C), 139.1 (C^5), 132.3 (C^3), 130.3, 129.8 (C^1 and C^4), 127.9 (C^2), 103.3 (C_5Me_5), 92.0 (C_5H_5), 22.5 (Me-4), 9.8 ($C_5\mathit{Me}_5$)
(4a)	1.64 [d, 9 H, MeP, $J(PH)$ 9, $J(PtH)$ 24], 1.67 [d, 9 H, MeP, $J(PH)$ 11, $J(PtH)$ 36], 2.35 (s, 3 H, Me-4), 4.75 [d, 5 H, C_5H_5, $J(PH)$ 1, $J(PtH)$ 4], 6.03 [d, 1 H, H^2, $J(H^3H^2)$ 6], 6.71 [d, 1 H, μ-CH, $J(PH)$ 7], 7.09 [d of d, 1 H, H^3, $J(H^2H^3)$ 6, $J(H^5H^3)$ 1], 7.17 [m, 1 H, H^6, $J(H^2H^6)$ 1, $J(H^5H^6)$ 9], 7.24 [m, 1 H, H^5, $J(H^3H^5)$ 1, $J(H^6H^5)$ 9]	224.1 [d, μ-CO, $J(PC)$ 22, $J(PtC)$ 139], 219.4 [CO, $J(PtC)$ 30, $J(WC)$ 163], 138.4 (C^4), 134.0 (C^5), 132.6 [d, C^6, $J(PC)$ 8], 131.0 (C^3), 116.3 [d of d, μ-C, $J(PC)$ 75 and 5, $J(PtC)$ 554, $J(WC)$ 30], 108.7 (C^1), 91.5 (C_5H_5), 79.5 [C^2, $J(PtC)$ 35], 20.9 (Me-4), 18.8 [d, MeP, $J(PC)$ 35, $J(PtC)$ 40], 15.9 [d, MeP, $J(PC)$ 31, $J(PtC)$ 31]
(4b)	1.44 [d, 3 H, MeP, $J(PH)$ 11, $J(PtH)$ 16], 1.65 [d, 3 H, MeP, $J(PH)$ 7, $J(PtH)$ 26], 1.67 [d, 3 H, MeP, $J(PH)$ 11, $J(PtH)$ 15], 1.75 [d, 3 H, MeP, $J(PH)$ 7, $J(PtH)$ 25], 2.34 (s, 3 H, Me-4), 4.78 [d, 5 H, C_5H_5, $J(PH)$ 1, $J(PtH)$ 5], 6.18 [d, 1 H, H^2, $J(H^3H^2)$ 6], 6.73 [d, 1 H, μ-CH, $J(PH)$ 7], 6.8—7.5 (m, 13 H, C_6H_4 and Ph)	222.9 [d, μ-CO, $J(PC)$ 21, $J(PtC)$ 121], 219.6 [CO, $J(PtC)$ 29, $J(WC)$ 168], 140—128 (Ph and C_6H_4), 116.9 [d of d, μ-C, $J(PC)$ 74 and 5, $J(PtC)$ 564, $J(WC)$ 30], 109.4 (C^1), 92.4 (C_5H_5), 79.5 [C^2, $J(PtC)$ 30], 21.5 (Me-4), 18.1 [d, MeP, $J(PC)$ 40, $J(PtC)$ 40], 17.3 [d, MeP, $J(PC)$ 35, $J(PtC)$ 42], 15.7 [d, MeP, $J(PC)$ 32, $J(PtC)$ 32], 14.1 [d, MeP, $J(PC)$ 31, $J(PtC)$ 20]
(4c)	[g] 1.69 [d, 3 H, MeP, $J(PH)$ 10, $J(PtH)$ 35], 2.10 [d, 3 H, MeP, $J(PH)$ 9, $J(PtH)$ 25], 2.33 (s, 3 H, Me-4), 4.73 [d, 5 H, C_5H_5, $J(PH)$ 1], 6.13 [d, 1 H, H^2, $J(H^3H^2)$ 6], 6.52 [d, 1 H, μ-CH, $J(PH)$ 8], 6.78—7.50 (m, 23 H, C_6H_4 and Ph)	[g] 221.5 [d, μ-CO, $J(PC)$ 17, $J(PtC)$ 107], 217.7 [CO, $J(PtC)$ 28, $J(WC)$ 166], 139.0 (C^4), 134—128 (Ph and C_6H_4), 119.2 [d, μ-C, $J(PC)$ 76, $J(PtC)$ 578], 107.4 (C^1), 92.0 (C_5H_5), 79.4 [C^2, $J(PtC)$ 25], 21.4 (Me-4), 16.4 [d, MeP, $J(PC)$ 34, $J(PtC)$ 34], 15.5 [d, MeP, $J(PC)$ 31, $J(PtC)$ 30]
(5)	[g] 1.58 [d, 9 H, MeP, $J(PH)$ 10, $J(PtH)$ 37], 1.64 [d, 9 H, MeP, $J(PH)$ 9, $J(PtH)$ 23], 2.37 (s, 3 H, Me-4), 3.03 [d of d, 3 H, μ-CMe, $J(PH)$ 6 and 3, $J(PtH)$ 17], 4.63 [d, 5 H, C_5H_5, $J(PH)$ 1, $J(PtH)$ 5], 5.90 [d, 1 H, H^2, $J(H^3H^2)$ 6], 7.12—7.31 (m, 3 H, C_6H_4)	220.7 [d, μ-CO, $J(PC)$ 19, $J(PtC)$ 115], 217.8 [CO, $J(PtC)$ 43], 137.5 (C^4), 135.3 (C^3), 133.1 [C^5, $J(PtC)$ 10], 128.4 [d of d, μ-C, $J(PC)$ 76 and 13, $J(PtC)$ 576, $J(WC)$ 24], 125.4 [d, C^6, $J(PC)$ 5, $J(PtC)$ 34], 121.4 [q, CF_3, $J(FC)$ 322] 111.4 (C^1), 94.4 (C_5H_5), 74.0 [C^2, $J(PtC)$ 31], 27.9 [d, μ-C*Me*, $J(PC)$ 3, $J(PtC)$ 16], 21.2 (Me-4), 19.6 [d, MeP, $J(PC)$ 34, $J(PtC)$ 44], 16.7 [d, MeP, $J(PC)$ 31, $J(PtC)$ 27],

[a] Coupling constants in Hz. [b] Measured in CD_2Cl_2 unless otherwise stated. [c] Measured in CD_2Cl_2—CH_2Cl_2 unless otherwise stated; hydrogen-1 decoupled chemical shifts in p.p.m., positive values representing shifts to high frequency of $SiMe_4$. [d] Measured at −20 °C. [e] Measured at −70 °C. [f] Measured at −40 °C. [g] Measured in $CDCl_3$.

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)
(4a) [d]	−10.2 [d, $J(PP)$ 15, $J(PtP)$ 3 408, $J(WP)$ 40] −14.2 [d, $J(PP)$ 15, $J(PtP)$ 2 663, $J(WP)$ 14]	−126 [d of d, $J(PPt)$ 3 408 and 2 663, $J(WPt)$ 74]
(4b) [d]	−0.35 [d, $J(PP)$ 16, $J(PtP)$ 3 444, $J(WP)$ 39] −3.23 [d, $J(PP)$ 16, $J(PtP)$ 2 720, $J(WP)$ 12]	−111 [d of d, $J(PPt)$ 3 444 and 2 720]
(4c) [e]	11.9 [d, $J(PP)$ 15, $J(PtP)$ 3 492, $J(WP)$ 40] 9.8 [d, $J(PP)$ 15, $J(PtP)$ 2 798, $J(WP)$ 14]	−150 [d of d, $J(PPt)$ 3 492 and 2 798]
(5) [e]	−11.8 [d, $J(PP)$ 12, $J(PtP)$ 3 588, $J(WP)$ 39] −15.6 [d, $J(PP)$ 12, $J(PtP)$ 2 510, $J(WP)$ 14]	32 [d of d, $J(PPt)$ 3 588 and 2 510]

[a] Hydrogen-1 decoupled chemical shifts in p.p.m., coupling constants in Hz. [b] Chemical shifts to high frequency of 85% H_3PO_4 (external). [c] Chemical shifts to high frequency of Ξ(^{195}Pt) 21.4 MHz. [d] Measured in CD_2Cl_2. [e] Measured in $CDCl_3$.

resonate at δ 338, 336, and 338 p.p.m.[2] respectively. No such low-field signals are seen in the spectra of (4a)—(4c).

It was apparent that in order to ascertain the nature of the bridging-ligand system in compounds (2)—(4c) an *X*-ray diffraction study on one or other of the species was required. Compound (4a) afforded crystals of good quality, and the results of the *X*-ray diffraction measurements are summarised in Table 4, with the cation shown in the Figure. From the

Table 4. Bond lengths (Å) and selected bond angles (°) for $[PtW\{\mu\text{-}\sigma:\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (4a), with estimated standard deviations in parentheses

Pt–W	2.795(1)	Pt–P(1)	2.281(4)	W–Pt–P(1)	138.5(1)	W–Pt–P(2)	121.8(1)
Pt–P(2)	2.314(4)	Pt–C(2)	2.272(16)	P(1)–Pt–P(2)	97.9(1)	W–Pt–C(2)	43.9(4)
Pt–C	2.053(14)	W–C(1)	1.966(17)	P(1)–Pt–C(2)	164.5(5)	P(2)–Pt–C(2)	86.6(4)
W–C(2)	1.956(15)	W–C(31)	2.376(11)	W–Pt–C	50.3(4)	P(1)–Pt–C	89.7(4)
W–C(32)	2.325(13)	W–C(33)	2.270(13)	P(2)–Pt–C	172.0(4)	Pt–W–C(1)	90.3(5)
W–C(34)	2.288(12)	W–C(35)	2.354(11)	Pt–W–C(2)	53.7(5)	C(1)–W–C(2)	84.2(7)
W–C	2.166(14)	W–C(41)	2.406(14)	Pt–W–C	46.8(4)	W–C(1)–O(1)	174.3(14)
W–C(42)	2.602(13)	P(1)–C(11)	1.819(21)	Pt–C(2)–W	82.4(6)	Pt–C(2)–O(2)	121.8(12)
P(1)–C(12)	1.834(19)	P(1)–C(13)	1.821(19)	W–C(2)–O(2)	155.1(14)	Pt–C–W	83.0(5)
P(2)–C(21)	1.824(24)	P(2)–C(22)	1.763(22)	Pt–C–C(41)	123.4(11)	C–C(41)–C(42)	117.0(12)
P(2)–C(23)	1.779(22)	C(1)–O(1)	1.178(22)	C–C(41)–C(46)	124.2(14)	C(42)–C(41)–C(46)	118.5(13)
C(2)–O(2)	1.218(20)	C–C(41)	1.411(20)	C(41)–C(42)–C(43)	118.4(12)	C(42)–C(43)–C(44)	122.3(15)
C(41)–C(42)	1.426(21)	C(41)–C(46)	1.430(20)	C(43)–C(44)–C(45)	117.8(15)	C(43)–C(44)–C(47)	122.4(17)
C(42)–C(43)	1.461(22)	C(43)–C(44)	1.351(22)	C(45)–C(44)–C(47)	119.8(14)	C(44)–C(45)–C(46)	121.1(14)
C(44)–C(45)	1.478(25)	C(44)–C(47)	1.492(28)	C(41)–C(46)–C(45)	121.8(16)		
C(45)–C(46)	1.348(24)	B–F(mean)	1.340(20)				

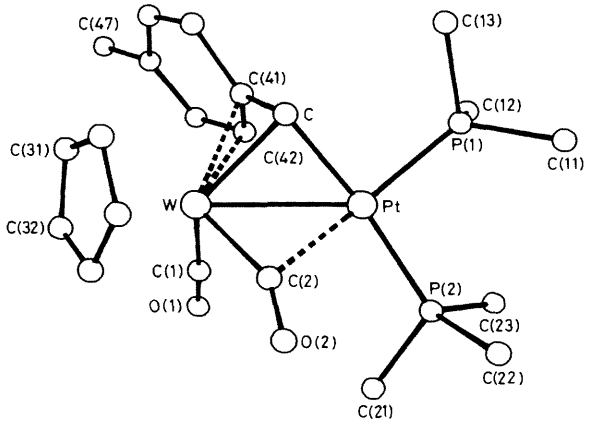
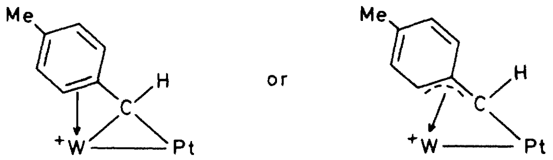


Figure. Molecular structure of the cation of $[PtW\{\mu\text{-}\sigma:\eta^3\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (4a), showing the crystallographic numbering scheme

latter it is immediately apparent that the Pt–W bond [2.795(1) Å] is bridged by the tolylmethylene ligand in such a manner that C, C(41), and C(42) are η^3-co-ordinated to the tungsten atom, while the atom C is also σ bonded to the platinum. This mode of attachment of a CC_6H_4Me-4 group has been found to occur in the compound $[Mo_2\{\mu\text{-}C(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$.[15] Moreover, one CC_6H_5 group in $[Ru_2(\mu\text{-}CPh_2)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_2]$ similarly σ:η^3-bridges the metal–metal bond.[16] In compound (4a) the metal–metal bond is semi-bridged by the C(2)O(2) ligand [W–C(2)–O(2) 155.1(14)°], thus accounting for certain i.r. and n.m.r. data, discussed above.

Interest centres on the μ-$CH(C_6H_4Me$-4) ligand. Although the important μ-CH hydrogen atom was not located, its presence was clearly revealed in the ^1H n.m.r. spectrum (Table 2) by a doublet signal at δ 6.71 p.p.m. [*J*(PH) 7 Hz] which was clearly distinguished from the C_6H_4 resonances by ^1H–^1H decoupling experiments. Moreover, the μ-C group gives rise in the ^{13}C-$\{^1H\}$ n.m.r. spectrum to a diagnostic resonance at δ 116.3 p.p.m., occurring as a doublet of doublets, due to coupling with two non-equivalent phosphorus nuclei [*J*(PC) 75 and 5 Hz] with ^{183}W and ^{195}Pt satellite peaks [*J*(WC) 30, *J*(PtC) 554 Hz].

The bonding of the CC_6H_4Me-4 group to the tungsten in compound (4a) can be formally described as involving either a vinyl carbene bridge or an allylic group. Either representation results in the tungsten atom acquiring an 18-electron



configuration. The near co-planarity of the atoms Pt, C, C(41), and C(42) favours the 'allylic' formulation, and this is supported by the similarity of the C–C(41) [1.41(2) Å] and C(41)–C(42) [1.43(2) Å] separations. Co-ordination of C(41)–C(42) to tungsten destroys aromatic delocalisation within the C_6H_4 ring and the short C(43)–C(44) [1.35(2) Å] and C(45)–C(46) [1.35(2) Å] separations are consistent with the presence of localised C=C bonds at these positions [*cf.* C(42)–C(43) 1.46(2), C(44)–C(45) 1.48(3), and C(46)–C(41) 1.43(2) Å]. The resulting electronic and steric constraints inherent in this unusual bonding mode are clearly reflected in the W–η^3-C distances which show a smooth increase along the series W–C [2.166(14) Å], W–C(41) [2.406(14) Å], and W–C(42) [2.602(13) Å]. Typically W–μ-C(carbene) or W–C(η-C_5H_5) separations lie in the range 2.10(2)—2.49(3) Å. Evidently, in compound (4a), the C_6H_4Me-4 group is only weakly co-ordinated to tungsten, and not surprisingly the chemistry of the compound is dominated by facile displacement of the co-ordinated ring by nucleophiles such as CO or PR_3.[10,17]

The relatively weak W–C(C_6H_4) interaction is offset by correspondingly strong bonding within the Pt–μ-C–W ring. Thus the W–μ-C [2.166(14) Å], Pt–μ-C [2.053(14) Å], and Pt–W [2.795(1) Å] distances are all comparable with those found in the closely related species $[PtW(\mu\text{-}H)\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ [W–μ-C 2.259(9), Pt–μ-C 2.109(9), and Pt–W 2.895(1) Å][17] and $[PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}CO)(PMe_3)_2(\eta\text{-}MeC_2Me)(\eta\text{-}C_5H_5)][BF_4]$ [W–μ-C 2.10(2), Pt–μ-C 2.110(15), and Pt–W 2.771(1) Å].[18]

The platinum atom is in an essentially planar environment, with the dihedral angle between the P(1),Pt,P(2) and Pt,C,W planes being only 12.2° (Table 5). The Pt–P(2) distance [2.314(4) Å] is significantly longer than Pt–P(1) [2.281(4) Å]. Similar asymmetry in the PtP_2 group bonding has been previously observed [19] in related complexes, and is thought to reflect the *trans* influence of the bridging carbon atoms.

Having established the molecular structure of (4a), and in particular the nature of the bridge bonding of the $CH(C_6H_4Me$-4) group, it is possible to interpret more clearly the n.m.r. data for the various compounds (2)—(4c). As mentioned

Table 5. Some least-squares planes for [PtW{μ-σ:η^3-CH(C$_6$H$_4$Me-4)}(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$] (4a), in the form $Ax + By + Cz = D$, where x, y, z are fractional co-ordinates. Distances (Å) of relevant atoms from the planes are given in square brackets

Plane (i): Pt, C, C(41), C(42)
$13.241x + 1.713y + 2.013z = -2.367$
[Pt −0.02, C 0.06, C(41) −0.06, C(42) 0.03, W 2.03]

Plane (ii): Pt, W, C, P(1), P(2)
$-0.403x + 3.549y + 11.524z = 4.507$
[Pt 0.11, W −0.12, C 0.12, P(1) −0.11, P(2) 0.01, C(1) −1.54, C(2) 0.90]

Plane (iii): Pt, P(1), P(2)
$-1.789x + 4.255y + 11.442z = 5.468$

Plane (iv): Pt, W, C
$1.121x + 3.771y + 11.296z = 4.267$

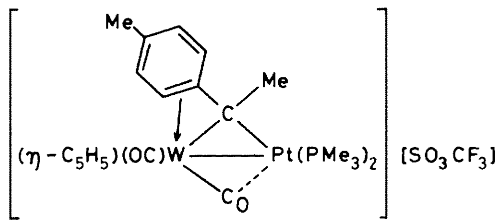
Angles (°) between planes:

	(ii)	(iii)	(iv)
(i)	74.1	79.7	67.8
(ii)		6.3	6.3
(iii)			12.2

above, the ^{13}C-{^{1}H} n.m.r. spectrum of compound (4a) showed a resonance for the μ-C nucleus at δ 116.3 p.p.m., with ^{195}Pt and ^{183}W satellite peaks. Similar signals are observed in the spectra of (4b) and (4c) (Table 2). In the spectrum of compound (2) the peak at 181.3 p.p.m. is assigned to the μ-C group. In the proton-coupled spectrum it appears as the expected doublet [J(HC) 122 Hz].

As mentioned above, both the ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra of compound (3) were found to vary with temperature, indicating dynamic behaviour. This probably involves rotation of the bridging ligand about an axis through μ-C,C(1), C(4) of the CC$_6$H$_4$Me-4 group (see diagram in Table 2) so that the proton sites H^2 and H^6, and H^3 and H^5, and the carbons to which these are attached, are averaged at room temperature on the n.m.r. time-scale. At −70 °C the fluxional behaviour ceases and the ^{1}H resonance assignments in Table 2 were made by selective-homonuclear-decoupling experiments. The peak at δ 4.80 p.p.m. may be assigned to H^2, because similar high-field shifts have been reported for protons in this environment in the spectra of [Mo$_2${μ-C(C$_6$H$_4$Me-4)$_2$}(CO)$_4$(η-C$_5$H$_5$)$_2$] [15] and in [Ru$_2$(μ-CPh$_2$)(μ-CO)(CO)(η-C$_5$H$_5$)$_2$].[16] Selective irradiation of the signal at δ 4.80 p.p.m. decoupled the peak at δ 7.05 p.p.m., which is, therefore, assigned to H^3. As the temperature is raised the peaks at 4.80 and 7.81 p.p.m. coalesce, hence the latter may be assigned to H^6. Also at 25 °C the signals at δ 7.05 and 7.28 p.p.m. give rise to a broad resonance at 7.16 p.p.m. Thus the resonance at δ 7.28 p.p.m. must be due to H^5.

In contrast with (3), compounds (2) and (4a)—(4c) do not show dynamic ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra. Evidently the CH(C$_6$H$_4$Me-4) group remains rigidly η^3-co-ordinated to the tungsten atom in these species, maintaining an 18-electron configuration at this metal centre. In this context it is interesting to compare the nature of the products (4a)—(4c) obtained by protonation of the tolylmethylidyne species [PtW(μ-CC$_6$H$_4$Me-4)(CO)$_2$(PR$_3$)$_2$(η-C$_5$H$_5$)] with the nature of the product obtained by protonating the ethylidyne complex [PtW(μ-CMe)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)]. With HBF$_4$·Et$_2$O, the latter affords the ethylene complex [PtW(μ-CO)$_2$(PMe$_3$)$_2$(η-C$_2$H$_4$)(η-C$_5$H$_5$)][BF$_4$] rather than the expected species [PtW(μ-CHMe)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$].[20] The latter may be an intermediate but it involves a formal 16-electron count at tungsten, whereas the ethylene complex gives rise to an 18-electron count, as attained in compounds (4a)—(4c).



(5)

We have also examined the methylation of [PtW(μ-CC$_6$H$_4$-Me-4)(CO)$_2$(PMe$_3$)$_2$(η-C$_5$H$_5$)] with CF$_3$SO$_3$Me in diethyl ether, a reaction which produces the yellow salt (5). Analytical and other data for (5) are given in Table 1. The ^{1}H, ^{13}C-{^{1}H}, ^{31}P-{^{1}H}, and ^{195}Pt-{^{1}H} n.m.r. spectra (Tables 2 and 3) are all in accord with the structure proposed, which, as with the other compounds discussed above, involves an σ:η^3-bonding mode for the bridging group. A similar σ:η^3-bridge system occurs in the rhodium–tungsten salt [RhW{μ-CH(C$_6$H$_4$Me-4)}-(CO)$_2$(PMe$_3$)(η-C$_9$H$_7$)(η-C$_5$H$_5$)][BF$_4$], obtained by protonation of the dimetal compound [RhW(μ-CC$_6$H$_4$Me-4)(CO)$_2$-(PMe$_3$)(η-C$_9$H$_7$)(η-C$_5$H$_5$)].[21]

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. The n.m.r. measurements were made with JEOL FX 90Q and FX 200 instruments, and i.r. spectra were recorded with a Nicolet 10 MX FT spectrophotometer. The compounds [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)],[11] [Cr(CO)$_2$(NO)(η-C$_5$H$_5$)],[22] [CoW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(η-C$_5$H$_5$)(η-C$_5$Me$_5$)],[3] and [PtW(μ-CC$_6$H$_4$-Me-4)(CO)$_2$(PR$_3$)$_2$(η-C$_5$H$_5$)] (PR$_3$ = PMe$_3$, PMe$_2$Ph, or PMePh$_2$) [2] were made by literature methods. The tetrafluoroboric acid–diethyl ether adduct used was from BDH (54% HBF$_4$). Analytical data for the new compounds are given in Table 1.

Preparation of the Complex [CrW(μ-CC$_6$H$_4$Me-4)(CO)$_3$-(NO)(η-C$_5$H$_5$)$_2$].—A red thf (40 cm^3) solution of [Cr(CO)$_2$-(NO)(η-C$_5$H$_5$)] (0.20 g, 1.0 mmol) was irradiated with u.v. light (500-W medium-pressure Hanovia mercury-vapour lamp) for 40 min at 0 °C to afford a yellow solution of [Cr(thf)(CO)(NO)(η-C$_5$H$_5$)]. Solid [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.41 g, 1.0 mmol) was added, and the mixture slowly warmed to room temperature with stirring. Solvent was removed *in vacuo* and the residue dissolved in dichloromethane–light petroleum (1 : 5) and chromatographed on an alumina column (10 × 3 cm). Elution with the same solvent mixture afforded some unreacted [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] followed by a band containing the product. Removal of solvent *in vacuo* followed by crystallisation of the residue from dichloromethane–light petroleum (1 : 3) at −20 °C gave deep red *needles* of [CrW(μ-CC$_6$H$_4$Me-4)(CO)$_3$(NO)(η-C$_5$H$_5$)$_2$] (1) (0.21 g); $\nu_{\text{max.}}$(CO) at 1 985s, 1 964(sh), 1 927vs, 1 925(sh), and 1 876w(br) cm^{-1}, $\nu_{\text{max.}}$(NO) at 1 657s and 1 651(sh) cm^{-1} (CH$_2$Cl$_2$); $\nu_{\text{max.}}$(CO) at 1 996m, 1 980m, 1 967m, 1 938s, 1 925vs, and 1 877w cm^{-1}, $\nu_{\text{max.}}$(NO) at 1 668s(br) cm^{-1} (Et$_2$O). N.m.r.: ^{1}H (CD$_2$Cl$_2$), δ 2.4 (s, 3 H, Me-4), 4.9 [s, 5 H, Cr(η-C$_5$H$_5$)], 5.5 [s, 5 H, W(η-C$_5$H$_5$)], and 7.2 (m, 4 H, C$_6$H$_4$); ^{13}C-{^{1}H} (CD$_2$Cl$_2$–CH$_2$Cl$_2$), δ 363.5 (μ-C), 252.7 (CrCO), 217.6 [WCO, J(WC) 99], 214.6 [WCO, J(WC) 99 Hz], 162.5—124.3 (C$_6$H$_4$), 96.9 [W(η-C$_5$H$_5$)], 92.0 [Cr(η-C$_5$H$_5$)], and 21.5

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

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	−2 940(1)	6 565(1)	1 878(1)	C(33)	239	5 619	2 977
W	−1 284(1)	5 574(1)	2 045(1)	C(34)	−397	5 409	3 784
P(1)	−4 582(3)	6 408(3)	1 680(4)	C(35)	−793	4 619	3 497
P(2)	−2 898(3)	7 942(2)	1 373(4)	C	−2 781(10)	5 336(9)	2 273(13)
C(11)	−5 342(14)	7 220(12)	2 155(19)	C(41)	−2 668(10)	4 719(8)	1 459(12)
C(12)	−5 036(14)	6 235(16)	182(16)	C(42)	−2 466(10)	4 989(8)	367(12)
C(13)	−5 040(13)	5 506(11)	2 358(17)	C(43)	−2 170(12)	4 374(10)	−424(13)
C(21)	−1 780(17)	8 297(11)	868(19)	C(44)	−2 135(12)	3 560(9)	−179(14)
C(22)	−3 017(18)	8 648(12)	2 478(19)	C(45)	−2 398(12)	3 297(9)	937(16)
C(23)	−3 747(17)	8 294(12)	232(19)	C(46)	−2 641(12)	3 854(9)	1 698(14)
C(1)	−892(12)	6 088(10)	670(14)	C(47)	−1 841(18)	2 931(11)	−990(21)
O(1)	−577(11)	6 393(10)	−110(11)	B	3 043(10)	5 934(7)	4 460(11)
C(2)	−1 356(12)	6 710(9)	2 581(17)	F(1)	3 703(11)	6 526(10)	4 735(22)
O(2)	−1 059(10)	7 321(8)	3 110(11)	F(2)	2 813(14)	5 916(15)	3 330(11)
C(31) *	−402(10)	4 340(6)	2 512(11)	F(3)	2 247(14)	6 093(14)	4 958(17)
C(32)	236	4 958	2 191	F(4)	3 411(19)	5 202(8)	4 818(19)

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

p.p.m. (Me-4). Compound (1) is stable in air for about 1—2 weeks, but its solutions in organic solvents are more air sensitive.

Protonation Studies.—(*a*) A dichloromethane (10 cm^3) solution of compound (1) (0.10 g, 0.20 mmol) at −50 °C was treated with excess of $HBF_4{\cdot}Et_2O$ (*ca.* 0.05 cm^3) and the resultant deep red solution stirred for 30 min. Solvent was removed *in vacuo* at −20 °C, and the residue washed with cold diethyl ether. Crystallisation from dichloromethane–diethyl ether (1 : 3) at −20 °C afforded deep red *crystals* of [CrW{μ-σ:η^3-$CH(C_6H_4Me$-4)}$(CO)_3(NO)(\eta$-$C_5H_5)_2$][BF_4] (2) (0.06 g).

(*b*) A diethyl ether (20 cm^3) solution of [CoW(μ-CC_6H_4Me-4)$(CO)_3(\eta$-$C_5H_5)(\eta$-$C_5Me_5)$] (0.43 g, 0.68 mmol) was treated with $HBF_4{\cdot}Et_2O$ (*ca.* 0.1 cm^3), thereby affording without further purification dark green *microcrystals* of the salt [CoW{μ-σ:η^3-$CH(C_6H_4Me$-4)}$(CO)_3(\eta$-$C_5H_5)(\eta$-$C_5Me_5)$][BF_4] (3) (0.45 g).

(*c*) The protonation of the tungsten–platinum complexes [PtW(μ-CC_6H_4Me-4)$(CO)_2(PR_3)_2(\eta$-$C_5H_5)$] was carried out similarly. For example, [PtW(μ-CC_6H_4Me-4)$(CO)_2(PMe_3)_2(\eta$-$C_5H_5)$] (0.38 g, 0.50 mmol) in diethyl ether (30 cm^3) with $HBF_4{\cdot}Et_2O$ (*ca.* 0.1 cm^3) gave yellow *microcrystals* of [PtW{μ-σ:η^3-$CH(C_6H_4Me$-4)}$(CO)_2(PMe_3)_2(\eta$-$C_5H_5)$][BF_4] (4a) (0.38 g).

Synthesis of [PtW{μ-σ:η^3-$CMe(C_6H_4Me$-4)}$(CO)_2(PMe_3)_2$-$(\eta$-$C_5H_5)$][SO_3CF_3].—A vigorously stirred diethyl ether (50 cm^3) solution of [PtW(μ-CC_6H_4Me-4)$(CO)_2(PMe_3)_2(\eta$-$C_5H_5)$] (0.38 g, 0.50 mmol) was treated dropwise with CF_3SO_3Me until no further precipitation occurred. After 30 min the yellow precipitate was allowed to settle and the solvent decanted. The residue was washed with diethyl ether (3 × 20 cm^3) and dried *in vacuo* to give yellow *microcrystals* of [PtW{μ-σ:η^3-CMe-$(C_6H_4Me$-4)}$(CO)_2(PMe_3)_2(\eta$-$C_5H_5)$][SO_3CF_3] (5) (0.39 g).

Crystal Structure Determination.—Crystals of compound (4a) grow as yellow hexagonal plates from CH_2Cl_2–Et_2O. Diffracted intensities were recorded at 293 K from a crystal of dimensions *ca.* 0.10 × 0.23 × 0.30 mm, having well developed faces of the type {1 0 0}, {0 1 0}, and {0 1 1}. Of the total 4 518 independent reflections ($2\theta \leqslant 50^\circ$) measured on a Nicolet *P*3*m* four-circle diffractometer, 3 430 satisfied the criterion $I \geqslant 2.5\sigma(I)$, and only these were used in the solution and refinement of the structure. The intensity data were corrected for Lorentz, polarisation, and *X*-ray absorption effects.

Crystal data. $C_{21}H_{31}BF_4O_2P_2PtW$, $M = 843.2$, monoclinic, $a = 13.903(3)$, $b = 16.213(3)$, $c = 11.859(2)$ Å, $\beta = 96.89(2)^\circ$, $U = 2\,654(1)$ Å^3, $Z = 4$, $D_c = 2.11$ g cm^{-3}, $F(000) = 1\,584$, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 99.1 cm^{-1}.

The structure was solved by conventional heavy-atom and electron-density difference methods. The cyclopentadienyl ring was treated as a rigid isotropic group (C–C 1.420 Å) and the BF_4^- anion was constrained to tetrahedral geometry. All remaining non-hydrogen atoms were refined with anisotropic thermal parameters. Methyl and cyclopentadienyl hydrogen atoms were included at calculated positions (C–H 0.960 Å) and chemically related hydrogen atoms were given common refined isotropic thermal parameters. The C_6H_4 and μ-CH hydrogen atoms could not be located with certainty and are not included. A weighting scheme of the form $w = [\sigma^2(F_o) + 0.0015|F_o|^2]^{-1}$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks > 1 e Å^{-3} except in the immediate vicinity of the metal atoms where peaks of *ca.* 3 e Å^{-3} were observed. Scattering factors and corrections for anomalous dispersion were from ref. 23. Refinement by blocked-cascade least squares converged at *R* 0.054 (*R′* 0.054). All calculations were carried out on an ' Eclipse ' S230 Data General computer with the SHELXTL system of programs.[24] The final atom co-ordinates are listed in Table 6.

Acknowledgements

We thank the S.E.R.C. for research studentships (to J. C. V. L. and I. M.) and the Syrian Ministry of Education and the University of Aleppo for a Scholarship (to H. R.).

References

1 Part 24, G. A. Carriedo, J. A. K. Howard, and F. G. A. Stone, preceding paper.
2 T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1609; M. J. Chetcuti, K. Marsden, I. Moore, F. G. A. Stone, and P. Woodward, *ibid.*, 1982, 1749; M. J. Chetcuti, J. A. K. Howard, R. M. Mills, F. G. A. Stone, and P. Woodward, *ibid.*, p. 1757.
3 J. A. Abad, L. W. Bateman, J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2075.

4 M. Green, J. C. Jeffery, S. J. Porter, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1982, 2475.

5 M. J. Chetcuti, P. A. M. Chetcuti, J. C. Jeffery, R. M. Mills, P. Mitrprachachon, S. J. Pickering, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1982, 699.

6 L. Busetto, J. C. Jeffery, R. M. Mills, F. G. A. Stone, M. J. Went, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 101.

7 G. M. Dawkins, M. Green, K. A. Mead, J-Y. Salaün, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 527.

8 U. Behrens and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1605.

9 F. G. A. Stone, in 'Inorganic Chemistry: Toward the 21st Century,' ed. M. H. Chisholm, *ACS Symp. Ser.*, 1983, **211**, 383.

10 J. C. Jeffery, I. Moore, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1981, 1255.

11 E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrick, F. R. Kreissl, and J. O. Besenhard, *Chem. Ber.*, 1977, **110**, 3397.

12 B. W. Hames, P. Legzdins, and D. T. Martin, *Inorg. Chem.*, 1978, **17**, 3644.

13 R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711.

14 J. A. K. Howard, K. A. Mead, J. R. Moss, R. Navarro, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 743.

15 L. Messerle and M. D. Curtis, *J. Am. Chem. Soc.*, 1980, **102**, 7789.

16 D. L. Davies, A. F. Dyke, S. A. R. Knox, and M. J. Morris, *J. Organomet. Chem.*, 1981, **215**, C30.

17 J. C. Jeffery, I. Moore, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, following paper.

18 J. C. Jeffery, I. Moore, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1581.

19 M. R. Awang, J. C. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 2091.

20 M. R. Awang, J. C. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 1426.

21 J. C. Jeffery, C. Sambale, M. F. Schmidt, and F. G. A. Stone, *Organometallics*, 1982, **1**, 1597.

22 J. K. Hoyano, P. Legzdins, and J. T. Malito, *Inorg. Synth.*, 1978, **18**, 126.

23 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

24 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *X*-ray system, University of Cambridge, 1976; updated at Göttingen, 1981.

Received 22nd September 1983; *Paper* 3/1679