# Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 26.[1] Reactions of the Compounds $[PtW\{\mu-\sigma:\eta^3-CH(C_6H_4Me-4)\}(CO)_2(PR_3)_2(\eta-C_5H_5)][BF_4]$ ($PR_3 = PMe_3$, $PMe_2Ph$, or $PMePh_2$) and $[PtW\{\mu-\sigma:\eta^3-C(Me)C_6H_4Me-4\}(CO)_2(PMe_3)_2(\eta-C_5H_5)]$-$[SO_3CF_3]$ with Nucleophiles; *X*-Ray Crystal Structure of $[PtW(\mu-H)\{\mu-CH(C_6H_4Me-4)\}(CO)_2(PMe_3)_2(\eta-C_5H_5)]$ *

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The salts $[PtW\{\mu-\sigma:\eta^3-CH(C_6H_4Me-4)\}(CO)_2(PR_3)_2(\eta-C_5H_5)][BF_4]$ react with carbon monoxide and with tertiary phosphines to afford, respectively, the complexes $[PtW\{\mu-CH(C_6H_4Me-4)\}(CO)_3(PR_3)_2(\eta-C_5H_5)][BF_4]$ ($PR_3 = PMe_3$, $PMe_2Ph$, or $PMePh_2$) and $[PtW\{\mu-CH(C_6H_4Me-4)\}(CO)_2(PR_3)_3(\eta-C_5H_5)][BF_4]$ ($PR_3 = PMe_3$ or $PMe_2Ph$), whereas treatment with $K[BH(CHMeEt)_3]$ or tetra-alkylammonium halide gives the species $[PtW(\mu-H)\{\mu-CH(C_6H_4Me-4)\}(CO)_2(PR_3)_2(\eta-C_5H_5)]$ ($PR_3 = PMe_3$ or $PMe_2Ph$) and $[PtWX\{\mu-CH(C_6H_4Me-4)\}(CO)_2(PR_3)_2(\eta-C_5H_5)]$ (X = Cl, Br, or I, $PR_3 = PMe_3$; X = I, $PR_3 = PMe_2Ph$), respectively. N.m.r. data ($^1H$, $^{13}C-\{^1H\}$, $^{31}P-\{^1H\}$, and $^{195}Pt-\{^1H\}$) are reported, and discussed in relation to the structures of the compounds. In solution, the bridged hydrido-complexes exist as an equilibrium mixture of diastereoisomers. An *X*-ray diffraction study of $[PtW(\mu-H)\{\mu-CH(C_6H_4Me-4)\}(CO)_2(PMe_3)_2(\eta-C_5H_5)]$ confirmed that the metal–metal bond is spanned by the $CH(C_6H_4Me-4)$ and H ligands [Pt–W 2.895(1), Pt–μ-C 2.109(9), and W–μ-C 2.259(9) Å], that the tungsten atom carries two terminally bonded CO groups and the $\eta-C_5H_5$ ligand, and that the platinum atom is part of a *cis*-$Pt(PMe_3)_2$ group. The platinum is in an essentially planar environment with the angle between the planes defined by $PtP_2$ and Pt(μ-C)W being only 7°. Crystals are monoclinic, space group $P2_1/c$; the structure has been refined to *R* 0.039 for 3 083 reflections measured to $2\theta = 50°$ at 220 K. Some reactions of the salt $[PtW\{\mu-\sigma:\eta^3-C(Me)C_6H_4Me-4\}(CO)_2(PMe_3)_2(\eta-C_5H_5)][SO_3CF_3]$ have also been studied. Thus $PMe_3$, $K[BH(CHMeEt)_3]$, and NaH afford, respectively, the compounds $[PtW\{\mu-C(Me)C_6H_4Me-4\}(CO)_2(PMe_3)_3(\eta-C_5H_5)][SO_3CF_3]$, $[PtW(\mu-H)\{\mu-C(Me)C_6H_4Me-4\}(CO)_2(PMe_3)_2(\eta-C_5H_5)]$, and $[PtW\{\mu-C(C_6H_4Me-4)=CH_2\}(CO)_2(PMe_3)_2(\eta-C_5H_5)]$. N.m.r. data show that the $PMe_3$ adduct and and the hydrido-species exist in solution as mixtures of diastereoisomers.

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In the preceding paper [1] we described the salts (1), obtained by protonation or methylation of the compounds $[PtW(\mu-CC_6H_4Me-4)(CO)_2(PR_3)_2(\eta-C_5H_5)]$ ($PR_3 = PMe_3$, $PMe_2Ph$, or $PMePh_2$). In these salts the bridging group adopts an interesting $\sigma:\eta^3-CH(C_6H_4Me-4)$ bonding mode also found in the compounds $[Mo_2\{\mu-C(C_6H_4Me-4)_2\}(CO)_4(\eta-C_5H_5)_2]$,[2] $[RhW\{\mu-CH(C_6H_4Me-4)\}(CO)_2(PMe_3)(\eta-C_5H_5)(\eta-C_9H_7)][BF_4]$ ($C_9H_7$ = indenyl),[3] and $[Ru_2(\mu-CPh_2)(\mu-CO)(CO)(\eta-C_5H_5)_2]$.[4] In this paper we describe reactions of the salts (1) with a variety of nucleophilic reagents which afford products in which platinum–tungsten bonds are bridged by the tolylmethylene or methyltolylmethylene groups. Formation of these new species *via* protonation or methylation of the species $[PtW(\mu-CC_6H_4Me-4)(CO)_2(PR_3)_2(\eta-C_5H_5)]$ corresponds to the conversion of alkylidyne into alkylidene groups at a dimetal centre. A preliminary account of some of the results has been given.[5]

## Results and Discussion

Treatment of dichloromethane solutions of the salts (1a)—(1c) with carbon monoxide at atmospheric pressure afforded quantitatively the tricarbonyl species (2), data for which are summarised in Table 1. The $^1H$ and $^{13}C-\{^1H\}$ n.m.r. spectra (Table 2) of the three compounds showed that the tolyl ring had been displaced from $\eta^2$ bonding to tungsten. Thus the signal for the $C_6H_4$ group in the $^1H$ spectrum of compound (2a) appears as a singlet whereas in the spectrum of (1a) the $C_6H_4$ moiety gives rise to four resonances.[1] Similarly, the $^{13}C-\{^1H\}$ n.m.r. spectrum of (2a) shows four resonances for the $C_6H_4$ ring whereas this group in (1a) has no equivalent carbon sites and thus produces six resonances.[1] The i.r. spectra of compounds (2) (Table 1) display three CO bands, one of which at *ca.* 1 860 $cm^{-1}$ is characteristic of a semi-bridging ligand.[3,6] In agreement, the $^{13}C-\{^1H\}$ n.m.r. spectra show three distinct CO resonances and hence no rapid carbonyl-exchange process is occurring at the tungsten centre. Moreover, each spectrum displays a signal [δ 76.1 (2a), 78.2 (2b), and 81.8 p.p.m. (2c)] due to the ligated μ-C atom, appearing as a doublet due to $^{31}P-^{13}C$ coupling with the transoid $PR_3$ group. The appearance of $^{195}Pt$ satellite peaks with *J*(PtC) 445—466 Hz (Table 2) is also diagnostic. For compound (2a) the spectrum was also of sufficient quality to show $^{183}W-^{13}C$ coupling. An interesting feature of the chemical shifts for the μ-C nuclei is that they are by far the most shielded of those as yet reported for a carbene-carbon ligand bridging two heteronuclear metal centres. The normal range of such signals is δ 100—200 p.p.m.[7]

Interestingly, the salts (2) release CO readily so that their formation is reversible, consequently the n.m.r. data (Tables 2 and 3) were measured on samples under an atmosphere of carbon monoxide. The $^{31}P-\{^1H\}$ and $^{195}Pt-\{^1H\}$ spectra were as expected for the proposed structures, being characteristic of species with *cis*-$Pt(PR_3)_2$ groups.[6]

The compounds (1a) and (1b) react with $PMe_3$ and $PMe_2Ph$, respectively, to afford the complexes (3a) and (3b). These

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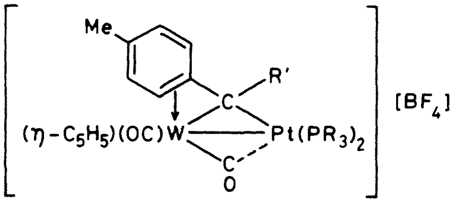
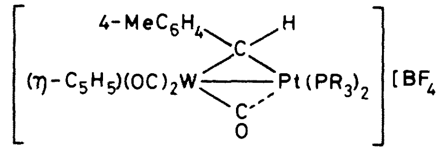
* 2,2-Dicarbonyl-2-η-cyclopentadienyl-μ-hydrido-μ-*p*-tolylmethylene-1,1-bis(trimethylphosphine)platinumtungsten(*Pt–W*).

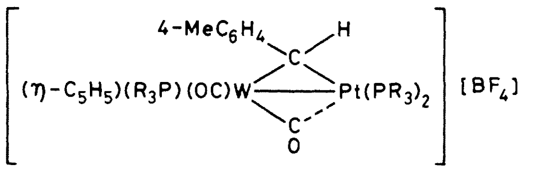
*Supplementary data available* (No. SUP 23930, 28 pp.): thermal parameters, H-atom co-ordinates, complete bond distances and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



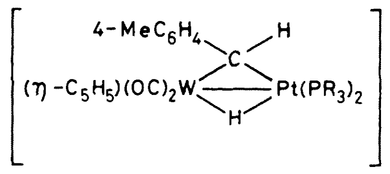
| | $PR_3$ | R' |
|---|---|---|
| (1a) | $PMe_3$ | H |
| (1b) | $PMe_2Ph$ | H |
| (1c) | $PMePh_2$ | H |
| (1d) | $PMe_3$ | Me |



| | $PR_3$ |
|---|---|
| (2a) | $PMe_3$ |
| (2b) | $PMe_2Ph$ |
| (2c) | $PMePh_2$ |



| | $PR_3$ |
|---|---|
| (3a) | $PMe_3$ |
| (3b) | $PMe_2Ph$ |



| | $PR_3$ |
|---|---|
| (4a) | $PMe_3$ |
| (4b) | $PMe_2Ph$ |

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

| Complex [b] | M.p. ($\theta_c$/°C) [c] | Colour | Yield (%) | $\tilde{\nu}$(CO) [d]/cm$^{-1}$ | Analysis (%) | |
|---|---|---|---|---|---|---|
| | | | | | C | H |
| (2a) $[PtW(\mu\text{-}CHR)(CO)_3(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$ | 156—160 | Orange | 100 | 2 026s, 1 978s, 1 861(br) | 29.7 (30.3) | 3.6 (3.6) |
| (2b) $[PtW(\mu\text{-}CHR)(CO)_3(PMe_2Ph)_2(\eta\text{-}C_5H_5)][BF_4]$ | 90—95 | Orange | 100 | 2 027s, 1 980s, 1 855m(br) | 38.7 (38.6) | 3.9 (3.5) |
| (2c) $[PtW(\mu\text{-}CHR)(CO)_3(PMePh_2)_2(\eta\text{-}C_5H_5)][BF_4]$ | 118—120 | Yellow | 100 | 2 030s, 1 983s, 1 866m(br) | 45.0 (45.0) | 3.6 (3.5) |
| (3a) $[PtW(\mu\text{-}CHR)(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)][BF_4]$ | 142—145 | Yellow | 100 | 1 942s, 1 804m(br) | 31.4 (31.3) | 4.2 (4.5) |
| (3b) $[PtW(\mu\text{-}CHR)(CO)_2(PMe_2Ph)_3(\eta\text{-}C_5H_5)][BF_4]$ | 110—115 | Orange | 100 | 1 942s, 1 804m(br) | 41.9 (42.4) | 4.3 (4.2) |
| (4a) $[PtW(\mu\text{-}H)(\mu\text{-}CHR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ | 146—150 | Yellow | 67 | 1 897s, 1 802s | 33.4 (33.3) | 4.7 (4.2) |
| (4b) $[PtW(\mu\text{-}H)(\mu\text{-}CHR)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ | 50—56 | Yellow | 70 | 1 899s, 1 804s | 41.7 (42.2) | 4.4 (4.1) |
| (5a) $[PtWCl(\mu\text{-}CHR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ | 150—154 | Orange | 88 | 1 959s, 1 764m(br) | [e] 31.8 (31.8) | 4.2 (3.9) |
| (5b) $[PtWBr(\mu\text{-}CHR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ | 166—170 | Orange | 93 | 1 959s, 1 770m(br) | [f] 30.1 (30.1) | 3.9 (3.8) |
| (5c) $[PtWI(\mu\text{-}CHR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ | 168—172 | Orange | 88 | 1 955s, 1 783m(br) | [g] 28.6 (28.5) | 3.8 (3.5) |
| (5d) $[PtWI(\mu\text{-}CHR)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ | 136—140 | Orange | 90 | 1 957s, 1 779m(br) | [h] 37.0 (37.0) | 3.5 (3.5) |
| (6) $[PtW\{\mu\text{-}C(Me)R\}(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)][SO_3CF_3]$ | 98—100 | Yellow | 100 | 1 911s, 1 794s | 31.5 (31.4) | 4.7 (4.2) |
| (7) $[PtW(\mu\text{-}H)\{\mu\text{-}C(Me)R\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ | 106—110 | Yellow | 78 | 1 898s, 1 800s | 34.0 (34.2) | 4.7 (4.4) |
| (8a) $[PtW\{\mu\text{-}C(R)=CH_2\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ | 194—200 | Yellow | 65 | 1 866s, 1 727m | 34.4 (34.3) | 4.6 (4.2) |
| (8b) $[PtW\{\mu\text{-}C(R)=CH_2\}(CO)_3(PMe_3)(\eta\text{-}C_5H_5)]$ | 152—156 | Yellow | 100 | 2 034s, 1 882s, 1 774m(br) | 33.6 (33.3) | 3.4 (3.2) |

[a] Calculated values are given in parentheses. [b] R = $C_6H_4Me\text{-}4$. [c] With decomposition. [d] In $CH_2Cl_2$. [e] Cl, 5.1 (4.5%). [f] Br, 9.5 (9.6%). [g] I, 14.3 (14.4%). [h] I, 13.0 (12.6%).

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reactions thus parallel those involving CO; the $\eta^2\text{-}C_6H_4Me\text{-}4$ bonding in the precursors is displaced by the $PR_3$ groups so that a formal 18-electron count is maintained at the tungsten atom in each species. The $^1H$ and $^{13}C\text{-}\{^1H\}$ n.m.r. data for compounds (3) (Table 2) are similar to those for (2) and call for no comment. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra (Table 3) show three resonances, as expected for the proposed structures. The presence of a tungsten-bonded $PR_3$ ligand in (3a) and (3b) is confirmed by one of the resonances showing large $^{183}W\text{-}^{31}P$ coupling. The spectrum of (3a) was second order and the chemical shifts for this compound were determined from the $^{195}Pt$ satellite peaks.

The cobalt–tungsten compound $[CoW\{\mu\text{-}\sigma\text{:}\eta^3\text{-}CH(C_6H_4\text{-}Me\text{-}4)(CO)_3(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)][BF_4]$ reacts with $PMe_2Ph$ to afford a product $[CoW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_3(PMe_2Ph)\text{-}(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)][BF_4]$ of similar structure to (3b), with the

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

| Complex [b] | $^1H$ (δ) | $^{13}C$ [c] (δ) |
|---|---|---|
| (2a) [d] | 1.54 [d, 9 H, MeP, *J*(PH) 11, *J*(PtH) 45, *J*(WH) 6], 1.71 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 22], 2.29 (s, 3 H, Me-4), 5.33 [d, 5 H, $C_5H_5$, *J*(PH) 1, *J*(PtH) 5], 5.83 [d of d, 1 H, μ-CH, *J*(PH) 4, 2, *J*(PtH) 12], 6.99 (s, 4 H, $C_6H_4$) | 218.3 [d, CO, *J*(PC) 16], 211.5 [d, CO, *J*(PC) 7], 205.9 [CO, *J*(PtC) 67], 154.0 [d, $C^1(C_6H_4)$, *J*(PC) 6], 135.7, 129.3, 128.3 ($C_6H_4$), 93.3 ($C_5H_5$), 76.1 [d, μ-C, *J*(PC) 60, *J*(PtC) 445, *J*(WC) 28], 21.0 (Me-4), 18.1 [d, MeP, *J*(PC) 35, *J*(PtC) 56], 17.5 [d, MeP, *J*(PC) 29, *J*(PtC) 30] |
| (2b) [e] | 1.30 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 44], 1.43 [d, 3 H, MeP, *J*(PH) 11, *J*(PtH) 45], 1.61 [d, 3 H, MeP, *J*(PH) 8], 1.71 [d, 3 H, MeP, *J*(PH) 9, *J*(PtH) 21], 2.29 (s, 3 H, Me-4), 5.29 (s, 5 H, $C_5H_5$), 5.86 [d of d. μ-CH, *J*(PH) 4, 1, *J*(PtH) 20], 7.0—7.8 (m, 14 H, $C_6H_4$, Ph) | 218.8 [d, CO, *J*(PC) 17, *J*(PtC) 96], 210.0 [d, CO, *J*(PC) 7, *J*(WC) 124], 205.4 [CO, *J*(PtC) 67, *J*(WC) 138], 153.6 [$C^1(C_6H_4)$], 139—127 ($C_6H_4$, Ph), 93.1 ($C_5H_5$), 78.2 [d, μ-CH, *J*(PC) 60, *J*(PtC) 452], 20.9 (Me-4), 16.1 [d, MeP, *J*(PC) 38, *J*(PtC) 58], 16.0 [d, MeP, *J*(PC) 29], 15.0 [d, MeP, *J*(PC) 27], 14.8 [d, MeP, *J*(PC) 31] |
| (2c) [e] | 1.70 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 45], 2.10 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 21], 2.20 (s, 3 H, Me-4), 5.30 [d, 5 H, $C_5H_5$, *J*(PH) 5], 6.5—7.6 (m, 24 H, $C_6H_4$, Ph) | 218.2 [d, CO, *J*(PC) 16], 206.9 [CO, *J*(PtC) 65, *J*(WC) 139], 206.7 [d, CO, *J*(PC) 9], 152.5 [d, $C^1(C_6H_4)$, *J*(PC) 5], 140—125 ($C_6H_4$, Ph), 93.0 ($C_5H_5$), 81.8 [d, μ-CH, *J*(PC) 57, *J*(PtC) 466], 20.9 (Me-4), 15.7 [d, MeP, *J*(PC) 29, *J*(PtC) 22], 15.0 [d, MeP, *J*(PC) 36, *J*(PtC) 44] |
| (3a) [f] | 1.42 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 38], 1.62 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 8], 1.65 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 22], 2.25 (s, 3 H, Me-4), 4.97 (s, 5 H, $C_5H_5$), 5.79 [d of d of d, 1 H, μ-CH, *J*(PH) 27, 3, 2, *J*(PtH) 25], 6.83—6.99 (m, 4 H, $C_6H_4$) | 228.1 [d of d, CO, *J*(PC) 18, 15, *J*(PtC) 126], 223.6 [d, CO, *J*(PC) 13], 157.0 [$C^1(C_6H_4)$], 133.9, 129.0, 126.5 ($C_6H_4$), 95.0 [d of d, μ-C, *J*(PC) 60, 7, *J*(PtC) 496, *J*(WC) 42], 91.9 ($C_5H_5$), 20.9 (Me-4), 19.1 [d, MeP, *J*(PC) 31, *J*(PtC) 24], 18.9 [d, MeP, *J*(PC) 38], 17.6 [d, MeP, *J*(PC) 31, *J*(PtC) 24] |
| (3b) [c] | 1.02 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 37], 1.26 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 38], 1.49 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 24], 1.78 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 22], 1.97 [d, 3 H, MeP, *J*(PH) 7], 2.01 [d, 3 H, MeP, *J*(PH) 7], 2.26 (s, 3 H, Me-4), 4.92 (s, 5 H, $C_5H_5$), 5.76 [d of d of d, 1 H, μ-CH, *J*(PH) 27, 3, 2, *J*(PtH) 25], 6.5—7.8 (m, 19 H, $C_6H_4$, Ph) | 229.1 [d of d, CO, *J*(PC) 19, 14, *J*(PtC) 130], 223.4 [d of d, CO, *J*(PC) 15, 7], 156.6 [$C^1(C_6H_4)$], 138—125 ($C_6H_4$, Ph), 99.5 [d(br), μ-CH, *J*(PC) 57, *J*(PtC) 592], 92.3 ($C_5H_5$), 21.0 [d, MeP, *J*(PC) 32, *J*(PtC) 28], 20.9 (Me-4), 17.3 [d, MeP, *J*(PC) 32, *J*(PtC) 32], 16.7 [d, MeP, *J*(PC) 28, *J*(PtC) 24], 15.4 [d, MeP, *J*(PC) 34, *J*(PtC) 48], 15.2 [d, MeP, *J*(PC) 36, *J*(PtC) 42], 13.6 [d, MeP, *J*(PC) 29, *J*(PtC) 29] |
| (4a) [f,g] | (A)[h] −7.92 [d of d, 1 H, μ-H, *J*(PH) 82, 15, *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, Me-4), 5.25 (s, 5 H, $C_5H_5$), 6.10 [d, 1 H, $C_6H_4$, *J*(HH) 7], 6.57 [t, 1 H, μ-CH, *J*(PH) 4], 6.74—6.93 (m, 3 H, $C_6H_4$) | 241.7 [CO, *J*(WC) 145], 232.8 [CO, *J*(WC) 184], 159.0 [$C^1(C_6H_4)$], 132.3, 129.5, 127.2, 126.1, 124.3 ($C_6H_4$), 105.3 [d, μ-C, *J*(PC) 57, *J*(PtC) 486, *J*(WC) 58], 88.4 ($C_5H_5$), 20.4 (Me-4), 19.2 [d, MeP, *J*(PC) 29, *J*(PtC) 29], 16.5 [d, MeP, *J*(PC) 33, *J*(PtC) 24] |
|  | (B)[i] −8.57 [d of d, 1 H, μ-H, *J*(PH) 83, 15, *J*(PtH) 473], 1.43 [d, 9 H, MeP, *J*(PH) 12], 1.67 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 24], 2.18 (s, 3 H, Me-4), 4.92 (s, 5 H, $C_5H_5$) | 237.7 (CO), 237.2 (CO), 160.7 [$C^1(C_6H_4)$], 133.0, 129.6, 128.4, 127.7, 126.8 ($C_6H_4$), 111.9 [d, μ-C, *J*(PC) 58], 90.0 ($C_5H_5$) |
| (4b) [f,j] | (A) −7.41 [d of d, 1 H, μ-H, *J*(PH) 82, 14, *J*(PtH) 528, *J*(WH) 52], 1.16 [d, 3 H, MeP, *J*(PH) 9], 1.38 [d, 3 H, MeP, *J*(PH) 10], 1.60 [d, 3 H, MeP, *J*(PH) 8], 1.71 [d, 3 H, MeP, *J*(PH) 8], 2.20 (s, 3 H, Me-4), 5.21 (s, 5 H, $C_5H_5$), 6.26 [d, 1 H, μ-CH, *J*(PH) 8], 6.6—7.5 (m, 14 H, $C_6H_4$, Ph) | 242.2 (CO), 233.0 (CO), 159.4 [$C^1(C_6H_4)$], 144—124 ($C_6H_4$, Ph), 108.9 [d, μ-C, *J*(PC) 56, *J*(PtC) 488], 89.1 ($C_5H_5$), 21.1 (Me-4), 18.9 [d, MeP, *J*(PC) 29, *J*(PtC) 28], 17.2 [d, MeP, *J*(PC) 29, *J*(PtC) 33], 15.5 [d, MeP, *J*(PC) 32, *J*(PtC) 37], 14.6 [d, MeP, *J*(PC) 34] |
|  | (B)[i] −7.98 [d of d, 1 H, μ-H, *J*(PH) 82, 15, *J*(PtH) 536], 4.85 (s, 5 H, $C_5H_5$) | 160.9 [$C^1(C_6H_4)$], 114.4 [d, μ-C, *J*(PC) 62], 90.8 ($C_5H_5$) |
| (5a) [c] | 1.39 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 35], 1.65 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 23], 2.27 (s, 3 H, Me-4), 5.00 [d, 5 H, $C_5H_5$, *J*(PH) 1, *J*(PtH) 6], 6.01 [d of d, 1 H, μ-CH, *J*(PH) 5, 3, *J*(PtH) 13], 6.94—7.10 (m, 4 H, $C_6H_4$) |  |
| (5b) [d] | 1.41 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 35], 1.66 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 23], 2.27 (s, 3 H, Me-4), 5.00 [d, 5 H, $C_5H_5$, *J*(PH) 1, *J*(PtH) 5], 6.36 [d of d, 1 H, μ-CH, *J*(PH) 5, 3, *J*(PtH) 12], 6.94—7.09 (m, 4 H, $C_6H_4$) | 237.6 [d, CO, *J*(PC) 16, *J*(PtC) 87], 221.8 [d, CO, *J*(PC) 3, *J*(PtC) 34], 158.3 [d, $C^1(C_6H_4)$, *J*(PC) 3], 131.9, 128.3 ($C_6H_4$), 109.8 [d, μ-C, *J*(PC) 59, *J*(PtC) 538, *J*(WC) 47], 92.5 ($C_5H_5$), 21.0 (Me-4), 19.2 [d, MeP, *J*(PC) 30, *J*(PtC) 45], 18.0 [d, MeP, *J*(PC) 28, *J*(PtC) 28] |
| (5c) [e] | 1.43 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 36], 1.68 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 22], 2.25 (s, 3 H, Me-4), 5.00 [d, 5 H, $C_5H_5$, *J*(PH) 1, *J*(PtH) 6], 7.0 (m, 5 H, $C_6H_4$, μ-CH) |  |
| (5d) [c] | 1.17 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 37], 1.44 [d, 3 H, MeP, *J*(PH) 10, *J*(PtH) 36], 1.58 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 23], 1.66 [d, 3 H, MeP, *J*(PH) 8, *J*(PtH) 23], 2.28 (s, 3 H, Me-4), 5.07 (s, 5 H, $C_5H_5$), 6.9—7.4 (m, 15 H, $C_6H_4$, Ph, μ-CH) | 234.9 [d, CO, *J*(PC) 16], 217.8 [d, CO, *J*(PC) 4], 158.5 [$C^1(C_6H_4)$], 139—127 ($C_6H_4$, Ph), 101.6 [d, μ-C, *J*(PC) 59, *J*(PtC) 541, *J*(WC) 47], 91.5 ($C_5H_5$), 20.9 (Me-4), 18.1 [d of d, MeP, *J*(PC) 40, 3, *J*(PtC) 44], 16.6 [d of d, MeP, *J*(PC) 50, 4, *J*(PtC) 46], 15.2 [d, MeP, *J*(PC) 33, *J*(PtC) 42], 15.1 [d, MeP, *J*(PC) 27, *J*(PtC) 26] |
| (6) [d] | (A) 1.45 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 40], 1.68 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 20], 1.81 [d, 9 H, MeP, *J*(PH) 10], 2.29 (s, 3 H, Me-4), 2.55 (br, 3 H, μ-CMe), 5.30 [d, 5 H, $C_5H_5$, *J*(PH) 2], 7.01, 7.08 [$(AB)_2$, 4 H, $C_6H_4$, *J*(AB) 8] | 225 (m, CO), 220.9 [d, CO, *J*(PC) 35], 154.8 [$C^1(C_6H_4)$, *J*(PtC) 36], 136.4, 128.2 ($C_6H_4$), 126.9 (br, μ-C), 121.5 [q, $CF_3$, *J*(FC) 326], 95.1 ($C_5H_5$), 37.3 (μ-C*Me*), 20.9 (Me-4), 20—16 (MeP) |
|  | (B)[i] 1.37 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 40], 1.66 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 22], 2.24 (s, 3 H, Me-4), 2.55 (br, 3 H, μ-CMe), 5.64 [d, 5 H, $C_5H_5$, *J*(PH) 2], 6.92, 7.01 [$(AB)_2$, 4 H, $C_6H_4$, *J*(AB) 8] | 156.8 [$C^1(C_6H_4)$], 134.6, 127.9 ($C_6H_4$), 38.1 (μ-C*Me*) |

**Table 2** (*continued*)

| | | |
|---|---|---|
| (7) [f,k] | (A) −7.98 [d of d, 1 H, $\mu$-H, *J*(PH) 78, 14, *J*(PtH) 566], 1.22 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 35], 1.68 [d, 9 H, MeP, *J*(PH) 8], 2.17 (s, 3 H, Me-4), 2.64 (br, 3 H, $\mu$-CMe), 4.95 (s, 5 H, $C_5H_5$), 6.3—7.4 (m, 4 H, $C_6H_4$) | 239.1 (CO), 236.2 [CO, *J*(WC) 178], 163.1 [$C^1(C_6H_4)$], 134.9, 133.9, 127.9, 126.5 ($C_6H_4$), 124.6 [d, $\mu$-C, *J*(PC) 63, *J*(PtC) 515], 89.7 ($C_5H_5$), 20.9 (Me-4), 19.6 [d, MeP, *J*(PC) 27, *J*(PtC) 28], 16.8 [d, MeP, *J*(PC) 34] |
| | (B)[i] −8.15 [d of d, 1 H, $\mu$-H, *J*(PH) 78, 14], 1.28 [d, 9 H, MeP, *J*(PH) 15, *J*(PtH) 37], 1.69 [d, 9 H, MeP, *J*(PH) 8], 2.17 (s, 3 H, Me-4), 2.64 (br, 3 H, $\mu$-CMe), 5.25 (s, 5 H, $C_5H_5$), 6.1—7.4 (m, 4 H, $C_6H_4$) | 237.7 (2 CO), 162.2 [$C^1(C_6H_4)$], 91.3 ($C_5H_5$) |
| (8a) [d] | 1.29 [d, 9 H, MeP, *J*(PH) 10, *J*(PtH) 33], 1.55 [d, 9 H, MeP, *J*(PH) 9, *J*(PtH) 22], 2.30 (s, 3 H, Me-4), 2.83 [d, 1 H, $H^2(CH_2)$, *J*(PH) 8, *J*(PtH) 16], 3.32 [d, 1 H, $H^1(CH_2)$, *J*(PH) 12, *J*(PtH) 110], 4.76 (s, 5 H, $C_5H_5$), 6.9—7.4 (m, 4 H, $C_6H_4$) | 236.7 [d, CO, *J*(PC) 11, *J*(PtC) 50], 226.7 [d, CO, *J*(PC) 3, *J*(WC) 174], 153.3 [$C^1(C_6H_4)$, *J*(PtC) 24], 142.4 [d, $\mu$-C, *J*(PC) 78, *J*(PtC) 608], 129.1, 128.3 ($C_6H_4$), 90.5 ($C_5H_5$), 26.7 ($CH_2$), 21.0 (Me-4), 19.0 [d, MeP, *J*(PC) 30, *J*(PtC) 42], 17.8 [d, MeP, *J*(PC) 27, *J*(PtC) 36] |
| (8b) [d] | 1.34 [d, 9 H, MeP, *J*(PH) 11, *J*(PtH) 33], 2.33 (s, 3 H, Me-4), 2.58 [d, 1 H, $H^2(CH_2)$, *J*(HH) 2, *J*(PtH) 20], 3.16 [d of d, 1 H, $H^1(CH_2)$, *J*(HH) 2, *J*(PH) 2, *J*(PtH) 107], 4.91 (s, 5 H, $C_5H_5$), 7.0—7.1 (m, 4 H, $C_6H_4$) | 233.9 [CO, *J*(PtC) 24], 224.7 [CO, *J*(WC) 176], 193.6 [d, CO, *J*(PC) 5, *J*(PtC) 1 342], 151.4 [$C^1(C_6H_4)$, *J*(PtC) 28], 147.1 [$\mu$-C, *J*(PtC) 653, *J*(WC) 39], 135.6, 128.6 ($C_6H_4$), 91.5 ($C_5H_5$), 21.7 (Me-4), 21.1 [$CH_2$, *J*(WC) 173], 17.2 [d, MeP, *J*(PC) 34, *J*(PtC) 43] |

[a] Chemical shifts ($\delta$) in p.p.m., coupling constants in Hz. Measurements at room temperature unless otherwise stated. [b] R = $C_6H_4Me$-4. [c] Hydrogen-1 decoupled, to high frequency of $SiMe_4$. [d] Hydrogen-1 spectrum measured in $CDCl_3$, and $^{13}C$ spectrum measured in $CD_2Cl_2$–$CH_2Cl_2$. [e] Spectra measured in $CDCl_3$. [f] Hydrogen-1 spectrum measured in $CD_2Cl_2$, and $^{13}C$ spectrum measured in $CD_2Cl_2$–$CH_2Cl_2$. [g] Spectra measured at −30 °C. [h] (A) refers to the major and (B) to the minor isomer. [i] Only signals clearly distinguishable from those of the major isomer (A) are listed. [j] Hydrogen-1 spectrum measured at −50 °C, and $^{13}C$ at −30 °C. [k] Spectra measured at −50 °C.

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

| Compound | | $^{31}P$ [b] ($\delta$) | $^{195}Pt$ [c] ($\delta$) |
|---|---|---|---|
| (2a) [d] | | −10.5 [d, *J*(PP) 10, *J*(PtP) 4 324, *J*(WP) 40]<br>−13.5 [d, *J*(PP) 10, *J*(PtP) 2 510] | 243.5 [d of d, *J*(PPt) 4 324, 2 510] |
| (2b) [e] | | −1.2 [d, *J*(PP) 11, *J*(PtP) 4 355, *J*(WP) 20]<br>−3.0 [d, *J*(PP) 11, *J*(PtP) 2 554] | 205.8 [d of d, *J*(PPt) 4 335, 2 554, *J*(WPt) 136] |
| (2c) [e] | | 12.2 [d, *J*(PP) 10, *J*(PtP) 4 461]<br>9.6 [d, *J*(PP) 10, *J*(PtP) 2 551] | 213.7 [d of d, *J*(PPt) 4 461, 2 551] |
| (3a) [d] | | −15.6 [ABX, $P^{\alpha}Pt$, *J*($P^{\beta}P^{\alpha}$) 8, *J*($PtP^{\alpha}$) 2 548]<br>−15.8 [ABX, $P^{\beta}Pt$, *J*($P^{\alpha}P^{\beta}$) 8, *J*($P^{\gamma}P^{\beta}$) 13, *J*($PtP^{\beta}$) 3 872]<br>−30.7 [ABX, $P^{\gamma}W$, *J*($P^{\beta}P^{\gamma}$) 13, *J*($PtP^{\gamma}$) 135, *J*($WP^{\gamma}$) 242] | −14.9 [d of d of d, *J*(PPt) 3 872, 2 548, 135] |
| (3b) [c] | | −5.2 [d, *J*(PP) 8, *J*(PtP) 2 560]<br>−6.5 [d of d, *J*(PP) 13, 8, *J*(PtP) 3 844]<br>−22.7 [d, *J*(PP) 13, *J*(PtP) 139, *J*(WP) 214] | −17.6 [d of d of d, *J*(PPt) 3 844, 2 560, 139] |
| (4a) [d,f] | (A) [g] | −26.5 [d, *J*(PP) 10, *J*(PtP) 3 944]<br>−25.9 [d, *J*(PP) 10, *J*(PtP) 2 251] | −1 006 [d of d, *J*(PPt) 3 944, 2 251] |
| | (B) | −23.6 [d, *J*(PP) 12, *J*(PtP) 2 160]<br>−27.8 [d, *J*(PP) 12, *J*(PtP) 3 891] | −1 023 [d of d, *J*(PPt) 3 891, 2 160] |
| (4b) [d,h] | (A) | −11.2 [d, *J*(PP) 8, *J*(PtP) 4 030]<br>−13.9 [d, *J*(PP) 8, *J*(PtP) 2 302] | −1 019 [d of d, *J*(PPt) 4 030, 2 302] |
| | (B) [i] | −6.2 [d, *J*(PP) 10, *J*(PtP) 2 798]<br>−15.5 [d, *J*(PP) 10, *J*(PtP) 3 980] | |
| (5a) [e] | | −9.1 [d, *J*(PP) 5, *J*(PtP) 3 694, *J*(WP) 32]<br>−14.2 [d, *J*(PP) 5, *J*(PtP) 2 627] | |
| (5b) [d] | | −10.0 [d, *J*(PP) 5, *J*(PtP) 3 734, *J*(WP) 29]<br>−14.9 [d, *J*(PP) 5, *J*(PtP) 2 626] | −79.1 [d of d, *J*(PPt) 3 734, 2 626] |
| (5d) [e] | | −2.4 [d, *J*(PP) 7, *J*(PtP) 3 831, *J*(WP) 30]<br>−4.2 [d, *J*(PP) 7, *J*(PtP) 2 663] | −21.6 [d of d, *J*(PPt) 3 831, 2 663] |
| (6) | (A) [e] | −10.9 [d, *J*(PP) 12, *J*(PtP) 34, *J*(WP) 214]<br>−17.9 [d, *J*(PP) 12, *J*(PtP) 4 187]<br>−22.0 [s, *J*(PtP) 2 335] | [d] 47.0 [d of d of d, *J*(PPt) 4 187, 2 335, 34] |
| | (B) | −9.5 [d, *J*(PP) 12, *J*(PtP) 38]<br>−18.5 [d, *J*(PP) 12, *J*(PtP) 4 171]<br>−21.2 [s, *J*(PtP) 2 358] | 37.3 [d of d of d, *J*(PPt) 4 171, 2 358, 38] |
| (7) [d,j] | (A) | −25.6 [d, *J*(PP) 8, *J*(PtP) 4 120]<br>−30.2 [d, *J*(PP) 8, *J*(PtP) 2 073] | |
| (8a) [e] | | −17.0 [d, *J*(PP) 10, *J*(PtP) 2 678]<br>−23.4 [d, *J*(PP) 10, *J*(PtP) 3 570, *J*(WP) 24] | [d] −238.0 [d of d, *J*(PPt) 3 570, 2 678] |
| (8b) [e] | | −24.0 [s, *J*(PPt) 3 159, *J*(WP) 19] | −106.0 [d, *J*(PPt) 3 159] |

[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) measured at room temperature unless otherwise stated. [c] Chemical shifts to high frequency of $\Xi(^{195}Pt)$ 21.4 MHz, measured at room temperature unless otherwise stated. [e] In $CD_2Cl_2$. [d] In $CDCl_3$. [f] Phosphorus-31 spectrum measured at −60 °C, $^{195}Pt$ spectrum measured at −30 °C. [g] (A) and (B) refer to isomers, see text. [h] Spectra measured at −30 °C. [i] Platinum-195 peaks for this minor isomer not observed. [j] Spectra measured at −50 °C, peaks for minor isomer (B) not observed, see $^1H$ data (Table 2).

**Table 4.** Selected internuclear distances (Å) and angles (°), with estimated standard deviations in parentheses, for [PtW(μ-H){μ-CH($C_6H_4$Me-4)}$(CO)_2(PMe_3)_2$(η-$C_5H_5$)] (4a)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Pt–W | 2.895(1) | Pt–P(1) | 2.265(3) | P(1)–C(13) | 1.826(13) | P(2)–C(21) | 1.820(12) |
| Pt–P(2) | 2.305(3) | Pt–C | 2.109(9) | P(2)–C(22) | 1.798(12) | P(2)–C(23) | 1.820(12) |
| W–C | 2.259(9) | W–C(1) | 1.949(10) | C(1)–O(1) | 1.173(12) | C(2)–O(2) | 1.141(13) |
| W–C(2) | 1.954(11) | W–C(31) | 2.345(7) | C–C(41) | 1.497(10) | C(44)–C(47) | 1.552(13) |
| W–C(32) | 2.285(7) | W–C(33) | 2.313(7) | C–H(1) | 1.05 * | Pt–H(2) | 1.80 * |
| W–C(34) | 2.388(7) | W–C(35) | 2.408(7) | W–H(2) | 1.72 * | C–C($C_5H_5$) | 1.420 * |
| P(1)–C(11) | 1.801(13) | P(1)–C(12) | 1.826(11) | C–C(aryl) | 1.395 * | | |
| W–Pt–P(1) | 142.6(1) | W–Pt–P(2) | 114.4(1) | W–C(1)–O(1) | 177.1(9) | W–C(2)–O(2) | 178.7(9) |
| P(1)–Pt–P(2) | 102.3(1) | W–Pt–C | 50.7(2) | Pt–C–W | 83.0(3) | Pt–C–C(41) | 117.5(5) |
| P(1)–Pt–C | 92.3(3) | P(2)–Pt–C | 165.1(3) | W–C–C(41) | 121.8(6) | Pt–C–H(1) | 118 * |
| Pt–W–C(1) | 86.8(3) | Pt–W–C(2) | 103.6(3) | W–C–H(1) | 114 * | C(41)–C–H(1) | 103 * |
| C(1)–W–C(2) | 75.3(4) | Pt–W–C | 46.3(2) | W–H(2)–Pt | 111 * | | |
| C(1)–W–C | 116.3(4) | C(2)–W–C | 77.8(4) | | | | |

* Parameter not refined, see Experimental section.

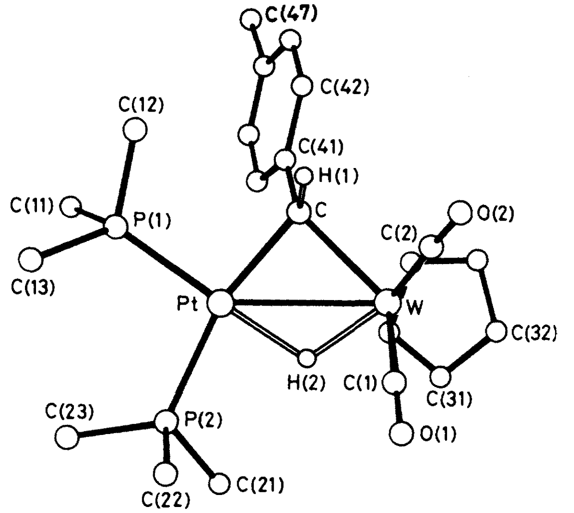


**Figure 1.** Molecular structure of the complex [PtW(μ-H){μ-CH($C_6H_4$Me-4)}$(CO)_2(PMe_3)_2$(η-$C_5H_5$)] (4a), showing the atom numbering scheme

$Pt(PMe_2Ph)_2$ group in the latter replaced by Co(CO)(η-$C_5Me_5$).[5,8] However, the compound [CoW{μ-CH($C_6H_4$Me-4)}$(CO)_3$($PMe_2$Ph)(η-$C_5H_5$)(η-$C_5Me_5$)][$BF_4$] exists as a pair of diastereoisomers which rapidly interconvert on the n.m.r. time-scale at room temperature. These diastereoisomers presumably differ in the orientation of the $PMe_2$Ph ligand with respect to the μ-CH($C_6H_4$Me-4) group. In contrast, the complexes (3) show only one set of sharp n.m.r. resonances in their spectra (Tables 2 and 3). This would occur if the high-temperature limit of a dynamic process had been achieved. However, as the less sterically crowded tricarbonyl complexes (2) (see above) and a more sterically crowded methyltolylmethylene analogue of (3a) (see below) show no dynamic behaviour at ambient temperatures, such a process seems unlikely for the species (3). An alternative and more plausible explanation for the n.m.r. data is that the latter compounds exist in one diastereoisomeric form. Perhaps, the stereoselective formation of (3) implies a reaction which has some $S_N2$ character, whereas the formation of [CoW{μ-CH($C_6H_4$-Me-4)}$(CO)_3$($PMe_2$Ph)(η-$C_5H_5$)(η-$C_5Me_5$)][$BF_4$] might proceed predominantly *via* an $S_N1$ process. A possible explanation for the difference between these cobalt–tungsten and platinum–tungsten salts may be associated with the properties of the two precursors [MW{μ-σ:$\eta^3$-CH($C_6H_4$Me-4)}$(CO)_2L_n$(η-$C_5H_5$)]-[$BF_4$] [$ML_n$ = $Pt(PMe_2Ph)_2$ or Co(CO)(η-$C_5Me_5$)]. Whereas compound (1b) has a rigid bridging ligand system,[1] the Co(CO)(η-$C_5Me_5$) analogue undergoes low-energy dynamic behaviour involving rotation of the $CC_6H_4$Me-4 group about the Co–μ-$CC_6H_4$Me-4 axis.[1,8]

Treatment of (1a) or (1b) with K[BH(CHMeEt)$_3$] affords the hydrido-bridged compounds (4), data for which are summarised in Tables 1—3. It was immediately apparent from the n.m.r. spectra that these species underwent dynamic behaviour in solution, involving interconversion of two isomers (A) and (B) present in *ca.* 4 : 1 proportions as judged from the relative intensity of n.m.r. peaks in low-temperature-limiting spectra. Discussion of the n.m.r. properties is deferred until the results of an *X*-ray diffraction study on compound (4a) are presented.

The molecule (4a) is shown in Figure 1, and selected internuclear distances and angles are summarised in Table 4. It is evident from the structure that the hydrido-ligand has formally added to the metal–metal bond with concomitant displacement of the $CC_6H_4$Me-4 group from its $\eta^2$-bonding mode to tungsten. The positions of the μ-CHR and W(μ-H)Pt hydrogen atoms were tentatively identified in the final electron-density difference map. In addition, possible μ-hydrido-sites were located using a steric-potential-energy-minimisation technique,[9] and the results of this calculation agree well with the observed μ-H location.

Compound (4a) is the first *X*-ray structurally characterised compound with both a carbene and a hydrido-ligand bridging a heteronuclear metal–metal bond. One diastereoisomeric form of (4a) is found in the crystal where packing forces may be sufficient to prevent the existence of the other form.

The dimensions of the $\overline{\mathrm{Pt}(\mu\text{-H})(\mu\text{-C})\mathrm{W}}$ core in (4a) are of interest and the data are summarised in Table 5, together with those for related compounds. It is apparent that the bonding within the ring system of (4a) is substantially weaker than in the two cationic carbene complexes (1a) and [PtW{μ-CH($C_6H_4$Me-4)}(μ-CO)(η-$MeC_2Me$)$(PMe_3)_2$(η-$C_5H_5$)][$BF_4$],[8] and that these compounds are in turn more weakly bonded at the core than the species [PtW(μ-$CC_6H_4$Me-4)-$(CO)_2(PMe_2Ph)_2$(η-$C_5H_5$)]. Perhaps not surprisingly, (4a) is the least thermally stable of the compounds listed in Table 5, decomposing slowly in solution at room temperature. The Pt–W bond is the longest we have observed,[10,11] reflecting the presence of the μ-H ligand.[12]

The platinum atom is approximately coplanar with its ligated atoms. Maximum deviation from the plane defined by Pt, W, C, P(1), P(2), and H(2) is 0.08 Å. The angle between the planes Pt,P(1),P(2) and W,Pt,C is only 7°. The ligand H(2)

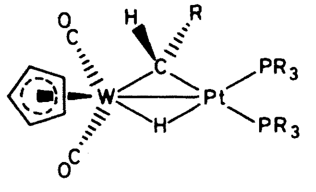
Table 5. Dimensions of three-membered rings in platinum–tungsten complexes [a]

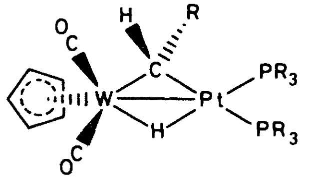
| Compound [b] | Pt–W | μ-C–Pt | μ-C–W | P–Pt [c] | Pt–μ-C–W |
|---|---|---|---|---|---|
| $[PtW(\mu\text{-}CR)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ [d] | 2.751(1) | 1.997(9) | 1.967(6) | 2.258(2)<br>2.325(2) | 87.9(3) |
| $[PtW(\mu\text{-}\sigma{:}\eta^3\text{-}CHR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (1a) [e] | 2.795(1) | 2.053(14) | 2.166(14) | 2.281(4)<br>2.314(4) | 83.0(5) |
| $[PtW(\mu\text{-}CHR)(\mu\text{-}CO)(\eta\text{-}MeC_2Me)(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$ [f] | 2.771(1) | 2.11(2) | 2.10(2) | 2.309(6)<br>2.316(5) | 82.3(6) |
| $[PtW(\mu\text{-}H)(\mu\text{-}CHR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (4a) | 2.895(1) | 2.109(9) | 2.259(9) | 2.265(3)<br>2.305(3) | 83.0(3) |

[a] Distances in Å, angles in °. [b] R = $C_6H_4Me$-4. [c] Longer distances correspond to the bond *trans* to the μ-C atom, see ref. 10. [d] Ref. 11. [e] Ref. 1. [f] Ref. 8.

occupies a position *trans* to P(1) and *cis* to P(2), hence in the $^1H$ n.m.r. spectrum, H(2) is strongly coupled to one phosphorus atom [P(1), *ca.* 80 Hz] and weakly coupled to the other [P(2), *ca.* 15 Hz].

As mentioned above, the n.m.r. data for the compounds (4) are interpretable if it is assumed that in solution these complexes exist as a mixture of two diastereoisomers (below). The isomers would be related by the relative orientations of the η-$C_5H_5$ and μ-$CH(C_6H_4Me\text{-}4)$ ligands with respect to the plane of the Pt(μ-C)W ring. Interconversion could occur *via* rotation of the $W(CO)_2(\eta\text{-}C_5H_5)$ moiety about an axis through the tungsten and the midpoint of the μ-C–Pt vector. Since in the two diastereoisomers the CO ligands are *trans* to similar groups in each, it is not surprising that in the i.r. spectrum two rather than four CO bands are observed (Table 1). Moreover, the spectrum had to be measured in $CH_2Cl_2$ rather than hexane, for reasons of solubility, and in the former solvent the bands are broadened.





At 35 °C, the $^1H$ n.m.r. spectrum of (4a) shows that interconversion of the isomers is approaching the high-temperature limit, with an averaging of the signals. Thus the μ-H group gives a resonance at δ −7.9 [d, *J*(PH) *ca.* 70, *J*(PtH) *ca.* 510 Hz]. At low temperatures (Tables 2 and 3) limiting spectra are observed. The $^1H$ spectra of (4a) and (4b) are, as expected, very similar, but the data for the latter species are superior and these are discussed in detail. At −50 °C (Figure 2), resonances for the μ-H ligand are seen at δ −7.41 [isomer (A)] and −7.98 p.p.m. [isomer (B)], both signals occurring as doublet of doublets due to $^{31}P$–$^1H$ coupling with the transoid and cisoid $PMe_2Ph$ groups. Also, $^{183}W$ and $^{195}Pt$ satellite peaks are observed. The magnitude of *J*(PtH) [528 (A) and 536 Hz (B)] is as expected for a hydrido-ligand bridging a metal–metal bond involving platinum.[13] Based on the behaviour of the distinctive η-$C_5H_5$ resonances for (A) and (B) of (4b), a coalescence temperature of *ca.* 0 °C was measured, leading to an estimate for $\Delta G^\ddagger$ for interconversion of the diastereoisomers of *ca.* 54 ± 4 kJ $mol^{-1}$. Interestingly, the cationic species $[Rh_2(\mu\text{-}H)(\mu\text{-}CH_2)(CO)_2(\eta\text{-}C_5H_5)_2]^+$ exists in solution as a mixture of two diastereoisomers [14] and a similar mechanism for interconversion as for (4) has been proposed.

The variable-temperature $^{13}C$-{$^1H$} (Table 2), $^{31}P$-{$^1H$}, and $^{195}Pt$-{$^1H$} (Table 3) n.m.r. spectra of the compounds (4) also reveal peaks due to two isomers for each species. Of particular interest in the $^{13}C$-{$^1H$} spectra of (4a) are the two CO signals for (A) and (B). For compound (4b) the spectrum was of insufficient quality to see the CO resonances of the minor isomer (B). From the $^{13}C$-{$^1H$} spectra of (4a) and (4b) the resonances due to the μ-C group of the predominant isomer (A) are readily identifiable from the *J*(PC) and *J*(PtP) couplings [(4a), δ 105.3, *J*(PC) 57, *J*(PtC) 486, and *J*(WC) 58; (4b), δ 108.9 p.p.m., *J*(PC) 56 and *J*(PtC) 488 Hz]. For the minor isomer (B) of (4a) and (4b), peaks for the μ-C nucleus are also seen as doublets at δ 111.9 [*J*(PC) 58] and 114.4 p.p.m. [*J*(PC) 62 Hz], respectively.

On treatment with $HBF_4{\cdot}Et_2O$ the compounds (4) surprisingly and readily revert to (1a) and (1b), respectively. Moreover, although treatment of (1a) and (1b) with $K[BH(CHMeEt)_3]$ affords (4a) and (4b), respectively, reaction of compounds (1) with NaH or $Na(C_5H_5)$ results in deprotonation to yield $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$. Interestingly, the hydrido-compounds (4) are also produced by treating the complexes (3) with $K[BH(CHMeEt)_3]$, a $PR_3$ group being displaced from tungsten in this reaction.

The complexes (4) can be regarded as hydrogenated forms of the species $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ ($PR_3$ = $PMe_3$ or $PMe_2Ph$),[6,11] the 'hydrogenation' being carried out *via* sequential treatment of the latter with $H^+$ and $H^-$. However, reaction of the complexes $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ with hydrogen [50 bar (5 × $10^6$ Pa)] in toluene failed to produce detectable amounts of (4).

Reactions of the cations (1a)—(1c) with halide anions were next investigated. Using tetraethylammonium salts as the halide source, the new compounds (5) were obtained (see Table 1 for physical and analytical data). The n.m.r. data are in accord with the proposed structure. The $^1H$ and $^{13}C$-{$^1H$} resonances for the $C_6H_4$ group (Table 2) show that it has been displaced from its $\eta^2$-bonding mode to tungsten. In the $^1H$ spectra of compounds (5a) and (5b) there is a well resolved signal for the μ-CH group appearing as a doublet of doublets through coupling with the non-equivalent $PR_3$ ligands; this signal also shows $^{195}Pt$ satellite peaks. In the spectrum of (5c) the resonance for μ-C*H* could not be unambiguously defined, but as in the spectrum of (5d) it was probably masked by that

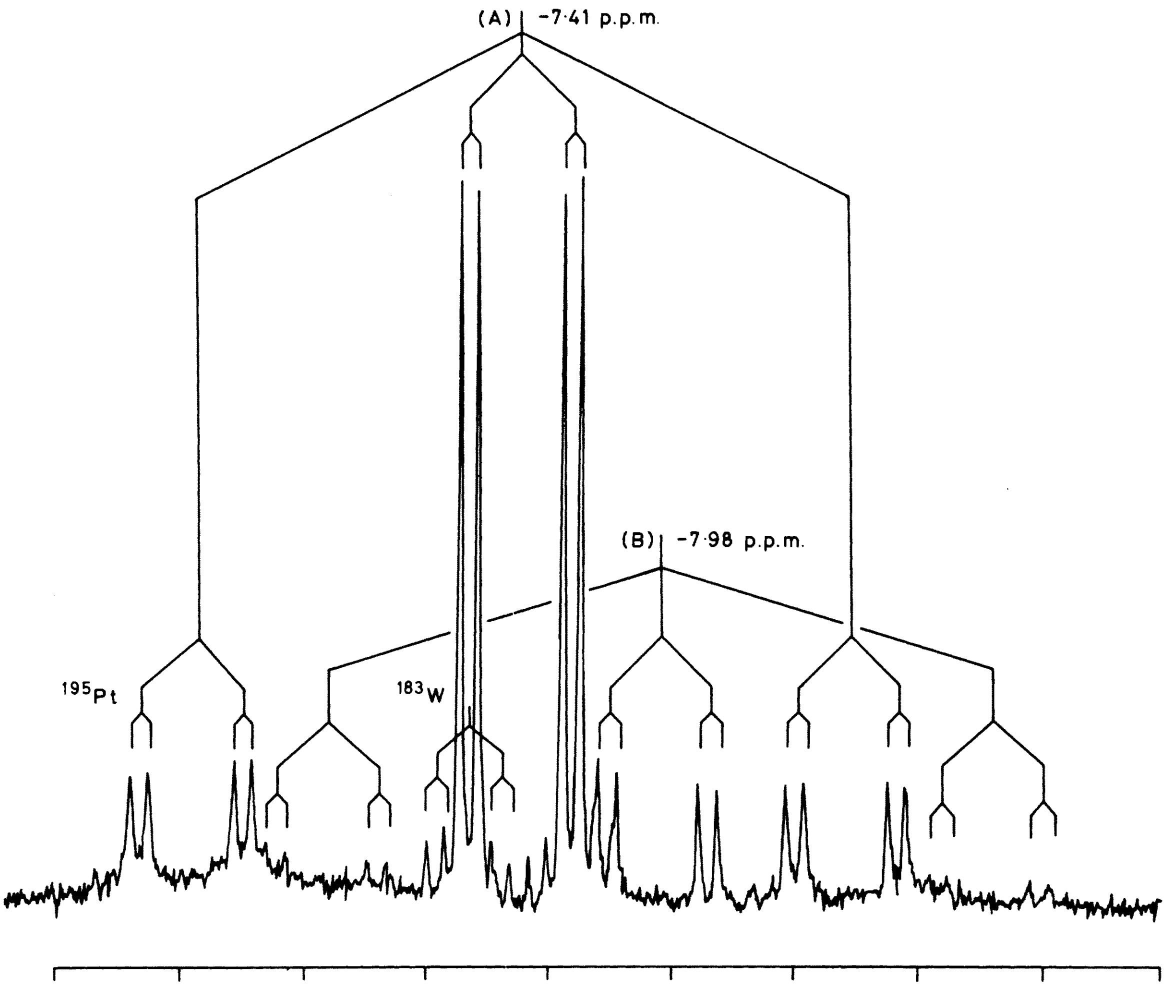


**Figure 2.** Hydrogen-1 n.m.r. spectrum of compound (4b) centred at δ −7.4 (width *ca.* 1 000 Hz), measured at −50 °C in $CD_2Cl_2$. Peaks for isomers (A) and (B) are marked

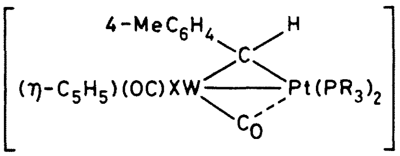
for the $C_6H_4$ protons. In the $^{13}C$-{$^1H$} spectrum of (5d), however, the resonance for the μ-C nucleus was clearly seen at δ 101.6 p.p.m. with characteristic couplings [*J*(PC) 59, *J*(PtC) 541, and *J*(WC) 47 Hz]. The $^{13}C$-{$^1H$} spectrum of compound (5b) also showed a diagnostic signal for the μ-C atom (Table 2). The corresponding spectra of (5a) and (5c) were not measured. The $^{31}P$-{$^1H$} spectra of (5a), (5b), and (5d) were measured (Table 3) and confirm the presence of the *cis*-$Pt(PR_3)_2$ groups in these species. Signals for two non-chemically equivalent $PR_3$ ligands are seen, with the expected $^{195}Pt-^{31}P$ coupling-constant values for groups cisoid and transoid to the Pt–W bond.[6,11]

The i.r. spectra of the compounds (5) show two CO-stretching bands (Table 1) of similar frequency to those of their precursors (1a)—(1c),[1] which is not surprising since in changing from the salts (1a)—(1c) to the neutral species (5), in which an electronegative halide ligand is attached to tungsten, the net charge at the latter would not substantially change. The band at *ca.* 1 770 cm$^{-1}$ in the spectra of (5) must be due to a semi-bridging carbonyl ligand.

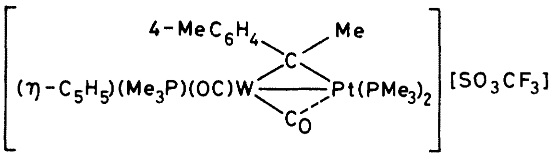
Compound (5b) could also be prepared by treating (2a) with $NEt_4Br$. Since (2a) might be expected to be substitution inert, it seems likely that this reaction proceeds by removal of (1a) from the equilibrium mixture which exists between it and (2a) in solution (see above). Treatment of compound (5b) with $AgBF_4$ in diethyl ether afforded (1a) and AgBr, but the yield was very dependent on the purity of the $AgBF_4$ used. As with compounds (2) and (3) the halide complexes (5) are produced in only one diastereoisomeric form.

In the preceding paper [1] we reported that alkylation of the compound [PtW(μ-$CC_6H_4Me$-4)$(CO)_2(PMe_3)_2$(η-$C_5H_5$)] with $MeSO_3CF_3$ afforded the salt [PtW{μ-σ:η$^3$-C(Me)$C_6H_4Me$-4}$(CO)_2(PMe_3)_2$(η-$C_5H_5$)][$SO_3CF_3$] (1d), structurally analogous to (1a). We have investigated some reactions of (1d) but it is less reactive than (1a). For example, no reaction occurs between the salt and CO, and surprisingly $NEt_4Br$ does not react either. However, there is a slow reaction with $PMe_3$, requiring several hours for completion, yielding compound (6). The spectroscopic data for the latter are similar to those for (3a) with the significant difference that the n.m.r. data (Tables 2 and 3) show that (6) exists in solution at room temperature as a pair of diastereoisomers in the ratio *ca.* 2 : 1 [resonances labelled (A) and (B) in the Tables]. The fact that the formation of compound (6) is less stereoselective than that of (3a) might suggest that it involves a transition state with more *S*$_N$1 character than the latter reaction, *i.e.* the tolyl ring dissociates its η$^2$ bonding to tungsten in the rate-determining step forming a 16-electron metal centre, thus allowing $PMe_3$ to attack from a different direction. Since the isomers are formed in unequal quantities, steric factors may make substitution from one direction more favourable.

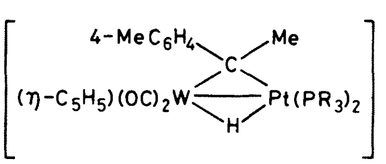
Treatment of (1d) with K[BH$(CHMeEt)_3$] gives the bridged



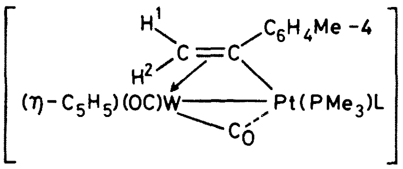
| | X | $PR_3$ |
|---|---|---|
| (5a) | Cl | $PMe_3$ |
| (5b) | Br | $PMe_3$ |
| (5c) | I | $PMe_3$ |
| (5d) | I | $PMe_2Ph$ |



(6)



(7)



| | L |
|---|---|
| (8a) | $PMe_3$ |
| (8b) | CO |

hydrido-complex (7), analogous to (4a). Like (4a), compound (7) has dynamic n.m.r. spectra (Tables 2 and 3) corresponding to the presence of two diastereoisomers, the interconversion of which is rapid on the n.m.r. time-scale at ambient temperatures but is slow at $-50$ °C so that limiting spectra can be measured. The data given in Tables 2 and 3 for (7) are similar to those for (4a), in accord with the similar structures of the compounds.

Reaction of compound (1d) with sodium hydride does not afford (7). Instead, deprotonation occurs to give the vinyl-bridged complex (8a), as well as a small amount of the compound (8b); both species were characterised in the usual manner (Table 1). The n.m.r. data (Tables 2 and 3) for (8a) are in agreement with the structure proposed. Moreover, the structure has been confirmed by an *X*-ray diffraction study, since (8a) has been prepared by an alternative and novel route.[15] Protonation of compound (8a) with $HBF_4 \cdot Et_2O$ regenerated the salt (1d). Interestingly, (8a) can also be prepared by treating (6) with NaH, a $PMe_3$ ligand being lost from tungsten in preference to a CO group.

Reaction of compound (8a) with $PMe_3$ in an attempt to displace the bridging vinyl ligand failed. Likewise, prolonged treatment with CO did not displace the $\eta^2$ bonding of the $C(C_6H_4Me\text{-}4)=CH_2$ moiety. Instead, the complex (8b) is produced in which a $PMe_3$ ligand in (8a) transoid to the μ-C group has been replaced by CO.[6] The presence of this carbonyl group is clearly revealed by a signal in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum (δ 193.6 p.p.m.) with a characteristically large *J*(PtC) of 1 342 Hz for a PtCO group.[16]

Finally, for the compounds reported herein containing a bridging $\mu\text{-}C(R')C_6H_4Me\text{-}4$ ($R' = H$ or Me) ligand, and having $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of sufficient quality to reveal $^{195}Pt\text{-}^{13}C$ coupling on the signal due to the μ-C nucleus, the coupling (445—540 Hz) is evidently diagnostic of this group. These values are substantially less than those found for *J*(PtC) (*ca.* 730—750 Hz) on the resonances for the μ-C atom in the dimetallacyclopropene ring compounds $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$.[6,11]

## Experimental

The techniques used and instrumentation employed have been described earlier.[1] Analytical and other data for the new compounds are given in Table 1. The syntheses described below are representative of those employed in this work. Light petroleum is that fraction of b.p. 40—60 °C. The salts (1) were prepared as described in the preceding paper.[1]

*Preparation of the Compounds* $[PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PR_3)_2L(\eta\text{-}C_5H_5)][BF_4]$ (L = CO *or* $PR_3$).—Carbon monoxide gas was bubbled through a dichloromethane (20 cm³) solution of compound (1a) (0.42 g, 0.50 mmol) for 4 h. Solvent was removed by placing a warm water-bath around the Schlenk tube, while increasing the rate of flow of CO gas. When the residue was dry it was washed with diethyl ether (10 × 10 cm³) and dried *in vacuo* to afford orange *microcrystals* of $[PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_3(PMe_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (2a) (0.44 g). Compounds (2b) and (2c) were similarly prepared.

An excess of $PMe_3$ in light petroleum (2 cm³) was added to a vigorously stirred dichloromethane solution (30 cm³) of compound (1a) (0.42 g, 0.50 mmol). After 10 min, solvent was removed *in vacuo* and the residue thoroughly washed with diethyl ether (10 × 10 cm³). Drying *in vacuo* gave yellow *microcrystals* of $[PtW\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_3(\eta\text{-}C_5H_5)][BF_4]$ (3a) (0.46 g). Compound (3b) was similarly obtained.

*Synthesis of Complexes* $[PtW(\mu\text{-}H)\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$.—A solution of $K[BH(CHMeEt)_3]$ (*ca.* 0.5 mmol) was added to a vigorously stirred dichloromethane (10 cm³) solution of compound (1a) (0.42 g, 0.50 mmol). After 30 min the mixture was filtered through alumina (*ca.* 5 cm). Solvent was removed *in vacuo*, and the residue dissolved in dichloromethane–light petroleum (1 : 1) and chromatographed on an alumina column (10 × 1 cm). Elution of the column commenced with dichloromethane–light petroleum (1 : 1) and increased to 100% dichloromethane. The only yellow eluate was collected, the solvent was removed *in vacuo*, thereby affording yellow *microcrystals* of $[PtW(\mu\text{-}H)\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (4a) (0.26 g). Compound (4b) was prepared in an analogous manner.

*Preparation of the Compounds* $[PtWX\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ (X = Cl, Br, *or* I).—A large excess of $NEt_4Br$ was added to a vigorously stirred dichloromethane

**Table 6.** Atomic positional (fractional co-ordinates) parameters, with estimated standard deviations in parentheses, for [PtW(μ-H){μ-CH($C_6H_4$Me-4)}$(CO)_2(PMe_3)_2$(η-$C_5H_5$)] (4a)

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Pt | 0.270 82(3) | 0.318 12(3) | 0.217 31(2) | C(31) | 0.021 6(7) | 0.260 6(7) | 0.389 4(4) |
| W | 0.135 44(3) | 0.176 69(3) | 0.306 35(2) | C(32) | 0.001 5(7) | 0.139 7(7) | 0.387 1(4) |
| P(1) | 0.328 8(3) | 0.327 2(3) | 0.109 11(13) | C(33) | −0.066 4(7) | 0.111 9(7) | 0.321 0(4) |
| P(2) | 0.390 5(3) | 0.463 7(3) | 0.274 38(13) | C(34) | −0.088 3(7) | 0.215 4(7) | 0.282 5(4) |
| C(11) | 0.237 (2) | 0.430 8(12) | 0.054 3(7) | C(35) | −0.033 9(7) | 0.307 3(7) | 0.324 7(4) |
| C(12) | 0.312 4(13) | 0.194 7(10) | 0.058 1(6) | C | 0.153 2(3) | 0.173 5(8) | 0.191 6(5) |
| C(13) | 0.494 3(12) | 0.362 5(14) | 0.099 9(7) | C(41) | 0.039 7(5) | 0.189 0(6) | 0.137 3(3) |
| C(21) | 0.318 8(12) | 0.523 4(11) | 0.346 9(6) | C(42) | 0.004 8(5) | 0.095 8(6) | 0.093 6(3) |
| C(22) | 0.541 2(12) | 0.410 1(12) | 0.316 1(7) | C(43) | −0.098 3(5) | 0.105 4(6) | 0.040 9(3) |
| C(23) | 0.434 1(12) | 0.593 9(10) | 0.230 9(6) | C(44) | −0.166 6(5) | 0.208 2(6) | 0.031 9(3) |
| C(1) | 0.295 0(11) | 0.170 3(10) | 0.369 7(5) | C(45) | −0.131 8(5) | 0.301 5(6) | 0.075 6(3) |
| O(1) | 0.389 5(9) | 0.161 8(8) | 0.408 7(4) | C(46) | −0.028 7(5) | 0.291 9(6) | 0.128 3(3) |
| C(2) | 0.202 2(10) | 0.022 2(10) | 0.294 3(6) | C(47) | −0.280 7(13) | 0.221 4(14) | −0.026 9(7) |
| O(2) | 0.242 0(9) | −0.067 9(7) | 0.288 4(5) | | | | |
| Co-ordinates obtained from final difference map | | | | | | | |
| H(1) | 0.196 0 | 0.098 5 | 0.175 1 | H(2) | 0.238 7 | 0.289 8 | 0.304 3 |
| Co-ordinate obtained by potential-energy-minimisation program 'HYDEX' * | | | | | | | |
| H(2) | 0.182 0 | 0.327 9 | 0.293 0 | | | | |

* See ref. 9.

(30 $cm^3$) solution of compound (1a) (0.42 g, 0.50 mmol). After 10 min, solvent was removed *in vacuo* and the residue extracted with diethyl ether (4 × 10 $cm^3$). The extracts were filtered through a Celite pad (5 cm). Evaporation of solvent *in vacuo* afforded orange *microcrystals* of [PtWBr{μ-CH($C_6H_4$Me-4)}$(CO)_2(PMe_3)_2$(η-$C_5H_5$)] (5b) (0.39 g). The compounds (5a), (5c), and (5d) were obtained in a similar manner.

*Reactions of the Salt* [PtW{μ-σ:$\eta^3$-C(Me)$C_6H_4$Me-4}$(CO)_2(PMe_3)_2$(η-$C_5H_5$)][$SO_3CF_3$].—An excess of NaH was added to a tetrahydrofuran (15 $cm^3$) solution of salt (1d) (0.46 g, 0.50 mmol), and the mixture stirred for 18 h. After filtration through a Celite pad (1 cm), solvent was removed *in vacuo* and the residue dissolved in dichloromethane–light petroleum (1 : 1) and chromatographed on an alumina column (20 × 1 cm). The column was eluted initially with dichloromethane–light petroleum (1 : 1) and subsequently with 100% dichloromethane. The first yellow eluate was collected and solvent evaporated *in vacuo* to give *microcrystals* of [PtW{μ-C($C_6H_4$-Me-4)=$CH_2$}$(CO)_3(PMe_3)$(η-$C_5H_5$)] (8b) (40 mg). The second and major yellow band afforded yellow *microcrystals* of [PtW{μ-C($C_6H_4$Me-4)=$CH_2$}$(CO)_2(PMe_3)_2$(η-$C_5H_5$)] (8a) (0.25 g).

The compounds (6) and (7) were prepared from (1d) in a similar manner to the syntheses of (3a) and (4a) from (1a). Compound (8b) can be obtained in essentially quantitative yield by bubbling CO through a toluene solution of (8a) for several days, followed by isolation *via* chromatography.

*Crystal Structure Determination of* [PtW(μ-H){μ-CH($C_6H_4$Me-4)}$(CO)_2(PMe_3)_2$(η-$C_5H_5$)] (4a).—Crystals of compound (4a) grow from dichloromethane–light petroleum as yellow prisms. Diffracted intensities were recorded at 220 K from a crystal of dimensions 0.14 × 0.15 × 0.25 mm, having well developed faces of the type {1, 0, 0}, {1, 1, 0}, and {0, 0, 1}. Of the total 4 767 independent reflections ($2\theta \leqslant 50°$) measured on a Nicolet *P*3*m* four-circle diffractometer, 3 083 satisfied the criterion $I \geqslant 3\sigma(I)$, 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.* $C_{21}H_{32}O_2P_2PtW$, $M = 757.4$, monoclinic, $a = 10.554(4)$, $b = 11.624(3)$, $c = 19.393(7)$ Å, $\beta = 97.64(3)°$, $U = 2\,358(1)$ Å$^3$, $Z = 4$, $D_c = 2.13$ g cm$^{-3}$, $F(000) = 1\,424$, space group $P2_1/c$ (no. 14), Mo-$K_\alpha$ *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu$(Mo-$K_\alpha$) = 111.2 cm$^{-1}$.

*Structure solution and refinement.* The structure was solved by conventional heavy-atom and electron-density difference methods. All non-hydrogen atoms were refined with anisotropic thermal parameters and the cyclopentadienyl and aryl rings were treated as rigid groups [C–C($C_5H_5$) 1.420 and C–C(aryl) 1.395 Å]. Methyl and aromatic hydrogen atoms were included in calculated positions (C–H 0.960 Å) and chemically related groups of hydrogen atoms were given common refined isotropic thermal parameters. Likely locations for the μ-C*H*R and W–μ-H–Pt hydrogen atoms were obtained from the final electron-density difference synthesis, but these atoms were not stable on refinement. Application of the potential-energy-minimisation technique of Orpen[9] afforded a W–μ-H–Pt hydride location which was in good agreement with that obtained as above. A weighting scheme of the form $w = [\sigma^2(F_o) + 0.0001|F_o|^2]^{-1}$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >1 or <−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. 17. Refinement by blocked-cascade least-squares converged at *R* 0.039 (*R'* 0.041). All calculations were carried out on an 'Eclipse' Data General computer with the SHELXTL system of programs.[18] The final atom co-ordinates are listed in Table 6.

## Acknowledgements

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