Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 3.[1] Synthesis of Bimetallic Platinum–Tungsten Complexes with μ-Tolylidyne Groups; Crystal Structure of $[\mathrm{PtW}(\mu\text{-C}\cdot\mathrm{C_6H_4Me}\text{-}p)(\mathrm{CO})_2(\mathrm{PMe_2Ph})_2(\eta\text{-C_5H_5})]$ †

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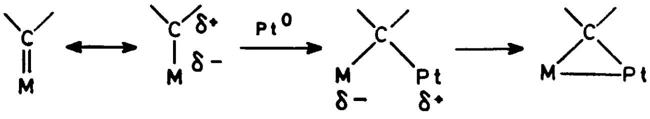
The tungsten–carbyne complex $[\mathrm{W}(\equiv\mathrm{C}\cdot\mathrm{C_6H_4Me}\text{-}p)(\mathrm{CO})_2(\eta\text{-C_5H_5})]$ reacts with the compounds $[\mathrm{Pt}(\mathrm{C_2H_4})(\mathrm{PR_3})_2]$ ($\mathrm{PR_3} = \mathrm{PMe_2Ph}$ or $\mathrm{PMe_3}$) to give the dimetal species $[\mathrm{PtW}(\mu\text{-C}\cdot\mathrm{C_6H_4Me}\text{-}p)(\mathrm{CO})_2(\mathrm{PR_3})_2(\eta\text{-C_5H_5})]$. A related complex $[\mathrm{PtWBr}(\mu\text{-C}\cdot\mathrm{C_6H_4Me}\text{-}p)(\mathrm{CO})_4(\mathrm{PMe_3})_2]$ is produced quantitatively from $[\mathrm{W}(\equiv\mathrm{C}\cdot\mathrm{C_6H_4Me}\text{-}p)(\mathrm{Br})(\mathrm{CO})_4]$ and $[\mathrm{Pt}(\mathrm{C_2H_4})(\mathrm{PMe_3})_2]$. In order to establish the molecular structure of this class of complex a single-crystal *X*-ray diffraction study was made on $[\mathrm{PtW}(\mu\text{-C}\cdot\mathrm{C_6H_4Me}\text{-}p)(\mathrm{CO})_2(\mathrm{PMe_2Ph})_2(\eta\text{-C_5H_5})]$, crystals of which are monoclinic, space group $P2_1/c$, $Z = 4$, in a unit cell with lattice parameters $a = 12.212(11)$, $b = 9.339(6)$, $c = 26.125(24)$ Å, and $\beta = 92.77(7)°$. The structure has been refined to R 0.031 (R' 0.029) for 3 803 reflections measured at 200 K for $2.9 \leqslant 2\theta \leqslant 55°$ (Mo-K_α *X*-radiation). In the molecule a Pt–W bond [2.751(1) Å] is bridged by a $\mathrm{C}\cdot\mathrm{C_6H_4Me}\text{-}p$ group forming a ' dimetallacyclopropene ' ring with Pt–C 1.997(9) Å and W–C 1.967(6) Å. The least-squares plane defined by the carbon atoms of the $\mathrm{C}\cdot\mathrm{C_6H_4Me}\text{-}p$ ligand is at 88.1° to the plane $\overline{\mathrm{Pt}(\mu\text{-C})\mathrm{W}}$. The ^{1}H, ^{31}P, and ^{13}C n.m.r. spectra of the compounds are discussed in relation to their structures.

In preceding papers[1,2] we have described the facile synthesis of bonds between platinum and chromium, molybdenum, tungsten, or manganese *via* reactions between the species $[\mathrm{Pt}(\mathrm{C_2H_4})(\mathrm{PR_3})_2]$, generated *in situ* from $[\mathrm{Pt}(\mathrm{C_2H_4})_3]$, and mononuclear metal–carbene compounds. In the products so produced a carbene or alkylidene ligand bridges the heteronuclear dimetal bond, and the process may be represented as shown in the Scheme. It is reasonable to assume that in these reactions the dipolar character[3,4] of the metal–carbon (carbene) bond in the mononuclear complexes facilitates attack by the zero-valent platinum species. In this context bonds between metals and carbyne or alkylidyne ligands are also dipolar. Hence these bonds should also react with low-valent metal complexes, thereby affording dimetallacyclopropene-type structures. Moreover, in the particular case of attack of Pt^0 on a group W≡CR there is an analogy with reactions of zero-valent platinum with electrophilic acetylenes for which ionic intermediates have been invoked.[5,6]



SCHEME

In order to investigate whether Pt^0 would complex with a metal–carbon triple bond the mononuclear tungsten compound $[\mathrm{W}(\equiv\mathrm{C}\cdot\mathrm{C_6H_4Me}\text{-}p)(\mathrm{CO})_2(\eta\text{-C_5H_5})]$ was chosen as a model because it has been especially well characterised by a single-crystal *X*-ray diffraction study and by ^{13}C n.m.r. spectroscopy.[7] A preliminary account of the work described herein has been given.[8]

Complexes with metal–metal bonds bridged by carbyne ligands are scarce, and none has been prepared by synthetic methods of wide applicability. The only dimetal complexes reported are the cationic species $[\mathrm{Fe_2}(\mu\text{-CR})(\mu\text{-CO})(\mathrm{CO})_2(\eta\text{-C_5H_5})_2]^+$ (ref. 9), and the compound $[\mathrm{W_2}(\mu\text{-CSiMe_3})_2(\mathrm{CH_2SiMe_3})_4]$[10] both containing homonuclear metal–metal bonds. Known trimetal complexes with bridging alkylidyne ligands include $[\mathrm{Co_3}(\mu_3\text{-CR})(\mathrm{CO})_9]$,[11,12] $[\mathrm{M_3H_3}(\mu_3\text{-CR})(\mathrm{CO})_9]$ (M = Ru, R = Me;[13] M = Os, R = H;[14] and M = Fe, Ru, or Os, R = OMe[15]), $[\mathrm{M_3H}(\mu_2\text{-COMe})(\mathrm{CO})_{10}]$ (M = Fe, Ru, or Os),[15] and $[\mathrm{Ni_3}(\mu_3\text{-CPh})(\eta\text{-C_5H_5})_3]$.[16] Very recently heteronuclear trimetallic complexes of the type $[\mathrm{Co_2M}(\mu_3\text{-CR})(\mathrm{CO})_8(\eta\text{-C_5H_5})]$ (M = Cr, Mo, or W) have been serendipitously prepared.[17]

RESULTS AND DISCUSSION

Addition of $[\mathrm{W}(\equiv\mathrm{C}\cdot\mathrm{C_6H_4Me}\text{-}p)(\mathrm{CO})_2(\eta\text{-C_5H_5})]$ in light petroleum to a suspension of $[\mathrm{Pt}(\mathrm{C_2H_4})(\mathrm{PMe_2Ph})_2]$ led to rapid formation in over 80% yield of a red complex (1), air stable and with an i.r. spectrum (in cyclohexane) having carbonyl stretching bands at 1 898s and 1 818s cm^{-1}. The ^{31}P(^{1}H-decoupled) n.m.r. spectrum showed doublet resonances at δ 3.8 [*J*(PP) 4, *J*(PtP) 4 113, *J*(WP) 14 Hz] and 10.6 p.p.m. [*J*(PP) 4, *J*(PtP) 2 743, *J*(WP) 6 Hz]. The two PMe$_2$Ph ligands in (1) are thus non-equivalent, the small value of *J*(PP) indicating a *cis*-$\mathrm{Pt}(\mathrm{PMe_2Ph})_2$ arrangement. The larger ^{195}Pt–^{31}P and ^{183}W–^{31}P couplings on the signal at 3.8 p.p.m. indicated that this resonance was due to a tertiary phosphine ligand *trans* to a Pt–W bond.[2] The ^{13}C(^{1}H-decoupled) spectrum was especially informative. A resonance was observed at 336 p.p.m., appearing as a doublet [*J*(PC) 59 Hz] with platinum satellites [*J*(PtC) 747 Hz]. The low-field shift of this signal characterised it as being due to the ligating carbon of a carbyne group, and the magnitude of the ^{195}Pt–^{13}C coupling showed that it was attached to platinum.[2,18] Unfortunately the

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† *de*-Dicarbonyl-*f*-1—5-η-cyclopentadienyl-*ab*-bis(dimethylphenylphosphine)-*c*-μ-*p*-methylbenzylidyne-platinumtungsten (*Pt–W*).

spectrum was not sufficiently strong to reveal ^{183}W–^{13}C coupling. However, in the mononuclear compound [W(≡C·C_6H_4Me-*p*)$(CO)_2$(η-C_5H_5)] the carbyne metal-bonded carbon atom resonates at 300 p.p.m.,[7] so that there is a 36 p.p.m. downfield shift on formation of (1). Interestingly, this shift is in the same direction as occurs for the ligating carbon atoms of acetylenes upon complexation with platinum.[19] In contrast, carbene–carbon atoms which bridge a metal–metal bond experience an upfield chemical shift compared with that of the parent mononuclear metal carbene complex.[2] The ^{1}H spectrum confirmed the presence of two environments for the PMe_2Ph ligands and displayed the expected signals for C_5H_5 and C_6H_4Me-*p*. The spectroscopic properties thus indicated that (1) was the desired compound [PtW(C·C_6H_4Me-*p*)$(CO)_2(PMe_2Ph)_2$(η-C_5H_5)] and very likely contained the Pt(μ-C·C_6H_4Me-*p*)W framework.

The complex [PtW(μ-C·C_6H_4Me-*p*)$(CO)_2(PMe_3)_2$(η-C_5H_5)] (2), analogous to (1), was prepared in quantitative yield by reacting [W(≡C·C_6H_4Me-*p*)$(CO)_2$(η-C_5H_5)] with [Pt(C_2H_4)$(PMe_3)_2$]. Compound (2) showed a molecular ion in its mass spectrum, $\nu_{max.}$ (CO) at 1 898 and 1 815 cm^{-1}, and ^{31}P n.m.r. signals at 16.0 [*J*(PP) 6, *J*(PtP) 4 021, *J*(WP) 15 Hz] and 24.0 p.p.m. [*J*(PP) 6, *J*(PtP) 2 642 Hz]. The ^{13}C n.m.r. spectrum showed a carbyne ligating-carbon resonance at 338 p.p.m. appearing as a doublet [*J*(PC) 61 Hz] with platinum-195 satellites [*J*(PtC) 732 Hz]. These properties establish that (2) is structurally similar to (1).

TABLE 1

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for complex (1)

Atom	*x*	*y*	*z*
Pt	0.203 13(3)	0.017 84(3)	0.150 71(1)
W	0.007 93(3)	0.114 27(3)	0.186 19(1)
C(001)	0.046 4(7)	−0.039 5(6)	0.138 8(3)
C(01)	−0.010 2(7)	−0.146 8(7)	0.106 7(2)
C(02)	−0.040 2(7)	−0.117 1(7)	0.055 3(3)
C(03)	−0.087 7(8)	−0.220 3(8)	0.023 6(3)
C(04)	−0.105 7(8)	−0.358 3(8)	0.042 0(3)
C(041)	−0.153 9(10)	−0.478 1(9)	0.006 4(4)
C(05)	−0.078 1(8)	−0.387 5(7)	0.092 0(3)
C(06)	−0.031 5(8)	−0.284 7(7)	0.124 6(3)
C(6)	0.081 8(8)	0.277 4(8)	0.154 8(3)
O(6)	0.117 5(6)	0.379 6(5)	0.136 0(2)
C(7)	0.124 7(8)	0.104 1(8)	0.240 4(3)
O(7)	0.184 5(6)	0.099 5(6)	0.277 2(2)
P(1)	0.357 0(2)	0.150 3(2)	0.176 9(1)
C(11)	0.460 3(8)	0.055 1(9)	0.216 2(3)
C(12)	0.339 4(8)	0.312 5(8)	0.215 4(3)
C(131)	0.430 5(9)	0.226 1(7)	0.124 9(3)
C(132)	0.373 7(8)	0.256 5(8)	0.078 2(3)
C(133)	0.422 3(10)	0.317 1(9)	0.037 3(3)
C(134)	0.532 3(12)	0.347 9(10)	0.042 6(4)
C(135)	0.594 3(10)	0.322 8(12)	0.088 5(4)
C(136)	0.542 4(11)	0.262 4(10)	0.128 7(3)
P(2)	0.283 6(2)	−0.149 1(2)	0.102 6(1)
C(21)	0.249 9(10)	−0.128 9(11)	0.034 7(3)
C(22)	0.240 2(9)	−0.333 0(9)	0.114 1(4)
C(231)	0.433 3(8)	−0.170 1(8)	0.104 7(3)
C(232)	0.498 0(12)	−0.084 5(8)	0.074 4(3)
C(233)	0.609 5(13)	−0.098 6(12)	0.076 0(3)
C(234)	0.660 4(10)	−0.197 8(14)	0.107 4(5)
C(235)	0.598 3(14)	−0.286 0(11)	0.138 0(4)
C(236)	0.483 6(12)	−0.271 5(10)	0.137 3(3)

In view of the novel nature of compounds (1) and (2) a single-crystal *X*-ray diffraction study was carried out on the former in order to establish the molecular structure beyond doubt. The results are given in Tables 1—3 and the molecule is illustrated in Figure 1, which also shows the crystallographic numbering system. It is at once evident that a C·C_6H_4Me-*p* group bridges a W–Pt bond [2.751(1) Å]. The latter is slightly but significantly shorter than the sum of the covalent radii (2.85 Å), and is also shorter than the W–Pt bonds in [$(OC)_5$W{μ-C(OMe)Ph}Pt$(PMe_3)_2$] [2.861(1) Å] [2] and in

TABLE 2

Bond lengths (Å) and angles (°) for the complex [(η-C_5H_5)-$(OC)_2$W(μ-C·C_6H_4Me-*p*)Pt$(PMe_2Ph)_2$] (1) with estimated standard deviations in parentheses

(*a*) Distances

Pt–W	2.751(1)	C(001)–C(01)	1.46(1)
Pt–C(001)	1.997(9)	C(01)–C(02)	1.40(1)
W–C(001)	1.967(6)	C(02)–C(03)	1.38(1)
W–C(6)	1.970(8)	C(03)–C(04)	1.40(1)
W–C(7)	1.963(8)	C(04)–C(041)	1.55(1)
C(6)–O(6)	1.17(1)	C(04)–C(05)	1.36(1)
C(7)–O(7)	1.18(1)	C(05)–C(06)	1.39(1)
W–C(1)	2.36(1)	C(06)–C(01)	1.40(1)
W–C(2)	2.34(1)	C(1)–C(2)	1.44(1)
W–C(3)	2.37(1)	C(2)–C(3)	1.41(1)
W–C(4)	2.36(1)	C(3)–C(4)	1.41(1)
W–C(5)	2.38(1)	C(4)–C(5)	1.43(1)
		C(5)–C(1)	1.44(1)
Pt–P(1)	2.325(2)	Pt–P(2)	2.258(2)
P(1)–C(11)	1.819(9)	P(2)–C(21)	1.812(8)
P(1)–C(12)	1.837(8)	P(2)–C(22)	1.826(9)
P(1)–C(131)	1.808(9)	P(2)–C(231)	1.837(1)
C(131)–C(132)	1.40(1)	C(231)–C(232)	1.40(1)
C(132)–C(133)	1.37(1)	C(232)–C(233)	1.37(2)
C(133)–C(134)	1.37(2)	C(233)–C(234)	1.37(2)
C(134)–C(135)	1.41(1)	C(234)–C(235)	1.40(2)
C(135)–C(136)	1.37(1)	C(235)–C(236)	1.41(2)
C(136)–C(131)	1.41(2)	C(236)–C(231)	1.40(1)

(*b*) Angles

W–Pt–C(001)	45.6(2)	Pt–W–C(001)	46.5(3)
Pt–C(001)–W	87.9(3)	C(6)–W–C(001)	100.0(3)
P(1)–Pt–P(2)	99.4(1)	C(7)–W–C(001)	103.4(3)
P(1)–Pt–W	115.3(1)	P(1)–Pt–C(001)	160.6(3)
P(2)–Pt–W	145.2(1)	P(2)–Pt–C(001)	99.7(2)
Pt–W–C(6)	72.0(3)	Pt–W–C(7)	67.4(2)
Pt–C(001)–C(01)	134.2(6)	W–C(001)–C(01)	137.9(7)
C(001)–C(01)–C(02)	120.6(6)		
C(001)–C(01)–C(06)	122.1(6)	C(6)–W–C(7)	90.4(3)
C(01)–C(02)–C(03)	121.2(7)	W–C(6)–O(6)	174.6(8)
C(02)–C(03)–C(04)	120.5(7)	W–C(7)–O(7)	171.7(8)
C(03)–C(04)–C(05)	118.7(7)		
C(04)–C(05)–C(06)	121.7(7)	C(1)–C(2)–C(3)	108.7(7)
C(05)–C(06)–C(01)	120.6(6)	C(2)–C(3)–C(4)	107.4(7)
C(06)–C(01)–C(02)	117.3(6)	C(3)–C(4)–C(5)	110.0(7)
C(03)–C(04)–C(041)	121.3(7)	C(4)–C(5)–C(1)	106.2(7)
C(05)–C(04)–C(041)	120.0(7)	C(5)–C(1)–C(2)	107.6(7)
Pt–P(1)–C(11)	115.8(3)	Pt–P(2)–C(21)	112.9(3)
Pt–P(1)–C(12)	119.0(3)	Pt–P(2)–C(22)	114.9(4)
Pt–P(1)–C(131)	114.3(3)	Pt–P(2)–C(231)	121.1(2)
C(11)–P(1)–C(12)	101.0(4)	C(21)–P(2)–C(22)	101.8(5)
C(11)–P(1)–C(131)	105.0(5)	C(21)–P(2)–P(231)	102.7(4)
C(12)–P(1)–C(131)	99.5(4)	C(22)–P(2)–C(231)	101.0(4)
P(1)–C(131)–C(132)	119.3(8)	P(2)–C(231)–C(232)	120.7(7)
P(1)–C(131)–C(136)	123.8(6)	P(2)–C(231)–C(236)	119.9(8)
C(131)–C(132)–C(133)	123(1)	C(231)–C(232)–C(233)	121(1)
C(132)–C(133)–C(134)	118(1)	C(232)–C(233)–C(234)	120(1)
C(133)–C(134)–C(135)	122(1)	C(233)–C(234)–C(235)	120(1)
C(134)–C(135)–C(136)	118(1)	C(234)–C(235)–C(236)	120(1)
C(135)–C(136)–C(131)	122(1)	C(235)–C(236)–C(231)	119(1)
C(136)–C(131)–C(132)	117(1)	C(236)–C(231)–C(232)	119(1)

the trimetallic complex $[Pt_2W\{\mu\text{-}C(OMe)Ph\}(CO)_6(PBu^t{}_2Me)_2]$ [2.830(2) Å].[20]

The bridging ligand $C{\cdot}C_6H_4Me\text{-}p$ is situated such that its carbon atoms define a plane almost perpendicular to the plane formed by the $Pt\{\mu\text{-}C(001)\}W$ ring (Table 3). The atom C(001) appears very slightly asymmetrically placed with respect to the metal atoms, with Pt–C(001) 1.997(9) Å and W–C(001) 1.967(6) Å. The Pt–C(001) separation is within the range [1.99—2.15 Å] generally observed for platinum–carbon σ bonds.[21] Interest centres on the W–C(001) distance in relation to the length of other tungsten–carbon bonds. In $[W(\equiv C{\cdot}C_6H_4Me\text{-}p)(CO)_2(\eta\text{-}C_5H_5)]$, the precursor to (1), the W–C(carbyne) distance is 1.82(2) Å.[7] Hence complexation of the $Pt(PMe_2Ph)_2$ moiety with the tungsten–carbon triple bond has resulted, not unexpectedly in an increase (0.15 Å) in length. Cotton and co-workers [22] have studied by *X*-ray diffraction several complexes containing W–C(alkyl) bonds and have measured these in the range 2.14—2.20 Å. Evidently in (1) the distance W–C(001) is shorter than that for a single bond. Indeed, following the 18-electron formalism, the W–C(001) bond would be a double bond with perhaps an internuclear separation similar to that between carbon and tungsten in a mononuclear carbene complex. In this context it is interesting that in $[W(CPh_2)(CO)_5]$ the C–W distance is 2.14(2) Å [23] *i.e.* longer than in complex (1) and just in the range found by others [22] for several W–C single bonds. Nevertheless, the C–W separation in $[W(CPh_2)(CO)_5]$ has been taken to imply [23] a W=C bond because it is significantly less than the corresponding distance [2.34(1) Å] in the anion $[W\{CH(OMe)Ph\}(CO)_5]^-$. Evidently W–C and W=C bond distances will vary depending on the oxidation state of the metal and the ligands present, but based on known W=W (2.488 Å) [24] and C=C (1.337 Å) distances, 1.91 Å seems a reasonable estimate for a W=C separation. In compound (1), therefore, the carbon–tungsten distance of 1.967(6) Å lies between the estimate of the sum of the radii (1.91 Å) and that found (2.14 Å) in $[W(CPh_2)(CO)_5]$, and thus seems to correspond well to a W=C interaction, although it is probable that the bonding in the $W(\mu\text{-}C)Pt$ ring system is delocalised.

TABLE 3

Some least-squares planes for $[(\eta\text{-}C_5H_5)(OC)_2W(\mu\text{-}CC_6H_4Me\text{-}p)Pt(PMe_2Ph)_2]$ (1) in the form $Ax + By + Cz = D$, where x, y, and z are fractional co-ordinates

Plane (i): Pt, W, C(001)
$0.668x - 5.978y + 19.927z = 3.032$

Plane (ii): Pt, P(1), P(2)
$1.151x - 5.466y + 20.896z = 3.286$

Plane (iii) [a]: C(001), C(01), C(02), C(03), C(04), C(041), C(05), C(06)
$11.245x - 2.686y - 8.030z = -0.557$

Plane (iv) [b]: C(1), C(2), C(3), C(4), C(5)
$11.813x - 0.442y - 7.708z = 3.415$

Angles (°) between planes: (i)—(ii), 4.5; (i)—(iii), 88.1; (i)—(iv), 96.2

[a] Maximum deviation, C(001) 0.07 Å. [b] Maximum deviation, C(3) 0.008 Å.

The platinum atom in (1) is in an essentially planar environment with respect to P(1), P(2), C(001), and W, since the dihedral angle between the planes defined by P(1)·Pt·P(2) and Pt·C(001)·W is only 4.5°. The Pt–P distances [2.291(2) Å average] fall within the range previously observed, namely 2.267(9)—2.331(5) Å.[21a] However, Pt–P(1) is somewhat longer than Pt–P(2) perhaps reflecting the *trans* influence of the carbyne–carbon atom. A similar effect was found in the two Pt–P separations in $[(OC)_5W\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$.[2] In the latter complex, the angle W(μ-C)Pt is 77.8(3)° compared with 87.9(3)° for Pt·C(001)·W in (1). The angle W·Pt·C(001) is 45.6(2)°, compared with 58.0(3)° for the corresponding angle in $[(OC)_5W\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$. The P·Pt·P angles in the two structures are the same.

If the cyclopentadienyl ligand is regarded as tridentate, then this ligand and C(6), C(7), and C(001) can be visualised as forming an approximately octahedral environment for the tungsten [C(6)·W·C(7) 90.4(3), C(6)·W·C(001) 100.0(3), C(7)·W·C(001) 103.4(3)°], with the metal–metal bond penetrating the C(6), C(7), C(001) face of the octahedron. The two carbonyl groups attached to the tungsten atom are bent back over the metal–metal bond [Pt·W·C(6) 72.0(3), Pt·W·C(7) 67.4°] as found (67.4°) in $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$.[25] In the latter molecule semi-bridging CO ligands are invoked even though the Mo·C·O angles average 176°. In complex (1) the angles W·C(6)·O(6) and W·C(7)·O(7) are 174.6(8) and 171.7(8)°, respectively, with Pt–C(6) 2.846 Å and Pt–C(7) 2.697 Å. These Pt–C(6) and Pt–C(7) distances are significantly longer than that found [2.21(3) Å] for the semi-bridging carbonyls in $[Pt_3(\mu\text{-}CO)_3\{P(C_6H_{11})_3\}_3]$.[26] Nevertheless, the CO stretching frequencies observed for (1) in solution (see above) seem too low for normal terminal carbonyls. The lowest

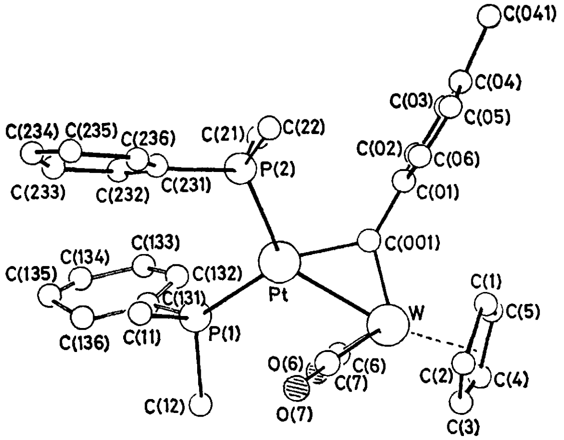

FIGURE 1 The molecular structure of $[(\eta\text{-}C_5H_5)(OC)_2W(\mu\text{-}CC_6H_4Me\text{-}p)Pt(PMe_2Ph)_2]$

energy band (1 818 cm^{-1}) is even lower than that observed (1 835 cm^{-1}) for the semi-bridging carbonyl in $[Mo_2(\mu\text{-}C_2H_2)(CO)_4(\eta\text{-}C_5H_5)_2]$, although in the structure of the latter the corresponding Mo·C·O angle is *ca.* 3° less at 168.5(4)°.[27] It may be that in complex (1) the small reach of the tolylidyne bridging ligand coupled with the necessity of equalizing charge distributions between the dissimilar metal atoms results in positioning of the CO groups so that transfer of charge from at least C(7)–O(7) to the platinum can occur. Moreover, the steric constraints of the $\mu\text{-}C{\cdot}C_6H_4Me\text{-}p$ ligand may also be responsible for the shortening of the W–Pt bond.

We have also investigated the reaction of $[Pt(C_2H_4)(PMe_3)_2]$ with the bromo(carbyne)tungsten complex $[WBr(C{\cdot}C_6H_4Me\text{-}p)(CO)_4]$.[28] The product (3) forms quantitatively in pentane–diethyl ether at −50 °C as a red microcrystalline solid. The ^{31}P n.m.r. spectrum shows two resonances at 8.7 and 21.8 p.p.m. appearing as doublets [*J*(PP) 13 Hz] with platinum satellites [*J*(PtP) 4 015 and 2 670 Hz, respectively]. The ^{1}H spectrum also revealed two environments for the PMe_3 ligands, and signals for the $\mu\text{-}C{\cdot}C_6H_4Me\text{-}p$ group. The ^{13}C spectrum was difficult to measure due to the insolubility of (3), except in dichloromethane or chloroform in which it decomposed, but a resonance characteristic of the contact carbon of a carbyne group was observed at 349 p.p.m. These properties, and the analytical data, establish (3) as $[(OC)_4(Br)\overline{W(\mu\text{-}C{\cdot}C_6H_4Me\text{-}p)Pt}(PMe_3)_2]$.

The inherent 'unsaturation' of the novel dimetallacyclopropene rings in compounds such as (1)—(3) should lead to an extensive chemistry. For example, compound (1) and $[Fe(CO)_5]$ react to give the trimetallic complex $[FePtW(\mu\text{-}C{\cdot}C_6H_4{\cdot}Me)(CO)_6(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ in which the carbyne ligand bridges three different transition metals.[29] This and other reactions will be described in subsequent papers.

EXPERIMENTAL

Instrumentation used and experimental techniques employed were as described in Part 1.[2] Light petroleum refers to that fraction of b.p. 40—60 °C. Hydrogen-1, ^{31}P, and $^{13}C(^{1}H$-decoupled) n.m.r. spectra were measured at 100, 40.48, and 25.15 MHz, respectively. Chemical shifts are in p.p.m. relative to 85% H_3PO_4 (external) for ^{31}P, with shifts to low frequency taken as positive; and in p.p.m. relative to $SiMe_4$ (positive values to high frequency) for ^{13}C. Spectra were measured in $[^{2}H_1]$chloroform at ambient temperatures unless otherwise stated.

The tungsten complexes $[W(\equiv C{\cdot}C_6H_4Me\text{-}p)(CO)_2(\eta\text{-}C_5H_5)]$ and $[WBr(C{\cdot}C_6H_4Me\text{-}p)(CO)_4]$ were prepared as described elsewhere.[7,28] The platinum compounds $[Pt(C_2H_4)(PR_3)_2]$ ($PR_3 = PMe_2Ph$ or PMe_3) were prepared *in situ* from $[Pt(C_8H_{12})_2]$.[30] Bis(cyclo-octa-1,5-diene)platinum (0.41 g, 1 mmol) was added portion-wise to rapidly stirred light petroleum (20 cm^3) at 0 °C under ethylene, allowing each portion to dissolve before adding the next. The resultant pale yellow solution was treated under ethylene with 2 mmol of PR_3 in light petroleum (5 cm^3). After stirring (5 min) the ethylene atmosphere was replaced by nitrogen and reactions were performed on the resultant suspensions of $[Pt(C_2H_4)(PR_3)_2]$ (1 mmol).

Synthesis of the Complexes $[PtW(\mu\text{-}C{\cdot}C_6H_4Me\text{-}p)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)]$ *and* $[PtWBr(\mu\text{-}C{\cdot}C_6H_4Me\text{-}p)(CO)_4(PMe_3)_2]$.—(*a*) A solution of $[W(\equiv C{\cdot}C_6H_4Me\text{-}p)(CO)_2(\eta\text{-}C_5H_5)]$ (0.41 g, 1 mmol) in light petroleum (30 cm^3) was added to a rapidly stirred suspension of $[Pt(C_2H_4)(PMe_2Ph)_2]$ (1 mmol) at 0 °C. A pale red precipitate formed within minutes. After stirring for 30 min, and then cooling to −20 °C for 1 h, the reaction solution was decanted and the red residue washed with cold (−20 °C) pentane (4 × 5 cm^3). Drying under high vacuum afforded red *micro-prisms* of $[PtW(\mu\text{-}C{\cdot}C_6H_4\text{-}Me\text{-}p)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ (1) (0.68 g, 84%), m.p. 150—151 °C (Found: C, 42.1; H, 3.9. $C_{31}H_{34}O_2P_2PtW$ requires C, 42.3; H, 3.9%); $\nu_{max.}$ (cyclohexane) at 1 898s and 1 818s (CO); $\nu_{max.}$ (Nujol) at 3 060w, 1 875s, 1 800s, 1 585w, 1 430w, 1 295w, 1 290w, 1 282w, 1 102w, 1 062w, 1 015w, 1 007w, 940m, 930s, 920s, 838w, 818w, 810m, 748w, 740m, 728s, 702w, 692m, 678w, and 663m cm^{-1}. The ^{1}H n.m.r. spectrum showed resonances at τ 2.4—3.0 (m, 10 H, C_6H_5), 3.16 and 3.46 [$(AB)_2$ system, 4 H, $C_6H_4Me\text{-}p$, *J*(AB) 8], 4.6 [s, 5 H, C_5H_5, *J*(PtH) 4], 7.75 (s, 3 H, $p\text{-}C_6H_4\text{-}CH_3$), 8.17 [d, 6 H, PCH_3, *J*(PH) 8, *J*(PtH) 22], and 8.94 [d, 6 H, PCH_3, *J*(PH) 9, *J*(PtH) 38 Hz]. The ^{31}P n.m.r. spectrum showed resonances at δ 3.8 [d, *J*(PP) 4, *J*(PtP) 4 113, *J*(WP) 14] and 10.6 p.p.m. [d, *J*(PP) 4, *J*(PtP) 2 743, *J*(WP) 6 Hz]. The ^{13}C n.m.r. spectrum showed resonances at δ 336 [d, $C{\cdot}C_6H_4{\cdot}Me$, *J*(PC) 59, *J*(PtC) 747], 221 [CO, *J*(PtC) 27], 164 [$C^{(1)}(C_6H_4Me)$, *J*(PtC) 61], 140 [d, $C^{(1)}(PC_6H_5)$, *J*(PC) 29], 139.5 [d, $C^{(1)}(PC_6H_5)$, *J*(PC) 27], 130—120 (aromatic C), 91 (C_5H_5), 21 ($CH_3C_6H_4$), 16 [d, MeP, *J*(PC) 25], and 15 p.p.m. [d, MeP, *J*(PC) 24 Hz].

(*b*) The compound $[PtW(\mu\text{-}C{\cdot}C_6H_4Me\text{-}p)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (2), m.p. 177—179 °C was obtained quantitatively as red *microcrystals* [Found: C, 33.6; H, 4.2%, *M* (mass spectrum) 755. $C_{21}H_{30}O_2P_2PtW$ requires C, 33.4; H, 4.0%, *M* 755] from $[Pt(C_2H_4)(PMe_3)_2]$ (1 mmol) and $[W(\equiv C{\cdot}C_6H_4Me\text{-}p)(CO)_2(\eta\text{-}C_5H_5)]$ (1 mmol) by the method used to obtain (1). $\nu_{max.}$ (cyclohexane) at 1 898s and 1 815s; $\nu_{max.}$ (Nujol) 1 872s, 1 795s, 1 590w, 1 418w, 1 298w, 1 280m, 1 108w, 1 010w, 1 000w, 960s, 948s, 938(sh), 845w, 815w, 798w, 733s, 725(sh), 715(sh), 678s, and 665(sh) cm^{-1}. The ^{1}H n.m.r. spectrum showed resonances at τ 2.94 and 3.32 [$(AB)_2$ system, 4 H, $C_6H_4Me\text{-}p$, *J*(AB) 8], 4.60 [s, 5 H, C_5H_5, *J*(PtH) 4], 7.65 (s, 3 H, $p\text{-}C_6H_4CH_3$), 8.28 [d, 9 H, MeP, *J*(PH) 8, *J*(PtH) 20], and 8.72 [d, 9 H, MeP, *J*(PH) 12, *J*(PtH) 36 Hz]. The ^{31}P n.m.r. spectrum showed resonances at δ 16.0 [d, *J*(PP) 6, *J*(PtP) 4 021, *J*(WP) 15] and 24.0 p.p.m. [d, *J*(PP) 6, *J*(PtP) 2 642 Hz]. The ^{13}C n.m.r. spectrum showed resonances at δ 338 [d, $C{\cdot}C_6H_4Me\text{-}p$, *J*(PC) 61, *J*(PtC) 732], 222 [CO, *J*(PtC) 25], 165 [$C^{(1)}(C_6H_4Me)$, *J*(PtC) 59], 132, 127, 119 (C_6H_4), 91 (C_5H_5), 21 ($p\text{-}C_6H_4Me$), and 19—17.7 (m, PMe).

(*c*) A solution of $[WBr(C{\cdot}C_6H_4Me\text{-}p)(CO)_4]$ (0.48 g, 1 mmol) in diethyl ether (20 cm^3) at −10 °C was added dropwise to a rapidly stirred suspension of $[Pt(C_2H_4)(PMe_3)_2]$ (1 mmol) in pentane at −50 °C. A red precipitate formed immediately and stirring was continued for 15 min. After decanting the solvent, the residue was washed with diethyl ether (3 × 5 cm^3) at 0 °C and dried *in vacuo* to afford quantitatively (0.71 g) red *microcrystals* of $[PtWBr(\mu\text{-}C{\cdot}C_6H_4Me\text{-}p)(CO)_4(PMe_3)_2]$ (3), m.p. 132—134 °C (Found: C, 25.7; H, 3.4. $C_{18}H_{25}BrO_4P_2PtW$ requires C, 26.2; H, 3.1%); $\nu_{max.}$ at 2 080s, 2 020s, 1 978s, br, 1 870s, br (CO), 1 422w, 1 300w, 1 282w, 960(sh), 945s, 920m, 732s, 722(sh)

695w, 675w, 670(sh), 640w, 575w, 552w, and 540m cm^{-1}. The ^{1}H n.m.r. spectrum (−20 °C) showed resonances at τ 2.83 and 2.98 [$(AB)_2$ system, 4 H, p-C_6H_4Me, J(AB) 8], 6.59 (s, 3 H, p-C_6H_4-*Me*), 8.26 [d, 9 H, MeP, J(PH) 8, J(PtH) 23] and 8.73 [d, 9 H, MeP, J(PH) 10, J(PtH) 38 Hz]. The ^{31}P n.m.r. spectrum (−30 °C) showed resonances at δ 8.7 [d, J(PP) 13, J(PtP) 4 015], and 21.8 p.p.m. [d, J(PP) 13, J(PtP) 2 670 Hz]. The ^{13}C n.m.r. spectrum (−50 °C, [$^{2}H_1$]chloroform–dichloromethane) showed resonances at δ 349 (μ-*C*·C_6H_4Me-p), 200 (CO), 135—118 (aromatic C), 21 (*Me*C_6H_4), and 19—16 (m, PMe).

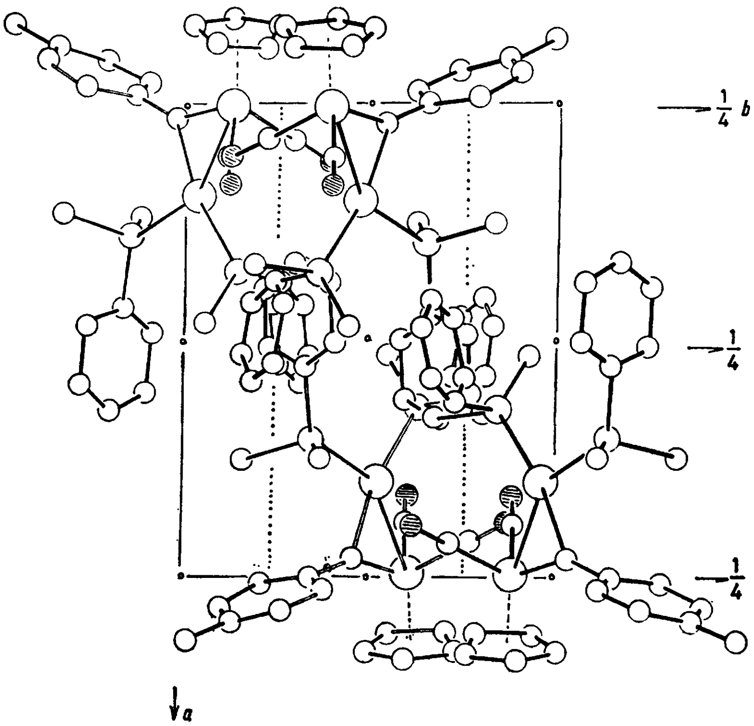

FIGURE 2 Contents of the monoclinic unit cell seen down c* towards the origin

Crystal-structure Determination of $[(\eta\text{-}C_5H_5)(OC)_2W(\mu\text{-}CC_6H_4Me\text{-}p)Pt(PMe_2Ph)_2]$ (1).—Crystals of (1) grow as red prisms from tetrahydrofuran–pentane mixtures; that for data collection was of dimensions *ca.* 0.1 × 0.2 × 0.06 mm, and diffracted intensities were recorded at 200 K for $2.9 \leqslant 2\theta \leqslant 55^{\circ}$ on a Syntex $P2_1$ four-circle diffractometer, according to methods described earlier.[31] Of the total 5 520 recorded intensities, 3 803 had $|F| \geqslant 2\sigma(F)$ where $\sigma(F)$ is the standard deviation based on counting statistics, and only these were used in the final refinement of the structure. Corrections were applied for Lorentz and polarisation effects and for the effects of X-ray absorption. Computations were carried out with the ' SHELX ' system of programs.[32]

Crystal data. $C_{31}H_{34}O_2P_2PtW$, $M = 879.5$, Monoclinic, $a = 12.212(11)$, $b = 9.339(6)$, $c = 26.125(24)$ Å, $\beta = 92.77(7)^{\circ}$, $U = 2\,975.8$ Å^3, $D_m = 1.96$ (flotation), $Z = 4$, $D_c = 1.97$ g cm^{-3}, $F(000) = 1\,676$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 91.6 cm^{-1}, space group $P2_1/c$.

Structure solution and refinement. The structure was solved by the heavy-atom method and all atoms (except H) were located by successive electron-density difference synthesis. The structure was refined by blocked-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms except one phenyl carbon [C(135)] which behaved anomalously when refined anisotropically. The hydrogen atoms were included at positions calculated for rigid group atoms and only common temperature factors for chemically equivalent hydrogen atoms were refined. Refinement for the structure converged at R 0.031 (R' 0.029) with a mean shift-to-error ratio in the final four cycles of 0.05 : 1 with a maximum of 0.5 : 1. A weighting scheme of the form $w = 1.090(\sigma^2F + 0.000\,2F^2)^{-1}$ where $\sigma(F)$ is the estimated error in the observed structure factor based on counting statistics only, gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >0.8 e Å^{-3}. Scattering factors were from ref. 33 for C, O, and P, ref. 34 for hydrogen, and ref. 35 for Pt and W, including corrections for the effects of anomalous dispersion for Pt ($\Delta f'$ −2.352, $\Delta f''$ 8.388), W ($\Delta f'$ −1.421, $\Delta f''$ 6.872), and P ($\Delta f'$ 0.090, $\Delta f''$ 0.095). Atomic positional parameters are in Table 1, interatomic distances and angles in Table 2, and some least-squares planes in Table 3. Contents of the unit cell as shown in Figure 2. Observed and calculated structure factors, all thermal parameters, and positional parameters for hydrogen atoms are listed in Supplementary Publication No. SUP 22768 (22 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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