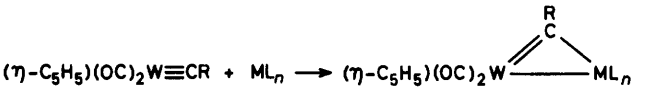
Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 13.[1] Synthesis of Platinumirontungsten Trimetal Compounds with μ_3-Tolylidyne Groups; Crystal Structures of $[FePtW(\mu_3\text{-}CR)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)]$ and $[FePtW(\mu_3\text{-}CR)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) †

By **Michael J. Chetcuti, Judith A. K. Howard, Rona M. Mills, F. Gordon A. Stone,** and **Peter Woodward,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The dimetal compounds $[PtW(\mu\text{-}CR)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4, PR'_3 = PMe_3, PMe_2Ph, $PMePh_2$, or PEt_3) react with $[Fe_2(CO)_9]$ in tetrahydrofuran at room temperature to afford trimetal complexes $[FePtW(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_5(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$, $[FePtW(\mu_3\text{-}CR)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)]$, and $[FePtW(\mu_3\text{-}CR)(CO)_6(PR'_3)(\eta\text{-}C_5H_5)]$ (PR'_3 = PMe_3, $PMePh_2$, or PEt_3). The reaction involving $[PtW(\mu\text{-}CR)(CO)_2(PEt_3)_2(\eta\text{-}C_5H_5)]$ also gave the non-iron containing compound $[Pt_2W(\mu_3\text{-}CR)(CO)_4(PEt_3)_2(\eta\text{-}C_5H_5)]$. Pathways for the formation of these heteronuclear trimetal complexes are discussed, and n.m.r. data (^1H, $^{31}P\text{-}\{^1H\}$, $^{13}C\text{-}\{^1H\}$) are reported for the dynamic platinumirontungsten species which contain a μ_3-CFePtW core. *X*-Ray diffraction studies on $[FePtW(\mu_3\text{-}CR)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)]$ and on $[FePtW(\mu_3\text{-}CR)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$ confirm that the molecular skeleton is the same for both; the Pt atom in the former carries two $PMePh_2$ ligands whereas in the latter it carries one terminal CO and one PEt_3 ligand. Interesting differences in detailed structure are revealed, however. The Fe–Pt bond lengths are similar [2.556(2) and 2.542(3) Å] for $[FePtW(\mu_3\text{-}CR)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)]$ and $[FePtW(\mu_3\text{-}CR)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$ respectively, but the Fe–W and Pt–W bond lengths are significantly different [2.694(2) *versus* 2.784(3), and 2.883(1) *versus* 2.775(1) Å]. The Pt–W bond in $[FePtW(\mu_3\text{-}CR)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)]$ is among the longest so far observed. These differences, and those between the bonds of the μ_3-CR ligand, are discussed. In the pentacarbonyl species the two P–Pt distances differ, that *trans* to the μ_3-C atom [2.331(4) Å] being notably longer than the other [2.289(3) Å]. Both molecules are chiral and both crystallise in non-centrosymmetric space groups. Crystals of $[FePtW(\mu_3\text{-}CR)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)]$ are monoclinic, space group $P2_1$ (no. 4) with $Z = 2$ in a unit cell of dimensions a = 10.005(2), b = 17.240(3), c = 12.928(4) Å, β = 115.98(2)°, and the structure has been refined to R 0.050 for 4 490 reflections. Crystals of $[FePtW(\mu_3\text{-}CR)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$ are orthorhombic, space group $Pna2_1$ (no. 33) with $Z = 4$ in a unit cell of dimensions a = 16.106(5), b = 8.958(5), c = 18.429(7) Å, and the structure has been refined to R 0.050 for 2 703 reflections.

We have recently shown [2-7] that the alkylidyne complex $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ [8] combines with low-valent metal species ML_n to afford a variety of dimetal compounds (Scheme 1). This discovery [9] followed from an appreciation of the isolobal relationship [10] between CR and $W(CO)_2(\eta\text{-}C_5H_5)$ (W: d^5, co-ordination number = 8) groups, suggesting that the alkylidynetungsten compound might display a co-ordination pattern similar to that of an alkyne. The products of the reactions are formulated with 'dimetallacyclopropene' rings with a double bond between the tungsten and the bridging carbon atom. *X*-Ray crystallographic studies on representative compounds [2,3] support this view, and hence the reactivity of the compounds should reflect the electron-rich character of the three-membered rings. In this context, an exciting possibility is the addition of other



SCHEME 1 R = C_6H_4Me-4; ML_n = $Pt(PR_3)_2$, $Co(CO)(\eta\text{-}C_5Me_5)$, $Rh(CO)(\eta\text{-}C_9H_7)$, $Fe(CO)_4$, $Mn(CO)_2(\eta\text{-}C_5H_4Me)$, $Re(CO)_2(\eta\text{-}C_5H_5)$, and $Cr(CO)_2(\eta\text{-}C_6Me_6)$

metal–ligand fragments in which the incoming metal species has the requisite three orbitals and sufficient electron pairs for cluster bonding.[11] The resulting metal cluster would have a 'tetrahedrane-like' structure with a carbon atom capping a metal triangle. Moreover, starting from $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4), and depending on the choice of reactants, the clusters could be so constructed that the metal atoms they contain would involve either two or three different elements.

In order to examine these possibilities several of the dimetal compounds of Scheme 1 have been reacted with low-valent metal complexes, and herein we report on the addition of iron carbonyl groups. A preliminary account of certain aspects of this work has been given.[12,13]

RESULTS AND DISCUSSION

The first reaction to be investigated was that between $[Fe_2(CO)_9]$ and the compound $[PtW(\mu\text{-}CR)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$. Tetrahydrofuran (thf) was used as solvent because it is known [14] that in this medium enneacarbonyldi-iron affords the labile complex $[Fe(CO)_4(thf)]$. When the reactants were mixed at room temperature a deep purple solution was produced. Chromatography on an alumina column led to the isolation of a purple compound in 70% yield, formulated as $[FePtW(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_5(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ (1). The proposed structure of complex (1) is based on spectroscopic evidence. Thus in the i.r. spectrum in the CO-stretching region there is a low-frequency band at 1 713 cm^{-1}

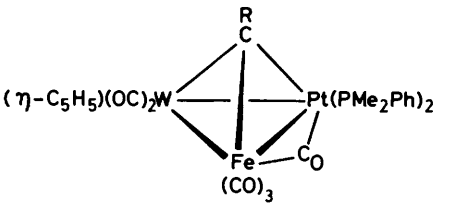
† 2,2,2,3,3-Pentacarbonyl-3-η-cyclopentadienyl 1,1-bis(methyldiphenylphosphine)-μ_3-*p*-tolymethyllidyne-*triangulo*-platinumirontungsten and 1,2,2,2,3,3-hexacarbonyl-3-η-cyclopentadienyl-μ_3-*p*-tolylmethylidyne-1-triethyl-phosphine-*triangulo*-platinumirontungsten.

attributable to a bridging CO ligand. N.m.r. studies (^{1}H, ^{13}C-{^{1}H}, ^{31}P-{^{1}H}, and ^{195}Pt-{^{1}H}) proved to be very informative, and showed that the compound underwent dynamic behaviour in solution.

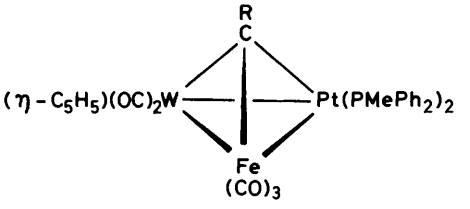
At ambient temperatures the ^{195}Pt spectrum showed a triplet signal [relative intensity 1 : 2 : 1, J(PPt) 3 339 Hz]. On cooling to −95 °C a doublet of doublets [J(PPt) 3 646 and 2 991 Hz] was observed. The ^{31}P n.m.r. data were in accord with these observations, although the broadness of the peaks indicated that neither the high-temperature nor low-temperature limiting spectra were attained. At room temperature a broad resonance with ^{195}Pt satellites [J(PP) 3 347 Hz] was seen (Experimental section), while at −100 °C two slightly broadened doublet signals were visible with ^{195}Pt satellites [J(PtP) 3 618 and 2 993 Hz]. The ^{31}P and ^{195}Pt data establish the presence of the $Pt(PMe_2Ph)_2$ group in (1), and show that the phosphine ligands undergo site exchange, with an activation energy ($\Delta G_{T_c}^{\ddagger}$) estimated [15] to be 46 ± 2 kJ mol^{-1} (T_c *ca.* 248 K). A possible mechanism for the process would be rotation of the $Pt(PMe_2Ph)_2$ group about an axis passing through the platinum and the middle of the CFeW face of the cluster. In this context it is interesting that theoretical calculations [16] on the hypothetical compound $[Fe_3Pt(CO)_{10}(PH_3)]^{2-}$ suggest that rotation of the $Pt(CO)(PH_3)$ moiety about an axis through the platinum and the middle of the Fe_3 triangle would involve a very low activation energy (*ca.* 25 kJ mol^{-1}). However, it was suggested that the presence of bulky tertiary phosphines and bridging ligands would increase the energy required for the process. Hence an activation energy of *ca.* 46 kJ mol^{-1} for rotation of the $Pt(PMe_2Ph)_2$ group in (1) is a reasonable value.

Measurement of the ^{13}C n.m.r. spectrum of (1) at various temperatures also confirmed the intramolecular exchange of the PMe_2Ph groups. At room temperature the μ_3-C ligated carbon signal {at δ 295 p.p.m. with J(PtC) 427 Hz, compared with δ 336 p.p.m. and J(PtC) 747 Hz for the precursor $[PtW(\mu\text{-}CR)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$} was a triplet (1 : 2 : 1), suggesting coupling with two equivalent PMe_2Ph ligands [J(PC) 11 Hz]. At −100 °C, this μ_3-C signal became a doublet [J(PC) 27 Hz], a pattern presumably arising through coupling with a single ^{31}P nucleus in a *transoid* position. Consistently at the low-temperature limit, the PMe_2Ph ligands give rise to four methyl signals with appropriate ^{31}P and ^{195}Pt coupling, and this confirms that the cluster is chiral. As expected, intramolecular phosphine exchange at ambient temperatures results in only two methyl signals and these appear as AA'X multiplets with poorly resolved ^{195}Pt satellites.

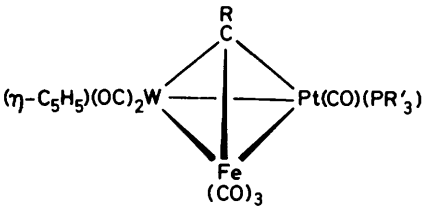
The ^{13}C n.m.r. data for ambient and low-temperature measurements showed that the CO groups were also undergoing site exchange. Three signals only were observed in the room-temperature spectrum. Two at δ 239 p.p.m. [J(WC) 181, J(PtC) 27 Hz] and 232 p.p.m. [J(WC) 172, J(PtC) 24 Hz] could be assigned to WCO groups on account of the ^{183}W–^{13}C coupling. The third resonance [δ 217 p.p.m., J(PtC) 34 Hz] is evidently due to FeCO groups. Using a ^{13}C-enriched sample of (1), data were obtained at −100 °C. Although the limiting spectrum had not been reached, three resonances were observed for the FeCO groups: a doublet signal at δ 225 p.p.m. [J(PC) 5, J(PtC) 39 Hz], and two broad signals at δ 221 and 216 p.p.m. (1 : 2). The more deshielded resonance at 225 p.p.m. is assigned to a $\overline{Fe(\mu\text{-}CO)Pt}$ group,[17] and it is notable that this is the only CO signal which shows ^{31}P coupling. At −100 °C the two resonances for the WCO groups are essentially unchanged from the room-temperature spectrum. It would appear that there are two CO-exchange processes, namely, bridge–



(1)



(2)

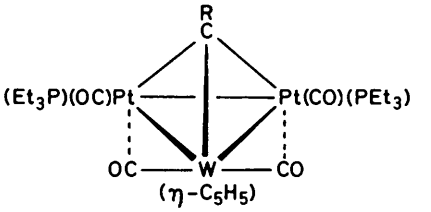


PR'_3

(3) $PMePh_2$

(4) PMe_3

(5) PEt_3



(6)

$R = C_6H_4Me\text{-}4$

terminal, and rotation of the $Fe(CO)_3$ group about an axis through the iron atom and CPtW face of the cluster, the latter process apparently still occurring at −100 °C, the lowest temperature at which experiments could be conducted.

In view of the i.r. and n.m.r. evidence for the presence of a $(OC)_3Fe(\mu\text{-}CO)Pt$ group in (1) it seemed important to confirm the structure by a single-crystal *X*-ray diffraction study. This was particularly desirable since for a platinum-containing cluster with a μ_3-CFePtW core, compound (1) is unusual in having 50 cluster valence electrons rather than 48 (see later). Unfortunately, crystals of (1) proved to be of poor quality and also decomposed in the *X*-ray beam.

The reaction between $[Fe_2(CO)_9]$ and $[PtW(\mu\text{-}CR)(CO)_2(PMePh_2)_2(\eta\text{-}C_5H_5)]$ was next investigated, and found to afford two cluster compounds (2) and (3). The former was a minor reaction product which was fortunately unambiguously characterised as a result of an *X*-ray diffraction study (discussed below) carried out on a crystal selected from the mixture. The spectroscopic properties of (3) are in accord with the proposed structure. Thus in contrast with (1), the i.r. spectrum of (3) showed no band in the bridging CO region. The ^{31}P n.m.r. spectrum showed a singlet resonance [δ −15.0 p.p.m., J(PtP) 3 654 Hz], while the ^{13}C n.m.r. spectrum displayed four resonances due to CO ligands. One of these, a doublet at δ 187 p.p.m. [J(PC) 7, J(PtC) 1 614 Hz], was clearly due to a PtCO group on account of the very large ^{195}Pt–^{13}C coupling.

From reactions between $[Fe_2(CO)_9]$ and the compounds $[PtW(\mu\text{-}CR)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)]$ (PR'_3 = PMe_3 or PEt_3), complexes (4) and (5) were isolated. The reaction which afforded (5) also gave the diplatinumtungsten compound (6). As described in the preceding paper,[1] compounds of structural type (6) are formed from the dimetal compounds $[PtW(\mu\text{-}CR)(CO)_3(PR'_3)(\eta\text{-}C_5H_5)]$, which in turn are produced by the action of CO on the species $[PtW(\mu\text{-}CR)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)]$.

As expected for compounds having similar structures, the i.r. spectra of (3)—(5) are very similar in the CO-stretching region (Experimental section). Similarly, the ^{13}C spectra all reveal a characteristic μ_3-C resonance in the range δ 320—330 p.p.m. with ^{31}P, ^{195}Pt, and ^{183}W coupling. The ^{195}Pt n.m.r. spectrum of (4) showed a doublet signal [δ 170 p.p.m., J(PPt) 3 650 Hz] in accord with the presence of a $Pt(PMe_3)$ group. In the ^{13}C spectra of all three complexes, the two CO ligands on the tungsten are distinct, whilst the three CO groups on the iron atom appear as a sharp singlet even at −100 °C. Dynamic behaviour of the $Fe(CO)_3$ group is evidently occurring, as discussed above for the similar group in (1). The platinum-bound CO ligands in (4) and (5) are seen as doublet signals [J(PC) *ca.* 8 Hz] at δ 187 p.p.m. with strong ^{195}Pt–^{13}C coupling (J *ca.* 1 500 Hz). The ^{31}P n.m.r. spectrum of (5) varies with temperature. At 25 °C, a single resonance is seen [δ −29.3 p.p.m., J(PtP) 3 617 Hz] while at −100 °C there are two signals [δ −38.6 and −27.8 p.p.m., relative intensity 1 : 6, with J(PPt) 3 629 and 3 593 Hz, respectively]. This suggests that the $Pt(CO)(PEt_3)$ group in (5) is rotating, in a manner similar to that proposed for the $Pt(PMe_2Ph)_2$ group in (1) discussed above. Apparently in solution at −100 °C two conformational isomers of (5) exist.

Fortunately, good quality crystals of (5) were obtained, thereby allowing the structure to be determined by *X*-ray diffraction. The results, and those of the *X*-ray diffraction study on (2) mentioned above, are summarised in Tables 1—4, and the two molecular structures are shown in Figures 1 and 2.

For both complexes the skeleton consists of a tetrahedrane-type linking of the three metal atoms and the tolylidyne carbon atom and, as expected, the structures

TABLE 1

Selected bond lengths (Å) and angles (°) for $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)]$ (2)

(*a*) Distances

Pt–W	2.883(1)	Pt–C(00)	2.11(1)
Pt–Fe	2.556(2)	Fe–C(00)	1.96(1)
W–Fe	2.694(2)	W–C(00)	2.02(1)
W–C (cp) mean *	2.36(2)	C(00)–C(01)	1.51(2)
C–C (cp) mean *	1.43(3)	C(01)–C(02)	1.39(2)
W–C(1)	1.97(1)	C(02)–C(03)	1.40(3)
C(1)–O(1)	1.14(2)	C(03)–C(04)	1.37(3)
W–C(2)	1.96(2)	C(04)–C(05)	1.37(3)
C(2)–O(2)	1.19(3)	C(05)–C(06)	1.39(3)
Fe–C(3)	1.80(1)	C(01)–C(06)	1.39(3)
C(3)–O(3)	1.18(2)	C(04)–C(001)	1.54(4)
Fe–C(4)	1.80(1)	Pt–P(1)	2.331(4)
C(4)–O(4)	1.13(2)	P(1)–C(100)	1.87(2)
Fe–C(5)	1.77(1)	P(1)–C(111)	1.84(1)
C(5)–O(5)	1.14(2)	P(1)–C(121)	1.82(1)
		Pt–P(2)	2.289(3)
		P(2)–C(200)	1.83(2)
C–C (Ph) mean	1.38(3)	P(2)–C(211)	1.82(1)
		P(2)–C(221)	1.82(2)

(*b*) Angles

W–Pt–Fe	59.0(1)	W–Pt–C(00)	44.5(3)
Pt–W–Fe	54.4(1)	Pt–W–C(00)	47.1(4)
Pt–Fe–W	66.5(1)	W–Fe–C(00)	48.4(3)
W–C(00)–Pt	88.4(5)	Fe–W–C(00)	46.5(3)
W–C(00)–Fe	85.1(4)	Pt–Fe–C(00)	53.9(4)
Pt–C(00)–Fe	77.6(5)	Fe–Pt–C(00)	48.6(3)
C(01)–C(00)–Fe	122.5(7)		
C(01)–C(00)–Pt	123.5(8)	C(3)–Fe–W	106.8(4)
C(01)–C(00)–W	139.8(9)	C(3)–Fe–Pt	114.1(5)
		C(4)–Fe–W	106.2(4)
C(1)–W–Fe	64.9(4)	C(4)–Fe–Pt	143.1(4)
C(1)–W–Pt	118.2(4)	C(5)–Fe–W	143.9(3)
C(2)–W–Fe	79.1(4)	C(5)–Fe–Pt	79.5(4)
C(2)–W–Pt	76.2(4)	C(3)–Fe–C(4)	102.7(6)
C(1)–W–C(2)	82.6(6)	C(3)–Fe–C(5)	97.8(6)
W–C(1)–O(1)	169(1)	C(4)–Fe–C(5)	93.3(6)
W–C(2)–O(2)	173(1)	Fe–C(3)–O(3)	177(1)
		Fe–C(4)–O(4)	176(1)
P(1)–Pt–Fe	102.2(1)	Fe–C(5)–O(5)	176(1)
P(1)–Pt–W	134.2(1)		
C(100)–P(1)–Pt	113.4(6)	P(2)–Pt–Fe	153.2(1)
C(100)–P(1)–C(111)	99.6(7)	P(2)–Pt–W	105.3(1)
C(100)–P(1)–C(121)	105.5(6)	C(200)–P(2)–Pt	114.8(5)
C(111)–P(1)–Pt	119.1(4)	C(200)–P(2)–C(211)	101.8(7)
C(121)–P(1)–Pt	115.5(5)	C(200)–P(2)–C(221)	101.1(8)
C(111)–P(1)–C(121)	101.5(6)	C(211)–P(2)–Pt	116.6(5)
P(1)–C(111)–C(112)	117(1)	C(221)–P(2)–Pt	117.5(3)
P(1)–C(121)–C(122)	120(1)	C(211)–P(2)–C(221)	102.6(7)
		P(2)–C(211)–C(212)	120(1)
		P(2)–C(221)–C(222)	120(1)

* cp = Cyclopentadienyl ligand.

TABLE 2

Selected bond lengths (Å) and angles (°) for [FePtW(μ_3-CC_6H_4Me-4)$(CO)_6(PEt_3)(\eta$-$C_5H_5)$] (5)

(*a*) Distances			
Pt–W	2.775(1)	Pt–C(1)	2.23(2)
Pt–Fe	2.542(3)	Fe–C(1)	1.90(2)
W–Fe	2.784(3)	W–C(1)	2.00(2)
W–C (cp) mean	2.34(3)	C(1)–C(11)	1.50(3)
C–C (cp) mean	1.43(4)	C(11)–C(12)	1.43(3)
W–C(2)	2.02(3)	C(12)–C(13)	1.39(3)
C(2)–O(2)	1.13(3)	C(13)–C(14)	1.44(4)
W–C(3)	2.00(3)	C(14)–C(15)	1.37(4)
C(3)–O(3)	1.12(3)	C(15)–C(16)	1.36(3)
Fe–C(4)	1.78(2)	C(16)–C(11)	1.38(3)
C(4)–O(4)	1.13(3)	C(14)–C(141)	1.47(4)
Fe–C(5)	1.74(2)	Pt–P	2.329(5)
C(5)–O(5)	1.17(3)	P–C(31)	1.81(3)
Fe–C(6)	1.82(2)	C(31)–C(32)	1.52(4)
C(6)–O(6)	1.14(3)	P–C(41)	1.84(3)
Pt–C(7)	1.90(2)	C(41)–C(42)	1.49(4)
C(7)–O(7)	1.14(3)	P–C(51)	1.79(3)
		C(51)–C(52)	1.58(3)
(*b*) Angles			
W–Pt–Fe	63.0(1)	W–Pt–C(1)	45.6(5)
Pt–W–Fe	54.4(1)	Pt–W–C(1)	52.7(5)
Pt–Fe–W	62.6(1)	W–Fe–C(1)	46.0(6)
W–C(1)–Pt	81.7(7)	Fe–W–C(1)	42.9(5)
W–C(1)–Fe	91.1(8)	Pt–Fe–C(1)	58.2(6)
Pt–C(1)–Fe	75.5(7)	Fe–Pt–C(1)	46.2(5)
C(11)–C(1)–Fe	128(1)		
C(11)–C(1)–Pt	117(1)	C(4)–Fe–W	103.1(9)
C(11)–C(1)–W	139(2)	C(4)–Fe–Pt	159.3(8)
		C(5)–Fe–W	143.4(8)
C(2)–W–Fe	69.7(7)	C(5)–Fe–Pt	92.3(9)
C(2)–W–Pt	119.8(7)	C(6)–Fe–W	106.0(6)
C(3)–W–Fe	83.7(6)	C(6)–Fe–Pt	94.6(7)
C(3)–W–Pt	72.2(6)	C(4)–Fe–C(5)	92.3(13)
C(2)–W–C(3)	82.1(9)	C(4)–Fe–C(6)	104.2(9)
W–C(2)–O(2)	171(2)	C(5)–Fe–C(6)	101.9(11)
W–C(3)–O(3)	179(2)	Fe–C(4)–O(4)	177(2)
		Fe–C(5)–O(5)	171(3)
P–Pt–Fe	103.9(2)	Fe–C(6)–O(6)	176(2)
P–Pt–W	158.3(1)		
Pt–P–C(31)	112.7(10)	C(7)–Pt–Fe	157.3(6)
Pt–P–C(41)	109.1(8)	C(7)–Pt–W	95.8(6)
Pt–P–C(51)	119.9(9)	C(7)–Pt–C(1)	113.4(8)
C(31)–P–C(41)	106(1)	C(7)–Pt–P	98.8(7)
C(31)–P–C(51)	103(1)	C(1)–Pt–P	137.9(5)
C(41)–P–C(51)	105(1)		
P–C(31)–C(32)	117(2)	Pt–C(7)–O(7)	178(2)
P–C(41)–C(42)	112(2)		
P–C(51)–C(52)	118(2)		

differ chemically in that in (5) the platinum atom carries one terminal CO group and one PEt_3 ligand, whereas in (2) the platinum atom carries two $PMePh_2$ ligands. Both molecules are chiral, and crystallise in non-centrosymmetric space groups. A study of the interatomic distances in the two molecules (Tables 1 and 2) reveals some interesting differences. The Fe–Pt bond lengths [2.556(2) and 2.542(3) Å for (2) and (5), respectively] are closely similar, and towards the lower end of the range observed in other cluster compounds,[15,18] and are very similar to those observed in trimetallic platinum–iron complexes.[19–21] In contrast, corresponding Fe–W and Pt–W bond lengths are significantly different [2.694(2) *versus* 2.784(3), and 2.883(1) *versus* 2.775(1) Å, respectively]. The metal triangle is therefore much nearer to isosceles in (5) than in (2), taking the Fe–Pt bond as the base of the triangle. A comparable Fe–W bond length is that found [12] in [FeRhW(μ_3-CC_6H_4Me-4)-

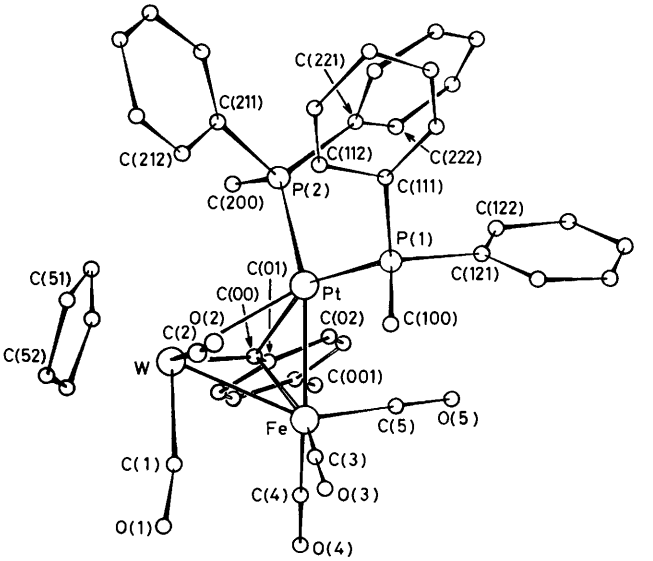


FIGURE 1 Molecular structure of [FePtW(μ_3-CC_6H_4Me-4)$(CO)_5$-$(PMePh_2)_2(\eta$-$C_5H_5)$] (2), showing the atom numbering scheme

(μ-CO)$(CO)_5(\eta$-$C_5H_5)(\eta$-$C_9H_7)$] which, at 2.772(1) Å, is much closer to that in (5) than to that in (2); however, the Pt–W distance in (2) [2.883(1) Å] is among the longest so far observed in a cluster compound. This may be a

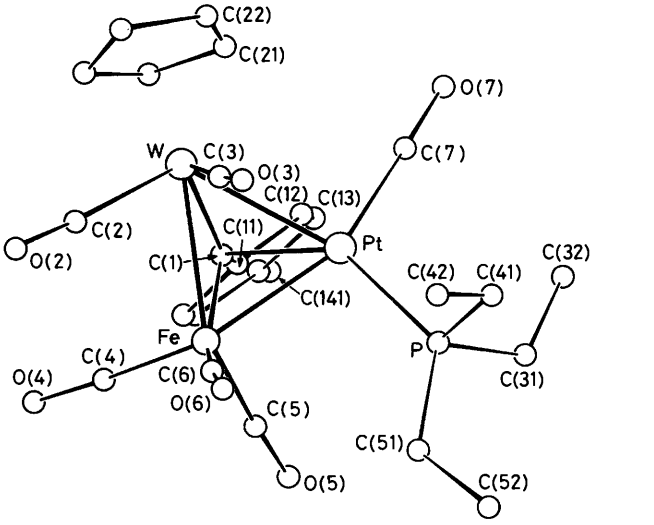


FIGURE 2 Molecular structure of [FePtW(μ_3-CC_6H_4Me-4)$(CO)_6$-$(PEt_3)(\eta$-$C_5H_5)$] (5), showing the atom numbering scheme

reflection of the fact that the bonding around the Pt atom is approximately square planar excluding the bond to the tungsten atom, whereas in (5) it is approximately square planar excluding the bond to the triply bridging carbon atom. A consequence of stronger Pt–W interaction might in turn be that the W–Fe bond in (5) is weakened.

The triply bridging alkylidyne carbon atom is asymmetrically related to the three metal atoms in both (2) and (5), but whereas the W–C and Fe–C interactions are

approximately equal to one another and are similar in both compounds, the Pt–C interaction is not only long compared with others that have been measured, but is even longer in (5) than in (2). There is clearly a significantly different electron density distribution in the two complexes, and this is further reflected in the different orientation of the $Fe(CO)_3$ moiety with respect to the metal triangle, seen in the stereopair drawings (Figures 3 and 4). The only further obvious difference

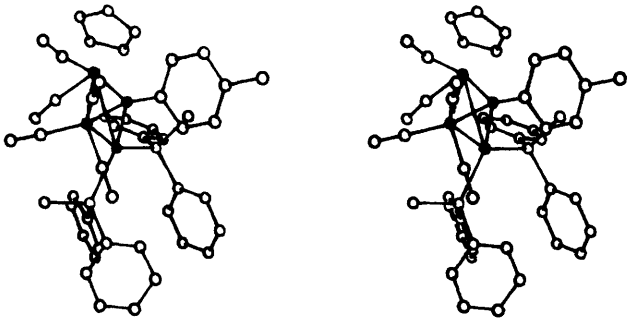


FIGURE 3 Stereopair drawing of the molecular structure of (2)

is that the plane of the tolyl ring is approximately parallel to the W–Pt bond in (2) but parallel to the Fe–Pt bond in (5), almost certainly as a consequence of inter- or intra-molecular packing requirements. Finally, it may be noted that the terminal carbonyl group on the W atom labelled C(1)–O(1) in (2) and C(2)–O(2) in (5) makes a rather acute angle with the Fe–W bond [65° in (2) and 70° in (5)] and might, therefore, be regarded as incipiently semi-bridging in the η^2 mode to the iron atom.

In complex (2) the two P–Pt distances are significantly different; P(1)–Pt, which lies in a *transoid* relationship to the carbyne carbon atom is appreciably longer [2.331(4) Å] than P(2)–Pt [2.289(3) Å]. Similar effects have been observed in other bis(tertiary phosphine)-platinum complexes [7,22-24] with alkylidene or alkylidyne groups bridging the metal–metal bonds.

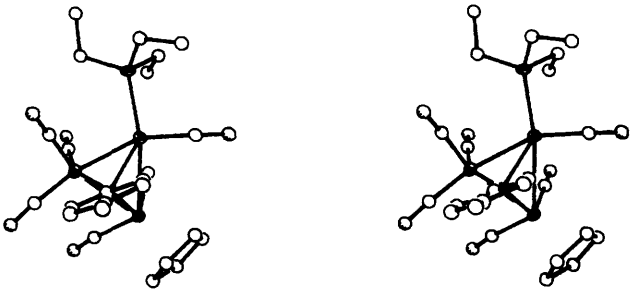
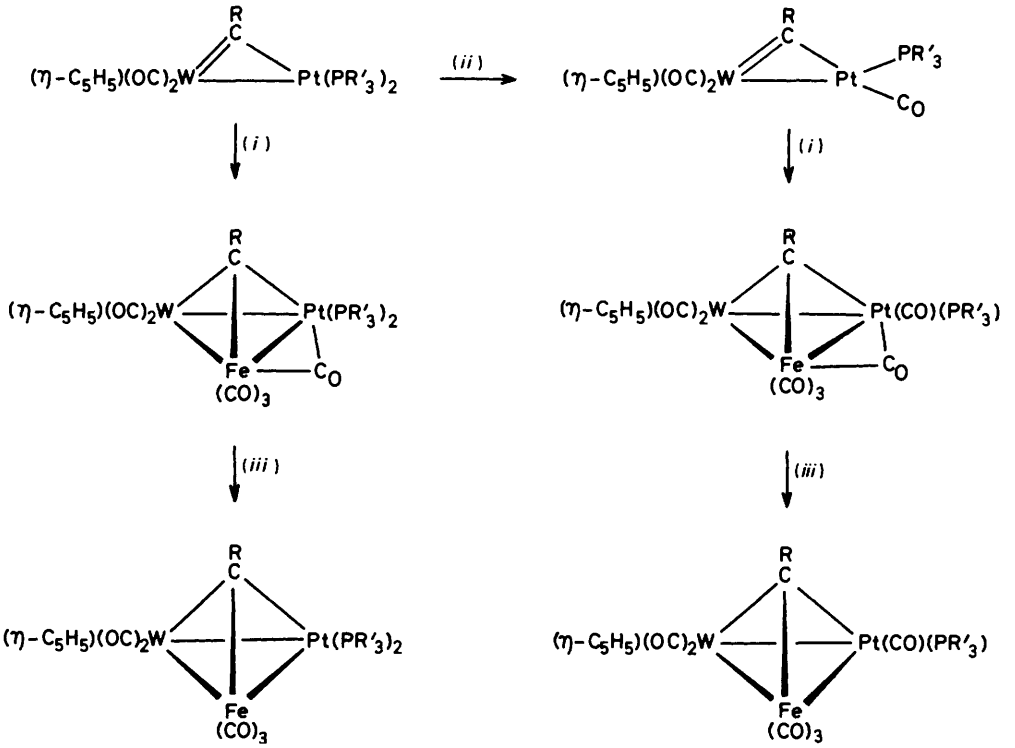


FIGURE 4 Stereopair drawing of the molecular structure of (5)

Formation of the various trimetal compounds described above can be accounted for as shown in Scheme 2. In thf, the di-iron carbonyl $[Fe_2(CO)_9]$ is believed to afford $[Fe(CO)_4(thf)]$ and $[Fe(CO)_5]$.[14] The latter is a ready source of CO, and it has previously been shown [1] that this reagent reacts with the compounds $[PtW(\mu\text{-}CR)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)]$ to give the tricarbonyl species $[PtW(\mu\text{-}CR)(CO)_3(PR'_3)(\eta\text{-}C_5H_5)]$. Both types of platinum–tungsten complex would thus be available for



SCHEME 2 (*i*) $Fe(CO)_4(thf)$, –thf; (*ii*) CO; (*iii*) –CO

reaction with $[Fe(CO)_4(thf)]$ to give initially the 50-electron clusters illustrated (Scheme 2) with Fe(μ-CO)Pt bridges. However, the latter would be expected to be relatively unstable, and only one such species, (1), was isolated. Loss of a molecule of CO would yield the 48-electron clusters (2)—(5) which possess the five skeletal bonding electron pairs which are expected for platinum-containing trimetallatetrahedrane structures.[25] It may well be that the donor ability and steric properties of the particular tertiary phosphine ligand influences the pathway followed in Scheme 2. The complexes $[FePtW(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_6(PR'_3)(\eta\text{-}C_5H_5)]$ (PR'_3 = $PMePh_2$, PMe_3, and PEt_3) are evidently very unstable since these species were not detected in the synthesis of (3)—(5).

EXPERIMENTAL

The techniques used, and the instrumentation employed, have been described previously.[7,26] For n.m.r. data, chemical shifts (p.p.m.) are relative to $SiMe_4$ (^1H and $^{13}C\text{-}\{^1H\}$), 85% H_3PO_4 (external) ($^{31}P\text{-}\{^1H\}$), and to Ξ 21.4 MHz ($^{195}Pt\text{-}\{^1H\}$), positive values representing shifts to high frequency of the reference. Unless otherwise stated, i.r. bands were measured in methylcyclohexane. The compounds $[PtW(\mu\text{-}CR)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)]$ were prepared as described previously,[1,2] except for PR'_3 = PEt_3, a new compound which was obtained as described below.

Light petroleum (20 cm^3) was saturated with ethylene at 0 °C, and powdered $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) (0.412 g, 1 mmol) was slowly added, followed by PEt_3 (2 mmol) so as to generate $[Pt(C_2H_4)(PEt_3)_2]$ *in situ*. The tungsten compound $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.408 g, 1 mmol) was then added, and the mixture stirred (2 h). Solvent was removed *in vacuo* to give orange *microcrystals* of $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PEt_3)_2(\eta\text{-}C_5H_5)]$ (0.80 g, 95%) (Found: C, 38.4; H, 5.1. $C_{37}H_{42}O_2P_2PtW$ requires C, 38.6; H, 5.0%), m.p. 128—130 °C; $\nu_{max.}$(CO) at 1 885vs and 1 805vs, br cm^{-1} (Nujol). N.m.r. ($[^2H_1]$chloroform): ^1H, δ 0.75—1.75 (m, 18 H, *Me*CH_2P), 1.96—2.28 (m, 12 H, CH_2), 2.37 (s, 3 H, Me-4), 5.28 (s, 5 H, C_5H_5), 6.63—6.95 (m, 4 H, C_6H_4); $^{31}P\text{-}\{^1H\}$, δ −20.6 [J(PP) 0, J(PtP) 4 061, J(WP) 15] and −3.1 p.p.m. [J(PtP) 2 717 Hz]; $^{195}Pt\text{-}\{^1H\}$, δ 524 p.p.m. [d of d, J(PPt) 4 066 and 2 768, J(PtW) 186 Hz]; ^{13}C ($[^2H_2]$dichloromethane), δ 337 [d, μ-C, J(PC) 59, J(PtC) 751, J(WC) 145], 164 [C^1 (C_6H_4), J(PtC) 64], 131, 126, 119 (C_6H_4), 91 (C_5H_5), 21 (Me-4), 17 [d, CH_2P, J(PC) 22, J(PtC) 24], 16 [d, CH_2P, J(PC) 24, J (PtC) 39], 8 p.p.m. [*Me*CH_2, J(PtC) 20 Hz].

Reactions of the Complexes $[PtW(\mu\text{-}CR)(CO)_2(PR'_3)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) *with* $[Fe_2(CO)_9]$.—(*a*) The compound $[PtW(\mu\text{-}CR)(CO)_2(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ (0.44 g, 0.5 mmol) was dissolved in thf (20 cm^3) and $[Fe_2(CO)_9]$ (0.18 g, 0.5 mmol) was added and the mixture stirred (4 h). All volatiles were removed *in vacuo*, and the residue dissolved in toluene (9 cm^3) and chromatographed on an alumina column (2 × 20 cm). Elution with light petroleum–diethyl ether (1 : 1) removed a deep purple band. Concentration of the eluate and cooling to −20 °C afforded purple *plates* of the compound $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_5(PMe_2Ph)_2(\eta\text{-}C_5H_5)]$ (1) (0.74 g, 70%) (Found: C, 40.4; H, 3.0. $C_{35}H_{34}FeO_6P_2PtW$ requires C, 40.1. H, 3.1%); $\nu_{max.}$(CO) at 2 017m, 1 995s, 1 953m, 1 927s, 1 913s, 1 879m, and 1 713m cm^{-1}. N.m.r.: ^1H ($[^2H_6]$benzene), δ 0.8—1.4 (m, 12 H, MeP), 1.86 (s, 3 H, Me-4), 5.04 (s, 5 H, C_5H_5), 6.90—7.05 (m, 10 H, Ph), 7.11—7.50 (m, 4 H, C_6H_4); $^{31}P\text{-}\{^1H\}$ ($[^2H_2]$dichloromethane, 25 °C), δ −5.6 p.p.m. [br, J(PtP) 3 347 Hz]; $^{31}P\text{-}\{^1H\}$ (−100 °C), δ −13.5 [d, J(PP) 46, J(PtP) 3 618], −0.6 p.p.m. [d, J(PP) 46, J(PtP) 2 993, J(WP) 32 Hz]; $^{195}Pt\text{-}\{^1H\}$ (25 °C), δ −390.7 p.p.m. [t, J(PPt) 3 339 Hz]; $^{195}Pt\text{-}\{^1H\}$ (−95 °C), δ −477.3 p.p.m. [d of d, J(PPt) 3 646 and 2 991 Hz]; $^{13}C\text{-}\{^1H\}$ (25 °C), δ 295.2 [t, μ_3-C, J(PC) 11, J(PtC) 427, J(WC) 111], 238.9 [WCO, J(PtC) 27, J(WC) 181], 231.8 [WCO, J(PtC) 24, J(WC) 172], 217.4 [FeCO, J(PtC) 34], 164.6 [C^1 (C_6H_4), J(PtC) 20], 134—125 (C_6H_4, Ph), 92.5 (C_5H_5), 21.2 (Me-4), 18.6 [AA'X system, MeP, N(PC) 31, J(PtC) not resolved *], 11.6 [AA'X system, MeP, N(PC) 28, J(PtC) not resolved]; $^{13}C\text{-}\{^1H\}$ (−100 °C, selected signals only), δ 293.9 [d, μ_3-C, J(PC) 27, J(PtC), 418], 242.3 [WCO, J(PtC) 22, J(WC) 184], 233.2 [WCO, J(PtC) 19, J(WC) 210], 224.8 [d, Fe(μ-*C*O)Pt, J(PC) 5, J(PtC) 39], 221.0, 216.7 [FeCO, br, relative intensity 1 : 2], 18.2 [d, MeP, J(PC) 29], 16.1 [d, MeP, J(PC) 32], 10.4 [d, MeP, J(PC) 29], 7.1 p.p.m. [d, MeP, J(PC) 27 Hz].

(*b*) The compound $[PtW(\mu\text{-}CR)(CO)_2(PMePh_2)_2(\eta\text{-}C_5H_5)]$ (0.48 g, 0.5 mmol) in thf (25 cm^3) was similarly reacted with $[Fe_2(CO)_9]$ (0.18 g, 0.5 mmol) at room temperature. Removal of volatile material *in vacuo*, addition of toluene (10 cm^3) and chromatography led to the isolation of brown *crystals* (0.44 g, 45%) of $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)]$ (2) and $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PMePh_2)(\eta\text{-}C_5H_5)]$ (3). Compound (2) was formed in minor amount and was characterised by *X*-ray diffraction (see below). Compound (3) (Found: C, 40.1; H, 2.7. $C_{32}H_{25}FeO_6PPtW$ requires C, 39.6; H, 2.6%), m.p. 152—156 °C; $\nu_{max.}$(CO) at 2 039m, 2 017s, 1 995s, 1 955s, 1 941s, and 1 881m cm^{-1}. N.m.r. ($[^2H_2]$dichloromethane): ^1H, δ 2.27 (s, 3 H, Me-4), 2.48 [d, 3 H, MeP, J(PH) 10, J(PtH) 19 Hz], 5.43 (s, 5 H, C_5H_5), 6.80—6.98 (m, 4 H, C_6H_4), 7.2—7.5 (m, 10 H, Ph); $^{31}P\text{-}\{^1H\}$, δ −15.0 p.p.m. [J(PtP) 3 654 Hz]; $^{13}C\text{-}\{^1H\}$, δ 327.0 [d, μ_3-C, J(PC) 7, J(PtC) 410, J(WC) 125], 220.5 [WCO, J(WC) 121], 218.9 [WCO, J(WC) 119], 216.5 [FeCO, J(PtC) 29], 187.2 [d, PtCO, J(PC) 7, J(PtC) 1 614], 163.8 [C^1 (C_6H_4)], 131—120 (C_6H_4, Ph), 93.3 (C_5H_5), 21.4 (Me-4), 18.2 p.p.m. [d, MeP, J(PC) 29, J(PtC) 59 Hz].

(*c*) A thf (25 cm^3) solution of $[PtW(\mu\text{-}CR)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]$ (0.38 g, 0.5 mmol) was stirred (3 h) with $[Fe_2(CO)_9]$ (0.18 g, 0.5 mmol). All volatiles were removed *in vacuo*, the dark brown residue dissolved in toluene and chromatographed. Trace amounts of a yellow product believed to be $[Fe(CO)_4(PMe_3)]$ were first eluted, followed by a dark brown band. Concentration by partial removal of the toluene *in vacuo* followed by addition of some pentane at −20 °C afforded brown-black *crystals* of $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PMe_3)(\eta\text{-}C_5H_5)]$ (4) (0.34 g, 40%) (Found: C, 31.1; H, 2.6. $C_{22}H_{21}FeO_6PPtW$ requires C, 31.2; H, 2.5%), m.p. 105—108 °C; $\nu_{max.}$(CO) at 2 036m, 2 013s, 1 982s, 1 954s, 1 934s, and 1 879m cm^{-1}. N.m.r. ($[^2H_1]$-chloroform): ^1H, δ 1.79 [d, 9 H, MeP, J(PH) 10, J(PtH) 16.5 Hz], 2.27 (s, 3 H, Me-4), 5.53 (s, 5 H, C_5H_5), 6.79—7.01 (m, 4 H, C_6H_4); $^{31}P\text{-}\{^1H\}$, δ 6.8 p.p.m. [J(PtP) 3 649 Hz]; $^{195}Pt\text{-}\{^1H\}$, δ 169.6 [d, J(PtP) 3 650 Hz]; $^{13}C\text{-}\{^1H\}$, δ 321 [d, μ_3-C, J(PC) 10, J(PtC) 408, J(WC) 121], 228 (WCO), 220 (WCO), 215 [FeCO, J(PtC) 29], 187 [d, PtCO, J(PC) 6, J(PtC) 1 449], 164 [C^1 (C_6H_4)], 133, 127, 120 (C_6H_4), 92 (C_5H_5), 21 (Me-4), 19 p.p.m. [d, MeP, J(PC) 31, J(PtC) 43 Hz].

(*d*) Similarly, $[PtW(\mu\text{-}CR)(CO)_2(PEt_3)_2(\eta\text{-}C_5H_5)]$ (0.42 g, 0.5 mmol) and $[Fe_2(CO)_9]$ (0.18 g, 0.5 mmol) gave by chrom-

* $N = J(AX) + J(A'X)$.

atography a trace of $[Fe(CO)_4(PEt_3)]$ (i.r., and ^{31}P n.m.r. identified) and then eluting with light petroleum–diethyl ether (1 : 1) an orange solution followed by a brown solution. Concentration of these solutions and cooling to −20 °C afforded red *microcrystals* of $[Pt_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_4(PEt_3)_2(\eta\text{-}C_5H_5)]$ (6) (0.11 g, 10%) (see ref. 1 for characterisation, and spectroscopic data) and black *crystals* of $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$ (5) (0.36 g, 40%) (Found: C, 33.6; H, 3.1. $C_{25}H_{27}FeO_6PPtW$ requires C, 33.8; H, 3.1%), m.p. 124—127 °C; $\nu_{max.}$(CO) at 2 035m, 2 013s, 1 985s, 1 954s, 1 933s, and 1 877m cm^{-1}. N.m.r. ($[^2H_2]$dichloromethane): ^1H, δ 1.06 [d of t, 9 H, $MeCH_2$, J(HH) 8, J(PH) 18 Hz], 1.5—2.0 (m, 6 H, CH_2), 2.26 (s, 3 H, Me-4), 5.5 (s, 5 H, C_5H_5), 6.76—6.99 (m, 4 H, C_6H_4); ^{31}P-{^1H}, δ −29.3 p.p.m. [J(PtP) 3 617 Hz]; ^{31}P-{^1H} ($[^2H_2]$dichloromethane–methylcyclohexane, −100 °C), δ −38.6 [J(PtP) 3 629] and −27.8 p.p.m. [J(PtP) 3 593 Hz]; ^{13}C-{^1H}, δ 323.1 [d, μ_3-C, J(PC) 9, J(PtC) 404, J(WC) 110], 221.8 (WCO), 221.6 (WCO), 216.0 [FeCO, J(PtC) 26], 186.9 [d, PtCO, J(PC) 11, J(PtC) 1 549], 163.6 [C^1 (C_6H_4)], 134, 128, 120 (C_6H_4), 92.8 (C_5H_5), 21.1 (Me-4), 19.2 [d, CH_2P, J(PC) 26, J(PtC) 40], 8 p.p.m. [$MeCH_2$, J(PtC) 22 Hz].

Crystal Structure Determination of $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_5(PMePh_2)_2(\eta\text{-}C_5H_5)]$ (2).—Red-brown crystals of (2) were grown at −20 °C from dichloromethane. Intensities were collected at 200 K from a crystal of dimensions *ca.* 0.4 × 0.2 × 0.1 mm in the range $2.9 \leqslant 2\theta \leqslant 55°$. Two check reflections (1 $\bar{1}$ 1 and 1 3 1) were remeasured every 50 reflections and showed no significant decay. Of the total 6 234 reflections measured, 4 490 had $|F_o| \geqslant 6\sigma(F_o)$ and only these were used in the solution and refinement of the structure. Corrections were made for Lorentz and polarisation effects.

Crystal data. $C_{44}H_{38}FeO_5P_2PtW$. M = 1 143.5, Monoclinic, a = 10.005(2), b = 17.240(3), c = 12.928(4) Å, β = 115.98(2)°, U = 2 005 Å^3, D_m = 1.88 g cm^{-3} (flotation), Z = 2, D_c = 1.89 g cm^{-3}, $F(000)$ = 1 100, space group $P2_1$ (no. 4), Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, μ(Mo-K_α) = 65.8 cm^{-1}.

The platinum and tungsten atoms were located from a Patterson synthesis, and all other non-hydrogen atoms by successive electron-density difference syntheses. The origin of the unit cell ($P2_1$) was fixed with reference to the Pt atom. Hydrogen atoms were incorporated at calculated positions. The structure was refined by a cascade least-squares process, with anisotropic thermal parameters for all non-hydrogen atoms and a common isotropic thermal parameter for chemically equivalent hydrogen atoms. Weights were applied according to the scheme $w = [\sigma^2(F_o) + 0.0025|F_o|^2]^{-1}$, where $\sigma(F_o)$ is the estimated error in $|F_o|$ based on counting statistics only, and this gave a satisfactory weight analysis. Convergence was obtained at R 0.050, R' 0.050. As the space group $P2_1$ is non-centrosymmetric, corrections were applied for anomalous dispersion: Pt, $\Delta f'$ −2.35, $\Delta f''$ 8.39; W, $\Delta f'$ −1.42, $\Delta f''$ 6.87; P, $\Delta f'$ 0.09, $\Delta f''$ 0.09; and the structure was refined for both enantiomorphs. One gave a significantly better refinement than the other, and the co-ordinates listed in Table 3 correspond to the enantiomorph present in the crystal investigated. All computations were carried out within the laboratory on an Eclipse (Data General) computer with the ' SHELXTL ' system of programs.[27] Atom co-ordinates for (2) are listed in Table 3.

TABLE 3

Atomic positional parameters (fractional co-ordinates) for complex (2)

Atom	x	y	z
Fe	1.074 6(2)	0.936 22(10)	0.959 72(14)
W	0.840 43(5)	0.850 78(3)	0.817 73(4)
Pt	0.924 24(4)	1.000 00	0.764 17(3)
P(1)	1.109 9(3)	1.042 6(2)	0.714 8(3)
P(2)	0.710 9(4)	1.050 5(3)	0.622 7(3)
O(1)	1.048 7(13)	0.754 7(7)	1.029 6(12)
O(2)	1.067 3(15)	0.816 4(9)	0.714 8(12)
O(3)	1.346 2(11)	0.852 4(9)	0.983 2(11)
O(4)	1.087 9(13)	0.922 8(9)	1.189 5(10)
O(5)	1.200 8(13)	1.091 4(7)	1.012 5(10)
C(1)	0.984(2)	0.795 8(8)	0.955 5(13)
C(2)	0.986(2)	0.825 7(9)	0.759 5(13)
C(3)	1.238 9(13)	0.886 8(8)	0.971 5(12)
C(4)	1.084 8(14)	0.925 0(8)	1.101 0(11)
C(5)	1.148 6(13)	1.031 2(8)	0.988 0(11)
C(00)	0.860 2(12)	0.957 0(7)	0.889 0(10)
C(01)	0.787 6(12)	1.006 3(9)	0.946 5(10)
C(02)	0.802 8(14)	1.086 4(9)	0.951 3(11)
C(03)	0.739 1(15)	1.128 7(9)	1.010 8(13)
C(04)	0.665 7(15)	1.093 8(10)	1.066 4(12)
C(05)	0.644 2(15)	1.014 9(9)	1.057 3(12)
C(06)	0.706 0(15)	0.972 1(8)	0.997 9(12)
C(001)	0.601(3)	1.141 7(13)	1.135(2)
C(51)	0.674(2)	0.770 4(10)	0.666 2(15)
C(52)	0.714(3)	0.729 8(10)	0.770(2)
C(53)	0.661(2)	0.776 3(11)	0.838 1(15)
C(54)	0.587 0(14)	0.843 1(11)	0.774 0(13)
C(55)	0.594 0(15)	0.840 9(11)	0.669 4(14)
C(100)	1.273(2)	0.975 3(9)	0.763 3(15)
C(111)	1.067 9(13)	1.051 6(9)	0.562 0(11)
C(112)	1.020(3)	0.984 6(9)	0.494(2)
C(113)	0.989(3)	0.986 4(12)	0.382(2)
C(114)	0.999(2)	1.056 2(11)	0.328 2(13)
C(115)	1.051(2)	1.118 5(11)	0.395 3(14)
C(116)	1.079(2)	1.118 1(9)	0.509 3(14)
C(121)	1.187 0(14)	1.137 6(7)	0.769 5(11)
C(122)	1.095 6(14)	1.195 4(9)	0.773 0(15)
C(123)	1.151(2)	1.269 5(8)	0.813 1(15)
C(124)	1.300(2)	1.285 3(9)	0.844 8(14)
C(125)	1.395(2)	1.228 0(11)	0.844(2)
C(126)	1.337 1(15)	1.154 8(9)	0.802 7(15)
C(200)	0.551 8(14)	1.053 2(11)	0.657 6(13)
C(211)	0.632 9(13)	0.999 8(12)	0.485 3(11)
C(212)	0.692(2)	0.929 4(11)	0.474 8(14)
C(213)	0.633(3)	0.886(2)	0.374(2)
C(214)	0.507(3)	0.916 7(14)	0.277 7(15)
C(215)	0.451(3)	0.985(2)	0.289 0(14)
C(216)	0.509(2)	1.028 5(12)	0.389 2(13)
C(221)	0.716 1(13)	1.150 6(10)	0.580 2(12)
C(222)	0.701(2)	1.213 0(11)	0.648(2)
C(223)	0.716(3)	1.288(2)	0.616(3)
C(224)	0.754(2)	1.304 7(12)	0.531(3)
C(225)	0.770(2)	1.244 6(12)	0.465(2)
C(226)	0.750(2)	1.167 9(11)	0.489 3(15)

Crystal Structure Determination of $[FePtW(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(PEt_3)(\eta\text{-}C_5H_5)]$ (5).—Crystals of (5) grow as dark brown truncated pyramids from dichloromethane. Diffracted intensities were collected at 220 K from a crystal of dimensions 0.25 × 0.40 × 0.25 mm (mounted under nitrogen in a Lindemann capillary) on a Syntex $P2_1$ four-circle diffractometer. Of the total 3 170 independent reflections for $2.9 \leqslant 2\theta \leqslant 55.0°$, 2 703 satisfied the criterion $I \geqslant 2.5\sigma(I)$, and only these were used in the solution and refinement of the structure. Two check reflections ($\bar{4}$ 2 6 and 2 $\bar{2}$ $\bar{5}$) were remeasured every 40 reflections and showed no significant change during the 97 h of crystal exposure to X-rays. The intensities were corrected for Lorentz, polarisation, and X-ray absorption effects.

Crystal data. $C_{25}H_{27}FeO_6PPtW$, M = 889.0, Orthorhombic, a = 16.106(5) b = 8.958(5), c = 18.429(7) Å, U = 2 659(2) Å^3, D_m = 2.10 g cm^{-3}, Z = 4, D_c = 2.22 g

cm^{-3}, $F(000) = 1\,672$, space group $Pna2_1$ (no. 33), μ(Mo-K_α) $= 97.8\ cm^{-1}$.

The structure was solved as for (2), and was refined with isotropic thermal parameters for C(1), C(3), C(7), C(11)—C(16), C(21)—C(25) and anisotropic thermal parameters for all other non-hydrogen atoms. Hydrogen atoms were incorporated at calculated positions and were given a common isotropic thermal parameter. Weights were ascribed according to the scheme $w = 2.4186\,[\sigma(F_o)^2 + 0.0010|F_o|^2]^{-1}$. Refinement by full-matrix least squares converged to R 0.050 (R' 0.050), and a final electron-density difference map showed no peaks >3.6 or <3.2 e $Å^{-3}$, the largest peaks being in the vicinity of the metal atoms. Scattering factors were taken from ref. 28 for C and O, ref. 29 for H, and ref. 30 for Fe, Pt, and W. Computational work was carried out with the SHELX system of programs [31] on the ICL System 4 computers of the South-Western Universities Computer Network. Atom co-ordinates for (5) are listed in Table 4.

TABLE 4

Atomic positional parameters (fractional co-ordinates) for complex (5)

Atom	x	y	z
Pt	0.127 6(0)	−0.017 4(1)	0.000 0
W	0.144 0(0)	−0.262 8(1)	−0.090 7(1)
Fe	0.257 1(2)	−0.029 1(3)	−0.078 7(2)
C(1)	0.149(1)	−0.047(2)	−0.118(1)
C(2)	0.258(2)	−0.330(3)	−0.122(1)
O(2)	0.319(1)	−0.385(2)	−0.137(1)
C(3)	0.188(1)	−0.320(2)	0.007(2)
O(3)	0.213(1)	−0.354(2)	0.061(1)
C(4)	0.320(1)	−0.050(3)	−0.157(1)
O(4)	0.357(1)	−0.063(2)	−0.209(1)
C(5)	0.266(2)	0.165(2)	−0.081(2)
O(5)	0.266(1)	0.294(2)	−0.090(1)
C(6)	0.326(1)	−0.079(2)	−0.004(1)
O(6)	0.366(1)	−0.112(2)	0.045(1)
C(7)	0.017(1)	−0.060(2)	0.029(1)
O(7)	−0.050(1)	−0.084(2)	0.044(1)
C(11)	0.106(1)	0.059(2)	−0.169(1)
C(12)	0.021(1)	0.096(2)	−0.153(1)
C(13)	−0.022(1)	0.185(3)	−0.202(1)
C(14)	0.015(2)	0.241(3)	−0.268(2)
C(15)	0.096(2)	0.201(3)	−0.278(2)
C(16)	0.141(1)	0.116(3)	−0.231(1)
C(141)	−0.031(2)	0.339(3)	−0.318(2)
P	0.161 9(3)	0.153 6(6)	0.090 4(3)
C(31)	0.095(2)	0.316(3)	0.090(2)
C(32)	0.002(2)	0.290(3)	0.087(2)
C(41)	0.148(2)	0.065(2)	0.179(2)
C(42)	0.211(2)	−0.052(3)	0.194(2)
C(51)	0.264(2)	0.234(3)	0.093(2)
C(52)	0.287(2)	0.334(3)	0.160(2)
C(21)	0.002(2)	−0.289(3)	−0.115(1)
C(22)	0.029(1)	−0.415(2)	−0.074(1)
C(23)	0.089(2)	−0.494(3)	−0.115(1)
C(24)	0.099(2)	−0.410(3)	−0.184(1)
C(25)	0.040(2)	−0.293(3)	−0.183(2)

Observed and calculated structure factors for (2) and (5), a complete list of bond lengths and angles for each structure, all hydrogen atom co-ordinates, and all thermal parameters, are listed in Supplementary Publication No. SUP 23334 (63 pp.).*

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

We thank the S.E.R.C. for support and for a research studentship (to R. M. M.), and the Commonwealth Scholarship Commission for a Scholarship (to M. J. C.).

[2/306 *Received*, 18*th February*, 1982]

REFERENCES

[1] Part 12, M. J. Chetcuti, K. Marsden, I. Moore, F. G. A. Stone, and P. Woodward, preceding paper.
[2] T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1609.
[3] M. J. Chetcuti, M. Green, J. C. Jeffery, F. G. A. Stone, and A. Wilson, *J. Chem. Soc., Chem. Commun.*, 1980, 948.
[4] L. Busetto, M. Green, J. A. K. Howard, B. Hessner, J. C. Jeffery, R. M. Mills, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1981, 1101.
[5] J. C. Jeffery, R. Navarro, H. Razay, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1981, 2471.
[6] J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, M. J. Went, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1981, 867.
[7] 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.
[8] E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreissl, and J. O. Besenhard, *Chem. Ber.*, 1977, **110**, 3397.
[9] T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1979, 42.
[10] B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585; A. R. Pinhas, T. A. Albright, P. Hofmann, and R. Hoffmann, *Helv. Chim. Acta*, 1980, **63**, 29, and refs. therein.
[11] K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1; 'Transition Metal Clusters,' ed. B. F. G. Johnson, Wiley, New York, 1980, ch. 3.
[12] M. J. Chetcuti, M. Green, J. A. K. Howard, J. C. Jeffery, R. M. Mills, G. N. Pain, S. J. Porter, F. G. A. Stone, A. A. Wilson, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1980, 1057; M. Green, J. C. Jeffery, S. J. Porter, H. Razay, and F. G. A. Stone, *J. Chem. Soc. Dalton Trans.*, in the press.
[13] T. V. Ashworth, M. J. Chetcuti, L. J. Farrugia, J. A. K. Howard, J. C. Jeffery, R. M. Mills, G N. Pain, F. G. A. Stone, and P. Woodward, 'Reactivity of Metal–Metal Bonds,' *ACS Symp. Ser.*, 155, 1981, pp. 299—313.
[14] F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, 1974, **96**, 3438.
[15] L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 155.
[16] B. E. R. Schilling and R. Hoffmann, *J. Am. Chem. Soc.*, 1979, **101**, 3456.
[17] B. E. Mann and B. F. Taylor, '^{13}C N.M.R. Data for Organometallic Compounds,' Academic Press, London, 1981.
[18] G. Longoni, M. Manassero, and M. Sansoni, *J. Am. Chem. Soc.*, 1980, **102**, 3342.
[19] L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 1134.
[20] V. G. Albano and C. Ciani, *J. Organomet. Chem.*, 1974, **66**, 311.
[21] R. Mason, J. Zubieta, A. T. T. Hsieh, J. Knight, and M. J. Mays, *J. Chem. Soc., Chem. Commun.*, 1972, 200.
[22] J. A. K. Howard, J. C. Jeffery, M. Laguna, R. Navarro, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1979, 1170.
[23] 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.
[24] T. V. Ashworth, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1593.
[25] F. G. A. Stone, *Inorg. Chim. Acta*, 1981, **50**, 33, and refs. therein.
[26] J. C. Jeffery, I. Moore, M. Murray, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1982, 1741.
[27] G. M. Sheldrick, SHELXTL, a system of crystallographic programs for use with the Nicolet *P3/m X*-ray system, University of Cambridge, 1976.
[28] D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.
[29] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
[30] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.
[31] G. M. Sheldrick, SHELX, a system of crystallographic computer programs, University of Cambridge, 1976.