

## Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 4.<sup>1</sup> Synthesis of *triangulo*-Diplatinum–Chromium and –Tungsten Complexes. Crystal Structure of [Pt<sub>2</sub>W{μ-C(OMe)Ph}(CO)<sub>6</sub>(PBU<sup>t</sup><sub>2</sub>Me)<sub>2</sub>] †

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The compounds [M{C(OMe)Ph}(CO)<sub>5</sub>] (M = Cr or W) react with bis(ethylene)(trialkylphosphine)platinum complexes [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] [PR<sub>3</sub> = PBU<sup>t</sup><sub>2</sub>Me or P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>] to give *triangulo*-trimetal compounds [MPt<sub>2</sub>{μ-C(OMe)Ph}(CO)<sub>6</sub>(PR<sub>3</sub>)<sub>2</sub>]. With [Cr{C(OMe)Ph}(CO)<sub>5</sub>], di- and tri-platinum complexes [Pt<sub>2</sub>{μ-C(OMe)Ph}(CO)<sub>2</sub>(PBU<sup>t</sup><sub>2</sub>Me)<sub>2</sub>], and [Pt<sub>3</sub>{μ-C(OMe)Ph}(μ-CO)<sub>2</sub>(PR<sub>3</sub>)<sub>3</sub>] [PR<sub>3</sub> = PBU<sup>t</sup><sub>2</sub>Me or P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>], are also produced in the reactions. In the compound [Pt<sub>2</sub>W{μ-C(OMe)Ph}(CO)<sub>6</sub>(PBU<sup>t</sup><sub>2</sub>Me)<sub>2</sub>] <sup>13</sup>C n.m.r. studies showed that the μ-C(OMe)Ph group bridged the Pt–Pt bond, and this was confirmed by a single-crystal X-ray diffraction study. Crystals are monoclinic, with space group *P*2<sub>1</sub>/*a* and *Z* = 4 in a unit cell of dimensions *a* = 16.003(5), *b* = 15.691(7), *c* = 15.261(9) Å, and β = 93.52(4)°. The structure has been determined by heavy-atom methods from automated diffractometer data for 2.9 ≤ 2θ ≤ 50° and refined to *R* 0.075 (*R'* 0.082) for 3 991 reflections. A triangle of metal atoms has Pt–Pt and Pt–W separations of 2.627(1) and 2.830(2) Å, respectively. The platinum–platinum bond is bridged by the C(OMe)Ph group [C–Pt 2.05(2) Å]. Each platinum atom is co-ordinated by a CO and by a PBU<sup>t</sup><sub>2</sub>Me group such that both PBU<sup>t</sup><sub>2</sub>Me ligands lie on the same side of the Pt–Pt bond [P–Pt–Pt 149(1)°] and are *cis* to the μ-C(OMe)Ph group, with the two carbonyl ligands semi-bridging across the Pt–W bonds to the formally 16-electron W(CO)<sub>4</sub> group [Pt–C–O 148(3)°]. The ease of transfer of a carbene group from a mononuclear metal carbene complex to platinum is reflected in the reactions of [Mn{C(OMe)Ph}(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)] with [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] [PR<sub>3</sub> = PMe<sub>3</sub> or PBU<sup>t</sup><sub>2</sub>Me] from which no compounds with Mn–Pt bonds were isolated. Instead, the products were the triplatinum species [Pt<sub>3</sub>{μ-C(OMe)Ph}<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>] and [Pt<sub>3</sub>{μ-C(OMe)Ph}<sub>2</sub>(μ-CO)(PR<sub>3</sub>)<sub>3</sub>]. These triplatinum compounds likely form *via* initial formation of an intermediate with a Mn{μ-C(OMe)Ph}Pt bridged system, since it was observed that the dimetal compound [(OC)<sub>5</sub>Cr{μ-C(OMe)Ph}Pt(PMe<sub>3</sub>)<sub>2</sub>] decomposes at 80 °C in toluene to give [Pt<sub>3</sub>{μ-C(OMe)Ph}<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>] and [Pt<sub>3</sub>{μ-C(OMe)Ph}<sub>2</sub>(μ-CO)(PMe<sub>3</sub>)<sub>3</sub>]. Bulky phosphine groups seem to favour formation of trimetal compounds since [W{C(OMe)Ph}(CO)<sub>5</sub>] and [Pt(C<sub>2</sub>H<sub>4</sub>)(PBU<sup>t</sup><sub>2</sub>Me)<sub>2</sub>] react to give [Pt<sub>2</sub>W{μ-C(OMe)Ph}(CO)<sub>6</sub>(PBU<sup>t</sup><sub>2</sub>Me)<sub>3</sub>], rather than [(OC)<sub>5</sub>-W{μ-C(OMe)Ph}Pt(PBU<sup>t</sup><sub>2</sub>Me)<sub>2</sub>]. The spectroscopic properties of the new compounds are reported.

In Part 1<sup>2</sup> of this series we reported ready reactions between Fischer's<sup>3</sup> mononuclear metal carbene compounds [M{C(OMe)Ph}(CO)<sub>5</sub>] [M = Cr, Mo, or W] and platinum complexes [Pt(C<sub>2</sub>H<sub>4</sub>)(PR<sub>3</sub>)<sub>2</sub>] (PR<sub>3</sub> = PMe<sub>3</sub> or PMe<sub>2</sub>Ph). The products were dimetal species with platinum–chromium, –molybdenum, or –tungsten bonds, the metal–metal bonds being bridged by the carbene group forming 'dimetallacyclopropane' structures. In these reactions the zerovalent platinum compounds [Pt(C<sub>2</sub>H<sub>4</sub>)(PR<sub>3</sub>)<sub>2</sub>] act as sources of Pt(PR<sub>3</sub>)<sub>2</sub> groups which attack the dipolar M–C bonds of the mononuclear metal carbene complexes; subsequent ring closure would then account for the observed products. In this paper we extend these studies, by investigating reactions of Fischer's carbene–metal complexes with the bis(ethylene)platinum compounds [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] [PR<sub>3</sub> = PBU<sup>t</sup><sub>2</sub>Me or P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>].<sup>4</sup> The chemistry of the latter is dominated by displacement of ethylene in reactions and so we have employed these species as sources of 'Pt(PR<sub>3</sub>)' groups in various syntheses.<sup>5,6</sup> Following the precedent set by the [Pt(C<sub>2</sub>H<sub>4</sub>)(PR<sub>3</sub>)<sub>2</sub>] compounds, it was reasonable to expect that the bis(ethylene)(trialkylphosphine)platinum complexes would initially produce, in reactions

† μ-Methoxyphenylmethylene-μ-tetracarbonyltungstenio-bis[carbonyl(methyl-di-*t*-butylphosphine)platinum](Pt–Pt).

with the carbene–metal compounds, species of the type [(OC)<sub>5</sub>M{μ-C(OMe)Ph}Pt(C<sub>2</sub>H<sub>4</sub>)(PR<sub>3</sub>)]. However, if such compounds formed, loss of ethylene, thereby creating a vacant site on the platinum atom, would probably result in subsequent reaction leading both to further metal–metal bond formation and to ligand migration processes. A preliminary account of some of the work described in this paper has been given.<sup>7</sup>

### RESULTS AND DISCUSSION

Reaction of [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PBU<sup>t</sup><sub>2</sub>Me)] with [W{C(OMe)Ph}(CO)<sub>5</sub>] in a 2 : 1 mol ratio at –20 °C in toluene afforded (50%) a red crystalline complex formulated as [Pt<sub>2</sub>W{C(OMe)Ph}(CO)<sub>6</sub>(PBU<sup>t</sup><sub>2</sub>Me)<sub>2</sub>] (1) on the basis of analysis (Table 1) and <sup>13</sup>C and <sup>31</sup>P n.m.r. spectroscopy. The <sup>13</sup>C (<sup>1</sup>H-decoupled) n.m.r. spectrum showed a resonance at 237 p.p.m. in the region expected for a bridging C(OMe)Ph ligand between two metal atoms.<sup>2</sup> Moreover, this signal showed characteristic <sup>195</sup>Pt satellite peaks [*J*(PtC) 771 Hz] but no <sup>13</sup>C–<sup>183</sup>W coupling, providing strong evidence that the carbene ligand was bridging the two platinum atoms rather than the Pt–W bonds. The <sup>31</sup>P (<sup>1</sup>H-decoupled) n.m.r. spectrum (Table 2) revealed a pattern indicative of the presence of a P–Pt–Pt–P arrangement.<sup>6</sup> A singlet was observed with two sets of

TABLE 1  
Analytical <sup>a</sup> and physical data for the complexes

Compound	M.p. (θ <sub>c</sub> /°C)	Colour	ν(CO) <sup>b</sup> /cm <sup>-1</sup>	Analysis (%)	
				C	H
(1) [Pt <sub>2</sub> W{μ-C(OMe)Ph}(CO) <sub>6</sub> (PBu <sup>t</sup> <sub>2</sub> Me) <sub>2</sub> ] <sup>c</sup>	175—180 decomp.	Red	2 032s, 1 940m, 1 922s, 1 914 (sh)	32.3 (32.5)	4.4 (4.3)
(2) [Pt <sub>2</sub> W{μ-C(OMe)Ph}(CO) <sub>6</sub> (P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ) <sub>2</sub> ] <sup>d</sup>	192—194	Red	2 028s, 1 940m, 1 924 (sh), 1 916s	42.7 (42.2)	5.7 (5.3)
(3) [CrPt <sub>2</sub> {μ-C(OMe)Ph}(CO) <sub>6</sub> (PBu <sup>t</sup> <sub>2</sub> Me) <sub>2</sub> ]	240—243 decomp.	Red	2 019vs, 1 936s, 1 908vs, 1 876m	36.4 (36.6)	5.0 (4.8)
(4) [CrPt <sub>2</sub> {μ-C(OMe)Ph}(CO) <sub>6</sub> (P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ) <sub>2</sub> ]	179—181	Red	2 016vs, 1 936vs, 1 908vs, 1 860w	46.8 (46.5)	6.0 (5.8)
(5) [Pt <sub>2</sub> {μ-C(OMe)Ph}(CO) <sub>5</sub> (PBu <sup>t</sup> <sub>2</sub> Me) <sub>2</sub> ]	193—195	Pale yellow	1 990vs, 1 953m	37.6 (37.9)	5.8 (5.7)
(6) [Pt <sub>3</sub> {μ-C(OMe)Ph}(μ-CO) <sub>2</sub> (PBu <sup>t</sup> <sub>2</sub> Me) <sub>3</sub> ]	248—250 decomp.	Yellow	1 816s, 1 776vs	35.7 (35.8)	5.7 (5.8)
(7) [Pt <sub>3</sub> {μ-C(OMe)Ph}(μ-CO) <sub>2</sub> (P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ) <sub>3</sub> ]	260—262 decomp.	Yellow	1 808vs, 1 757vs	48.7 (48.6)	7.2 (6.7)
(8) [Pt <sub>3</sub> {μ-C(OMe)Ph} <sub>2</sub> (μ-CO)(PBu <sup>t</sup> <sub>2</sub> Me) <sub>3</sub> ]	236	Red	1 797s	39.8 (39.6)	6.1 (5.9)
(9) [Pt <sub>3</sub> {μ-C(OMe)Ph} <sub>2</sub> (μ-CO)(PMe <sub>3</sub> ) <sub>3</sub> ]	228 decomp.	Orange	1 793s <sup>e</sup>	29.0 (28.9)	4.2 (4.0)
(10) [Pt <sub>3</sub> {μ-C(OMe)Ph} <sub>2</sub> (PMe <sub>3</sub> ) <sub>3</sub> ]	238—239	Violet		33.9 (33.8)	4.7 (4.4)
(11) [Pt <sub>2</sub> W{μ-C(OMe)Ph}(CO) <sub>6</sub> (PBu <sup>t</sup> <sub>2</sub> Me) <sub>3</sub> ] <sup>f</sup>	166 decomp.	Red	1 961vs, 1 889s, 1 869s, 1 800m br	36.8 (36.7)	5.4 (5.4)

<sup>a</sup> Calculated values are given in parentheses. <sup>b</sup> In cyclohexane. <sup>c</sup> Mol. wt: Found: 1 150 (benzene). Calc. 1 154. <sup>d</sup> Mol. wt: Found: 1 502 (benzene). Calc. 1 423. <sup>e</sup> Second isomer ν<sub>max</sub>. 1 785 cm<sup>-1</sup>. <sup>f</sup> Mol. wt: Found: 1 426 (benzene). Calc. 1 343.

<sup>195</sup>Pt satellites arising from molecules with one active <sup>195</sup>Pt nucleus. Molecules with two <sup>195</sup>Pt atoms gave rise to a superimposed AA'XX' spectrum. The observation of only a very small *J*(<sup>183</sup>W—<sup>31</sup>P) coupling indicated that no PBu<sup>t</sup><sub>2</sub>Me ligand was directly bonded to tungsten. Another diplatinumtungsten complex (2), similar to (1), was prepared by treating [W{C(OMe)Ph}(CO)<sub>5</sub>] with

[Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>{P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>}]<sub>2</sub>. The <sup>31</sup>P n.m.r. spectrum of (2) was very similar to that of (1) (Table 2).

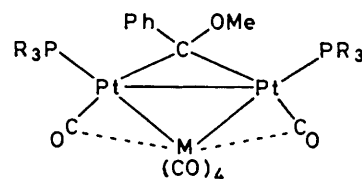
The mononuclear chromium carbene complex [Cr{C(OMe)Ph}(CO)<sub>5</sub>] also reacted with the compounds [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PR<sub>3</sub>)] [PR<sub>3</sub> = PBu<sup>t</sup><sub>2</sub>Me or P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>] to give chromium diplatinum species (3) and (4) (Tables 1

TABLE 2

Phosphorus-31 n.m.r. data <sup>a</sup> for the complexes

Compound	δ(p.p.m.) <sup>b</sup>
(1)	−53.7 [ <i>J</i> (PP) 68, <i>J</i> (PtP) 3 758, 291, <i>J</i> (PtPt) 2 241, <i>J</i> (WP) 34]
(2)	−58.8 [ <i>J</i> (PP) 62, <i>J</i> (PtP) 3 682, 257, <i>J</i> (PtPt) 1 748, <i>J</i> (WP) 32]
(3)	−45.4 [ <i>J</i> (PP) 67, <i>J</i> (PtP) 3 688, 278, <i>J</i> (PtPt) 2 092]
(4)	−45.8 [ <i>J</i> (PP) 61, <i>J</i> (PtP) 3 678, 219]
(5)	−33.1 [ <i>J</i> (PP) 101, <i>J</i> (PtP) 3 440, 392, <i>J</i> (PtPt) 2 582]
(6) <sup>c</sup>	−86.7 (P <sup>b</sup> ) [ <i>J</i> (P <sup>a</sup> P <sup>a</sup> ) 69, <i>J</i> (P <sup>a</sup> P <sup>b</sup> ) 56, <i>J</i> (Pt <sup>a</sup> P <sup>a</sup> ) 4 150, <i>J</i> (Pt <sup>b</sup> P <sup>b</sup> ) 5 100, −57.1 (P <sup>a</sup> ) [ <i>J</i> (Pt <sup>b</sup> P <sup>a</sup> ) 276, <i>J</i> (Pt <sup>a</sup> P <sup>a</sup> ) 303, <i>J</i> (Pt <sup>a</sup> P <sup>b</sup> ) 474]
(7) <sup>c,d</sup>	−85.2 (P <sup>b</sup> ) [ <i>J</i> (P <sup>a</sup> P <sup>b</sup> ) 60, <i>J</i> (Pt <sup>b</sup> P <sup>a</sup> ) 376, <i>J</i> (Pt <sup>a</sup> P <sup>b</sup> ) 485]
(9) <sup>c,e</sup>	−62.3 (P <sup>a</sup> )
Isomer A	−34.7 (P <sup>a</sup> ) [ <i>J</i> (P <sup>a</sup> P <sup>a</sup> ) 72, <i>J</i> (P <sup>a</sup> P <sup>b</sup> ) 79, <i>J</i> (Pt <sup>a</sup> P <sup>a</sup> ) 3 999, <i>J</i> (Pt <sup>b</sup> P <sup>b</sup> ) 3 586, −16.2 (P <sup>b</sup> ) [ <i>J</i> (Pt <sup>b</sup> P <sup>a</sup> ) 406, <i>J</i> (Pt <sup>a</sup> P <sup>a</sup> ) 496, <i>J</i> (Pt <sup>a</sup> P <sup>b</sup> ) 283]
Isomer B	−33.5 (P <sup>a</sup> ) [ <i>J</i> (P <sup>a</sup> P <sup>a</sup> ) 73, <i>J</i> (P <sup>a</sup> P <sup>b</sup> ) 81, <i>J</i> (Pt <sup>a</sup> P <sup>a</sup> ) 4 025, <i>J</i> (Pt <sup>b</sup> P <sup>b</sup> ) 3 551, −16.7 (P <sup>b</sup> ) [ <i>J</i> (Pt <sup>b</sup> P <sup>a</sup> ) 412, <i>J</i> (Pt <sup>a</sup> P <sup>a</sup> ) 510, <i>J</i> (Pt <sup>a</sup> P <sup>b</sup> ) 284]
(10) <sup>c,d</sup>	−31.1 (P <sup>b</sup> ) [ <i>J</i> (P <sup>a</sup> P <sup>a</sup> ) 82.4, <i>J</i> (P <sup>a</sup> P <sup>b</sup> ) 81.8, <i>J</i> (Pt <sup>a</sup> P <sup>a</sup> ) 3 606, <i>J</i> (Pt <sup>b</sup> P <sup>b</sup> ) 3 659, −30.0 (P <sup>a</sup> ) [ <i>J</i> (Pt <sup>b</sup> P <sup>a</sup> ) 395, <i>J</i> (Pt <sup>a</sup> P <sup>a</sup> ) 399, <i>J</i> (Pt <sup>a</sup> P <sup>b</sup> ) 386]
(11) <sup>f</sup>	−57.6 [ <i>J</i> (PP) 75, <i>J</i> (PtP) 3 725, 303] −32.3 [ <i>J</i> (WP) 211]

<sup>a</sup> Hydrogen-1 decoupled, chemical shifts in p.p.m. to low frequency of 85% H<sub>3</sub>PO<sub>4</sub> (external). Spectra measured in [<sup>2</sup>H<sub>6</sub>]chloroform unless otherwise stated. <sup>b</sup> Coupling constants in Hz. <sup>c</sup> Pt atoms are non-equivalent, for labelling Pt<sup>a</sup> and Pt<sup>b</sup> see structural formula in text. Phosphorus nuclei carry same superscripts as platinum to which they are attached. <sup>d</sup> In [<sup>2</sup>H<sub>6</sub>]benzene. <sup>e</sup> In [<sup>2</sup>H<sub>2</sub>]dichloromethane. <sup>f</sup> In [<sup>2</sup>H<sub>6</sub>]toluene.



M	PR <sub>3</sub>
(1)	W PBu <sup>t</sup> <sub>2</sub> Me
(2)	W P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>
(3)	Cr PBu <sup>t</sup> <sub>2</sub> Me
(4)	Cr P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>

and 2), but in low yield. These reactions were accompanied by the formation of non-chromium containing di- and tri-platinum compounds discussed further below. In the i.r. spectra of (3) and (4), bands at 1 876 and 1 860 cm<sup>-1</sup> suggested the presence of semi-bridging CO ligands. The <sup>31</sup>P n.m.r. spectra of (3) and (4) (Table 2) were similar to those of (1) and (2), indicating that the chromium compounds also contained R<sub>3</sub>P—Pt—Pt—PR<sub>3</sub> groups. However, in order to establish firmly the structures of (1)—(4) an X-ray diffraction study was carried out on (1), for which a suitable single crystal was obtainable.

The results of the X-ray diffraction study are summarised in Tables 3—5, and a view of the molecule with the atomic numbering scheme is shown in Figure 1. The *triangulo*-Pt<sub>2</sub>W arrangement is immediately apparent. The Pt—Pt separation [2.627(1) Å] is very similar to those found in [Pt<sub>3</sub>(μ-CNBU<sup>t</sup>)<sub>3</sub>(CNBU<sup>t</sup>)<sub>3</sub>] [2.632(2) Å]<sup>8</sup> and [Pt<sub>3</sub>(μ-CO)<sub>3</sub>{P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>}<sub>3</sub>] [2.654(2) Å].<sup>9</sup> The

TABLE 3

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Pt(1)	0.124 75(9)	0.201 53(7)	0.336 37(6)
Pt(2)	0.139 92(9)	0.196 20(6)	0.166 02(6)
W	0.089 18(10)	0.045 26(7)	0.249 51(8)
C(1)	0.170(2)	0.292(1)	0.253(1)
O(1)	0.262(1)	0.312(1)	0.268(1)
C(01)	0.321(2)	0.244(2)	0.280(2)
C(11)	0.135(2)	0.371(1)	0.245(2)
C(12)	0.048(3)	0.370(2)	0.233(2)
C(13)	0.000(2)	0.444(2)	0.222(2)
C(14)	0.037(3)	0.524(2)	0.231(2)
C(15)	0.122(3)	0.528(2)	0.243(2)
C(16)	0.170(2)	0.451(2)	0.251(2)
Carbonyl groups			
C(02)	0.072(3)	0.115(2)	0.107(3)
O(02)	0.015(2)	0.100(2)	0.051(2)
C(03)	0.045(3)	0.124(2)	0.374(2)
O(03)	-0.015(2)	0.112(1)	0.416(1)
C(21)	0.100(2)	-0.049(2)	0.171(2)
O(21)	0.107(2)	-0.104(1)	0.117(1)
C(22)	0.080(2)	-0.043(2)	0.337(2)
O(22)	0.078(2)	0.095(1)	0.392(2)
C(23)	-0.039(3)	0.035(2)	0.229(2)
O(23)	-0.109(2)	0.026(2)	0.219(2)
C(24)	0.214(4)	0.040(2)	0.265(2)
O(24)	0.285(2)	0.029(2)	0.278(2)
Phosphine ligands			
P(1)	0.163 1(6)	0.263 7(5)	0.473 1(5)
C(3)	0.246(3)	0.343(2)	0.468(2)
C(4)	0.215(3)	0.182(2)	0.550(2)
C(41)	0.287(3)	0.133(3)	0.510(3)
C(42)	0.247(3)	0.222(2)	0.639(2)
C(43)	0.143(3)	0.114(3)	0.576(3)
C(5)	0.067(3)	0.330(2)	0.518(2)
C(51)	0.029(3)	0.385(3)	0.448(3)
C(52)	0.102(3)	0.390(3)	0.595(3)
C(53)	0.105(3)	0.270(3)	0.551(2)
P(2)	0.201 0(5)	0.249 4(5)	0.041 1(4)
C(6)	0.275(2)	0.336(2)	0.067(2)
C(7)	0.260(2)	0.163(2)	-0.015(2)
C(71)	0.325(3)	0.130(2)	0.057(2)
C(72)	0.307(3)	0.197(2)	-0.088(2)
C(73)	0.215(3)	0.086(2)	-0.039(2)
C(8)	0.131(2)	0.306(2)	-0.043(2)
C(81)	0.180(2)	0.361(2)	-0.107(2)
C(82)	0.076(3)	0.372(2)	0.011(2)
C(83)	0.069(3)	0.245(3)	-0.088(3)

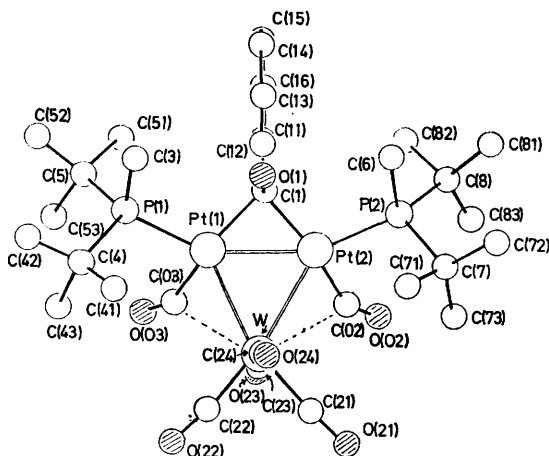


FIGURE 1 Molecular structure of the complex  $[\text{Pt}_2\text{W}\{\text{C}(\text{OMe})\text{Ph}\}(\text{CO})_6(\text{PBu}_2\text{Me})_2]$  (1) showing the atomic numbering scheme, but with the methyl substituent  $[\text{C}(01)]$  of the OMe group omitted for clarity

$\text{C}(\text{OMe})\text{Ph}$  group symmetrically bridges the Pt-Pt bond  $[\text{Pt}-\text{C}(1) 2.05(2) \text{ \AA}]$  with the plane of the carbene ligand at  $90^\circ$  to the plane defined by the atoms  $\text{Pt}_2\text{W}$ . The

TABLE 4

Bond lengths and angles for the complex  $[\text{Pt}_2\text{W}\{\text{C}(\text{OMe})\text{Ph}\}(\text{CO})_6(\text{PBu}_2\text{Me})_2]$  (1)

(a) Distances (Å)		
Pt(1)-Pt(2)	2.627(1)	
Pt(1)-W	2.828(2)	Pt(2)-W 2.832(2)
Pt(1)-C(1)	2.07(2)	Pt(2)-C(1) 2.04(2)
Pt(1)-C(03)	1.88(4)	Pt(2)-C(02) 1.86(4)
C(03)-O(03)	1.20(5)	C(02)-O(02) 1.23(5)
C(1)-O(1)	1.50(4)	O(1)-C(01) 1.45(4)
C(1)-C(11)	1.36(4)	C(11)-C(12) 1.39(6)
C(12)-C(13)	1.41(4)	C(13)-C(14) 1.39(4)
C(14)-C(15)	1.36(6)	C(15)-C(16) 1.43(4)
C(16)-C(11)	1.39(4)	
W-C(21)	1.91(3)	C(21)-O(21) 1.21(4)
W-C(22)	1.93(3)	C(22)-O(22) 1.18(4)
W-C(23)	2.06(5)	C(23)-O(23) 1.13(6)
W-C(24)	2.00(6)	C(24)-O(24) 1.16(7)
Pt(1)-P(1)	2.350(7)	Pt(2)-P(2) 2.349(7)
P(1)-C(3)	1.82(4)	P(2)-C(6) 1.83(3)
P(1)-C(4)	1.89(4)	P(2)-C(7) 1.88(3)
C(4)-C(41)	1.54(7)	C(7)-C(71) 1.56(5)
C(4)-C(42)	1.56(5)	C(7)-C(72) 1.48(5)
C(4)-C(43)	1.63(6)	C(7)-C(73) 1.44(5)
P(1)-C(5)	2.00(4)	P(2)-C(8) 1.87(3)
C(5)-C(51)	1.48(5)	C(8)-C(81) 1.55(5)
C(5)-C(52)	1.59(6)	C(8)-C(82) 1.62(5)
C(5)-C(53)	1.48(6)	C(8)-C(83) 1.51(6)
(b) Angles (°)		
Pt(1)-Pt(2)-W	62.3(2)	Pt(1)-C(1)-Pt(2) 79.5(8)
Pt(2)-W-Pt(1)	55.3(2)	C(1)-Pt(2)-Pt(1) 50.7(7)
W-Pt(1)-Pt(2)	62.4(2)	Pt(2)-Pt(1)-C(1) 49.8(6)
P(1)-Pt(1)-Pt(2)	148.9(2)	P(2)-Pt(2)-Pt(1) 149.3(2)
Pt(1)-C(03)-O(03)	148(3)	Pt(2)-C(02)-O(02) 148(3)
Pt(1)-C(03)-W	81.4(7)	Pt(2)-C(02)-W 81.1(7)
W-C(21)-O(21)	175(2)	W-C(22)-O(22) 177(3)
W-C(23)-O(23)	177(3)	W-C(24)-O(24) 172(3)
C(21)-W-C(22)	84(1)	C(22)-W-C(23) 86(1)
C(21)-W-C(23)	88(1)	C(22)-W-C(24) 90(1)
C(21)-W-C(24)	86(1)	C(23)-W-C(24) 173(1)
Pt(1)-C(1)-O(1)	115(2)	Pt(2)-C(1)-O(1) 117(2)
Pt(1)-C(1)-C(11)	121(2)	Pt(2)-C(1)-C(11) 122(2)
O(1)-C(1)-C(11)	102(2)	
C(1)-C(11)-C(12)	114(3)	C(1)-C(11)-C(16) 131(3)
C(11)-C(12)-C(13)	123(3)	C(12)-C(13)-C(14) 120(3)
C(13)-C(14)-C(15)	118(3)	C(14)-C(15)-C(16) 120(3)
C(15)-C(16)-C(11)	123(3)	C(16)-C(11)-C(12) 115(3)
Pt(1)-P(1)-C(3)	113(1)	Pt(2)-P(2)-C(6) 112(1)
Pt(1)-P(1)-C(4)	111(1)	Pt(2)-P(2)-C(7) 111(1)
Pt(1)-P(1)-C(5)	111(1)	Pt(2)-P(2)-C(8) 118(1)
C(3)-P(1)-C(4)	103(2)	C(6)-P(2)-C(7) 107(1)
C(3)-P(1)-C(5)	102(1)	C(6)-P(2)-C(8) 99(1)
C(4)-P(1)-C(5)	117(1)	C(7)-P(2)-C(8) 109(1)
P(1)-C(4)-C(41)	113(3)	P(2)-C(7)-C(71) 104(2)
P(1)-C(4)-C(42)	112(2)	P(2)-C(7)-C(72) 112(2)
P(1)-C(4)-C(43)	107(3)	P(2)-C(7)-C(73) 118(3)
C(41)-C(4)-C(42)	110(3)	C(71)-C(7)-C(72) 107(3)
C(41)-C(4)-C(43)	109(3)	C(71)-C(7)-C(73) 101(3)
C(42)-C(4)-C(43)	104(3)	C(72)-C(7)-C(73) 113(3)
P(1)-C(5)-C(51)	110(3)	P(2)-C(8)-C(81) 113(3)
P(1)-C(5)-C(52)	109(3)	P(2)-C(8)-C(82) 106(2)
P(1)-C(5)-C(53)	109(3)	P(2)-C(8)-C(83) 111(2)
C(51)-C(5)-C(52)	107(3)	C(81)-C(8)-C(82) 106(3)
C(51)-C(5)-C(53)	112(4)	C(81)-C(8)-C(83) 114(3)
C(52)-C(5)-C(53)	110(3)	C(82)-C(8)-C(83) 106(3)

Pt-C(1) separation is the same as that found<sup>2</sup> for the bridging C atom in  $[(\text{OC})_5\text{W}\{\mu\text{-C}(\text{OMe})\text{Ph}\}\text{Pt}(\text{PMe}_3)_2]$ , and within the range generally observed for carbon-platinum  $\sigma$  bonds.<sup>10</sup> The Pt-W bonds [mean  $2.830(2) \text{ \AA}$ ] are close

to the sum of the covalent radii, and to the metal-metal bond distance in  $[(OC)_5W\{\mu-C(OMe)Ph\}Pt(PMe_3)_2]$  [2.861(1) Å].<sup>2</sup>

In addition to being bonded to each other, to the tungsten atom, and the bridging C(OMe)Ph group, the platinum atoms each carry a CO and a PBu<sub>2</sub>Me ligand. The Pt-P separations [2.350(7) Å] are at the upper end of the range generally observed.<sup>10b,c</sup> There is an essentially *trans*-P-Pt-Pt arrangement [P-Pt-Pt

TABLE 5

Equations of least-squares planes for [Pt<sub>2</sub>W{C(OMe)Ph}(CO)<sub>6</sub>(PBu<sub>2</sub>Me)<sub>2</sub>] (1) in the form  $Ax + By + Cz = D$ , where  $x, y$ , and  $z$  are fractional co-ordinates. Distances, (Å) of relevant atoms from the planes are given in square brackets

Plane (i): Pt(1), Pt(2), W	$15.191x - 4.284y + 1.487z = 1.532$
Plane (ii): Pt(1), Pt(2), C(1)	$14.594x - 5.969y + 1.486z = 1.118$
Plane (iii): C(1), O(1), C(11)	$-2.567x + 0.393y + 15.181z = 3.519$
Plane (iv): C(1), O(1), C(01)	$-2.577x + 0.442y + 15.178z = 3.531$
Plane (v): P(1), C(03), Pt(1), Pt(2), P(2), C(02)	$11.570x - 10.626y + 1.406z = -0.247$
[P(1) 0.0, C(03) -0.02, Pt(1) 0.02, Pt(2) 0.02, P(2) -0.02, C(02) 0.01, W 1.11]	
Plane (vi): C(11), C(12), C(13), C(14), C(15), C(16)	$-2.434x + 0.005y + 15.198z = 3.404$
[C(11) -0.01, C(12) 0.02, C(13) -0.03, C(14) 0.02, C(15) -0.01, C(16) 0.0]	
Plane (vii): Pt(1), C(03), W	$10.781x - 7.064y + 8.294z = 2.711$
Plane (viii): Pt(2), C(02), W	$13.340x - 7.368y - 5.214z = 0.445$

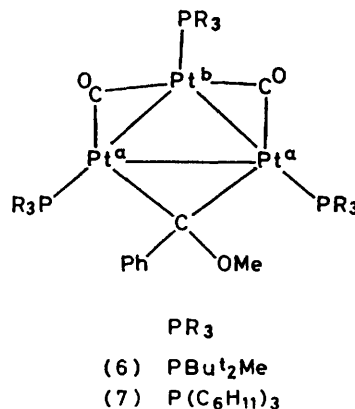
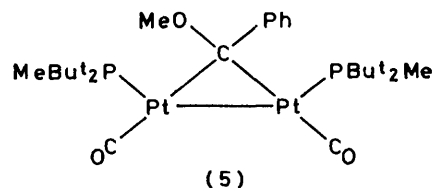
Angles (°) between planes:

	(ii)	(iii)	(iv)	(v)	(vii)	(viii)
(i)	6.5	90.3	90.4	26.8	31.4	29.1
(ii)		90.2	90.3	20.3	28.9	26.6

149.1(2)°], as predicted by the large  $^1J(\text{PtP})$  value observed in the <sup>31</sup>P n.m.r. spectrum, discussed earlier. The Pt-C(O) distances [1.87(4) Å] fall within the range (1.74–1.94 Å) found for terminal carbonyl ligands in a variety of mononuclear carbonyl platinum complexes.<sup>11–13</sup> However, in compound (1) the angles Pt(1)-C(03)-O(03) and Pt(2)-C(02)-O(02) are markedly bent [148(3)°] reflecting semi-bridging of these CO ligands to the tungsten. The latter, with only four terminal CO ligands has formally 16 valence electrons, and interaction with the carbonyls on the platinum atoms would reduce its electron deficiency. The distance between the tungsten atom and C(02) or C(03) averages 2.43(3) Å, which, although greater than the sum of the covalent radii (1.91 Å), can be compared with 2.14 Å found<sup>14</sup> for the W-CPh<sub>2</sub> distance in [W(CPh<sub>2</sub>)(CO)<sub>5</sub>]. The bond distances and angles within the W(CO)<sub>4</sub> group are normal (Table 4).

As mentioned earlier, the reactions which gave (3) and (4) led also to the formation of homonuclear di- and tri-

platinum species. Compounds (5) and (6) were isolated from the reaction of [Cr{C(OMe)Ph}(CO)<sub>5</sub>] with [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PBu<sub>2</sub>Me)]. The <sup>31</sup>P n.m.r. spectrum of (5) (Table 2) was as expected for a diplatinum molecule containing a R<sub>3</sub>P-Pt-Pt-PR<sub>3</sub> system.<sup>15</sup> Unfortunately it was isolated in insufficient quantity for <sup>13</sup>C n.m.r. studies, but the <sup>1</sup>H spectrum showed the expected signals for the μ-C(OMe)Ph ligand. The latter is probably *cis* to the PBu<sub>2</sub>Me groups as in compound (1). A complex probably analogous to (5), *viz.* [Pt<sub>2</sub>{μ-C(OMe)Ph}(CO)<sub>2</sub>{P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>}]<sub>2</sub>, was found in trace amounts in the reaction between [Cr{C(OMe)Ph}(CO)<sub>5</sub>] and [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>{P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>}]<sub>2</sub>. Evidence for this came from the <sup>31</sup>P n.m.r. spectrum of (4) which revealed a weak resonance at -28.0 p.p.m., due to an impurity having coupling constants [ $J(\text{PP})$  93;  $J(\text{PtP})$  3 405, 354; and  $J(\text{PtPt})$  2 264 Hz] very similar to those obtained from the spectrum of the analogue (5).

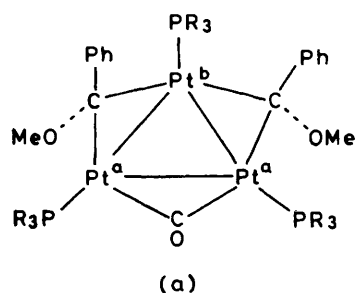


Microanalysis and <sup>31</sup>P n.m.r. studies established compounds (6) and (7) as triplatinum species. Two signals were observed corresponding to the expected A<sub>2</sub>B pattern together with satellite peaks, although the limited solubility of (7) prevent measurements of all the coupling constants. In their i.r. spectra, (6) and (7) showed ν<sub>max</sub>(CO) bands (Table 1) as expected for bridging carbonyl ligands. Indeed, we may compare the CO bands in (6) and (7) with those at 1 836 and 1 773 cm<sup>-1</sup> observed in the spectrum of [Pt<sub>3</sub>{μ-CO)<sub>3</sub>(PBu<sub>2</sub>Ph)<sub>3</sub>].<sup>16</sup>

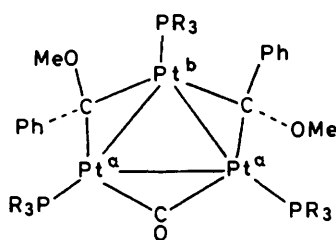
In view of the formation of compounds (1)–(4) from reactions between [M{C(OMe)Ph}(CO)<sub>5</sub>] (M = Cr or W) and [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PR<sub>3</sub>)], it was of interest to investigate reactions of the latter species with the mononuclear manganese carbene complex [Mn{C(OMe)Ph}(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)]. We have previously shown that the man-

ganese compound reacts with  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$  to give the dimetal complex  $[(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{Mn}\{\mu\text{-C}(\text{OMe})\text{Ph}\}\text{Pt}(\text{PMe}_3)_2]$ .<sup>17</sup> Formation of the latter is similar to the synthesis of the compounds  $[(\text{OC})_5\text{M}\{\mu\text{-C}(\text{OMe})\text{Ph}\}\text{Pt}(\text{PMe}_3)_2]$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{or W}$ ) from  $[\text{M}\{\text{C}(\text{OMe})\text{Ph}\}(\text{CO})_5]$  and  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$ .<sup>2</sup> If the reaction of  $[\text{Mn}\{\text{C}(\text{OMe})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  with  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{P}^t\text{Bu}_2\text{Me})]$  paralleled those with the chromium or tungsten compounds  $[\text{M}\{\text{C}(\text{OMe})\text{Ph}\}(\text{CO})_5]$  ( $\text{M} = \text{Cr or W}$ ), then a complex  $[\text{MnPt}_2\{\mu\text{-C}(\text{OMe})\text{Ph}\}(\text{CO})_3(\text{P}^t\text{Bu}_2\text{Me})_2(\eta\text{-C}_5\text{H}_5)]$  might be isolable. However, reaction occurred at room temperature to yield as the only isolable compound the non-manganese containing species (8). The reaction between  $[\text{Mn}\{\text{C}(\text{OMe})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  and  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)]$  was next investigated and found to give the triplatinum compounds (9) and (10).

Chromatography of the product mixture of (9) and (10) on alumina allowed the separation of (9) into two isomers [ $\nu_{\text{max.}}(\text{CO})$  1 793 and 1 785  $\text{cm}^{-1}$ ], the <sup>31</sup>P n.m.r. data for

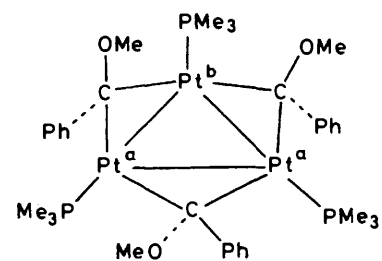


(a)



(b)

PR<sub>3</sub>  
(8) P<sup>t</sup>Bu<sub>2</sub>Me  
(9) PMe<sub>3</sub>



(10)

which are summarised in Table 2. Both spectra show a basic A<sub>2</sub>B pattern for molecules containing no <sup>195</sup>Pt nuclei, together with a large number of satellite peaks due to the molecules with one, two, or three <sup>195</sup>Pt nuclei. Analysis of these satellite spectra, which also yields values of  $J(\text{PtPt}')$ , and the results of <sup>1</sup>H{<sup>195</sup>Pt} INDOR spectroscopy, will be presented elsewhere.<sup>18</sup> The two isomers of (9) would arise according to whether the Ph or the OMe substituents on the bridging carbene ligands are on the same or opposite sides of the *triangulo*-triplatinum rings. The <sup>1</sup>H spectra of (9a) and (9b) showed different  $\tau$  values for the OMe groups. Without an X-ray crystallographic study on one or other isomer, it is not possible to establish which isomer A or B of Table 2 corresponds to (9a) or (9b). Interestingly, although isomers of the triplatinum compound (10) are possible, only one isomer was isolated in the reaction of  $[\text{Mn}\{\text{C}(\text{OMe})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  with  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)]$ , and its <sup>31</sup>P n.m.r. spectrum (Table 2) was of similar pattern to those of the other triplatinum compounds discussed.

Formation of the triplatinum complexes in the reactions of  $[\text{Cr}\{\text{C}(\text{OMe})\text{Ph}\}(\text{CO})_5]$  or  $[\text{Mn}\{\text{C}(\text{OMe})\text{Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  with the compounds  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$  [ $\text{PR}_3 =$

$\text{P}^t\text{Bu}_2\text{Me}$ ,  $\text{P}(\text{cyclo-C}_6\text{H}_{11})_3$ , or  $\text{PMe}_3$ ] is related to an earlier observation of Fischer and Beck<sup>19</sup> who have briefly reported that the carbene-molybdenum complex  $[\text{Mo}\{\text{C}(\text{OMe})\text{Ph}\}(\text{CO})(\text{NO})(\eta\text{-C}_5\text{H}_5)]$  reacts with  $[\text{Ni}(\text{CO})_4]$  to give  $[\text{Ni}_3\{\mu\text{-C}(\text{OMe})\text{Ph}\}_3(\text{CO})_3]$ .

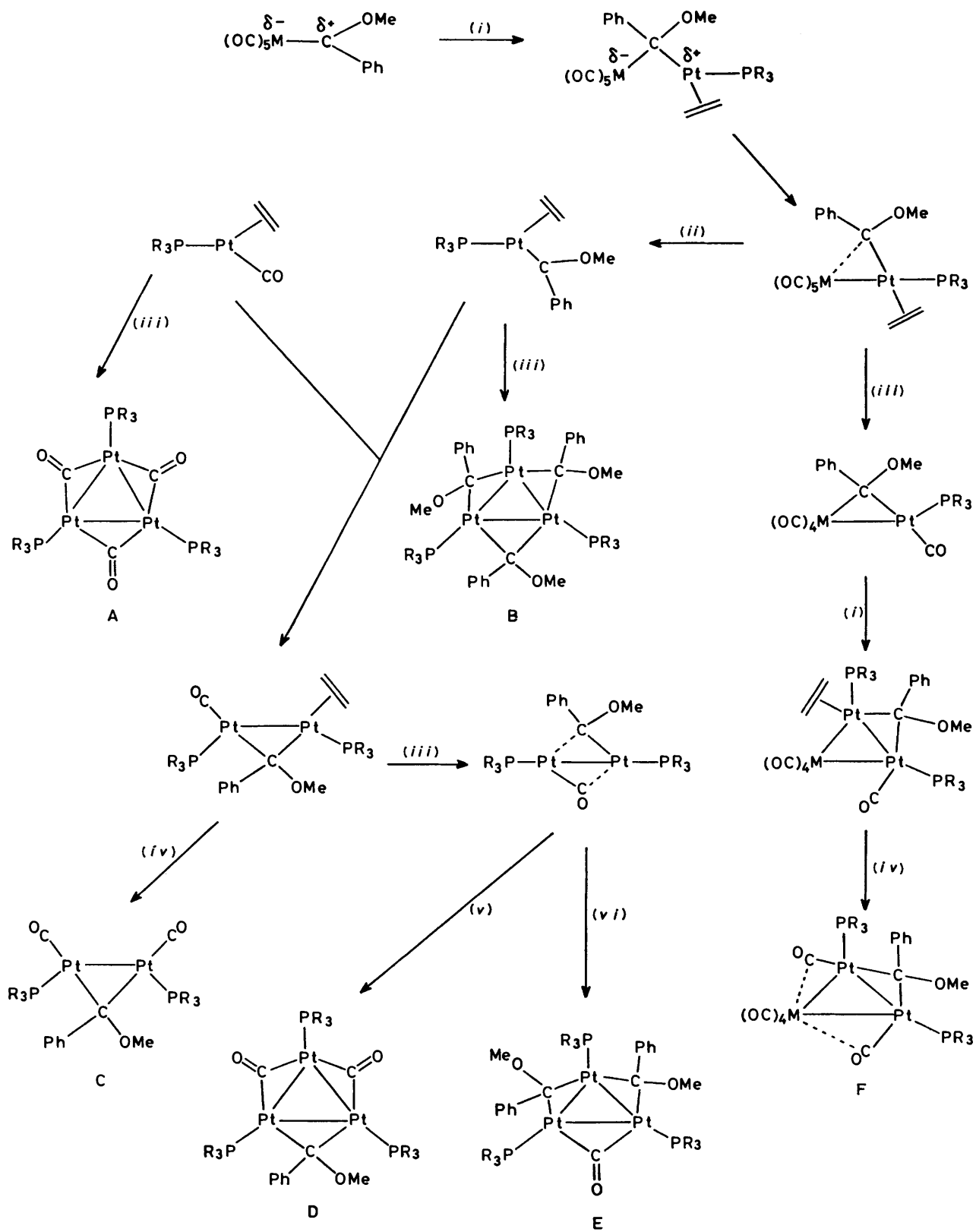
The Scheme illustrates possible pathways by which the various di- and tri-metal compounds of structural type A–F might form from  $[\text{M}\{\text{C}(\text{OMe})\text{Ph}\}(\text{CO})_5]$  ( $\text{M} = \text{Cr or W}$ ) via an initial adduct  $[(\text{OC})_5\text{M}\{\mu\text{-C}(\text{OMe})\text{Ph}\}\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)]$ . For manganese, the  $\text{M}(\text{CO})_5$  group would be replaced by  $\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ .<sup>17</sup> In the case of tungsten, the homonuclear di- or tri-platinum species were not isolated and reaction proceeds to give heteronuclear trimetal compounds (1) and (2) which are of structural type F. For chromium or manganese, the initially formed heteronuclear dimetal adducts

$[\text{L}_n\text{M}\{\mu\text{-C}(\text{OMe})\text{Ph}\}\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)]$  [ $\text{ML}_n = \text{Cr}(\text{CO})_5$  or  $\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ ] are evidently unstable, presumably releasing co-ordinatively unsaturated  $\text{Cr}(\text{CO})_5$  or  $\text{Mn}$

$(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$  species which could abstract  $\text{C}_2\text{H}_4$  or  $\text{CO}$ , both of which are likely to be freely available from the labile reactants involved. We have previously observed<sup>2</sup>

that in  $[(\text{OC})_5\text{W}\{\mu\text{-C}(\text{OMe})\text{Ph}\}\text{Pt}(\text{PMe}_3)_2]$  the  $\mu\text{-C}(\text{OMe})\text{Ph}$  group lies much closer to the platinum than to the tungsten atom, evidently reflecting a tendency for the carbene ligand to transfer from one metal atom to another. Elimination of  $\text{ML}_n$  from the initial dimetal adduct would release a species  $[\text{Pt}\{\text{C}(\text{OMe})\text{Ph}\}(\text{C}_2\text{H}_4)(\text{PR}_3)]$  (Scheme) which by loss of  $\text{C}_2\text{H}_4$  and trimerisation would give a compound of type B, viz. (10). The reactants  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ <sup>4</sup> are highly reactive towards  $\text{CO}$  giving the compounds of type A, presumably via an intermediate  $[\text{Pt}(\text{CO})(\text{C}_2\text{H}_4)(\text{PR}_3)]$ .<sup>6</sup> Although the tricarbonyltriplatinum compounds A were not detected in the present work, reaction of  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)]$  with  $[(\text{OC})_5\text{Mn-Mn}(\text{CCH}_2\text{CH}_2\text{CH}_2\text{O})(\text{CO})_4]$  affords, among other compounds,  $[\text{Pt}_3(\mu\text{-CO})_3(\text{PMe}_3)_3]$ .<sup>17</sup> Combination of  $[\text{Pt}(\text{CO})(\text{C}_2\text{H}_4)(\text{PR}_3)]$  with  $[\text{Pt}\{\text{C}(\text{OMe})\text{Ph}\}(\text{C}_2\text{H}_4)(\text{PR}_3)]$  could lead in stages to the other structural types C, D, and E isolated in this work.

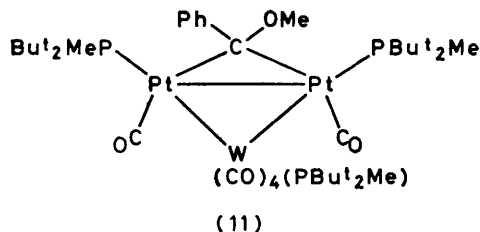
We have also found that the compound  $[(\text{OC})_5\text{-}$



SCHEME M = Cr or W,  $PR_3 = P Bu_2 Me$  or  $P(cyclo-C_6H_{11})_3$  (i)  $[Pt(C_2H_4)_2(PR_3)]$ ,  $-C_2H_4$ ; (ii)  $+C_2H_4$ ,  $-[M(CO)_5(C_2H_4)]$ ; (iii)  $-C_2H_4$ ; (iv)  $+CO$ ; (v)  $[Pt(C_2H_4)(CO)(PR_3)]$ ,  $-C_2H_4$ ; (vi)  $[Pt\{C(OMe)Ph\}(C_2H_4)(PR_3)]$ ,  $-C_2H_4$

$\text{Cr}\{\mu\text{-C(OMe)Ph}\}\text{Pt(PMe}_3)_2$ ] is unstable with respect to the formation of triplatinum compounds. In toluene at 80 °C, the dimetal compound affords complexes (9a), (9b), and (10). The isomer of (10) produced was identical to that formed in the reaction of  $[\text{Mn}\{\text{C(OMe)Ph}\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  with  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)]$ , mentioned above. The  $^1\text{H}$  n.m.r. spectrum revealed two singlet resonances for the OMe groups of relative intensity 1 : 2, as expected for a structure in which one of the OMe groups is below the  $\text{Pt}_3$  ring and the other two are above. Formation of (10) would arise *via* trimerisation of the 14-electron species  $[\text{Pt}\{\text{C(OMe)Ph}\}(\text{PMe}_3)]$  which might be produced by elimination of  $[\text{Cr}(\text{CO})_5(\text{PMe}_3)]$  from  $[(\text{OC})_5\text{Cr}\{\mu\text{-C(OMe)Ph}\}\text{Pt(PMe}_3)_2]$ . We have previously shown<sup>2</sup> that the  $\text{PMe}_3$  group *trans* to the carbene ligand in the latter compound is readily substituted, and is evidently labilised by the *trans* influence of the  $\mu\text{-C(OMe)Ph}$  group. The process would be analogous to the formation of  $[\text{Ni}_3\{\mu\text{-C(OMe)Ph}\}_3(\text{CO})_3]$ , referred to above, which is presumably accompanied by release of  $[\text{Mo}(\text{CO})_2(\text{NO})(\eta\text{-C}_5\text{H}_5)]$ . Formation of (9a) and (9b) in the decomposition of  $[(\text{OC})_5\text{Cr}\{\mu\text{-C(OMe)Ph}\}\text{Pt(PMe}_3)_2]$  is less readily accounted for, but presumably involves the intermediacy of  $[\text{Pt}(\text{CO})(\text{PMe}_3)]$ .

Finally, it should be mentioned that complexes having the *triangulo*- $\text{Pt}_2\text{W}$  structure (type F of Scheme) can be synthesized from 14-electron bis(trialkylphosphine)-platinum complexes provided bulky  $\text{PR}_3$  ligands are involved. Thus  $[\text{W}\{\text{C(OMe)Ph}\}(\text{CO})_5]$  and  $[\text{Pt}(\text{P}^t\text{Bu}_2\text{Me})_2]$ <sup>20</sup> react in 1 : 2 mol ratio in toluene at -60 °C to afford the compound  $[\text{Pt}_2\text{W}\{\mu\text{-C(OMe)Ph}\}(\text{CO})_6(\text{P}^t\text{Bu}_2\text{Me})_3]$  (11). Examination of the  $^{31}\text{P}$  n.m.r. spectrum of



(11) (Table 2) confirmed the presence of the  $\text{Bu}^t_2\text{MePt-PtP}^t\text{Bu}_2\text{Me}$  group in the structure, and also established that the third  $\text{P}^t\text{Bu}_2\text{Me}$  ligand present was attached to the tungsten since its resonance at -32.3 p.p.m. showed strong  $^{183}\text{W}\text{-}^{31}\text{P}$  coupling (211 Hz). The  $^1\text{H}$  n.m.r. spectrum of (11) also showed the presence of three  $\text{P}^t\text{Bu}_2\text{Me}$  ligands, while a resonance at 251 p.p.m. in the  $^{13}\text{C}$  n.m.r. spectrum can be assigned to the contact carbon  $\text{Pt}(\mu\text{-C})\text{Pt}$ , but limited solubility prevented detection of  $^{195}\text{Pt}\text{-}^{13}\text{C}$  coupling.

The presence in the i.r. spectrum of (11) of CO bands as low as 1869 and 1800  $\text{cm}^{-1}$  suggests that the semi-bridging CO groups present in (1) may have become fully bridging in (11).

Evidently in the formation of (11), bulky  $\text{P}^t\text{Bu}_2\text{Me}$  groups are displaced from platinum and transferred to

the tungsten. Moreover, the interesting observation was made that recrystallization of (11) from chloroform-hexane mixtures resulted in partial conversion into complex (1). These results demonstrate both the lability of the peripheral ligands in these systems and the delicate

balance between the isolation of  $[\text{M}\{\mu\text{-C(OMe)Ph}\}\text{Pt}]$  or  $[\text{MPT}_2\{\mu\text{-C(OMe)Ph}\}]$  ( $\text{M} = \text{Cr}$  or  $\text{W}$ ) structures from the reactions of the  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$  or  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$  species with the carbene compounds  $[\text{M}\{\text{C(OMe)Ph}\}(\text{CO})_5]$ .

#### EXPERIMENTAL

Instrumentation used and experimental techniques employed were as described in Part 1.<sup>2</sup> Light petroleum refers to that fraction with b.p. 40–60 °C. Hydrogen-1 and  $^{31}\text{P}$  and  $^{13}\text{C}$  ( $^1\text{H}$ -decoupled) n.m.r. spectra were measured at 100, 40.48, and 25.15 MHz respectively. The solvent was  $[\text{^2H}]$ -chloroform unless otherwise specified. For  $^{31}\text{P}$ , chemical shifts are in p.p.m. relative to 85%  $\text{H}_3\text{PO}_4$  (external) with shifts to low frequency taken as positive. For  $^{13}\text{C}$ , chemical shifts have positive values to high frequency relative to  $\text{SiMe}_4$ . The complexes  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ <sup>4</sup> and  $[\text{M}\{\text{C(OMe)Ph}\}(\text{CO})_5]$  ( $\text{M} = \text{Cr}$  or  $\text{W}$ )<sup>21</sup> were prepared as described previously. Infrared spectra were measured in Nujol, unless otherwise stated. Analytical data for the new compounds are given in Table 1.

*Reactions of the Complexes*  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$  [ $\text{PR}_3 = \text{PMe}_3$ ,  $\text{P}^t\text{Bu}_2\text{Me}$  or  $\text{P}(\text{cyclo-C}_6\text{H}_{11})_3$ ].—(a) *With*  $[\text{W}\{\text{C(OMe)Ph}\}(\text{CO})_5]$ . (i) The compound  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{P}^t\text{Bu}_2\text{Me})]$  {1 mmol, prepared from  $[\text{Pt}(\text{cod})_2]$  (cod = cyclo-octa-1,5-diene) (0.41 g, 1 mmol) in light petroleum saturated with ethylene and treated with  $\text{P}^t\text{Bu}_2\text{Me}$  (1 mmol) in toluene (5  $\text{cm}^3$ ) cooled to -20 °C was treated dropwise with a toluene (5  $\text{cm}^3$ ) solution of  $[\text{W}\{\text{C(OMe)Ph}\}(\text{CO})_5]$  (0.22 g, 0.5 mmol) over a 1 h period. The mixture was warmed to room temperature, stirred (0.5 h), and solvent removed *in vacuo*. The residue was extracted with hexane (15  $\text{cm}^3$ ) and recrystallised from tetrahydrofuran-hexane to give red prisms of  $[\text{Pt}_2\text{W}\{\mu\text{-C(OMe)Ph}\}(\text{CO})_6(\text{P}^t\text{Bu}_2\text{Me})_2]$  (1) (0.30 g, 50%);  $\nu_{\text{max}}$  at 2 020s, 1 952s, 1 890s, 1 880s, 1 850(sh), 1 830(sh), 1 580vw, 1 292vw, 1 282w, 1 170m, 1 160m, 1 100(sh), 1 090m, 1 065w, 1 010w, 972m, 880m, 870m, 800w, 750w, 720m, 685m, 632w, 590m, and 565  $\text{cm}^{-1}$ . N.m.r.:  $^1\text{H}$ ,  $\tau$  2.2–3.3 (m, 5 H, Ph), 6.36 (s, 3 H, OMe), 8.52 [d, 6 H, MeP,  $J(\text{PH})$  8,  $J(\text{PtH})$  38], 8.67 [d, 18 H,  $\text{Bu}^t$ ,  $J(\text{PH})$  14], and 9.13 [d, 18 H,  $\text{Bu}^t$ ,  $J(\text{PH})$  14 Hz];  $^{13}\text{C}$ ,  $\delta$ , 237 [ $\text{Pt}(\mu\text{-C})\text{Pt}$ ,  $J(\text{PtC})$  771], 209 [CO,  $J(\text{PtC})$  161], 150 [ $\text{C}^{(1)}(\text{Ph})$ ], 131, 127, 126, 118 (aromatic), 61 [OMe,  $J(\text{PtC})$  38 Hz], 36, 35, 29 ( $\text{Bu}^t$ ), and 3 p.p.m. (PMe).

(ii) A solution of  $[\text{W}\{\text{C(OMe)Ph}\}(\text{CO})_5]$  (0.11 g, 0.25 mmol) in toluene (10  $\text{cm}^3$ ) was added dropwise (1 h) to a solution of  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{P}(\text{C}_6\text{H}_{11})_3)_2]$  (0.26 g, 0.5 mmol) in toluene (5  $\text{cm}^3$ ) at 20 °C. The dark red solution was stirred (1 h), solvent was removed *in vacuo*, and the residue treated with light petroleum (15  $\text{cm}^3$ ). The solvent was then decanted and the red-brown residue washed with light petroleum (3  $\times$  2  $\text{cm}^3$ ), and recrystallized from tetrahydrofuran-hexane to give bright red prisms of  $[\text{Pt}_2\text{W}\{\mu\text{-C(OMe)Ph}\}(\text{CO})_6\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$  (2) (0.15 g, 40%);  $\nu_{\text{max}}$  at 2 040s, 1 945m, 1 935m, 1 905s, 1 838m, 1 825(sh), 1 300w, 1 260m, 1 225w, 1 190w, 1 180w, 1 105m, 1 077w, 977m, 918w, 895w, 770w, 735w, 725w, 705w, 600m, 565w, 515w, and 490  $\text{cm}^{-1}$ . Hydrogen-1 n.m.r.:  $\tau$  2.4–3.2 (m, 5 H, Ph), 6.20 (s, 3 H, OMe), and 7.4–9.3 (m, 66 H,  $\text{C}_6\text{H}_{11}$ ).

(b) *With*  $[\text{Cr}\{\text{C(OMe)Ph}\}(\text{CO})_5]$ . (i) To a toluene solution

(10 cm<sup>3</sup>) of [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PBU<sub>2</sub>Me)] (1 mmol) was added slowly (10 min) the compound [Cr{C(OMe)Ph}(CO)<sub>5</sub>] (0.16 g, 0.5 mmol) in toluene (5 cm<sup>3</sup>). After 1 h solvent was reduced in volume to ca. 2 cm<sup>3</sup>, light petroleum added (5 cm<sup>3</sup>), and the mixture chromatographed on an alumina column (5 cm). Elution with hexane followed by evaporation of solvent afforded pale yellow *crystals* of [Pt<sub>2</sub>{μ-C(OMe)Ph}(CO)<sub>2</sub>-(PBU<sub>2</sub>Me)<sub>2</sub>] (5) (29 mg, 6%);  $\nu_{\max}$  at 1 990vs br, 1 952s, 1 589w, 1 509m, 1 470m, 1 362m, 1 289m, 1 260w, 1 178m br, 1 102s, 1 027w, 1 018m, 970m, 932w, 909w, 895m, 885s, 879s, 812m, 762w, 728m, 702s, 648m, 638s, 599w, 570w, 512w, and 470s cm<sup>-1</sup>. Hydrogen-1 n.m.r.:  $\tau$  2.6—3.4 (m, 5 H, Ph), 6.45 (s, 3 H, OMe), 8.73 [d, 24 H, MeP, Bu<sup>t</sup>, J(PH) 13], and 9.08 [d, 18 H, Bu<sup>t</sup>, J(PH) 13 Hz]. Further elution with hexane and evaporation of solvent gave bright yellow *crystals* of [Pt<sub>3</sub>{μ-C(OMe)Ph}(μ-CO)<sub>2</sub>(PBU<sub>2</sub>Me)<sub>3</sub>] (6) (31 mg, 5%);  $\nu_{\max}$  at 1 798vs, 1 752vs br, 1 594w, 1 362s, 1 288m, 1 177m br, 1 095s, 1 070s, 1 025m, 1 015m, 994w, 970m, 930w, 880m br, 810m, 760m, 716m, 692m, 639w, 585w, 568w, 528w, 468m, 455w, and 420w cm<sup>-1</sup>. Hydrogen-1 n.m.r.:  $\tau$  2.4—3.2 (m, 5 H, Ph), 6.46 (s, 3 H, OMe), 8.67 [d, 27 H, Bu<sup>t</sup>, J(PH) 14], 8.74 [d, 27 H, Bu<sup>t</sup>, J(PH) 14], and 9.10 [d, 9 H, MeP, J(PH) 14 Hz].

Elution of the chromatography column with 1 : 9 diethyl ether–light petroleum and evaporation of solvent gave red *crystals* of [CrPt<sub>2</sub>{μ-C(OMe)Ph}(CO)<sub>6</sub>(PBU<sub>2</sub>Me)<sub>2</sub>] (3) (21 mg, 4%);  $\nu_{\max}$  at 2 007vs, 1 916vs br, 1 878vs br, 1 591vw, 1 295w, 1 210w, 1 185m, 1 173(sh), 1 116(sh), 1 108m, 1 076w, 1 031w, 1 018w, 1 000w, 988m, 929w, 888m, 881(sh), 876m, 809w, 766w, 725w, 698m, 676m, 641m, 610m, 566w br, 518w, 456(sh), and 450 cm<sup>-1</sup>. Hydrogen-1 n.m.r.:  $\tau$  2.4—3.2 (m, 5 H, Ph), 6.30 (s, 3 H, OMe), 8.56 [d, 6 H, MeP, J(PH) 9, J(PtH) 42], 8.61 [d, 18 H, Bu<sup>t</sup>, J(PH) 15], and 9.20 [d, 18 H, Bu<sup>t</sup>, J(PH) 15 Hz].

(ii) To a solution of [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>{P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>}] (1 mmol) in toluene (10 cm<sup>3</sup>) at room temperature was added [Cr{C(OMe)Ph}(CO)<sub>5</sub>] (0.156 g, 1 mmol) in toluene (5 cm<sup>3</sup>). After 1 h, the volume was reduced to ca. 2 cm<sup>3</sup> and light petroleum (5 cm<sup>3</sup>) added. The mixture was chromatographed on an alumina column (30 cm). Elution with hexane and evaporation of solvent gave yellow *crystals* of [Pt<sub>3</sub>{μ-C(OMe)Ph}(μ-CO)<sub>2</sub>{P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>}<sub>3</sub>] (7) (80 mg, 10%);  $\nu_{\max}$  at 1 808vs, 1 757vs br, 1 342w, 1 330w, 1 306(sh), 1 300w, 1 292w, 1 259m, 1 229w, 1 218w, 1 200w, 1 194w, 1 180m, 1 132m, 1 115(sh), 1 101s, 1 078m, 1 032w, 1 008m, 978s, 920m, 892m br, 855m, 821m, 810w br, 765w, 742m, 700m, 641w, 593m, 532w, 521w, 517w, 482m, 455w, 432w, 421w, and 385w cm<sup>-1</sup>. Hydrogen-1 n.m.r. ([<sup>2</sup>H<sub>6</sub>]benzene):  $\tau$  2.0—3.0 (m, 5 H, Ph), 5.99 (s, 3 H, OMe), and 7.9—8.8 (m, 99 H, C<sub>6</sub>H<sub>11</sub>).

Elution of the column with diethyl ether–light petroleum and evaporation of solvent gave red *crystals* of [CrPt<sub>2</sub>{μ-C(OMe)Ph}(CO)<sub>6</sub>{P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>}<sub>2</sub>] (4) (175 mg, 25%);  $\nu_{\max}$  at 2 006vs, 1 938vs, 1 895vs br, 1 591vw, 1 326vw, 1 300w, 1 268w, 1 237w, 1 200w, 1 183m, 1 127w, 1 108m, 1 082m, 1 050m br, 1 006m, 968m, 918w, 899w br, 851w br, 817w, 772w, 747w, 705m, 665m, 628w, 598m, 566w, 516w, 490w, 477w, 449w, and 440w cm<sup>-1</sup>. Hydrogen-1 n.m.r. ([<sup>2</sup>H<sub>6</sub>]benzene):  $\tau$  2.3—3.2 (m, 5 H, Ph), 6.15 (s, 3 H, OMe), and 8.2—9.0 (m, 66 H, C<sub>6</sub>H<sub>11</sub>).

(c) With [Mn{C(OMe)Ph}(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)]. (i) The complex [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] {1 mmol, prepared from [Pt(cod)<sub>2</sub>] (0.41 g, 1 mmol) saturated with ethylene in light petroleum at 0 °C and treated with PMe<sub>3</sub> (1 mmol)} was treated with [Mn{C(OMe)Ph}(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)] (0.30 g, 1 mmol) in toluene

(4 cm<sup>3</sup>). After stirring at room temperature (24 h), solvent was removed *in vacuo* and the red residue dissolved in toluene and chromatographed on alumina. Elution with 10 : 1 light petroleum–toluene gave unreacted [Mn{C(OMe)Ph}(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)] (40 mg). Elution with 5 : 1 light petroleum–toluene gave, after evaporation of solvent and recrystallisation from light petroleum, red-violet *crystals* of [Pt<sub>3</sub>{μ-C(OMe)Ph}<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>] (10) (10 mg, 3%). Elution of the column with 5 : 1 light petroleum–diethyl ether caused an orange band to move down the column and partially separate. The two fractions were evaporated and the residues recrystallised by adding light petroleum to toluene saturated solutions and cooling (−78 °C). The less soluble fraction gave orange red *crystals* of one isomer (A, Table 2) of [Pt<sub>3</sub>{μ-C(OMe)Ph}<sub>2</sub>(μ-CO)(PMe<sub>3</sub>)<sub>3</sub>] (9) (80 mg, 22%);  $\nu_{\max}$  at 3 072vw br, 3 042vw br, 1 783s br, 1 585w, 1 479m, 1 426m, 1 418m, 1 300m, 1 282m, 1 258w, 1 219m, 1 179m, 1 164w, 1 150w, 1 098(sh), 1 090s, 1 071m, 1 025w, 996w, 984m, 964s, 952s, 885m, 848(sh), 843w, 815(sh), 798w br, 771(sh), 766m, 732m, 726(sh), 702m, 695m, 675m, 641m, 583s, and 475w br cm<sup>-1</sup>. Hydrogen-1 n.m.r.:  $\tau$  2.10—3.02 (m, 10 H, Ph), 6.07 (s, 6 H, OMe), and 8.44—9.22 (m, 27 H, MeP).

The other fraction from the column gave orange *crystals* of the more soluble second isomer (B, Table 2) of [Pt<sub>3</sub>{μ-C(OMe)Ph}<sub>2</sub>(μ-CO)(PMe<sub>3</sub>)<sub>3</sub>] (9) (90 mg, 25%);  $\nu_{\max}$  at 3 075vw br, 3 054vw br, 1 786s, 1 585w br, 1 480m, 1 441m, 1 422m br, 1 302w, 1 284m, 1 261w br, 1 223w, 1 216(sh), 1 181m, 1 169m, 1 154vw, 1 108s br, 1 082m br, 1 075m, 1 028w, 1 000w, 977m, 970s br, 955s br, 880m, 802w br, 767(sh), 763m, 741m br, 700(sh), 695m br, 676m, 672(sh), 648vw, 640w, 588s, and 472w br cm<sup>-1</sup>. Hydrogen-1 n.m.r. ([<sup>2</sup>H<sub>6</sub>]acetone):  $\tau$  2.15—3.00 (m, 10 H, Ph), 6.24 (s, 6 H, OMe), and 8.25—9.25 (m, 27 H, MeP).

(ii) The compound [Mn{C(OMe)Ph}(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)] (0.148g, 0.5 mmol) in toluene (2 cm<sup>3</sup>) was added to [Pt(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(PBU<sub>2</sub>Me)] (1 mmol) in light petroleum (40 cm<sup>3</sup>) at 0 °C. The solution was stirred for 24 h, solvent was removed *in vacuo*, and the residue was dissolved in toluene and chromatographed on alumina. Elution with 20 : 1 light petroleum–toluene, followed by evaporation and recrystallisation from light petroleum, gave red *crystals* of [Pt<sub>3</sub>{μ-C(OMe)Ph}<sub>2</sub>(μ-CO)(PBU<sub>2</sub>Me)<sub>3</sub>] (8) (20 mg);  $\nu_{\max}$  at 3 077vw br, 3 052vw br, 1 793s, 1 586w, 1 364m, 1 298w br, 1 287w, 1 258w, 1 177m br, 1 167m, 1 091m, 1 073m, 1 026(sh), 1 018w, 974w, 957m, 888m, 877(sh), 874m, 865(sh), 812m, 804(sh), 766m, 762(sh), 715(sh), 711w, 699m, 635w, 593w, 568w, 470w, and 459w cm<sup>-1</sup>. Hydrogen-1 n.m.r.: ([<sup>2</sup>H<sub>6</sub>]benzene):  $\tau$  1.43—2.99 (m, 10 H, Ph), 6.10 (s, 6 H, OMe), and 8.30—9.08 (m, 63 H, PBU<sub>2</sub>Me).

*Decomposition of the Complex* [CrPt{μ-C(OMe)Ph}(CO)<sub>5</sub>(PMe<sub>3</sub>)<sub>2</sub>].—A 1 mmol sample of [CrPt{μ-C(OMe)Ph}(CO)<sub>5</sub>(PMe<sub>3</sub>)<sub>2</sub>] was heated at 80 °C (1 h) in toluene (20 cm<sup>3</sup>). Chromatography, followed by elution with toluene–light petroleum and evaporation of solvent gave compound (10) (16%); <sup>1</sup>H n.m.r. ([<sup>2</sup>H<sub>6</sub>]benzene):  $\tau$  1.5—2.8 (m, 15 H, Ph), 5.84 (s, 3 H, OMe), 5.90 (s, 6 H, OMe), and 8.96 (m, 27 H, MeP). Further elution with toluene–light petroleum allowed separation of the two isomers of complex (9) in 11 and 13% yields, after recrystallisation.

*Reaction of* [W{C(OMe)Ph}(CO)<sub>5</sub>] *with* [Pt(PBU<sub>2</sub>Me)<sub>2</sub>].—A solution of [Pt(PBU<sub>2</sub>Me)<sub>2</sub>] (1 mmol) in toluene (8 cm<sup>3</sup>) was added to a solution of [W{C(OMe)Ph}(CO)<sub>5</sub>] (0.26 g, 0.6 mmol) in toluene (6 cm<sup>3</sup>) at −60 °C. The mixture was stirred as it warmed to room temperature (2 h). Solvent was removed *in vacuo* and the red residue was washed with



light petroleum ( $7 \times 3 \text{ cm}^3$ ). Recrystallisation from toluene–light petroleum gave red *microcrystals* of  $[\text{Pt}_2\text{W}\{\mu\text{-C}(\text{OMe})\text{Ph}\}(\text{CO})_6(\text{PBU}^t_2\text{Me})_2]$  (11) (0.38 g, 58%). Hydrogen-1 n.m.r.:  $\tau$  2.2–3.4 (m, 5 H, Ph) 6.29 (s, 3 H, OMe), 8.30 (m, 27 H,  $\text{Bu}^t$ , MeP), 8.66 [d, 9 H,  $\text{Bu}^t$ ,  $J(\text{PH})$  14], 8.70 [d, 18 H,  $\text{Bu}^t$ ,  $J(\text{PH})$  12], and 9.10 [d, 9 H,  $\text{Bu}^t$ ,  $J(\text{PH})$  14 Hz]. Carbon-13 ( $^{13}\text{H}_2$ ) dichloromethane– $\text{CH}_2\text{Cl}_2$ ,  $\delta$  251 [Pt( $\mu\text{-C}$ )Pt], 231, 219 (CO), 132–118 (aromatic C), 62 (OMe), 36 ( $\text{CMe}_3$ ), 30, 29 (C– $\text{CH}_3$ ), 8 [d, MeP,  $J(\text{PC})$  18 Hz], and 4 p.p.m. (m, MeP).

*Crystal-structure Determination of  $[\text{Pt}_2\text{W}\{\mu\text{-C}(\text{OMe})\text{Ph}\}(\text{CO})_6(\text{PBU}^t_2\text{Me})_2]$ .*—The complex (1) crystallises as ruby red prisms and that used for data collection was of dimensions *ca.*  $0.20 \times 0.28 \times 0.014 \text{ mm}$ . Diffracted intensities were recorded on a Syntex  $P2_1$  four-circle diffractometer for

all the remaining non-hydrogen atoms by successive electron-density difference syntheses. The structure was refined by blocked-matrix least squares with anisotropic thermal parameters for metal and phosphorus atoms only. The refinement is not stable if anisotropic thermal parameters are introduced for the tertiary-butyl groups and for carbonyls. The hydrogen atoms were not located. Refinement converged at  $R$  0.075 ( $R'$  0.082) with a mean shift-to-error ratio in the final cycle of 0.01 : 1 with a maximum of 0.2 : 1. A weighting scheme of the form  $w^{-1} = \sigma^2(F) + \alpha|F|^2$  where  $\alpha = 0.004$  gave a reasonable weight analysis. The final electron-density difference synthesis showed no peaks  $> 0.9$  or  $< -0.9 \text{ e } \text{\AA}^{-3}$  except in the vicinity of the metal atoms. Scattering factors were from ref. 24 for C, O, and P, and ref. 25 for Pt and W, including corrections for the

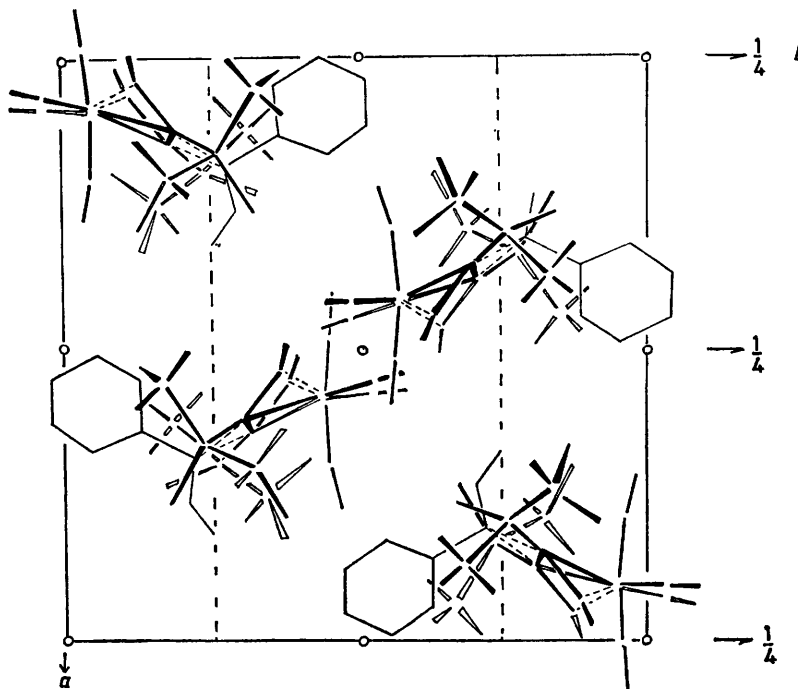


FIGURE 2 Contents of the monoclinic unit cell of (1) viewed down  $c^*$  towards the origin

$2.9 \leq 2\theta \leq 50^\circ$ , according to methods described earlier.<sup>22</sup> Of the total of 6 323 reflections, 3 991 were 'observable' according to the criterion  $I \geq 2\sigma(I)$  where  $\sigma(I)$  is the estimated standard deviation of the measured intensity based on counting statistics, and only these were used in the solution and refinement of the structure. Corrections were applied for Lorentz and polarisation effects and for the effects of X-ray absorption. All the computations were carried out with the 'X-Ray' system of programs<sup>23</sup> available for the CDC 7600 at the London Computing Centre.

*Crystal data.*  $\text{C}_{32}\text{H}_{56}\text{O}_7\text{P}_2\text{Pt}_2\text{W}$ ,  $M = 1182.7$ , Monoclinic,  $a = 16.003(5)$ ,  $b = 15.691(7)$ ,  $c = 15.261(9) \text{ \AA}$ ,  $\beta = 93.52(4)^\circ$ ,  $U = 3825.0 \text{ \AA}^3$ ,  $D_m = 2.00$  (floatation),  $Z = 4$ ,  $D_c = 2.01 \text{ g cm}^{-3}$ ,  $F(000) = 2176$ , Mo- $K_\alpha$  X-radiation (graphite monochromator),  $\lambda = 0.71069 \text{ \AA}$ ,  $\mu(\text{Mo-}K_\alpha) = 109.7 \text{ cm}^{-1}$ , space group  $P2_1/a$ .

*Structure solution and refinement.* The platinum and tungsten atoms were located from a Patterson synthesis, and

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 3, interatomic distances in Table 4, and some least-squares planes in Table 5. The contents of the unit cell are shown in Figure 2. Observed and calculated structure factors and the thermal parameters are listed in Supplementary Publication No. SUP 22783 (18 pp.).\*

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

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