Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 11.[1] Some Reactions of the Compound $[PtW\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}(CO)_5(\eta\text{-}C_8H_{12})]$ and the Crystal Structure of One Isomer of $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_3(CO)_3]$ †

By **John C. Jeffery, Iain Moore, Martin Murray, and F. Gordon A. Stone**, School of Chemistry, The University of Bristol, Bristol BS8 1TS

The compound $[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(cod)]$ (cod = cyclo-octa-1,5-diene) reacts with PMe_3, dppe ($Ph_2PCH_2CH_2PPh_2$), and pdma [$C_6H_4(AsMe_2)_2$-1,2] to give the bis-phosphine complexes $[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}PtL_2]$ [L_2 = $(PMe_3)_2$, dppe, or pdma] in which the dimetallacyclopropane rings are preserved. In contrast, reactions with CO or $CNBu^t$ afford triplatinum compounds $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_3L_3]$ (L = CO or $CNBu^t$) (two isomers). For L = CO the isomers were separated, and a single-crystal *X*-ray diffraction study was carried out on one species thereby establishing its configuration. The crystals are orthorhombic, space group $P2_12_12_1$, $Z = 4$, in a unit cell with lattice parameters a = 11.085(2), b = 15.554(3), and c = 18.733(5) Å. The structure has been refined to R 0.046 (R' 0.045) for 2 699 reflections to $2\theta \leqslant 50°$ [Mo-K_α *X*-radiation] collected at room temperature. The molecule consists of an essentially equilateral triangle of platinum atoms [mean Pt–Pt 2.624(1) Å], each metal atom carrying a terminally bonded CO ligand [mean Pt–CO 1.82(3) Å]. The three metal–metal vectors are bridged by $C(OMe)C_6H_4Me$ ligands [mean Pt–μ-C 2.15(3) Å], such that the plane defined by the metal atoms and the three ligated carbon atoms is perpendicular to the planes of these μ-C atoms and the O and C atoms to which they are bonded. Moreover, two of these groups have the same orientation with respect to the Pt_3 plane whilst the third is inverted. The ^{195}Pt n.m.r. spectrum of this ' asymmetric ' isomer has been measured and analysed. Spectroscopic data for all the new compounds are given.

SEVERAL bridged dimetal complexes of the type $[(OC)_5M\{\mu\text{-}C(OMe)R\}PtL_2]$ [M = Cr, Mo, or W; R = Ph, C_6H_4Me-4, or Me; L_2 = cod (cyclo-octa-1,5-diene) or $(PR_3)_2$] have been synthesised [2,3] by reacting zerovalent platinum compounds, which function as sources of PtL_2 groups, with mononuclear metal carbene species $[M\{C(OMe)R\}(CO)_5]$. The geometries of the dimetallacyclopropane rings in the compounds are of considerable interest. A single-crystal *X*-ray diffraction study [2] on $[(OC)_5W\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ revealed that in the W–C–Pt ring the carbon atom is markedly displaced towards platinum [C–Pt 2.04(1), C–W 2.48(1) Å]. The complex $[(Me_3P)(OC)_4W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$ also shows this asymmetry, but it is less marked [C–Pt 2.03(1), C–W 2.37(1) Å].[3] Moreover, in the latter compound the Pt–W distance [2.825(1) Å] is significantly shorter than in the former complex [2.861(1) Å]. Evidently replacement of one CO ligand of the $W(CO)_5$ group by PMe_3 results in an appreciable tightening of the W–C–Pt ring and enhanced stability.[3] The asymmetry of the bridging carbon atom in the pentacarbonyl species appears to be reflected in a tendency for complete transfer of the carbene group to platinum, a process accompanied by fragmentation of the heteronuclear metal–metal bond. Thus in toluene at 80 °C, $[(CO)_5Cr\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ affords a mixture of the triplatinum compounds $[Pt_3\{\mu\text{-}C(OMe)Ph\}_2(\mu\text{-}OC)(PMe_3)_3]$ and $[Pt_3\{\mu\text{-}C(OMe)Ph\}_3(PMe_3)_3]$.[4]

In order to obtain more information about the effect of the peripheral ligands in these compounds on the migratory tendency of the bridging carbene group, some ligand-substitution reactions of the title complex $[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(cod)]$ (1) have been investigated, and are described herein. Since the earlier studies [4] showed that replacement of CO (π acceptor) at chromium or tungsten by PMe_3 (σ donor) lowered the tendency of the carbene group to migrate across the metal–metal bond, it was of interest to determine how this property was influenced by changing the ligands on the platinum centre *via* displacement of the cod ligand.

RESULTS AND DISCUSSION

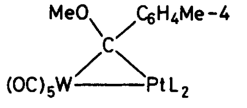
Compound (1) was readily obtained from the reaction between $[Pt(cod)_2]$ and $[W\{C(OMe)C_6H_4Me\text{-}4\}(CO)_5]$, and was characterised by analysis (Table 1) and n.m.r. spectroscopy (Table 2). Reaction of (1) with two equivalents of PMe_3 in light petroleum results in ready displacement of the cod group to give complex (2). The platinum–tungsten compounds (3) and (4) were similarly prepared in high yield by addition of one equivalent of dppe ($Ph_2PCH_2CH_2PPh_2$) or pdma [$C_6H_4(AsMe_2)_2$-1,2] to (1). Compound (2) has been previously prepared [3] from $[Pt(C_2H_4)(PMe_3)_2]$ and $[W\{C(OMe)C_6H_4Me\text{-}4\}(CO)_5]$ and its synthesis from (1) serves only to demonstrate the clean displacement of cod from the latter by a monodentate phosphine. Compounds (3) and (4) were characterised by microanalysis (Table 1) and by their ^1H and ^{13}C n.m.r. spectra (Table 2). These spectra were in accord with the structures proposed. Noteworthy from the ^{13}C data are the resonances at δ 218.3 p.p.m. [d of d,

---

† *cyclo*-Tris[carbonyl-μ-methoxy(4-tolyl)methylene-platinum](3 *Pt–Pt*).

J(PC) 90 and 18 Hz] for (3) and at δ 210.5 p.p.m. [J(PtC) 1 252 Hz] for (4), which are due to the μ-C groups in the dimetallacyclopropane rings.

The relatively large ^{195}Pt–^{13}C coupling observed for the



	L_2
(1)	cod
(2)	$(PMe_3)_2$
(3)	dppe
(4)	pdma

bridged carbon atom in the ^{13}C n.m.r. spectrum of (4) may reflect substantial asymmetry in the W–C–Pt ring, with the μ-C(OMe)C_6H_4Me-4 group displaced towards the platinum. If so, a similar argument applies to (1) for which J(PtC) = 1 390 Hz. Information on J(^{195}Pt–^{13}C) values from the spectra of compounds containing M(μ-CRR′)Pt ring systems is as yet limited. This is due in part to the difficulty of observing ^{195}Pt satellite peaks on carbon atoms not linked to protons, and with signals split by ^{31}P–^{13}C coupling if phosphine ligands are present. Indeed no satellite peaks were detectable in the spectrum of (3). However, in the platinum–tungsten compound [$(OC)_4$W{μ-CH(C_6H_4Me-4)}(μ-dppm)Pt(CO)] (dppm = $Ph_2PCH_2PPh_2$)[5] and the platinum–manganese complex [(η-C_5H_5)$(OC)_2$Mn{μ-C(OMe)C_6H_4Me-4}Pt(cod)][6] the ^{195}Pt–μ-^{13}C couplings are 973 and 975 Hz, respectively. These values may be compared with J(PtC) 1 704 Hz in the compound [$(OC)_4$Mn(μ-I)Pt($COCH_2CH_2CH_2$)-($PBu^t{}_2Me$)][7] in which the carbene ligand is known to be terminally bound to platinum. Hence the J(PtC) values for (1) (1 390 Hz) and (4) (1 252 Hz) are suggestive of the presence of semibridging carbene ligands. Further X-ray diffraction studies are in progress to place the correlation between ^{195}Pt–^{13}C couplings and asymmetric bonding of the carbene ligand on a firmer basis.

Treatment of a dichloromethane solution of (1) with CO results in the immediate formation of a brilliant cherry-red solution. Chromatography of this solution gave [$W(CO)_6$] and a triplatinum compound [Pt_3{μ-C(OMe)C_6H_4Me-4}$_3$$(CO)_3$] (5), produced as a mixture of isomers. Small amounts of other products were observed but not characterised. It was possible to separate the two isomers (5a) and (5b) of the triplatinum compound by thin-layer chromatography on alumina, and it was observed that they were formed in a *ca.* 4 : 1 ratio. Mass spectra showed molecular ions for both isomers at *m/e* 1 071, and the i.r. spectra revealed a single strong CO stretching band [at 2 029 cm^{-1} (5a), 2 031 cm^{-1} (5b)]. In order to establish the structure of these species a single-crystal X-ray diffraction study was carried out on (5a). The results are summarised in Tables 3—5, and a view of the molecule is shown in Figure 1, together with the atomic numbering scheme.

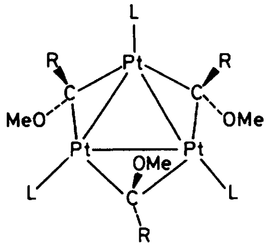
The *triangulo* arrangement of the three platinum atoms is confirmed, with each metal atom linked to a terminal CO group. The edges of the metal cluster are bridged by C(OMe)C_6H_4Me-4 groups. Two of these carbene groups have the same orientation with respect to the Pt_3 plane whilst the third is inverted, thereby distinguishing this isomer from the more symmetric structure proposed for (5b). In (5a) the metal-bridging carbon atoms and the carbon and oxygen atoms to which these three carbon atoms are bonded define planes which are perpendicular to the plane formed by the platinum

TABLE 1

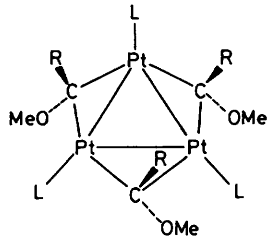
Analytical [a] and physical data for the di- and tri-metal complexes

Compound [b]	M.p. (θ_c/°C) (decomp.)	Colour	$\tilde{\nu}_{max.}$(CO) [c]/ cm^{-1}	Yield (%)	Analysis (%)	
					C	H
(1) [PtW{μ-C(OMe)(C_6H_4Me-4)}$(CO)_5$(cod)]	95—100	Orange	2 046s, 1 981s, 1 957s, 1 929s, 1 919 (sh)	70	34.5 (34.7)	3.0 (2.9)
(3) [PtW{μ-C(OMe)C_6H_4Me-4}$(CO)_5$(dppe)]	108—112	Yellow	2 043s, 1 966m, 1 923s, vbr	70	45.9 (45.7)	3.4 (3.2)
(4) [PtW{μ-C(OMe)C_6H_4Me-4}$(CO)_5$(pdma)]	138—141	Orange	2 043s, 1 967s, 1 939s, 1 919s, 1 903s	78	30.7 (30.7)	2.9 (2.8)
(5) [Pt_3{μ-C(OMe)C_6H_4Me-4}$_3$$(CO)_3$] [d]	—	Red	2 031s, 2 029m	45	34.0 (33.6)	3.1 (2.8)
(6) [Pt_3{μ-C(OMe)C_6H_4Me-4}$_3$($CNBu^t$)$_3$] [d]	—	Dark red	[e] 2 117s, br, 2 087(sh)	90	[f] 41.2 (40.8)	4.8 (4.6)

[a] Calculated values are given in parentheses. [b] Data for complex (2) in ref. 3. [c] In cyclohexane. [d] Mixture of isomers, see text. [e] $\nu_{max.}$(NC). [f] N 3.2 (3.4%).



(*a*)



(*b*)

	L	R
(5)	CO	C_6H_4Me-4
(6)	$CNBu^t$	C_6H_4Me-4

TABLE 2

Hydrogen-1 and ^{13}C n.m.r. data [a]

Complex	^1H (δ)	^{13}C (δ) [b]
(1) $[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(cod)]$	2.0—2.8 (m, 11 H, CH_2 and Me-4), 3.7 (s, 3 H, OMe), 4.2—5.8 [m, 4 H, CH (cod)], 7.0—7.3 (m, 4 H, C_6H_4)	206.0 (CO, 1 C), 200.9 [CO, 4 C, J(PtC) 71, J(WC) 122], 199.7 [μ-C, J(PtC) 1 390], 153.5 [C^1 (C_6H_4), J(PtC) 83], 135.7, 127.4, 125.5 (C_6H_4), 118.8, 107.9, 96.8, 94.3 [CH (cod), with J(PtC) 59, 45, 143, and 154], 61.3 [OMe, J(PtC) 50], 33.1, 32.7, 26.6, 26.1 [CH_2 (cod), with J(PtC) 10, 10, 11, and 11], 20.9 (Me-4)
(2) $[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$ [c]		207.2 [CO, 1 C, J(PtC) 49], 203.5 [CO, 4 C, J(WC) 123], 202.4 [d of d, μ-C, J(PC) 74 and 5], 157.1 [d, C^1 (C_6H_4), J(PC) 7, J(PtC) 89], 138.1, 128.4 (C_6H_4), 60.1 [OMe, J(PtC) 58], 21.9 (Me-4), 16.3 [d, PMe, J(PC) 25, J(PtC) 26], 16.0 [d, PMe, J(PC) 33, J(PtC) 62]
(3) $[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(dppe)]$	1.9—2.4 (m, 7 H, CH_2 and Me-4), 3.3 (s, 3 H, OMe), 6.4—8.0 (m, 24 H, C_6H_4 and Ph)	218.3 [d of d, μ-C, J(PC) 90 and 18], 206.4 [CO, 1 C, J(PtC) 17], 202.9 [CO, 4 C, J(PtC) 23, J(WC) 120], 153.7 [d, C^1 (C_6H_4), J(PtC) 100, J(PC) 4], 134—125 (C_6H_4, Ph), 60.3 [OMe, J(PtC) 52], 29.9 [d of d, CH_2, J(PC) 37 and 14], 20.8 (Me-4)
(4) $[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(pdma)]$	1.2 [s, 3 H, AsMe, J(PtH) 32], 1.6 [s, 3 H, AsMe, J(PtH) 30], 1.7 [s, 3 H, AsMe, J(PtH) 12], 1.75 [s, 3 H, AsMe, J(PtH) 12], 2.3 (s, 3 H, Me-4), 3.8 (s, 3 H, OMe), 6.8—8.0 (m, 8 H, C_6H_4)	210.5 [μ-C, J(PtC) 1 252], 208.2 [CO, 1 C, J(PtC) 24], 204.4 [CO, 4 C, J(PtC) 30, J(WC) 152], 155.1 [C^1 (C_6H_4), J(PtC) 107], 143.8—125.9 (C_6H_4), 61.2 [OMe, J(PtC) 62], 21.1 (Me-4), 11.9, 11.4, 11.3, 10.6 [AsMe, with J(PtC) 74, 84, 86, and 66]
(5a) $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_3(CO)_3]$ [d]	2.20 (s, 9 H, Me-4), 4.16 (s, 9 H, OMe), 7.0—7.8 (m, 12 H, C_6H_4)	255.5 (μ-C, 2 C), 254.3 (μ-C, 1 C), 198.3 [CO, 1 C, ^2J(PtC) 166], 197.9 [CO, 2 C, ^2J(PtC) 166], 154.1 [C^1 (C_6H_4), J(PtC) 26], 153.1 [C^1 (C_6H_4), 2 C, J(PtC) 26], 139.1, 129.0, 123.4, 123.2 (C_6H_4), 63.2 [OMe, 1 C, J(PtC) 47], 62.9 [OMe, 2 C, J(PtC) 45], 21.6 (Me-4)
(5b) $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_3(CO)_3]$ [d]	2.15 (s, 9 H, Me-4), 4.10 (s, 9 H, OMe), 7.0—7.8 (m, 12 H, C_6H_4)	254.8 (μ-C), 197.3 [CO, ^2J(PtC) 166], 152.0 [C^1 (C_6H_4), J(PtC) 26], 138.8, 128.6, 123.4 (C_6H_4), 64.0 [OMe, J(PtC) 41], 21.6 (Me-4)
(6) $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_3(CNBu^t)_3]$ [e]	1.12, 1.15, 1.19 (s, 27 H, $CNBu^t$), 2.10 (s, 9 H, Me-4), 4.08 (s, 9 H, OMe), 7.1—8.2 (m, 12 H, C_6H_4)	

[a] Measured in $CDCl_3$. Coupling constants in Hz. [b] Hydrogen-1 decoupled, chemical shifts in p.p.m., positive values representing shifts to high frequency of $SiMe_4$. [c] For ^1H and ^{31}P data see ref. 3. [d] ^1J(PtCO) *ca.* 2 000 Hz, accurate assignment precluded due to poor signal-to-noise ratio. [e] Isomeric mixture, see text.

atoms and the carbon atoms to which the metal atoms are linked (Table 5).

The molecule (5a) possesses a pseudo-mirror plane which is normal to the metal plane and is defined by Pt(3), the midpoint of the Pt(1)–Pt(2) vector, and the midpoints of all other related atom pairs. The unique Pt(1)–Pt(2) separation [2.621(1) Å] is little different from those of the pseudo-symmetry related pair, Pt(1)–Pt(3) [2.619(1) Å] and Pt(2)–Pt(3) [2.632(1) Å]. The average Pt–Pt separation [2.624(1) Å] is similar to those found in $[Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3]$ [2.632(2) Å] [8] and $[Pt_3(\mu\text{-}CO)_3\{P(cyclo\text{-}C_6H_{11})_3\}_3]$ [2.654(2) Å].[9] The mean Pt–μ-C distance [2.15(3) Å] in (5a) is within the range reported for Pt–C σ bonds [1.99(3)—2.15(2) Å] [10] but is somewhat longer than those observed in the bridged carbene complexes $[(OC)_5W\{\mu\text{-}C(OMe)Ph\}Pt(PMe_3)_2]$ and $[(Me_3P)(OC)_4W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}Pt(PMe_3)_2]$ [2.04(1) (ref. 2) and 2.031(1) Å (ref. 3), respectively]. The longer Pt–μ-C distance in (5a) may reflect a mutual *trans* destabilisation due to the transoid arrangement of the carbene ligands [mean μ-C–Pt–μ-C 165(1)°]. The Pt–CO distances (Table 4) are typical for terminal carbonyl ligands on platinum. The geometries of the OMe and C_6H_4Me-4 groups are unremarkable and require no comment.

The presence of non-equivalent μ-$C(OMe)C_6H_4Me$-4 groups in (5a) is not reflected in the ^1H n.m.r. spectrum (Table 2), the inequivalence being apparently insufficient to produce detectable chemical shift differences. Moreover, the ^1H n.m.r. spectrum of (5b) is almost indistinguishable from that of (5a), and thus does not afford any information about the structure of this isomer.

The ^{13}C n.m.r. spectra of (5a) and (5b) are informative. In agreement with the results of the *X*-ray diffraction study, the spectrum of (5a) shows a pair of resonances for the μ-C groups at δ 255.5 and 254.3 p.p.m. (relative intensity 2 : 1). The spectrum of (5b) shows one μ-C

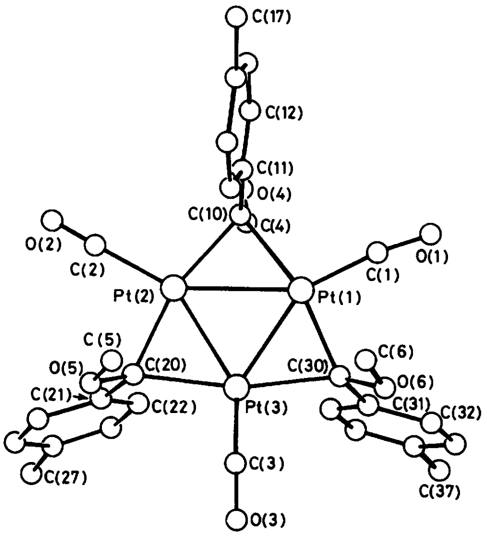


FIGURE 1 The molecular structure of $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_3(CO)_3]$ (5a) showing the atom numbering scheme

TABLE 3

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for the complex $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_3(CO)_3]$ (5a)

Atom	*x*	*y*	*z*
Pt(1)	0.648 47(8)	0.018 26(6)	0.107 11(5)
Pt(2)	0.651 92(9)	−0.010 31(5)	−0.030 76(5)
Pt(3)	0.584 74(9)	0.140 65(5)	0.018 78(5)
C(10)	0.714(3)	−0.094 8(14)	0.055(2)
C(20)	0.593(3)	0.102 3(13)	−0.090 4(12)
C(30)	0.587(3)	0.144 8(13)	0.131 6(12)
C(1)	0.678(3)	−0.017(3)	0.198(2)
C(2)	0.685(3)	−0.084(2)	−0.108(2)
C(3)	0.556(3)	0.249(2)	0.003 8(13)
C(4)	0.526(3)	−0.173(2)	0.072(2)
C(5)	0.792(3)	0.159 4(15)	−0.110(2)
C(6)	0.782(3)	0.202(2)	0.145(2)
O(1)	0.690(3)	−0.032(3)	0.259 8(15)
O(2)	0.708(3)	−0.126 0(13)	−0.152 6(13)
O(3)	0.525(3)	0.325 3(13)	−0.006 3(14)
O(4)	0.657 3(15)	−0.171 0(9)	0.067 8(11)
O(5)	0.671(2)	0.138 8(11)	−0.135 8(9)
O(6)	0.658 4(15)	0.199 3(11)	0.168 6(11)
C(11)	0.847 6(12)	−0.104 1(10)	0.057 9(10)
C(12)	0.899 5(12)	−0.182 5(10)	0.076 9(10)
C(13)	1.024 6(12)	−0.192 4(10)	0.075 1(10)
C(14)	1.097 7(12)	−0.123 8(10)	0.054 4(10)
C(15)	1.045 8(12)	−0.045 3(10)	0.035 4(10)
C(16)	0.920 7(12)	−0.035 5(10)	0.037 2(10)
C(17)	1.236(3)	−0.138(3)	0.057(2)
C(21)	0.473 1(13)	0.087 4(10)	−0.128 3(9)
C(22)	0.371 9(13)	0.063 3(10)	−0.088 8(9)
C(23)	0.260 1(13)	0.055 2(10)	−0.122 4(9)
C(24)	0.249 5(13)	0.071 2(10)	−0.195 4(9)
C(25)	0.350 7(13)	0.095 2(10)	−0.234 9(9)
C(26)	0.462 5(13)	0.103 3(10)	−0.201 3(9)
C(27)	0.128(4)	0.070(3)	−0.228(2)
C(31)	0.460 9(12)	0.148 3(10)	0.167 5(9)
C(32)	0.446 1(12)	0.186 0(10)	0.234 5(9)
C(33)	0.333 1(12)	0.185 8(10)	0.267 3(9)
C(34)	0.234 8(12)	0.147 9(10)	0.233 0(9)
C(35)	0.249 6(12)	0.110 3(10)	0.166 0(9)
C(36)	0.362 6(12)	0.110 5(10)	0.133 2(9)
C(37)	0.112(4)	0.151(3)	0.267(3)

TABLE 4

Internuclear distances (Å) and angles (°) for $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_3(CO)_3]$ (5a), with estimated standard deviations in parentheses

(*a*) Distances

Pt(1)–Pt(2)	2.621(1)	Pt(1)–Pt(3)	2.619(1)
Pt(1)–C(10)	2.14(3)	Pt(1)–C(30)	2.13(3)
Pt(1)–C(1)	1.82(4)	Pt(2)–Pt(3)	2.632(1)
Pt(2)–C(10)	2.18(3)	Pt(2)–C(20)	2.18(3)
Pt(2)–C(2)	1.89(3)	Pt(3)–C(20)	2.13(3)
Pt(3)–C(30)	2.11(3)	Pt(3)–C(3)	1.74(4)
C(10)–O(4)	1.35(3)	C(10)–C(11)	1.49(3)
C(20)–O(5)	1.34(3)	C(20)–C(21)	1.52(3)
C(30)–O(6)	1.35(3)	C(30)–C(31)	1.56(3)
C(1)–O(1)	1.18(5)	C(2)–O(2)	1.09(4)
C(3)–O(3)	1.25(4)	O(4)–C(4)	1.45(4)
O(5)–C(5)	1.47(3)	O(6)–C(6)	1.44(4)
C(11)–C(12)	1.395	C(11)–C(16)	1.395
C(12)–C(13)	1.395	C(13)–C(14)	1.395
C(14)–C(15)	1.395	C(14)–C(17)	1.55(4)
C(16)–C(15)	1.395	C(21)–C(22)	1.395
C(21)–C(26)	1.395	C(22)–C(23)	1.395
C(23)–C(24)	1.395	C(24)–C(25)	1.395
C(24)–C(27)	1.48(4)	C(26)–C(25)	1.395
C(31)–C(32)	1.395	C(31)–C(36)	1.395
C(32)–C(33)	1.395	C(33)–C(34)	1.395
C(34)–C(35)	1.395	C(34)–C(37)	1.50(4)
C(36)–C(35)	1.395		

(*b*) Angles

Pt(2)–Pt(1)–Pt(3)	60.3(0)	Pt(2)–Pt(1)–C(10)	53.4(7)
Pt(3)–Pt(1)–C(10)	113.5(7)	Pt(2)–Pt(1)–C(30)	111.9(6)
Pt(3)–Pt(1)–C(30)	51.6(6)	C(10)–Pt(1)–C(30)	164.8(9)
Pt(2)–Pt(1)–C(1)	150.3(10)	Pt(3)–Pt(1)–C(1)	149.2(10)
C(10)–Pt(1)–C(1)	96.9(12)	C(30)–Pt(1)–C(1)	97.7(11)
Pt(1)–Pt(2)–Pt(3)	59.8(0)	Pt(1)–Pt(2)–C(10)	51.9(7)
Pt(3)–Pt(2)–C(10)	111.5(7)	Pt(1)–Pt(2)–C(20)	111.4(5)
Pt(3)–Pt(2)–C(20)	51.6(5)	C(10)–Pt(2)–C(20)	162.8(8)
Pt(1)–Pt(2)–C(2)	149.9(8)	Pt(3)–Pt(2)–C(2)	150.3(8)
C(10)–Pt(2)–C(2)	98.0(11)	C(20)–Pt(2)–C(2)	98.8(10)
Pt(1)–Pt(3)–Pt(2)	59.9(0)	Pt(1)–Pt(3)–C(20)	113.1(5)
Pt(2)–Pt(3)–C(20)	53.2(5)	Pt(1)–Pt(3)–C(30)	52.2(6)
Pt(2)–Pt(3)–C(30)	112.1(6)	C(20)–Pt(3)–C(30)	165.2(8)
Pt(1)–Pt(3)–C(3)	148.9(8)	Pt(2)–Pt(3)–C(3)	149.4(8)
C(20)–Pt(3)–C(3)	97.1(9)	C(30)–Pt(3)–C(3)	97.7(10)
Pt(1)–C(10)–Pt(2)	74.7(7)	Pt(1)–C(10)–O(4)	119(2)
Pt(2)–C(10)–O(4)	121(2)	Pt(1)–C(10)–C(11)	113.4(15)
Pt(2)–C(10)–C(11)	113.4(15)	O(4)–C(10)–C(11)	111(2)
Pt(2)–C(20)–Pt(3)	75.3(7)	Pt(2)–C(20)–O(5)	118(2)
Pt(3)–C(20)–O(5)	121.1(15)	Pt(2)–C(20)–C(21)	112.3(12)
Pt(3)–C(20)–C(21)	117.1(15)	O(5)–C(20)–C(21)	109(2)
Pt(1)–C(30)–Pt(3)	76.2(7)	Pt(1)–C(30)–O(6)	120(2)
Pt(3)–C(30)–O(6)	123(2)	Pt(1)–C(30)–C(31)	114.3(13)
Pt(3)–C(30)–C(31)	114.9(14)	O(6)–C(30)–C(31)	106.(2)
Pt(1)–C(1)–O(1)	173(3)	Pt(2)–C(2)–O(2)	177(3)
Pt(3)–C(3)–O(3)	175(3)	C(10)–O(4)–C(4)	119(2)
C(20)–O(5)–C(5)	118(2)	C(30)–O(6)–C(6)	114(2)
C(10)–C(11)–C(12)	120.3(10)	C(10)–C(11)–C(16)	119.6(10)
C(12)–C(11)–C(16)	120.0(0)	C(11)–C(12)–C(13)	120.0(0)
C(12)–C(13)–C(14)	120.0(0)	C(13)–C(14)–C(15)	120.0(0)
C(13)–C(14)–C(17)	117.3(15)	C(15)–C(14)–C(17)	122.6(15)
C(14)–C(15)–C(16)	120.0(0)	C(11)–C(16)–C(15)	120.0(0)
C(20)–C(21)–C(22)	119.6(10)	C(20)–C(21)–C(26)	120.3(10)
C(22)–C(21)–C(26)	120.0(0)	C(21)–C(22)–C(23)	120.0(0)
C(22)–C(23)–C(24)	120.0(0)	C(23)–C(24)–C(25)	120.0(0)
C(23)–C(24)–C(27)	118.8(15)	C(25)–C(24)–C(27)	121.0(15)
C(24)–C(25)–C(26)	120.0(0)	C(21)–C(26)–C(25)	120.0(0)
C(30)–C(31)–C(32)	120.6(10)	C(30)–C(31)–C(36)	119.3(10)
C(32)–C(31)–C(36)	120.0(0)	C(31)–C(32)–C(33)	120.0(0)
C(32)–C(33)–C(34)	120.0(0)	C(33)–C(34)–C(35)	120.0(0)
C(33)–C(34)–C(37)	120(2)	C(35)–C(34)–C(37)	120(2)
C(34)–C(35)–C(36)	120.0(0)	C(31)–C(36)–C(35)	120.0(0)

signal (δ 254.8 p.p.m.) in accord with three equivalent bridging carbene groups. Moreoever, the spectrum of (5b) shows one signal for the OMe group, whereas that for (5a) has two peaks for this group.

TABLE 5

Some least-squares planes for the complex $[Pt_3\{\mu\text{-}C(OMe)\text{-}C_6H_4Me\text{-}4\}_3(CO)_3]$ (5a) 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), Pt(3), C(1), C(2), C(3), C(10), C(20), C(30)

$$10.518x + 4.369y - 0.786z = 6.876$$

[Pt(1) −0.05, Pt(2) −0.05, Pt(3) −0.06, C(1) 0.02, C(2) 0.004, C(3) 0.18, C(10) 0.12, C(20) −0.08, C(30) −0.10]

Plane (ii): C(10), C(11), O(4)

$$-0.200x + 3.280y + 18.309z = 0.550$$

Plane (iii): C(20), C(21), O(5)

$$-3.469x + 14.083y + 5.373z = 1.101$$

Plane (iv): C(30), C(31), O(6)

$$2.932x - 11.599y + 11.455z = 1.550$$

Angles (°) between least-squares planes:

	(ii)	(iii)	(iv)
(i)	89.6	9.15	90.5

The ^{195}Pt n.m.r. spectrum of (5a) is particularly interesting, and its analysis initially caused some difficulty. The spectrum is shown in Figure 2(*i*), the signal marked with an asterisk being due to the symmetrical isomer (5b), for which all the platinum atoms are equivalent. The remaining lines arise from the superimposition of the spectra of the various isotopomers of the asymmetric isomer, the spin systems being A, B, B_2 (singlets marked A and B), AB, and AB_2. The AB and AB_2 patterns are extremely second order, due to the large value of J_{AB} (3 115 Hz), and the positions of the corresponding weak lines are indicated in the Figure by arrows. The spectrum was simulated using ISO, a computer program which calculates and plots the spectra of all the isotopomers of platinum compounds. The results are presented in Table 6, along with the theoretical spectrum [Figure 2(*ii*)].

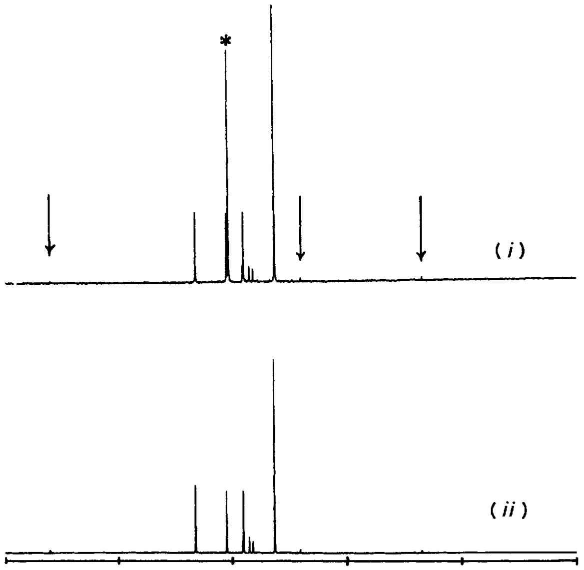


FIGURE 2 Observed (*i*) and calculated (*ii*) ^{195}Pt n.m.r. data for compound (5). The signal marked with an asterisk is due to the symmetrical isomer (5b). The arrows indicate the positions of weak signals (see text). Spectrum measured at 19.14 MHz, spectral width 10 000 Hz

Treatment of the isomeric mixture of (5) with $CNBu^t$ replaces the CO groups to give the two isomers of (6). These species show an intense broad band in their i.r. spectra (Table 1) due to the NC groups. The ^{1}H n.m.r. spectrum of the mixture of isomers shows the expected new signals for the isocyanide ligands (Table 2).

TABLE 6

Platinum-195 n.m.r. data for isomer (5a)

Observed		Calculated		
Frequency [a]	Intensity	Frequency	Intensity	Spin system [b]
18 989.6	70	18 987.8	86	AB (2 × 43)
16 418.8	1 768	16 418.8	2 123	AB_2 (131), A (1 992)
15 874.4	1 732	15 872.8	1 942	AB (2 × 971)
15 593.6	413	15 593.5	379	AB_2
15 578.9	1 772	15 578.1	1 942	AB (2 × 971)
15 476.4	391	15 477.1	507	AB_2
15 412.9	331	15 412.4	383	AB_2
15 032.1	6 916	15 032.1	6 017	B_2 (2 033), B (2 × 1 992)
14 585.3	111	14 587.1	134	AB_2
12 463.7	100	12 463.1	87	AB (2 × 43)

[a] Frequency in Hz. [b] Relative intensities are given in parentheses.

Compounds (6a) and (6b) may also be readily identified in the mixture of triplatinum species obtained by treating (1) with $CNBu^t$. However, this reaction gave a complex mixture of products, including $[W(CO)_4(CNBu^t)_2]$, and no attempt was made to identify all the $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_x(CNBu^t)_y(CO)_z]$ species formed. However, a partial separation of the products by chromatography afforded a compound having a molecular ion in its mass spectrum at *m/e* 1 127, a terminal CO stretch in its i.r. spectrum at 2 011 cm^{-1}, and a NC stretch at 2 129 cm^{-1}. These data suggest a complex of formulation $[Pt_3\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}_3(CO)_2(CNBu^t)]$ (7).

The results described above show that the cod ligand in (1) may be replaced by the σ-donor ligands PMe_3, dppe, or pdma with retention of the Pt–C–W ring system, whereas the reactions with the π-acceptor groups CO or $CNBu^t$ lead to fission of the metal-metal bond. Formation of (5) and (6) is clearly related to the observation[11] that the mononuclear molybdenum complex $[Mo\{C(OMe)Ph\}(CO)(NO)(\eta\text{-}C_5H_5)]$ reacts with $[Ni(CO)_4]$ to give the trinickel compound $[Ni_3\{\mu\text{-}C(OMe)Ph\}_3(CO)_3]$. Formation of (5) or (6) from (1) probably involves highly reactive intermediates $[(OC)_5W\{\mu\text{-}C(OMe)C_6H_4Me\text{-}4\}PtL_2]$ (L = CO or $CNBu^t$) which fragment affording $[W(CO)_6]$ or its isocyanide derivatives, and mononuclear platinum carbene species $[Pt\{C(OMe)C_6H_4Me\text{-}4\}L]$. Trimerisation of the latter would subsequently give (5) or (6). Similar reaction pathways have been proposed[4] to account for the synthesis of various triplatinum compounds $[Pt_3\{\mu\text{-}C(OMe)Ph\}_3(PR_3)_3]$, obtained by reacting mononuclear carbene complexes of chromium, tungsten, or manganese with the species $[Pt(C_2H_4)_2(PR_3)]$. The formation of compounds such as (7) can be accounted for by facile carbonyl–CNBu^t exchange processes giving intermediates such as the complex [(Bu^{t}NC)(OC)$_4$W{μ-C(OMe)C$_6$H$_4$Me-4}Pt(CO)(CNBu^t)] which fragment by migration to tungsten of either CNBu^t or CO. Finally, compounds (5) and (6) belong to a growing class of triplatinum cluster complexes, being members of the sub-group having 42 valence electrons.[12]

EXPERIMENTAL

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere, with solvents dried and distilled under nitrogen prior to use. The n.m.r. measurements were made with JEOL PS-100, JNM-FX 90Q, and FX 200 instruments, and i.r. spectra with Perkin-Elmer 257 spectrometers. Hydrogen-1 and ^{13}C-{^{1}H} n.m.r. data are given in Table 2. Phosphorus-31{^{1}H} chemical shifts (see below) are positive to high frequency of 85% H$_3$PO$_4$ (external). Platinum-195{^{1}H} chemical shifts are to high frequency of Ξ(^{195}Pt) 21.4 MHz. The compounds [Pt(cod)$_2$] [13] and [W{C(OMe)C$_6$H$_4$Me-4)}(CO)$_5$] [14] were made by literature methods.

Synthesis of the Compound [PtW{μ-C(OMe)C$_6$H$_4$Me-4}(CO)$_5$(cod)].—A sample of [W{C(OMe)C$_6$H$_4$Me-4}(CO)$_5$] (0.46 g, 1 mmol) was added portion-wise to a vigorously stirred ethylene-saturated solution of [Pt(cod)$_2$] (0.41 g, 1 mmol) in light petroleum (20 cm^3) at 0 °C. The mixture was stirred (1 h at 0 °C) and the precipitate allowed to settle, the mother-liquor decanted, and the residue washed (3 × 2 cm^3) with light petroleum. Drying *in vacuo* afforded orange-brown *microcrystals* of [(OC)$_5$W{μ-C(OMe)C$_6$H$_4$Me-4}Pt(cod)] (1) (0.53 g).

Reactions of the Complex [PtW{μ C(OMe)C$_6$H$_4$Me-4}(CO)$_5$(cod)] (1).—(*a*) *With* PMe$_3$. A light petroleum (10 cm^3) solution of (1) (0.38 g, 0.5 mmol) was treated with PMe$_3$ (1.1 mmol in 5 cm^3 of light petroleum) and the reactants stirred (18 h). Removal of solvent *in vacuo* and chromatography of the residue with toluene on an alumina column afforded an orange solution which on removal of solvent gave orange crystals of the known compound [3] [PtW{μ-C(OMe)C$_6$H$_4$Me-4}(CO)$_5$(PMe$_3$)$_2$] (2) (0.27 g), identified spectroscopically and by analysis.

(*b*) *With* Ph$_2$PCH$_2$CH$_2$PPh$_2$. Solid dppe (0.29 g, 0.55 mmol) was added to a dichloromethane (10 cm^3) solution of (1) (0.38 g, 0.5 mmol) and the resulting solution stirred for 18 h. Chromatography (toluene on alumina) afforded yellow *crystals* of [PtW{C(OMe)C$_6$H$_4$Me-4}(CO)$_5$(dppe)] (3) (0.37 g); ^{31}P-{^{1}H} n.m.r., δ 52.8 [d, P *trans* to μ-C, *J*(PP) 17, *J*(PtP) 2 508 Hz] and 44.0 p.p.m. [d, P *trans* to W, *J*(PP) 17, *J*(PtP) 3 909, *J*(WP) 11 Hz].

(*c*) *With* C$_6$H$_4$(AsMe$_2$)$_2$-1,2. A dichloromethane (10 cm^3) solution of (1) (0.38 g, 0.50 mmol) was added to a solution of pdma (0.53 mmol) in light petroleum (10 cm^3) and the resulting solution was stirred for 18 h. Chromatography and isolation of product as in (*a*) above gave dark orange *crystals* of [PtW{μ-C(OMe)C$_6$H$_4$Me-4}(CO)$_5$(pdma)] (4) (0.37 g).

(*d*) *With* CO. Carbon monoxide was bubbled through a solution of (1) (0.75 g, 1.0 mmol) in dichloromethane (10 cm^3) producing a brilliant cherry-red solution. Removal of solvent *in vacuo* and chromatography on alumina, eluting with light petroleum–dichloromethane (4 : 1), gave initially [W(CO)$_6$] (i.r. identified) followed by a red band from which red *crystals* of [Pt$_3${μ-C(OMe)C$_6$H$_4$Me-4}$_3$(CO)$_3$] (5) [0.16 g, *ca.* 4 : 1 of (5a) : (5b)] were obtained. Further elution with dichloromethane gave traces of a higher-molecular-weight triplatinum species, not identified. The isomers of (5) were readily separated by thin-layer chromatography (alumina–light petroleum). Reasonable quantities of the faster moving isomer (5a) may be obtained substantially pure by chromatography on a 60-cm alumina column using light petroleum as eluant.

Formation of [Pt$_3${μ-C(OMe)C$_6$H$_4$Me-4}$_3$(CNBu^t)$_3$].—(*a*) An isomeric mixture of (5) (0.1 g, 0.1 mmol) was treated with CNBu^t (0.28 mmol) in light petroleum. After 1 h solvent was removed *in vacuo* and the residue was dissolved in dichloromethane and filtered through an alumina pad. Removal of solvent *in vacuo* afforded dark red *microcrystals* of [Pt$_3${μ-C(OMe)C$_6$H$_4$Me-4}$_3$(CNBu^t)$_3$] (6) (0.1 g). (Field desorption mass spectroscopy revealed a molecular ion at *m/e* 1 236.)

(*b*) A diethyl ether (10 cm^3) solution of (1) (0.38 g, 0.5 mmol) was treated with CNBu^t (1.5 mmol) in light petroleum (10 cm^3), and after stirring (30 min) solvent was removed *in vacuo*. The residue was chromatographed on alumina using light petroleum–dichloromethane (9 : 1), allowing partial separation of products into a fast moving yellow band, a red band, and a slower moving dark yellow band. The first band eluted to give pale yellow crystals of [W(CO)$_4$(CNBu^t)$_2$] (Found: C, 36.6; H, 4.1; N, 6.2. C$_{14}$H$_{18}$NO$_4$W requires C, 36.4; H, 3.9; N, 6.1%), $\nu_{max.}$ 2 151m br (NC), 2 030s, 2 017vs, 1 933m, and 1 919s (CO) cm^{-1}. The red band was further separated by thin-layer chromatography (alumina–light petroleum) into the isomeric mixture (6) and a red compound for which field desorption mass spectrometry showed a molecular ion at *m/e* 1 127, suggesting the formulation [Pt$_3${μ-C(OMe)C$_6$H$_4$Me-4}$_3$(CO)$_2$(CNBu^t)] (7), $\nu_{max.}$ 2 129 (NC) and 2 011 cm^{-1} (CO). The third band contained various amounts of unidentified isomers.

Crystal-structure Determination of Compound (5a).—Crystals of (5a) were grown with difficulty by slow evaporation of light petroleum solutions under a stream of dry, oxygen-free, nitrogen. That used for data collection was a small but well formed plate of approximate dimensions 0.25 × 0.15 × 0.06 mm. The relatively weak diffracted intensities were recorded (room temperature, $2.9 \leqslant 2\theta \leqslant 50°$) on a Nicolet *P3m* four-circle diffractometer. Of the total 3 436 unique recorded intensities, 2 699 had $|F| \geqslant 5\sigma(F)$, where $\sigma(F)$ is the standard deviation based on counting statistics, and these were used in the solution and final refinement of the structure. Corrections were applied for Lorentz and polarisation effects, and for the effects of *X*-ray absorption. Computations were carried out using the SHELXTL series of programs [15] on a Data General ' Eclipse ' computer.

Crystal data. C$_{30}$H$_{30}$O$_6$Pt$_3$, M = 1 071.3, Orthorhombic, a = 11.085(2), b = 15.554(3), c = 18.733(5) Å, U = 3 230(1) Å^3, Z = 4, D_c = 2.20 g cm^{-3}, F(000) = 1 968, space group $P2_12_12_1$, Mo-K_α *X*-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 131.4 cm^{-1}.

Structure solution and refinement. The structure was solved, and all non-hydrogen atoms were located, by conventional heavy-atom methods and electron-density difference syntheses. Owing to the relatively poor quality of the data set the C$_6$H$_4$Me-4 rings were refined as rigid isotropic groups, whilst all other atoms were refined with anisotropic temperature factors. Refinement by a block-cascade matrix least-squares method converged at R 0.046 (R'

0.045) with a mean shift-to-error ratio in the final cycles of 0.05. A satisfactory weighting scheme was of the form $w^{-1} = [\sigma^2(F) + 0.001 |F_o|^2]$, where $\sigma(F)$ is the estimated error based on counting statistics only. The final electron-density difference synthesis showed no peaks >1.2 or <1 e Å^{-3}, except in the vicinity of the Pt atoms where residual peaks were *ca.* 2.3 e Å^{-3}. Scattering factors for all elements, including corrections for the effects of anomalous dispersion, were from ref. 16. Observed and calculated structure factors, temperature factors, and hydrogen-atom positional parameters are listed in Supplementary Publication No. SUP 23309 (20 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 I. M.).

[2/229 *Received, 8th February, 1982*]

REFERENCES

[1] Part 10, 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.

[2] T. V. Ashworth, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1593.

[3] 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.

[4] T. V. Ashworth, M. Berry, J. A. K. Howard, M. Laguna, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1615.

[5] I. Moore and F. G. A. Stone, unpublished work.

[6] M. Berry, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1601.

[7] M. Berry, J. Martin-Gil, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1625.

[8] M. Green, J. A. K. Howard, M. Murray, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, 1509.

[9] A. Albinati, *Inorg. Chim. Acta*, 1977, **22**, L31.

[10] G. K. Barker, M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1978, 1839; R. Mason, G. B. Robertson, and P. O. Whimp, *J. Chem. Soc. A*, 1970, 535; M. R. Truter and R. C. Watling, *ibid.*, 1967, 1955.

[11] E. O. Fischer and H. J. Beck, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 72.

[12] F. G. A. Stone, *Inorg. Chim. Acta*, 1981, **50**, 33.

[13] J. L. Spencer, *Inorg. Synth.*, 1979, **19**, 213.

[14] E. O. Fischer, U. Schubert, W. Kleine, and H. Fisher, *Inorg. Synth.*, 1979, **19**, 164.

[15] G. M. Sheldrick, SHELXTL programs for use with the Nicolet *P*3*m* *X*-ray system, Cambridge, 1976.

[16] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.