Organo-complexes of Platinum derived from Methyl Vinyl Ketone and Bis(cyclo-octa-1,5-diene)platinum; *X*-Ray Crystal Structure of (1,3-Diacetylbutane-1,4-diyl)bis(triphenylphosphine)platinum

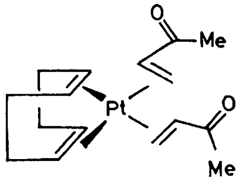
By **Michael Green, Judith A. K. Howard, Pachanee Mitrprachachon, Michel Pfeffer, John L. Spencer, F. Gordon A. Stone,* and Peter Woodward,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Bis(cyclo-octa-1,5-diene)platinum reacts with methyl vinyl ketone at *ca.* −20 °C to give either $[\mathrm{Pt\{\eta^2\text{-}CH_2{:}CHC(Me){:}O\}_2(cod)}]$ (cod = cyclo-octa-1,5-diene) or $[\mathrm{Pt\{\eta^2\text{-}CH_2{:}CHC(Me){:}O\}_3}]$. The former complex readily isomerises to a platinacyclopentane $[\mathrm{Pt\{CH_2{\cdot}CH[C(Me){:}O]{\cdot}CH_2{\cdot}CH[C(Me){:}O]\}(cod)}]$, from which the cod group may be replaced by CNBu^t or PPh$_3$ to give $[\mathrm{Pt\{CH_2{\cdot}CH[C(Me){:}O]{\cdot}CH_2{\cdot}CH[C(Me){:}O]\}L_2}]$ (L = CNBu^t or PPh$_3$). In order to establish the molecular structure of this class of complex a single-crystal *X*-ray diffraction study was made on the PPh$_3$ derivative, crystals of which are triclinic, space group $P\bar{1}$, Z = 2, in a unit cell with lattice parameters a = 10.755(3), b = 18.172(3), c = 11.780(2) Å, α = 110.26(1), β = 114.89(2), and γ = 95.77(2)°. The structure has been refined to R 0.044 (R' 0.041) for 8 596 independent reflections to $2\theta \leqslant 60°$ (Mo-K_α *X*-radiation) collected at room temperature. The platinacyclopentane ring has a head-to-tail arrangement for the $\mathrm{CH_2{\cdot}CH[C(Me){:}O]}$ groups, is non-planar, and is disordered about the β-carbon atom carrying a C(Me):O group, revealing for this derivative the presence of two isomers. Reaction of $[\mathrm{Pt\{\eta^2\text{-}CH_2{:}CHC(Me){:}O\}_2(cod)}]$ with oxygen, hexafluoroacetone, or $\mathrm{(CF_3)_2C{:}C(CN)_2}$ affords five-membered platina-ring complexes $[\mathrm{Pt\{X{\cdot}Y{\cdot}CH[C(Me){:}O]{\cdot}CH_2\}(cod)}]$ [X·Y = O·O, $\mathrm{O{\cdot}C(CF_3)_2}$, or $\mathrm{C(CN)_2{\cdot}C(CF_3)_2}$], while treatment with PPh$_3$, CNBu^t, or C$_2$F$_4$ gives $[\mathrm{Pt\{\eta^2\text{-}CH_2{:}CHC(Me){:}O\}L_2}]$ (L = PPh$_3$ or CNBu^t) and $[\mathrm{Pt(CF_2{\cdot}CF_2)(cod)}]$, respectively. The latter dimerises in solution to yield $[\mathrm{Pt_2(\mu\text{-}CF_2{\cdot}CF_2)_2(cod)_2}]$.

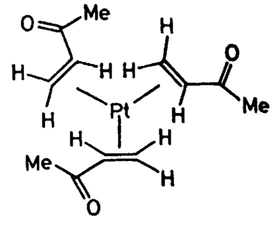
THE platinum complex $[\mathrm{Pt(cod)_2}]$ (cod = cyclo-octa-1,5-diene) shows a variety of reactivity patterns towards olefins and dienes. Thus ethylene, dimethyl fumarate, and tetrafluoroethylene react with $[\mathrm{Pt(cod)_2}]$ to give, respectively, $[\mathrm{Pt(C_2H_4)_3}]$,[1] $[\mathrm{Pt\{\mathit{trans}\text{-}CH(CO_2Me){:}CH(CO_2Me)\}(cod)}]$,[2] and $[\mathrm{Pt_2(\mu\text{-}CF_2{\cdot}CF_2)_2(cod)_2}]$.[3] Moreover, whereas 2,3-dimethylbuta-1,3-diene undergoes a 1,4 oxidative-addition reaction with $[\mathrm{Pt(cod)_2}]$ to give a product $[\mathrm{Pt\{CH_2{\cdot}C(Me){:}C(Me){\cdot}CH_2\}(cod)}]$ containing a platinacyclopentene ring, in contrast buta-1,3-diene affords a 2,5-divinylplatinacyclopentane derivative $[\mathrm{Pt\{CH(CH{:}CH_2){\cdot}CH_2{\cdot}CH_2{\cdot}CH(CH{:}CH_2)\}(cod)}]$.[4] This diverse behaviour towards unsaturated olefins and dienes has prompted a study of the reaction between methyl vinyl ketone and $[\mathrm{Pt(cod)_2}]$. This unsaturated ketone is of interest because it is known from previous work to act either as a unidentate olefin species as in $[\mathrm{Mn(CO)_2\{\eta^2\text{-}CH_2{:}CHC(Me){:}O\}(\eta\text{-}C_5H_4R)}]$,[5,6] or as a bidentate pseudo-buta-1,3-diene group as in $[\mathrm{W\{CH_2{:}CHC(Me){:}O\}_3}]$.[7,8] The former pattern of behaviour might be thought more likely with platinum in view of the earlier isolation of $[\mathrm{Pt\{\eta^2\text{-}CH_2{:}CHC(Me){:}O\}(PPh_3)_2}]$.[9] However, the lability of the cod ligands in $[\mathrm{Pt(cod)_2}]$ suggested that more than one methyl vinyl ketone molecule might become co-ordinated to platinum *via* displacement of cod groups, and this could be followed by cyclisation processes similar to those observed earlier[4] with buta-1,3-diene.

RESULTS AND DISCUSSION

Diethyl ether solutions of $[\mathrm{Pt(cod)_2}]$ at *ca.* −20 °C react with methyl vinyl ketone (mvk) in a 1 : 2 mol ratio to give a yellow crystalline complex $[\mathrm{Pt(mvk)_2(cod)}]$ (1). If the same reaction is carried out with an excess of mvk the white microcrystalline complex $[\mathrm{Pt(mvk)_3}]$ (2) is obtained in high yield. The i.r. spectra of (1) and (2) show C=O stretching frequencies at 1 655 and 1 643, and at 1 660 cm^{-1}, respectively. This indicates that the platinum is bonded only to the vinyl groups of the mvk ligands in these complexes, the α,β-unsaturated ketone functioning as a unidentate group, as in $[\mathrm{Pt\{\eta^2\text{-}CH_2{:}CHC(Me){:}O\}(PPh_3)_2}]$.[9] In contrast, when mvk acts as a bidentate ligand there is no i.r. band near 1 650 cm^{-1}, but an absorption near 1 495 cm^{-1} which is assigned to a metal-co-ordinated ketone group.[7]



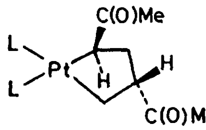
(1)

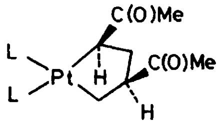


(2)

Complex (2) is stable under nitrogen at room temperature, apparently for several weeks. It is of comparable stability to tris(bicyclo[2.2.1]heptene)platinum,[1] and it probably has a similar structure in the solid state with the carbon atoms of the double bonds coplanar with the platinum.

Complex (1), in contrast to (2), is unstable in solution making it impossible to obtain definitive n.m.r. data as an aid to establishing the structure. The cod ligand probably adopts an η^4 co-ordination, as shown, although a trigonal structure involving an η^2-bonded cod group cannot be ruled out. That (1) contains two co-ordinated mvk groups is very strongly supported by analysis, and by its conversion over a period of hours in diethyl ether–light petroleum solutions into another species (3) of the same composition. Complex (3) shows strong bands in the i.r. at 1 694 and 1 636 cm^{-1} corresponding to unco-ordinated ketone groups. In free mvk this band occurs at 1 675 cm^{-1}. The ^{13}C n.m.r. spectrum of (3) indicated that it contains a platinacyclopentane ring, with a head-to-tail arrangement for the $CH_2{\cdot}CH[C(Me){:}O]$ groups.





(3a) 2L = cod (3b)
(4a) L = CNBu^t (4b)
(5a) L = PPh$_3$ (5b)

Particularly diagnostic are two resonances at 60.2 and 35.4 p.p.m. with coupling constants $J(^{195}Pt-^{13}C)$ of 642 and 778 Hz, respectively, characteristic of carbon atoms σ-bonded to platinum.[10] However, the n.m.r. study could not distinguish between the isomeric forms (3a) and (3b). The n.m.r. spectra did, nevertheless, show that a solution of (3) apparently consists of one isomer, assuming that (3a) and (3b) did not have identical ^{13}C n.m.r. shifts.

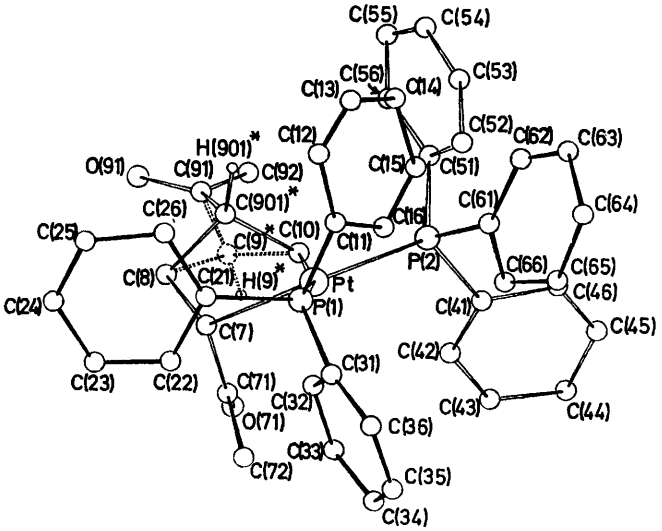


FIGURE 1 Molecular structure of complex (5)

Treatment of (3) with CNBu^t or PPh$_3$ displaces the cod and gives quantitatively (4) and (5), respectively. The i.r. spectrum of the isocyanide derivative shows two strong N≡C stretches at 2 202 and 2 176 cm^{-1} characteristic of a *cis* arrangement for the two CNBu^t groups. Similarly, the ^{31}P n.m.r. spectrum of (5) shows the typical AB pattern for a *cis*-$Pt(PPh_3)_2$ arrangement, with shifts at −25.93 and −25.07 p.p.m. [$J(^{31}P-^{31}P)$ 10.5; $J(^{195}Pt-^{31}P)$ 2 405 and 1 983 Hz].

In order to establish the nature of the ring system in complexes (3)—(5) a single-crystal *X*-ray diffraction study was made on (5), the only complex of the group for which crystals of sufficient quality could be obtained. The results of this study are given in Tables 1—3 and are

TABLE 1

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for complex (5)

Atom	*x*	*y*	*z*
Pt	0.143 04(2)	0.241 48(1)	0.043 84(2)
Triphenylphosphine group 1			
P(1)	0.094 61(16)	0.229 07(8)	−0.174 51(13)
C(11)	−0.098 0(6)	0.193 5(3)	−0.295 2(5)
C(12)	−0.179 3(6)	0.129 4(3)	−0.292 9(5)
C(13)	−0.326 6(7)	0.101 2(4)	−0.377 7(6)
C(14)	−0.397 6(7)	0.135 8(4)	−0.462 6(6)
C(15)	−0.316 3(7)	0.203 6(4)	−0.464 3(6)
C(16)	−0.169 5(7)	0.230 1(3)	−0.380 0(5)
C(21)	0.163 8(6)	0.148 9(3)	−0.250 4(5)
C(22)	0.298 5(9)	0.171 8(5)	−0.240 1(7)
C(23)	0.362 1(9)	0.110 6(6)	−0.278 5(8)
C(24)	0.288 8(11)	0.024 5(5)	−0.331 3(8)
C(25)	0.160 8(11)	0.007 4(5)	−0.343 5(10)
C(26)	0.094 9(8)	0.067 1(4)	−0.304 5(8)
C(31)	0.164 8(6)	0.312 8(3)	−0.203 6(5)
C(32)	0.153 0(7)	0.298 5(4)	−0.334 2(6)
C(33)	0.217 2(9)	0.360 9(5)	−0.350 3(8)
C(34)	0.291 4(8)	0.438 5(5)	−0.239 6(9)
C(35)	0.298 9(8)	0.453 1(4)	−0.117 3(8)
C(36)	0.236 5(6)	0.390 1(4)	−0.096 1(6)
Triphenylphosphine group 2			
P(2)	−0.024 78(16)	0.300 67(8)	0.077 49(13)
C(41)	0.066 2(6)	0.398 7(3)	0.233 0(5)
C(42)	0.212 0(7)	0.422 3(4)	0.316 4(6)
C(43)	0.280 0(7)	0.497 2(4)	0.434 8(6)
C(44)	0.202 8(9)	0.547 3(4)	0.465 7(6)
C(45)	0.054 5(8)	0.524 6(4)	0.385 5(6)
C(46)	−0.008 7(7)	0.451 6(4)	0.270 7(5)
C(51)	−0.137 1(6)	0.239 5(3)	0.115 0(5)
C(52)	−0.141 3(8)	0.266 4(4)	0.236 0(7)
C(53)	−0.225 8(10)	0.214 9(5)	0.258 5(8)
C(54)	−0.299 8(8)	0.138 2(5)	0.163 6(9)
C(55)	−0.299 6(9)	0.109 7(4)	0.040 0(8)
C(56)	−0.215 8(8)	0.160 5(4)	0.016 3(7)
C(61)	−0.153 8(6)	0.331 3(3)	−0.045 6(5)
C(62)	−0.301 0(7)	0.303 0(4)	−0.104 2(6)
C(63)	−0.391 7(7)	0.330 5(4)	−0.194 3(7)
C(64)	−0.335 4(8)	0.388 0(4)	−0.224 7(6)
C(65)	−0.188 7(7)	0.417 5(4)	−0.169 1(6)
C(66)	−0.101 2(6)	0.388 7(3)	−0.080 4(6)
Platinacyclopentane ring			
C(7)	0.325 0(6)	0.195 7(3)	0.078 7(5)
H(7)	0.320	0.170	−0.020
C(8)	0.311 5(8)	0.130 0(4)	0.130 8(7)
H(81)	0.270	0.060	0.050
H(82)	0.374	0.075	0.134
C(9) *	0.265 9(18)	0.165 3(9)	0.245 4(15)
H(9) *	0.360	0.200	0.280
C(901) *	0.181 5(15)	0.128 7(7)	0.160 0(13)
H(901) *	0.080	0.100	0.070
C(10)	0.182 6(8)	0.219 7(4)	0.217 6(7)
H(101)	0.170	0.260	0.320
H(102)	0.080	0.180	0.190
C(Me):O ligands			
C(71)	0.447 3(7)	0.269 9(4)	0.184 3(6)
O(71)	0.506 5(6)	0.289 1(3)	0.307 9(5)
C(72)	0.500 6(9)	0.328 5(5)	0.139 8(8)
C(91)	0.208 0(11)	0.096 7(6)	0.267 1(9)
O(91)	0.240 2(8)	0.034 1(4)	0.243 5(7)
C(92)	0.178 8(14)	0.120 2(7)	0.381 7(12)

* Disordered.

illustrated in Figure 1, which also shows the crystallographic numbering system. It is at once apparent that the two methyl vinyl ketone moieties have indeed joined head-to-tail and formed a non-planar platinacyclopentane ring, leaving the two other (*cis*) positions around the square-planar platinum atom to be occupied by the triphenylphosphine ligands.

TABLE 2

Bond lengths (Å) and angles (°) for complex (5)

(*a*) Distances

(*i*) Triphenylphosphine group 1

Pt–P(1)	2.320 6(17)	C(23)–C(24)	1.457(13)
P(1)–C(11)	1.829(5)	C(24)–C(25)	1.315(17)
C(11)–C(12)	1.399(9)	C(25)–C(26)	1.404(14)
C(12)–C(13)	1.385(8)	C(26)–C(21)	1.375(9)
C(13)–C(14)	1.366(11)	P(1)–C(31)	1.831(7)
C(14)–C(15)	1.449(12)	C(31)–C(32)	1.414(11)
C(15)–C(16)	1.381(9)	C(32)–C(33)	1.380(13)
C(16)–C(11)	1.396(9)	C(33)–C(34)	1.396(9)
P(1)–C(21)	1.831(7)	C(34)–C(35)	1.336(15)
C(21)–C(22)	1.407(12)	C(35)–C(36)	1.416(12)
C(22)–C(23)	1.405(14)	C(36)–C(31)	1.379(6)

(*ii*) Triphenylphosphine group 2

Pt–P(2)	2.295 4(19)	C(53)–C(54)	1.332(10)
P(2)–C(41)	1.835(4)	C(54)–C(55)	1.368(15)
C(41)–C(42)	1.372(8)	C(55)–C(56)	1.401(14)
C(42)–C(43)	1.400(7)	C(56)–C(51)	1.379(7)
C(43)–C(44)	1.351(12)	P(2)–C(61)	1.833(6)
C(44)–C(45)	1.392(11)	C(61)–C(62)	1.385(9)
C(45)–C(46)	1.362(7)	C(62)–C(63)	1.385(10)
C(46)–C(41)	1.389(10)	C(63)–C(64)	1.380(13)
P(2)–C(51)	1.847(8)	C(64)–C(65)	1.386(11)
C(51)–C(52)	1.360(11)	C(65)–C(66)	1.380(10)
C(52)–C(53)	1.406(15)	C(66)–C(61)	1.395(10)

(*iii*) Platinacyclopentane ring

Pt–C(7)	2.139(7)	C(9)*–C(91)	1.485(23)
C(7)–C(8)	1.540(11)	C(901)*–C(91)	1.500(20)
C(7)–C(71)	1.484(7)	C(91)–C(92)	1.446(21)
C(71)–C(72)	1.500(14)	C(91)–O(91)	1.196(14)
C(71)–O(71)	1.213(8)	C(9)*–C(10)	1.430(20)
C(8)–C(9)*	1.579(23)	C(901)*–C(10)	1.552(15)
C(8)–C(901)*	1.574(21)	C(10)–Pt	2.094(9)

(*b*) Angles

(*i*) Triphenylphosphine group 1

Pt–P(1)–C(11)	111.6(2)	P(1)–C(21)–C(26)	121.8(6)
Pt–P(1)–C(21)	109.6(2)	C(21)–C(22)–C(23)	119.0(7)
Pt–P(1)–C(31)	123.0(2)	C(22)–C(23)–C(24)	120.7(9)
C(11)–P(1)–C(21)	104.4(2)	C(23)–C(24)–C(25)	116.9(9)
C(21)–P(1)–C(31)	101.4(3)	C(24)–C(25)–C(26)	123.8(8)
C(31)–P(1)–C(11)	105.0(3)	C(25)–C(26)–C(21)	120.4(9)
P(1)–C(11)–C(12)	117.0(4)	C(26)–C(21)–C(22)	119.1(7)
P(1)–C(11)–C(16)	124.5(5)	P(1)–C(31)–C(32)	120.7(4)
C(11)–C(12)–C(13)	120.3(6)	P(1)–C(31)–C(36)	120.2(6)
C(12)–C(13)–C(14)	121.9(7)	C(31)–C(32)–C(33)	119.7(5)
C(13)–C(14)–C(15)	118.9(6)	C(32)–C(33)–C(34)	120.5(9)
C(14)–C(15)–C(16)	118.1(7)	C(33)–C(34)–C(35)	120.0(9)
C(15)–C(16)–C(11)	122.3(7)	C(34)–C(35)–C(36)	121.1(6)
C(16)–C(11)–C(12)	118.4(5)	C(35)–C(36)–C(31)	119.7(7)
P(1)–C(21)–C(22)	118.8(5)	C(36)–C(31)–C(32)	119.0(7)

(*ii*) Triphenylphosphine group 2

Pt–P(2)–C(41)	109.3(2)	P(2)–C(51)–C(56)	117.5(6)
Pt–P(2)–C(51)	112.4(2)	C(51)–C(52)–C(53)	120.5(6)
Pt–P(2)–C(61)	124.3(2)	C(52)–C(53)–C(54)	120.7(10)
C(41)–P(2)–C(51)	104.5(3)	C(53)–C(54)–C(55)	120.2(10)
C(51)–P(2)–C(61)	103.6(3)	C(54)–C(55)–C(56)	119.5(6)
C(61)–P(2)–C(41)	100.6(2)	C(55)–C(56)–C(51)	120.5(8)
P(2)–C(41)–C(42)	120.6(5)	C(56)–C(51)–C(52)	118.5(7)
P(2)–C(41)–C(46)	121.7(4)	P(2)–C(61)–C(62)	124.4(5)
C(41)–C(42)–C(43)	120.0(7)	P(2)–C(61)–C(66)	118.3(4)
C(42)–C(43)–C(44)	120.2(6)	C(61)–C(62)–C(63)	121.1(7)
C(43)–C(44)–C(45)	121.5(5)	C(62)–C(63)–C(64)	119.9(6)
C(44)–C(45)–C(46)	117.0(7)	C(63)–C(64)–C(65)	120.9(7)
C(45)–C(46)–C(41)	123.6(6)	C(64)–C(65)–C(66)	117.8(7)
C(46)–C(41)–C(42)	117.6(4)	C(65)–C(66)–C(61)	123.0(6)
P(2)–C(51)–C(52)	124.0(4)	C(66)–C(61)–C(62)	117.3(6)

TABLE 2 (*Continued*)

(*iii*) Platinacyclopentane ring

P(1)–Pt–P(2)	102.8(1)	C(7)–C(8)–C(901)*	109.4(8)
P(1)–Pt–C(7)	94.5(2)	C(8)–C(9)*–C(91)	109.0(11)
P(1)–Pt–C(10)	164.8(2)	C(8)–C(901)*–C(91)	108.5(10)
P(2)–Pt–C(7)	162.4(2)	C(9)*–C(91)–C(92)	115.6(10)
P(2)–Pt–C(10)	86.7(3)	C(901)*–C(91)–C(92)	131.1(11)
C(7)–Pt–C(10)	77.1(3)	C(9)*–C(91)–O(91)	123.2(14)
Pt–C(7)–C(8)	108.6(5)	C(901)*–C(91)–O(91)	114.7(11)
Pt–C(7)–C(71)	103.2(4)	O(91)–C(91)–C(92)	113.3(12)
C(8)–C(7)–C(71)	113.1(5)	C(8)–C(9)*–C(10)	110.4(13)
C(7)–C(71)–C(72)	119.5(6)	C(8)–C(901)*–C(10)	104.6(10)
C(7)–C(71)–O(71)	124.4(8)	C(9)*–C(10)–Pt	118.7(10)
O(71)–C(71)–C(72)	116.1(6)	C(901)*–C(10)–Pt	99.6(7)
C(7)–C(8)–C(9) *	107.2(8)		

Interest centres on this platinacyclopentane ring and its two C(Me):O substituents. Of the five atoms in the ring [Pt, and C(7)—C(10) inclusive], atoms C(7) and C(9) carry C(Me):O substituents. The ring itself, however, is highly puckered and atom C(9) is disordered about two positions [listed as C(9)* and C(901)* in the Tables, the asterisk indicating disorder]. Surprisingly, the ligand attached to C(9) is not obviously disordered (see below).

TABLE 3

Some least-squares planes [a] and torsion angles; distances (Å) of atoms from the planes are given in square brackets

Plane (*i*): Pt, P(1), P(2)

$$4.1564x + 13.8210y - 1.7874z = 3.9052$$

[C(7) 0.13, C(8) −0.93, C(9)* −0.86, C(10) −0.43, C(71) 1.51, O(71) 1.83, C(72) 2.65, C(91) −2.11, O(91) −2.78, C(92) −2.12, C(901)* −1.59]

Plane (*ii*): Pt, C(7), C(10)

$$3.0905x + 12.9804y + 0.9206z = 3.6170$$

[C(8) −0.84, C(9)* −0.42, C(71) 1.44, O(71) 1.98, C(72) 2.32, C(91) −1.47, O(91) −2.21, C(92) −1.15, C(901)* −1.24]

Plane (*iii*): C(71), O(71), C(72)

$$-9.2861x + 10.5711y + 2.8009z = -0.7845$$

[C(7) 0.06, Pt 2.13]

Plane (*iv*): C(91), O(91), C(92)

$$7.8091x + 3.5423y + 1.2626z = 2.3039$$

[C(9)* 0.67, C(901)* −0.23, Pt −0.28]

Angles (°) between the least-squares planes:

(*i*)–(*ii*) 13; (*i*)–(*iii*) 86; (*i*)–(*iv*) 38

Torsion angles (°) in the two forms of the platinacyclopentane ring:

C(10)–Pt–C(7)–C(8)	35	C(10)–Pt–C(7)–C(8)	35
Pt–C(7)–C(8)–C(9)*	−45	Pt–C(7)–C(8)–C(901)*	−8
C(7)–C(8)–C(9)*–C(10)	30	C(7)–C(8)–C(901)*–C(10)	−36
C(8)–C(9)*–C(10)–Pt	1	C(8)–C(901)*–C(10)–Pt	63
C(9)*–C(10)–Pt–C(7)	−20	C(901)*–C(10)–Pt–C(7)	−54

Twist angle (°) [b] between the least-squares plane of the phenyl ring and corresponding Pt–P–C plane

Pt–P(1)–C(11) and C(11)—C(16)	46
Pt–P(1)–C(21) and C(21)—C(26)	80
Pt–P(1)–C(31) and C(31)—C(36)	10
Pt–P(2)–C(41) and C(41)—C(46)	6
Pt–P(2)–C(51) and C(51)—C(56)	61
Pt–P(2)–C(61) and C(61)—C(66)	59

[a] x, y, and z are fractional crystal co-ordinates. [b] The twist angle is here taken to be the acute dihedral angle between the Pt–P–C and C_6 planes.

It will be seen from Table 3, which includes the torsion angles around the platinacyclopentane ring, that C(9)* gives rise to a ring of envelope conformation in which Pt, C(10), C(9)*, and C(8) are nearly coplanar (torsion angle 1°). Atoms C(7) and C(9)* also carry hydrogen atoms giving an essentially tetrahedral arrangement, so in this envelope conformation the two C(Me):O substituents are on ' opposite sides ' of the ring, with the substituent on C(7) deviating in the same sense as C(7) itself, *viz* downwards as drawn in Figure 1. In the alternative position for C(9) [*viz.* C(901)*], however, the atoms Pt, C(7), C(8), and C(901)* are now more nearly coplanar (torsion angle 8°) while C(10) deviates substantially but again in the same sense as did C(7) in the first conformation. This now places the ligand C(91) on the *same* side of the ring as C(71). Moreover, there is evidence from electron-density maps that the hydrogen atom occupies sites on both sides of the ring, *viz.* H(9)* and H(901)*. Thus in the crystal both isomeric forms, (a) and (b), of (5) are present.

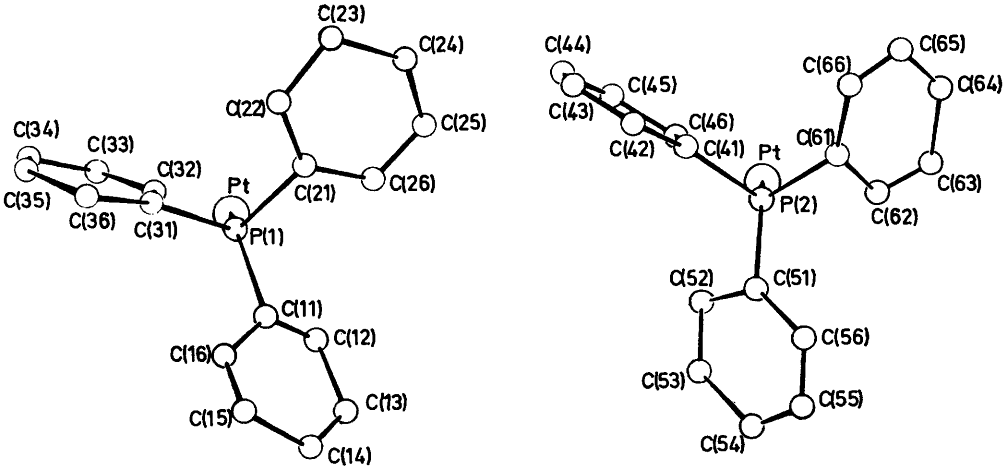


FIGURE 2 Conformations of the two triphenylphosphine ligands viewed along the P–Pt bonds

The C(Me):O group should be coplanar with the ring atom to which it is attached. In the case of C(7) the deviation of the ring atoms from the plane of the ligand is only 0.06 Å, whereas for the two C(9) positions the deviation is 0.67 Å for C(9)* and −0.23 Å for C(901)*. However, the thermal parameters for C(92) and O(91) are both high, suggesting short-range disorder in the position of the C(Me):O group which is being compensated by an apparent increase in thermal activity. There are also residual peaks on the final electron-density difference maps suggestive of a second set of overlapping positions for these ligand atoms.

The valence configuration around the central platinum atom, although loosely interpretable as square planar, is in fact neither square nor planar. The platinacyclopentane ring constrains the angle C(7)–Pt–C(10) to 77°, while the angle P(1)–Pt–P(2) is opened out to 103°. The two phosphine ligands are also not symmetrically related to the ring system, perhaps because of steric interaction between the phenyl groups and the groups on C(7); thus angle C(7)–Pt–P(1) is 95° compared with 87° for C(10)–Pt–P(2) (Table 2). Moreover, the plane defined by P(1)–Pt–P(2) makes a dihedral angle of 13° with that defined by C(7)–Pt–C(10), introducing a significant twist into the configuration (see Table 3).

In many compounds containing co-ordinated PPh_3 groups [11] it is found that the plane of one of the phenyl rings essentially contains the metal–phosphorus vector, another phenyl ring is twisted *ca.* 90° about its P–C bond with respect to the first ring, while the third phenyl ring assumes an intermediate orientation. Complex (5) conforms only approximately to this stereochemistry (Figure 2). Of the phenyl groups attached to P(1), ring C(31)—C(36) lies close to the plane defined by Pt, P(1), and C(31), while ring C(21)—C(26) lies nearly at right angles to the plane Pt, P(1), C(21). The third ring, C(11)—C(16), is in an intermediate position with respect to the plane Pt, P(1), C(11) (Table 3). For P(2), however, while the ring C(41)—C(46) lies close to the plane Pt, P(2), C(41), the other two rings, C(51)—C(56) and C(61)—C(66) are both at angles of *ca.* 60° with respect to their corresponding Pt–P–C planes. The P–C and C–C distances are within the ranges expected, averaging 1.834(6) * and 1.386(18) * respectively. The packing of the molecules in the unit cell is shown in Figure 3.

The presence of the metallacyclopentane ring system in (5), together with the head-to-tail arrangement, is reminiscent of numerous five-membered metallacycles obtained from reactions between unsaturated fluorocarbons and compounds of zerovalent nickel, palladium, and platinum.[12,13] The *X*-ray crystallographic study of (5), revealing relative *cis* and *trans* configurations for the C(Me):O substituents, does not allow any deduction to be made about the isomeric nature of its precursor (3), which in solution appeared from its spectroscopic properties to consist of only one isomer. Reaction of (3) with triphenylphosphine could disturb an equilibrium

---

* Estimated standard deviations are computed from: $\sigma^2 = \left[\sum_{i=1}^{i=N}(\chi_i - \bar{\chi})^2\right]/(N-1)$ where N is the number of measurements, χ_i is the ith value, and $\bar{\chi}$ the mean value.

between isomers, for example, *via* keto–enol tautomerism, or *via* ring opening as in the conversion of $[\mathrm{Pt\{CH(CH{:}CH_2)\cdot CH_2\cdot CH_2\cdot CH(CH{:}CH_2)\}(cod)}]$ into $[\mathrm{Pt(\eta^3\text{-}CH_2\cdot CH{:}CH\cdot CH_2\cdot CH_2\cdot CH{:}CH\cdot CH_2)(PR_3)}]$.[4] Unfortunately, as mentioned above, it was not possible to grow crystals of (3) suitable for *X*-ray diffraction work. This was particularly disappointing because it was observed in some experiments that if (1) was dissolved in diethyl ether saturated with ethylene gas it rearranged to a complex [$\nu_{max.}$(C=C) at 1 685vs and 1 638vs cm^{-1}] having a ^{13}C n.m.r. spectrum virtually identical with that of (3), but an i.r. spectrum (Nujol) very different in the region 500—1 800 cm^{-1}. Formation of this species was, however, hard to reproduce but the species was possibly one of the forms (3a) or (3b). It may, on the other hand, be merely another crystalline form of the first isomer. This compound reacted with CNBu^t to give a product with spectroscopic properties very similar to those of (4).

Although complex (1) readily affords (3), nevertheless, by generating (1) *in situ* at −20 °C it was possible to study several interesting reactions of the bis(methyl vinyl ketone)platinum complex. With oxygen, complex (1) reacts to give the stable peroxy-derivative (6a), from which the cyclo-octa-1,5-diene ligand can be displaced by t-butyl isocyanide to afford (6b). The structural assignments for the peroxy-compounds (6) are supported by elemental analyses, their i.r. spectra [$\nu_{max.}$(C=O) at 1 680 (6a) and 1 682 cm^{-1} (6b); and $\nu_{max.}$(N≡C) at 2 230 and 2 195 cm^{-1} (6b)], and the ^{13}C n.m.r. spectrum of (6a). The latter shows signals corresponding to the presence of one σ-bonded Pt·CH$_2$·CH[C(Me):O] group with $J(^{195}\mathrm{Pt}-^{13}C\mathrm{H_2})$ 617 Hz, and a co-ordinated cod ligand. Complexes (6) are structurally related to $[\mathrm{Pt\{O\cdot O\cdot C(O)\cdot O\}(PPh_3)_2}]$[14] and $[\mathrm{Pt(O\cdot O\cdot CMe_2\cdot O)(PPh_3)_2}]$,[15] prepared from CO$_2$ or acetone, respectively, and $[\mathrm{Pt(O\cdot O)(PPh_3)_2}]$. These peroxy-derivatives show a characteristic $\nu_{max.}$(O–O) near 780 cm^{-1}.[14] The i.r. bands in the spectra of (6a) and (6b) at 759m and 758m cm^{-1}, respectively, absorptions which are absent in the spectra of the precursor (1), may also be due to $\nu_{max.}$(O–O).

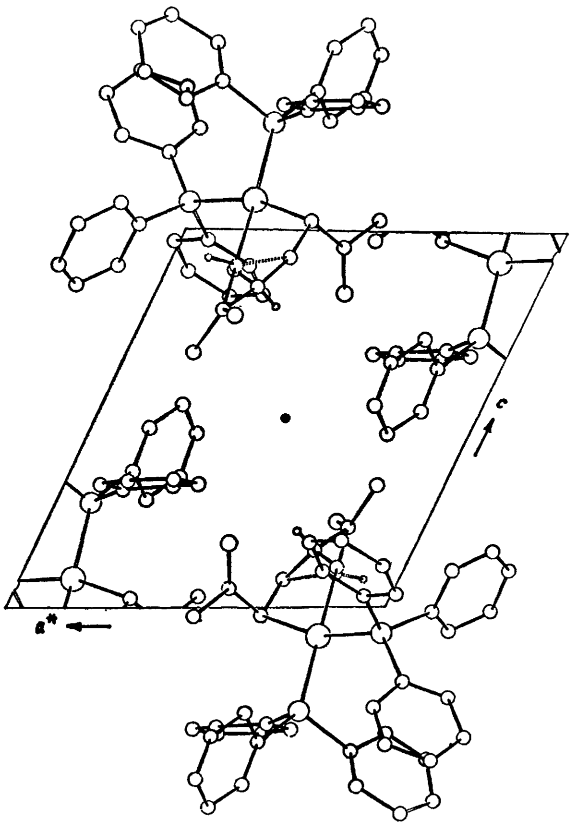
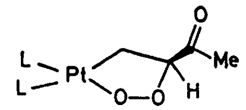
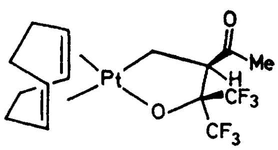


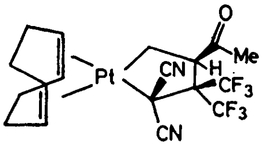
FIGURE 3 Contents of the triclinic unit cell seen in projection looking towards the origin



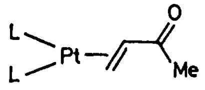
(6a) 2L = cod
(6b) L = CNBu^t



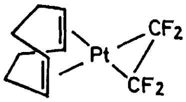
(7)



(8)



(9a) L = PPh3
(9b) L = CNBu^t



(10)

The electrophilic unsaturated compounds (CF$_3$)$_2$C:O and (CF$_3$)$_2$C:C(CN)$_2$ also react with (1) to give the five-membered ring complexes (7) and (8), the spectroscopic properties of which are in accord with the structures proposed. Thus the ^{19}F n.m.r. spectrum of (7) shows two quartet signals at 72.4 and 76.1 p.p.m. [J(FF) 9.5 Hz] with the former resonance displaying only weak coupling with platinum [$J(^{195}\mathrm{Pt}-^{19}\mathrm{F})$ 11.3 Hz]. This low coupling constant and the chemical shifts correspond to a Pt·O·C(CF$_3$)$_2$· group, as in $[\mathrm{Pt\{O\cdot C(CF_3)_2\cdot C(CF_3)_2\cdot O\}(PEt_3)_2}]$ [δ 71.3 p.p.m., J(PtF) 0 Hz].[16] In complexes containing the Pt·C(CF$_3$)$_2$·O· unit the ^{19}F chemical shifts occur at lower field (*ca.* 67 p.p.m.) with J(PtF) 68—80 Hz.[12,13] Similarly, the ^{19}F chemical shifts and coupling constants for (8) correspond very closely with those observed in the spectrum of the 1 : 1 adduct of [Pt(cod)$_2$] with (CF$_3$)$_2$C:C(CN)$_2$ which contains a Pt·C(CN)$_2$·C(CF$_3$)$_2$·CH fragment.[17] The ^{13}C n.m.r. spectrum of (7) also supports the structural formulation, with resonances assignable to the cod ligand and to the

$\overline{\mathrm{Pt\{CH_2{\cdot}CH[C(Me){:}O]{\cdot}C(CF_3)_2{\cdot}O}}\}$ group, *viz.* for the latter 204.5 (C=O), 124.4 and 124.1 [q, CF_3, J(CF) 290 Hz], 62.0 (CH), 30.5 (CH_3), and 27.7 p.p.m. [$CH_2{\cdot}Pt$, J(PtC) 693 Hz]. The non-observation of a resonance due to $C(CF_3)_2$ is not unexpected since the ^{13}C spectrum was not ^{19}F-decoupled.

Reaction of (1) with PPh_3 gives the complex $[\mathrm{Pt\{\eta^2\text{-}CH_2{:}CHC(Me){:}O\}(PPh_3)_2}]$ (9a), previously prepared by treating $[Pt(PPh_3)_3]$ with mvk.[9] Complex (9a) has an AB-type ^{31}P n.m.r. spectrum, with resonances at −30.26 and −29.61 p.p.m. [J(PP) 40.3, J(PPt) 4 091 and 3 622 Hz] in accord with a rigid platinacyclopropane structure. Complex (1) similarly reacts with $CNBu^t$ to form $[\mathrm{Pt\{\eta^2\text{-}CH_2{:}CHC(Me){:}O\}(CNBu^t)_2}]$ (9b), an air-sensitive complex better prepared from mvk and the cluster compound $[Pt_3(CNBu^t)_6]$.[18] Like (9a), the i.r. spectrum of (9b) shows a band (1 635vs cm^{-1}) indicating that the carbonyl groups is not co-ordinated to platinum. The unidentate nature of mvk with η^2 bonding *via* the vinyl group in (9b) is further substantiated by the ^{13}C spectrum. In diethyl ether or benzene the complex appears to dissociate partially into $[Pt_3(CNBu^t)_6]$ (orange solution) and mvk, but this can be reversed by addition of the ketone.

In contrast to the reactions of (1) with $(CF_3)_2C{:}O$ or $(CF_3)_2C{:}C(CN)_2$, which afford platinacyclopentane ring systems, tetrafluoroethylene gives the complex $[\overline{\mathrm{Pt(CF_2{\cdot}CF_2}})(\mathrm{cod})]$ (10). This result is of considerable interest because $[Pt(cod)_2]$ and tetrafluoroethylene react to give the octafluorodiplatinacyclohexane complex $[\mathrm{Pt_2(\mu\text{-}CF_2{\cdot}CF_2)_2(cod)_2}]$ [3] rather than the platinacyclopropane species (10). Although (10) is stable in the solid state, it dimerises to give $[\mathrm{Pt_2(\mu\text{-}CF_2{\cdot}CF_2)_2(cod)_2}]$ in many solvents. In diethyl ether this process is complete in *ca.* 2 h. In benzene, formation of the diplatinum complex is slow so that the ^{19}F n.m.r. spectrum of (10) can be readily examined in this solvent. The single resonance observed at 124.3 p.p.m. [J(PtF) 414 Hz] is characteristic of a $[\overline{\mathrm{Pt(CF_2{\cdot}CF_2}})\mathrm{L_2}]$ complex.[19-21] Complex (10) reacts with $CNBu^t$ at −20 °C to give $[\overline{\mathrm{Pt(CF_2{\cdot}CF_2}})(\mathrm{CNBu^t})_2]$ (11). The latter dimerises more slowly than (10), giving *ca.* 50% conversion into $[\mathrm{Pt_2(\mu\text{-}CF_2{\cdot}CF_2)_2(CNBu^t)_4}]$ after 12 h in diethyl ether at room temperature.

In conclusion, it is interesting to contrast the results described herein leading to the formation of the complexes (1) and (3) with the reaction of methyl vinyl ketone with $[Ni(cod)_2]$. The latter affords a product formulated as $[Ni(mvk)_2]$ [22] the nature of which is far from clear.

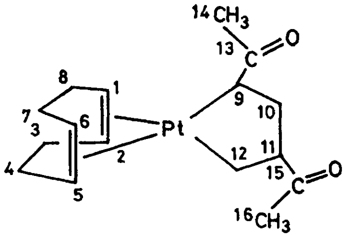
EXPERIMENTAL

N.m.r. spectra (^1H, ^{19}F, hydrogen-1 decoupled ^{13}C and ^{31}P) were recorded on JEOL PFT and PS 100 spectrometers, with ^{13}C shifts relative to $SiMe_4$ (0.0 p.p.m.), ^{19}F shifts relative to CCl_3F (0.0 p.p.m.), and ^{31}P shifts relative to H_3PO_4 (external). Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer 457 spectrophotometer. 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. Methyl vinyl ketone was dried over potassium carbonate for 2 d, and distilled prior to use. Light petroleum refers to that fraction having b.p. 40—60 °C.

*Reactions of Bis(cyclo-octa-*1,5-*diene)platinum with Methyl Vinyl Ketone.*—A diethyl ether solution (5 cm^3) of methyl vinyl ketone (70 mg, 1 mmol) was treated with $[Pt(cod)_2]$ (205 mg, 0.5 mmol) at −20 °C. Within 5 min a heavy yellow precipitate formed. The mixture was cooled to −70 °C and the supernatant liquid removed. The product was washed with light petroleum (3 × 10 cm^3) at −70 °C and dried *in vacuo* (1 min at 25 °C, and 2 h at −50 °C) to give yellow *crystals* of $[Pt(mvk)_2(cod)]$ (1) (155 mg, 70%) (Found: C, 43.3; H, 5.6. $C_{16}H_{24}O_2Pt$ requires C, 43.3; H, 5.4%); $\nu_{max.}$ at 1 655vs and 1 643vs (C=O), 1 342m, 1 333m, 1 265w, 1 205s, 1 196 (sh), 1 169s, 1 085 (sh), 1 077m, 1 023w, 965w, 935 (sh), 927m, 864w, 832w, 804w, 792w, 774w, and 600m,br cm^{-1}.

In another reaction, using an excess of methyl vinyl ketone (350 mg, 5 mmol) in diethyl ether (10 cm^3) and $[Pt(cod)_2]$ (205 mg, 0.5 mmol) at −20 °C, a yellow solution [complex (1)] formed initially which after *ca.* 15 min gave an almost colourless solution. The latter was frozen at −196 °C and then warmed to −70 °C giving a white powder. Supernatant liquid was removed after 0.5 h and the solid washed with light petroleum (2 × 10 cm^3) and dried *in vacuo* (2 h, −10 °C) to give white *microcrystals* of $[Pt(mvk)_3]$ (2) (150 mg, 75%) (Found: C, 36.1; H, 4.7. $C_{12}H_{18}O_3Pt$ requires C, 35.5; H, 4.4); $\nu_{max.}$ at 1 660vs,br (C=O), 1 367vs,br, 1 252s, 1 240vs, 1 211s, 1 060m, 1 017m, 980m, 940m, 930 (sh), 802w, 762w, 598w, 568m, and 505m cm^{-1}. The ^1H n.m.r. spectrum ([$^2H_8$]toluene, −30 °C) was very complicated with multiplets at τ 6.0 [3 H, CH, J(PtH) *ca.* 60], 6.8 [6 H, CH_2, J(PtH) *ca.* 70 Hz], and 8.6 (9 H, CH_3).

Isomerisation of Complex (1) *to the Platinacyclopentane Complexes* (3).—Light petroleum (20 cm^3) was added to (1) (1 mmol) in diethyl ether (40 cm^3) at −10 °C, and the solution cooled in a refrigerator overnight. This produced crystals; the volume of solution was reduced (*ca.* 30 cm^3) *in vacuo* and light petroleum (20 cm^3) added. Cooling produced more solid which was washed (2 × 10 cm^3 light petroleum) and dried *in vacuo* affording white *crystals* of (3) (260 mg, 59%), m.p. 87—89 °C (Found: C, 43.0; H, 5.7. $C_{16}H_{24}O_2Pt$ requires C, 43.3; H, 5.4%); $\nu_{max.}$ at 1 694vs and 1 636vs (C=O), 1 526w, 1 434s, 1 425 (sh), 1 415m, 1 364s, 1 344s, 1 319m, 1 272m, 1 236vs, 1 230vs, 1 187vw, 1 170m, 1 152w, 1 126w, 1 094w, 1 085w, 1 067m, 1 005m, 997sh, 985w, 956s, 904w, 867m, 851w, 835m, 804 (sh), 794m, 777m, 650m, 624w, 563m, 554m, 517w, 473w, 462w, 435w, and 417w cm^{-1}. The ^1H n.m.r. spectrum in C_6D_6 showed resonances at τ 4.60 (m, 1 H), 5.76 [m, 4 H, CH⁚CH, J(PtH) 48 Hz], 6.80 (m, 1 H), 7.50 (m, 2 H), 7.96 (s, 3 H, CH_3),



8.06 (s, 3 H, CH_3), 8.06 (m, 2 H), 8.14 (m, br, 4 H, $CH_2{\cdot}CH_2$), and 8.96 (m, 4 H, $CH_2{\cdot}CH_2$). The ^{13}C n.m.r. spectrum in C_6D_6 solution showed resonances at 209.9 [C^{13}, *J*(PtC) 98], 209.3 [C^{15}, *J*(PtC) 35], 104.8 [$C^{5,6}$, *J*(PtC) 50], 95.7 and 94.9 [C^1 and C^2, *J*(PtC) 82 and 78], 60.2 [C^9, *J*(PtC) 642], 59.8 (C^{11}), 38.6 (C^{10}), 35.4 [C^{12}, *J*(PtC) 778 Hz], 31.6, 30.3, 28.5, 28.1 (C^3, C^4, C^7, and C^8), and 28.1 and 27.2 p.p.m. (C^{14} and C^{16}).

When complex (1) (1 mmol) was allowed to rearrange in diethyl ether (10 cm^3) at −10 °C in the presence of ethylene gas to solubilise (1) a pale yellow solution was formed. Cooling of this mixture in its Schlenk tube for 4 d at −10 °C gave white *needles* of a complex (200 mg, 45%), similar to (3) (see text), m.p. 92—94 °C (Found: C, 42.7; H, 5.4. $C_{16}H_{24}O_2Pt$ requires C, 43.3; H, 5.4%); $\nu_{max.}$ at 1 685vs and 1 638vs (C=O), 1 430m, 1 362s, 1 352vs, 1 307m, 1 260m, 1 250s, 1 232vs, 1 209m, 1 167m, 1 122w, 1 078w, 1 049w, 999 (sh), 990m, 979 (sh), 950m, 892w, 862m, 841w, 828m, 790m, 770m, 738m, 640w, 590m, 569m, 553m, and 409w cm^{-1}. The ^1H n.m.r. spectrum in C_6D_6 showed resonances at τ 4.64 (m, 1 H), 5.76 [m, 4 H, CH:CH, *J*(PtH) 46 Hz], 6.80 (m, 1 H), 7.52 (m, 2 H), 7.96 (s, 3 H, CH_3), 8.06 (s, 3 H, CH_3), 8.06 (m, 2 H), 8.20 (m, 4 H, $CH_2{\cdot}CH_2$), and 8.48 (m, 4 H, $CH_2{\cdot}CH_2$). The ^{13}C n.m.r. spectrum in C_6D_6 solution showed resonances at 209.7 [C^{13}, *J*(PtC) 98], 209.3 [C^{15}, *J*(PtC) 38], 104.9 [$C^{5,6}$, *J*(PtC) 50], 95.5 and 94.8 [C^1 and C^2, *J*(PtC) 81 and 76], 60.4 [C^9, *J*(PtC) 644], 59.8 (C^{11}), 38.8 (C^{10}), 35.6 [C^{12}, *J*(PtC) 780 Hz], 31.6, 30.3, 28.5, and 28.2 (C^3, C^4, C^7, and C^8), and 28.0 and 27.2 p.p.m. (C^{14} and C^{16}).

Displacement of the Cyclo-octa-1,5-*diene Ligand from Complex* (3).—(*a*) *With t-butyl isocyanide*. A solution of (3) (220 mg, 0.5 mmol) in diethyl ether (15 cm^3) was treated with t-butyl isocyanide (90 mg, 1.1 mmol). After stirring (5 min), solvent was removed *in vacuo*, and the residue was dissolved in the minimum amount of diethyl ether to which light petroleum (20 cm^3) had been added. Cooling afforded white *crystals* of (4) (90%), m.p. 102—104 °C (Found: C, 43.1; H, 6.1; N, 5.6. $C_{18}H_{30}N_2OPt$ requires C, 43.1; H, 6.0; N, 5.6%); $\nu_{max.}$ at 2 202vs and 2 176vs (N≡C), 1 700vs and 1 647vs (C=O), 1 352s, 1 270w, 1 234s, 1 200s,br, 1 169s, 1 127w, 970m, 871w, 830w, 762w, 742w, 642w, 540w, and 526m cm^{-1}. The ^1H n.m.r. spectrum in C_6D_6 showed resonances at τ 6.50, 7.20, and 7.70 (m, 6 H), 7.74 (s, 3 H, CH_3), 7.96 (s, 3 H, CH_3), 8.90 (s, 9 H, CH_3), and 9.14 (s, 9 H, CH_3). The ^{13}C n.m.r. spectrum in C_6D_6 solution showed resonances at 211.8 [C^{13}, *J*(PtC) 86], 211.0 [C^{15}, *J*(PtC) 29], 61.3 [C^{11}, *J*(PtC) 11], 57.1 (CMe_3), 53.3 [C^9, *J*(PtC) 534], 38.1 [C^{10}, *J*(PtC) 9], 29.7 (CMe_3), 28.9 and 27.5 (C^{14} and C^{16}), and 24.2 p.p.m. [C^{12}, *J*(PtC) 613 Hz].

(b) *With triphenylphosphine*. A solution of (3) (220 mg, 0.5 mmol) in diethyl ether (15 cm^3) was treated with PPh_3 (262 mg, 1 mmol) giving a quantitative yield of white crystals (5) (washed with 2 × 10 cm^3 light petroleum and dried *in vacuo*), m.p. 162—166 °C (decomp.) (Found: C, 61.3; H, 4.9. $C_{44}H_{42}O_2P_2Pt$ requires C, 61.3; H, 4.9%); $\nu_{max.}$ at 1 677vs and 1 632s (C=O), 1 347s, 1 305w, 1 262w, 1 183w, 1 170m, 1 159 (sh), 1 093s, 1 029w, 1 000w, 970w, 758s, 740s, 705vs, 695vs, 538s, 522vs, 512s, and 496s cm^{-1}. The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 2.52 and 2.88 (m, 30 H, Ph), 7.10 and 7.60 (m,br, 3 H), 7.90 (s, 3 H, CH_3), 8.20 (s, 3 H, CH_3), and 8.22 and 8.80 (m, 3 H). The ^{31}P n.m.r. spectrum in $CDCl_3$ showed AB-type resonances at −25.93 and −25.07 p.p.m. with platinum satellites [*J*(PPt) 2 405 and 1 983, *J*(PP) 10.5 Hz].

Reactions of (*Cyclo-octa*-1,5-*diene*)*bis*(*methyl vinyl ketone*)-*platinum* (1).—For the following reactions, complex (1) (0.5 mmol) was prepared *in situ* at −20 °C by adding $[Pt(cod)_2]$ (205 mg, 0.5 mmol) to a solution of methyl vinyl ketone (0.2 mmol excess) in diethyl ether.

(*a*) *With oxygen*. A solution of (1) (0.5 mmol) in diethyl ether (20 cm^3) was added to light petroleum (50 cm^3) which had previously been vigorously stirred in air. After 5 min a pale yellow precipitate began to form. The mixture was stirred (12 h) in air, filtered, and the residue crystallised from dichloromethane–light petroleum as pale yellow *microcrystals* of (6a) (180 mg, 90%), m.p. 122—130 °C (decomp.) (Found: C, 35.4; H, 4.5; O, 11.8. $C_{12}H_{18}O_3Pt$ requires C, 35.6; H, 4.4; O, 11.9%); $\nu_{max.}$ at 3 160m,br, 1 680vs (C=O), 1 367m, 1 344w, 1 319w, 1 240m, 1 179s, 1 122vs, 1 112 (sh), 1 100 (sh), 1 039 (sh), 1 030w, 1 014w, 1 001m, 937vs, 922 (sh), 910m, 876m, 856w, 831w, 824w, 790m, 778 (sh), 759m,br, 699w, 623s, 603s, 552w, 492w, 480w, and 441w, cm^{-1}. The ^1H n.m.r. spectrum in CD_2Cl_2 solution showed resonances at τ 4.60 [m, 2 H, CH:CH, *J*(PtH) 40], 5.60 [m, 2 H, CH:CH, *J*(PtH) 52 Hz], 6.90 (m, 1 H), 7.1—8.3 (m,br, 10 H, CH_2), and 8.68 (s, 3 H, CH_3). The ^{13}C n.m.r. spectrum in CD_2Cl_2 solution showed resonances at 111.4 [CH:CH *trans* to CH_2Pt, *J*(PtC) 61], 96.3 (CH), 78.4 [CH:CH *trans* to O, *J*(PtC) 190], 37.5 [CH_2Pt, *J*(PtC) 617], 32.1 and 28.2 [CH_2 of cod, *J*(PtC) 17 and 10 Hz], and 26.1 p.p.m. (CH_3).

t-Butyl isocyanide (166 mg, 2 mmol) was added to a vigorously stirred suspension of (6a) (200 mg, 0.5 mmol) in diethyl ether (10 cm^3). The pale yellow suspension turned dark yellow and after 5 min the solvent was decanted and the powder washed with diethyl ether and light petroleum (2 × 10 cm^3). Recrystallisation from dichloromethane–light petroleum gave pale yellow *microcrystals* of (6b) (105 mg, 45%), m.p. 120—124 °C (decomp.) (Found: C, 36.4; H, 5.5; N, 5.9; O, 11.0. $C_{14}H_{24}N_2O_3Pt$ requires C, 36.3; H, 5.2; N, 6.0; O, 10.4%); $\nu_{max.}$ at 3 140s,br, 2 230vs, and 2 195vs (N≡C), 1 682vs (C=O), 1 400w, 1 345w, 1 318w, 1 240m, 1 212s, 1 178s, 1 127s, 1 112 (sh), 1 091w, 1 029w, 1 000w, 940vs, 912w, 908w, 870w, 812w, 798w, 758m,br, 623vs, 607 (sh), 541m, 528m, 486m, and 456w, cm^{-1}.

(*b*) *With hexafluoroacetone*. A solution of (1) (0.5 mmol) in diethyl ether (20 cm^3) was placed in a Schlenk tube attached to a vacuum line, cooled to −196 °C, and evacuated. Hexafluoroacetone (270 mg, 1.5 mmol) was condensed into the tube which was then removed from the vacuum line and warmed to room temperature. Solvent was partially (10 cm^3) removed *in vacuo*, light petroleum added (20 cm^3), and the solution cooled to −10 °C (3 h), affording white *crystals* of (7) (175 mg, 64%), m.p. 146—150 °C (decomp.) (Found: C, 33.5; H, 3.4. $C_{15}H_{18}F_3O_2Pt$ requires C, 33.4; H, 3.3%); $\nu_{max.}$ at 1 711s (C=O), 1 370m, 1 342w, 1 313m, 1 290s, 1 268s, 1 228 (sh), 1 219s, 1 201s, 1 190s, 1 162s, 1 108s, 1090s, 1 011m, 987m, 963w, 948s, 900w, 871w, 828w, 811w, 800w, 770w, 761m, 726s, 690w, 660w, 593m, 568w, 553w, 539w, 489w, and 471w, cm^{-1}. The ^1H n.m.r. spectrum in $CDCl_3$ solution showed resonances at τ 4.46 [m, 2 H, CH:CH, *J*(PtH) 36], 5.76 [m, 2 H, CH:CH, *J*(PtH) 68], 6.50 [m, 1 H, *J*(HH) 7], 7.48 (m, 8 H, CH_2CH_2), 7.76 (s, 3 H, CH_3), and 7.68 [m, 2 H, CH_2Pt, *J*(PtH) 92 Hz]. The ^{19}F n.m.r. spectrum in $CDCl_3$ solution showed resonances at 72.4 [q, 3 F, CF_3, *J*(FF) 9.5, *J*(PtF) 11.3] and 76.1 p.p.m. [q, 3 F, CF_3, *J*(FF) 9.5 Hz]. The ^{13}C n.m.r. spectrum in $CDCl_3$ solution showed resonances at 204.5 (C=O), 124.4 and 124.1 [q, CF_3, *J*(CF) 290], 111.7 [CH:CH, *trans* to CH_2Pt, *J*(PtC) 41], 76.9 and 76.4 [CH:CH *trans* to O, *J*(PtC) 112 and 115], 62.0 [*C*·C(O)Me], 31.9 and 31.4 [CH_2, *J*(PtC) 21], 30.5 (CH_3), 27.7 [CH_2Pt, *J*(PtC) 693], and 27.7 and 27.4 p.p.m. [CH_2, *J*(PtC) 15 and 21 Hz].

(*c*) *With* 1,1-*dicyano*-2,2-*bis*-(*trifluoromethyl*)*ethylene*. A solution of (1) (0.5 mmol) in diethyl ether (10 cm^3) was treated with $(CF_3)_2C{:}C(CN)_2$ (234 mg, 1 mmol) at −20 °C. The mixture was warmed to room temperature for 10 min, the volume reduced to *ca*. 5 cm^3 *in vacuo*, and light petroleum (20 cm^3) added. Cooling to −10 °C gave white *crystals* of complex (8) (175 mg, 60%), m.p. 196—198 °C (Found: C, 37.1; H, 3.3; N, 4.8. $C_{18}H_{18}F_6N_2OPt$ requires C, 36.8; H, 3.1; N, 4.8%); $\nu_{max.}$ 2 238m and 2 219m (C≡N), 1 719s (C=O), 1 361m, 1 349w, 1 330w, 1 319w, 1 267 (sh), 1 258s, 1 219 (sh), 1 210s, 1 190w, 1 179m, 1 170m, 1 150m, 1 138m, 1 129m, 1 098w, 1 030w, 1 018w, 1 009w, 958s, 914w, 904w, 871w, 859w, 836w, 805w, 798w, 788w, 765m, 741s, 703w, and 586w cm^{-1}. The ^1H n.m.r. spectrum in $CDCl_3$ solution showed resonances at τ 4.52 [m, 2 H, CH:CH, *J*(PtH) 32], 4.90 [m, 2 H, CH:CH, *J*(PtH) 68], 6.54 (m, 1 H), 7.36 (m, 4 H, CH_2), 7.60 (m, 4 H, CH_2), 7.72 (s, 3 H, CH_3), and 8.24 (m, 2 H, CH_2Pt). The ^{19}F n.m.r. spectrum in $CDCl_3$ solution showed resonances at 59.1 [q, 3 F, CF_3, *J*(FF) 10.5] and 63.5 p.p.m. [q, 3 F, CF_3, *J*(FF) 10.5 Hz].

(*d*) *With triphenylphosphine*. A solution of (1) 0.5 mmol) in diethyl ether (10 cm^3) at −10 °C was treated with PPh_3 (262 mg, 1 mmol) to give immediately a white solid which was washed with diethyl ether and light petroleum and dried *in vacuo* to afford white *crystals* of complex (9a) (460 mg, 95%), m.p. 144—150 °C (decomp.) (Found: C, 60.1; H, 4.6; P, 7.2. Calc. for $C_{34}H_{42}OP_2Pt$: C, 60.8; H, 4.6; P, 7.9%); $\nu_{max.}$ at 3 041m, 1 647vs (C=O), 1 479s, 1 434vs, 1 312w, 1 183s, 1 163w, 1 102s, 1 076w, 1 067w, 1 035m, 1 006m, 954m, 926w, 881w, 857w, 768m, 756s, 706vs, 620w, 604w, 551s, 534s, 523vs, 518vs, 509vs, 464m, and 431m cm^{-1}. The ^1H n.m.r. spectrum showed resonances at 2.84 (m, 30 H, C_6H_5), 6.50 (m,br, 1 H, CH), 7.92 (m,br, 2 H, CH_2), and 8.62 (s, 3 H, CH_3). The ^{31}P n.m.r. spectrum in C_6D_6 solution showed AB-type resonances at −30.26 and −29.61 p.p.m. [*J*(PP) 40.3, *J*(PPt) 4 091 and 3 622 Hz].

(*e*) *With tetrafluoroethylene*. A Schlenk tube containing (1) (1 mmol) in diethyl ether (20 cm^3) was attached through a stopcock to a vacuum line and cooled to −196 °C and evacuated. Tetrafluoroethylene (300 mg, 3 mmol) was added and the tube warmed to room temperature. After a few minutes a yellow precipitate formed. Solvent was decanted, light petroleum (20 cm^3) added, and the mixture cooled giving, after washing with light petroleum, pale yellow *crystals* of $[Pt(C_2F_4)(cod)]$ (10) (255 mg, 64%) (Found: C, 29.5; H, 3.1. $C_{10}H_{12}F_4Pt$ requires C, 29.8; H, 3.0%). This complex, although stable as a solid, dimerises in various solvents to give the known complex $[Pt_2(\mu\text{-}CF_2{\cdot}CF_2)_2(cod)_2]$, which was also recovered from the mother liquors of the above reaction and identified by comparison of its i.r. spectrum with an authentic sample.[3] Complex (10) dimerises only slowly in benzene, enabling measurement of its ^{19}F n.m.r. spectrum which showed a signal at 124.3 p.p.m. [*J*(PtF) 414 Hz]. The i.r. spectrum of (10) showed $\nu_{max.}$ at 1 423m, 1 392s, 1 346w, 1 320m, 1 239w, 1 189w, 1 095 (sh), 1 087vs, 1 060vs, 986w, 862m, 849s, 826vs, 797vw, 778w, 760vw, and 616m, cm^{-1}.

Treatment of (10) (200 mg, 0.5 mmol) with $CNBu^t$ (166 mg, 2 mmol) at −20 °C in diethyl ether (10 cm^3) gave, after addition of light petroleum (20 cm^3) and removal of supernatant liquid, pale yellow *microcrystals* of $[Pt(C_2F_4)(CNBu^t)_2]$ (11) (160 mg, 70%) (Found: C, 31.4; H, 4.3; N, 6.0. $C_{12}H_{18}F_4N_2Pt$ requires C, 31.2; H, 3.9; N, 6.1%); $\nu_{max.}$ at 2 210vs and 2 185vs (N≡C), 1 395m, 1 240m, 1 200s, 1 081vs, 1 063vs, 940w, 868w, 836 (sh), 820vs, 812 (sh), 608m, 562w, 531w, and 521w cm^{-1}. The ^{19}F n.m.r. spectrum in C_6H_6 solution showed a resonance at 129.5 p.p.m. [*J*(PtF) 294 Hz].

Reaction of Tris-μ-(*t-butyl isocyanide*)-*tris*(*t-butyl isocyanide*)-triangulo-*triplatinum with Methyl Vinyl Ketone*.—A solution of $[Pt_3(CNBu^t)_6]$ (200 mg, 0.18 mmol) in diethyl ether (10 cm^3) was treated with methyl vinyl ketone (500 mg, 7 mmol) for 30 min. The volume of the almost colourless solution was reduced to *ca*. 5 cm^3, light petroleum (20 cm^3) was added, and the mixture cooled in a refrigerator for 3 d to give white *crystals* of (9b) (120 mg, 44%) (Found: C, 39.1; H, 5.9; N, 6.4. $C_{14}H_{24}N_2OPt$ requires C, 39.0; H, 5.9; N, 6.5%); $\nu_{max.}$ at 2 172vs and 2 136vs (N≡C), 1 635vs (C=O), 1 338m, 1 238m, 1 197vs, 1 181vs, 1 142m, 1 157m, 963 (sh), 953s, 885m, 874m, 805w, 777w, 761w, 746m, 642w, 603w, 541m, 520s, 511 (sh), 457m, and 407w cm^{-1}. The ^1H n.m.r. spectrum in C_6D_6 solution showed resonances at τ 6—7.5 (m, 3 H, $CH_2{:}CH$), 7.72 (s, 3 H, CH_3), and 9.08 (s, 18 H, Bu^t). The ^{13}C n.m.r. spectrum in C_6D_6 solution showed resonances at 200.9 [C=O, *J*(PtC) 46], 56.5 (*C*Me_3), 51.5 [CH, *J*(PtC) 198], 29.9 (C*Me*$_3$), 27.7 (CH_3), and 25.5 p.p.m. [CH_2, *J*(PtC) 269 Hz].

Crystal-structure Determination of $[Pt\{CH_2{\cdot}CH[C(Me){:}O]{\cdot}CH_2{\cdot}CH[C(Me){:}O]\}(PPh_3)_2]$ (5).—Crystals of (5) grow as colourless prisms; that for data collection was of dimensions 0.10 × 0.23 × 0.40 mm, and diffracted intensities were recorded at room temperature for $2\theta \leqslant 60°$ on a Syntex $P2_1$ four-circle diffractometer. Of the total 10 245 recorded intensities, 8 596 had $I \geqslant 2\sigma(I)$, where $\sigma(I)$ is the standard deviation 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 [23] available for the CDC 7600 at the London Computing Centre.

Crystal data. $C_{44}H_{42}O_2P_2Pt$, $M = 861.5$, Triclinic, $a = 10.755(3)$, $b = 18.172(3)$, $c = 11.780(2)$ Å, $\alpha = 110.26(1)$, $\beta = 114.89(2)$, $\gamma = 95.77(2)°$, $U = 1\,875.3$ Å^3, $D_m = 1.49$ (flotation), $Z = 2$, $D_c = 1.52$ g cm^{-3}, $F(000) = 860$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 40.6$ cm^{-1}, space group $P\bar{1}$ (no. 2).

Structure solution and refinement. The platinum and phosphorus atoms were located from a Patterson synthesis, and all the remaining atoms (including hydrogen) by successive electron-density difference syntheses. The structure was refined by blocked-matrix least squares with anisotropic thermal parameters for all the non-hydrogen atoms except the two disordered atoms C(9)* and C(901)*. The hydrogen atoms were incorporated in the structure-factor calculations, but neither their positional nor thermal parameters were refined [U_{iso}(H) 6.33]. A disorder in the position of one of the carbon atoms of the platinacyclopentane ring was shown, by refinement of a population parameter, to correspond to a 0.5 : 0.5 distribution of the electron density between the two sites. Refinement converged at *R* 0.044 (*R′* 0.041) with a mean shift-to-error ratio in the last cycle of 0.2. A weighting scheme of the form $w = 1/\sigma^2(F_o)$, where $\sigma(F_o)$ is the estimated error in the observed structure factor based on counting statistics only, gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >0.4 or <-0.4 e Å^{-3}. Scattering factors were from ref. 24 for C, O, and P, ref. 25 for H, and ref. 26 for Pt, including corrections for the effects of anomalous dispersion for Pt($\Delta f'$ -2.352, $\Delta f''$ 8.388) and P($\Delta f'$ 0.096, $\Delta f''$ 0.095). Atomic positional parameters are in Table 1, interatomic distances in Table 2, and some least-squares planes, torsion angles, and twist angles in Table 3. Observed and calculated structure factors, all thermal parameters, positional parameters for hydrogen atoms, and details of the planarities of the phenyl rings are listed in Supplementary Publication No. SUP 22375 (38 pp.).*

We thank the C.N.R.S.–Royal Society European Exchange Programme for the award of a Fellowship (to M. P.), Zonta International for an Amelia Earhart Fellowship (to P. M.), and the S.R.C. for support.

[8/912 *Received*, 16*th May*, 1978]

REFERENCES

[1] M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 271.

[2] M. T. Chicote, M. Green, J. L. Spencer, F. G. A. Stone, and J. Vicente, *J. Organometallic Chem.*, 1977, **137**, C8.

[3] M. Green, A. Laguna, J. L. Spencer, and F. G. A. Stone *J.C.S. Dalton*, 1977, 1010.

[4] G. K. Barker, M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1976, **98**, 3373; *J.C.S. Dalton*, 1978, 1839.

[5] M. Giffard and P. Dixneuf, *J. Organometallic Chem.*, 1975, **85**, C26.

[6] W. A. Herrmann, *Chem. Ber.*, 1975, **108**, 486.

[7] R. B. King and A. Fronzaglia, *Inorg. Chem.*, 1966, **5**, 1837.

[8] R. E. Moriarty, R. D. Ernst, and R. Bau, *J.C.S. Chem. Comm.*, 1972, 1242.

[9] S. Cenini, R. Ugo, and G. La Monica, *J. Chem. Soc.* (*A*), 1971, 409.

[10] B. E. Mann, *Adv. Organometallic Chem.*, 1974, **12**, 193.

[11] V. G. Albano, P. Bellon, and M. Sansoni, *J. Chem. Soc.* (*A*), 1971, 2420.

[12] J. Browning, H. D. Empsall, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 381.

[13] F. G. A. Stone, *Pure Appl. Chem.*, 1972, **30**, 551.

[14] P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, 1970, **92**, 5873.

[15] R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Comm.*, 1968, 1498.

[16] H. D. Empsall, Ph.D. Thesis, Bristol University, 1971.

[17] M. Green, J. A. K. Howard, A. Laguna, L. E. Smart, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 278.

[18] M. Green, J. A. K. Howard, M. Murray, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 1509.

[19] M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2525.

[20] R. D. W. Kemmitt and R. D. Moore, *J. Chem. Soc.* (*A*), 1971, 2472.

[21] P. K. Maples, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 388.

[22] R. Van der Linde and B. Bogdanović, *Proc. 4th Internat. Conf. Organometallic Chem.*, Bristol, 1969, Abstract U8.

[23] ' *X*-Ray ' Program System, University of Maryland, Technical Report TR-192, June 1972.

[24] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[25] R. F. Stewart, E. R. Davidson, and W. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[26] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.