Chemistry of Metallacyclobutanones. Part 1. Synthesis and Ring Inversion of some Highly Puckered Metallacyclobutan-3-one (Slipped Oxodimethylenemethane) Complexes of Platinum; Crystal Structure of 2,4-Bis(methoxycarbonyl)-1,1-bis(triphenylphosphine)platinacyclobutan-3-one Monohydrate †

David A. Clarke, Raymond D. W. Kemmitt,* Muhammed A. Mazid, Peter McKenna, David R. Russell,* Michael D. Schilling, and Lesley J. S. Sherry
Department of Chemistry, The University, Leicester LE1 7RH

The reactions of the carbonato-complexes $[Pt(CO_3)L_2]$ with esters of 3-oxopentanedioic acid, RCH_2COCH_2R, in warm ethanol afford, in high yield, the formally platinacyclobutan-3-one compounds $[\overline{Pt(CHRCOCHR})L_2]$ ($R = CO_2Me$, $L = PPh_3$, $AsPh_3$, $PMePh_2$ or PMe_2Ph; $2L = Ph_2PCH_2CH_2PPh_2$; $R = CO_2Et$, $L = PPh_3$, or $AsPh_3$; $R = CO_2Pr^n$, $L = PPh_3$, or $AsPh_3$). The compounds $[\overline{Pt(CHRCOCHR})L_2]$ ($R = CO_2Me$, $L = PPh_3$, $AsPh_3$, $PMePh_2$, or PMe_2Ph; $R = CO_2Et$, $L = PPh_3$ or $AsPh_3$) are also formed upon treatment of benzene solutions of $[PtL_4]$ with RCH_2COCH_2R in the presence of air. Using the latter method, the triphenylphosphine derivative $[\overline{Pt\{CH(CO_2Me)COCH}(CO_2Me)\}(PPh_3)_2]$ is often contaminated with the peroxo-ring compound $[\overline{Pt\{OOC(CH_2CO_2Me)_2O}\}(PPh_3)_2]$ which is the major product if the reaction is carried out in diethyl ether. The reaction of $[Pt(O_2)(PPh_3)_2]$ with $MeO_2CCH_2COCH_2CO_2Me$ in diethyl ether also gives the peroxo-ring compound. Treatment of $MeO_2CCH_2COCH_2CO_2Me$ with either $[Pt(\textit{trans}\text{-}PhCH{=}CHPh)(PPh_3)_2]$ in benzene in the presence of air, $[\overline{PtOOC(O)O}(PPh_3)_2]$ in ethanol, *cis*-$[Pt(OCOPh)_2(PPh_3)_2]$ in ethanol, or *cis*-$[PtCl_2(PPh_3)_2]$ and silver oxide in dichloromethane also affords $[\overline{Pt\{CH(CO_2Me)COCH}(CO_2Me)\}(PPh_3)_2]$. A single-crystal *X*-ray diffraction study has been carried out on $[\overline{Pt\{CH(CO_2Me)COCH}(CO_2Me)\}(PPh_3)_2]\cdot H_2O$ (3a). The crystals are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with $a = 17.59(1)$, $b = 12.736(6)$, $c = 10.27(1)$ Å, $\alpha = 118.2(1)$, $\beta = 94.7(1)$, and $\gamma = 74.0(1)°$. The structure has been refined to R 0.035 (R' 0.036) for 7 263 reflections with $I \geqslant 3\sigma(I)$. It can be considered to be based either upon a highly puckered platinacyclobutan-3-one ring [fold angle = 50.4(4)°] with a weak transannular Pt–C bond of 2.416(5) Å, or as a slipped η^3-oxodimethylenemethane compound. N.m.r. data (^1H, ^{13}C-$\{^1H\}$, and ^{31}P-$\{H\}$) are reported and variable-temperature ^1H n.m.r. data for the compounds $[\overline{Pt(CHRCOCHR})L_2]$ ($R = CO_2Me$, $L = PPh_3$ or $AsPh_3$) are interpreted in terms of inversion of the platinacyclobutan-3-one ring through a planar transition state. The magnitude of the platinum-195 coupling to the axial and equatorial ring hydrogens of the platinacyclobutan-3-one ring is dependent upon the orientation of of the CH bonds with respect to the square planar platinum function and the magnitudes of ^3J(*cis*-PPtCH) are controlled by the dihedral angle.

Interest in organometallic derivatives of the 1,3-dipoles trimethylenemethane and oxodimethylenemethane derives from their role as key intermediates in a range of cyclo-addition reactions.[1–5] However, although organometallic complexes of trimethylenemethane have been well characterised[6–9] there is little information on complexes containing the oxodimethylenemethane ligand (1). The structure of the allylic species (2) derived from reactions of α,α'-dibromoketones and iron carbonyls[4] is not known. The η^3-β-diketonato(2–)-complexes of palladium(II)[10,11] and platinum(II)[12] of the type $[M(\eta^3\text{-}CH_2COCHR)L_2]$ ($M = Pd$, $R = COMe$ or CO_2Et, L = N-donor ligand; $M = Pt$, $R = COMe$, L = P-donor ligand) have been considered to contain oxodimethylenemethane ligands on the basis of n.m.r. studies. However the oxodimethylenemethane species present in the iridium complex $[\overline{Ir(CH_2COCH_2})H(PMe_3)_3]$[13] probably co-ordinates to the metal as an η^2-ligand to give a planar iridacyclobutan-3-one ring in order for the iridium to maintain an 18-electron configuration.

In this paper we now describe the preparations and properties of some highly puckered metallacyclobutan-3-one complexes of platinum(II) (3). We have obtained evidence from a single-crystal *X*-ray structure determination of the triphenylphosphine complex (3a) and from other data which indicate that a bonding description of (3a) should include a contribution from the slipped η^3-oxodimethylenemethane structure (4) analogous to the proposed structure for the η^3-trimethylenemethane palladium complex (5a).[1] Preliminary accounts of some aspects of the work described herein have been reported.[14,15]

Results and Discussion

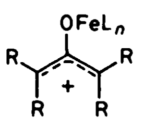
Reaction of $[Pt(PPh_3)_4]$ with dimethyl 3-oxopentanedioate (6a) in benzene at room temperature in the presence of air

---

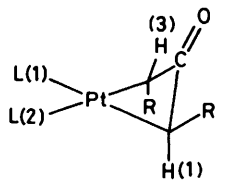
† [1,3-Bis(methoxycarbonyl)-2-oxopropane-1,3-diyl]bis(triphenylphosphine)platinum.

Supplementary data available (No. SUP 23963, 45 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

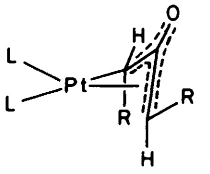
(1)



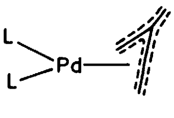
(2)



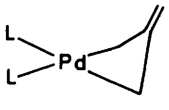
(3a) L = PPh_3, R = CO_2Me
(3b) L = PPh_3, R = CO_2Et
(3c) L = PPh_3, R = CO_2Pr^n
(3d) L = $AsPh_3$, R = CO_2Me
(3e) L = $AsPh_3$, R = CO_2Et
(3f) L = $AsPh_3$, R = CO_2Pr^n
(3g) L = $PMePh_2$, R = CO_2Me
(3h) L = PMe_2Ph, R = CO_2Me
(3i) 2L = $Ph_2PCH_2CH_2PPh_2$, R = CO_2Me



(4)



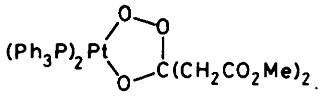
(5a)



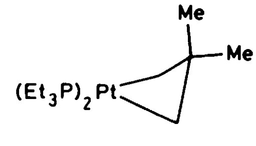
(5b)

RCH_2COCH_2R

(6a) R = CO_2Me
(6b) R = CO_2Et
(6c) R = CO_2Pr^n



(7)

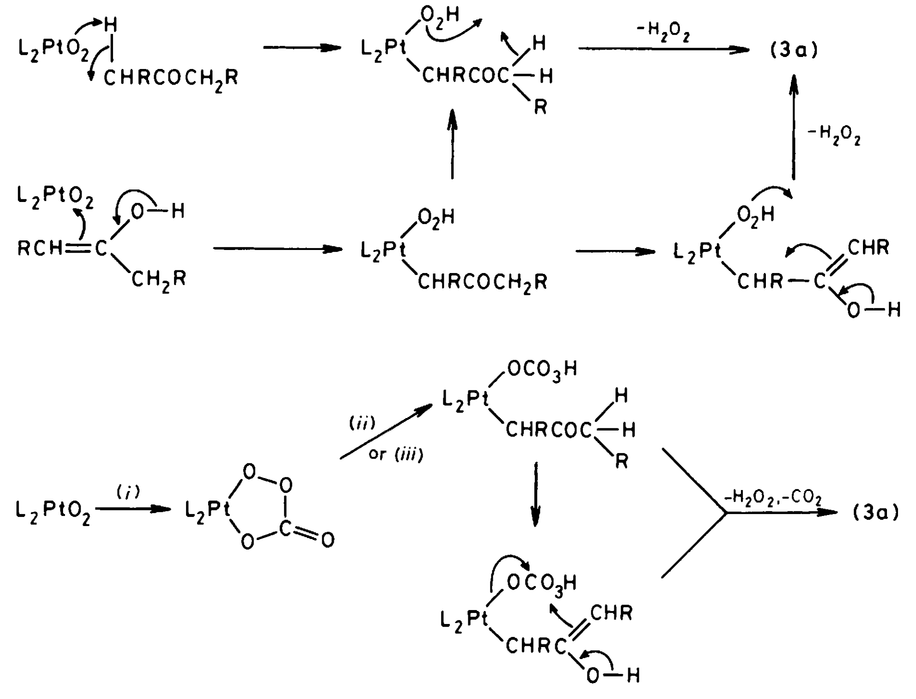


(8)

affords in 60—70% yield a white air-stable compound formulated formally as the platinacyclobutan-3-one species (3a) on the basis of microanalysis, spectroscopic properties, and an *X*-ray crystallographic study. Since it is well known that ketones react with $[Pt(PPh_3)_4]$ in the presence of dioxygen to afford peroxo-ring complexes $[Pt(OOCR_2O)(PPh_3)_2]$,[16,17] the formation of the novel platinum–carbon species (3a) was not anticipated. However, the expected peroxo-ring complex (7) is formed upon treatment of a suspension of the dioxygen complex $[Pt(O_2)(PPh_3)_2]$ in diethyl ether with (6a). The i.r. spectrum of (7) showed strong bands due to C=O stretching frequencies at 1 742, 1 725, and 1 696 cm^{-1} and a weak band at 776 cm^{-1} which can be assigned to ν(O–O). The ^{1}H n.m.r. spectrum of (7) showed a singlet at δ 3.39 p.p.m. due to methyl protons, the diastereotopic methylene groups appearing as an AB pattern. Further evidence for the structure of compound (7) was provided by its reaction with hexafluoroacetone which gave the known complex $[Pt\{OOC(CF_3)_2O\}(PPh_3)_2]$.[18] Displacement of acetone by hexafluoroacetone is known to occur upon treatment of $[Pt(OOCMe_2O)(PPh_3)_2]$ with hexafluoroacetone.[18]

The differences between the i.r. spectra of the platinacyclobutan-3-one (3a) and the peroxo-compound (7) allow a clear distinction to be made between these compounds, and examination of the i.r. spectra of samples of (3a) obtained from reaction of a benzene solution of $[Pt(PPh_3)_4]$ in air with (6a) reveals that in some preparations of (3a) the platinacyclobutan-3-one is contaminated by small amounts of the peroxo-ring compound. The quantity of the peroxo-compound formed varies in each reaction. Often it was not detectable and when it was present there was less than 5% in the crude product before recrystallisation. The quantity of peroxo-ring compound formed is also dependent upon the solvent medium since treatment of a suspension of $[Pt(PPh_3)_4]$ in diethyl ether in air with compound (6a) gave a mixture of (3a) and (7) in which the peroxo-compound was the major component. Thus, as illustrated in the Scheme, the reaction of (6a) with $[Pt(PPh_3)_4]$ in the presence of air can be understood in terms of formation of the dioxygen compound $[Pt(O_2)(PPh_3)_2]$,[19] followed by two different competitive reactions of the latter with the ketone (6a) to produce either the platinacyclobutan-3-one (3a) or the peroxo-compound (7). The formation of an initial platinum–carbon σ bond could proceed *via* transfer of hydrogen from the ketone either to co-ordinated dioxygen or peroxocarbonato-species which could form in air. Alternatively, direct attack at platinum by the enolate anion leads to a Pt–C bond. Either of the pathways involving attack at co-ordinated dioxygen, or a combination of both, is plausible as demonstrated in the Scheme, and is very similar to the mechanism proposed for the formation of acetonylcobalt(III) complexes which result upon treatment of cobalt(II) complexes with acetone in the presence of dioxygen.[20–23] Furthermore, a number of platinum(II)–carbon bonded compounds have been obtained by the action of weak carbon acids upon platinum(II)–oxygen bonded species.[24–29] γ-Hydrogen elimination from an intermediate $Pt\{CH(CO_2Me)COCH_2(CO_2Me)\}$ species provides an attractive route to the platinacyclobutan-3-one since similar eliminations from the organometal systems MCH_2COMe and MCH_2CMe_3 have been shown to afford the metallacyclic rings MCH_2COCH_2 and $MCH_2CMe_2CH_2$ respectively.[13,30,31] In addition, γ-hydrogen elimination from the systems MCH_2COCH_2R (M = Pd, R = COMe or CO_2Et; M = Pt, R = COMe) has been shown to give the derivatives $[M(\eta^3\text{-}CH_2COCHR)L_2]$.[10–12] Consistent with the mechanism outlined in the Scheme, there is no reaction between $[Pt(PPh_3)_4]$ and compound (6a) at room temperature in the absence of dioxygen. Besides the mechanism outlined in the Scheme we have also considered the possibility that the peroxo-compound (7) could be a source of the platinacyclobutan-3-one. Thus, treatment of (7) in dichloromethane with triphenylphosphine and (6a) for 4 d affords the platinacyclobutan-3-one (3a). However, the length of time needed for this reaction to go to completion suggests that this is not an important reaction path for the formation of (3a) from $[Pt(PPh_3)_4]$ and (6a) in air. Interestingly, treatment of compound (7) in dichloromethane with either PPh_3 or (6a) separately for 4 d leaves (7) unchanged.

The reaction of compound (6b) with a benzene solution of $[Pt(PPh_3)_4]$ in the presence of air afforded the platinacyclobutan-3-one (3b) and similar reactions of the zerovalent com-



Scheme. (*i*) CO_2; (*ii*) RCH_2COCH_2R; (*iii*) $RCH_2C(OH)=CHR$

plexes $[PtL_4]$ (L = $AsPh_3$, $PMePh_2$, or PMe_2Ph) with the appropriate ketone gave the platinacyclobutan-3-one compounds (3d), (3e), (3g), and (3h). The i.r. spectrum of the platinacyclobutan-3-one (3b) indicated that the sample contained a small amount of the peroxo-compound $[Pt\{OOC(CH_2CO_2Et)_2O\}(PPh_3)_2]$, although interestingly no peroxo-compounds could be detected in samples of the compounds (3d), (3e), (3g), and (3h).

The observation that platinum(II)–alkyl compounds can be prepared by reactions of platinum(II)–oxygen bonded species with weak carbon acids [24–29] coupled with our knowledge on the reactions of compounds (6) with zerovalent platinum complexes suggested to us the possibility of developing alternative syntheses of the platinacyclobutan-3-ones (3) *via* reactions of suitable platinum(II)–oxygen bonded compounds with compounds (6). In agreement with this idea we have found that compound (6a) reacts with either *cis*-$[Pt(OCOPh)_2(PPh_3)_2]$ in refluxing ethanol or a mixture of *cis*-$[PtCl_2(PPh_3)_2]$ and silver(I) oxide in refluxing dichloromethane to afford good yields of the platinacyclobutan-3-one (3a). However, we find that the best route to the platinacyclobutan-3-ones (3) is simply to treat the carbonate complexes $[Pt(CO_3)L_2]$ (L = PPh_3, $AsPh_3$, $PMePh_2$, or PMe_2Ph; L_2 = $Ph_2PCH_2CH_2PPh_2$) with the appropriate compound (6) in refluxing ethanol.

In order to determine the exact structure of a platinacyclobutan-3-one complex a single-crystal *X*-ray diffraction study was carried out on the bis(triphenylphosphine) complex (3a). The results of the *X*-ray work are summarised in Table 1. The molecular structure is shown in Figure 1. Compound (3a) crystallises with one molecule of water per molecule of compound incorporated in a 'hole' in the lattice (see Figure 2). There are no short intermolecular contacts between the platinum compound and the water molecule.

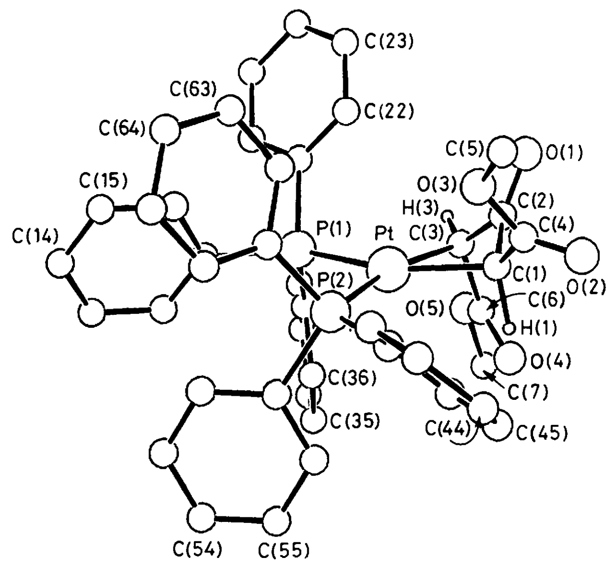


Figure 1. Molecular structure of (3a) showing the atom-numbering scheme. Atoms are drawn as circles with arbitrary radii. Phenyl- and methyl-hydrogen atoms have been excluded

The structures of known platinacyclobutanes have been summarised.[32–34] One structure of comparable accuracy with that of (3a) is the platinacyclobutane $[Pt(CH_2CMe_2CH_2)(PEt_3)_2]$ (8).[31] In both compounds the co-ordination about platinum is essentially square planar (Table 2), with similar bond angles about platinum and similar twist angles between PPtP and CPtC planes [8.1(2)° in (3a) and 1.8° in (8)]. The Pt–P distances are also similar [2.282(2) and 2.287(1) Å in (8)].

A major difference between compounds (3a) and (8) is in the degree of non-planarity of the Pt–C–C–C ring system, as measured by the fold angle between planes C(1)–Pt–C(3) and C(1)–C(2)–C(3). In (3a) this angle is 50.4(4)°, much larger than is found in saturated platinacyclobutanes where the range [31–36] is from 0 to 30° [22.4° in (8)]. Cyclobutanones are

Table 1. Selected intramolecular bond lengths (Å) and angles (°) in $[\overline{\mathrm{Pt}\{\mathrm{CH(CO_2Me)COC}}\mathrm{H(CO_2Me)}\}(\mathrm{PPh_3})_2]\cdot\mathrm{H_2O}$ (3a) with estimated standard deviations in parentheses

		CH(CO$_2$Me)COCH(CO$_2$Me) ligand				Triphenylphosphine ligands	
Pt–P(1)	2.300(1)	C(1)–C(2)	1.470(9)	O(3)–C(5)	1.452(16)	P(1)–C(11)	1.825(3)
Pt–P(2)	2.272(2)	C(2)–C(3)	1.493(9)	C(3)–C(6)	1.483(8)	P(1)–C(21)	1.830(3)
Pt–C(1)	2.133(5)	C(2)–O(1)	1.232(7)	C(6)–O(4)	1.187(7)	P(1)–C(31)	1.819(6)
Pt–C(2)	2.416(5)	C(1)–C(4)	1.482(11)	C(6)–O(5)	1.333(10)	P(2)–C(41)	1.837(5)
Pt–C(3)	2.155(6)	C(4)–O(2)	1.199(7)	O(5)–C(7)	1.447(10)	P(2)–C(51)	1.832(4)
		C(4)–O(3)	1.323(8)			P(2)–C(61)	1.807(3)

P(1)–Pt–P(2)	101.9(1)	P(1)–Pt–C(3)	91.2(2)	P(2)–Pt–C(1)	99.1(2)	C(1)–Pt–C(3)	68.4(2)

CH(CO$_2$Me)COCH(CO$_2$Me) ligand				Triphenylphosphine ligands	
C(1)–C(2)–C(3)	108.8(5)	C(4)–O(3)–C(5)	116.2(6)	Pt–P(1)–C(11)	125.2(2)
C(1)–C(2)–O(1)	126.7(7)	Pt–C(3)–C(2)	80.7(4)	Pt–P(1)–C(21)	109.9(1)
C(3)–C(2)–O(1)	122.9(6)	Pt–C(3)–H(3)	121(5)	Pt–P(1)–C(31)	110.2(1)
Pt–C(1)–H(1)	97.7(3.5)	Pt–C(3)–C(6)	107.5(3)	C(11)–P(1)–C(31)	101.9(2)
Pt–C(1)–C(2)	82.0(3)	H(3)–C(3)–C(6)	106(6)	C(11)–P(1)–C(21)	98.8(2)
Pt–C(1)–C(4)	125.9(4)	C(2)–C(3)–C(6)	118.3(4)	C(21)–P(1)–C(31)	109.8(2)
H(1)–C(1)–C(4)	111(5)	C(2)–C(3)–H(3)	121(6)	Pt–P(2)–C(41)	118.0(1)
H(1)–C(1)–C(2)	121(5)	C(3)–C(6)–O(5)	109.9(5)	Pt–P(2)–C(51)	109.0(2)
C(4)–C(1)–C(2)	115.5(5)	C(3)–C(6)–O(4)	127.5(7)	Pt–P(2)–C(61)	114.9(1)
C(1)–C(4)–O(2)	123.2(6)	O(4)–C(6)–O(5)	122.6(6)	C(41)–P(2)–C(51)	103.6(2)
C(1)–C(4)–O(3)	113.5(5)	C(6)–O(5)–C(7)	116.2(6)	C(41)–P(2)–C(61)	102.7(2)
O(2)–C(4)–O(3)	123.3(8)	Pt–C(2)–O(1)	134.0(3)	C(51)–P(2)–C(61)	107.6(1)
		Pt–C(2)–C(1)	60.9(2)		
		Pt–C(2)–C(3)	61.7(3)		

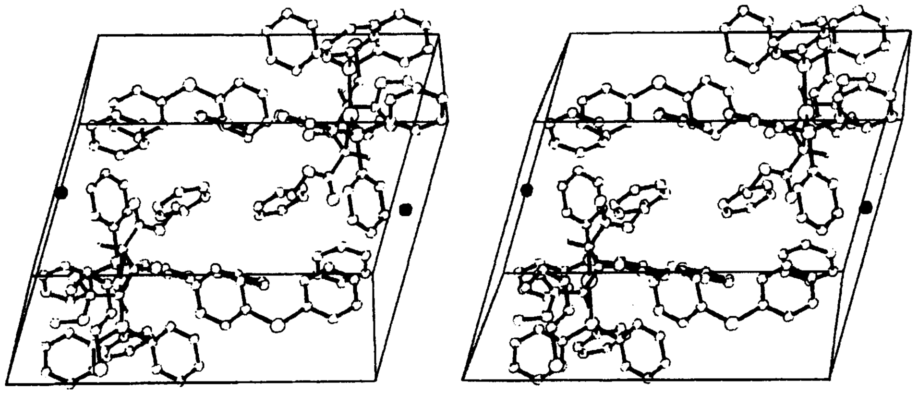


Figure 2. Stereoscopic view of the unit-cell contents (excluding all hydrogen atoms). Complete molecules are shown about the two platinum atoms. The water-oxygen atoms are shaded

only slightly non-planar, *e.g.* in *cis*-2,4-dibromo-2,4-di-t-butylcyclobutan-1-one the fold angle is 10°.[37]

A consequence of the large fold angle in compound (3a) is that the Pt–C(2) distance is only 2.416(5) Å compared with 2.698(6) Å in (8). Although this is longer than the sum of the covalent radii [C(sp^2) 0.76, Pt 1.31 Å],[38,39] there must be considerable orbital interaction between Pt and C(2) in (3a). Additional evidence for such an interaction is provided by the ^{1}H-decoupled ^{13}C n.m.r. spectrum discussed below. The orientation of the PtC$_3$ ring atoms is reminiscent of an η^3-metal allyl complex; an alternative description of (3a) could be given as in (4). A similar description to (4) has been proposed for the trimethylenemethane compound (5a); evidence suggests that in (5a) the trimethylenemethane is asymmetrically bound. Calculations show that a dihedral angle of 96° (*i.e.* a fold angle of 84°) between the PPdP and trimethylenemethane planes gives the minimum-energy conformation, although the three Pd–C distances were held equal in the calculation.[1,40] The Pt–C(1) and Pt–C(3) distances are longer in compound (3a) than in (8) [2.080(6) and 2.086(6) Å].

Consistent with a contribution of the η^3-allyl or 'slipped' oxodimethylenemethane structure (4) for (3a) are the shorter C(1)–C(2) and C(2)–C(3) distances in (3a) compared with those in platinacyclobutanes [1.535(9) and 1.536(9) Å in (8)]. The C(2)–O(1) bond is longer than the C=O bond lengths C(4)–O(2) and C(6)–O(4), and is inclined by 11.6(5)° out of the C(1)–C(2)–C(3) plane towards the platinum. Similar displacements of the central carbon substituents have been observed in η^3-allyl complexes.[41,42]

The torsion angles P(1)–Pt–C(3)–C(6) and P(2)–Pt–C(1)–C(4) are −96.5(4) and −43.0(5)° respectively, one methoxycarbonyl substituent occupying a pseudo-axial position and the other a pseudo-equatorial position. This is presumably the sterically favoured isomer since the *cis*-2,4-diaxial isomer would possess steric interactions between the two ester groups and in the diequatorial isomer there would be steric inter-

Table 2. Equations of some least-squares planes in the form $Ax + By + Cz = D$, where x, y, and z are fractional co-ordinates: distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): Pt, P(1), P(2), C(1), C(2)
$17.5878x + 3.5714y - 1.0332z = 3.4980$
[C(1) 0.114, C(3) −0.118, P(1) 0.081, P(2) −0.076, Pt −0.001, C(2) 0.661]

Plane (2): C(1), C(2), C(3)
$10.9544x - 1.8793y - 5.3309z = -4.6403$
[O(1) 0.247]

actions between the ring carbonyl and each ester group. Hydrogen-atom positions for H(1) and H(3) were located from a Fourier difference map.

Overall the geometry of the platinacyclobutan-3-one ring in (3a) bears a strong resemblance to the μ-2-oxo-1,3-diphenylpropanediylidene complex [(Bu^{t}NC)$_2$Pt{μ-(PhC)$_2$CO}Pt(CNBu^t)$_2$] which could also be viewed as a platinacyclobutan-3-one derivative: the fold angles for the rings are 55 and 52°, the mean transannular Pt–C distance is 2.50(2) Å, the mean terminal carbon Pt–C distances are 2.11 Å, and the C_3 fragment shows C–C separations which average to 1.43(2) Å.[43]

On the basis of n.m.r. studies, compounds of palladium(II) and platinum(II) containing dianions of pentane-2,4-dione and ethyl acetoacetate [10–12] have been formulated with η^3-β-diketonato(2−)-ligands. However, with the establishment of the structure of (3a) in the solid state, these derivatives of pentane-2,4-dione and ethyl acetoacetate could also be viewed as puckered metallacyclobutan-3-ones [M(CH$_2$COCHR)L$_2$] (M = Pd, R = COMe or CO$_2$Et; M = Pt, R = COMe) with the substituent R occupying an axial position of a puckered ring.

The role that the CO$_2$Me ester substituents play in determining the extent of the non-planarity of the platinacyclobutan-3-one ring in compound (3a) is not clear. N.m.r. data for the compounds [M(CH$_2$COCHR)L$_2$] indicate that the four-membered ring in these systems is also puckered. An important factor which probably accounts for ring puckering is the presence of a co-ordinatively unsaturated platinum centre and an unsaturated ring-carbon atom in (3a) which can lead to a transannular Pt–C bonding interaction.

The ^{1}H n.m.r. spectrum of the platinacyclobutan-3-one (3a), measured at −115 °C in CD$_2$Cl$_2$, showed the expected features for the illustrated static structure with two resonances at δ 3.16 and 2.64 p.p.m. for the methyl protons and signals due to the axial and equatorial ring protons at δ 4.05 and 3.23 p.p.m. respectively. The assignment of the higher-frequency signal at δ 4.05 to the axial proton is consistent with the ^{1}H n.m.r. data for the compounds [M(CH$_2$COCHR)L$_2$] [10–12] which show that for the CH$_2$ group the axial proton is more deshielded than the equatorial proton. We have also previously indicated that in metallacyclobutan-3-ones [15] the magnitudes of the three-bond couplings (*cis*-P–Pt–C–H) involving the axial and equatorial ring protons are under dihedral angle control as in the well known Karplus relations for vicinal H–C–C–H couplings.[44] Thus, in the ^{1}H n.m.r. spectrum of (3a), measured at −115 °C in CD$_2$Cl$_2$, the equatorial hydrogen H(3) exhibited coupling to both the *cis*-phosphorus [P(1)–Pt–C(3)–H(3) torsion angle 25(7)°] and *trans*-phosphorus ligands, but the axial hydrogen H(1) showed no discernible coupling to its *cis*-phosphorus ligand [P(2)–Pt–C(1)–H(1) torsion angle 80(5)°] and appeared as a doublet due to *trans*-phosphorus coupling only. Similar results have been found for [Pt{CH(COMe)COCH(COMe)}(PPh$_3$)$_2$] [15] and for a series of palladacyclobutan-3-ones.[45] Evidence that P(1) P(2), and H(3) can be treated as 'first order' with similar P–H couplings is provided by the ^{1}H-{^{31}P} broad-band-decoupled n.m.r. spectrum of (3a), measured at 360 MHz in CD$_2$Cl$_2$ at −115 °C, which consisted of resonances at δ 3.14 and 2.63 p.p.m. for the methyl protons and resonances for the CH protons at δ 4.01 [s, H(1), ^2J(PtH) 72 Hz] and 3.18 p.p.m. [s, H(3), ^2J(PtH) not discernible]. Furthermore, in a ^{1}H-{^{31}P} selectively decoupled n.m.r. spectrum of compound (3a), irradiation of the P(1) resonance caused the H(1) signal to collapse to a singlet, however, on irradiation of the P(2) resonance the H(1) signal remained unchanged as a doublet. Upon irradiation of either P(1) or P(2) the H(3) signal appeared as a doublet [^3J(PH) 4—5 Hz], which was partially obscured by one of the methyl signals. The ^{31}P-{^{1}H} n.m.r. spectrum of (3a) measured at 146 MHz in CD$_2$Cl$_2$ at −115 °C exhibited two resonances at δ 16.71{d, P(2), ^2J[P(1)P(2)] 11.3} and 14.38 p.p.m. {d, P(1), ^2J[P(2)P(1)] 11.3 Hz}.

The low-temperature ^{1}H n.m.r. spectra of compounds (3a) and (3d) also reveal that platinum-195 axial-hydrogen coupling is larger than platinum-195 equatorial-hydrogen coupling. In cyclic organophosphorus compounds it has been observed that ^2J(PH) is much larger when the coupled proton lies close to the orbital of the phosphorus(III) lone pair, and is quite small when remote.[46] Similar effects have been observed in imines, hydrazones, oximes, and aziridines, the magnitude of ^2J(^{15}NH) being enhanced if the nitrogen of the lone pair approaches the coupled hydrogen.[47] Location of the axial and equatorial hydrogens in (3a) by the *X*-ray study establishes that the C–H$_{\text{axial}}$ vector is aligned with the vector on platinum (defined as the *z* direction) perpendicular to the C(1)PtC(3) plane, whereas the C–H$_{\text{equatorial}}$ vector is not [the angles between the vector on platinum perpendicular to the C(1)PtC(3) plane and the C(1)–H(1) and C(3)–H(3) vectors being 8(4) and 117(6)° respectively]. The axial hydrogen atom is also closer to the platinum [Pt–H(1) 2.56(6), Pt–H(3) 2.74(9) Å]. We therefore suggest that the axial hydrogen experiences a greater coupling to the ^{195}Pt nucleus than the equatorial hydrogen, because the former lies closer to non-bonding electron density on platinum, possibly an electron pair in a $d_{z^2} + s + p_z$ hybrid orbital. This effect is also transmitted to the *trans*-phosphorus ligand in (3a) since the three-bond coupling ^3J(*trans*-PH) is greater for axial than equatorial hydrogen. Similar effects are observed in other platinacyclobutan-3-ones [15] and palladacyclobutan-3-ones [45] and in static η^3-allyls of both palladium(II) and platinum(II). In η^3-allyl compounds of platinum(II) ^2J(PtH) coupling to *anti*-hydrogens is greater than to *syn*-hydrogens,[48,49] the *anti*- and *syn*-hydrogens being oriented with respect to the platinum in a similar fashion to respectively the axial and equatorial hydrogens in compound (3a). Similarly, in η^3-allyls of palladium(II) [50,51] and platinum(II) [49] ^3J(*trans*-PH) is greater for *anti*- than *syn*-hydrogens.

Upon warming to room temperature the Me and CH ring signals in the ^{1}H n.m.r. spectrum of compound (3a) undergo reversible changes. Thus, the methyl resonances observed at δ 3.16 and 2.64 at −115 °C collapsed to a singlet at δ 3.046 and the CH resonances collapsed to the A part of an AA′XX′ spin system (X = ^{31}P) with ^{195}Pt satellites. This dynamic process is consistent with an inversion of the ring through a planar transition state resulting in a conformational transformation in which two axial positions become equatorial and *vice versa*. The free energy of activation, $\Delta G^{\ddagger}$, calculated for this process from the coalescence temperature T_c of the CH protons using the Gutowsky-Holm equations [52] is 36.1 kJ

mol^{-1}. The same value is also obtained from the coalescence temperature of the methyl protons and this conclusively demonstrates that the ring inversion is a concerted process. The value of $\Delta G^{\ddagger}_{T_c}$ determined for the triphenylarsine compound (3d) is 35.3 kJ mol^{-1}. The coalescence temperatures for the CH and methyl protons of (3a) were −79.6 and −83.6 °C respectively. For compound (3d) the respective temperatures were −90.2 and −92.2 °C. In contrast the 'frozen-out' spectra for the compounds (3g)—(3i) could not be obtained since these derivatives undergo fast exchange even at −115 °C. These values of $\Delta G^{\ddagger}_{T_c}$ are smaller than those found for analogous palladium(II) complexes [45] and are consistent with the presence of smaller fold angles and longer metal–carbon transannular interactions in platinum(II) as compared to palladium(II) metallacyclobutan-3-ones. These differences are probably a reflection of the greater tendency of four-co-ordinate palladium(II) to become five-co-ordinate as compared to platinum(II).

The compounds (3a) and (3d) provide the first examples in which the barrier to ring inversion of a four-membered metallacyclic ring has been determined. In platinacyclobutanes the fold angle ranges from 0 to 30°, transannular platinum–carbon distances being in the range 2.6—2.7 Å.[31–36] Barriers to ring inversion would therefore be expected to be lower than those found for (3a) and (3d). Interestingly, although the crystal structure of $[Pt(CH_2CH_2CH_2)(bipy)]$ (bipy = 2,2′-bipyridyl) shows the molecule to be almost completely planar, the possibility of a facile puckering motion in solution has been considered since the ^1H n.m.r. spectrum exhibits a large ^{195}Pt coupling to the β-hydrogens.[36]

The ^{13}C-{^1H-decoupled} n.m.r. spectrum of compound (3a) recorded at room temperature showed peaks corresponding to the carbon nuclei present, the carbon atoms C^1 and C^3 attached to platinum being equivalent due to rapid ring inversion. The observation that the $J(Pt-C)$ values are significantly greater for the ring carbons C^1, C^2, and C^3 than for the C=O carbons of the CO_2Me groups is consistent with a bonding interaction between the platinum and the ring carbons. The relative magnitudes of $J(Pt-C^1)$ and $^2J(Pt-C^2)$ are similar to those found for platinacyclobutanes [32] and for the η^3-2,4-pentanedionato(2−)-compound $[Pt(CH_2COCHR)\{P(C_6H_4Cl\text{-}p)_3\}_2]$ (R = COMe) [12] which could also be formulated as a platinacyclobutan-3-one derivative. This compound does not appear to undergo ring inversion in solution at room temperature, the substituent R preferring to be in an axial rather than equatorial site. The ^{13}C-{^1H-decoupled} n.m.r. spectra of compounds (3d) and (3g)—(3i) exhibited similar features to those observed for (3a), the ring carbonyl carbon C^2 exhibiting coupling to platinum and to both phosphorus nuclei. The room-temperature ^{31}P-{^1H-decoupled} n.m.r. spectra of (3a)—(3c) and (3g)—(3i) exhibited a single resonance with ^{195}Pt coupling which is again consistent with rapid inversion of the four-membered rings.

In conclusion we note that it is not possible to describe the bonding in compound (3a) in terms of a single structure, and the compound can be considered to be either a puckered platinacyclobutan-3-one or a slipped oxodimethylenemethane compound. Interestingly, the available structural data on the slipped trimethylenemethane compound (5a) can also be interpreted in terms of the palladacycle (5b) and it has been noted that there is no experimental or theoretical basis to differentiate between the η^3 (5a) or σ forms (5b).[1] It is also apparent from our studies that the oxodimethylenemethane compounds (3) are considerably more robust than the related palladium trimethylenemethane compound (5), attempts to isolate the latter being unsuccessful.[1]

Experimental

Melting points (Table 3) were measured on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on a Perkin-Elmer 580 spectrophotometer. Hydrogen-1 n.m.r. spectra were recorded on a JEOL JNM-PS-100 spectrometer at 100 MHz and on a Bruker Spectrospin WH 400 spectrometer at 400.13 MHz with $SiMe_4$ (0.0 p.p.m.) as internal reference, positive values being to high frequency (low field) in [$^2H_1$]chloroform unless otherwise stated. Carbon-13, hydrogen-1 decoupled, n.m.r. spectra were recorded on a Bruker Spectrospin WH 400 spectrometer at 100.62 MHz with $SiMe_4$ (0.0 p.p.m.) as internal reference. Phosphorus-31, hydrogen-1 decoupled, n.m.r. spectra were recorded on a JEOL JNM-FX60 spectrometer at 24.15 MHz with $[P(OH)_4]^+$ in [$^2H_2$]water (0.0 p.p.m.) as external reference,[53] and on a Bruker WH 360 spectrometer at 146 MHz with H_3PO_4 in [$^2H_2$]water at 0 °C. The hydrogen-1, phosphorus-31 decoupled, n.m.r. spectra were recorded on either Varian T60 or Bruker 360 spectrometers operating at 60 and 360 MHz respectively.

Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere unless otherwise stated, using solvents which were dried and distilled under nitrogen prior to use. The compounds $[Pt(PPh_3)_4]$,[54] $[Pt(AsPh_3)_4]$,[54] $[Pt(PMePh_2)_4]$,[55] $[Pt(PMe_2Ph)_4]$,[56] *cis*-$[PtCl_2(PPh_3)_2]$,[57] *cis*-$[Pt(OCOPh)_2(PPh_3)_2]$,[19] $[Pt(O_2)(PPh_3)_2]$,[19] $[Pt\{OOC(O)O\}(PPh_3)_2]$,[16] and $[Pt(CO_3)L_2]$ (L = PPh_3,[16] $PMePh_2$,[58] PMe_2Ph,[59] or $AsPh_3$;[16] L_2 = $Ph_2PCH_2CH_2PPh_2$[16]) were prepared as described in the literature. The dialkyl 3-oxopentanedioates RCH_2COCH_2R (R = CO_2Me, CO_2Et, or CO_2Pr^n) were commercial samples which were redistilled under nitrogen prior to use. The ^1H n.m.r. spectrum of a 50% solution of dimethyl 3-oxopentanedioate in [$^2H_1$]chloroform exhibited a broad singlet centred at δ 11.9 p.p.m. due to the hydroxyl group of the enol form, $RCH{=}C(OH)CH_2R$ (R = CO_2Me), a singlet at 3.7 p.p.m. due to the methyl groups, and a singlet at 3.6 p.p.m. due to the methylene protons. With the exception of the methyl protons, all the other protons undergo exchange upon shaking the solution with [$^2H_2$]water. It is apparent that rapid keto–enol tautomerism occurs with about 15% of the enol tautomer present.

Analytical data and yields for the new complexes are given in Table 3.

Preparation of 2,4-*Bis*(*alkoxycarbonyl*)-1,1-*bis*(*ligand*)*platinacyclobutan*-3-*ones*.—(*a*) *From carbonatobis*(*ligand*)*platinum*(II). *General method.* A mixture of $[Pt(CO_3)L_2]$ and the dialkyl 3-oxopentanedioate in ethanol (50 cm^3) was slowly heated to between 45 and 65 °C with stirring under nitrogen until a clear solution was formed. The resulting pale yellow solution was filtered and the filtrate was evaporated under reduced pressure to afford a pale yellow oil. Dissolution of the oil in dichloromethane (3—5 cm^3) followed by addition of diethyl ether (50 cm^3) gave, after standing for several hours, a white to pale yellow crystalline solid. Recrystallisation from dichloromethane–light petroleum (b.p. 40—60 °C) gave a white microcrystalline solid which was dried *in vacuo* (0.4 mmHg, *ca.* 54 Pa) at 40 °C.

$[Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]$. The compound $[Pt(CO_3)(PPh_3)_2]\cdot C_6H_6$ (0.40 g, 0.47 mmol) and dimethyl 3-oxopentanedioate (0.5 cm^3, 3.4 mmol) gave compound (3a) (0.34 g, 0.4 mmol). N.m.r. spectra: ^1H ([$^2H_2$]dichloromethane–CH_2Cl_2, 400 MHz), δ 7.39—7.24 (m, 30 H, Ph), 3.729 [d, second order, 2 H, CH$|^3J(PH)_{trans} + {}^3J(PH)_{cis}|$ 4.43, $^2J(PtH)$ 54.17 Hz], and 3.046 (s, 6 H, Me); ^1H([$^2H_2$]dichloromethane–CH_2Cl_2, −115 °C, 400 MHz), δ 7.99—6.56 (m, br, 30 H, Ph), 4.046 [d, 1 H, CH, $^3J(PH)$ 11.82, $^2J(PtH)$ 73.98], 3.230 [t, 1 H, CH, ^{3}J(PH)$_{trans}$ + ^{3}J(PH)$_{cis}$ 4.74, ^{2}J(PtH) 27.74 Hz], 3.160 (s, 3 H, Me), and 2.646 (s, 3 H, Me); ^{1}H-{^{31}P} ([^{2}H$_1$]chloroform, 60 MHz, irradiated at 24.29092 MHz), δ 7.4—7.2 (m, 30 H, Ph), 3.89 [s, 2 H, CH, ^{2}J(PtH) 74 Hz], and 3.06 (s, 6 H Me); ^{1}H-{^{31}P} ([^{2}H$_2$]dichloromethane, 360 MHz, broad-band irradiation, −115 °C), δ 4.01 [s, 1 H, CH, ^{2}J(PtH) 72], 3.18 [s, 1 H, CH, ^{2}J(PtH) not discernible], 3.14 (s, 3 H, Me), and 2.63 (s, 3 H, Me); ^{1}H-{^{31}P} ([^{2}H$_2$]dichloromethane, 360 MHz, irradiated at 145.787236 MHz {P(1)}, −115 °C), 4.01 [s, 1 H, CH, ^{2}J(PtH) 72], δ 3.18 [d, 1 H, ^{3}J(PH) *ca.* 3—4 Hz], 3.14 (s, 3 H, Me), and 2.63 (s, 3 H, Me); ^{1}H-{^{31}P} ([^{2}H$_2$]dichloromethane, 360 MHz, irradiated at 145.787576 MHz {P(2)}, −115 °C), δ 4.00 [d, 1 H, CH, ^{3}J(PH) 11.7, ^{2}J(PtH) 72], 3.18 [d, 1 H, ^{3}J(PH) *ca.* 3—4 Hz], 3.13 (s, 3 H, Me), and 2.62 (s, 3 H, Me); ^{13}C-{^{1}H} ([^{2}H$_1$]dichloromethane), δ 178.30 [t, CO, ring, ^{3}J(PC) 5.3, ^{2}J(PtC) 175.5], 171.68 [s, C=O, CO$_2$Me, ^{2}J(PtC) 35.1], 134.02 [t, second order, Ph, C-β, |^{2}J(PC) + ^{4}J(PC)| 9.5], 131.03 [d, second order, Ph, C-α, |^{1}J(PC) + ^{3}J(PC)| 54.69], 130.12 (s, Ph, C-δ), 127.85 [t, second order, Ph, C-γ, |^{3}J(PC) + ^{5}J(PC) 9.77], 56.427 {d,d, second order, CH, |^{2}J(PC)$_{trans}$ + ^{2}J(PC)$_{cis}$| 54.93, ^{1}J(PtC) 273.9 Hz], and 50.255 (s, Me); ^{31}P-{^{1}H} ([^{2}H$_1$]chloroform, 24 MHz), δ 16.94 [s, ^{1}J(PtP) 3 081 Hz]; ^{31}P-{^{1}H} ([^{2}H$_2$]dichloromethane, 146 MHz,), δ 16.71 {d, P(2), *J*[P(1)P(2)] 11.3} and 14.38 p.p.m. {d, P(1), *J*[P(2)P(1)] 11.3 Hz}. ν$_{max.}$ at 3 144vw, 3 076w, 3 056w, 3 022w, 3 008w, 2 988w, 2 940m, 2 834vw, 1 712vs, 1 694vs, 1 617vs, 1 584m, 1 570m, 1 480s, 1 456w, 1 432vs, 1 384w, 1 315s, 1 237s, 1 191s, 1 146(sh),s, 1 135vs, 1 095s, 1 074m, 1 036m, 1 028s, 1 000m, 977w, 960m, 911m, 892w, 863w, 845w, 797w, 766m, 755s, 744s, 695vs, 620w, 602w, 542s, 526vs, 511vs, 495s, 461m, 438w, 425m, 382w, and 359vw cm^{-1}.

[Pt{CH(CO$_2$Et)COCH(CO$_2$Et)}(PPh$_3$)$_2$]. The compound [Pt(CO$_3$)(PPh$_3$)$_2$]·C$_6$H$_6$ (0.30 g, 0.35 mmol) and diethyl 3-oxopentanedioate (0.5 cm^3, 2.7 mmol) gave compound (3b) (0.26 g, 0.29 mmol). N.m.r. spectra: ^{1}H (400 MHz), δ 7.36—7.15 (m, 30 H, Ph), 3.895 [d, second order, 2 H, CH, |^{3}J(PH)$_{trans}$ + ^{3}J(PH)$_{cis}$| 4.27, ^{2}J(PtH) 52.2], 3.469 [d,d,q, second-order AB spin system, 4 H, CH$_2$, ^{3}J(HH) 7.2, ^{2}J(HH) 10.67, δ$_A$ − δ$_B$ 0.562], and 0.670 [t, 6 H, Me, ^{3}J(HH) 7.2 Hz]; ^{31}P-{^{1}H} ([^{2}H$_1$]chloroform 24 MHz), δ 16.94 p.p.m. [s, ^{1}J(PtP) 3 066 Hz]. ν$_{max.}$ (1 800—1 500 cm^{-1}) at 1 712s, 1 683vs, 1 636vs, 1 586m, and 1 571m cm^{-1}.

[Pt{CH(CO$_2$Pr^n)COCH(CO$_2$Pr^n)}(PPh$_3$)$_2$]. The compound [Pt(CO$_3$)(PPh$_3$)$_2$]·C$_6$H$_6$ (0.25 g, 0.29 mmol) and di-n-propyl 3-oxopentanedioate (0.5 cm^3, 2.4 mmol) gave compound (3c) (0.19 g, 0.21 mmol). N.m.r. spectra: ^{1}H (400 MHz), δ 7.35—7.15 (m, 30 H, Ph), 3.915 [d, second order, 2 H, CH, |^{3}J(PH)$_{trans}$ + ^{3}J(PH)$_{cis}$| 4.27, ^{2}J(PtH) 52.8], 3.360 [d,d,t, second-order AB spin system, 4 H, CH$_2$, ^{3}J(HH) 7.2, ^{2}J(HH) 10.50, δ$_A$ − δ$_B$ 0.660], 1.174 [sextet, 4 H, CH$_2$, ^{3}J(HH) 7.2], and 0.670 [t, 6 H, Me, ^{3}J(HH) 7.2 Hz]; ^{31}P-{^{1}H} ([^{2}H$_1$]chloroform, 24 MHz), δ 16.94 p.p.m. [s, ^{1}J(PtP) 3 076 Hz].ν$_{max.}$ (1 800—1 500 cm^{-1}) at 1 720vs, 1 683vs, 1 644vs, 1 582m, and 1 573m, cm^{-1}.

[Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(AsPh$_3$)$_2$]. The compound [Pt(CO$_3$)(AsPh$_3$)$_2$]·C$_6$H$_6$ (0.27 g, 0.29 mmol) and dimethyl 3-oxopentanedioate (0.5 cm^3, 3.4 mmol) gave compound (3d) (0.24 g, 0.25 mmol). N.m.r. spectra: ^{1}H (100 MHz), δ 7.4—7.1 (m, 30 H, Ph), 4.16 [s, 2 H, 3H, ^{2}J(PtH) 71.64 Hz], and 3.04 (s, 6 H, Me); ^{1}H ([^{2}H$_2$]dichloromethane–CH$_2$Cl$_2$, −98 °C, 400 MHz), δ 7.98—6.60 (m, 30 H, Ph), 4.02 [s, 1 H, CH, ^{2}J(PtH) 81], 3.67 [s, 1 H, CH, ^{2}J(PtH) 36 Hz], 2.96 (s, 3 H, Me), and 2.67 (s, 3 H, Me); ^{13}C-{^{1}H} ([^{2}H$_1$]chloroform), δ 179.26 [s, C=O, ring, ^{2}J(PtC) 195], 171.48 [s, C=O, ester, ^{2}J(PtC) 41.2], 133.09 (s, Ph, C-β), 129.86 (s, Ph, C-δ), 128.39 (s, Ph, C-γ), 51.21 [s, CH, *J*(PtC) 313.9 Hz], and 50.23 p.p.m. (s, Me). ν$_{max.}$ (1 800—1 500 cm^{-1}) at 1 714vs, 1 697vs, 1 627vs, 1 580m, and 1 572m cm^{-1}.

[Pt{CH(CO$_2$Et)COCH(CO$_2$Et)}(AsPh$_3$)$_2$]. The compound [Pt(CO$_3$)(AsPh$_3$)$_2$]·C$_6$H$_6$ (0.26 g, 0.28 mmol) and diethyl 3-oxopentanedioate (0.5 cm^3, 3.4 mmol) gave compound (3e) (0.20 g, 0.21 mmol). N.m.r. spectrum: ^{1}H (400 MHz), δ 7.30—7.14 (m, 30 H, Ph), 4.09 [s, 2 H, CH, ^{2}J(PtH) 69.9], 3.45 [d,d,q, second-order AB spin system, 4 H, CH$_2$, ^{3}J(HH) 7.2, ^{2}J(HH) 10.6, δ$_A$ − δ$_B$ 0.56], and 0.74 p.p.m. [t, 6 H, Me, ^{3}J(HH) 7.2 Hz]. ν$_{max.}$ (1 800—1 500 cm^{-1}) at 1 714s, 1 689vs, 1 645vs, 1 581m, and 1 572m cm^{-1}.

[Pt{CH(CO$_2$Pr^n)COCH(CO$_2$Pr^n)}(AsPh$_3$)$_2$]. The compound [Pt(CO$_3$)(AsPh$_3$)$_2$]·C$_6$H$_6$ (0.50 g, 0.53 mmol) and di-n-propyl 3-oxopentanedioate (0.5 cm^3, 2.4 mmol) gave compound (3f) (0.38 g, 0.38 mmol). N.m.r. spectrum: ^{1}H (400 MHz), δ 7.30—7.14 (m, 30 H, Ph), 4.12 [s, 2 H, CH, ^{2}J(PtH) 69.6], 3.33 [d,d,t, second-order AB spin system, 4 H, CH$_2$, ^{3}J(HH) 7.2, ^{2}J(HH) 10.8, δ$_A$ − δ$_B$ 0.69], 1.106 [d,d, sextet, second-order AB spin sytem, 4 H, CH$_2$, ^{3}J(HH) 7.2, ^{2}J(HH) 13.5, δ$_A$ − δ$_B$ 0.09], and 0.65 p.p.m. [t, 6 H, Me, ^{3}J(HH) 7.2 Hz]. ν$_{max.}$ (1 800—1 500 cm^{-1}) at 1 718vs, 1 685vs, 1 648vs, 1 580m, and 1 574m cm^{-1}.

[Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(PMePh$_2$)$_2$]. The compound [Pt(CO$_3$)(PMePh$_2$)$_2$] (0.36 g, 0.55 mmol) and dimethyl 3-oxopentanedioate (0.5 cm^3, 3.4 mmol) gave compound (3g) (0.31 g, 0.39 mmol). N.m.r. spectra: ^{1}H (100 MHz), δ 7.4—7.0 (m, 20 H, Ph), 3.96 (d, second order, 2 H, CH, |^{3}J(PH)$_{trans}$ + ^{3}J(PH)$_{cis}$| 4.8, ^{2}J(PtH) 55.5], 3.04 (s, 6 H, CO$_2$Me), and 1.86 [d, second order, 6 H, PMe, |^{2}J(PH) + ^{4}J(PH)| 9.0, ^{3}J(PtH) 31.5 Hz]; ^{13}C-{^{1}H} ([^{2}H$_1$]chloroform), δ 179.73 [t, C=O, ring, ^{3}J(PC) 5.3, ^{2}J(PtC) 170], 172.18 [s, C=O, ester, ^{2}J(PtC) 35.2], 132.34 [t, second-order, Ph, C-β, |^{2}J(PC) + ^{4}J(PC)| 11.1], 131.69 [t, second order, Ph, C-β, |^{2}J(PC) + ^{4}J(PC)| 11.6] (NB. C-α of Ph obscured by signals due to C-β), 130.48 (s, Ph, C-δ), 130.08 (s, Ph, C-δ), 128.34 [d^f (filled doublet), second order, Ph, C-γ, |^{3}J(PC) + ^{5}J(PC)| 10.58], 128.23 [d^f, second order, Ph, C-γ, |^{3}J(PC) + ^{5}J(PC) 10.58], 54.84 [d, second order, CH, |^{2}J(PC)$_{trans}$ + ^{2}J(PC)$_{cis}$| 51.19, *J*(PtC) 245], 50.13 (s, Me, CO$_2$Me), and 15.55 p.p.m. (d, second order, Me, PMePh$_2$, |^{1}J(PC) + ^{3}J(PC)| 39.04, ^{2}J(PtC) 17 Hz]; ^{31}P-{^{1}H} (dichloromethane, 24 MHz), δ −1.01 p.p.m. [s, *J*(PPt) 2 988 Hz]. ν$_{max.}$ (1 800—1 500 cm^{-1}) at 1 720vs, 1 686vs, 1 630vs, 1 587m, and 1 572m cm^{-1}.

[Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(PMe$_2$Ph)$_2$]. The compound [Pt(CO$_3$)(PMe$_2$Ph)$_2$] (0.27 g, 0.51 mmol) and dimethyl 3-oxopentanedioate (0.5 cm^3, 3.4 mmol) gave compound (3h) (0.21 g, 0.33 mmol). N.m.r. spectra ^{1}H (100 MHz), δ 7.3—7.2 (m, 10 H, Ph), 4.07 [d, second order, 2 H, CH, |^{3}J(PH)$_{trans}$ + ^{3}J(PH)$_{cis}$| 5.6, ^{2}J(PtH) 55.2], 3.50 (s, 6 H, CO$_2$Me), 1.61 [d, second order, 6 H, PMe, | ^{2}J(PH) + ^{4}J(PH)| 10.0, ^{3}J(PtH) 31.2], and 1.57 [d, second order, 6 H, PMe, |^{2}J(PH) + ^{4}J(PH)| 30.8 Hz]; ^{13}C-{^{1}H} ([^{2}H$_1$]chloroform), δ 179.00 [t, C=O, ring, ^{3}J(PC) 5.03, ^{2}J(PtC) 171], 172.83 [s, C=O, ester, ^{2}J(PtC) 33.25], 134.03 [d, second order, Ph, C-α, |^{1}J(PC) + ^{3}J(PC)| 53.1], 130.57 [t, second order, Ph, C-β, |^{2}J(PC) + ^{4}J(PC)| 11.4], 130.46 (s, Ph, C-δ), 128.50 [t, second order, Ph, C-γ, |^{3}J(PC) + ^{5}J(PC)| 10.19], 53.24 [d, second order, CH, |^{2}J(PC)$_{trans}$ + ^{2}J(PC)$_{cis}$| 52.25, ^{1}J(PtC) 229.3], 50.44 (s, Me, CO$_2$Me), 15.94 {d, second order, Me, PMe$_2$Ph, |^{1}J(PC) + ^{3}J(PC)| 39.02], and 14.72 [d, second order, Me, PMe$_2$Ph, |^{1}J(PC) + ^{3}J(PC)| 37.80 Hz]; ^{31}P-{^{1}H} (dichloromethane, 24 MHz), −15.93 p.p.m. [s, *J*(PPt) 2 949 Hz]. ν$_{max.}$ (1 800—1 500 cm^{-1}) at 1 692vs, 1 676vs, 1 630vs, 1 587m, and 1 572m cm^{-1}.

[Pt{CH(CO$_2$Me)COCH(CO$_2$Me)}(Ph$_2$PCH$_2$CH$_2$PPh$_2$)]. The compound [Pt(CO$_3$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)] (0.60 g, 0.92 mmol) and dimethyl 3-oxopentanedioate (0.5 cm^3, 3.4 mmol)

Table 3. Preparations, yields, melting points, and analytical data [a]

Complex	Reaction time (h) using $[PtL_4]$	Yield (%) using		M.p. (θ_c/°C)	Analysis (%)	
		$[PtL_4]$	$[Pt(CO_3)L_2]$		C	H
(3a)	64	73 [b]	82	218—221 [c]	57.8 (57.9)	4.4 (4.3)
(3b)	64	49 [b]	81	215—220 [c]	58.8 (58.8)	4.7 (4.6)
(3c)			69	211—213 [c]	59.3 (59.6)	5.0 (4.9)
(3d)	64	69	86	205—207 [c]	52.9 (52.7)	4.0 (3.9)
(3e)	120	57	72	205 [c]	53.4 (53.6)	4.3 (4.2)
(3f)			67	204 [c]	54.4 (54.5)	4.5 (4.4)
(3g)	16	68	71	230—232	51.7 (51.6)	4.4 (4.5)
(3h)	16	63	64	174—175	42.9 (42.9)	4.7 (4.7)
(3i)			71	>220 [d]	51.9 (51.8)	4.3 (4.2)

[a] Calculated values are given in parentheses. [b] Compound prepared by this method often contains some peroxo-compound. [c] With decomposition. [d] Melts at 249—251 °C to give a red liquid.

Table 4. Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for $[Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]\cdot H_2O$ (3a)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	0.260 89(1)	0.024 61(2)	1.141 61(2)	C(24)	0.549 52(17)	−0.267 3(3)	1.259 8(4)
P(1)	0.303 82(8)	−0.182 10(11)	1.078 19(14)	C(25)	0.511 29(17)	−0.360 6(3)	1.185 6(4)
P(2)	0.244 75(8)	0.018 10(12)	0.916 37(15)	C(26)	0.436 59(17)	−0.334 4(3)	1.132 6(4)
C(1)	0.235 7(3)	0.220 0(4)	1.277 3(6)	C(31)	0.232 4(2)	−0.225 2(4)	1.148 5(5)
C(2)	0.280 6(3)	0.182 7(5)	1.382 6(6)	C(32)	0.252 0(2)	−0.293 7(4)	1.225 6(5)
C(3)	0.257 6(3)	0.075 0(5)	1.373 4(5)	C(33)	0.193 5(2)	−0.329 1(4)	1.266 6(5)
C(4)	0.264 4(4)	0.305 8(5)	1.247 1(7)	C(34)	0.115 4(2)	−0.296 0(4)	1.230 6(5)
C(5)	0.362 0(6)	0.331 1(10)	1.128 5(12)	C(35)	0.095 8(2)	−0.227 6(4)	1.153 6(5)
C(6)	0.175 0(3)	0.094 1(5)	1.418 9(6)	C(36)	0.154 3(2)	−0.192 2(4)	1.112 6(5)
C(7)	0.096 5(4)	0.030 1(9)	1.528 2(9)	C(41)	0.203 4(2)	0.164 9(3)	0.910 6(5)
O(1)	0.339 2(3)	0.214 3(4)	1.445 6(5)	C(42)	0.235 3(2)	0.190 3(3)	0.812 2(5)
O(2)	0.232 0(4)	0.414 2(4)	1.298 2(6)	C(43)	0.201 0(2)	0.300 8(3)	0.806 7(5)
O(3)	0.330 3(3)	0.251 7(4)	1.161 1(6)	C(44)	0.134 9(2)	0.385 7(3)	0.899 6(5)
O(4)	0.117 2(3)	0.166 2(5)	1.412 8(6)	C(45)	0.103 1(2)	0.360 2(3)	0.998 1(5)
O(5)	0.173 4(2)	0.019 3(4)	1.475 0(5)	C(46)	0.137 3(2)	0.249 8(3)	1.003 6(5)
O(6)	0.013 1(8)	0.490 5(7)	0.377 1(11)	C(51)	0.174 26(19)	−0.071 9(3)	0.817 8(4)
H(1)	0.167(4)	0.242(7)	1.279(8)	C(52)	0.198 59(19)	−0.192 8(3)	0.703 3(4)
H(3)	0.289(5)	0.025(7)	1.408(8)	C(53)	0.142 96(19)	−0.259 1(3)	0.635 1(4)
C(11)	0.326 3(2)	−0.308 7(3)	0.889 7(3)	C(54)	0.062 98(19)	−0.204 4(3)	0.681 3(4)
C(12)	0.280 3(2)	−0.391 9(3)	0.821 9(3)	C(55)	0.038 66(19)	−0.083 5(3)	0.795 8(4)
C(13)	0.300 0(2)	−0.486 0(3)	0.676 8(3)	C(56)	0.094 29(19)	−0.017 2(3)	0.864 0(4)
C(14)	0.365 7(2)	−0.496 7(3)	0.599 4(3)	C(61)	0.334 40(15)	−0.049 9(3)	0.798 9(3)
C(15)	0.411 6(2)	−0.413 4(3)	0.667 1(3)	C(62)	0.406 33(15)	−0.053 2(3)	0.867 1(3)
C(16)	0.391 9(2)	−0.319 4(3)	0.812 2(3)	C(63)	0.477 52(15)	−0.108 3(3)	0.781 6(3)
C(21)	0.400 12(17)	−0.214 9(3)	1.153 8(4)	C(64)	0.476 82(15)	−0.160 1(3)	0.627 9(3)
C(22)	0.438 35(17)	−0.121 6(3)	1.228 0(4)	C(65)	0.404 91(15)	−0.156 7(3)	0.559 6(3)
C(23)	0.513 04(17)	−0.147 8(3)	1.281 0(4)	C(66)	0.333 70(15)	−0.101 6(3)	0.645 1(3)

gave compound (3i) (0.50 g, 0.65 mmol). N.m.r. spectra: ^1H (400 MHz), δ 7.88—7.36 (m, 20 H, Ph), 4.37 [d, second order, 2 H, CH, $|^3J(PH)_{trans} + {}^3J(PH)_{cis}|$ 6.37, $^2J(PtH)$ 53.6 Hz], 2.97 (s, 6 H, Me), and 2.38—2.16 (m, 4 H, CH_2CH_2); ^{13}C-{^1H} ([$^2H_1$]chloroform), δ 178.47 [t, C=O, ring, $^3J(PC)$ 5.75, $^2J(PtC)$ 161], 172.14 [s, C=O, ester, $^2J(PtC)$ 35.98], 132.77 [d, Ph, C−β, $^2J(PC)$ 11.45], 132.66 [d, Ph, C-β, $^2J(PC)$ 10.94] (NB. C-α of Ph obscured by signals due to C-β), 131.37 (s, Ph, C-δ), 131.12 (s, Ph, C-δ), 128.98 [d, Ph, C-γ, $^3J(PC)$ 10.93], 128.67 [d, Ph, C-γ, $^3J(PC)$ 11.70], 54.89 [d, CH, $^2J(PC)$ 53.71, $^1J(PtC)$ 231.0], 49.77 (s, Me, CO_2Me), and 28.72 [d of d, second order, CH_2CH_2, $|^1J(PC) + {}^2J(PC)|$ 25.28 Hz]; ^{31}P-{^1H} (dichloromethane, 24 MHz), 43.56 p.p.m. [s, $^1J(PPt)$ 2 939 Hz]. $\nu_{max.}$ (1 800—1 500 cm^{-1}) at 1 716vs, 1 682vs, 1 635s, 1 586m, and 1 574m cm^{-1}.

(*b*) *From tetrakis*(*ligand*)*platinum*(0). *General method.* A mixture of the platinum(0) complex (*ca.* 0.4 mmol) and the dialkyl 3-oxopentanedioate (0.5 cm^3) in benzene (30 cm^3) was stirred in a flask in the presence of air for several hours (16—120 h). Addition of diethyl ether (100 cm^3) followed by recrystallisation of the fine white precipitate from dichloromethane–light petroleum (b.p. 40—60 °C) gave a white microcrystalline solid which was dried *in vacuo* (0.4 mmHg, *ca.* 54 Pa, at 40 °C). Reaction times are given in Table 3.

(*c*) *Preparation of* $[Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]$. (*i*) *From* $[Pt\{OOC(O)O\}(PPh_3)_2]$. A suspension of $[Pt\{OOC(O)O\}(PPh_3)_2]\cdot C_6H_6$ (0.30 g, 0.34 mmol) in ethanol (40 cm^3) and dimethyl 3-oxopentanedioate (0.5 cm^3, 3.4 mmol) were heated together under reflux for 15 min. The resulting clear solution was filtered and the solvent was evaporated under reduced pressure to give a pale yellow oil. The oil was dissolved in dichloromethane (*ca.* 3 cm^3) and addition of diethyl ether (50 cm^3) gave, on standing, a white crystalline solid, which was recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C) and dried *in vacuo* (0.4 mmHg at 40 °C) to afford compound (3a) (0.25 g, 81.7%).

(*ii*) *From* $[\mathrm{Pt(OCOPh)_2(PPh_3)_2}]$. As above, $[\mathrm{Pt(OCOPh)_2(PPh_3)_2}]$ (0.293 g, 0.31 mmol) and dimethyl 3-oxopentanedioate (0.5 cm^3, 3.4 mmol) after refluxing for 1 h gave compound (3a) (0.19 g, 69.8%).

(*iii*) *From cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$. A mixture of *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ (0.20 g, 0.25 mmol), silver(I) oxide (0.60 g, 2.6 mmol), and dimethyl 3-oxopentanedioate (0.1 cm^3, 0.68 mmol) in dichloromethane (40 cm^3) was heated under reflux for 1 h. It was filtered and the filtrate evaporated under reduced pressure to a small volume (5 cm^3). Addition of light petroleum (b.p. 40—60 °C), with stirring, gave compound (3a) (0.14 g, 62.0%).

(*iv*) *From* [Pt(*trans*-PhCH=CHPh)$(\mathrm{PPh_3})_2$]. An excess of dimethyl 3-oxopentanedioate (0.20 g, 1.15 mmol) and [Pt(*trans*-PhCH=CHPh)$(\mathrm{PPh_3})_2$] (0.31 g, 0.34 mmol) in benzene were stirred together in an open flask for 4 d. The white microcrystalline powder was filtered off and washed with diethyl ether to give compound (3a) (0.16 g, 52.0%).

Reaction of $[\mathrm{Pt(O_2)(PPh_3)_2}]$ *with Dimethyl* 3-*Oxopentanedioate*.—An excess of dimethyl 3-oxopentanedioate (0.20 g, 1.15 mmol) and $[\mathrm{Pt(O_2)(PPh_3)_2}]$ (0.30 g, 0.40 mmol) suspended in diethyl ether were stirred together for 1 h. The resulting white microcrystalline substance was filtered off, washed with diethyl ether, and dried *in vacuo* to give $[\mathrm{Pt\{OOC(CH_2CO_2Me)_2O\}(PPh_3)_2}]$ (7) (0.25 g, 68%), m.p. 158—159 °C (decomp.) (Found: C, 55.1; H, 4.4; O, 11.9. $\mathrm{C_{43}H_{40}O_7P_2Pt}$ requires C, 55.8; H, 4.4; O, 12.1%). N.m.r. spectrum: ^{1}H (100 MHz), δ 7.20 (m, 30 H, Ph), 3.39 (s, 6 H, Me), 3.34, 3.20, 3.07, and 2.93 p.p.m. [AB spin system, 4 H, CH$_2$, ^2J(HH) 14, Δν 23.1 Hz]. $\nu_{\mathrm{max.}}$ (Nujol mull) at 1 742s, 1 725s(sh), 1 696m, 1 589w, 1 573w, 1 316m(sh), 1 298s, 1 223m, 1 215m(sh), 1 186m, 1 170s, 1 149m, 1 114m, 1 100s, 1 074m, 1 046w, 1 030w, 1 020w, 1 000m, 979w, 938w, 850w, 776w(sh), 758m, 747s, 726w, 706s(sh), 699s, 621w, 574m, 553s, 530s, 523s, 518s, 504s, 468w, 452w, 424w, 361w, and 320w cm^{-1}.

Reaction of $[\mathrm{Pt(PPh_3)_4}]$ *suspended in Diethyl Ether with Dimethyl* 3-*Oxopentanedioate*.—An excess of dimethyl 3-oxopentanedioate (0.20 g, 1.15 mmol) and $[\mathrm{Pt(PPh_3)_4}]$ (0.50 g, 0.40 mmol) suspended in diethyl ether were stirred together in an open flask for 24 h. A sample of the white powder was filtered from the reaction mixture, and shown to be a mixture of compounds (3a) and (7) by its i.r. and ^{1}H n.m.r. spectra with the peroxo-compound (7) as the major component. The remainder of the mixture was stirred for a total of 12 d and the resulting white solid identified as compound (3a) (0.32 g, 89%) by its i.r. and ^{1}H n.m.r. spectra. Alternatively, the mixture of complexes could be converted into pure (3a) by stirring in dichloromethane solution in an open flask for 4 d. Overall yield 87%.

Reaction of Hexafluoroacetone with the Peroxo-ring Complex $[\mathrm{Pt\{OOC(CH_2CO_2Me_2)O\}(PPh_3)_2}]$.—An excess of hexafluoroacetone (1.0 cm^3) was condensed (−196 °C) onto a suspension of $[\mathrm{Pt\{OOC(CH_2CO_2Me)_2O\}(PPh_3)_2}]$ (0.30 g, 0.33 mmol) in diethyl ether contained in a Carius tube. The tube was sealed, shaken at room temperature for 7 d, cooled, opened, and volatile material removed. The white solid was filtered off, washed with diethyl ether, and recrystallised from dichloromethane–light petroleum (b.p. 40—60 °C) to give white *crystals* of $[\mathrm{Pt\{OOC(CF_3)_2O\}(PPh_3)_2}]$ (0.24 g, 84%), m.p. 212—214 °C (decomp.) (lit.,[18] 215—216 °C, decomp.) (Found: C, 50.7; H, 3.2; F, 11.7. Calc. for $\mathrm{C_{39}H_{30}F_6O_3P_2Pt}$: C, 51.0; H, 3.3; F, 12.4%).

X-*Ray Data Collection and Structure Determination*.—*Crystal data*. (3a), $\mathrm{C_{43}H_{38}O_5P_2Pt{\cdot}H_2O}$, $M = 909.8$, triclinic, space group $P\bar{1}$, $a = 17.59(1)$, $b = 12.736(6)$, $c = 10.27(1)$ Å, $\alpha = 118.2(1)$, $\beta = 94.7(1)$, $\gamma = 74.0(1)°$, $U = 1\,946.4$ Å^3, $Z = 2$, $D_c = 1.53$ g cm^{-3}, $F(000) = 462$; Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 17.83 cm^{-1}.

Measurements. The crystal (*ca*. 0.15 × 0.15 × 0.2 mm) was mounted about the *c* axis in air. The cell dimensions were determined from an oscillation photograph about the *c* axis of the crystal and from its optimised counter angles for zero- and upper-layer reflections on a Weissenberg diffractometer. Intensity data were collected at room temperature on a Stoe Weissenberg diffractometer with an ω-scan technique in the range $7 \leqslant 2\theta \leqslant 60°$. The 7 263 reflections, collected from Weissenberg layers *hk*(0—10), having $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarisation effects. Subsequent calculations were carried out using the computer program SHELX.[60]

Structure solution and refinement. The molecular structure (Figure 1) was solved by conventional Patterson and Fourier difference techniques. Scattering factors for the atoms were taken from ref. 61. In the final stages of blocked-matrix least-squares refinement all non-hydrogen atoms were given anisotropic thermal parameters. All the phenyl rings were treated as rigid bodies with D_{6h} symmetry and C–C distances of 1.395(5) Å. The hydrogen-atom positions for H(1) and H(3) were located from a Fourier difference map. They were then refined subject to a weak constraint that the corresponding C–H distances were 1.08(5) Å; the angular orientation of the C–H vector was not constrained. The hydrogen thermal parameters refined to reasonable values. The hydrogen atoms of the phenyl rings and methyl groups were refined at calculated positions [C–H 1.08(5) Å]. Final cycles employed weights calculated from $w = 1/(\sigma^2F_o + gF_o^2)$, $g = 0.000\,743$. The final residual indices were $R[=\Sigma(||F_o| - |F_c||)/\Sigma|F_o|] = 0.0349$, $R'[= \Sigma w(||F_o| - |F_c||)/\Sigma w|F_o|] = 0.0362$. The atomic co-ordinates are given in Table 4.

Acknowledgements

We thank the S.E.R.C. for support and for provision of high-field n.m.r. facilities, Johnson Matthey Ltd. for the generous loan of platinum metal salts, Drs. O. Howarth and E. Curzon (University of Warwick) for high-field ^{1}H and ^{13}C n.m.r. spectra, and Dr. I. H. Sadler (University of Edinburgh) for low-temperature ^{31}P n.m.r. spectra and heteronuclear decoupling experiments.

References

1 B. M. Trost and D. M. T. Chan, *J. Am. Chem. Soc.*, 1983, **105**, 2315, 2326.
2 P. Binger, M. Cetinkaya, M. J. Doyle, A. Germer, and U. Schuchardt, *Fundam. Res. Homogeneous Catal.*, 1979, **3**, 271.
3 R. Noyori, M. Yamakawa, and H. Takaya, *Tetrahedron Lett.*, 1978, 4823.
4 R. Noyori, *Acc. Chem. Res.*, 1979, **12**, 61.
5 H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 819.
6 A. J. Deeming, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 4, p. 447.
7 R. Davis and L. A. P. Kane-Maguire, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 3, pp. 960, 1175.
8 S. G. Barnes and M. Green, *J. Chem. Soc., Chem. Commun.*, 1980, 267.
9 J. M. Mayer, C. J. Curtis, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1983, **105**, 2651.
10 N. Yanase, Y. Nakamura, and S. Kawaguchi, *Inorg. Chem.*, 1980, **19**, 1575.

11 Y. Otani, Y. Nakamura, S. Kawaguchi, S. Okeya, and T. Hinomoto, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1467.
12 S. Okeya, Y. Nakamura, S. Kawaguchi, and T. Hinomoto, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 477.
13 T. H. Tulip and D. L. Thorn, *J. Am. Chem. Soc.*, 1981, **103**, 2448.
14 D. A. Clarke, R. D. W. Kemmitt, M. A. Mazid, M. D. Schilling, and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1978, 744.
15 R. D. W. Kemmitt, P. McKenna, D. R. Russell, and L. J. S. Sherry, *J. Organomet. Chem.*, 1983, **253**, C59.
16 P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Am. Chem. Soc.*, 1970, **92**, 5873,
17 G. M. Zanderighi, R. Ugo, A. Fusi, and Y. Ben Taarit, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 729.
18 P. J. Hayward and C. J. Nyman, *J. Am. Chem. Soc.*, 1971, **93**, 617.
19 C. J. Nyman, C. E. Wymore, and G. Wilkinson, *J. Chem. Soc. A*, 1968, 561.
20 R. D. W. Kemmitt and D. R. Russell, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 5, p. 1.
21 M. E. Kastner and W. R. Scheidt, *J. Organomet. Chem.*, 1978, **157**, 109.
22 W. P. Schaefer, R. Waltzman, and B. T. Huie, *J. Am. Chem. Soc.*, 1978, **100**, 5063.
23 A. Nashinaga, K. Nishizawa, Y. Nakayama, and T. Matsuura, *Tetrahedron Lett.*, 1977, 85.
24 F. R. Hartley, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, p. 471.
25 T. G. Appleton and M. A. Bennett, *Inorg. Chem.*, 1978, **17**, 738.
26 D. P. Arnold and M. A. Bennett, *J. Organomet. Chem.*, 1980, **199**, 119.
27 M. A. Cairns, K. R. Dixon, and M. A. R. Smith, *J. Organomet. Chem.*, 1977, **135**, C33.
28 M. E. Fakley and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 1977, 1444.
29 R. Ros, R. A. Michelin, R. Bataillard, and R. Roulet, *J. Organomet. Chem.*, 1978, **161**, 75.
30 P. Foley, R. DiCosimo, and G. M. Whitesides, *J. Am. Chem. Soc.*, 1980, **102**, 6713.
31 J. A. Ibers, R. DiCosimo, and G. M. Whitesides, *Organometallics*, 1982, **1**, 13.
32 R. J. Puddephatt, *Coord. Chem. Rev.*, 1980, **33**, 149.
33 S. S. Moore, R. DiCosimo, A. F. Sowinski, and G. M. Whitesides, *J. Am. Chem. Soc.*, 1981, **103**, 948.
34 D. J. Yarrow, J. A. Ibers, M. Lenarda, and M. Graziani, *J. Organomet. Chem.*, 1974, **70**, 133.
35 J. W. Bruno, T. J. Marks, and V. W. Day, *J. Am. Chem. Soc.*, 1982, **104**, 7357.
36 R. J. Klinger, J. C. Huffman, and J. K. Kochi, *J. Am. Chem. Soc.*, 1982, **104**, 2147.
37 C. Riche, *Acta Crystallogr., Sect. B*, 1974, **30**, 587.
38 R. McWeeny, 'Coulsons Valence,' 3rd edn., Oxford University Press, Oxford, 1979.
39 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.
40 D. J. Gordon, R. F. Fenske, T. N. Nanninga, and B. M. Trost, *J. Am. Chem. Soc.*, 1981, **103**, 5974.
41 R. Mason and A. G. Wheeler, *J. Chem. Soc. A*, 1968, 2549.
42 P. M. Maitlis, P. Espinet, and M. J. H. Russell, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, p. 385.
43 W. E. Carroll, M. Green, J. A. K. Howard, M. Pfeffer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1978, 1472.
44 S. F. Dyke, A. J. Floyd, M. Sainsbury, and R. S. Theobald, 'Organic Spectroscopy,' 2nd edn., Longman, London and New York, 1978, p. 142.
45 M. K. Deh, R. D. W. Kemmitt, P. McKenna, D. R. Russell, and L. J. S. Sherry, *J. Chem. Soc., Chem. Commun.*, 1982, 505; unpublished work.
46 J. P. Albrand, D. Gagnaire, M. Picard, and J. B. Robert, *Tetrahedron Lett.*, 1970, 4593.
47 W. B. Jennings, D. R. Boyd, C. G. Watson, E. D. Becker, R. B. Bradley, and D. M. Jerina, *J. Am. Chem. Soc.*, 1972, **94**, 8501.
48 See, for example, N. M. Boag, M. Green, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1200; D. J. Mabbott, B. E. Mann, and P. M. Maitlis, *ibid.*, 1977, 294.
49 H. Kurosawa and N. Asada, *J. Organomet. Chem.*, 1981, **217**, 259.
50 J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 1967, 1839.
51 J. Powell and A. W-L. Chan, *J. Organomet. Chem.*, 1972, **35**, 203.
52 H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 1956, **25**, 1228.
53 T. Glonek and J. R. van Wazer, *J. Magn. Reson.*, 1974, **13**, 390.
54 L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.
55 B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc. A*, 1968, 167.
56 R. G. Pearson, W. Louw, and J. Rajaram, *Inorg. Chim. Acta*, 1974, **9**, 251.
57 J. C. Bailar, jun., and H. Itatani, *Inorg. Chem.*, 1965, **4**, 1618.
58 D. M. Blake and L. M. Leung, *Inorg. Chem.*, 1972, **11**, 2879.
59 C. Eaborn, A. Pidcock, and B. R. Steele, *J. Chem. Soc., Dalton Trans.*, 1975, 809.
60 G. M. Sheldrick, SHELX 76 Program for crystal structure determination, University of Cambridge, 1976.
61 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

Received 7*th November* 1983; *Paper* 3/1987