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 †

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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

[Pt(CHRCOCHR)L₂] (R = CO₂Me, L = PPh₃, AsPh₃, PMePh₂ or PMe₂Ph; 2L = Ph₂PCH₂CH₂PPh₂; R = CO₂Et, L = PPh₃, or AsPh₃; R = CO₂Prⁿ, L = PPh₃, or AsPh₃). The compounds [Pt(CHRCOCHR)-L₂] (R = CO₂Me, L = PPh₃, AsPh₃, PMePh₂, or PMe₂Ph; R = CO₂Et, L = PPh₃ or AsPh₃) are also formed upon treatment of benzene solutions of [PtL₄] with RCH₂COCH₂R in the presence of air.

Using the latter method, the triphenylphosphine derivative $[P_{1}^{\dagger}(CH(CO_{2}Me)COCH(CO_{2}Me))(PPh_{3})_{2}]$

is often contaminated with the peroxo-ring compound $[Pt{OOC(CH_2CO_2Me)_2O}(PPh_3)_2]$ 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 $[Pt(trans-PhCH=CHPh)(PPh_3)_2]$ in benzene in the presence of

air, [PtOOC(0)O(PPh₃)₂] in ethanol, cis-[Pt(OCOPh)₂(PPh₃)₂] in ethanol, or cis-[PtCl₂(PPh₃)₂] and

silver oxide in dichloromethane also affords [Pt{CH(CO₂Me)COCH(CO₂Me)}(PPh₃)₂]. A single-crystal

X-ray diffraction study has been carried out on $[Pt{CH(CO_2Me)COCH(CO_2Me)}(PPh_3)_2]\cdot H_2O$ (3a). The crystals are triclinic, space group PI, 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 $\gamma = 74.0(1)^\circ$. The structure has been refined to R 0.035 (R' 0.036) for 7 263 reflections with $l \ge 3\sigma(l)$. It can be considered to be based either upon a highly puckered platina-cyclobutan-3-one ring [fold angle = $50.4(4)^\circ$] 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, ¹³C-{¹H}, and ³¹P-{H}) are

reported and variable-temperature ¹H n.m.r. data for the compounds [Pt(CHRCOCHR)L₂] (R = CO_2Me , L = PPh₃ or AsPh₃) 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(11) ^{10,11} and platinum(11) ¹² of the type [M(η^3 -CH₂COCHR)L₂] (M = Pd, R = COMe or CO₂Et, 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 $[[r(CH_2COCH_2)H(PMe_3)_3]^{13}$ 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(11) (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(triphenyl-phosphine)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.



(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) $2L = Ph_2PCH_2CH_2PPh_2$, $R = CO_2Me$



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(OOCR₂O)(PPh₃)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 v(O-O). The ¹H 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(CF₃)₂O}(PPh₃)₂].¹⁸ Dis-

placement of acetone by hexafluoroacetone is known to occur upon treatment of $[Pt(OOCMe_2O)(PPh_3)_2]$ with hexa-fluoroacetone.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 peroxoView Article Online



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(PPh₃)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-(PPh₃)₄] in the presence of air can be understood in terms of formation of the dioxygen compound [Pt(O₂)(PPh₃)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(CO₂Me)COCH₂(CO₂Me)} species provides an attractive route to the platinacyclobutan-3-one since similar eliminations from the organometal systems MCH₂COMe and MCH₂CMe₃ have been shown to afford the

metallacyclic rings $\dot{M}CH_2CO\dot{C}H_2$ and $\dot{M}CH_2CMe_2\dot{C}H_2$ 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 $[M(\eta^3-CH_2COCHR)L_2]^{.10-12}$ Consistent with the mechanism outlined in the Scheme, there is no reaction between [Pt-(PPh₃)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 peroxocompound (7) could be a source of the platinacyclobutan-3one. Thus, treatment of (7) in dichloromethane with triphenylphosphine and (6a) for 4 d affords the platinacyclobutan-3one (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(PPh₃)₄] and (6a) in air. Interestingly, treatment of compound (7) in dichloromethane with either PPh₃ 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) CO₂; (ii) RCH₂COCH₂R; (iii) RCH₂C(OH)=CHR

plexes [PtL₄] (L = AsPh₃, PMePh₂, or PMe₂Ph) 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(CH₂CO₂Et)₂O}(PPh₃)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-(PPh₃)₂] in refluxing ethanol or a mixture of cis-[PtCl₂(PPh₃)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(CO₃)L₂] (L = PPh₃, AsPh₃, PMePh₂, or PMe₂Ph; L₂ = Ph₂PCH₂CH₂PPh₂) 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.

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



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

platinum is essentially square planar (Table 2), with similar bond angles about platinum and similar twist angles between PPtP and CPtC planes $[8.1(2)^{\circ}$ 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

CH(CO ₂ Me)COCH(CO ₂ Me) ligand							nylphosphi	ne 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) 1.82	5(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) 1.83	0(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) 1.81	9(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) 1.83	7(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) 1.83	2(4)
		C(4)-O(3)	1.323(8)			P(2)-C	(61) 1.80	07(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)
Cł	H(CO₂Me)COC	H(CO₂Me) ligar	nd	Triphenylphosphine ligand:			e 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)	
CÌ	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	2(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	2(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)				

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



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-tbutylcyclobutan-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(sp²) 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 ¹H-decoupled ¹³C n.m.r. spectrum discussed below. The orientation of the PtC₃ 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 $-43.0(5)^\circ$ 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'NC)₂Pt{ μ -(PhC)₂CO}Pt-(CNBu')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 C₃ 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 $[\dot{M}(CH_2CO\dot{C}HR)L_2]$ (M = Pd, R = COMe or CO₂Et; M = Pt, R = COMe) with the substituent R occupying an axial position of a puckered ring.

The role that the CO_2Me ester substituents play in determining the extent of the non-planarity of the platinacyclobutan-3one ring in compound (3a) is not clear. N.m.r. data for the compounds [M(CH₂COCHR)L₂] indicate that the fourmembered 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 ¹H n.m.r. spectrum of the platinacyclobutan-3-one (3a), measured at -115 °C in CD₂Cl₂, 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 ¹H

n.m.r. data for the compounds $[M(CH_2COCHR)L_2]^{10-12}$ which show that for the CH₂ group the axial proton is more deshielded than the equatorial proton. We have also previously indicated that in metallacyclobutan-3-ones¹⁵ 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 ¹H n.m.r. spectrum of (3a), measured at -115 °C in CD₂Cl₂, 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 ¹H-{³¹P} broad-band-decoupled n.m.r. spectrum of (3a), measured at 360 MHz in CD₂Cl₂ 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 ¹H-{³¹P} 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 [${}^{3}J(PH)$ 4—5 Hz], which was partially obscured by one of the methyl signals. The ³¹P-{¹H} n.m.r. spectrum of (3a) measured at 146 MHz in CD₂Cl₂ 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 ¹H 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 ${}^{2}J(PH)$ 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 ${}^{2}J({}^{15}NH)$ 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_{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_{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 ¹⁹⁵Pt 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 ${}^{3}J(trans-PH)$ 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 antiand 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 ¹H 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 = ³¹P) with ¹⁹⁵Pt 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, ΔG^{\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 $\Delta G_{T_c}^{\ddagger}$ 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(11) as compared to palladium(II) metallacyclobutan-3-ones. These differences are probably a reflection of the greater tendency of four-coordinate 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 platinumcarbon 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(CH₂CH₂CH₂)(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 ¹⁹⁵Pt coupling to the β -hydrogens.³⁶

The ¹³C-{¹H-decoupled} n.m.r. spectrum of compound (3a) recorded at room temperature showed peaks corresponding to the carbon nuclei present, the carbon atoms C¹ and C³ 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 C¹, C², and C³ than for the C=O carbons of the CO₂Me groups is consistent with a bonding interaction between the platinum and the ring carbons. The relative magnitudes of $J(Pt-C^1)$ and ² $J(Pt-C^2)$ are similar to those found for platinacyclobutanes ³² and for the η^3 -2,4-

pentanedionato(2–)-compound [Pt(CH₂COCHR){P(C₆H₄Clp)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 ¹³C-{¹H-decoupled} n.m.r. spectra of compounds (3d) and (3g)—(3i) exhibited similar features to those observed for (3a), the ring carbonyl carbon C² exhibiting coupling to platinum and to both phosphorus nuclei. The room-temperature ³¹P-{¹H-decoupled} n.m.r. spectra of (3a)—(3c) and (3g)—(3i) exhibited a single resonance with ¹⁹⁵Pt 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 hotstage 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 SiMe₄ (0.0 p.p.m.) as internal reference, positive values being to high frequency (low field) in [²H₁]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 SiMe₄ (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 $[^{2}H_2]$ 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 [²H₂]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(PPh₃)₄],⁵⁴ [Pt(AsPh₃)₄],⁵⁴ [Pt(PMePh₂)₄],⁵⁵ [Pt-(PMe₂Ph)₄],⁵⁶ cis-[PtCl₂(PPh₃)₂],⁵⁷ cis-[Pt(OCOPh)₂(PPh₃)₂],¹⁹ [Pt(O₂)(PPh₃)₂],¹⁹ [Pt{OOC(O)O}(PPh₃)₂],¹⁶ and [Pt(CO₃)L₂] $(L = PPh_{3})^{16} PMePh_{2}^{58} PMe_{2}Ph_{5}^{59} \text{ or } AsPh_{3}; {}^{16} L_{2} = Ph_{2}^{-1}$ PCH₂CH₂PPh₂¹⁶) 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 'H n.m.r. spectrum of a 50% solution of dimethyl 3-oxopentanedioate in $[{}^{2}H_{1}]$ 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 = CO₂Me), 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 [²H₂]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 cm³) 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 cm³) followed by addition of diethyl ether (50 cm³) 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(CO₂Me)COCH(CO₂Me)}(PPh₃)₂]. The compound [Pt(CO₃)(PPh₃)₂]·C₆H₆ (0.40 g, 0.47 mmol) and dimethyl 3oxopentanedioate (0.5 cm³, 3.4 mmol) gave compound (3a) (0.34 g, 0.4 mmol). N.m.r. spectra: ¹H ([²H₂]dichloromethane-CH₂Cl₂, 400 MHz), δ 7.39—7.24 (m, 30 H, Ph), 3.729 [d, second order, 2 H, CH]³J(PH)_{trans} + ³J(PH)_{cts}| 4.43, ²J(PtH) 54.17 Hz], and 3.046 (s, 6 H, Me); ¹H([²H₂]dichloromethane-CH₂Cl₂, -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); ¹H-{³¹P} ([²H₁]chloroform, 60 MHz, irradiated at 24.29092 MHz), 8 7.4-7.2 (m, 30 H, Ph), 3.89 [s, 2 H, CH, ²J(PtH) 74 Hz], and 3.06 (s, 6 H Me); ¹H-{³¹P} ([²H₂]dichloromethane, 360 MHz, broad-band irradiation, -115 °C), 8 4.01 [s, 1 H, CH, ²J(PtH) 72], 3.18 [s, 1 H, CH, ²J(PtH) not discernible], 3.14 (s, 3 H, Me), and 2.63 (s, 3 H, Me); ¹H-{³¹P} ([²H₂]dichloromethane, 360 MHz, irradiated at 145.787236 MHz {P(1)}, -115 °C), 4.01 [s, 1 H, CH, ²J(PtH) 72], & 3.18 [d, 1 H, ³J(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, ³J(PH) 11.7, ²J(PtH) 72], 3.18 [d, 1 H, ³J(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, ³J(PC) 5.3, ²J(PtC) 175.5], 171.68 [s, C=O, CO₂Me, ²J(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 , $|^{3}J(PC)$ + ⁵J(PC) 9.77], 56.427 {d,d, second order, CH, $|^{2}J(PC)_{trans}$ + ²J(PC)_{cts} 54.93, ¹J(PtC) 273.9 Hz], and 50.255 (s, Me); ³¹P-{¹H} ([²H₁]chloroform, 24 MHz), δ 16.94 [s, ¹J(PtP) 3 081 Hz]; ³¹P-{¹H} ([²H₂]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}. v_{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(CO₂Et)COCH(CO₂Et)}(PPh₃)₂]. The compound [Pt(CO₃)(PPh₃)₂]·C₆H₆ (0.30 g, 0.35 mmol) and diethyl 3oxopentanedioate (0.5 cm³, 2.7 mmol) gave compound (3b) (0.26 g, 0.29 mmol). N.m.r. spectra: ¹H (400 MHz), δ 7.36— 7.15 (m, 30 H, Ph), 3.895 [d, second order, 2 H, CH, |³J-(PH)_{trans} + ³J(PH)_{cts}| 4.27, ²J(PtH) 52.2], 3.469 [d,d,q, secondorder AB spin system, 4 H, CH₂, ³J(HH) 7.2, ²J(HH) 10.67, $\delta_A - \delta_B$ 0.562], and 0.670 [t, 6 H, Me, ³J(HH) 7.2 Hz]; ³¹P-{¹H} ([²H₁]chloroform 24 MHz), δ 16.94 p.p.m. [s, ¹J-(PtP) 3 066 Hz]. v_{max}. (1 800—1 500 cm⁻¹) at 1 712s, 1 683vs, 1 636vs, 1 586m, and 1 571m cm⁻¹.

[Pt{CH(CO₂Prⁿ)COCH(CO₂Prⁿ)}(PPh₃)₂]. The compound [Pt(CO₃)(PPh₃)₂]·C₆H₆ (0.25 g, 0.29 mmol) and di-n-propyl 3-oxopentanedioate (0.5 cm³, 2.4 mmol) gave compound (3c) (0.19 g, 0.21 mmol). N.m.r. spectra: ¹H (400 MHz), δ 7.35— 7.15 (m, 30 H, Ph), 3.915 [d, second order, 2 H, CH, |³J-(PH)_{trans} + ³J(PH)_{c1s}| 4.27, ²J(PtH) 52.8], 3.360 [d,d,t, secondorder AB spin system, 4 H, CH₂, ³J(HH) 7.2, ²J(HH) 10.50, $\delta_{A} - \delta_{B}$ 0.660], 1.174 [sextet, 4 H, CH₂, ³J(HH) 7.2], and 0.670 [t, 6H, Me, ³J(HH) 7.2 Hz]; ³¹P-{¹H} ([²H₁]chloroform, 24 MHz), δ 16.94 p.p.m. [s, ¹J(PtP) 3 076 Hz].v_{max}. (1 800—1 500 cm⁻¹) at 1 720vs, 1 683vs, 1 644vs, 1 582m, and 1 573m, cm⁻¹.

[Pt{CH(CO₂Me)COCH(CO₂Me)}(AsPh₃)₂]. The compound [Pt(CO₃)(AsPh₃)₂]·C₆H₆ (0.27 g, 0.29 mmol) and dimethyl 3-oxopentanedioate (0.5 cm³, 3.4 mmol) gave compound (3d) (0.24 g, 0.25 mmol). N.m.r. spectra: ¹H (100 MHz), δ 7.4—7.1 (m, 30 H, Ph), 4.16 [s, 2 H, 3H, ²J(PtH) 71.64 Hz], and 3.04 (s, 6 H, Me); ¹H ([²H₂]dichloromethane-CH₂Cl₂, -98 °C, 400 MHz), δ 7.98—6.60 (m, 30 H, Ph), 4.02 [s, 1 H, CH, ²J(PtH) 81], 3.67 [s, 1 H, CH, ²J(PtH) 36 Hz], 2.96 (s, 3 H, Me), and 2.67 (s, 3 H, Me); ¹³C-{¹H} ([²H₁]chloroform), δ 179.26 [s, C=O, ring, ²J(PtC) 195], 171.48 [s, C=O, ester, ²J(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). v_{max}. (1 800—1 500 cm⁻¹) at 1 714vs, 1 697vs, 1 627vs, 1 580m, and 1 572m cm⁻¹.

[Pt(CO₂Et)COCH(CO₂Et)}(AsPh₃)₂]. The compound [Pt(CO₃)(AsPh₃)₂]·C₆H₆ (0.26 g, 0.28 mmol) and diethyl 3oxopentanedioate (0.5 cm³, 3.4 mmol) gave compound (3e) (0.20 g, 0.21 mmol). N.m.r. spectrum: ¹H (400 MHz), δ 7.30— 7.14 (m, 30 H, Ph), 4.09 [s, 2 H, CH, ²J(PtH) 69.9], 3.45 [d,d,q, second-order AB spin system, 4 H, CH₂, ³J(HH) 7.2, ²J(HH) 10.6, $\delta_A - \delta_B$ 0.56], and 0.74 p.p.m. [t, 6 H, Me, ³J-(HH) 7.2 Hz]. v_{max.} (1 800—1 500 cm⁻¹) at 1 714s, 1 689vs, 1 645vs, 1 581m, and 1 572m cm⁻¹.

[Pt{CH(CO₂Prⁿ)COCH(CO₂Prⁿ)}(AsPh₃)₂]. The compound [Pt(CO₃)(AsPh₃)₂]·C₆H₆ (0.50 g, 0.53 mmol) and di-n-propyl 3-oxopentanedioate (0.5 cm³, 2.4 mmol) gave compound (3f) (0.38 g, 0.38 mmol). N.m.r. spectrum: ¹H (400 MHz), δ 7.30— 7.14 (m, 30 H, Ph), 4.12 [s, 2 H, CH, ²J(PtH) 69.6], 3.33 [d,d,t, second-order AB spin system, 4 H, CH₂, ³J(HH) 7.2, ²J(HH) 10.8, $\delta_A - \delta_B$ 0.69], 1.106 [d,d, sextet, second-order AB spin sytem, 4 H, CH₂, ³J(HH) 7.2, ²J(HH) 13.5, $\delta_A - \delta_B$ 0.09], and 0.65 p.p.m. [t, 6 H, Me, ³J(HH) 7.2 Hz]. v_{max} (1 800—1 500 cm⁻¹) at 1 718vs, 1 685vs, 1 648vs, 1 580m, and 1 574m cm⁻¹.

 $[Pt{CH(CO_2Me)COCH(CO_2Me)}(PMePh_2)_2]$. The compound [Pt(CO₃)(PMePh₂)₂] (0.36 g, 0.55 mmol) and dimethyl 3-oxopentanedioate (0.5 cm³, 3.4 mmol) gave compound (3g) (0.31 g, 0.39 mmol). N.m.r. spectra: ¹H (100 MHz), δ 7.4-7.0 (m, 20 H, Ph), 3.96 (d, second order, 2 H, CH, $|{}^{3}J(PH)_{trans}$ + ³J(PH)_{cts} 4.8, ²J(PtH) 55.5], 3.04 (s, 6 H, CO₂Me), and 1.86 [d, second order, 6 H, PMe, $|{}^{2}J(PH) + {}^{4}J(PH)|$ 9.0, ${}^{3}J(PtH)$ 31.5 Hz]; ¹³C-{¹H} ([²H₁]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. $C-\alpha$ 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 CH, $|^{2}J(PC)_{trans} + {}^{2}J(PC)_{cts}|$ 51.19, J(PtC) 245], order, 50.13 (s, Me, CO₂Me), and 15.55 p.p.m. (d, second order, Me, PMePh₂, $|^{1}J(PC) + {}^{3}J(PC)|$ 39.04, ${}^{2}J(PtC)$ 17 Hz]; ³¹P-{¹H} (dichloromethane, 24 MHz), δ -1.01 p.p.m. [s, J(PPt) 2 988 Hz]. v_{max} (1 800—1 500 cm⁻¹) at 1 720vs, 1 686vs, 1 630vs, 1 587m, and 1 572m cm⁻¹.

 $[Pt{CH(CO_2Me)COCH(CO_2Me)}(PMe_2Ph)_2]$. The compound [Pt(CO₃)(PMe₂Ph)₂] (0.27 g, 0.51 mmol) and dimethyl 3-oxopentanedioate (0.5 cm³, 3.4 mmol) gave compound (3h) (0.21 g, 0.33 mmol). N.m.r. spectra ¹H (100 MHz), δ 7.3-7.2 (m, 10 H, Ph), 4.07 [d, second order, 2 H, CH, |³J(PH)_{trans} $+ {}^{3}J(PH)_{cis}$ 5.6, ${}^{2}J(PtH)$ 55.2], 3.50 (s, 6 H, CO₂Me), 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]; ¹³C-{¹H} ([²H₁]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, CO₂-Me), 15.94 {d, second order, Me, PMe_2Ph , $|^{1}J(PC) + {}^{3}J(PC)|$ 39.02], and 14.72 [d, second order, Me, PMe₂Ph, $|{}^{1}J(PC) + {}^{3}J(PC)|$ 37.80 Hz]; ${}^{31}P-{}^{1}H$ (dichloromethane, 24 MHz), -15.93 p.p.m. [s, J(PPt) 2 949 Hz]. v_{max} (1 800-1 500 cm⁻¹) at 1 692vs, 1 676vs, 1 630vs, 1 587m, and 1 572m cm⁻¹.

 $[Pt{CH(CO_2Me)COCH(CO_2Me)}(Ph_2PCH_2CH_2PPh_2)].$ The compound $[Pt(CO_3)(Ph_2PCH_2CH_2PPh_2)]$ (0.60 g, 0.92 mmol) and dimethyl 3-oxopentanedioate (0.5 cm³, 3.4 mmol)

Table 3.	Preparations,	yields,	melting	points,	and	analytical	data	a
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	Reaction time (h)	Yield (%) using			Analysis (%)		
Complex	using [PtL ₄]	[PtL ₄]	[Pt(CO ₃)L ₂]	M.p. (θ _c /°C)	C	Н	
(3a)	64	73 ^ø	82	218	57.8 (57.9)	4.4 (4.3)	
(3b)	64	49 ^o	81	215—220 °	58.8 (58.8)	4.7 (4.6)	
(3c)			69	211—213 °	59.3 (59.6)	5.0 (4.9)	
(3d)	64	69	86	205—207 °	52.9 (52.7)	4.0 (3.9)	
(3e)	120	57	72	205 °	53.4 (53.6)	4.3 (4.2)	
άń			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	У	z	Atom	x	У	Ζ
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)	-0.3606(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)	-0.3344(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)	-0.2252(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, $|^{3}J(PH)_{trans} + {}^{3}J(PH)_{cts}|$ 6.37, ${}^{2}J(PtH)$ 53.6 Hz], 2.97 (s, 6 H, Me), and 2.38—2.16 (m, 4 H, CH₂CH₂); ${}^{13}C-{}^{1}H$ } ([${}^{2}H_{1}$]chloroform), δ 178.47 [t, C=O, ring, ${}^{3}J(PC)$ 5.75, ${}^{2}J(PtC)$ 161], 172.14 [s, C=O, ester, ${}^{2}J(PtC)$ 35.98], 132.77 [d, Ph, C- β , ${}^{2}J(PC)$ 11.45], 132.66 [d, Ph, C- β , ${}^{2}J(PC)$ 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 , ${}^{3}J(PC)$ 53.71, ${}^{1}J(PC)$ 231.0], 49.77 (s, Me, CO₂Me), and 28.72 [d of d, second order, CH₂CH₂, $|{}^{1}J(PC) + {}^{2}J(PC)|$ 25.28 Hz]; ${}^{31}P-{}^{1}H$ } (dichloromethane, 24 MHz), 43.56 p.p.m. [s, ${}^{1}J(PT)$ 2 939 Hz]. v_{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 cm³) 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 cm³) and dimethyl 3-oxopentanedioate (0.5 cm³, 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 cm³) and addition of diethyl ether (50 cm³) 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 $[Pt(OCOPh)_2(PPh_3)_2]$. As above, $[Pt(OCOPh)_2(PPh_3)_2]$ (0.293 g, 0.31 mmol) and dimethyl 3-oxopentanedioate (0.5 cm³, 3.4 mmol) after refluxing for 1 h gave compound (3a) (0.19 g, 69.8%).

(*iii*) From cis-[PtCl₂(PPh₃)₂]. A mixture of cis-[PtCl₂(PPh₃)₂] (0.20 g, 0.25 mmol), silver(1) oxide (0.60 g, 2.6 mmol), and dimethyl 3-oxopentanedioate (0.1 cm³, 0.68 mmol) in dichloromethane (40 cm³) was heated under reflux for 1 h. It was filtered and the filtrate evaporated under reduced pressure to a small volume (5 cm³). Addition of light petroleum (b.p. 40-60 °C), with stirring, gave compound (3a) (0.14 g, 62.0%).

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

Reaction of $[Pt(O_2)(PPh_3)_2]$ with Dimethyl 3-Oxopentanedioate.—An excess of dimethyl 3-oxopentanedioate (0.20 g, 1.15 mmol) and $[Pt(O_2)(PPh_3)_2]$ (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 $[Pt{OOC(CH_2CO_2Me)_2O}(PPh_3)_2]$ (7) (0.25 g, 68%), m.p. 158—159 °C (decomp.) (Found: C, 55.1; H, 4.4; O, 11.9. C₄₃H₄₀O₇P₂Pt requires C, 55.8; H, 4.4; O, 12.1%). N.m.r. spectrum: ¹H (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, CH₂, ²J(HH) 14, Δv 23.1 Hz]. v_{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

Reaction of $[Pt(PPh_3)_4]$ suspended in Diethyl Ether with Dimethyl 3-Oxopentanedioate.—An excess of dimethyl 3oxopentanedioate (0.20 g, 1.15 mmol) and $[Pt(PPh_3)_4]$ (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 ¹H 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 ¹H 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

 $[Pt{OOC(CH_2CO_2Me_2)O}(PPh_3)_2]$.—An excess of hexafluoroacetone (1.0 cm³) was condensed (-196 °C) onto a suspension

of $[Pt{OOC(CH_2CO_2Me)_2O}(PPh_3)_2]$ (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 crys-

tals of $[Pt\{OOC(CF_3)_2O\}(PPh_3)_2]$ (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 $C_{39}H_{30}F_6O_3P_2Pt$: C, 51.0; H, 3.3; F, 12.4%).

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X-Ray Data Collection and Structure Determination.— Crystal data. (3a), $C_{43}H_{38}O_5P_2Pt \cdot H_2O$, M = 909.8, triclinic, space group PI, a = 17.59(1), b = 12.736(6), c = 10.27(1) Å, $\alpha = 118.2(1)$, $\beta = 94.7(1)$, $\gamma = 74.0(1)^\circ$, U = 1 946.4 Å³, 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. $0.15 \times 0.15 \times 0.2$ 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 $7 \le 20 \le 60^\circ$. The 7 263 reflections, collected from Weissenberg layers hk(0-10), having $I \ge 3\sigma(I)$ 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 leastsquares 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 $w = 1/(\sigma^2 F_0 + gF_0^2)$, g = 0.000 743. The final residual indices were $R[=\Sigma(||F_0| - |F_c|)/\Sigma|F_0]] =$ 0.0349, $R'[= \Sigma w(||F_o| - |F_c||)/\Sigma w|F_o|] = 0.0362$. The atomic co-ordinates are given in Table 4.

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