Chemistry of Metallacyclobutanones. Part 3.[1] Reactions of Heptane-2,4,6-trione and 1,5-Diphenylpentane-1,3,5-trione with some Carbonate Complexes of Platinum(II); X-Ray Crystal Structures of $[Pt\{CH(COMe)COCH(COMe)\}(PPh_3)_2]$ and $[Pt\{OC(CHCOPh)CHC(Ph)O\}(PPh_3)_2]$†

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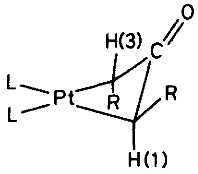
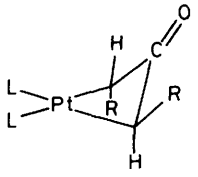
Heptane-2,4,6-trione reacts with the carbonate complexes $[Pt(CO_3)L_2]$ in warm ethanol to afford high yields of the platinacyclobutan-3-one complexes $[Pt(CHRCOCHR)L_2]$ (R = COMe, L = PPh_3 or $AsPh_3$). A single-crystal X-ray diffraction study has been carried out on the complex $[Pt\{CH(COMe)COCH(COMe)\}(PPh_3)_2]$. The molecular structure can be considered to be based upon a highly puckered platinacyclobutan-3-one ring complex [fold angle 48.0(4)°] with a weak transannular Pt–C bond of 2.486(6) Å, the allylic structure $[Pt\{\eta^3\text{-}CH(COMe)COCH(COMe)\}(PPh_3)_2]$ making a significant contribution to the bonding. N.m.r. data (^1H, ^{13}C-$\{^1H\}$) are reported and variable-temperature ^1H n.m.r. data for the complexes $[Pt\{CH(COMe)COCH(COMe)\}L_2]$ (L = PPh_3 or $AsPh_3$) are interpreted in terms of inversion of the platinacyclobutan-3-one ring through a planar transition state. In contrast, 1,5-diphenylpentane-1,3,5-trione reacts with $[Pt(CO_3)(PPh_3)_2]$ in warm ethanol to afford the dienediolate complex $[Pt\{OC(CHCOPh)CHC(Ph)O\}(PPh_3)_2]$ which was characterised by X-ray crystallography.

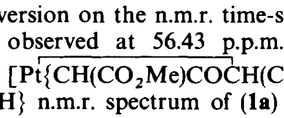
We have previously shown that esters of 3-oxopentanedioic acid RCH_2COCH_2R (R = CO_2Me, CO_2Et, or CO_2Pr^n) react with dioxygen or carbonate complexes of palladium(II)[1] or platinum(II)[2] to afford high yields of the air-stable metallacyclobutanones $[M(CHRCOCHR)L_2]$ (M = Pd or Pt; L = tertiary-phosphine or -arsine ligand). X-Ray structural studies on some of these complexes have established the presence of highly non-planar metallacyclic rings and have indicated that a bonding description of these complexes should include contribution from the allylic structure $[M(\eta^3\text{-}CHRCOCHR)L_2]$. It seemed possible that the substituents R might exert an influence on the structures of these complexes and it was therefore decided to examine some different derivatives. In this paper we describe the preparations and structures of some metallacyclobutanones containing acetyl substituents and attempts to obtain related benzoyl derivatives. A preliminary account of some of the work has been given.[3]



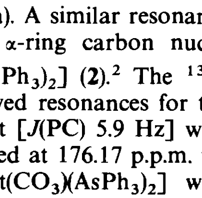
(1a) L = PPh_3
(1b) L = $AsPh_3$
R = COMe



(2) L = PPh_3
R = CO_2Me



(3)



(4)

Results and Discussion

Reaction of an excess of heptane-2,4,6-trione, $MeCOCH_2COCH_2COMe$, with $[Pt(CO_3)(PPh_3)_2]$ gave a yellow crystalline air-stable complex (**1a**) in high yield (88%). Complex (**1a**) was fully identified spectroscopically, particularly by its ^{13}C-$\{^1H\}$ n.m.r. spectrum. The latter had a resonance at δ 67.06 p.p.m. with ^{31}P coupling and ^{195}Pt satellites [J(PtC) 246.9 Hz]. This signal is characteristic for the presence of platinum–carbon bonds of a platinacyclobutan-3-one ring undergoing rapid ring inversion on the n.m.r. time-scale in (**1a**). A similar resonance is observed at 56.43 p.p.m. for the α-ring carbon nuclei of $[Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]$ (**2**).[2] The ^{13}C-$\{^1H\}$ n.m.r. spectrum of (**1a**) also showed resonances for the other groups present including a triplet [J(PC) 5.9 Hz] with ^{195}Pt satellites [J(PtC) 173.7 Hz] centred at 176.17 p.p.m. for the ring carbonyl. Treatment of $[Pt(CO_3)(AsPh_3)_2]$ with heptane-2,4,6-trione afforded the triphenylarsine derivative (**1b**).

A single-crystal X-ray diffraction study established the molecular structure of (**1a**), which is illustrated in Figure 1 with the crystallographic numbering. Relevant bond lengths and angles are given in Tables 1 and 2. Overall the geometry of (**1a**)

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* (1,3-Diacetyl-2-oxopropane-1,3-diyl)bis(triphenylphosphine)-platinum(II) and (5-oxo-1,5-diphenylpenta-1,3-diene-1,3-diolato)-bis(triphenylphosphine)platinum(II).

Supplementary data available (No. SUP 56117, 16 pp.): structure factors, thermal parameters, full atomic co-ordinates, full bond distances and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

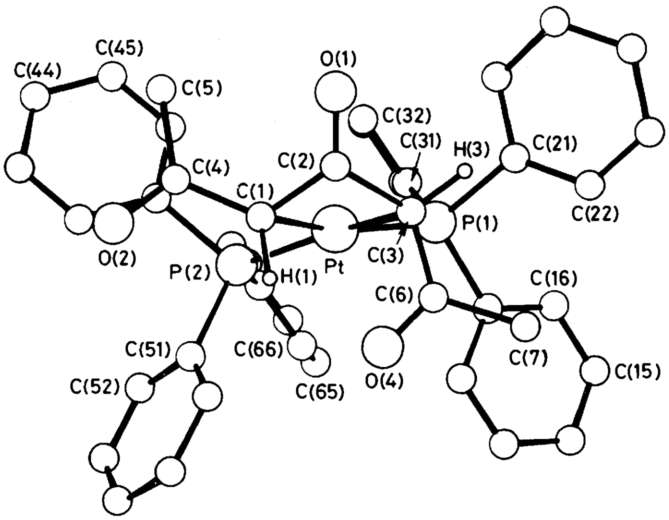


Figure 1. Molecular structure of (**1a**) showing the atom numbering scheme. Atoms are drawn as circles with arbitrary radii. Phenyl and methyl hydrogen atoms have been excluded

Table 1. Selected intramolecular bond lengths (Å) in the complex [Pt{CH(COMe)COCH(COMe)}(PPh$_3$)$_2$] (**1a**) with estimated standard deviations in parentheses

Pt–P(1)	2.295(2)	Pt–C(1)	2.183(7)
Pt–P(2)	2.309(1)	Pt–C(2)	2.486(6)
		Pt–C(3)	2.153(5)
CH(COMe)COCH(COMe) ligand			
C(1)–C(2)	1.496(9)	C(4)–C(5)	1.483(9)
C(2)–C(3)	1.491(9)	C(3)–C(6)	1.468(6)
C(2)–O(1)	1.219(7)	C(6)–O(4)	1.206(11)
C(1)–C(4)	1.463(9)	C(6)–C(7)	1.540(11)
C(4)–O(2)	1.236(13)		
Triphenylphosphine ligands			
P(1)–C(11)	1.832(2)	P(2)–C(41)	1.844(2)
P(1)–C(21)	1.839(3)	P(2)–C(51)	1.834(3)
P(1)–C(31)	1.832(2)	P(2)–C(61)	1.847(4)

bears a strong resemblance to that of the platinacyclobutan-3-one complex (**2**). In (**1a**) the presence of a puckered platinacyclobutan-3-one ring with a transannular Pt–C(2) bonding interaction is confirmed. The fold angle between planes C(1)–Pt–C(3) and C(1)–C(2)–C(3) is 48.0(4)° and the Pt–C(2) distance is 2.486(6) Å. We have previously discussed the structure of the platinacyclobutan-3-one ring in (**2**) and have indicated that the orientation of the PtC$_3$ ring atoms is reminiscent of an η^3-metal allyl or 'slipped' oxodimethylenemethane complex.[2] A similar bonding description can be used to describe the platinacyclobutan-3-one ring in (**1a**) but in this compound there is a longer Pt–C(2) bond and consequent shorter C(2)–O(1) bond [1.219(7) Å in (**1a**) and 1.232(7) Å in (**2**)]. These results indicate that replacement of CO$_2$Me by COMe groups in the platinacyclobutan-3-one ring leads to a decrease in the allylic contribution to the bonding in (**1a**) as compared to (**2**). In line with this trend, the C(2)–O(1) bond in (**1a**) is inclined by only 8.7(5)° out of the C(1)–C(2)–C(3) plane towards the platinum. In (**2**) this angle is 11.6(5)°.[2] In both complexes the co-ordination about platinum is essentially square planar (Table 3), with similar bond angles about

Table 2. Selected bond angles (°) in [Pt{CH(COMe)COCH(COMe)}-(PPh$_3$)$_2$] (**1a**) with estimated standard deviations in parentheses

P(1)–Pt–P(2)	102.3	P(1)–Pt–C(3)	94.4(2)
P(2)–Pt–C(1)	96.8(1)	C(1)–Pt–C(3)	67.3(2)
CH(COMe)COCH(COMe) ligand			
C(1)–C(2)–C(3)	107.2(4)		
C(1)–C(2)–O(1)	127.0(6)		
C(3)–C(2)–O(1)	124.8(7)		
Pt–C(1)–C(2)	82.8(4)	Pt–C(3)–C(2)	84.0(3)
Pt–C(1)–H(1)	96(4)	Pt–C(3)–H(3)	116(3)
Pt–C(1)–C(4)	124.7(4)	Pt–C(3)–C(6)	104.0(4)
H(1)–C(1)–C(4)	120(4)	H(3)–C(3)–C(6)	115(2)
H(1)–C(1)–C(2)	106(3)	H(3)–C(3)–C(2)	114(3)
C(4)–C(1)–C(2)	121.0(5)	C(6)–C(3)–C(2)	120.8(6)
C(1)–C(4)–O(2)	119.2(5)	C(3)–C(6)–O(4)	124.6(6)
C(1)–C(4)–C(5)	121.7(8)	C(3)–C(6)–C(7)	116.9(7)
O(2)–C(4)–C(5)	119.1(7)	O(4)–C(6)–C(7)	118.5(5)
Triphenylphosphine ligands			
Pt–P(1)–C(11)	117.6(1)	Pt–P(2)–C(41)	114.8(1)
Pt–P(1)–C(21)	111.0(2)	Pt–P(2)–C(51)	110.8(1)
Pt–P(1)–C(31)	112.5(1)	Pt–P(2)–C(61)	120.6(1)
C(11)–P(1)–C(31)	107.5(1)	C(41)–P(2)–C(51)	105.1(2)
C(11)–P(1)–C(21)	103.2(1)	C(41)–P(2)–C(61)	104.1(1)
C(21)–P(1)–C(31)	103.8(2)	C(51)–P(2)–C(61)	99.3(2)

Table 3. Equations of some least-squares planes in the form $Ax + By + Cz = D$, where x, y, and z are fractional co-ordinates, for complexes (**1a**) and (**3**); distances (Å) of relevant atoms from these planes are given in square brackets

(*a*) [Pt{CH(COMe)COCH(COMe)}(PPh$_3$)$_2$] (**1a**)
Plane (1): Pt, P(1), P(2), C(1), C(3)

$$2.3192x + 13.2038y + 1.3294z = 3.9157$$

[C(1) −0.142, C(3) 0.154, P(1) −0.096, P(2) 0.102,
Pt −0.017, C(2) −0.638]

Plane (2): C(1), C(2), C(3)

$$-9.6915x - 5.8127y + 3.2658z = -3.1611$$

[O(1) 0.185]

(*b*) [Pt{OC(CHCOPh)CHC(Ph)O}(PPh$_3$)$_2$] (**3**)
Plane (1): P(1), Pt, P(2)

$$-6.8966x + 15.7438y + 10.1696z = 4.1741$$

Plane (2): O(1), Pt, O(2)

$$-6.8299x + 15.9202y + 9.9997z = 4.2533$$

Plane (3): O(2), C(3), C(2), C(1), O(1)

$$-6.5918x + 16.8912y + 8.7250z = 4.8375$$

[O(2) −0.011, C(3) 0.017, C(2) −0.010, C(1) −0.002,
O(1) 0.006, C(4) 0.085, C(81) −0.070]

Plane (4): C(4), C(5), O(3), C(71)

$$4.9008x - 18.5041y - 7.7643z = -5.5076$$

[C(4) 0.012, C(5) −0.033, O(3) 0.012, C(71) 0.009, C(3) −0.054]

Plane (5): C(71), C(72), C(73), C(74), C(75), C(76)

$$-1.3471x - 20.2538y + 5.6254z = -10.2075$$

Plane (6): C(81), C(82), C(83), C(84), C(85), C(86)

$$3.8582x - 17.7357y - 9.6721z = -5.4860$$

Angles (°) between normals to planes in (**3**)

(1)–(2)	0.73	(1)–(3)	5.64
(3)–(4)	8.87	(4)–(5)	46.85
(2)–(3)	4.93	(3)–(6)	15.41

platinum and similar twist angles between PPtP and CPtC planes [10.4(1)° in (**1a**) and 8.1(2)° in (**2**)].

Previous studies on substituted metallacyclobutan-3-ones of four-co-ordinate platinum(II)[2] and palladium(II)[1] have indicated that *trans*-(2,4-axial–equatorial) substitution of the metallacyclic ring is preferred. This conformation is also adopted by the COMe substituents in (**1a**). In metallacyclobutanes of the type $[\overline{M(CHRCH_2C}HR)Cl_4]$, theoretical studies have indicated that a puckered conformation is preferred with 2,4-diequatorial substitution.[4]

It was anticipated that the platinacyclobutan-3-one complexes (**1a**) and (**1b**) might show dynamic behaviour in solution, due to inversion of the metallacyclic ring, but that on decreasing the temperature of the measurements a slow-exchange limit on the n.m.r. time-scale would be reached.[1,2] From previous studies on metallacyclobutan-3-ones it has been possible to estimate the activation energies for ring inversion.[1,2] Examination of the ^1H n.m.r. spectra of (**1a**) in the temperature range 25 to −90 °C revealed the anticipated temperature-dependent behaviour, the CH protons of the platinacyclobutan-3-one ring appearing equivalent at room temperature and splitting into two signals centred at δ 4.53 and 3.80 p.p.m. which are assigned to the axial H(1) and equatorial H(3) protons of (**1a**) respectively by analogy with related systems.[1,2] The coalescence temperature was found to be −76 °C and application of the relation (1)[5] gave a value for the free energy

$$\Delta G_{T_c}^{\ddagger} = -RT_c\ln(\pi\Delta\nu h/2^{\frac{1}{2}}kT_c) \qquad (1)$$

of activation of 37.0 ± 1 kJ mol^{-1}. A value of 37.3 ± 1 kJ mol^{-1} was calculated from the coalescence temperature (−85 °C) of the methyl groups in (**1a**). Similarly for the triphenylarsine derivative (**1b**) a free energy of activation of 36.6 ± 1 kJ mol^{-1} was calculated from the coalescence temperature of −82 °C for the CH protons and −84 °C for the methyl groups. These values for the free energy of activation for ring inversion of (**1a**) and (**1b**) are very similar to those observed for the complexes $[\overline{Pt\{CH(CO_2Me)COC}H(CO_2Me)\}L_2][L = PPh_3$ (**2**), $L = AsPh_3]$.[2]

In (**1a**) the axial hydrogen H(1) is closer to the platinum than H(3) [Pt–H(1) 2.53(3), Pt–H(3) 2.79 Å] and the C–H$_{\text{axial}}$ vector is aligned with the vector on platinum 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 are 13 and 126° respectively]. For (**1a**) we find that ^2J[Pt–H(1)] = 49.9 Hz and ^2J[Pt–H(3)] = 29 Hz, and as discussed previously[2,3] these different values for 195-platinum–hydrogen coupling can be correlated with the relative orientation of the axial and equatorial platinacyclobutan-3-one ring hydrogens with respect to the square-planar platinum function.

In an attempt to obtain a platinacyclobutan-3-one derivative containing axial and equatorial benzoyl substituents the action of $PhCOCH_2COCH_2COPh$ upon $[Pt(CO_3)(PPh_3)_2]$ was investigated. This reaction afforded yellow crystals of the complex (**3**). However, the spectroscopic data for complex (**3**) were insufficient for structural characterisation of the complex. The $\overline{PtCH(COPh)COC}H(COPh)$ group was clearly not present, as shown by the absence of C=O absorptions typical of a platinacyclobutan-3-one ring in the i.r. spectrum and the absence of resonances ascribable to PtCH groups in the ^1H n.m.r. spectrum. Thus to establish the structure of (**3**) a single-crystal *X*-ray diffraction study was undertaken. The molecular parameters for compound (**3**) are summarised in Tables 4 and 5; the molecular structure is illustrated in Figure 2.

Table 4. Selected bond lengths (Å) in $[\overline{Pt\{OC(CHCOPh)CHC(Ph)O}\}(PPh_3)_2]$ (**3**) with estimated standard deviations in parentheses

Pt–P(1)	2.254(2)	Pt–O(1)	2.033(10)
Pt–P(2)	2.236(4)	Pt–O(2)	2.026(6)
OC(CHCOPh)CHC(Ph)O ligand			
O(1)–C(1)	1.305(16)	C(3)–C(4)	1.434(14)
O(2)–C(3)	1.296(17)	C(4)–C(5)	1.389(19)
C(1)–C(2)	1.355(14)	C(5)–O(3)	1.27(2)
C(2)–C(3)	1.427(19)	C(5)–C(71)	1.497(13)
C(1)–C(81)	1.503(16)		
Triphenylphosphine ligands			
P(1)–C(11)	1.799(9)	P(2)–C(41)	1.833(6)
P(1)–C(21)	1.807(10)	P(2)–C(51)	1.804(8)
P(1)–C(31)	1.790(9)	P(2)–C(61)	1.792(10)

Table 5. Selected bond angles (°) in $[\overline{Pt\{OC(CHCOPh)CHC(Ph)O}\}(PPh_3)_2]$ (**3**)

P(1)–Pt–P(2)	97.0(1)	P(2)–Pt–O(2)	86.7(3)
P(1)–Pt–O(1)	84.5(2)	O(1)–Pt–O(2)	91.7(3)
OC(CHCOPh)CHC(Ph)O ligand			
Pt–O(1)–C(1)	122.6(7)	C(2)–C(3)–C(4)	125(1)
Pt–O(2)–C(3)	126.5(7)	O(2)–C(3)–C(4)	112(1)
O(1)–C(1)–C(2)	129(1)	C(3)–C(4)–C(5)	125(1)
O(1)–C(1)–C(81)	110.9(8)	C(4)–C(5)–O(3)	128(1)
C(2)–C(1)–C(81)	120(1)	C(4)–C(5)–C(71)	118(1)
C(1)–C(2)–C(3)	127(1)	O(3)–C(5)–C(71)	114(1)
C(2)–C(3)–O(2)	123(1)		
Triphenylphosphine ligands			
Pt–P(1)–C(11)	112.1(3)	Pt–P(2)–C(41)	114.0(3)
Pt–P(1)–C(21)	119.5(3)	Pt–P(2)–C(51)	111.1(4)
Pt–P(1)–C(31)	111.7(3)	Pt–P(2)–C(61)	112.8(3)
C(11)–P(1)–C(31)	103.5(4)	C(41)–P(2)–C(51)	103.0(4)
C(11)–P(1)–C(21)	105.4(4)	C(41)–P(2)–C(61)	101.1(4)
C(21)–P(1)–C(31)	103.1(5)	C(51)–P(2)–C(61)	114.0(5)

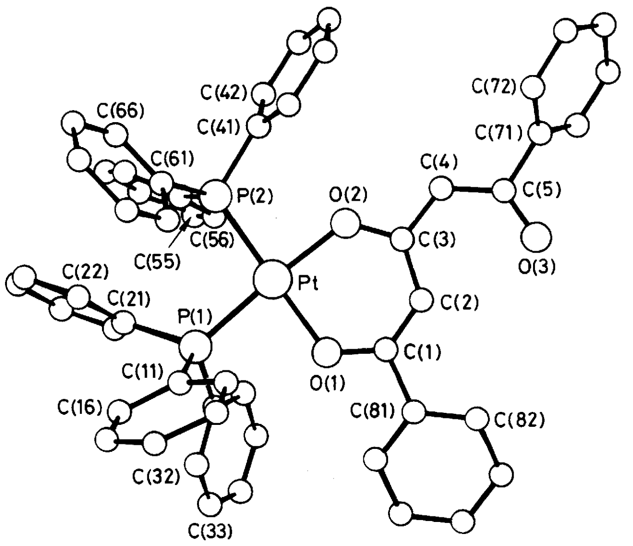
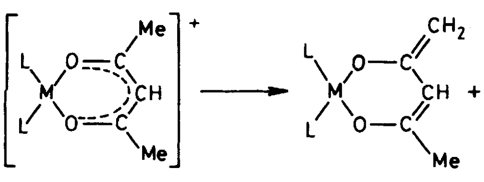
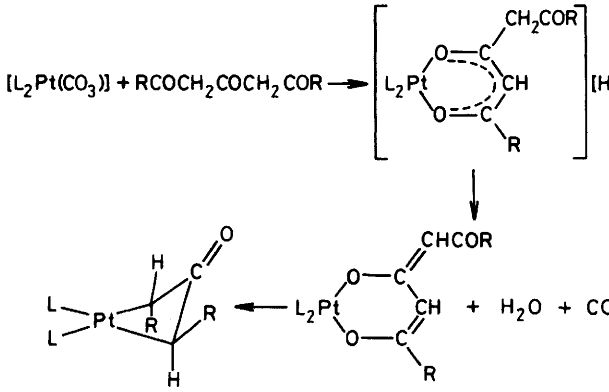


Figure 2. Molecular structure of (**3**) showing the atom numbering scheme. Hydrogen atoms have been excluded

The platinum atom is part of a six-membered ring formed by co-ordination of a dienediolate group. The six-membered ring is essentially planar (Table 3), and shows C–C and C–O bond lengths intermediate between those of single and double bonds.



Scheme 1.



Scheme 2.

This feature has been well established in many β-diketoenolate complexes[6–8] and is indicative of a relationship between these two types of ligand systems. Deprotonation of a chelating β-diketoenolate ligand will produce a dienediolate ligand (Scheme 1) and although dienediolate bonding has been observed for the phosphorus derivative P{OC(CH$_2$)CHC(Me)O}Ph co-ordinated to the fragments Mn(CO)$_2$(η-C$_5$H$_5$), Cr(CO)$_5$, or W(CO)$_5$,[9,10] complex (**3**) represents the first dienediolate derivative of a transition metal. The CHC(Ph)O substituent is planar (Table 3) and the C(3)–C(4), C(4)–C(5), and C(5)–O(3) distances are indicative of a highly conjugated system. The angle between the C(4)–C(5)–O(3)–C(71) and O(2)–C(3)–C(2)–C(1)–O(1) planes is 8.9° and as a consequence O(3) is brought within 2.93 Å of C(2). The geometry about the platinum is square planar (Table 3), the short Pt–P bonds being typical of bonds *trans* to ligand atoms of low *trans* influence.[11] Although the Pt–O(2) and Pt–O(1) distances are essentially equal, the Pt–P(1) bond is significantly longer than Pt–P(2) bond. Lengthening of Pt–P bonds by steric interactions with large *cis* ligands has been noted previously.[11,12] Examination of the detailed geometry of the phenyl groups on atom P(1) [*e.g.*, C(21)–P(1)–Pt 119.5(3)°] suggests that they have significant interactions both with the rings on atom P(2) and the phenyl group attached to atom C(1). In view of these interactions it is surprising that this latter phenyl group is almost coplanar with the six-membered chelate ring (Table 3).

Previously we have suggested that the formation of platinacyclobutan-3-ones from the ketones RCOCH$_2$COCH$_2$COR (R = Me, Et, or Pr^n) and dioxygen or carbonate complexes of platinum proceeds *via* initial Pt–C bond formation.[2] However, the isolation of the dienediolate derivative (**3**) suggests an alternative pathway as outlined in Scheme 2. Previous studies[13] have suggested that the dienediolate complex (**3**) would be unstable and would transform either to a platinacyclobutan-3-one or to a *C,O*-chelate complex of the type (**4**). Clearly the presence of phenyl groups in (**3**) inhibits transformations of this type.

Experimental

The experimental techniques used and the instrumentation employed have been described previously.[1,2] For n.m.r. measurements, chemical shifts (δ p.p.m.) are relative to SiMe$_4$ for the ^{1}H and ^{13}C-{^{1}H} spectra and to [P(OH)$_4$]$^+$ in D$_2$O (external) for ^{31}P-{^{1}H} spectra. Light petroleum refers to that fraction of b.p. 40—60 °C. The compounds [Pt(CO$_3$)L$_2$] (L = PPh$_3$ or AsPh$_3$),[14] heptane-2,4,6-trione,[15] and 1,5-diphenylpentane-1,3,5-trione[16] were prepared as described in the literature.

Syntheses.—[Pt{CH(COMe)COCH(COMe)}(PPh$_3$)$_2$]. A mixture of [Pt(CO$_3$)(PPh$_3$)$_2$]·C$_6$H$_6$ (0.50 g, 0.58 mmol and heptane-2,4,6-trione (0.17 g, 1.20 mmol) in ethanol (50 cm^3) was stirred and slowly heated to 45—65 °C until a clear solution was formed. The resulting 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 on standing a yellow solid which was recrystallised from dichloromethane–light petroleum to afford yellow crystals of [Pt{CH(COMe)COCH(COMe)](PPh$_3$)$_2$] (**1a**) (0.44 g, 88%), m.p. 220—222 °C (decomp.) (Found: C, 59.7; H, 4.5. C$_{43}$H$_{38}$O$_3$P$_2$Pt requires C, 60.1; H, 4.4%); $\nu_{max.}$ (1 800—1 500 cm^{-1}) 1 650vs, 1 642vs, 1 622vs, 1 600s (sh), 1 585m, and 1 564m cm^{-1}. N.m.r.: ^{1}H (400 MHz, [^{2}H$_2$]dichloromethane), δ 7.36—7.18 (m, 30 H, Ph), 4.20 [d, second order, 2 H, CH,|^3J(PH)$_{trans}$ + ^3J(PH)$_{cis}$| 4.3, ^2J(PtH) 47.8], and 1.33 (s, 6 H, Me); ^{1}H (400 MHz, [^{2}H$_2$]dichloromethane, −90 °C), δ 7.4—7.1 (m, br, 30 H, Ph), 4.53 [d, 1 H, CH, ^3J(PH) 7.9, ^2J(PtH) 49.9], 3.80 [t, 1 H, CH,|^3J(PH)$_{trans}$ + ^3J(PH)$_{cis}$| 0.8, ^2J(PtH) 29], 1.16 (s, 3 H, Me), and 0.98 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 205.32 [s, CO, COMe, ^2J(PtC) 31.9], 176.17 [s, CO ring, ^3J(PC) 5.9, ^2J(PtC) 173.7], 133.95 [t, second order, Ph, C-β,|^2J(PC) + ^4J(PC)| 11.0], 131.05 [d, second order, Ph, C-α,|^1J(PC) + ^3J(PC)| 55.0], 130.27 (s, Ph, C-δ), 127.92 [t, second order, Ph, C-γ, |^3J(PC) + ^5J(PC)|15.0], 67.06 [d of d, second order, CH,|^2J(PC)$_{trans}$ + ^2J(PC)$_{cis}$| 49.1, ^1J(PtC) 246.9], and 31.68 (s, Me); ^{31}P-{^{1}H} (24 MHz, [^{2}H$_1$]chloroform), δ 15.73 p.p.m. [s, ^1J(PPt) 3 129.9 Hz].

[Pt{CH(COMe)COCH(COMe)}(AsPh$_3$)$_2$]. As above, [Pt(CO$_3$)(AsPh$_3$)$_2$]·C$_6$H$_6$ (0.50 g, 0.53 mmol) and heptane-2,4,6-trione (0.15 g, 1.06 mmol) gave pale yellow *microcrystals* of [Pt{CH(COMe)COCH(COMe)}(AsPh$_3$)$_2$] (**1b**) (0.41 g, 82%), m.p. 229—232 °C (decomp.) (Found: C, 54.3; H, 4.1. C$_{43}$H$_{38}$As$_2$O$_3$Pt requires C, 54.5; H, 4.0%); $\nu_{max.}$ (1 800—1 500 cm^{-1}) 1 649vs, 1 622vs, 1 578m, and 1 572m (sh) cm^{-1}. N.m.r.: ^{1}H (400 MHz, [^{2}H$_2$]dichloromethane), δ 7.37—7.25 (m, 30 H, Ph), 4.31 [s, 2 H, CH, ^2J(PtH) 65.6], and 1.44 (s, 6 H, Me); ^{1}H (400 MHz, [^{2}H$_2$]dichloromethane, −90 °C), 7.78—7.18 (m, br, 30 H, Ph), 4.52 [s, 1 H, CH, ^2J(PtH) 81.2], 4.09 [s, 1 H, CH, ^2J(PtH) 51.2], 1.39 (s, 3 H, Me), and 1.06 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 205.94 [s, CO, COMe, ^2J(PtC) 37.7], 179.08 [s, CO, ring, ^2J(PtC) 196.3], 134.09 (s, Ph, C-β), 130.93 (s, Ph, C-δ), 129.45 (s, Ph, C-γ), 63.28 [s, CH, ^1J(PtC) 298.1 Hz], and 32.17 p.p.m. (s, Me).

[Pt{OC(CHCOPh)CHC(Ph)O}(PPh$_3$)$_2$]. A mixture of [Pt(CO$_3$)(PPh$_3$)$_2$]·C$_6$H$_6$ (0.38 g, 0.44 mmol) and 1,5-diphenylpentane-1,3,5-trione (0.39 g, 1.46 mmol) in ethanol (50 cm^3) was stirred and heated at 70 °C for 3 h. The solution was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in dichloromethane (1 cm^3) and addition of a 1 : 1 mixture of dichloromethane–light petroleum (100 cm^3) precipitated a yellow powder which was recrystallised from dichloromethane–light petroleum to give yellow *crystals* of [Pt{OC(CHCOPh)CHC(Ph)O}(PPh$_3$)$_2$] (**3**) (0.24 g, 56%), m.p. 235—238 °C (Found: C, 64.4; H, 4.5. C$_{53}$H$_{42}$O$_3$P$_2$Pt

Table 6. Atomic positional (fractional co-ordinates) parameters, with estimated standard deviations in parentheses, for [Pt{CH(COMe)COCH(COMe)}$(PPh_3)_2$] (**1a**)

Atom	*x*	*y*	*z*
Pt	0.163 21(1)	0.232 35(1)	0.340 11(2)
P(2)	−0.009 87(10)	0.286 70(6)	0.191 60(11)
P(1)	0.091 96(10)	0.224 09(6)	0.487 19(11)
O(2)	0.215 2(7)	0.233 1(4)	0.018 4(6)
O(4)	0.520 7(5)	0.323 4(3)	0.558 5(6)
O(1)	0.336 6(5)	0.088 8(2)	0.245 7(5)
C(1)	0.275 9(5)	0.214 0(3)	0.231 7(5)
C(4)	0.202 9(7)	0.185 2(4)	0.065 4(7)
C(5)	0.112 8(9)	0.100 1(5)	−0.048 3(9)
C(3)	0.362 9(4)	0.198 0(3)	0.461 5(6)
C(6)	0.473 9(5)	0.276 0(4)	0.582 4(7)
C(7)	0.532 5(7)	0.298 1(4)	0.750 8(7)
C(2)	0.334 4(5)	0.158 6(3)	0.306 8(6)
C(41)	−0.120 0(3)	0.222 61(16)	−0.019 8(2)
C(42)	−0.123 9(3)	0.249 52(16)	−0.120 5(2)
C(43)	−0.217 2(3)	0.200 84(16)	−0.281 7(2)
C(44)	−0.306 6(3)	0.125 29(16)	−0.342 2(2)
C(45)	−0.302 6(3)	0.098 43(16)	−0.241 5(2)
C(46)	−0.209 3(3)	0.147 08(16)	−0.080 3(2)
C(51)	0.077 9(3)	0.383 44(14)	0.224 7(3)
C(52)	−0.011 2(3)	0.429 69(14)	0.158 1(3)
C(53)	0.051 3(3)	0.502 60(14)	0.177 9(3)
C(54)	0.203 0(3)	0.529 25(14)	0.264 4(3)
C(55)	0.292 1(3)	0.483 00(14)	0.331 0(3)
C(56)	0.229 5(3)	0.410 11(14)	0.311 1(3)
C(61)	−0.146 6(2)	0.319 69(16)	0.225 3(3)
C(62)	−0.297 0(2)	0.284 36(16)	0.114 1(3)
C(63)	−0.393 8(2)	0.314 73(16)	0.146 2(3)
C(64)	−0.340 3(2)	0.380 47(16)	0.289 5(3)
C(65)	−0.190 0(2)	0.415 81(16)	0.400 7(3)
C(66)	−0.093 1(2)	0.385 42(16)	0.368 7(3)
C(11)	0.158 9(3)	0.314 78(13)	0.667 3(2)
C(12)	0.235 8(3)	0.386 52(13)	0.697 8(2)
C(13)	0.302 4(3)	0.454 69(13)	0.841 7(2)
C(14)	0.292 1(3)	0.451 08(13)	0.955 3(2)
C(15)	0.215 2(3)	0.379 31(13)	0.924 8(2)
C(16)	0.148 6(3)	0.311 16(13)	0.780 8(2)
C(21)	0.157 5(3)	0.145 89(15)	0.553 6(3)
C(22)	0.270 1(3)	0.166 25(15)	0.709 5(3)
C(23)	0.323 9(3)	0.105 37(15)	0.753 5(3)
C(24)	0.265 2(3)	0.024 12(15)	0.641 5(3)
C(25)	0.152 7(3)	0.003 76(15)	0.485 6(3)
C(26)	0.098 8(3)	0.064 64(15)	0.441 7(3)
C(31)	−0.107 75(20)	0.190 44(16)	0.376 0(3)
C(32)	−0.182 96(20)	0.123 80(16)	0.228 8(3)
C(33)	−0.334 73(20)	0.095 26(16)	0.138 1(3)
C(34)	−0.411 30(20)	0.133 35(16)	0.194 6(3)
C(35)	−0.336 09(20)	0.200 00(16)	0.341 8(3)
C(36)	−0.184 33(20)	0.228 54(16)	0.432 5(3)
H(1)	0.357 (5)	0.271 8(17)	0.313 (6)
H(3)	0.358 (5)	0.156 (2)	0.504 (5)

requires C, 64.7; H, 4.3%); $\nu_{max.}$ (1 800—1 500 cm^{-1}) 1 590mw, 1 580w, 1 570m, and 1 540ms cm^{-1}. N.m.r. ^1H (90 MHz, [$^2H_1$]chloroform), δ 8.2 (s, 1 H, CH), 7.2 (m, 40 H, Ph), and 4.9 (s, 1 H, CH).

Table 7. Atomic positional (fractional co-ordinates) parameters, with estimated standard deviations in parentheses, for [Pt{OC(CHCOPh)CHC(Ph)O}$(PPh_3)_2$] (**3**)

Atom	*x*	*y*	*z*
Pt	0.046 39(4)	0.343 98(2)	−0.090 61(3)
P(1)	0.207 5(2)	0.339 03(16)	0.026 29(19)
P(2)	−0.058 3(2)	0.274 52(15)	−0.054 06(20)
O(1)	0.138 7(7)	0.406 6(4)	−0.127 3(5)
O(2)	−0.092 6(6)	0.352 3(4)	−0.198 8(5)
O(3)	−0.172 5(8)	0.433 5(5)	−0.434 3(6)
C(11)	0.225 1(7)	0.407 5(4)	0.089 5(5)
C(12)	0.167 9(7)	0.462 1(4)	0.051 7(5)
C(13)	0.179 4(7)	0.516 4(4)	0.098 2(5)
C(14)	0.248 1(7)	0.516 1(4)	0.182 4(5)
C(15)	0.305 3(7)	0.461 5(4)	0.220 2(5)
C(16)	0.293 8(7)	0.407 2(4)	0.173 7(5)
C(21)	0.228 2(8)	0.273 4(4)	0.095 2(5)
C(22)	0.182 4(8)	0.274 9(4)	0.155 7(5)
C(23)	0.195 2(8)	0.223 4(4)	0.207 1(5)
C(24)	0.253 8(8)	0.170 3(4)	0.198 0(5)
C(25)	0.299 6(8)	0.168 7(4)	0.137 5(5)
C(26)	0.286 8(8)	0.220 2(4)	0.086 1(5)
C(31)	0.336 2(5)	0.338 2(4)	0.005 3(5)
C(32)	0.436 2(5)	0.370 4(4)	0.054 5(5)
C(33)	0.535 9(5)	0.366 4(4)	0.037 6(5)
C(34)	0.535 6(5)	0.330 2(4)	−0.028 3(5)
C(35)	0.435 6(5)	0.297 9(4)	−0.077 4(5)
C(36)	0.335 9(5)	0.301 9(4)	−0.060 6(5)
C(41)	−0.205 6(5)	0.263 2(4)	−0.131 5(4)
C(42)	−0.238 3(5)	0.207 5(4)	−0.176 0(4)
C(43)	−0.349 4(5)	0.201 4(4)	−0.237 2(4)
C(44)	−0.427 9(5)	0.250 8(4)	−0.253 7(4)
C(45)	−0.395 3(5)	0.306 5(4)	−0.209 2(4)
C(46)	−0.284 1(5)	0.312 6(4)	−0.148 0(4)
C(51)	0.003 8(7)	0.197 3(4)	−0.043 3(6)
C(52)	0.000 9(7)	0.153 0(4)	0.014 1(6)
C(53)	0.044 5(7)	0.093 0(4)	0.013 9(6)
C(54)	0.091 0(7)	0.077 2(4)	−0.043 7(6)
C(55)	0.093 9(7)	0.121 5(4)	−0.101 1(6)
C(56)	0.050 3(7)	0.181 5(4)	−0.100 9(6)
C(61)	−0.087 5(7)	0.299 4(4)	0.033 0(5)
C(62)	−0.059 1(7)	0.360 9(4)	0.059 9(5)
C(63)	−0.084 5(7)	0.383 8(4)	0.125 1(5)
C(64)	−0.138 2(7)	0.345 2(4)	0.163 4(5)
C(65)	−0.166 6(7)	0.283 7(4)	0.136 6(5)
C(66)	−0.141 2(7)	0.260 8(4)	0.071 3(5)
C(1)	0.100 5(9)	0.429 7(5)	−0.201 8(8)
C(2)	−0.003 7(10)	0.420 9(5)	−0.264 5(8)
C(3)	−0.098 1(10)	0.384 7(6)	−0.262 4(8)
C(4)	−0.209 5(9)	0.379 5(6)	−0.328 9(7)
C(5)	−0.239 0(11)	0.406 5(6)	−0.406 1(9)
C(71)	−0.360 5(6)	0.398 0(5)	−0.487 9(6)
C(72)	−0.453 9(6)	0.410 3(5)	−0.445 9(6)
C(73)	−0.567 0(6)	0.401 9(5)	−0.503 3(6)
C(74)	−0.586 7(6)	0.381 2(5)	−0.582 7(6)
C(75)	−0.493 3(6)	0.368 8(5)	−0.604 8(6)
C(76)	−0.380 1(6)	0.377 3(5)	−0.547 3(6)
C(81)	0.192 3(6)	0.468 2(4)	−0.214 7(6)
C(82)	0.166 4(6)	0.502 2(4)	−0.287 3(6)
C(83)	0.255 2(6)	0.530 6(4)	−0.303 9(6)
C(84)	0.369 9(6)	0.525 0(4)	−0.247 9(6)
C(85)	0.395 8(6)	0.491 0(4)	−0.175 2(6)
C(86)	0.307 0(6)	0.462 6(4)	−0.158 6(6)

X-Ray Crystal Structure Determinations of Complexes.—(*a*) [Pt{CH(COMe)COCH(COMe)}$(PPh_3)_2$] (**1a**). Crystals of (**1a**) were grown from dichloromethane–light petroleum. A crystal of dimensions *ca.* 0.449 × 0.224 × 0.163 mm was mounted in air. The cell dimensions were determined from an oscillation photograph about the *c* axis of the crystal and from its optimized counter angles for zero- and upper-layer reflections on a Weissenberg diffractometer. Intensity data were collected at 293 K on a Stöe Weissenberg diffractometer with an ω scan technique in the range $7 < 2\theta < 60$ °. The 8 307 reflections, collected from Weissenberg layers *hk*(0—14), having $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarization effects. Subsequent calculations were carried out using the computer program SHELX.[17]

Crystal data. $C_{43}H_{38}O_3P_2Pt$, $M = 859.8$, triclinic, $a = 11.337(1)$, $b = 18.341(1)$, $c = 11.545(8)$ Å, $\alpha = 111.8(1)$, $\beta = 123.6(1)$, $\gamma = 90.0(1)^\circ$, $U = 1\,791.8$ Å^3, $Z = 2$, $D_c = 1.6$ g cm^{-3}, $F(000) = 856$, space group $P\bar{1}$, Mo-K_α X-radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 38.63 cm^{-1}.

The structure was solved by conventional Patterson and difference Fourier techniques. Scattering factors were taken from ref.18. In the final stages of block-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 difference Fourier map. They were then refined 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 temperature factors 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 a weighting factor w calculated from $w = k/(\sigma^2F + gF^2)$, where $k = 1.36$, $g = 0.000\,656$. Final values of R and R' are 0.0329 and 0.0343. Fractional atomic co-ordinates are given in Table 6.

(*b*) $[\overline{\mathrm{Pt}\{\mathrm{OC(CHCOPh)CHC(Ph)O}}\}(\mathrm{PPh}_3)_2]$ (**3**). Conditions were as for (**1a**), except for the following: crystal size 0.15 × 0.17 × 0.20 mm; intensity data were collected in the range $7 \leqslant 2\theta \leqslant 50^\circ$ for 3 279 reflections from Weissenberg layers hk(0—24); final weighting parameter $k = 1.63$, $g = 0.000\,539$; final R and R' values are 0.0478 and 0.0438.

Crystal data. $C_{53}H_{42}O_3P_2Pt$, $M = 984.1$, monoclinic, $a = 12.534(1)$, $b = 21.377(1)$, $c = 17.619(8)$ Å, $\beta = 113.0(4)^\circ$, $U = 4\,345.5$ Å^3, $Z = 4$, $D_c = 1.51$ g cm^{-3}, $F(000) = 1\,943$, space group $P2_1/c$, μ(Mo-K_α) = 31.91 cm^{-1}.

Fractional atomic co-ordinates are given in Table 7.

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