Cyclopentadiene-, Furan- and Thiophene-derived 1,2-Dioxolene Complexes of Platinum(II) and the Crystal Structure of $[Pt\{OCC(CO_2Me)CH_2C(CO_2Me)CO\}(PPh_3)_2]$

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The synthesis of a number of platinum(II)-dioxolene complexes of the type $[Pt\{OCC(CO_2Me)XC(CO_2Me)CO\}L_2]$ was readily achieved in high yields *via* the silver(I) oxide-mediated reactions of the cyclic α,β-diketone compounds $XCH(CO_2R)C(O)C(O)CH(CO_2R)$ (X = CH_2, O or S) with platinum(II) chloride complexes *cis*-$[PtCl_2L_2]$ [L = PPh_3 or L_2 = cycloocta-1,5-diene (cod)]. The complexes can be considered to be derived from cyclopentadiene, furan or thiophene, and are related to metal–catecholates. A single-crystal structure determination on the cyclopentadiene-derived complex $[Pt\{OCC(CO_2Me)CH_2C(CO_2Me)CO\}(PPh_3)_2]$ revealed the presence of a planar platinum–oxolene ring system. Silver(I) oxide can also be used to synthesise the related tetrachlorocatecholato complexes $[Pt(1,2\text{-}O_2C_6Cl_4)L_2]$ (L = PPh_3 or L_2 = cod) in high yields and purities.

Complexes **1** [M = transition metal, L_n = ancillary donor ligand(s)] containing the catecholate ligand have been known for many years,[1,2] however, there has been continued interest in the chemistry of such ligands.[3–5] In addition, the related nitrogen (*o*-phenylene-1,2-diamido) **2**[6,7] and sulfur (*e.g.* benzene-1,2-dithiolato **3**[8] and maleonitriledithiolato **4**[9]) analogues have been found to have a similarly extensive co-ordination chemistry. These types of ligands are known to be capable of stabilising transition metals in high oxidation states.[2,7,10] In addition, a rich ligand-based redox chemistry has been described in many cases,[1–3,11–13] and consequently these are an important class of metal–ligand complexes. A variety of methods have been developed for their synthesis. The oxidative addition of *o*-quinones to low-valent metal complexes has been extensively studied,[1–3,12–16] and represents a general route for the synthesis of catecholate complexes of *e.g.* Pd^{II}, Pt^{II}, Rh^{III}, Ir^{III} and Ru^{IV}. The reaction of catechol dianion salts $M_2[1,2\text{-}O_2C_6R_4]$ with metal halide complexes has also been reported to be a general route to such complexes.[2,5,11,13,17]

During the course of our studies into the reactions of platinum-group metal halide complexes with organic compounds containing activated, or acidic, hydrogens, which lead to small-ring metallacycles,[18] we embarked on a study of the reactions of cyclic diketone compounds **I** with platinum halide complexes. These compounds can be viewed as precursors either to bicyclic platinum complexes **5**, or to platinum dioxolene rings **6**. There has been recent interest in the synthesis of functionalised catecholato ligands, for example 1,10-phenanthroline-5,6-diolate.[3] Platinum, palladium and ruthenium complexes of these ligands have potentially interesting electro- and photo-chemical properties, and can be used in the synthesis of multinuclear complexes.

Results and Discussion

Reaction of the complexes *cis*-$[PtCl_2(PPh_3)_2]$ or $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene) with the cyclic diketones **I**, and an excess of silver(I) oxide in refluxing dichloromethane, gave after work-up, high yields of air-stable pale yellow microcrystalline complexes **6a**–**6d**. These products were formulated as O-bonded dioxolene derivatives based upon their $^{31}P\text{-}\{^1H\}$, $^{13}C\text{-}\{^1H\}$ and ^1H NMR and IR spectroscopic properties, elemental analytical data, and a single-crystal X-ray diffraction study carried out on the cyclopentadiene analogue **6a**. Overall the complexes bear a strong resemblance to the large number of metal catecholato complexes which have been reported.

Complex **6a** crystallises with two non-symmetry-related molecules in the unit cell. The differences between these lies mainly in the orientations of the phenyl rings of the triphenylphosphine ligands, however overall the two molecules appear very similar, and only one (molecule 1) will be subsequently discussed in detail. The molecular structure of molecule 1 is shown in Fig. 1, which also gives the crystallographic atom numbering scheme. Crystal data are presented in Table 1, selected bond distances and angles in Table 2 and fractional atomic coordinates in Table 3.

The organic fragment is co-ordinated to platinum *via* the two adjacent oxygen atoms, derived from the α,β-diketone, to form a highly planar five-membered dioxolene ring system, with no atom in molecule 1 being more than 0.025 Å from the plane formed by Pt(1), O(1), C(1), C(2) and O(2), with a very slight twist in the ring. A close examination of the corresponding parameters for molecule 2 suggests that this ring system is very slightly puckered. The platinum atom of molecule 1 also adopts the expected square-planar geometry, with no atom being more than 0.023 Å from the least-squares plane formed by Pt(1), P(1), P(2), O(1), and O(2), and the co-ordination sphere about Pt(2) in molecule 2 is even more regular (maximum deviation 0.009 Å). The Pt–O(1) and Pt–O(2) bonds of molecule 1 [2.044(7) and 2.052(9) Å] are comparable to those in other related platinum and palladium catecholate complexes. Thus, for example, in the palladium(II) tetrachlorocatecholato complex **7a**[14] the Pd–O bond distances average 2.033(5) Å. The ligand forms a bite angle of 83.3(3)° at the platinum atom, which compares very favourably with the corresponding value for **7a** of 82.6(2)°. The oxolene C(1)–O(1) and C(2)–O(2) bonds [1.314(18) and

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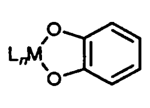
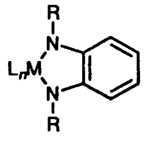
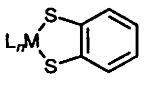
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



1



2
R = H, alkyl, or aryl



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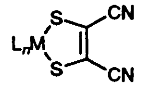

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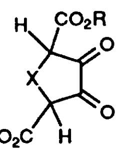
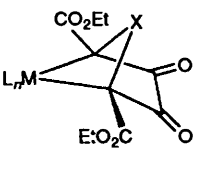


	X	R
Ia	CH_2	Me
Ib	O	Et
Ic	S	Et



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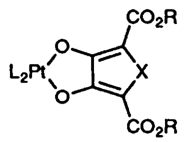
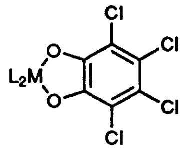
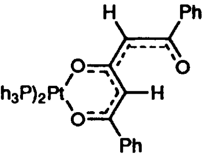


6a X = CH_2, L = PPh_3, R = Me
6b X = O, L = PPh_3, R = Et
6c X = O, L_2 = cod, R = Et
6d X = S, L = PPh_3, R = Et



7a M = Pd, L = PPh_3
7b M = Pt, L = PPh_3
7c M = Pt, L_2 = cod



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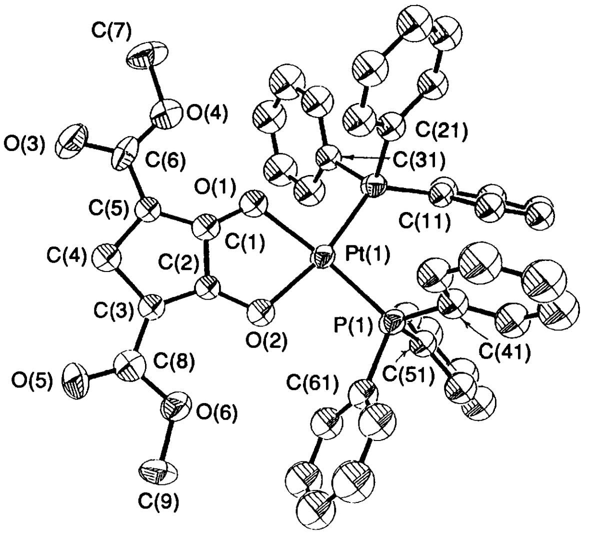

Fig. 1 Molecular structure of [Pt{OCC(CO_2Me)CH_2C(CO_2Me)CO}-(PPh_3)$_2$] **6a**, with hydrogen atoms omitted for clarity. Atoms are represented by thermal ellipsoids at the 50% probability level

Table 1 Crystal data and intensity collection for [Pt-{OCC(CO_2Me)CH_2C(CO_2Me)CO}(PPh_3)$_2$] **6a**

Empirical formula	$C_{45}H_{38}O_6P_2Pt$
M	931.8
Colour	Pale yellow
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	17.98(1)
b/Å	15.26(1)
c/Å	16.00(2)
α/°	72.3(1)
β/°	102.6(1)
γ/°	104.7(1)
U/Å^3	3998(6)
D_c/g cm^{-3}	1.55
Z	4 (2 × 2 independent molecules)
Radiation	Mo-Kα (λ 0.710 69 Å)
T/K	293
Reflections collected	11 056
Unique reflections	9433 (R_{int} 0.0126)
Reflections used	8722 [$I > 3\sigma(I)$]
F(000)	1851.82
Absorption coefficient/mm^{-1}	3.472

1.334(13) Å respectively] are notably longer than the ester carbonyl C=O bonds C(6)–O(3) and C(8)–O(5) [1.218(17) and 1.217(18) Å], and are comparable to the ester C–O single bonds C(6)–O(4) [1.352(20) Å] and C(8)–O(6) [1.357(13) Å]. It is considered that the carbon–oxygen bond distance in the series metal–catecholate, metal–semiquinone, metal–quinone decreases from 1.35 to 1.29 to 1.23 Å.[2] The cyclic C(1)–C(5) and C(2)–C(3) bonds [1.383(17) and 1.361(19) Å respectively] are significantly shorter than the C(4)–C(5) [1.530(20) Å] and C(3)–C(4) [1.529(14) Å] single bonds. In comparison, the average C=C and (sp^3–sp^2) C–C bond distances in the lead(IV) σ-cyclopentadienide complex $PbPh_3$(Cp) are 1.385 and 1.49 Å respectively.[19] The C(1)–C(2) bond, at 1.479(16) Å, appears to be intermediate in length, although the relatively large standard deviations on the data preclude any detailed comparisons. On consideration of the bond distances in the dioxolene moiety, it is clear that a representation of the type indicated, with C=C double and C–O single oxolene bonds, has a large contribution to the bonding in **6**.

We note that the platinum–dioxolene complexes are formed exclusively, with the crude reaction products being highly pure, as evidenced by $^{31}P-\{^1H\}$ NMR spectroscopy. Specifically we do not observe any bicyclic products of the type **5**, containing platinum–carbon bonds. Although such a ring system would not be expected to have any significant degree of ring strain, it would appear that the formation of a planar conjugated dioxolene ring system is a strong driving force for the formation of the observed product. We have observed similar behaviour previously, in reactions of RC(O)CH_2C(O)CH_2C(O)R with [Pt(CO_3)(PPh_3)$_2$], with a highly puckered four-membered platinacyclobutan-3-one (also termed η^3-oxodimethylene-methane) complex [Pt{MeC(O)CHC(O)CHC(O)Me}(PPh_3)$_2$] being formed when R = Me.[20] However, when R = Ph, a planar, conjugated dienediolato complex **8** was formed. Although platinum is typically considered to have a strong preference for binding to softer donor atoms,[21] for example carbon, often other factors can dictate the preferential formation of platinum–oxygen bonds, and a good example comes from the chemistry of acetylacetonate, which can have a variety of bonding modes, including C- and O-bonded forms.[1]

The spectroscopic properties of complexes **6a**–**6d** are entirely consistent with their formulation as dioxolene complexes. The $^{31}P-\{^1H\}$ NMR spectra show a single resonance with satellites

Table 2 Selected intramolecular bond distances (Å) and angles (°) for complex **6a** with estimated standard deviations in parentheses

Platinum–oxolene moiety			
Pt(1)–P(1)	2.234(3)	Pt(1)–P(2)	2.259(4)
Pt(1)–O(1)	2.044(7)	Pt(1)–O(2)	2.052(9)
O(1)–C(1)	1.314(18)	O(2)–C(2)	1.334(13)
O(3)–C(6)	1.218(17)	O(4)–C(6)	1.352(20)
O(4)–C(7)	1.440(16)	O(5)–C(8)	1.217(18)
O(6)–C(8)	1.357(13)	O(6)–C(9)	1.480(20)
C(1)–C(2)	1.479(16)	C(1)–C(5)	1.383(17)
C(2)–C(3)	1.361(19)	C(3)–C(4)	1.529(14)
C(3)–C(8)	1.438(18)	C(4)–C(5)	1.530(20)
C(5)–C(6)	1.449(15)		
Triphenylphosphine ligands			
P(1)–C(41)	1.828(7)	P(1)–C(51)	1.831(9)
P(1)–C(61)	1.833(10)	P(2)–C(11)	1.838(9)
P(2)–C(21)	1.826(7)	P(2)–C(31)	1.836(7)
P(1)–Pt(1)–P(2)	100.9(1)	P(2)–Pt(1)–O(1)	85.3(3)
P(1)–Pt(1)–O(2)	90.4(2)	O(1)–Pt(1)–O(2)	83.3(3)
Platinum–oxolene moiety			
Pt(1)–O(1)–C(1)	109.4(6)	Pt(1)–O(2)–C(2)	111.0(7)
C(6)–O(4)–C(7)	117.7(11)	C(8)–O(6)–C(9)	115.3(11)
O(1)–C(1)–C(2)	120.4(10)	O(1)–C(1)–C(5)	132.8(11)
C(2)–C(1)–C(5)	106.7(12)	O(2)–C(2)–C(1)	115.7(11)
O(2)–C(2)–C(3)	132.7(10)	C(1)–C(2)–C(3)	111.6(9)
C(2)–C(3)–C(4)	108.9(10)	C(2)–C(3)–C(8)	131.9(10)
C(4)–C(3)–C(8)	119.3(12)	C(3)–C(4)–C(5)	102.0(10)
C(1)–C(5)–C(4)	110.9(9)	C(1)–C(5)–C(6)	127.4(13)
C(4)–C(5)–C(6)	121.7(11)	O(3)–C(6)–O(4)	121.4(11)
O(3)–C(6)–C(5)	123.4(14)	O(4)–C(6)–C(5)	115.1(11)
O(5)–C(8)–O(6)	122.0(12)	O(5)–C(8)–C(3)	126.8(10)
O(6)–C(8)–C(3)	111.1(12)		
Triphenylphosphine ligands			
Pt(1)–P(1)–C(41)	112.6(3)	Pt(1)–P(1)–C(51)	116.9(3)
C(41)–P(1)–C(51)	110.3(5)	Pt(1)–P(1)–C(61)	111.9(3)
C(41)–P(1)–C(61)	104.3(4)	C(51)–P(1)–C(61)	99.6(4)
Pt(1)–P(2)–C(11)	123.6(3)	Pt(1)–P(2)–C(21)	112.9(3)
C(11)–P(2)–C(21)	101.9(4)	Pt(1)–P(2)–C(31)	106.4(3)
C(11)–P(2)–C(31)	104.5(4)	C(21)–P(2)–C(31)	106.1(4)

due to coupling to ^{195}Pt, with ^1J(PtP) values of *ca.* 3610 Hz being observed for all of the triphenylphosphine complexes. This is consistent with the oxygen-donor ligands having a low *trans* influence, somewhat similar in magnitude to that of chloride.[22] The ^{13}C-{^{1}H} NMR spectra display a rather broad resonance in the region δ 165–166, attributed to the Pt–O–C–*C* oxolene carbon, and the ester carbonyls are identified as a sharper resonance at around δ 159–160. The Pt–O–C carbon is observed for all of the complexes at around δ 121, and in the case of the triphenylphosphine furan dioxolene complex **6b**, coupling to ^{31}P could be resolved. The cyclooctadiene complex also shows the expected resonances for the cod ligand, with no evidence for attack of an alkoxide-like moiety at the olefinic carbon. Identical behaviour has been documented previously in the KOH-directed syntheses of catecholato complexes of Pt(cod).[17] In this regard it is interesting that the reaction of [PtCl$_2$(cod)] with the lithium salt of a semiquinone has been reported to result in the formation of Pt metal.[4] The CH carbons of **6c** appear at δ 92.1 showing coupling to ^{195}Pt of 171.9 Hz, similar to the value for the complex [PtCl$_2$(cod)] (152.6 Hz). The ^{1}H NMR spectroscopic features were as expected for complexes of this type, with ^2J(PtH) for the cod complex **7c** being 62.7 Hz.

A characteristic feature of catecholato and related complexes is the rich redox chemistry which they display.[1–3,11–13] Metal–catecholato, –semiquinone, and –quinone complexes form a redox series, and studies have shown that the redox process is largely centred on the ligand itself.[4] Oxidations can be accomplished either electrochemically or chemically, and silver(I) trifluoroacetate has been reported as an oxidant for metal–catechol complexes.[11] In this regard it is somewhat surprising that the dioxolene complexes described in this paper are stable towards silver(I) oxide, and we observe no evidence for paramagnetic species (very sharp resonances were observed in the NMR spectra of all the complexes described).

The successful synthesis of platinum–dioxolene complexes using silver(I) oxide led us to investigate the synthesis of platinum–catecholato complexes *via* the same route, which does not appear to have been reported previously. Thus, reaction of tetrachlorocatechol monohydrate with *cis*-[PtCl$_2$(PPh$_3$)$_2$] and silver(I) oxide in dichloromethane gave the known[15,16,23]

Table 3 Fractional atomic coordinates (× 10^4) for complex **6a**

Atom	*x*	*y*	*z*
Pt(1)	1324(1)	3677(1)	3943(1)
P(1)	2488(2)	4629(2)	3817(2)
P(2)	1204(2)	2958(2)	2863(2)
O(1)	242(4)	2892(5)	4141(5)
O(2)	1205(4)	4199(5)	4936(5)
O(3)	−1932(5)	1899(7)	5249(7)
O(4)	−1354(5)	1872(6)	4151(7)
O(5)	77(5)	4590(6)	6967(6)
O(6)	1163(4)	5039(6)	6333(6)
C(1)	−2(7)	3132(8)	4741(8)
C(2)	513(6)	3821(7)	5203(7)
C(3)	167(6)	3950(7)	5820(8)
C(4)	−645(7)	3321(8)	5823(8)
C(5)	−683(6)	2831(7)	5106(8)
C(6)	−1370(7)	2168(8)	4861(10)
C(7)	−2056(8)	1307(10)	3805(11)
C(8)	430(7)	4540(8)	6420(8)
C(9)	1488(8)	5670(10)	6924(10)
C(11)	2030(4)	2925(5)	2377(5)
C(12)	2301	2099	2543
C(13)	2940	2109	2177
C(14)	3309	2944	1645
C(15)	3038	3770	1479
C(16)	2398	3760	1845
C(21)	531(4)	3393(5)	1875(5)
C(22)	7	3899	1935
C(23)	−533	4202	1197
C(24)	−549	4000	399
C(25)	−25	3495	339
C(26)	515	3191	1077
C(31)	772(5)	1718(4)	3313(6)
C(32)	1146	1193	4092
C(33)	844	239	4413
C(34)	167	−192	3954
C(35)	−207	333	3175
C(36)	96	1287	2855
C(41)	2492(5)	5534(5)	2762(5)
C(42)	1819	5906	2446
C(43)	1796	6670	1698
C(44)	2446	7061	1266
C(45)	3118	6689	1582
C(46)	3141	5926	2330
C(51)	3326(4)	4071(6)	4044(7)
C(52)	4080	4610	4069
C(53)	4716	4173	4283
C(54)	4598	3198	4471
C(55)	3844	2659	4446
C(56)	3208	3095	4232
C(61)	2786(5)	5290(6)	4661(5)
C(62)	2828	6256	4453
C(63)	3070	6723	5123
C(64)	3271	6224	5999
C(65)	3230	5258	6206
C(66)	2987	4791	5537

catecholato complex **7b**, and with [PtCl$_2$(cod)] gave the new derivative **7c**, both in high yield and purity. These results demonstrate the general applicability to the synthesis of chelate-ring complexes of this type, in a one-pot procedure, giving by-products (AgCl and water) which are readily removed. The synthesis of related complexes is under investigation.

Experimental

Melting points were recorded on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on a Bio-Rad FTS-40 spectrophotometer, ^{1}H NMR spectra in CDCl$_3$ solution on a Bruker AC300P spectrometer at 300.13 MHz with chemical shifts referenced to SiMe$_4$ (δ 0.0), ^{13}C-{^{1}H} NMR spectra in CDCl$_3$ on a Bruker AC300P spectrometer at 75.47 MHz relative to SiMe$_4$ and ^{31}P-{^{1}H} NMR spectra in CDCl$_3$ on a JEOL FX90Q spectrometer at 36.23 MHz respectively, with external 85% H$_3$PO$_4$ (δ 0.0) as reference.

All the compounds described are air-stable, and reactions were carried out and products recrystallised from solvents without regard for the exclusion of air. Solvents were dried and distilled from appropriate drying agents prior to use. Light petroleum refers to the fraction of b.p. 40–60 °C. Tetrachlorocatechol monohydrate was used as supplied by Aldrich. The compound [PtCl$_2$(cod)] was prepared *via* the literature procedure,[24] and *cis*-[PtCl$_2$(PPh$_3$)$_2$] was generated from this compound by addition of 2 mole equivalents of triphenylphosphine to a dichloromethane solution.

The cyclic diketones XCH(CO$_2$R)C(O)C(O)CH(CO$_2$R) **I** (X = CH$_2$, O or S) were prepared by the sodium alkoxide-induced condensation of the appropriate dialkyl glutarate, diglycolate, or thiodiglycolate with the dialkyl oxalate having the same alkyl group, *via* a modification of a process described in the literature for these compounds.[25] The resulting sodium salts were converted into the free cyclic diketones by acidification followed by work-up. The purity was confirmed by ^{1}H NMR spectroscopy and for **Ia** by GC–mass spectrometry (M^+ at m/z 214) and elemental analysis (Found: C, 50.20; H, 4.65. Calc. for C$_9$H$_{10}$O$_6$: C, 50.45; H, 4.70%).

Syntheses.—[Pt{OCC(CO$_2$Me)CH$_2$C(CO$_2$Me)CO}(PPh$_3$)$_2$] **6a**. To a solution of [PtCl$_2$(cod)] (0.100 g, 0.267 mmol) in dichloromethane (30 cm^3) were added in succession triphenylphosphine (0.140 g, 0.535 mmol), diketone **Ia** (0.057 g, 0.266 mmol) and silver(I) oxide (0.7 g, excess) and the mixture refluxed for 4 h. Filtration to remove the silver salts gave a pale yellow solution which was evaporated to dryness under reduced pressure to give a pale yellow solid. The latter was recrystallised from dichloromethane–light petroleum to give the product as pale yellow needles (0.173 g, 70%) (Found: C, 57.70; H, 4.20. C$_{45}$H$_{38}$O$_6$P$_2$Pt requires C, 58.00; H, 4.10%), decomp. > 200 °C, melting to a red liquid at 235–238 °C; ν(C=O) at 1686 cm^{-1}. ^{31}P-{^{1}H} NMR: δ 5 [s, ^1J(PtP) 3603 Hz]. Crystallographic quality crystals were grown slowly by vapour diffusion of light petroleum into a dichloromethane solution of the complex.

[Pt{OCC(CO$_2$Et)OC(CO$_2$Et)CO}(PPh$_3$)$_2$]·CH$_2$Cl$_2$ **6b**. To a solution of [PtCl$_2$(cod)] (0.300 g, 0.802 mmol) in dichloromethane (30 cm^3) were added in succession triphenylphosphine (0.420 g, 1.603 mmol), diketone **Ib** (0.196 g, 0.803 mmol), and silver(I) oxide (0.8 g, excess), and the mixture was refluxed for 18 h. Filtration to remove the silver salts gave a yellow solution which was evaporated to dryness under reduced pressure to give a pale yellow microcrystalline solid. Recrystallisation from dichloromethane–light petroleum gave complex **6b** as pale yellow microcrystals (0.684 g, 81%) (Found: C, 54.1; H, 3.8. C$_{46}$H$_{40}$O$_7$P$_2$Pt·CH$_2$Cl$_2$ requires C, 53.95; H, 4.0%), m.p. 260–280 °C (decomp.); ν(C=O) at 1696 cm^{-1}. NMR: ^{31}P-{^{1}H}, δ 7.1 [s, ^1J(PtP) 3611]; ^{1}H, δ 7.49–7.14 (m, 30 H, PPh$_3$), 4.02 [q, 4 H, CH$_2$, ^3J(HH) 7.0], and 0.98 [t, 6 H, CH$_3$, ^3J(HH) 7.0]; ^{13}C-{^{1}H}, δ 166.1 (s, br, Pt-O-C-*C*), 159.9 (s, CO$_2$Et), 134.4–127.3 (m, Ph), 121.8 [t, Pt-O-C, ^3J(PC)$_{cis}$ + ^3J(PC)$_{trans}$ 2.2 Hz], 58.7 (s, CH$_2$) and 14.4 (s, CH$_3$). The presence of CH$_2$Cl$_2$ of crystallisation in this complex was confirmed by ^{1}H and ^{13}C-{^{1}H} NMR spectroscopy.

[Pt{OCC(CO$_2$Et)OC(CO$_2$Et)CO}(cod)] **6c**. A mixture of [PtCl$_2$(cod)] (0.200 g, 0.525 mmol), diketone **Ib** (0.131 g, 0.536 mmol) and silver(I) oxide (0.7 g, excess) in dichloromethane (30 cm^3) was refluxed for 20 h. Filtration to remove the silver salts gave a yellow solution which was evaporated to dryness under reduced pressure to afford a yellow oil which crystallised on standing. Recrystallisation from dichloromethane–light petroleum gave pale yellow microcrystals of complex **6c** (0.209 g, 72%) (Found: C, 38.95; H, 3.90. C$_{18}$H$_{22}$O$_7$Pt requires C, 39.65; H, 4.05%), softens and darkens > 170 °C with no melting; ν(C=O) at 1685 cm^{-1}. NMR: ^{1}H, δ 5.52 [s, 4 H, cod CH, ^2J(PtH) 62.7], 4.27 [q, 4 H, CH$_2$ (ester), ^3J(HH) 7.1], 2.67 (m, 4 H, br, CH$_2$ of cod), 2.26 (m, 4 H, CH$_2$ of cod), and 1.30 [t, 6 H, CH$_3$, ^3J(HH) 7.1]; ^{13}C-{^{1}H}, δ 165.3 (s, Pt-O-C-*C*), 158.8 (s, CO$_2$Et), 120.5 (s, Pt-O-C), 92.1 [s, CH of cod, ^1J(PtC) 171.9 Hz], 60.1 [s, CH$_2$ (ester)], 29.5 (s, CH$_2$ of cod), and 14.3 (s, CH$_3$).

[Pt{OCC(CO$_2$Me)SC(CO$_2$Me)CO}(PPh$_3$)$_2$] **6d**. A solution of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.150 g, 0.190 mmol) in dichloromethane (30 cm^3) with diketone **Ic** (0.044 g, 0.190 mmol) and silver(I) oxide (*ca.* 0.7 g, excess) was refluxed for 2 h. Work-up as for complex **6a** gave a pale yellow solid (0.141 g, 81%) which was recrystallised from dichloromethane–light petroleum to give fine pale yellow needles (Found: C, 54.85; H, 3.90. C$_{44}$H$_{36}$O$_6$P$_2$PtS requires C, 55.65; H, 3.80%), m.p. 268–272 °C (decomp.); ν(C=O) at 1684 cm^{-1}. NMR: ^{31}P-{^{1}H}, δ 4.8 [s, ^1J(PtP) 3609]; ^{1}H, δ 7.5–7.0 (m, 30 H, Ph) and 3.46 (s, 6 H, Me); ^{13}C-{^{1}H}, δ 170.7 (s, br, Pt-O-C-*C*), 164.1 (s, CO$_2$Me), 134.6–128.2 (m, Ph), 100.4 (s, br, Pt-O-C) and 50.0 (s, CH$_3$).

[Pt(1,2-O$_2$C$_6$Cl$_4$)(PPh$_3$)$_2$] **7b**. To a solution of [PtCl$_2$(cod)] (0.200 g, 0.535 mmol) in dichloromethane (40 cm^3) was added in succession triphenylphosphine (0.280 g, 1.068 mmol), tetrachlorocatechol monohydrate (0.142 g, 0.535 mmol), and silver(I) oxide (0.7 g, excess), and the mixture refluxed for 18 h. Work-up as for complex **6a** gave a yellow crystalline solid. Recrystallisation from dichloromethane–light petroleum gave a bright yellow microcrystalline solid which was filtered off, washed with light petroleum and dried *in vacuo* to give **7b** (0.419 g, 81%) (Found: C, 51.95; H, 2.95. Calc. for C$_{42}$H$_{30}$Cl$_4$O$_2$P$_2$Pt: C, 52.25; H, 3.15%), m.p. 260–270 °C (with sublimation and decomposition). ^{31}P-{^{1}H} NMR: δ 8.1 [s, ^1J(PtP) 3613 Hz].

[Pt(1,2-O$_2$C$_6$Cl$_4$)(cod)] **7c**. A mixture of [PtCl$_2$(cod)] (0.200 g, 0.535 mmol), tetrachlorocatechol monohydrate (0.142 g, 0.535 mmol) and silver(I) oxide (0.7 g, excess) in dichloromethane (30 cm^3) was refluxed for 6 h. Filtration to remove the silver salts gave a bright yellow solution which afforded a yellow microcrystalline solid on reduction in the volume to *ca.* 5 cm^3 and addition of light petroleum (50 cm^3). The solid was filtered off and dried *in vacuo* to give complex **7c** (0.243 g, 83%) (Found: C, 30.65; H, 1.95. C$_{14}$H$_{12}$Cl$_4$O$_2$Pt requires C, 30.60; H, 2.2%), decomp. > 200 °C. ^{1}H NMR: δ 5.55 [s, 4 H, cod CH, ^2J(PtH) 66.3 Hz], 2.72 (m, br, 4 H, cod CH$_2$) and 2.40 (m, 4 H, cod CH$_2$). The relatively low solubility of **7c** precluded full NMR characterisation, however the ^{13}C-{^{1}H} spectrum clearly displayed resonances due to cod CH carbons at δ 90.3 [s, ^1J(PtC) 174.5 Hz] and cod CH$_2$ carbons at δ 29.6 (s).

Crystal Structure Determination.—A very pale yellow crystal of complex **6a** of approximate dimensions 0.28 × 0.13 × 0.07 mm was mounted in air and the unit-cell dimensions were determined from oscillation photographs about the *c* axis and from optimised counter angles for zero- and upper-layer reflections. Data were collected on a Stoe STADI-2 diffractometer with an ω-scan technique in the range $7 \leqslant 2\theta \leqslant 54°$. The 8722 unique reflections collected from

Weissenberg layers *hk*(0–17) having $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarisation effects. Subsequent calculations were carried out using the programs SHELX 76[26] and SHELXTL PC.[27]

The molecular structure was solved by conventional Patterson and Fourier-difference techniques. Scattering factors were taken from SHELXTL. An analytical absorption correction was applied to the data using the Gaussian integration method of SHELX 76, the maximum and minimum transmission factors being 0.8103 and 0.5906 respectively. In the final stages of full-matrix least-squares refinements all atoms with the exception of the phenyl carbons were given anisotropic thermal parameters. All phenyl rings were treated as rigid bodies with D_{6h} symmetry and C–C distances of 1.395(5) Å. The phenyl and methylenic hydrogen atoms were not included in refinement cycles. The total number of refined parameters was 399, with a ratio of reflections: parameters of 22 : 1. Final cycles employed a weighting factor w calculated from $k/(\sigma^2F + gF^2)$ where $k = 1.4453$ and $g = 0.000\,630$. Final values of R and R' are 0.0551 and 0.0536. The maximum and minimum electron densities in the final ΔF map were 1.37 and -1.63 e Å^{-3} respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles for both independent molecules of the structure.

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