Side-bonded Ketone Complexes of Platinum(0). Indan-1,2,3-trione Complexes; Molecular and Crystal Structure of [2,2',-Bis(indan-1,2,3-trionato)(2–)-$O^2O^{2'}$]bis(triphenylphosphine)platinum

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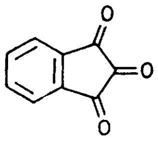
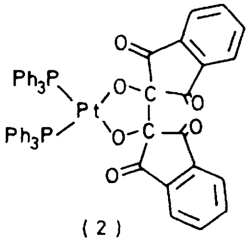
Reactions of equimolar quantities of [PtL_4] (L = PPh_3 or $AsPh_3$) with either indan-1,2,3-trione (int) or 2,2-dihydroxyindan-1,3-dione afford the side-bonded ketone complexes [Pt(int)L_2] which undergo ring-expansion reactions with int to give [Pt{(int)$_2$}L_2]. Crystals of the adduct [Pt{(int)$_2$}(PPh_3)$_2$] are monoclinic, space group *Cc* with a = 22.08, b = 14.47, c = 30.72 Å, β = 95.1°, and Z = 8. Least-squares refinement of the structural parameters reduced R to 0.078 for 2 382 reflections. The adduct has the two indan-1,2,3-trione moieties linked *via* the carbon atoms of the central carbonyl groups and bonded by the oxygen atoms at these groups to the platinum to give a five-membered 1,3-dioxa-2-platinolan ring. Ring-expansion reactions of [Pt(int)L_2] and ring-substitution reactions of [Pt{(int)$_2$}L_2], with hexafluoropropan-2-one and hexafluorobut-2-yne are also described. Reactions with hexafluoropropan-2-one give both five- and seven-membered ring systems. The side-bonded complexes [Pt(int)L_2] react with dioxygen to give cyclic dicarboxylato-complexes.

ALTHOUGH hexafluoropropan-2-one is known to co-ordinate to low-valent metal complexes *via* its p_π–p_π orbitals,[1] examples of other ketones behaving in this manner are restricted to certain α,β-unsaturated ketones,[2-5] which act as bidentate ligands, and the fluoroketones, chloropentafluoropropan-2-one,[6] 1,3-dichlorotetrafluoropropan-2-one,[6] and CF_3COCN.[7] A feature of fluorinated ketones is the electrophilic behaviour of the carbonyl group and we wished to investigate the organometallic chemistry of the electrophilic ketone indan-1,2,3-trione [int,(1)],[8] in particular the possibility of ring-opening reactions. We had previously discovered that platinum(0) causes ring opening of benzocyclobutene-1,2-dione.[9]


(1) int

RESULTS AND DISCUSSION

Treatment of a benzene solution of tetrakis(triphenylphosphine)platinum(0) with an excess of indan-1,2,3-trione (1) gave a yellow complex of formula [Pt{(int)$_2$}(PPh_3)$_2$] (2). In order to clarify the exact nature of (2) a single-crystal *X*-ray diffraction study was carried out thereby establishing (2) as the five-membered ring complex.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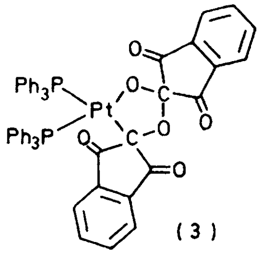
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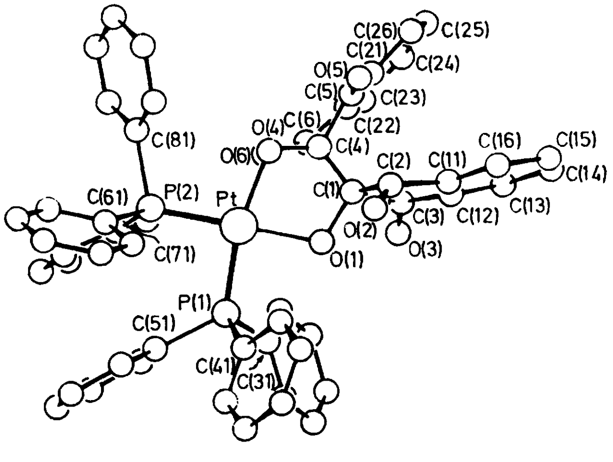
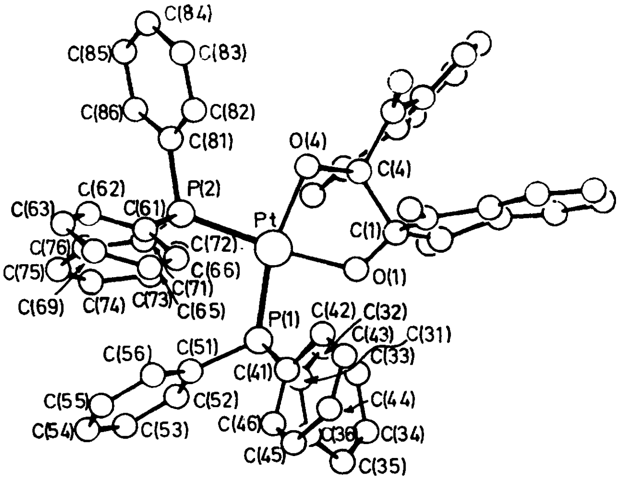


Molecule 2



Molecule 1

FIGURE 1 Molecular geometry and atom numbering for the two molecules

The molecular geometry and atom numbering are illustrated in Figure 1. The two molecules in the asymmetric unit have almost identical geometries. The large estimated standard deviations (e.s.d.s) prohibit detailed discussion of bond lengths and angles (listed in Table 1) but the mean values are unexceptional.

The co-ordination about platinum is planar to within experimental error for both molecules. The Pt–O–C–C–O ring is non-planar in both molecules, the carbon atoms being on the same side (but at different distances) of the plane defined by the platinum and oxygen atoms. This conformation achieves a staggering of the indan-1,2,3-trione residues as illustrated in Figure 2. The five-membered ring of each indan-1,2,3-trione residue is non-planar with the carbon atom linking the two residues 0.4 Å on average from the mean plane of the other four carbon atoms and the oxygen atoms of the two ketonic groups 0.2 Å on the opposite side of this plane.

TABLE 1

Bond lengths (Å) and angles (°) *

	Molecule 1	Molecule 2
Pt–P(1)	2.30	2.15
Pt–P(2)	2.25	2.16
	mean 2.22(7)	
P(1)–C(31)	1.81	1.84
P(1)–C(41)	1.82	1.81
P(1)–C(51)	1.80	1.95
P(2)–C(61)	1.77	1.77
P(2)–C(71)	1.80	1.73
P(2)–C(81)	1.93	1.93
	mean 1.83(7)	
Pt–O(1)	2.15	2.05
Pt–O(4)	2.05	1.97
	mean 2.06(7)	
C(2)–O(2)	1.32	1.28
C(3)–O(3)	1.11	1.14
C(5)–O(5)	1.30	1.06
C(6)–O(6)	1.42	1.22
	mean 1.23(12)	
C(1)–O(1)	1.54	1.43
C(4)–O(4)	1.28	1.38
	mean 1.41(11)	
C(1)–C(4)	1.73	1.41
	mean 1.57	
C(1)–C(2)	1.69	1.60
C(1)–C(3)	1.66	1.76
C(4)–C(5)	1.38	1.53
C(4)–C(6)	1.44	1.45
	mean 1.56(13)	
C(2)–C(11)	1.46	1.51
C(3)–C(12)	1.58	1.37
C(5)–C(21)	1.50	1.56
C(6)–C(22)	1.58	1.44
	mean 1.50(7)	

	Molecule 1	Molecule 2
P(1)–Pt–P(2)	102	93
P(1)–Pt–O(1)	92	87
P(2)–Pt–O(4)	85	100
O(1)–Pt–O(4)	83	80
Pt–O(1)–C(1)	97	108
Pt–O(4)–C(4)	118	112
	mean 109(9)	
O(1)–C(1)–C(4)	106	115
O(4)–C(4)–C(1)	102	108
	mean 108(5)	
C(2)–C(1)–C(3)	107	104
C(5)–C(4)–C(6)	102	103
	mean 104(2)	
C(1)–C(2)–C(11)	101	102
C(1)–C(3)–C(12)	94	103
C(14)–C(5)–C(21)	118	103
C(4)–C(6)–C(22)	110	111
	mean 105(7)	
C(2)–C(11)–C(12)	119	115
C(3)–C(12)–C(11)	110	115
C(5)–C(21)–C(22)	106	109
C(6)–C(22)–C(21)	103	107
	mean 111(5)	
C(1)–C(2)–O(2)	137	118
C(11)–C(2)–O(2)	123	128
C(1)–C(3)–O(3)	117	124
C(12)–C(3)–O(3)	148	120
C(4)–C(5)–O(5)	130	127
C(21)–C(5)–O(5)	112	129
C(4)–C(6)–O(6)	125	131
C(22)–C(6)–O(6)	120	116
	mean 125(8)	

* Individual e.s.d.s are 0.03 for Pt–P, 0.04 for Pt–O, 0.07 for P–C, and 0.09 Å for C–C and C–O. Individual e.s.d.s for the angles lie between 5 and 8°.

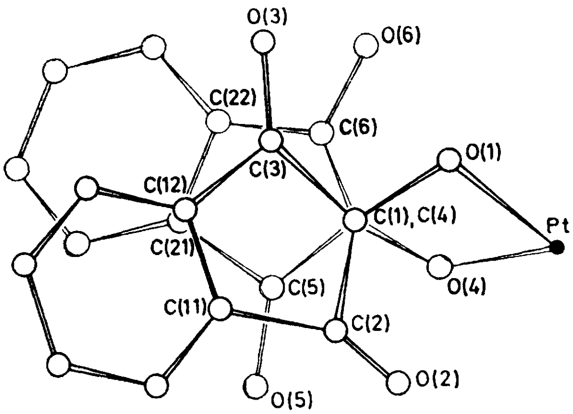
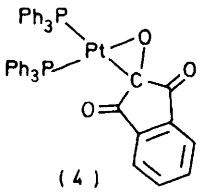


FIGURE 2 Relative orientation of the two indantrione residues for molecule 1. Molecule 2 is similar

It is apparent from Figure 1 that a head-to-tail linkage of the ketones, structure (3), would bring the indantriketone moiety adjacent to the platinum into close proximity with the phenyl groups of the triphenylphosphine ligands and this may be a reason why the head-to-head linking of the two trione molecules is preferred in this system. In similar reactions involving hexafluoropropan-2-one only head-to-tail linkage of this ketone has been observed.[10]

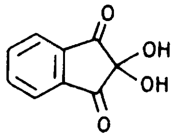
The formation of (2) may proceed *via* co-ordination of the central, most electrophilic, carbonyl group of indan-1,2,3-trione to the platinum to give (4), followed by ring expansion of the three-membered ring, a process analogous to that proposed for the ring expansion of similar complexes of hexafluoropropan-2-one.[10] Evidence that this mechanism operates in the formation of (2) is provided by the observation that treatment of



(4)

[$Pt(PPh_3)_4$] with an equimolar quantity of indan-1,2,3-trione gave a complex [$Pt(int)(PPh_3)_2$] (4) which reacts with a further equimolar quantity of indan-1,2,3-trione to give (2). The physical and chemical properties of (4) strongly support a structure in which the central carbonyl group of the trione is co-ordinated to platinum *via* its p_π–p_π orbitals as is found in [$Pt\{OC(CF_3)_2\}(PPh_3)_2$].[1] Thus the i.r. spectrum of (4) exhibits two carbonyl absorptions at 1 709 and 1 678 cm^{-1}, typical of the CO groups of indan-1,3-dione.[11,12] Furthermore, the formation of (4) would be consistent with the observation that indan-1,2,3-trione is known to act as a dienophile in Diels–Alder reactions.[12]

The side-bonded indan-1,2,3-trione complex (4) may also be obtained by reaction of the diol (5) with [$Pt(PPh_3)_4$] as well as by the reactions of (1) or (5) with either [Pt(*trans*-PhCH=CHPh)($PPh_3)_2$] or [$Pt(PhC{\equiv}CPh)(PPh_3)_2$]. It is surprising that both (1) and (5) form the same three-membered ring complex (4) and this observation suggests that Pt^0 is a powerful enough nucleophile to displace water from the diol (5). However, reactions with (5) were approximately four times slower than with indan-1,2,3-trione.

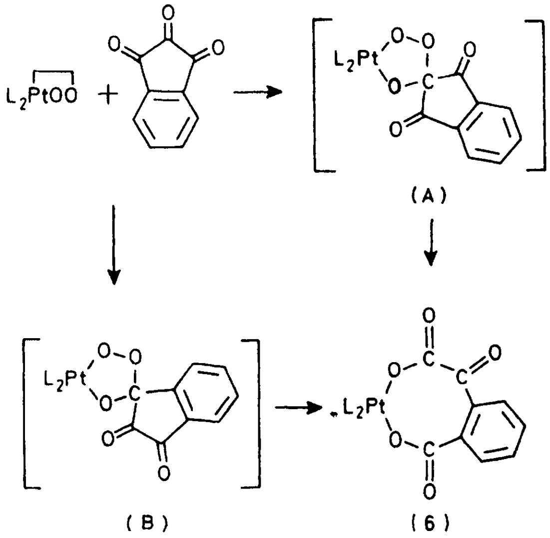


(5)

The reactions of [$Pt(AsPh_3)_4$] with the appropriate quantity of (1) gave the triphenylarsine derivatives of (2) and (4). The triphenylarsine ligands in [$Pt(C_2F_4)(AsPh_3)_2$] are readily displaced by tertiary phosphines.[13] However, only intractable red oils or solids were obtained by treating [$Pt(int)(AsPh_3)_2$] with either 1,2-bis(diphenylphosphino)ethane or methyldiphenylphosphine.

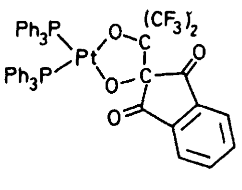
The indan-1,2,3-trione ligand in (4) was readily displaced by hydrogen chloride gas and tetrachloro-*o*-benzoquinone to give *cis*-[$PtCl_2(PPh_3)_2$] and [$Pt(O_2C_6Cl_4)(PPh_3)_2$] respectively. When stored under dinitrogen, complex (4) was indefinitely stable but in the atmosphere it reacted slowly with dioxygen and its yellow colour faded. In benzene solution the reaction of dioxygen with (4) was rapid and elemental analyses and molecular-weight data for the white crystalline product indicate the formation of a 1 : 1 adduct (6). The complex exhibits strong carbonyl absorptions at 1 752 and 1 675 cm^{-1} and strong absorptions at 1 315 and 1 275 cm^{-1}. The same complex (6) could be isolated from the reaction between (1) and [$PtO_2(PPh_3)_2$], and surprisingly from the reaction between the diol (5) and [$PtO_2(PPh_3)_2$]. This one complex (6) isolated from these three reactions might be expected to have a five-membered ring structure involving a peroxy-group analogous to the systems formed with aldehydes and ketones.[14,15] However, it has been shown that α-diketones, when involved in this type of five-membered ring structure, rearrange to give dicarboxylato-complexes.[16] By analogy, it seems reasonable to expect indan-1,2,3-trione to undergo a similar reaction to yield the dicarboxylato-complex (6) *via* an unstable five-membered peroxy-ring complex (Scheme). The strong absorptions in the i.r. spectrum at 1 315 and 1 275 cm^{-1} can be assigned to ν_{sym}(OCO) for the carboxylato-complex (6); these fall in the region characteristic of carboxylate groups bonded to platinum.[17] An absorption at 1 675 cm^{-1} can be assigned to ν_{asym}(OCO). Further evidence for the formulation of (6) as a carboxylato-complex rather than a five-membered peroxy-ring complex is provided by the observation that (6) can be recovered unchanged after refluxing a suspension of the complex for 1 d in isopropyl alcohol. Similarly, dioxygen reacts with [$Pt(int)(AsPh_3)_2$] to give a carboxylato-complex analogous to (6).

In the mechanism we propose for this reaction (Scheme), two different intermediate five-membered peroxy-ring systems, (A) and (B), initially form, which can both collapse to the same carboxylato-complex (6). The reaction of dioxygen with (4) presumably proceeds *via* (A). However, it seems more likely that reactions involving the diol (5) proceed *via* formation of a five-membered peroxy-ring intermediate involving a carbonyl group adjacent to the aromatic nucleus. This intermediate would then dehydrate to give (B) which collapses to (6). In these reactions we have not observed the formation of an intermediate peroxy-ring system. This may be a steric effect since it is known that bulky substituents enhance the formation of carboxylato-complexes.[16]

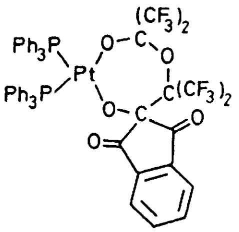


SCHEME L = PPh_3 or $AsPh_3$

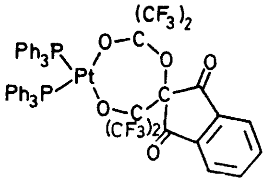
Although complex (4) readily undergoes a ring-expansion reaction with indan-1,2,3-trione this is not the case with propan-2-one or fluoren-9-one. However, when (4) was treated with hexafluoropropan-2-one at room temperature in benzene two products were isolated. The major product was a yellow crystalline air-stable solid. Microanalytical and molecular-weight data indicate a 1 : 1 adduct (7) between (4) and hexafluoropropan-2-one. The i.r. spectrum of (7) shows a strong absorption in the carbonyl region at 1 705 cm^{-1} and weaker absorptions at 1 760 and 1 733 cm^{-1}. The ^{19}F n.m.r. spectrum shows one singlet. The data are consistent with a structure in which the two ketones are present in a five-membered ring system. The absence of ^{31}P and ^{195}Pt splitting in the ^{19}F n.m.r. spectrum indicates carbonyl oxygen–platinum bonding for the hexafluoropropan-2-one and, in view of the structure found for (2), structure (7) is proposed for this 1 : 1 adduct. Treatment of (7) with hydrogen chloride gas or trifluoroacetic acid gave *cis*-$[PtCl_2(PPh_3)_2]$ and $[Pt(O_2CCF_3)_2(PPh_3)_2]$ respectively. However, with hydrochloric acid, (7) gave *cis*-$[PtCl_2(PPh_3)_2]$ and the oxygen adduct (6).



(7)



(8a)

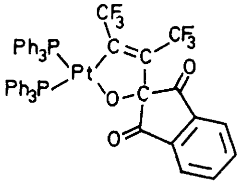


(8b)

The second product, (8), isolated from the reaction of hexafluoropropan-2-one with (4), was a white crystalline solid for which elemental analyses suggest a 1 : 2 adduct between (4) and hexafluoropropan-2-one. The i.r. spectrum shows a strong absorption in the carbonyl region at 1 732 cm^{-1} and the ^{19}F n.m.r. spectrum contains four quartets centred at 5.98, 7.98, 15.6, and 17.8 p.p.m. each showing approximately equal ^{19}F–^{19}F coupling. It seems probable that this adduct contains a seven-membered ring, the absence of ^{31}P and ^{195}Pt coupling in the ^{19}F n.m.r. spectrum again implying the absence of platinum–carbon bonding of the hexafluoropropan-2-one. Puckering of the seven-membered ring would render each CF_3 group non-equivalent and the *gem*-CF_3 groups can thus couple to give the observed quartets in the ^{19}F n.m.r. spectrum. Complex (8) may have a structure (8a) analogous to that found for the seven-membered ring formed from $[Pt(O_2)(PPh_3)_2]$ and hexafluoropropan-2-one.[15] However, structure (8b) would also be consistent with the ^{19}F n.m.r. data and confirmation of the structure must await additional data.

Treatment of (7) with hexafluoropropan-2-one at 70 °C also gave a low yield of the seven-membered ring complex (8). This would appear to be a novel five- to seven-membered ring-expansion reaction. However, it is possible that the reaction goes *via* dissociation of the five-membered ring followed by recombination to give the observed product. The observation that unchanged (7) and a low yield of $[Pt\{OC(CF_3)_2\}(PPh_3)_2]$ could be isolated from the reaction mixture is in agreement with this suggestion. The five-membered ring complex (7) appears to be more reactive towards hexafluoropropan-2-one than is $[\overline{Pt\{OC(CF_3)_2OO}\}(PPh_3)_2]$, since this last dioxygen ring complex does not undergo further ring expansion with hexafluoropropan-2-one.[15]

The reaction of (4) with hexafluorobut-2-yne at 60 °C led to displacement of the ketone and formation of $[Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2]$. However, at room temperature three products were formed: (2), $[Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2]$, and a 1 : 1 adduct between (4) and the acetylene. The i.r. and ^{19}F n.m.r. data for this latter complex are consistent with a five-membered ring structure and assuming that the ketone again forms a platinum–oxygen bond in the ring then the structure (9) can be assigned to this complex. The complex $[Pt(int)(AsPh_3)_2]$ undergoes a much more rapid reaction with hexafluorobut-2-yne than does (4). However, the only two products which could be isolated were $[Pt(CF_3C{\equiv}CCF_3)(AsPh_3)_2]$ and the triphenylarsine derivative of (2). These reactions with hexafluorobut-2-yne thus lead to some displacement of the triketone from the platinum, in contrast to the reactions observed with hexafluoropropan-2-one in which no simple displacement products were obtained.



(9)

Our observation that hexafluoropropan-2-one would ' ring expand ' (7) to (8) prompted an investigation of the reactions of the five-membered ring system (2) with hexafluoropropan-2-one and hexafluorobut-2-yne. At room temperature (2) reacted with hexafluoropropan-2-one to give (1), (7), and (8) together with a small amount of a complex which appears to be another 1 : 1 adduct of (4) with hexafluoropropan-2-one. However, this product is not identical to (7). It may be an isomer of (7) in which there is head-to-tail linking of the carbonyl groups in the five-membered ring. Insufficient material and low solubility precluded a ^{19}F n.m.r. study. In contrast, hexafluorobut-2-yne did not react with (2) at room temperature but at 60 °C both molecules of indan-1,2,3-trione were displaced from the platinum and $[Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2]$ was isolated.

The results described in this paper indicate that other electrophilic ketones besides hexafluoropropan-2-one can form side-bonded complexes with Pt^0. The present indan-1,2,3-trione complexes, however, are considerably more reactive than the hexafluoropropan-2-one complexes of Pt^0 so far described. This increased reactivity of indan-1,2,3-trione complexes is probably a consequence of steric effects and the poorer π-accepting ability of indan-1,2,3-trione as compared to hexafluoropropan-2-one, factors which would weaken the attachment of indan-1,2,3-trione to Pt^0. Indeed, unlike hexafluoropropan-2-one,[1] we find that (1) does not form an adduct with *trans*-$[IrCl(CO)(PPh_3)_2]$.

EXPERIMENTAL

Melting points (Table 2) were measured on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded using Nujol and hexachlorobutadiene mulls on a Perkin-Elmer model 225 spectrophotometer between KBr (400—4 000 cm^{-1}) and Polythene (200—400 cm^{-1}) plates. Fluorine-19 n.m.r. spectra were obtained at 56.4 MHz on a Varian Associates DA60 instrument, ^1H spectra at 60 MHz on a Varian Associates T60 instrument. Molecular-weight determinations were carried out by Beller Mikroanalytisches Laboratorium and microanalyses by Pascher Mikroanalytisches Laboratorium (Table 2).

TABLE 2

Melting points, yields, and microanalytical data for the complexes

	Complex	(θ_c/°C)	Yield (%)	Analysis (%)						
				Found			Calc.			
				C	H	O	C	H	O	M[a]
(4)	$[Pt(int)(PPh_3)_2]$	210—214[b]	85	61.3	4.1	5.8	61.5	3.9	5.4	893 (880)
	$[Pt(int)(AsPh_3)_2]$	149—151	84	56.5	3.8	5.5	55.8	3.5	5.0	970 (968)
(2)	$[Pt\{(int)_2\}(PPh_3)_2]$	157—161	68	61.6	4.3	9.6	62.4	3.7	9.2	1 030 (1 040)
	$[Pt\{(int)_2\}(AsPh_3)_2]$	152—156	61	58.3	3.8	8.4	57.5	3.4	8.5	1 135 (1 128)
(6)	$[Pt\{O_2C{\cdot}o\text{-}C_6H_4{\cdot}C(O)CO_2\}(PPh_3)_2]$	168—171	60	58.8	4.0	8.7	59.3	3.8	8.8	1 020 (912)
	$[Pt\{O_2C{\cdot}o\text{-}C_6H_4{\cdot}C(O)CO_2\}(AsPh_3)_2]$	230—240[b]	76	53.9	3.7	8.0	54.1	3.4	9.0	1 078 (1 000)
(7)	$[Pt\{OC(CF_3)_2{\cdot}int\}(PPh_3)_2]$	210—220	62	55.0	3.4	*c*	55.2	3.3		1 020 (1 046)
(8)	$[Pt\{2\ OC(CF_3)_2{\cdot}int\}(PPh_3)_2]$	182—185[d]	26	50.7	2.9	*e*	50.5	2.8		1 203 (1 212)
(9)	$[Pt(C_4F_6{\cdot}int)(PPh_3)_2]$	164—168	11	56.7	3.3	*f*	56.4	3.3		951 (1 042)

[a] Molecular weights determined osmometrically in $CHCl_3$; calculated values are given in parentheses. [b] With decomposition. [c] F, 10.7 (requires 10.9%). [d] Gas evolved with decomposition. [e] F, 18.3 (requires 18.8%). [f] F, 11.1 (requires 10.9%).

Indan-1,2,3-trione,[18] $[Pt(PPh_3)_4]$,[19] $[Pt(AsPh_3)_4]$,[18] [Pt(*trans*-PhCH=CHPh)$(PPh_3)_2]$,[20] $[Pt(PhC{\equiv}CPh)(PPh_3)_2]$,[21] $[PtO_2(PPh_3)_2]$,[22] and *trans*-$[IrCl(CO)(PPh_3)_2]$ [23] were prepared as described in the literature. The light petroleum used had b.p. 30—40 °C. All the reactions were carried out in a dinitrogen atmosphere unless otherwise stated.

Reactions.—Tetrakis(triphenylphosphine)platinum(0) *with an equimolar quantity of indan*-1,2,3-*trione*. The complex $[Pt(PPh_3)_4]$ (1 g, 0.8 mmol) and indan-1,2,3-trione (0.13 g, 0.8 mmol) were stirred together in benzene (100 cm^3) for 30 min to produce a dark brown solution. The volume of the solution was reduced (to *ca*. 20 cm^3) by evaporation under reduced pressure and an excess of diethyl ether (100 cm^3) was added. Yellow *crystals* of (indan-1,2,3-trione)bis(triphenylphosphine)platinum(0) (4) were slowly deposited. These were filtered off, washed with diethyl ether, dried *in vacuo*, and stored under nitrogen. Yield 0.6 g (85%); ν(C=O) at 1 709m and 1 678s cm^{-1}.

The same general method was used for the reactions of (*trans*-stilbene)bis(triphenylphosphine)platinum(0) (1 g, 1.1 mmol) and (diphenylacetylene)bis(triphenylphosphine)platinum(0) (1 g, 1.11 mmol) with indan-1,2,3-trione (0.18 g, 1.1 mmol and 0.18 g, 1.1 mmol respectively) to yield in each case (4) (0.8 g, 81% and 0.76 g, 73% respectively). In each case a yellow, rather than dark brown, solution was produced during the reaction.

Tetrakis(triphenylphosphine)platinum(0) *with an equimolar quantity of ninhydrin*. The complex $[Pt(PPh_3)_4]$ (1 g, 0.8 mmol) and ninhydrin (0.14 g, 0.8 mmol) were stirred together in benzene (100 cm^3) for 2 h to produce a dark brown solution. The volume of the solution was reduced (*ca*. 20 cm^3) by evaporation under reduced pressure and an excess of diethyl ether (*ca*. 100 cm^3) was added. Yellow *crystals* were slowly deposited which were filtered off, washed with diethyl ether, dried *in vacuo*, and stored under nitrogen. These were shown to be (4) by their m.p. 212—220 °C (decomp.), i.r. spectra, and microanalysis (Found: C, 61.5; H, 3.7%).

As with indan-1,2,3-trione, ninhydrin reacted with [Pt(*trans*-PhCH=CHPh)$(PPh_3)_2]$ and $[Pt(PhC{\equiv}CPh)(PPh_3)_2]$ to give (4).

Tetrakis(triphenylarsine)platinum(0) *with an equimolar quantity of indan*-1,2,3-*trione*. The complex $[Pt(AsPh_3)_4]$ (2 g, 1.4 mmol) and indan-1,2,3-trione (0.2 g, 1.4 mmol) were stirred together in benzene (150 cm^3) for 1 h. The resulting clear yellow solution was reduced in volume (*ca*. 50 cm^2) by evaporation under reduced pressure and an excess of diethyl ether (*ca*. 150 cm^3) was added. Yellow *crystals* of (indan-1,2,3-trione)bis(triphenylarsine)platinum(0) were slowly deposited. These were filtered off, washed with diethyl ether, dried *in vacuo*, and stored under nitrogen; ν(C=O) at 1 712m and 1 684s cm^{-1}. The complex, unless stored under nitrogen, turned brown-yellow after several days.

Similarly, the reaction of $[Pt(AsPh_3)_4]$ with ninhydrin gave $[Pt(int)(AsPh_3)_2]$.

Of (indan-1,2,3-*trione)bis(triphenylphosphine)platinum*(0) (4). (*a*) *With indan*-1,2,3-*trione*. Complex (4) (0.25 g, 0.28 mmol) and indan-1,2,3-trione (0.055 g, 0.29 mmol) were stirred together in benzene (20 cm^3) for 48 h. The resulting bright yellow solution was filtered and reduced in volume (*ca*. 10 cm^3) by evaporation under reduced pressure. Slow addition of diethyl ether gave yellow *crystals* (prisms) of $[Pt\{(int)_2\}(PPh_3)_2]$ (2) which were filtered off, washed with diethyl ether, and dried *in vacuo*.

(*b*) *With hydrogen chloride*. Hydrogen chloride gas was passed through a solution of (4) (0.5 g, 0.56 mmol) in benzene (50 cm^3) for 5 min. The white suspension was filtered off and another crop of the white solid was obtained by reducing the volume of the filtrate by evaporation under reduced pressure. Recrystallisation of the white solid from methylene chloride–ethanol gave white *crystals* of *cis*-dichlorobis(triphenylphosphine)platinum(II) (0.39 g, 90%) identified by i.r. and m.p. 306—310 °C (lit.,[24] 310—312 °C).

(*c*) *With* 3,4,5,6-*tetrachloro*-o-*benzoquinone*. Complex (4) (0.25 g, 0.28 mmol) was stirred with 3,4,5,6-tetrachloro-*o*-benzoquinone (0.07 g, 0.28 mmol) for 12 h. The yellow-orange solution was filtered and reduced in volume (*ca.* 10 cm^3) by evaporation under reduced pressure. Addition of ethanol precipitated a yellow solid which upon recrystallisation from methylene chloride–ethanol gave yellow crystals of $[Pt(O_2C_6Cl_4)(PPh_3)_2]$ (0.24 g, 88%) identified by i.r. and m.p. 240 °C (lit.,[25] 246 °C).

(*d*) *With dioxygen*. A suspension of (4) (0.8 g, 0.9 mmol) in oxygenated benzene (100 cm^3) was shaken for 5 d. The white suspension was filtered off, washed with a small portion of benzene, and recrystallised from methylene chloride–benzene–diethyl ether to afford white needles of a 1 : 1 *adduct* between dioxygen and (4) (0.5 g, 60%). Infrared spectrum: 1 752s [ν(C=O)], 1 675s [ν(OCO)], 1 583vw, 1 568vw, 1 480m, 1 438s, 1 433s, 1 315m [ν(OCO)], 1 298vw, 1 275s [ν(OCO)], 1 231w, 1 188w, 1 158w, 1 147vw, 1 113w, 1 095s, 1 072w, 1 028vw, 1 008w, 859m, 848w, 819w, 807vw, 776vw, 766m, 760m (sh), 758m, 748m, 720m, 712m, 706m (sh), 696s, 662vw, 634vw, 624vw, 560m, 544m, 532s, 527m (sh), 517m, and 512s cm^{-1}.

(*e*) *With hexafluoropropan*-2-*one*. Hexafluoropropan-2-one (*ca.* 1.5 cm^3) was condensed into a Carius tube (−196 °C) containing (4) (0.7 g, 0.8 mmol) suspended in benzene (25 cm^3). The tube was sealed and shaken at room temperature for 3 d. The resulting pale yellow solid was filtered off and washed with diethyl ether and two more crops of the pale yellow solid were obtained by evaporation of the filtrate under reduced pressure followed by addition of diethyl ether. The three crops were combined and recrystallised from methylene chloride–diethyl ether to yield pale yellow *crystals* of $[Pt\{OC(CF_3)_2\cdot int\}(PPh_3)_2]$ (7). These were filtered off, washed with diethyl ether, and dried *in vacuo*. Yield 0.5 g (62%); ν(C=O) at 760vw, 1 733m, and 1 705s cm^{-1}. The ^{19}F n.m.r. spectrum in CH_2Cl_2 exhibited a singlet at 7.1 p.p.m. relative to internal α,α,α-trifluorotoluene.

The solvents from the filtrate and ether washings were completely removed by evaporation under reduced pressure and diethyl ether was added to the residue. A cream solid slowly precipitated from the solution and precipitation was completed by slow addition of light petroleum. The precipitate was recrystallised from methylene chloride–methanol to give white *crystals* (prisms) of $[Pt\{2\ OC(CF_3)_2\cdot int\}(PPh_3)_2]$ (8). These were filtered off, washed with methanol, and dried *in vacuo*. Yield 0.26 g (26%); ν(C=O) at 1 732 cm^{-1}. The ^{19}F n.m.r. spectrum in CH_2Cl_2 showed four signals at δ 5.98 [3 F, q, *J*(FF) 10.5], 7.98 [3 F, br q, *J*(FF) *ca.* 10.5], 15.6 [3 F, q, *J*(FF) 10.5], and 17.8 p.p.m. [3 F, q, *J*(FF) 10.5 Hz] relative to internal $C_6H_5CF_3$.

(*g*) *With hexafluorobut*-2-*yne at* 60 °C. Hexafluorobut-2-yne (*ca.* 2 cm^3) was condensed into a Carius tube (−196 °C) containing (4) (0.25 g, 0.3 mmol) suspended in benzene (20 cm^3). The tube was sealed and shaken at 60 °C for 1 d. The solvent was removed under reduced pressure. The residue was dissolved in diethyl ether and the solution was filtered and reduced in volume. Addition of light petroleum gave white *crystals* of $[Pt(C_4F_6)(PPh_3)_2]$ (0.15 g, 60%), m.p. 212 °C (lit.,[26] 215—216 °C); $\nu(C\equiv C)$ at 1 762s, cm^{-1} (lit.,[26] 1 775 cm^{-1}).

(*f*) *With hexafluorobut*-2-*yne at room temperature*. Hexafluorobut-2-yne (*ca.* 2 cm^3) and (4) (1 g, 1 mmol) suspended in benzene (*ca.* 25 cm^3) were shaken in a Carius tube at room temperature for 2 months. The resulting yellow solid was filtered off, washed with diethyl ether, and recrystallised from methylene chloride–diethyl ether. The bright yellow *crystals* (0.35 g, 30%) were identified as (2), m.p. 160—162 °C; ν(C=O) at 1 743m, 1 728vw, and 1 706s cm^{-1}.

Evaporation of the filtrate and ether washings under reduced pressure afforded a pale yellow residue. The residue was dissolved in methylene chloride and addition of methanol and slow evaporation under reduced pressure gave a pale yellow solid which was filtered off and washed with light petroleum. Recrystallisation from methylene chloride–methanol gave white crystals of $[Pt(C_4F_6)(PPh_3)_2]$ (0.25 g, 25%), m.p. 214 °C, $\nu(C\equiv C)$ at 1 762s cm^{-1}.

The filtrate and petrol washings were slowly evaporated under reduced pressure to give a yellow solid which was filtered off. Recrystallisation from benzene–diethyl ether–light petroleum gave yellow *crystals* (needles) of $[Pt(CF_3C=CCF_3\cdot int)(PPh_3)_2]$ (9) (0.13 g, 11%). Infrared spectrum: 1 751w, 1 744w, 1 738vw (sh), 1 718s, 1 704s, 1 604w, 1 598w, 1 587w, 1 482m, 1 440s, 1 436m (sh), 1 344vw, 1 307w (sh), 1 298m, 1 288m, 1 281w, 1 242s, 1 233s, 1 182w (sh), 1 178m, 1 160s, 1 136m (sh), 1 125, 1 115m (sh), 1 100s, 1 088m (sh), 1 028vw, 1 016vw, 994m, 921vw, 856vw, 838w, 820w, 774w, 768w, 762m, 756m, 749s, 743m, 732w, 712s, 703s, 697s (sh), 640w (sh), 636m, 628, 548m, 536s, 531s, 527s, and 506m cm^{-1}. The ^{19}F n.m.r. spectrum in CH_2Cl_2 showed two signals at δ −7.05 [3 F, q, *J*(FF) 15 Hz] and −13.6 p.p.m. (3 F, m) relative to internal $C_6H_5CF_3$.

(*Indan*-1,2,3-*trione*)*bis*(*triphenylarsine*)*platinum*(0). (*a*) *With indan*-1,2,3-*trione*. As for the corresponding triphenylphosphine complex, indan-1,2,3-trione (0.04 g, 0.2 mmol) and $[Pt(int)(AsPh_3)_2]$ (0.2 g, 0.2 mmol) gave after 4 h yellow crystals of $[Pt\{(int)_2\}(AsPh_3)_2]$ (0.15 g, 61%); ν(C=O) at 1 745m, 1 733vw, and 1 711s cm^{-1}.

(*b*) *With dioxygen*. A suspension of $[Pt(int)(AsPh_3)_2]$ (0.8 g, 0.86 mmol) in oxygenated benzene (100 cm^3) was shaken for 1 week. The white crystalline suspension was recrystallised from methylene chloride–diethyl ether and gave white needles of $[\overline{Pt\{O_2C\cdot o\text{-}C_6H_4\cdot C(O)C}O_2\}(AsPh_3)]$ (6; L = $AsPh_3$) (0.65 g, 76%). Infrared spectrum: 1 755s [ν(CO)], 1 679s [ν(OCO)], and 1 313m cm^{-1} [ν(OCO)].

(*c*) *With hexafluorobut*-2-*yne*. Hexafluorobut-2-yne (*ca.* 2 cm^3), $[Pt(int)(AsPh_3)_2]$ (0.6 g, 0.6 mmol), and benzene (25 cm^3) were shaken at room temperature for 2 d. The yellow-green solution was filtered off and evaporated to small bulk. Addition of diethyl ether gave a yellow solid, which was washed with diethyl ether and recrystallised from methylene chloride–benzene–diethyl ether to give unchanged $[Pt(int)(AsPh_3)_2]$ (0.11 g, 31%), m.p. 150—154 °C; ν(C=O) at 1 745m, 1 733vw, and 1 711s cm^{-1}.

Removal of the solvents from the filtrate and ether washings and addition of diethyl ether and light petroleum gave a white solid which was washed with petroleum. This was shown to be $[Pt(C_4F_6)(AsPh_3)_2]$ (0.42 g, 63%) from its i.r. and ^{19}F n.m.r. spectra; $\nu(C\equiv C)$ at 1 776 cm^{-1} (lit.,[26] 1 775 cm^{-1}).

Of $[Pt(O_2)(PPh_3)_2]$. (*a*) *With indan*-1,2,3-*trione*. Indan-1,2,3-trione (0.11 g, 0.67 mmol) and $[Pt(O_2)(PPh_3)_2]$ (0.5 g, 0.67 mmol) in benzene (50 cm^3) were stirred for 3 h. The resulting white suspension was filtered off, washed with benzene, and recrystallised from methylene chloride–benzene–diethyl ether to give white needles of (6; L = PPh_3) (0.3 g, 50%), m.p. 170—172 °C; ν(C=O) at 1 752s and 1 675s cm^{-1}.

(*b*) *With ninhydrin.* As above, ninhydrin (0.06 g, 0.3 mmol) and $[Pt(O_2)(PPh_3)_2]$ (0.25 g, 0.3 mmol) gave (6; L = PPh_3) (0.2 g, 67%).

Of $[Pt\{OC(CF_3)_2\cdot int\}(PPh_3)_2]$ (7). (*a*) *With hexafluoropropan-2-one.* Hexafluoropropan-2-one (*ca.* 2 cm^3) and (7) (0.5 g, 0.48 mmol) in benzene (20 cm^3) were shaken at 70 °C for 2 d. The resulting yellow solution was evaporated to *ca.* 5 cm^3 and diethyl ether (60 cm^3) was added. The yellow solution was shaken with activated charcoal at room temperature, filtered, and the filtrate was evaporated to *ca.* 20 cm^3. Light petroleum was added and the solution was allowed to stand for 12 h. The yellow solid was filtered off, washed with petroleum, and recrystallised from methylene chloride–diethyl ether to give yellow *crystals* of unchanged (7) (0.19 g, 38%), m.p. 190—210 °C (decomp.).

Addition of methanol to the filtrate and slow evaporation under reduced pressure gave a white solid which was washed with methanol. Recrystallisation from methylene chloride–methanol gave white *crystals* of (8) (0.19 g, 33%), m.p. 178—183 °C (decomp.), ν(C=O) at 1 732s cm^{-1}.

On concentrating the above filtrate another white solid was obtained. This was washed with diethyl ether and its i.r. spectrum indicated it to be a mixture mainly of $[Pt\{OC(CF_3)_2\}(PPh_3)_2]$ and another unidentified product. Recrystallisation from methylene chloride–diethyl ether yielded a white crystalline solid which was shown to be mainly $[Pt\{OC(CF_3)_2\}(PPh_3)_2]$ (0.03 g, 7%) by comparison of its i.r. spectrum with that of an authentic sample.[1]

(*b*) *With aqueous hydrochloric acid.* Hydrochloric acid (1.2 cm^3, 0.100 2 mol dm^{-3}, 0.115 mmol HCl) was added to a solution of (7) (0.12 g, 0.12 mmol) in methylene chloride (20 cm^3). The mixture was shaken for 3 d and the white solid which formed was filtered off. Addition of diethyl ether to the filtrate and concentration of the mixture gave another crop of the white solid which was shown to be *cis*-$[PtCl_2(PPh_3)_2]$ (0.03 g, 65%) by its m.p. and i.r. spectrum, m.p. 305—310 °C (lit.,[24] 310—312 °C).

The filtrates were evaporated to dryness and addition of diethyl ether to the residue gave an off-white solid. Recrystallisation from chloroform–diethyl ether gave white needles of (6; L = PPh_3) (0.04 g, 35%), m.p. 167—173 °C; ν(C=O) at 1 750s and 1 674s cm^{-1}.

(*c*) *With hydrogen chloride gas.* Passage of hydrogen chloride gas through a solution of (7) (0.1 g, 0.1 mmol) in methylene chloride (10 cm^3) gave *cis*-$[PtCl_2(PPh_3)_2]$ (0.06 g, 80%), m.p. 308—312 °C.

(*d*) *With trifluoroacetic acid.* Excess of trifluoroacetic acid (0.05 g, 0.4 mmol) was added to a solution of (7) (0.2 g, 0.2 mmol) in methylene chloride (10 cm^3). Diethyl ether was added to the colourless solution and evaporation under reduced pressure gave white crystals of $[Pt(O_2CCF_3)_2(PPh_3)_2]$ (0.13 g, 70%), m.p. 220—223 °C (lit.,[22] 230—235 °C).

Of $[Pt\{(int)_2\}(PPh_3)_2]$ (2). (*a*) *With hexafluorobut-2-yne.* Hexafluorobut-2-yne (*ca.* 1.5 cm^3) and (2) (0.44 g 0.42 mmol) in benzene (25 cm^3) were shaken at 60 °C for 4 h. The yellow-green solution was evaporated to dryness. The residue was dissolved in diethyl ether and the solution was filtered. Addition of methanol and evaporation to small bulk gave a white solid which was recrystallised from methylene chloride–methanol to give white *crystals* of $[Pt(C_4F_6)(PPh_3)_2]$ (0.26 g, 70%), m.p. 213 °C (lit.,[26] 215—216 °C).

(*b*) *With hexafluoropropan-2-one.* Hexafluoropropan-2-one (*ca.* 1.5 cm^3) and (2) (0.56 g, 0.54 mmol) in benzene (30 cm^3) were shaken at room temperature for 3 d. The red crystals which formed were filtered from the blue-green solution and were identified as indan-1,2,3-trione (0.04 g, 47%), m.p. 240—244 °C (lit.,[14] 241—243 °C).

The filtrate was evaporated to *ca.* 10 cm^3 and addition of diethyl ether gave a pale yellow solid contaminated with red crystals of indan-1,2,3-trione. The mixture was filtered off, washed with diethyl ether, and recrystallised from methylene chloride–diethyl ether. The yellow *crystals* (0.24 g, 43%) were shown to be identical to (7), m.p. 190—210 °C (decomp.); ν(C=O) at 1 760vw, 1 733m, and 1 705s cm^{-1}.

The filtrate and diethyl ether washings were evaporated to *ca.* 2 cm^3 and addition of diethyl ether gave a pale yellow solid which was filtered off and washed with diethyl ether. Recrystallisation from methylene chloride–diethyl ether gave white *crystals* having a stoicheiometry corresponding to a 1 : 1 adduct between (4) and hexafluoropropan-2-one (0.06 g, 11%), m.p. 270—290 °C (decomp.) (Found: C, 54.2; H, 3.2; F, 10.0. $C_{48}H_{34}F_6O_4P_2Pt$ requires C, 55.2; H, 3.3; F, 10.9%); ν(C=O) at 1 728s cm^{-1}. Infrared spectrum: 1 728s, 1 608w, 1 600vw, 1 587vw, 1 572vw, 1 483m, 1 439s, 1 341vw, 1 312m, 1 292m, 1 278s, 1 223s, 1 212s, 1 191vw, 1 180m, 1 159m, 1 150m, 1 121s, 1 104m, 1 096m, 1 081m, 1 042s, 1 009m, 972s, 943m, 902m, 879m, 804vw, 778m, 763m, 752m, 727s, 714m, 700s, 623w, 562m, 549m, 538m, 526m, 518m, and 504m cm^{-1}.

The solvents from the filtrate and diethyl ether washings were evaporated to dryness and diethyl ether was added to the residue. A white solid slowly precipitated and two additional crops were obtained in this way. The white precipitates were recrystallised from methylene chloride–methanol to give white *crystals* of (8) (0.22 g, 34%) identified by its i.r. spectrum and m.p. 174—184 °C (decomp.) (gas evolved); ν(C=O) at 1 731s cm^{-1}.

X-*Ray Crystallographic Study*.—Recrystallisation from a variety of solvents did not yield good-quality crystals of the adduct (2). However, an irregular bright yellow crystal of dimensions *ca.* 0.057 × 0.027 × 0.025 cm was isolated from benzene–diethyl ether solution and used for the measurement of cell constants and intensities. Unit-cell dimensions were obtained from precession photographs using Mo-K_α radiation.

Crystal data. $C_{54}H_{38}O_6P_2Pt$, $M = 1\,039.9$, Monoclinic, $a = 22.08(2)$, $b = 14.47(1)$, $c = 30.72(2)$ Å, $\beta = 95.1(5)°$, $U = 9\,438$ Å^3, $D_c = 1.46$ g cm^{-3}, $Z = 8$, μ(Mo-K_α) = 32.4 cm^{-1}, space group *Cc*.

Intensities were measured in 14 layers, $h0l$ through $h13l$, on a Stoe Weissenberg diffractometer using monochromatic Mo-K_α radiation ($\lambda = 0.710\,7$ Å) and an ω-scan technique. The 2 382 reflections with significant intensity $[I > 2\sigma(I)]$ and $0.1 < (\sin\theta)\lambda < 0.7$ Å^{-1} were corrected for Lorentz, polarisation, and absorption [27] effects.

Scattering factors for the atoms were taken from ref. 28. The three-dimensional Patterson function indicated that both unique platinum atoms had y co-ordinates of *ca.* $\frac{1}{4}$ with the result that only 314 reflections with significant intensity break the pseudo-*F*-centring thus introduced. Nevertheless, the remaining non-hydrogen atoms could be distinguished and the two molecules resolved using

TABLE 3

Final atomic co-ordinates * with estimated standard deviations in parentheses

	Molecule 1			Molecule 2		
	x/a	y/b	z/c	x/a	y/b	z/c
Pt	0.281 3(1)	0.256 7(3)	0.260 8(1)	0.0	0.243 0(3)	0.0
P(1)	0.256 1(7)	0.138 1(11)	0.306 5(4)	0.064 1(9)	0.138 6(16)	−0.15 4(6)
P(2)	0.213 3(6)	0.366 1(11)	0.274 4(4)	0.032 4(8)	0.340 6(14)	−0.045 6(5)
C(1)	0.355(3)	0.208(5)	0.195(2)	−0.072(3)	0.199(6)	0.069(2)
C(2)	0.423(3)	0.166(6)	0.183(2)	−0.135(3)	0.145(6)	0.060(2)
C(3)	0.303(3)	0.151(6)	0.163(2)	−0.051(3)	0.175(6)	0.125(2)
C(4)	0.350(3)	0.327(6)	0.192(2)	−0.073(3)	0.296(5)	0.066(3)
C(5)	0.408(3)	0.361(6)	0.201(2)	−0.133(3)	0.333(6)	0.080(2)
C(6)	0.339(3)	0.348(6)	0.146(2)	−0.027(3)	0.346(6)	0.093(2)
O(1)	0.361(2)	0.184(3)	0.244(1)	−0.030(2)	0.151(3)	0.044(1)
O(2)	0.478(2)	0.162(3)	0.204(1)	−0.143(2)	0.100(3)	0.024(1)
O(3)	0.256(2)	0.152(3)	0.173(1)	−0.003(2)	0.155(3)	0.138(1)
O(4)	0.303(2)	0.344(3)	0.212(1)	−0.065(2)	0.317(3)	0.023(1)
O(5)	0.441(2)	0.367(3)	0.238(1)	−0.177(2)	0.324(3)	0.064(1)
O(6)	0.291(2)	0.309(3)	0.118(1)	0.021(2)	0.381(3)	0.085(1)
C(11)	0.410	0.142	0.137	−0.148	0.114	0.105
C(12)	0.347	0.135	0.126	−0.101	0.132	0.139
C(21)	0.442	0.394	0.164	−0.115	0.376	0.126
C(22)	0.400	0.378	0.127	−0.051	0.375	0.133

* Co-ordinates for the remaining phenyl carbon atoms have been deposited with the structure-factor table.

successive Fourier syntheses. Hydrogen atoms were not included in the structure-factor calculations and in view of the limited and poor-quality data the phenyl groups were given a fixed geometry (*viz.* planar with C–C 1.395 Å and C–C–C 120°) and only the position and orientation of the groups was varied. Carbon and oxygen atoms were given temperature factors B of 5.0 and 3.0 Å^2 respectively. These light-atom temperature factors were not refined.

Limitations on computer storage necessitated the refinement of the parameters for the two independent molecules in alternate least-squares cycles. The above mentioned pseudo-centring together with the use of a block-diagonal approximation probably means that the e.s.d.s from the least-squares refinement are underestimated. Refinement converged with R 0.078 for the 2 382 reflections. The function minimised was $\Sigma w\Delta^2$ where the weighting scheme given by $w = (656.0 - 8.1|F_o| + 0.04|F_o|^2)^{-1}$ was introduced in order that $w\Delta^2$ be approximately independent of $|F_o|$. The maximum shift in the final cycle was 0.3σ. Final atomic parameters are listed in Table 3. A list of observed and calculated structure factors and thermal parameters is available as Supplementary Publication No. SUP 22371 (16 pp.).*

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