Reactions of Bis(cyclo-octa-1,5-diene)platinum with Quinones; Crystal Structure of $[Pt\{\eta^4-C_6H_2O_2(Bu^t_2-2,6)\}(\eta^4-C_8H_{12})]$†

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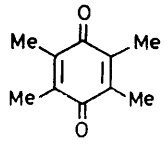
Bis(cyclo-octa-1,5-diene)platinum reacts with benzo-1,4-quinone, 2,3,5,6-tetramethyl-, 2,6-dimethyl-, 2,6-di-t-butyl-, 2,5-dimethyl-, and 2,5-diphenyl-benzo-1,4-quinone to give complexes [Pt(quinone)(cod)] (cod = cyclo-octa-1,5-diene). Carbon-13 n.m.r. studies on these compounds failed to establish whether the quinone ligands were η^4 or η^2 bonded to platinum, and so *X*-ray diffraction studies have been carried out on the 2,3,5,6-tetramethyl- and 2,6-di-t-butylbenzo-1,4-quinone derivatives. Although crystals of the former exhibited some disorder, preventing complete solution of the structure, it could be deduced that the bonding mode was η^4. Crystals of the 2,6-di-t-butylbenzo-1,4-quinone complex were monoclinic, space group $P2_1/n$, $Z = 4$, in a unit cell with lattice parameters $a = 10.652(5)$, $b = 12.541(4)$, $c = 14.971(4)$ Å, and $\beta = 93.17(3)°$. The structure has been refined to R 0.025 (R' 0.027) for 4 258 independent reflections collected at 200 K to $2.9 \leqslant 2\theta \leqslant 60°$ (Mo-K_α *X*-radiation). The results establish that the 2,6-di-t-butylbenzo-1,4-quinone ligand is attached to the metal by both C=C bonds so that with the cod group the platinum atom is in a distorted tetrahedral environment (dihedral angle between the pairs of double bonds of the ligands is 69°). In the complexes [Pt(quinone)(cod)] (quinone = 2-methylbenzo-1,4-quinone or naphtho-1,4-quinone), ^{13}C n.m.r. studies reveal an η^2-quinone attachment. Reactions between $[Pt(cod)_2]$ and 2,3-dichloronaphtho-1,4-quinone and phenanthrene-9,10-quinone are also described.

THE development of a practical synthesis of bis(cyclo-octa-1,5-diene)platinum[1] has enabled this compound to be used as a precursor in many syntheses. With buta-1,3-diene[2] or methyl vinyl ketone,[3] the complex $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) affords platinum-containing five-membered ring structures, resulting from cyclisation of two molecules of the reactants on the metal. Organoplatinum cyclic compounds are also formed in reactions of $[Pt(cod)_2]$ with the electrophilic species hexafluoroacetone[4] and tetrafluoroethylene.[5]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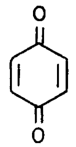
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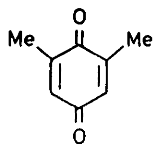
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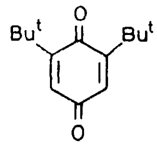
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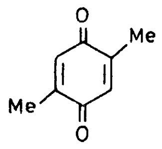
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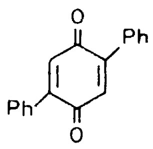
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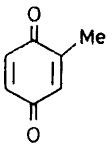
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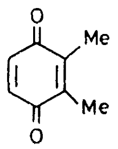
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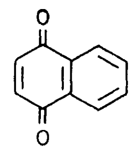
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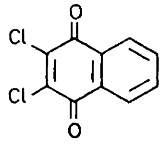
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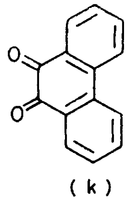
(k)

In this paper we report on the nature of the complexes formed by reacting $[Pt(cod)_2]$ with the quinones (a)—(k). The object of this study was two-fold. Firstly, the benzo-1,4-quinones (a)—(i) are relatively strong π-acceptor ligands, and we wished to compare their complexing ability with those of maleic anhydride, dimethyl- or diethyl-maleate and -fumarate, and 2-methyl-2,4,6-tris(trifluoromethyl)pyran. These reagents have been shown to form stable trigonal 16-electron platinum complexes, *viz.* [Pt{CH=CHC(O)OC(O)}(cod)], [Pt(RCH=CHR)(cod)] (R = CO_2Me or CO_2Et),[6] and $[Pt\{CH=C(CF_3)CH=C(CF_3)OC(CF_3)Me\}(cod)]$,[7] in reactions with $[Pt(cod)_2]$. Secondly, we wished to make comparisons with $[Ni(cod)_2]$ which has long been known to form compounds of the type [Ni(benzo-1,4-quinone)(cod)].[8,9] From an *X*-ray diffraction study of the tetramethylbenzo-1,4-quinonenickel complex the ligand (a) is known to be η^4 co-ordinated to the metal.[10] It was of interest to establish whether the quinones in complexes [Pt(benzo-1,4-quinone)(cod)] bond to platinum *via* an η^4 or an η^2 mode, and whether the type of bonding depends on the nature and the positions of the substituents on the rings. Prior to our work, two $[Pt(quinone)(PPh_3)_2]$ complexes had been prepared by reacting the quinones (b) and (i) with $[Pt(PPh_3)_3]$ in diethyl ether or benzene.[11] From ^1H n.m.r. studies it was concluded that the product from benzo-1,4-quinone was η^4 bonded while that from naphthoquinone was probably η^2 co-ordinated to the CH=CH group. The possibility of dynamic behaviour was not considered.

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† (1—2; 5—6-η-Cyclo-octa-1,5-diene)(2—3; 5—6-η-2,6-di-t-butylbenzo-1,4-quinone)platinum.

RESULTS AND DISCUSSION

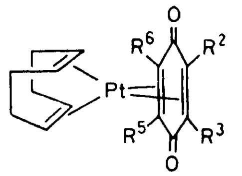
Bis(cyclo-octa-1,5-diene)platinum, suspended in diethyl ether, reacts with the quinones (a) to (i) to afford complexes of composition [Pt(quinone)(cod)] in good yield (Table 1). Except for the products from benzo-1,4-quinone, and from 2-methyl- and 2,3-dimethylbenzo-1,4-quinone, these yellow compounds are generally stable in air as solids, or in toluene solutions. Both (1b) and (1g) were prepared at —30 to —50 °C and crystallised below room temperature. Complex (1b) could not be obtained analytically pure, and compound (1h) decomposes so readily it could not be analysed. Although soluble in chloroform and in dichloromethane, several of the complexes are slowly decomposed by these particular solvents. However, with the majority, the rate of decomposition is not sufficiently rapid to inhibit n.m.r. studies, the data from which are summarised in Table 2. In their i.r. spectra the complexes all show (Table 1) C=O absorptions shifted to lower frequencies than those in the free quinone.[11]

TABLE 1

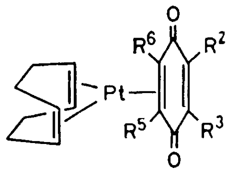
Analytical [a] and physical data for the complexes (1a)—(1k)

Compound [b]	M.p.[c] (θ_c/°C)	Yield (%)	ν(C=O) [d] (cm^{-1})	Analysis (%) C	H
(1a)	158—162	90	1 566vs	46.3 (46.2)	5.1 (5.2)
(1b)	150—154	90	1 621s, 1 604vs	37.5 (40.8)	4.2 (3.9)
(1c)	150—156	70	1 579vs	43.7 (43.7)	4.6 (4.7)
(1d)	160—165	60	1 631vs, 1 606vs	50.0 (50.4)	6.5 (6.2)
(1e)	157—160	75	1 626vs, 1 608vs	43.4 (43.7)	4.8 (4.7)
(1f) [e]	179—184	95	1 613vs, 1 592vs	55.2 (55.4)	4.4 (4.3)
(1g)	>142	85	1 626s, 1 603 (sh)	42.2 (42.4)	4.5 (4.3)
(1h)	152—156	90	1 615 (sh), 1 599vs		
(1i)	150—152	87	1 644vs, 1 592 (sh)	46.6 (46.8)	4.0 (3.9)
(1j)	222—226	95	1 668vs, 1 643s	40.7 (40.8)	3.0 (3.0)
(1k) [f]	202—210	90	1 612m, 1 589s	51.7 (51.7)	4.0 (3.9)

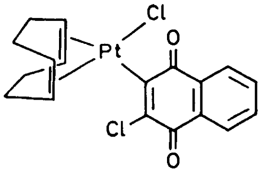
[a] Calculated values are given in parentheses. [b] All compounds are yellow unless otherwise stated. [c] With decomposition *in vacuo*. [d] In Nujol. [e] Orange. [f] Red.



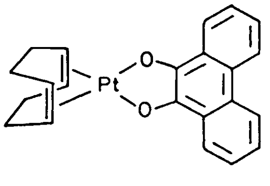
	R2	R3	R5	R6
(1a)	Me	Me	Me	Me
(1b)	H	H	H	H
(1c)	Me	H	H	Me
(1d)	Bu^t	H	H	Bu^t
(1e)	Me	H	Me	H
(1f)	Ph	H	Ph	H



	R2	R3	R5	R6
(1g)	Me	H	H	H
(1h)	Me	Me	H	H
(1i)	CH	CH	H	H



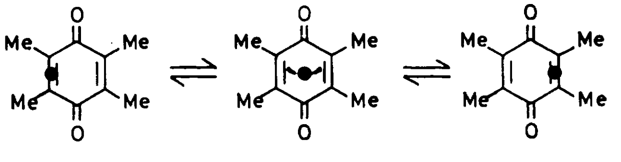
(1j)



(1k)

Between room temperature and —90 °C the ^{13}C n.m.r. spectrum of complex (1a) showed no change, one resonance being observed for the ring carbon atoms of the quinone and one signal for the CH groups of the cod ligand, both absorptions having ^{195}Pt satellites. The data imply either a rigid structure with the 2,3,5,6-tetramethylbenzo-1,4-quinone η^4 bonded to the platinum or a low-energy degenerate rearrangement of a ground-state η^2 bound ligand, as indicated in the Scheme, with this dynamic behaviour being rapid even at —90 °C.

Although very unstable in solution, it was possible to record the ^{13}C n.m.r. spectrum of (1b) at —60 and at —90 °C. At the lower temperature there are two resonances, assignable to *C*H groups of the benzo-1,4-quinone and the cod ligands, respectively. Both peaks, with ^{195}Pt satellites (Table 2), are broad, and the broadening is enhanced at —60 °C but with loss of ^{195}Pt–^{13}C satellites. Thus no firm structural inferences can be made from the spectrum.



● = Pt(cod)

SCHEME

The ^{13}C n.m.r. spectra of the symmetrically disubstituted quinone complexes (1c)—(1f) do not change between room temperature and —90 °C and again the results could be interpreted as for (1a), *i.e.* a static structure with η^4 quinone–metal bonding, or rapid exchange between η^2 structures. Thus the spectrum of (1e) displayed two resonances for the *C*H(cod) groups and one signal only for the *C*H and *C*Me groups of the quinone ligand. This pattern can be explained by either 2,5-dimethylbenzo-1,4-quinone acting as an η^4-diene-type ligand or by rapid exchange between two degenerate η^2-quinone bonded structures which averages the signals

TABLE 2

Hydrogen-1 and carbon-13 n.m.r. data [a] for the complexes [Pt(1,4-quinone)(cod)] [b]

Complex	Hydrogen-1 [c]	Carbon-13 [d] (δ)
(1a) $[Pt(\eta^4\text{-}C_6Me_4O_2)(cod)]$ [e]	5.77 [s, 4 H, CH(cod), *J*(PtH) 78], 7.73 [s, 8 H, CH_2(cod)], 7.83 [s, 12 H, Me, *J*(PtC) 16]	159 [C=O, *J*(PtC) 29], 109 [CMe, *J*(PtC) 32], 84 [CH(cod), *J*(PtC) 192], 32 (CH_2), 13 (Me)
(1b) $[Pt(\eta^4\text{-}C_6H_4O_2)(cod)]$ [f]	4.68 (m br, 8 H, CH), 7.72 (m, 8 H, CH_2)	177 (br, C=O), 98 [br, CH(Q), *J*(PtC) 92], 91 [br, CH(cod), *J*(PtC) 143], 31 (CH_2)
(1c) $[Pt\{\eta^4\text{-}C_6H_2O_2(Me_2\text{-}2,6)\}(cod)]$ [g]	4.08 [s, 2 H, CH(Q), *J*(PtH) 10], 4.86 [s, 2 H, CH(cod), *J*(PtH) 76], 5.68 [s, 2 H, CH(cod), *J*(PtH) 84], 7.64 (m, 8 H, CH_2), 7.88 [s, 6 H, Me, *J*(PtH) 20]	164 (C=O), 162 [C=O, *J*(PtC) 24], 112 [CMe, *J*(PtC) 46], 99 [CH(Q), *J*(PtC) 47], 86 [CH(cod), *J*(PtC) 188], 83 [CH(cod), *J*(PtC) 171], 31 (CH_2), 16 (Me)
(1d) $[Pt\{\eta^4\text{-}C_6H_2O_2(Bu^t{}_2\text{-}2,6)\}(cod)]$ [h]	4.26 [s, 2 H, CH(Q), *J*(PtH) 14], 4.86 [s, 2 H, CH(cod), *J*(PtH) 81], 5.01 [s, 2 H, CH(cod), *J*(PtH) 72], 7.63 (m br, 8 H, CH_2), 8.67 (s, 18 H, Bu^t)	172 [C=O, *J*(PtC) 60], 161 [C=O, *J*(PtC) 18], 121 [CBu^t, *J*(PtC) 52], 94 [CH(Q), *J*(PtC) 37], 85.4 [CH(cod), *J*(PtC) 160], 76 [CH(cod), *J*(PtC) 209], 35 (CMe_3), 33, 31 (CH_2), 29 (Me)
(1e) $[Pt\{\eta^4\text{-}C_6H_2O_2(Me_2\text{-}2,5)\}(cod)]$ [f]	3.94 [s, 2 H, CH(q), *J*(PtH) 12], 5.00—5.62 [' AB ' system, 4 H, CH(cod), *J*(AB) 9, *J*(PtA) 85, *J*(PtB) 81], 7.65 (m br, 8 H, $CH)_2$, 7.94 [s, 6 H, Me, *J*(PtH) 18]	162 [C=O, *J*(PtC) 32], 112 [CMe, *J*(PtC) 40], 98 [CH(Q), *J*(PtC) 50], 87 [CH(cod), *J*(PtC) 185], 83 [CH(cod), *J*(PtC) 177], 31 (CH_2), 15 (Me)
(1f) $[Pt\{\eta^4\text{-}C_6H_2O_2(Ph_2\text{-}2,5)\}(cod)]$	2.21—2.77 (m, 10 H, Ph), 3.90 [s, 2 H, CH(Q), *J*(PtH) 12], 4.73 [m, 2 H, CH(cod), *J*(PtH) 78], 5.11 [m, 2 H, CH(cod), *J*(PtH) 72], 7.43—8.20 (m, 8 H, CH_2)	170 [C=O, *J*(PtC) 46], 134, 129, 128.7, 128.4 (Ph), 113 [CPh, *J*(PtC) 64], 98 [CH(Q), *J*(PtC) 92], 92 [CH(cod), *J*(PtC) 157], 86 [CH(cod), *J*(PtC) 159], 32, 30 (CH_2)
(1g) $[Pt\{\eta^2\text{-}C_6H_3O_2(Me\text{-}2)\}(cod)]$ [i]	3.58 [s, 1 H, CH(Q)], 4.2—5.5 (m br, 6 H, CH), 7.70 (m, 8 H, CH_2), 8.04 (s, 3 H, Me)	183 [C=O, *J*(PtC) 52], 144 (CMe), 131 [CH(Q)], 97 [CH(cod), *J*(PtC) 127], 95 [CH(cod), *J*(PtC) 125], 92 [2 C, CH(cod), *J*(PtC) 125], 63.2 [CH(Q), *J*(PtC) 250], 63 [CH(Q), *J*(PtC) 241], 30.8 (CH_2), 30.5 (CH_2), 17 (Me)
(1h) $[Pt\{\eta^2\text{-}C_6H_2O_2(Me_2\text{-}2,3)\}(cod)]$ [j]	4.40 [s, 2 H, CH(Q), *J*(PtH) 19], 4.70 [d, 2 H, CH(cod), *J*(HH) *ca.* 8, *J*(PtH) 75], 5.50 [d, 2 H, CH(cod), *J*(HH) *ca.* 8, *J*(PtH) 78], 7.70 (m br, 8 H, CH_2), 7.79 (s, 6 H, Me)	
(1i) $[Pt(\eta^2\text{-}C_{10}H_6O_2)(cod)]$ [e]	1.88—2.52 [m, 4 H, CH(Q)], 4.63 [s, 2 H, CH(cod), *J*(PtH) 66], 4.95 [s, 2 H, CH (cod), *J*(PtH) 75], 5.69 [s, 2 H, CH(Q), *J*(PtH) 65], 7.6—7.8 (m br, 8 H, CH_2)	186 [C=O, *J*(PtC) 56], 132, 125 [CH(Q)], 112 [C, *J*(PtC) 55], 100 [CH(cod), *J*(PtC) 121], 95 [CH(cod), *J*(PtC) 101], 57 [CH(Q), *J*(PtC) 284], 30 (CH_2)

[a] Measured in $[^2H_1]$chloroform at room temperature unless otherwise stated. Coupling constants in Hz. [b] Q denotes quinone ligand in peak assignments. [c] Chemical shifts in τ. [d] Hydrogen-1 decoupled, chemical shifts in p.p.m. to high frequency of $SiMe_4$. [e] Carbon-13 spectrum measured at −90 °C in $[^2H_2]$dichloromethane. [f] Hydrogen-1 spectrum measured at −60 °C, ^{13}C spectrum measured at −90 °C. [g] Hydrogen-1 spectrum measured at −90 °C. [h] Carbon-13 spectrum measured at −90 °C in $[^2H_1]$chloroform–CH_2Cl_2 (4 : 1 mixture); ^1H spectrum measured at −90 °C in $[^2H_1]$chloroform. [i] Measured at −50 °C. [j] Hydrogen-1 spectrum measured at —60 °C. ^{13}C spectrum not measured due to decomposition.

of the two *C*H and the two *C*Me environments which would be present in the static structure. Similarly, the spectrum of (1d) (Table 2) shows, for the cod ligand, two resonances for the *C*H groups, and for the quinone one signal for the *C*H groups and one signal for the CBu^t groups.

It is highly probable that in the ground state all the quinones (a)—(f) bond to platinum in the complexes (1a)—(1f) by the same mode. Since the n.m.r. data could not provide an unambiguous structural assignment recourse was made to *X*-ray diffraction studies.

Crystals of (1a) exhibited disorder, but from the data obtained (see below) the co-ordination of the quinone to the metal atom is strongly suggested to be η^4, as found in the nickel analogue.[10] Fortunately, crystals of the related compound (1d) proved to be satisfactory for *X*-ray studies, and the results obtained are summarised in Tables 3—5. The molecular structure is shown in Figure 1 together with the atomic numbering scheme.

It is seen that the ligand (d) is co-ordinated to the platinum *via* both double bonds which are elongated [mean 1.399(5) Å] with respect to those [1.322(8) Å] in free benzo-1,4-quinone,[12] but comparable with those for the duroquinone ligand in the nickel complex [1.40(1) Å].[10] The cod ligand adopts the usual tub conformation, but is twisted, as found in several other cyclo-octa-1,5-diene complexes.[10,13] The dihedral angle between the planes defined by the midpoints of C(2)–C(3) and C(5)–C(6) and the platinum atom and the midpoints of C(7)–C(14) and C(10)–C(11) and the metal atom is 69°, hence the platinum atom is in a very distorted tetrahedral environment. By comparison this dihedral angle is 90° in $[Ni(\eta^4\text{-}C_6Me_4O_2)(cod)]$.[10]

The average distance [2.182(4) Å] between the platinum atom and the ligated carbon atoms of the cod ligand is shorter than those in some previously studied compounds,[13] but compares well with the mean distance (2.21 Å) in $[Pt(cod)_2]$.[14] In the latter compound the

TABLE 3

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for complex (1d)

Atom	x	y	z
Pt	0.081 14(1)	0.128 48(1)	0 315 41(1)
C(1)	0.040 7(3)	−0.061 7(3)	0.267 2(2)
O(1)	0.068 1(3)	−0.150 1(2)	0.299 7(2)
C(2)	−0.067 7(3)	0.000 7(3)	0.292 3(2)
C(3)	−0.119 6(3)	0.087 5(3)	0.245 2(2)
C(03)	−0.248 5(4)	0.132 4(3)	0.265 1(3)
C(31)	−0.346 1(4)	0.084 3(5)	0.196 9(4)
C(32)	0.284 4(5)	0.103 8(6)	0.359 4(5)
C(33)	−0.250 2(5)	0.253 7(4)	0.256 0(4)
C(4)	−0.057 6(3)	0.119 5(3)	0.162 8(2)
O(4)	−0.110 6(3)	0.171 9(2)	0.102 3(2)
C(5)	0.078 9(3)	0.091 0(3)	0.163 9(2)
C(05)	0.162 1(4)	0.144 6(3)	0.094 9(2)
C(51)	0.302 4(4)	0.124 6(4)	0.120 7(3)
C(52)	0.129 4(5)	0.094 1(4)	0.003 1(3)
C(53)	0.140 0(5)	0.266 2(3)	0.088 8(3)
C(6)	0.121 4(3)	−0.000 5(3)	0.210 1(2)
C(7)	0.088 8(4)	0.122 3(3)	0.462 0(2)
C(8)	0.091 7(5)	0.230 9(3)	0.505 8(3)
C(9)	0.051 7(5)	0.319 4(3)	0.439 3(3)
C(10)	0.095 1(4)	0.298 9(3)	0.346 2(3)
C(11)	0.213 0(4)	0.258 6(3)	0.328 5(2)
C(12)	0.321 2(4)	0.236 8(4)	0.396 7(3)
C(13)	0.323 8(5)	0.122 5(4)	0.432 4(4)
C(14)	0.194 9(4)	0.070 5(3)	0.431 9(2)

TABLE 4

Important internuclear separations (Å) and angles (°) for the complex [Pt{$C_6H_2O_2(Bu^t_2$-2,6)}(cod)] (1d)

(*a*) Distances

Pt–C(1)	2.521(3)	Pt–C(2)	2.268(3)
Pt–C(3)	2.386(3)	Pt–C(4)	2.654(3)
Pt–C(5)	2.316(3)	Pt–C(6)	2.315(3)
Pt–C(7)	2.193(4)	Pt–C(10)	2.189(4)
Pt–C(11)	2.154(4)	Pt–C(14)	2.192(4)
C(1)–O(1)	1.239(4)	C(4)–O(4)	1.230(4)
C(1)–C(2)	1.461(5)	C(2)–C(3)	1.395(5)
C(2)–H(2)	0.96(4)	C(6)–H(6)	0.96(4)
C(3)–C(4)	1.487(5)	C(4)–C(5)	1.496(5)
C(5)–C(6)	1.403(5)	C(1)–C(6)	1.462(5)
C(3)–C(03)	1.528(5)	C(5)–C(05)	1.549(5)
C(03)–C(31)	1.539(7)	C(05)–C(51)	1.544(6)
C(03)–C(32)	1.528(7)	C(05)–C(52)	1.536(6)
C(03)–C(33)	1.527(6)	C(05)–C(53)	1.545(6)
C(7)–C(14)	1.400(6)	C(10)–C(11)	1.393(6)

(*b*) Angles *

C(2)–Pt–C(3)	34.8(1)	C(5)–Pt–C(6)	35.3(1)
C(7)–Pt–C(14)	37.2(2)	C(10)–Pt–C(11)	37.4(2)
C(2,3)–Pt–C(5,6)	67.4	C(10,11)–Pt–C(7,14)	86.1
O(1)–C(1)–C(2)	123.4(3)	O(1)–C(1)–C(6)	124.4(3)
C(1)–C(2)–C(3)	125.8(3)	C(2)–C(3)–C(4)	116.6(3)
C(3)–C(4)–O(4)	123.2(3)	O(4)–C(4)–C(5)	122.8(3)
C(3)–C(4)–C(5)	113.8(3)	C(4)–C(5)–C(6)	119.2(3)
C(5)–C(6)–C(1)	122.3(3)	C(6)–C(1)–C(2)	111.6(3)
C(5)–C(6)–H(6)	112(2)	C(1)–C(2)–H(2)	114(2)
C(1)–C(6)–H(6)	126(2)	C(3)–C(2)–H(2)	120(2)
C(2)–C(3)–C(03)	121.6(3)	C(03)–C(3)–C(4)	120.5(3)
C(4)–C(5)–C(05)	118.7(3)	C(05)–C(5)–C(6)	120.2(3)

* C(*n,m*) refers to midpoint of bond joining atoms C(*n*) and C(*m*).

angle of ' bite ' of the cod ligand is 85° and that in (1d) is essentially the same (86°). In (1d) the co-ordinated C=C bonds of the cod ligand [mean 1.396(6) Å] are characteristically increased from the value (1.341 Å) in free cyclo-octa-1,5-diene.[15]

The C=O distances [mean 1.234(4) Å] are essentially unaltered from those observed in the free ligands (a) (1.23 Å) [16] and (b) (1.22 Å).[12] The separations between the metal atom and C(1) or C(4) are 2.521(3) and 2.654(3) Å, respectively, and are too long to be considered bonding distances, and the difference between them reflects the deviation of the ligand from a symmetrical η^4 co-ordination.

TABLE 5

Molecular planes for complex (1d) represented by $px + qy + rz = s$, where x, y, and z are the atomic fractional co-ordinates, and deviations (Å) from the planes are in square brackets

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

$$2.484x + 10.814y + 6.527z = 2.241$$

[C(3) 0.009, C(4) −0.030, C(5) 0.009, O(4) 0.012]

Plane (ii): C(2), C(1), O(1), C(6)

$$4.983x + 5.012y + 11.397z = 2.984$$

[C(1) −0.045, C(2) 0.013, C(6) 0.014, O(1) 0.018]

Plane (iii): C(2), C(3), C(5), C(6)

$$4.207x + 7.509y + 10.089z = 2.648$$

[C(2) 0.021, C(3) −0.020, C(5) 0.020, C(6) −0.021, C(03) −0.024, C(05) 0.077, Pt 1.84]

Plane (iv): * Pt, C(5,6), C(2,3)

$$-3.076x + 10.293y - 7.129z = -1.176$$

Plane (v): Pt, C(10,11), C(7,14)

$$9.583x - 3.866y - 5.370z = -1.412$$

Dihedral angles (°)	Plane	(i)	(ii)	(iv)
	(iii)	13.3	22.8	88.1
	(v)			111.1

* C(*n,m*) indicates the midpoint of the line joining atoms C(*n*) and C(*m*).

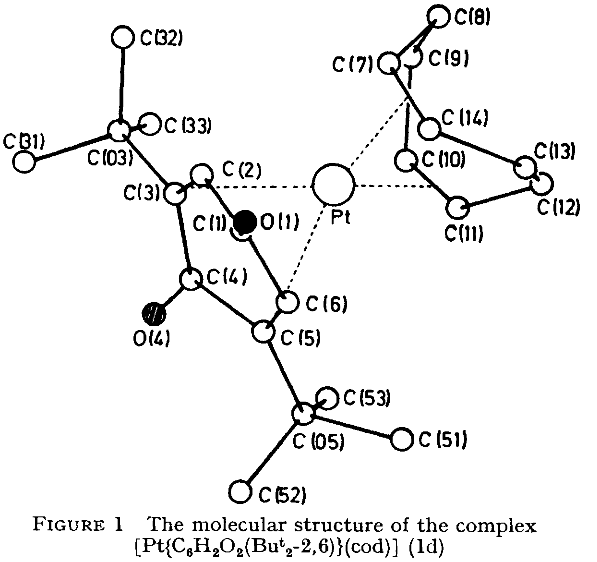
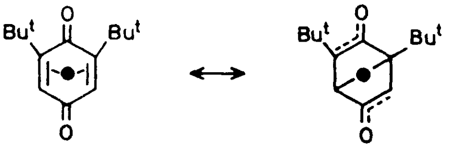


FIGURE 1 The molecular structure of the complex [Pt{$C_6H_2O_2(Bu^t_2$-2,6)}(cod)] (1d)

The C=O groups are bent away from the metal atom as shown by the angles of 13.3 and 22.8° between the plane defined by C(2), C(3), C(5), and C(6) and those defined by C(3), C(4), O(4), C(5), and C(2), C(1), O(1), and C(6), respectively. These angles are substantially larger than the comparable angle (6°) in [Ni(η^4-$C_6Me_4O_2$)(cod)],[10] and differ from each other due to the influence of the Bu^t groups attached to C(3) and C(5). Whereas in the nickel structure the methyl substituents are bent slightly towards the metal atom, in (1d) one of the Bu^t groups [C(05)] bends slightly towards the platinum atom while the other [C(03)] bends away (Table 5).

One might predict for symmetrical η^4 bonding of the ligand (d), C(3) and C(5) would be equivalently related to the platinum atom, but further away than the C(2), C(6) pair due to the steric effect of the Bu^t groups. However, C(5) and C(6) are essentially equidistant and C(2) is closer to the metal than C(3) by more than 0.1 Å (*ca.* 30 σ). To account for this, and the 21° distortion from a tetrahedral structure, discussed above, we suggest that the bonding for a particular molecule in the crystal is not entirely diene-like for Pt^0 as in (i) but involves a slight degree of platinum–carbon σ bonding for Pt^{II} as in the resonance hybrid (ii).



(i) (ii)

● = Pt(cod)

Although it is likely that the complexes formed by the other symmetrically substituted quinones (b), (c), (e), and (f) also have structures in which the ligands are bonded to the metal *via* both double bonds, the ^{13}C n.m.r. spectrum of (1g) at −50 °C shows that in this complex the quinone (g) is rigidly η^2 co-ordinated to the platinum *via* the CH=CH group. Thus the peaks due to the carbon atoms of the MeC=CH group at δ 131 and 144 p.p.m. are little changed in chemical shift from those observed (133 and 146 p.p.m.) in the free quinone. Moreover, these ligand resonances show no $^{195}Pt-^{13}C$ coupling. However, two signals at 63.2 and 63.0 p.p.m. can be assigned to the quinone's η^2 metal-bonded *C*H=*C*H group, shifted *ca.* 80 p.p.m. upfield from those in the free ligand, and with strong $^{195}Pt-^{13}C$ coupling (*ca.* 250 Hz). An asymmetric static structure in which the platinum is η^2 bonded to the CH=CH group of (g) might be expected to afford four environments for the cod ligand CH groups. However, two of these sites would be distinctly different from each other and from the other two, while the latter pair could give rise to coincident peaks because they are more remote from the CMe group. We propose that this accounts for the appearance of three CH(cod) signals (Table 2). Moreover, if rapid rotation occurred about the platinum η^2-bonded CH=CH (quinone) axis, as in platinum–olefin complexes,[17] the CH(cod) resonances should occur as two peaks. Since three are observed this process does not occur in this compound at −50 °C. Unfortunately the instability of (1g) prevented measurements at higher temperatures so that this type of dynamic behaviour could not be tested.

Complex (1h) was the most unstable in solution of all those studied, and its ^{13}C spectrum could not be measured. At −60 °C the ^1H spectrum shows two C*H*(cod) resonances [*J*(HH) *ca.* 8, *J*(PtH) *ca.* 75 Hz], as expected for either an η^2 or an η^4 co-ordinated ligand (h). However, a dynamic process occurs, since on warming to room temperature these signals merged, but decomposition prevents any analysis as to whether a dissociative or non-dissociative mechanism is involved.

Naphtho-1,4-quinone (i) would be most unlikely to act as a bidentate ligand to platinum in compound (1i), since by doing so the aromatic ring would be destabilized. Moreover, we found that 9,10-anthraquinone did not react with $[Pt(cod)_2]$. Not surprisingly, therefore, the ^{13}C spectrum (Table 2) of (i) is in accord with the rigid structure with the CH=CH group of (i) η^2 bonded to the platinum. The resonance for this group (δ 57 p.p.m.) is shifted from 138.6 p.p.m. in the free ligand and shows strong $^{195}Pt-^{13}C$ coupling (284 Hz). In contrast the signal for the two bridgehead carbon nuclei is only shifted from 132 to 112 p.p.m. with $J(^{195}Pt-^{13}C)$ 55 Hz. In the ^1H spectrum the resonance for the C*H*=C*H* protons, seen at τ 3.0 in the free ligand, occurs at τ 5.69 [*J*(PtH) 65 Hz]. Both the ^1H and ^{13}C spectra show two CH(cod) signals, but rotation of the CH=CH entity about the bonding axis with the metal atom might occur at higher temperatures. However, measurements of spectra above 30 °C were not informative due to ligand dissociation, as evidenced by loss of ^{195}Pt coupling in both the ^1H and ^{13}C spectra.

Thus the evidence for an η^2 bonding of the ligands (g) and (i) in compounds (1g) and (1i), which do not contain a centre or mirror plane of symmetry is strong. Indeed, if dynamic behaviour occurred for (1g) of similar mechanism to that depicted in the Scheme it would involve two non-degenerate structures likely to differ significantly in energy. It is interesting to note that in the ^{13}C spectra of compounds (1g) and (1i) the $^{195}Pt-^{13}CH$ (quinone) couplings are 240—280 Hz, in contrast to the η^4 bonded structures where these couplings are much smaller at 37—92 Hz. The reverse holds for the $^{195}Pt-^{13}CH$(cod) couplings which are larger for (1c), (1d), (1e), and (1f) than for (1g) or (1i). A comparison of chemical-shift changes on co-ordination with platinum is also interesting.

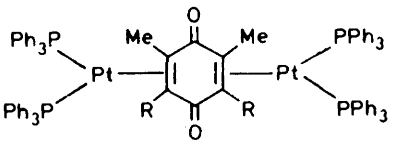
In the spectra of the ligands (c)—(f) the *C*H resonances occur at 130—134 p.p.m.. On forming the η^4 complexes (1c)—(1f) these signals are shifted by 27—34 p.p.m. upfield. In contrast, there is a larger upfield shift of 74 and 82 p.p.m., respectively, for the *C*H signals in going from the free ligands (g) and (i) to the η^2 bonded compounds (1g) and (1i).

The two quinones (j) and (k) react with $[Pt(cod)_2]$ to give different types of product to those afforded by (a)—(i). 2,3-Dichloronaphtho-1,4-quinone undergoes an oxidative-elimination reaction to give the platinum(II) complex (1j). This formulation is favoured by the appearance in the i.r. spectrum of a band at 320 cm^{-1} ascribed to a Pt–Cl stretch. In $[PtCl_2(cod)]$ metal–halogen stretches are observed at 316 and 338 cm^{-1} (ref. 18). Moreover, the ^{13}C spectrum shows (Experimental section) many more resonances for the quinone moiety than expected for a more symmetrical structure in which the ClC=CCl group of (j) is η^2 co-ordinated to the [Pt(cod)] group. The resonances of the CH group of the cod ligand appear as three signals 114.5, 114.2, and 89.1

p.p.m. The latter shows a higher $J(^{195}PtC)$ coupling (190 Hz) than do the other two resonances (*ca.* 51 Hz) and is therefore assigned to the CH=CH group *trans* to PtCl. The relatively strong *trans* effect of the σ-bonded quinone ligand compared with Cl could produce this effect. Moreover, the observation of two CH resonances for the cod CH=CH group *trans* to the Pt–C(quinone) linkage together with five signals for the *C* and *C*H atoms of the C_6H_4 ring suggests that there is restricted rotation about the Pt–C σ bond.

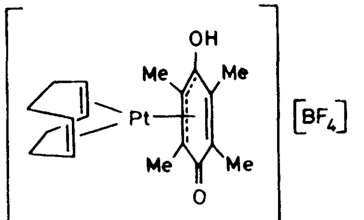
The air and solution stable product (1k) is very likely an oxygen-bonded platinum(II) complex formulated as shown. It differs from all the other compounds in being bright red, and having no strong bands in its i.r. spectrum at or just above 1 600 cm^{-1}. In this respect the properties are similar to those reported [11] for the product from $[Pt(PPh_3)_3]$ and phenanthrene-9,10-quinone. The ^{13}C and ^1H n.m.r. spectra each show only one resonance for the CH(cod) groups in accord with the proposed structure.

Several reactions of complex (1a) were investigated. With $P(OMe)_3$ and with $CNBu^t$, the cod and quinone ligands are displaced to give $[Pt\{P(OMe)_3\}_4]$ and $[Pt_3(CNBu^t)_6]$, respectively. With PPh_3, compound (1a) yields (2a), a complex first prepared [11] from $[Pt(PPh_3)_3]$ and 2,3,5,6-tetramethylbenzo-1,4-quinone. Compound (1c) reacts to give an analogous diplatinum compound (2c).



(2a) R = Me

(2c) R = H



(3a)

Protonation of (1a) with HBF_4 affords a pale yellow salt (3a) in which the C_6 ligand is probably η^3 bonded to the metal as reported [19] for the C_7H_7 group in the salt $[Pt(1\text{—}3\text{-}\eta\text{-}C_7H_7)(cod)][BF_4]$. However, the ^1H and ^{13}C n.m.r. spectra of (3a) measured at room temperature and at −90 °C indicated equivalent environments for the CH groups of the cod ligand and for the carbon atoms and the methyl groups of the protonated ligand. This spectrum can be understood as arising through dynamic behaviour, involving permutation of the η^3-bonding system among the five sp^2 carbon atoms of the six-membered ring, accompanied by rapid exchange of the proton between oxygen sites. Indeed, in the ^1H spectrum at room temperature the resonance due to the hydroxy-group (τ 2.30) was very broad, and the signal was not observable at −90 °C.

EXPERIMENTAL

Hydrogen-1 and ^{13}C n.m.r. spectra were recorded on JEOL PS- and PFT-100 spectrometers at 100 and 25.15 MHz respectively. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Experiments were carried out in Schlenk tubes under a dry, oxygen-free, nitrogen atmosphere using solvents which were dried and distilled under nitrogen prior to use. Bis(cyclo-octa-1,5-diene)-platinum was prepared as described elsewhere.[20] The various quinones were obtained commercially or were prepared by oxidising the corresponding phenol using Fremy's salt.[21,22] Light petroleum refers to that fraction of b.p. 40—60 °C.

During the course of the work, the ^{13}C n.m.r spectra of the quinones (a)—(k) were recorded. Data are as follows δ (p.p.m.) in $[^2H_1]$chloroform: (a) 187.0 (C=O), 140.3 (*C*Me), 12.3 (Me); (b) 187.1 (C=O), 136.5 (*C*H); (c) 187.8, 187.2 (C=O), 145.4 (*C*Me), 132.9 (*C*H), 15.7 (Me); (d) 188.8, 187.6 (C=O), 157.6 (CBu^t), 130.1 (*C*H), 35.6 (CMe_3), 29.4 (Me); (e) 188 (C=O), 145.7 (*C*Me), 133.6 (*C*H), 15.5 (Me); (f) 186.3 (C=O), 145.6 (*C*Ph), 133.1 [C^1(Ph)], 132.4 (*C*H), 130.1, 129.3, 128.5 (Ph); (g) 187.5, 187.4 (C=O), 145.7 (*C*Me), 136.5, 136.4, 133.2 (*C*H), 15.7 (Me); (h) 187.3 (C=O), 140.9 (*C*Me), 136.0 (CH), 12.2 (Me); (i) 184.9 (C=O), 138.6 (*C*H), 133.8, 131.8, 126.3 (C_6H_4 ring); (j) 175.9 (C=O), 143.5 (*C*Cl), 134.6, 131.1, 127.8 (C_6H_4 ring); (k) 180.1 (C=O), 136.0, 135.7, 130.9, 130.4, 129.5, 123.9.

Synthesis of the Complexes [Pt(quinone)(cod)].—Most of the compounds were prepared similarly, and the following two syntheses are illustrative. Analytical data for the compounds are given in Table 1.

(*i*) 2,6-Di-t-butylbenzo-1,4-quinone (162 mg, 0.73 mmol) was added to a stirred suspension of $[Pt(cod)_2]$ (274 mg, 0.66 mmol) in diethyl ether (10 cm^3). The $[Pt(cod)_2]$ rapidly dissolved and within 5 min fine yellow crystals were deposited. The suspension was stirred for 45 min at room temperature, after which the precipitate was allowed to settle and the solvent removed with a syringe. The residue was washed with light petroleum (3 × 5 cm^3) and dried *in vacuo* for several hours to give yellow *crystals* of $[Pt\{C_6H_2O_2(Bu^t{}_2\text{-}2,6)\}(cod)]$ (1d).

(*ii*) 2,3,5,6-Tetramethylbenzo-1,4-quinone (164 mg, 1 mmol) in diethyl ether (15 cm^3) was treated with $[Pt(cod)_2]$ (411 mg, 1 mmol). After *ca.* 10 min the heavy deep yellow precipitate was washed with light petroleum (2 × 10 cm^3) and dried *in vacuo* giving yellow *crystals* of $[Pt(C_6Me_4O_2)(cod)]$ (1a).

Because of their high solubility in diethyl ether, in the synthesis of (1c) and (1e) the volume of diethyl ether was reduced to under 5 cm^3 *in vacuo* prior to removal of the remaining solvent with a syringe. Complexes (1f) and (1i) were recrystallised from toluene–hexane mixtures. Because of their low stability, complexes (1b)—(1h) were prepared between −30 and −50 °C, and the crystals washed with light petroleum at −30 °C.

*Reaction of Bis(cyclo-octa-*1,5*-diene)platinum with* 2,3*-Dichloronaphtho-*1,4*-quinone.*—The quinone (j) (118.5 mg, 0.5 mmol) was suspended in diethyl ether (15 cm^3) and treated with $[Pt(cod)_2]$ (206 mg, 0.5 mmol). A heavy greenish yellow precipitate formed within minutes. After 0.5 h the mother-liquor was removed (syringe) and the product washed with light petroleum (2 × 5 cm^3) and dried *in vacuo* to give *microcrystals* of the complex $[Pt(C_{10}H_4Cl_2O_2)(cod)]$ (1j) (240 mg, 90%). N.m.r.: ^{1}H, τ 1.81—2.35 (m, 4 H, CH), 4.10 [s, 2 H, CH(cod), J(PtC) 40], 5.01 [s, 2 H, CH(cod), J(PtH) 72 Hz], 7.03—7.9 (m, 8 H, CH_2). ^{13}C, δ 186.6, 176.6 (*C*=O), 161 (*C*Cl), 143 (*C*Pt), 133 (*C*H), 132.8, 131.4 (C), 126.9, 126.7 (*C*H), 114.5 [CH(cod), J(PtC) 52], 114.2 [CH(cod), J(PtC) 50], 89 [CH(cod), J(PtC) 190], 32 [CH_2, J(PtC) 21], 28.8 [CH_2, J(PtC) 18], 28.0 p.p.m. [CH_2, J(PtC) 15 Hz].

*Reaction of Bis(cyclo-octa-*1,5*-diene)platinum with Phenanthrene-*9,10*-quinone*.—This reactant (k) (104 mg, 0.5 mmol) was dissolved in diethyl ether (10 cm^3) and treated with $[Pt(cod)_2]$ (206 mg, 0.5 mmol) portion-wise. The brownish solution turned red depositing red crystals (30 min). The solvent was removed with a syringe and the precipitate washed (5 cm^3) with light petroleum to give red *crystals* of complex $[Pt(C_{14}H_8O_2)(cod)]$ (1k) (230 mg, 90%). N.m.r. spectra: ^{1}H, τ 1.38—2.67 (m, 8 H, aromatic), 4.44 [s, 4 H, CH(cod), J(PtH) 64 Hz], 7.26—7.93 (m, 8 H, CH_2); ^{13}C, δ (p.p.m.) 158.4, 149.9, 136.8, 125.7, 122.4, 120.2, 111.9, 87.7 [J(PtC) 176 Hz], and 29.9.

Reaction of Complex (1c) *with Triphenylphosphine*.—Compound (1c) (117 mg, 0.25 mmol) in diethyl ether (10 cm^3) was treated with PPh_3 (131 mg, 0.5 mmol). Solvent was removed *in vacuo* and the residue washed with light petroleum (2 × 10 cm^3) giving orange *microcrystals* of $[Pt_2\{\mu\text{-}C_6H_2O_2(Me_2\text{-}2,6)\}(PPh_3)_4]$ (2c) (155 mg, 80%), m.p. 160—164 °C (decomp.) (Found: C, 62.0; H, 4.6. Calc. for $C_{80}H_{68}O_2P_4Pt_2$: C, 61.0; H, 4.3%), $\nu_{max.}$ (C=O) 1 621vs and 1 605vs, ^{1}H n.m.r. ([$^{2}H_1$]chloroform), τ 2.84 (m, 60 H, Ph), 5.08 [s, 2 H, CH(Q), J(PH) 6, J(PtH) 24], and 8.48 [s, 6 H, Me, J(PtH) 28 Hz].

Protonation of Complex (1a).—Treatment of a suspension of (1a) (233 mg, 0.5 mmol) in diethyl ether (20 cm^3) with HBF_4 (0.75 mmol) gave after 1 h a pale yellow powder which was washed with diethyl ether and light petroleum to give $[Pt\{C_6Me_4O(OH)\}(cod)][BF_4]$ (3a) (250 mg, 90%) as yellow *microcrystals* (Found: C, 38.7; H, 4.6. $C_{18}H_{25}BF_4O_2Pt$ requires C, 38.9; H, 4.5%), m.p. 170—174 °C (decomp.), $\nu_{max.}$ (C=O) 1 559m cm^{-1}. N.m.r. ([$^{2}H_2$]dichloromethane): ^{1}H (25 °C), τ 2.30 (s br, 1 H, OH), 5.48 [m, 4 H, CH, J(PtH) 80], 7.62 (m, 8 H, CH_2), 7.80 [s, 12 H, Me, J(PtH) 19 Hz]. ^{13}C (−90 °C), δ (p.p.m.) 144 (C=O), 111 (*C*Me), 86 (CH), 32 (CH_2), 12 (Me). In [$^{2}H_3$]nitromethane at 25 °C, δ (p.p.m.) 146 (C=O), 118 (*C*Me), 96 [CH, J(PtC) 179 Hz], 32.5 (CH_2), 13 (Me).

Crystal-structure Determination of Compound (1d).—As mentioned in the Discussion, the first complex to be studied crystallographically was (1a). Data [2 193 reflections with $F \geqslant 4\sigma(F)$] were obtained [23] at 200 K, assuming the orthorhombic space groups *Pmmn* or *P*2$_1$*mn*, with lattice parameters a = 13.930(7), b = 14.132(9), c = 8.219(5) Å, with Z = 4 and M 467.5. The Patterson synthesis applied to these data indicated two independent molecules per asymmetric unit, the platinum atoms necessarily occupying positions of site symmetry *mm* (or *m*), and hence co-ordination of the quinone to the metal being η^4. However, internal disorder of the duroquinone ligand in one molecule and of the cod in the other precluded a satisfactory refinement [R 0.127 (R' 0.128)] Attention was then directed to crystals of (1d) which were grown by evaporation under a nitrogen stream from a diethyl ether–hexane solution. Preliminary photographs of a yellow needle-shaped crystal indicated the space group *Pbca*. The crystal was mounted on a Syntex *P*2$_1$ four-circle diffractometer but on cooling to 200 K it appeared to undergo a reversible phase change, since on slow warming to room temperature the previously obtained diffracted intensities for specific reflections, and the orthorhombic systematic absences, returned. Accordingly, it was decided to collect data from another crystal at ambient temperatures. This second crystal of dimensions *ca.* 0.2 × 0.08 × 0.05 mm, with morphology apparently similar to the previous one, appeared to belong to the monoclinic system from an investigation of diffracted intensities and further photographs. Moreover, cooling to 200 K produced no phase change and, therefore, data were recorded at this temperature for 2.9 ⩽ 2θ ⩽ 60° on a *P*3 four-circle automated diffractometer.[23] Two reflections (0 $\bar{2}$ 1 and 0 6 1) were used as check reflections and were monitored once every batch of 50 reflections, but observed intensity fluctuations were only of a random nature. Of the total 6 656 recorded intensities, 4 258 unique reflections had $|F| \geqslant 6\sigma(F)$ where $\sigma(F)$ is the standard deviation based on counting statistics, and only these were used in the final refinement of the structure, after corrections had been applied for Lorentz, polarization, and the effect of *X*-ray absorption. For the latter a method of employing azimuthal scan data was applied. All computations were carried out using the 'SHELXTL' system [24] of programs on the ECLIPSE (Data General) computer.

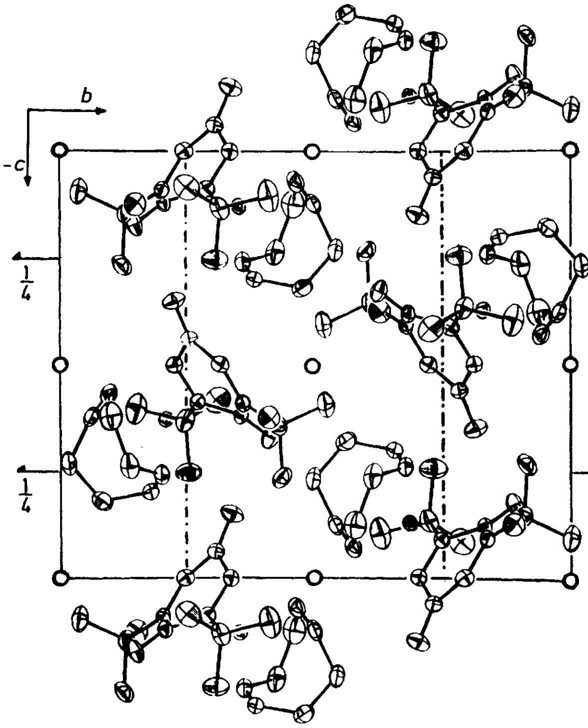


FIGURE 2 Contents of the unit cell of (1d) viewed down a^* towards the origin

Crystal data. (a) $C_{22}H_{32}O_2Pt$, Orthorhombic, M = 523.6, a = 10.546(2), b = 16.133(4), c = 23.815(8) Å, U = 4 052 Å^3, Z = 8, D_c = 1.72 g cm^{-3}, $F(000)$ = 2 064, space group *Pbca* (no. 61).

(b) $C_{22}H_{32}O_2Pt$, Monoclinic, $M = 523.6$, $a = 10.652(5)$, $b = 12.541(4)$, $c = 14.971(4)$ Å, $\beta = 93.17(3)^\circ$, $U = 1\,997$ Å^3, $D_m = 1.74$ (estimated), $Z = 4$, $D_c = 1.75$ g cm^{-3}, $F(000) = 1\,032$, Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 67.8 cm^{-1}, space group $P2_1/n$ (non-standard $P2_1/c$, no. 14).

Structure solution and refinement. Patterson techniques were used to locate the platinum atom and all remaining atoms, including the hydrogen atoms, were located by difference electron-density syntheses. In subsequent refinement (block cascaded) all non-hydrogen atoms were given anisotropic thermal parameters. The hydrogen atoms were allowed to refine freely, except that they were given common, refined, isotropic temperature factors for chemically equivalent hydrogen types, *e.g.* methyl, olefinic, methylenic, *etc.* Convergence was obtained at R 0.025 (R' 0.027). A weighting scheme of the form $w^{-1} = [\sigma^2(F_o) + 0.016|F_o|^2]$, where $\sigma(F_o)$ is the estimated error in $|F_o|$ based on counting statistics, gave a satisfactory analysis in terms of sin 0 and F_o. There were no residual electron-density maxima greater than 0.5 e Å^{-3}, except in the vicinity of the Pt atom. Scattering factors were from ref. 25 for C and O, ref. 26 for hydrogen, and ref. 27 for Pt, including corrections for the effect of anomalous dispersion. Atomic positional parameters are in Table 3, internuclear distances and angles in Table 4, and some selected planes in Table 5. The packing of the molecules in the unit cell is shown in Figure 2. Observed and calculated structure factors, all thermal parameters, and molecular parameters for the hydrogen atoms are listed in Supplementary Publication No. SUP 22916 (32 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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