Reactions of Bis(ethylene)(tricyclohexyl- and triphenyl-phosphine)platinum with Quinones. Crystal Structure of Ethylene(2—3-η-2,3,5,6-tetramethylbenzo-1,4-quinone)(tricyclohexylphosphine)platinum

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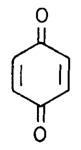
A series of complexes $[Pt(\eta^2\text{-quinone})(C_2H_4)\{P(cyclo\text{-}C_6H_{11})_3\}]$ has been prepared by treating $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ with benzo-1,4-quinones. Carbon-13 n.m.r. studies on the compounds containing the ligands 2,3-dimethyl-, 2,5-dimethyl-, 2,5-diphenyl-benzo-1,4-quinone, and naphtho-1,4-quinone revealed that although the C_2H_4 group is undergoing rapid rotation, the η^2-bonded quinone is rigid on the n.m.r. time scale. In contrast, in the derivatives from 2,6-dimethyl-, 2,6-di-t-butyl-, 2,6-dimethoxy-, and 2,3,5,6-tetramethyl-benzo-1,4-quinone, the quinone ligands are also undergoing dynamic behaviour. The η^2 ground-state structure was established by an *X*-ray diffraction study on the compound $[Pt(\eta^2\text{-}C_6Me_4O_2)(C_2H_4)\{P(cyclo\text{-}C_6H_{11})_3\}]$. Crystals are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with lattice parameters $a = 9.818(3)$, $b = 10.489(3)$, $c = 14.486(3)$ Å, $\alpha = 97.27(2)$, $\beta = 97.93(2)$, and $\gamma = 91.33(3)°$. The structure has been refined to R 0.027 (R' 0.033) for 6 467 independent reflections collected at 200 K for $2.9 \leqslant 2\theta \leqslant 55°$ (Mo-K_α *X*-radiation). The results establish that the 2,3,5,6-tetramethylbenzo-1,4-quinone ligand is attached to the platinum by two carbon atoms of one C(Me)=C(Me) group, and the metal is in a trigonal planar environment with the midpoint of this group, the phosphorus atom, and the midpoint of the C–C bond of the ethylene ligand, with all these co-ordinated atoms lying within 0.1 Å of the co-ordination plane.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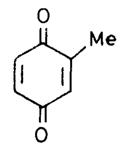
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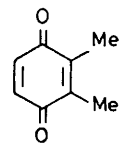
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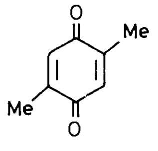
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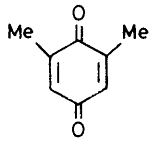
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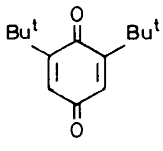
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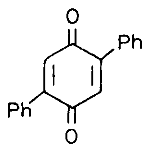
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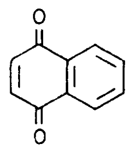
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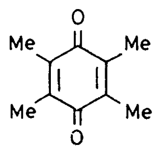
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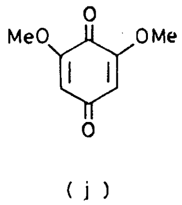
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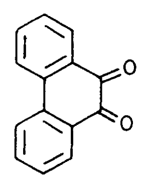
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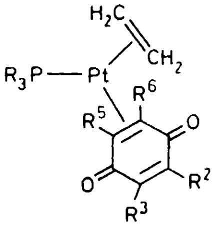
BIS(CYCLO-OCTA-1,5-DIENE)PLATINUM reacts with the benzo-1,4-quinones (a)—(i) to give complexes [Pt(quinone)(cod)] [(1a)—(1i)].[1] The compounds involving ligands (a), (d), (e), (f), (g), and (i) were formulated with structures in which both C=C bonds of the quinone are bonded to platinum, and this was confirmed by an *X*-ray crystallographic study on the derivative from 2,6-di-t-butylbenzo-1,4-quinone (f).[1] In contrast, in those complexes of the type [Pt(quinone)(cod)] having unsymmetrically substituted quinone ligands (b), (c), and (h), ^{13}C n.m.r. studies either established conclusively or indicated an η^2-mode of quinone–metal bonding *via* the CH=CH group. As a consequence of these results, it was decided to investigate reactions between the various quinones and the platinum(0) compounds $[Pt(C_2H_4)_2(PR_3)]$,[2] in the expectation that a new type of platinum–benzo-1,4-quinone complex would be formed

RESULTS AND DISCUSSION

Addition of the quinone ligands (a)—(j) to a suspension of the compound $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ [2] in diethyl ether afforded in good yield complexes $[Pt(quinone)(C_2H_4)\{P(cyclo\text{-}C_6H_{11})_3\}]$ [(2a)—(2j)], characterised by microanalysis (Table 1), and by ^1H, ^{31}P (Table 2), and ^{13}C (Table 3) n.m.r. spectroscopy. All the compounds are soluble in chloroform, dichloromethane, and toluene, and are moderately soluble in light petroleum. The complexes containing a triphenylphosphine group [(3g)—(3i)] were similarly prepared from $[Pt(C_2H_4)_2(PPh_3)]$.

The ^{13}C n.m.r. spectra of the compounds (Table 3) were very informative concerning the nature of the quinone–platinum bonding, with the exception of (2a), which was insufficiently stable to allow data accumulation, and (2b) which formed as a mixture of isomers (discussed below). The spectra of (2c), (2d), (2g), and (2h) are all interpretable in terms of the metal atom being η^2 bonded to the quinone ligands. Thus in the spectrum of (2d) there are two resonances at δ 145 and 136 p.p.m. which may be assigned to the *C*Me and *C*H groups, respectively, since in the spectrum of the free ligand these signals occur at δ 145.7 (*C*Me) and 133.6 (*C*H).[1] Moreover, the peaks at

145 and 136 p.p.m. have no ^{195}Pt satellites confirming that the metal is not bonded to this CH=C(Me) group. In contrast, the other *C*H=*C*(Me) group gives rise to resonances at δ 69 p.p.m. (*C*Me) and 64 p.p.m. (*C*H), markedly shifted upfield from those in the free quinone and showing strong ^{195}Pt–^{13}C coupling of 136 and 195 Hz, respectively, providing clear evidence of metal bonding to this CH=C(Me) group. As discussed previously,[1] in η^4 bonded quinone–platinum complexes *J*(PtC) values are smaller than those observed in the η^2 bonded species such as (2d), being in the range 40—90 Hz. Thus in the ^{13}C spectrum of [Pt{η^4-$C_6H_2O_2(Me_2$-2,5)}(cod)], the *C*Me and *C*H nuclei (δ 112 and 98 p.p.m.) have *J*(PtC) values of 40 and 50 Hz, respectively.



	R^2	R^3	R^5	R^6	R
(2a)	H	H	H	H	C_6H_{11}
(2b)	Me	H	H	H	C_6H_{11}
(2c)	Me	Me	H	H	C_6H_{11}
(2d)	Me	H	Me	H	C_6H_{11}
(2e)	Me	H	H	Me	C_6H_{11}
(2f)	Bu^t	H	H	Bu^t	C_6H_{11}
(2g)	Ph	H	Ph	H	C_6H_{11}
(2h)	CH	CH	H	H	C_6H_{11}
(2i)	Me	Me	Me	Me	C_6H_{11}
(2j)	OMe	H	H	OMe	C_6H_{11}
(3g)	Ph	H	Ph	H	Ph
(3h)	CH	CH	H	H	Ph
(3i)	Me	Me	Me	Me	Ph

An interesting feature of the ^{13}C n.m.r. spectra of (2c), (2d), (2g), and (2h), containing rigidly bonded quinone ligands, is the pattern of signals arising from the cyclohexyl groups. As a consequence of the environment of the platinum (see later) and the rigidity of the quinone ligands, the molecules lack a plane of symmetry and thus within each cyclohexyl group there are two diastereotopic pairs of carbon atoms at the C^2 and C^6, and the C^3 and C^5 ring positions. Hence in the spectra of (2c), (2d), (2g), and (2h) the C_6H_{11} rings show six resonances.

A further feature of the ^{13}C n.m.r. spectra of (2c), (2d), (2g), and (2h), and indeed of the other new compounds discussed herein, is that the resonances of the ethylenic-carbon atoms appear as one signal but with ^{195}Pt satellites. However, the ^{195}Pt–$^{13}C_2H_4$ couplings in the spectra of (2c), (2d), (2g), and (2h) are smaller than the ^{195}Pt–^{13}C (quinone) couplings. In the rigid structure, with the platinum atom coplanar with the phosphorus, the carbon atoms of the ethylene, and the metal-bonded quinone atoms, the *C*H_2 nuclei are non-equivalent and would afford two signals. The appearance of one resonance indicates rapid rotation on the n.m.r. time scale about an axis through the platinum and the midpoint of the C=C double bond of the ethylene, as observed in the spectra of the complexes [Pt$(C_2H_4)_2(PR_3)$].[2] Cooling to −90 °C did not freeze out this dynamic behaviour. Indeed, it is interesting to compare these results with those obtained for the compound [Pt$(C_2H_4)(C_2F_4)${P$(C_6H_{11})_3$}]. An *X*-ray crystallographic study [3] on the latter established the ground-state trigonal structure with the ligated carbon atoms and the phosphorus atom coplanar with the platinum. However, in this molecule the presence of the strong π-acceptor C_2F_4 ligand results in a lower barrier for C_2H_4 rotation than those found for the species [Pt$(C_2H_4)_2(PR_3)$].[2] Similarly, in the [Pt(quinone)$(C_2H_4)(PR_3)$] compounds described herein, the ethylene ligands would be expected to have a relatively low energy barrier for rotation because quinone ligands are strong π acceptors [4] thereby reducing back-bonding between the platinum and the ethylene ligand.

TABLE 1

Analytical [a] and physical data for the complexes [Pt(quinone)$(C_2H_4)(PR_3)$]

Compound [b]	M.p. [c] (θ_c/°C)	Yield (%)	ν(C=O) [d] (cm^{-1})	Analysis (%)	
				C	H
(2a)	189—192	90	1 623 (sh), 1 610vs	51.6 (51.1)	6.7 (6.8)
(2b) [e]	171—180	85		51.4 (51.8)	6.9 (6.9)
(2c)	177—180	95	1 628vs	52.7 (52.7)	7.1 (7.1)
(2d)	172—177	79	1 647s, 1 624vs	52.4 (52.7)	7.2 (7.1)
(2e)	138—144	50	1 643vs, 1 630vs	52.6 (52.7)	7.0 (7.1)
(2f)	191—195	75	1 632vs, 1 603vs	56.3 (56.4)	8.3 (8.0)
(2g)	180—184	95	1 639s, 1 624vs	59.3 (59.8)	6.3 (6.5)
(2h)	180—186	70	1 647 (sh), 1 643vs	54.1 (54.4)	7.0 (6.6)
(2i)	140—146	85	1 619vs, 1 608vs	53.6 (54.0)	7.7 (7.3)
(2j) [f]	163—164	92	1 668s, 1 603s	50.3 (50.1)	7.1 (6.8)
(2k) [g]		60	1 675w, 1 609m	57.1 (57.4)	6.8 (6.4)
(3g) [h]	104—107	85	1 642s, 1 626vs	61.1 (61.2)	4.2 (4.2)
(3h)	180—186	95	1 663vs, 1 596m	55.8 (56.0)	3.8 (3.9)
(3i)	154—158	90	1 610vs, 1 588m	55.2 (55.5)	4.7 (4.8)

[a] Calculated values are given in parentheses. [b] All compounds are yellow unless otherwise stated. [c] With decomposition, in sealed tube. [d] In Nujol. [e] Isomeric mixture, see text. [f] Orange-yellow. [g] Brown-red. [h] Orange-red.

The ^{13}C n.m.r. spectra of the complexes (2e), (2f), (2i), and (2j), formed by the symmetrical ligands (e), (f), (i), and (j), show fewer resonances than those in the spectra of the compounds discussed above, indicating that the quinone ligands, as well as the ethylene groups, are undergoing dynamic behaviour. Moreover, cooling to −90 °C did not lead to limiting spectra, although some changes were observed as discussed below. The dynamic behaviour shown by (2e), (2f), (2i), and (2j) results in the appearance of four resonances for the cyclohexyl nuclei rather than the six signals seen in the spectra of the compounds with rigidly bound η^2-quinone ligands.

TABLE 2

Hydrogen-1 and phosphorus-31 n.m.r. data [a] for the complexes $[Pt(quinone)(C_2H_4)(PR_3)]$

	Complex	Hydrogen-1 [b]	Phosphorus-31 [c]	
			δ	$J(PtP)$
(2a)	$[Pt(\eta^2\text{-}C_6H_4O_2)(C_2H_4)\{P(C_6H_{11})_3\}]$	4.6—5.0 (m,br, 4 H, CH), 7.14 [s, 4 H, CH_2, $J(PtH)$ 57], 8.0—8.8 (m, 33 H, C_6H_{11})	19.7	3 406
(2b)	$[Pt(\eta^2\text{-}C_6H_3O_2Me\text{-}2)(C_2H_4)\{P(C_6H_{11})_3\}]$ [d]		24.6 25.1 19.3 19.8	3 502 3 505 3 415 3 412
(2c)	$[Pt\{\eta^2\text{-}C_6H_2O_2(Me_2\text{-}2,3)\}(C_2H_4)\{P(C_6H_{11})_3\}]$ [e]	5.70 [m, 1 H, CH, $J(HH)$ 8, $J(PH)$ 8, $J(PtH)$ 54], 6.05 [m, 1 H, CH, $J(HH)$ 8, $J(PH)$ 3, $J(PtH)$ 54], 6.94 [m, 2 H, CH_2, $N(HH)$ 9.0, $J(PtH)$ 56], 7.59 [m, 2 H, CH_2, $N(HH)$ 10, $J(PtH)$ 53], 7.5—9.0 (m, 33 H, C_6H_{11}), 8.19 and 8.23 (s, 6 H, Me)	24.5	3 508
(2d)	$[Pt\{\eta^2\text{-}C_6H_2O_2(Me\text{-}2,5)\}(C_2H_4)\{P(C_6H_{11})_3\}]$ [e]	3.90 (m,br, 1 H, CH), 6.01 [d, 1 H, CH, $J(PH)$ 2, $J(PtH)$ 53], 7.16 [m, 2 H, CH_2, $N(HH)$ 8, $J(PtH)$ 56], 7.45 [m, 2 H, CH_2, $N(HH)$ 8, $J(PtH)$ 53], 7.5—9.0 (m, 33 H, C_6H_{11}), 8.20, 8.26, (s, 3 H, Me)	23.9	3 408
(2e)	$[Pt\{\eta^2\text{-}C_6H_2O_2(Me_2\text{-}2,6)\}(C_2H_4)\{P(C_6H_{11})_3\}]$	5.09 [m, 2 H, CH, $J(PtH)$ 27], 7.39 [s, 4 H, CH_2, $J(PtH)$ 57], 7.6—8.9 (m, 33 H, C_6H_{11}), 8.23 (s, 6 H, Me)	24.7	3 413
(2f)	$[Pt\{\eta^2\text{-}C_6H_2O_2(Bu^t_2\text{-}2,6)\}(C_2H_4)\{P(C_6H_{11})_3\}]$	4.96 [m, 2 H, CH, $J(PtH)$ 23], 7.17 [s, 4 H, CH_2, $J(PtH)$ 57], 7.55—8.9 (m, 33 H, C_6H_{11}), 8.80 (s, 18 H, Bu^t)	22.8	3 373
(2g)	$[Pt\{\eta^2\text{-}C_6H_2O_2(Ph_2\text{-}2,5)\}(C_2H_4)\{P(C_6H_{11})_3\}]$ [e]	2.4—2.9 (m, 10 H, Ph), 3.53 (s, 1 H, CH), 5.69 [d, 1 H, CH, $J(PH)$ 3, $J(PtH)$ 49], 6.93 [m, 2 H, CH_2, $N(HH)$ 11, $J(PtH)$ 56], 7.31 [m, 2 H, CH_2, $N(HH)$ 11, $J(PtH)$ 54], 7.56—8.95 (m, 33 H, C_6H_{11})	23.9	3 512
(2h)	$[Pt(\eta^2\text{-}C_{10}H_6O_2)(C_2H_4)\{P(C_6H_{11})_3\}]$ [e]	2.02—2.68 (m, 4 H, CH), 5.59 [m, 1 H, CH, $J(HH)$ 8, $J(PH)$ 8, $J(PtH)$ 49], 5.90 [m, 1 H, CH, $J(HH)$ 8, $J(PH)$ 2, $J(PtH)$ 55], 6.86 [m, 2 H, CH_2, $N(HH)$ 10, $J(PtH)$ 57], 7.54 [m, 2 H, CH_2, $N(HH)$ 10, $J(PtH)$ 50], 7.5—9.0 (m, 33 H, C_6H_{11})	24.2	3 530
(2i)	$[Pt(\eta^2\text{-}C_6Me_4O_2)(C_2H_4)\{P(C_6H_{11})_3\}]$	7.32 [s, 4 H, CH_2, $J(PtH)$ 54], 7.80—8.85 (m, 33 H, C_6H_{11}), 8.14 (s, 6 H, Me), 8.22 (s, 6 H, Me)	20.9	3 569
(2j)	$[Pt\{\eta^2\text{-}C_6H_2O_2[(OMe)_2\text{-}2,6]\}(C_2H_4)\{P(C_6H_{11})_3\}]$	5.18 [s, 2 H, CH, $J(PtH)$ 27], 6.43 (s, 6 H, OMe), 7.18 [s, 4 H, CH_2, $J(PtH)$ 59], 7.45—8.8 (m, 33 H, C_6H_{11})	25.3	3 377
(3g)	$[Pt\{\eta^2\text{-}C_6H_2O_2(Ph_2\text{-}2,5)\}(C_2H_4)(PPh_3)]$	2.22—3.1 (m, 25 H, Ph), 3.50 (s, 1 H, CH), 5.30 [d, 1 H, CH, $J(PH)$ 3, $J(PtH)$ 44], 6.93 [s, 4 H, CH_2, $J(PtH)$ 59]	24.0	3 512
(3h)	$[Pt(\eta^2\text{-}C_{10}H_6O_2)(C_2H_4)(PPh_3)]$	2.4—2.8 (m, 21 H, Ph and CH), 5.64 [s, 4 H, CH_2, $J(PtH)$ 56]	18.9	3 643
(3i)	$[Pt(\eta^2\text{-}C_6Me_4O_2)(C_2H_4)(PPh_3)]$	2.7 (m, 15 H, Ph), 5.71 [s, 4 H, CH_2, $J(PtH)$ 77], 7.79 [s, 6 H, Me, $J(PtH)$ 19], 8.46 [d, 6 H, Me, $J(PH)$ 2, $J(PtH)$ 17]	29.1	3 883

[a] Measured in $[^2H_1]$chloroform, at room temperature, coupling constants in Hz. [b] Chemical shifts in τ. [c] Hydrogen-1 decoupled, chemical shifts in p.p.m. to low frequency of 85% H_3PO_4 (external). [d] Isomeric mixture, see text. [e] $N(AB) = |J(AB) + J(AB')|$ for an AA'BB' spin system of the co-ordinated C_2H_4.

At room temperature, the ^{13}C n.m.r. spectrum of (2f) (Table 3) did not show resonances due to the *C*H and *C*Bu^t carbon atoms of the co-ordinated quinone (f). On cooling to −90 °C, however, broad signals appear at δ(p.p.m.) 51.3 and 81.1, the latter peak being a doublet [$J(PC)$ 17, $J(PtC)$ 140 Hz], and at 131.5 and 160.2. The peaks at 131.5 and 160.2 p.p.m. are assigned to carbon atoms of a *C*H=*C*Bu^t group not bonded to platinum since in the spectrum of the free quinone these nuclei give resonances at δ 130.1 (*C*H) and 157.6 (*C*Bu^t).[1] Changes in the ^1H n.m.r. spectrum of (2f) are also observed on cooling. Whereas at room temperature (Table 2) only one resonance is observed for the protons of the C*H* (quinone) and C*H*$_2$ (C_2H_4) groups at τ 4.96 and 7.17, respectively, both with ^{195}Pt satellites, coalescence of the quinone C*H* peaks occurs at *ca.* −35 °C. At −100 °C (CCl_3F solution), the C*H*(quinone) protons give broad peaks at τ 4.10 and 6.26, only the latter showing ^{195}Pt–^{13}C coupling (48 Hz). The C*H*$_2$(C_2H_4) proton resonance became very broad at −90 °C showing no fine structure. Thus, whereas at the low temperature the ethylene ligand is still rotating, the quinone ligand is commencing to show the peaks expected for an η^2 bonding mode to the platinum. Similar changes with temperature were observed in the ^1H n.m.r. spectra of compound (2e). At room temperature (Table 2) the C*H*(quinone) protons give a resonance at τ 5.09. At −100 °C (CD_2Cl_2) the C*H*-(quinone) protons show two broad peaks at τ 4.07 and 6.20. The coalescence temperature is *ca.* −65 °C. At −90 °C there are no changes from the ^{13}C n.m.r. measured at room temperature.

TABLE 3

Carbon-13 n.m.r. data[a] for the complexes $[Pt(quinone)(C_2H_4)(PR_3)]$

	Complex	δ[b]
(2c)	$[Pt\{\eta^2\text{-}C_6H_2O_2(Me_2\text{-}2,3)\}(C_2H_4)\{P(C_6H_{11})_3\}]$	191 [C=O, *J*(PtC) 41], 189 [d, C=O, *J*(PC) 5, *J*(PtC) 35], 143, 142 (*C*Me), 56.1 [d, CH, *J*(PC) 5, *J*(PtC) 198], 55.9 [d, CH, *J*(PC) 14, *J*(PtC) 131], 52 [CH_2, *J*(PtC) 116], 35 [d, C^1 (C_6H_{11}), *J*(PC) 24, *J*(PtC) 33], 30.0 [*J*(PtC) 15], 29.9 [*J*(PtC) 21], 27.6 [d, *J*(PC) 5], 27.2 [d, *J*(PC) 5], 26.6 (C_6H_{11}), 12.9, 12.7 (Me)
(2d)	$[Pt\{\eta^2\text{-}C_6H_2O_2(Me_2\text{-}2,5)\}(C_2H_4)\{P(C_6H_{11})_3\}]$	191 [C=O, *J*(PtC) 43], 187 [d, C=O, *J*(PC) 4, *J*(PtC) 35], 145 (*C*Me), 136 (CH), 69 [d, *C*Me, *J*(PC) 15, *J*(PtC) 136], 64 [d, CH, *J*(PC) 3, *J*(PtC) 195], 54 [CH_2, *J*(PtC) 125], 34.5 [d, $C^1(C_6H_{11})$, *J*(PC) 23, *J*(PtC) 32], 29.9 [*J*(PtC)11], 29.8 [*J*(PtC) 11], 27.5, 27.2 [d, *J*(PC) 2], 26.6 (C_6H_{11}), 18, 16 (Me)
(2e)	$[Pt\{\eta^2\text{-}C_6H_2O_2(Me\text{-}2,6)\}(C_2H_4)\{P(C_6H_{11})_3\}]$	191 (C=O), 190.5 (C=O), 99 [CH, *J*(PtC) 87], 54 [CH_2, *J*(PtC) 127], 34 [d, C(1)(C_6H_{11}), *J*(PC) 23, *J*(PtC) 33], 30 [*J*(PtC) 18], 27.5 [d, *J*(PC) 11], 26.8 (C_6H_{11}), 17 (Me)
(2f)	$[Pt\{\eta^2\text{-}C_6H_2O_2(Bu^t{}_2\text{-}2,6)\}(C_2H_4)\{P(C_6H_{11})_3\}]$	192 [d, C=O, *J*(PC) 3, *J*(PtC) 43], 186 [d, C=O, *J*(PC) 6, *J*(PtC) 44], 50 [CH_2, *J*(PtC) 127], 36 (*C*Me_3), 34 [d, $C^1(C_6H_{11})$, *J*(PC) 23], 30.2 (Me), 30 [*J*(PtC) 18], 27.6 [d, *J*(PC) 11], 27 (C_6H_{11})
(2g)	$[Pt\{\eta^2\text{-}C_6H_2O_2(Ph_2\text{-}2,5)\}(C_2H_4)\{P(C_6H_{11})_3\}]$	189 [C=O, *J*(PtC) 43], 184 [d, C=O, *J*(PC) 6, *J*(PtC) 38], 143, 139.5, 139.4, 137, 135, 129.2, 128.9, 128.4, 128, 127.7, 126 (CH and Ph), 75 [d, *C*(Ph), *J*(PC) 14, *J*(PtC) 170], 65 [d, CH, *J*(PC) 4, *J*(PtC) 200], 59 [CH_2, *J*(PtC) 116], 35 [d, $C^1(C_6H_{11})$, *J*(PC) 23, *J*(PtC) 35], 30 [*J*(PtC) 15], 29.8 [*J*(PtC) 24], 27.4 [d, *J*(PC) 9], 27 [d, *J*(PC) 11], 26.5 (C_6H_{11})
(2h)	$[Pt(\eta^2\text{-}C_{10}H_6O_2)(C_2H_4)\{P(C_6H_{11})_3\}]$	190 [C=O, *J*(PtC) 41], 187 [d, C=O, *J*(PC) 5, *J*(PtC) 34], 135, 132.3, 131.8, 131.2, 125.5, 125.2 (C, CH), 57.3 [d, CH, *J*(PC) 14, *J*(PtC) 125], 57.2 [d, CH, *J*(PC) 5, *J*(PtC) 195], 54 [CH_2, *J*(PtC) 116], 35 [d, $C^1(C_6H_{11})$, *J*(PC) 24, *J*(PtC) 33], 30 [*J*(PtC) 18], 29.6 [*J*(PtC) 24], 27.5 [d, *J*(PC) 5], 27.1 [d, *J*(PC) 5], 26.5 (C_6H_{11})
(2i)	$[Pt(\eta^2\text{-}C_6Me_4O_2)(C_2H_4)\{P(C_6H_{11})_3\}]$	188 [C=O, *J*(PtC) 50], 186 [d, C=O, *J*(PC) 5, *J*(PtC) 42], 105.6 [d, *C*Me, *J*(PC) 7, *J*(PtC) 68], 105.4 [*C*Me, *J*(PtC) 110], 56 [CH_2, *J*(PtC) 111], 35 [d, $C^1(C_6H_{11})$, *J*(PC) 22, *J*(PtC) 33], 30 [*J*(PtC) 20], 27.4 [d, *J*(PC) 11], 26.6 (C_6H_{11}), 14.1 (Me), 13.8 (Me)
(2j)	$[Pt\{\eta^2\text{-}C_6H_2O_2[(OMe)_2\text{-}2,6]\}(C_2H_4)\{P(C_6H_{11})_3\}]$	189 [d, C=O, *J*(PC) 3, *J*(PtC) 24], 175 (C=O), 132 [d, *C*(OMe), *J*(PC) 9], 80 [CH, *J*(PtC) 92], 56 [OMe, *J*(PtC) 15], 54 [CH_2, *J*(PtC) 124], 34 [d, $C^1(C_6H_{11})$, *J*(PC) 23, *J*(PtC) 28], 30 [*J*(PtC) 20], 27 [d, *J*(PC) 11], 27 (C_6H_{11})
(3g)	$[Pt\{\eta^2\text{-}C_6H_2O_2(Ph_2\text{-}2,5)\}(C_2H_4)(PPh_3)]$	188 [C=O, *J*(PtC) 18], 184 [d, C=O, *J*(PC) 6, *J*(PtC) 28], 134 [d, C^1(Ph), *J*(PC) 11, *J*(PtC) 39], 139.4—126.5 (Ph), 81 [d, *C*Ph, *J*(PC) 15], 72 [CH, *J*(PtC) 125], 63 [CH_2, *J*(PtC) 117]
(3h)	$[Pt(\eta^2\text{-}C_{10}H_6O_2)(C_2H_4)(PPh_3)]$	184 [C=O, *J*(PtC) 35], 135—125 (Ph), 66 [CH, *J*(PtC) 171], 60 [CH_2, *J*(PtC) 113]
(3i)	$[Pt(\eta^2\text{-}C_6Me_4O_2)(C_2H_4)(PPh_3)]$	207 [C=O, *J*(PtC) 31], 135—128 (Ph), 109 [*C*Me, *J*(PtC) 35], 106 [*C*Me, *J*(PtC) 35], 84 [CH_2, *J*(PtC) 194], 14 (Me), 12 (Me)

[a] Measured in $[^2H_1]$chloroform at room temperature. [b] Hydrogen-1 decoupled, chemical shifts in p.p.m. to high frequency of $SiMe_4$, coupling constants in Hz.

Although the quality of the spectra make deductions less certain, it would appear from the ^{13}C n.m.r. data that the triphenylphosphine complex (3i) is fluxional. In contrast, the observation of ^{195}Pt–^{13}C coupling of magnitude 171 Hz for the *C*H carbon atoms (δ 66 p.p.m.) in the spectrum of (3h) implies that (h) is η^2 bonded to the platinum in this compound, as would be expected.[1]

The nature of the n.m.r. spectra discussed above for the compounds (2e), (2f), (2i), and (2j) suggests low-energy dynamic behaviour on the part of the quinone ligands, by a mechanism which most likely involves rapid exchange between two degenerate η^2 quinone–platinum bonded structures. In order to confirm this supposition it was necessary to establish the ground-state structure of one of the 'dynamic' quinone ligand complexes. Fortunately, crystals of compound (2i) were suitable for *X*-ray diffraction study. The results are summarised in Tables 4—6, and the molecular structure is shown in Figure 1, together with the crystallographic numbering scheme.

It is immediately apparent that the duroquinone ligand is indeed η^2 bonded to the platinum at C(2) and C(3) (Pt–C, 2.15 Å mean), the distances from the platinum to C(1), C(4), C(5), and C(6) (2.88, 2.91, 3.40, and 3.35 Å respectively) being too long for any significant bonding interaction between these carbon atoms and the metal. The co-ordination around the platinum is trigonal planar as we have previously found for $[Pt(C_2H_4)(C_2F_4)\{P\text{-}(cyclo\text{-}C_6H_{11})_3\}]$,[3] $[Pt(C_2H_4)_2(C_2F_4)]$,[5] $[Pt(C_2H_4)_3]$,[6] and $[Pt(C_7H_{10})_3]$.[7] The contiguous atoms Pt, P, C(2), C(3), C(111), and C(112) deviate only slightly (<0.1 Å) from the mean plane calculated through their centres (Table 6), while the co-ordination angles at the platinum between the phosphorus and the midpoints of the C(2)–C(3) and the C(111)–C(112) bonds are, respectively, 124° and 109°, compared with the idealised angle of 120°. The larger

TABLE 4

Atomic positional parameters (fractional co-ordinates) for complex (2i) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt	0.087 25(1)	0.032 94(1)	0.242 15(1)
P(1)	0.098 38(9)	−0.182 84(8)	0.263 74(6)
Ethylene			
C(111)	−0.070 5(7)	0.123 1(6)	0.157 5(5)
H(1)	−0.131(8)	0.136(7)	0.198(5)
H(2)	−0.042(8)	0.192(8)	0.134(5)
C(112)	−0.093 7(5)	−0.010 0(5)	0.135 5(4)
H(3)	−0.078(6)	−0.048(5)	0.066(4)
H(4)	−0.156(5)	−0.064(5)	0.156(3)
Cyclohexyl groups			
C(101)	0.173 1(4)	−0.284 4(3)	0.171 4(2)
C(102)	0.087 0(4)	−0.298 7(4)	0.073 3(3)
C(103)	0.154 9(5)	−0.389 1(5)	0.004 1(3)
C(104)	0.300 7(5)	−0.342 9(6)	−0.001 4(3)
C(105)	0.384 4(5)	−0.322 4(6)	0.094 3(3)
C(106)	0.318 1(4)	−0.232 5(5)	0.165 3(3)
C(201)	0.208 4(4)	−0.211 8(3)	0.374 4(2)
C(202)	0.266 3(5)	−0.346 4(4)	0.376 7(3)
C(203)	0.363 3(6)	−0.351 4(6)	0.467 4(4)
C(204)	0.296 5(7)	−0.309 8(6)	0.554 8(4)
C(205)	0.238 0(6)	−0.177 9(5)	0.552 8(3)
C(206)	0.138 4(4)	−0.174 5(4)	0.461 5(3)
C(301)	−0.074 9(4)	−0.259 2(3)	0.259 2(2)
C(302)	−0.168 9(4)	−0.183 1(4)	0.321 4(3)
C(303)	−0.316 3(4)	−0.236 8(4)	0.298 6(3)
C(304)	−0.324 4(5)	−0.380 6(5)	0.308 7(4)
C(305)	−0.229 9(5)	−0.455 2(4)	0.250 1(4)
C(306)	−0.081 7(4)	−0.401 2(4)	0.272 7(3)
Duroquinone			
C(1)	0.214 2(5)	0.270 6(4)	0.209 5(3)
O(1)	0.158 9(4)	0.365 6(3)	0.180 0(3)
C(2)	0.178 0(4)	0.220 5(3)	0.293 6(3)
C(21)	0.092 1(7)	0.307 3(5)	0.351 9(5)
C(3)	0.261 4(4)	0.126 9(3)	0.335 5(3)
C(31)	0.275 2(7)	0.125 0(5)	0.441 1(3)
C(4)	0.382 9(4)	0.084 3(4)	0.293 0(3)
O(4)	0.468 9(3)	0.017 1(3)	0.332 9(3)
C(5)	0.404 9(4)	0.123 8(4)	0.199 7(3)
C(51)	0.524 6(7)	0.064 1(8)	0.157 6(7)
C(6)	0.322 1(5)	0.207 7(4)	0.160 2(3)
C(61)	0.338 2(9)	0.250 7(8)	0.066 7(5)

angle between the duroquinone and the phosphorus almost certainly reflects the greater steric requirements of the ligand (i) compared with C_2H_4.

Co-ordination of the ethylene molecule to platinum is as expected from previous structural work. For instance the mean Pt–C bond length [2.169(6) Å] lies between that in [$Pt(C_2H_4)_3$] [2.177(3) Å][6] and that in

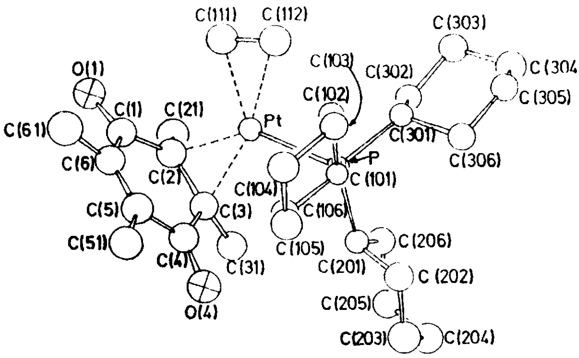


FIGURE 1 The molecular structure of compound (2i). Hydrogen atoms are omitted for clarity

TABLE 5

Interatomic distances (Å) and bond angles (°) in [$Pt(C_6Me_4O_2)(C_2H_4)\{P(C_6H_{11})_3\}$] (2i)

(*a*) Distances

Pt–P(1)	2.326 6(9)	C(111)–C(112)	1.398(8)
Pt–C(111)	2.153(7)	C(111)–H(1)	0.89(8)
Pt–C(112)	2.186(5)	C(111)–H(2)	0.90(8)
Pt–C(2)	2.141(4)	C(112)–H(3)	1.07(6)
Pt–C(3)	2.161(4)	C(112)–H(4)	0.93(5)
Cyclohexyl groups			
P(1)–C(101)	1.846(4)	P(1)–C(301)	1.853(4)
C(101)–C(102)	1.539(5)	C(301)–C(302)	1.523(6)
C(102)–C(103)	1.524(6)	C(302)–C(303)	1.518(6)
C(103)–C(104)	1.516(7)	C(303)–C(304)	1.535(7)
C(104)–C(105)	1.498(7)	C(304)–C(305)	1.508(3)
C(105)–C(106)	1.529(7)	C(305)–C(306)	1.526(6)
C(106)–C(101)	1.531(6)	C(306)–C(301)	1.528(5)
P(1)–C(201)	1.869(4)		
C(201)–C(202)	1.536(6)		
C(202)–C(203)	1.520(7)		
C(203)–C(204)	1.525(9)		
C(204)–C(205)	1.512(9)		
C(205)–C(206)	1.538(6)		
C(206)–C(201)	1.531(6)		
Duroquinone ligand			
C(1)–C(2)	1.470(7)	C(5)–C(6)	1.339(7)
C(2)–C(3)	1.432(6)	C(6)–C(61)	1.508(10)
C(2)–C(21)	1.514(8)	C(6)–C(1)	1.479(7)
C(3)–C(31)	1.521(6)		
C(3)–C(4)	1.469(6)	C(1)–O(1)	1.240(6)
C(4)–C(5)	1.505(7)	C(4)–O(4)	1.240(6)
C(5)–C(51)	1.511(9)		

(*b*) Angles

C(111)–Pt–C(112)	37.6(2)	H(1)–C(111)–C(112)	97(5)
		H(2)–C(111)–C(112)	142(5)
H(3)–C(112)–C(111)	115(3)	H(1)–C(111)–H(2)	116(7)
H(4)–C(112)–C(111)	129(3)	H(3)–C(112)–H(4)	109(4)
C(111,112)–Pt–P(1) *	109.3(2)		
C(2,3)–Pt–P(1) *	124.0(1)	C(2)–Pt–C(3)	38.9(1)
C(111,112)–Pt–C(2,3) *	126.6(3)		
Cyclohexyl groups			
Pt–P(1)–C(101)	114.2(1)	Pt–P(1)–C(201)	114.0(1)
Pt–P(1)–C(301)	111.9(1)	C(201)–P(1)–C(101)	103.3(2)
C(101)–P(1)–C(301)	103.3(2)	C(201)–P(1)–C(301)	109.3(2)
P(1)–C(101)–C(102)	114.8(3)	P(1)–C(201)–C(206)	112.2(3)
P(1)–C(101)–C(106)	109.9(2)	P(1)–C(201)–C(202)	116.8(2)
C(101)–C(102)–C(103)	110.3(3)	C(201)–C(202)–C(203)	110.5(4)
C(102)–C(103)–C(104)	111.7(4)	C(202)–C(203)–C(204)	112.6(5)
C(103)–C(104)–C(105)	110.8(4)	C(203)–C(204)–C(205)	111.6(5)
C(104)–C(105)–C(106)	112.9(4)	C(204)–C(205)–C(206)	110.2(4)
C(105)–C(106)–C(101)	109.9(3)	C(205)–C(206)–C(201)	111.6(4)
C(106)–C(101)–C(102)	109.2(3)	C(206)–C(201)–C(202)	109.9(3)
P(1)–C(301)–C(302)	114.5(2)	P(1)–C(301)–C(306)	117.0(2)
C(301)–C(302)–C(303)	111.0(3)	C(302)–C(303)–C(304)	111.0(4)
C(303)–C(304)–C(305)	111.2(4)	C(304)–C(305)–C(306)	112.1(4)
C(305)–C(306)–C(301)	110.4(3)	C(306)–C(301)–C(302)	109.8(3)
Duroquinone ligand			
Pt–C(2)–C(3)	71.3(2)	Pt–C(3)–C(2)	69.8(2)
Pt–C(2)–C(21)	115.1(3)	Pt–C(3)–C(31)	121.2(4)
Pt–C(2)–C(1)	104.4(2)	Pt–C(3)–C(4)	105.2(2)
C(1)–C(2)–C(21)	115.2(4)	C(4)–C(3)–C(31)	114.4(4)
C(3)–C(2)–C(21)	120.4(4)	C(2)–C(3)–C(31)	119.4(4)
C(1)–C(2)–C(3)	119.9(4)	C(2)–C(3)–C(4)	118.6(4)
C(2)–C(1)–C(6)	118.9(4)	C(3)–C(4)–C(5)	119.5(4)
C(2)–C(1)–O(1)	121.8(4)	C(3)–C(4)–O(4)	121.4(4)
C(6)–C(1)–O(1)	119.3(5)	O(4)–C(4)–C(5)	119.0(4)
C(1)–C(6)–C(5)	121.4(4)	C(4)–C(5)–C(6)	120.1(4)
C(1)–C(6)–C(61)	115.7(5)	C(4)–C(5)–C(51)	115.3(5)
C(5)–C(6)–C(61)	122.8(5)	C(6)–C(5)–C(51)	124.5(6)

* C(*n*,*m*) indicates the midpoint of the bond joining atom C(*n*) to C(*m*).

$[Pt(C_2H_4)(PPh_3)_2]$ [2.11(1) Å].[8] The shorter metal–carbon distance in the latter case is attributable to the greater degree of metal–olefin back-bonding promoted by the two electron-donating PPh_3 groups. Indeed, this effect is probably responsible for significant asymmetry in the Pt–CH_2 separations observed in (2i). Thus C(111) which is *transoid* with respect to the P(cyclo-$C_6H_{11})_3$ ligand is closer to platinum [2.153(7) Å] than is C(112) [2.186(5) Å] which is *transoid* to the duroquinone. The latter would be a more effective π acceptor and less efficient σ donor than tricyclohexylphosphine. A similar result has been observed in the structure of $[Pt(C_2H_4)(C_2F_4)\{P(cyclo\text{-}C_6H_{11})_3\}]$ [3] where the asymmetric Pt–CH_2 separations are 2.02(1) and 2.18(1) Å.

TABLE 6

Equations of least-squares planes for complex (2i) in the form $Ax + By + Cz = D$, where x, y, and z are fractional co-ordinates. Deviations (Å) of atoms from a plane are given in square brackets

Plane (1): Pt, P(1), C(111), C(112), C(2), C(3)
$-6.688x + 0.418y + 11.723z = 2.298$
[Pt −0.029, P(1) 0.059, C(111) 0.072, C(112), −0.087, C(2) 0.046, C(3) −0.061]

Plane (2): C(1), C(2), C(3), C(4), C(5), C(6)
$5.124x + 6.973y + 5.064z = 3.966$
[C(1) 0.079, C(2) −0.030, C(3) −0.043, C(4) 0.067, C(5) −0.017, C(6) −0.056, O(1) 0.309, C(21) 0.430, C(31) 0.549, O(4) 0.241, C(51) −0.033, C(61) −0.148]

Plane (3): C(21), C(2), C(3), C(31)
$7.135x + 6.820y - 0.389z = 2.630$
[C(21) −0.014, C(2) 0.030, C(3) −0.029, C(31) 0.014]

Plane (4): C(1), C(2), C(3), C(4)
$4.579x + 6.867y + 6.102z = 4.118$
[C(5) −0.196, C(6) −0.239, C(21) 0.561, C(31) 0.692]

Plane (5): C(1), C(6), C(61), C(5), C(51), C(4)
$5.428x + 7.139y + 4.158z = 3.923$
[C(1) 0.043, C(6) −0.025, C(61) −0.020, C(5) −0.011, C(51) 0.038, C(4) −0.025, C(2) −0.161, C(3) −0.203]

Plane (6): * C(111), H(1), C(112), H(4)
$5.958x - 2.789y + 9.984z = 0.815$

Plane (7): * C(111), H(2), C(112), H(3)
$9.011x - 2.289y + 3.440z = -0.364$

Plane (8): * C(111), H(1), H(2)
$6.403x + 0.500y + 9.324z = 1.078$

Plane (9): * C(112), H(3), H(4)
$7.098x - 6.241y + 5.021z = 0.078$

Dihedral angles (°)

Plane	(1)	(3)	(4)	(5)	(6)
(2)	87.7	23.7	4.9	3.8	
(3)	111.1				
(4)	82.8	28.6			
(5)	91.3	8.7	8.7		
(6)	82.4				
(7)	112.2				29.9

* H(1)—H(4) are hydrogen atoms of C_2H_4 ligand.

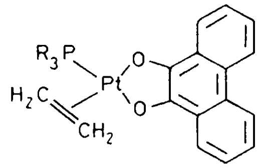
There is also asymmetry in the platinum–duroquinone separations with C(2), *transoid* to the phosphorus atom, at 2.141(4) Å and C(3) at 2.161(4) Å. In considering whether the asymmetry in the two pairs of Pt–C(olefin) distances could be attributed entirely to electronic effects, all possible non-bonded intramolecular contacts were examined. The larger Pt–C distances occur *cis* to the bulky P(cyclo-$C_6H_{11})_3$ ligand and the shortest H ⋯ H contact is between hydrogen atoms on C(112) and C(302). However, with the relative uncertainty in the hydrogen-atom co-ordinates and since the largest angle around the platinum atom occurs between the midpoints of the two co-ordinated C=C bonds (126.6°), the ethylene molecule would have little difficulty in increasing its distance from the phosphorus atom if steric interactions with the cyclo-C_6H_{11} groups were the most important influence on its observed co-ordination position.

The six ring atoms C(1)–C(6) of the duroquinone are essentially coplanar (max. deviation 0.07 Å) but there is a slight fold in the ring along the C(1)–C(4) axis, such that C(5) and C(6) and their bonded Me groups are bent slightly towards the metal atom. Alternatively, the ring distortion may be viewed as a bending of the C=O groups away from the metal. Thus the small deviation of C(1) and C(4) from the ligand mean plane is accentuated at O(1) and O(4), which deviate from this plane by 0.3 and 0.4 Å. Both Me groups attached to C(2) and C(3) are bent away from the platinum, the mean plane through C(2), C(21), C(3), and C(31) being inclined at 111.1° to the co-ordination plane of the metal. The latter plane is at 87.7° to the mean plane of the C_6 ring of the quinone. Within this ring there are some small but significant variations in geometry, namely, the shorter C(1)–C(2) and C(3)–C(4) bonds (mean 1.469 Å) compared with the C(1)–C(6) and C(4)–C(5) separations (1.492 Å). It is possible that these values reflect some degree of delocalisation extending beyond that seen in the lengthening of C(2)–C(3) on co-ordination to the platinum, and that a weak interaction between this delocalised system and the metal is keeping the C_6 quinone ring more nearly perpendicular to the central co-ordination plane than might have been expected. Moreover, this effect would favour a low-energy pathway for transfer in solution of the metal bonding from C(2)–C(3) to C(5)–C(6) *via* an 18-electron η^4 bonded duroquinone intermediate.

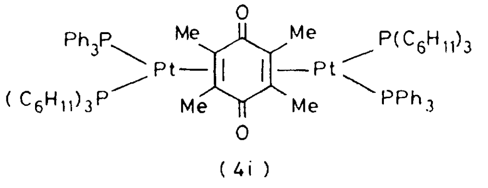
Mention was made earlier of the formation of an isomeric mixture in the reaction of the quinone (b) with $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$. This was most clearly demonstrated by the ^{31}P n.m.r. spectrum (Table 2). Whereas all the other complexes $[Pt(quinone)(C_2H_4)(PR_3)]$ showed the expected single resonance with ^{195}Pt–^{31}P satellite peaks, after mixing (b) with $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ two resonances are observed at δ 24.6 and 25.1 p.p.m. of relative intensity corresponding to a 6 : 4 mixture. Within a few minutes two additional resonances appear at δ 18.9 and 19.3 p.p.m. and after 24 h these are the only signals observed. Chromatography and fractional crystallisation failed to separate any of these species. The ^1H and ^{13}C n.m.r. spectra were very complicated, with many signals, and were not interpretable. We can advance no reason as to why the reaction with (b) proceeds differently from that of the other ligands.

Phenanthrene-9,10-quinone (k) reacts with $[Pt(C_2H_4)_2$-

$\{P(cyclo\text{-}C_6H_{11})_3\}]$ to give the compound (2k). This complex is formulated as a platinum(II) species with metal-oxygen bonds, as proposed for [Pt(phenanthrenequinone)(cod)].[1] In the ^{13}C n.m.r. spectrum of (2k) there are no resonances assignable to C=O groups, which in the spectrum of (k) occur at 180.1 p.p.m. All the compounds in Table 3 show resonances due to the oxygen-bonded carbon atoms only slightly shifted from those observed in the spectra of the free quinones.



(2k, R = C_6H_{11})



(4i)

Reaction of compound (2i) with PPh_3 affords the diplatinum compound (4i) as a single isomer, as inferred from the ^{31}P n.m.r. spectrum which showed only two resonances (Experimental section). The spectroscopic data do not establish whether the PPh_3 groups are *trans* as shown (4i) or *cis*. A related compound $[Pt_2(\mu\text{-}duroquinone)(PPh_3)_4]$ was first prepared [9] some years ago by reacting $[Pt(PPh_3)_3]$ with (i), and $[Pt\{\eta^4\text{-}C_6H_2O_2(Me_2\text{-}2,6)\}(cod)]$ reacts with PPh_3 to give a similar diplatinum complex.[1]

EXPERIMENTAL

The techniques used and instrumentation employed have been previously described.[1] The complexes $[Pt(C_2H_4)_2(PR_3)]$ were prepared as described elsewhere,[2,10] and the quinones were either commercially obtained or synthesised.[1]

Synthesis of the Complexes $[Pt(quinone)(C_2H_4)(PR_3)]$ (2a—2k).—All the compounds were prepared similarly by adding either a slight excess or a stoicheiometric amount of the quinone to the $[Pt(C_2H_4)_2(PR_3)]$ complex as a stirred suspension in diethyl ether at room temperature. The following syntheses are representative.

(*i*) 2,3,5,6-Tetramethylbenzo-1,4-quinone (180 mg, 1.1 mmol) was added portion-wise to a vigorously stirred suspension of $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ (531 mg, 1 mmol) in diethyl ether (20 cm^3), and the mixture was stirred for 30 min. The heavy yellow precipitate produced was removed from the mother-liquor and washed with light petroleum (10 cm^3). The washings were added to the mother-liquor and the solution was reduced in volume giving additional yellow solid. The combined yellow *microcrystals* of $[Pt(\eta^2\text{-}C_6Me_4O_2)(C_2H_4)\{P(cyclo\text{-}C_6H_{11})_3\}]$ (2i) (580 mg, 85%) were washed with light petroleum (3 × 10 cm^3).

(*ii*) Naphtho-1,4-quinone (158 mg, 1 mmol) was added to a stirred suspension of $[Pt(C_2H_4)_2(PPh_3)]$ (513 mg, 1 mmol) in diethyl ether (10 cm^3). Gas evolution was observed and a light yellow precipitate formed. Stirring was continued for 40 min, and solvent was then removed *in vacuo*. The residue was washed with light petroleum (4 × 5 cm^3) and dried *in vacuo* affording pale yellow *microcrystals of* $[Pt(\eta^2\text{-}C_{10}H_6O_2)(C_2H_4)(PPh_3)]$ (3 h) (611 mg, 95%).

Compounds (2g), (2i), and (2j) were recrystallised from toluene–hexane solutions. Complex (2k) was purified by chromatography on alumina, using toluene as eluant, with crystallisation at −78 °C.

Reaction of Compound (2i) *with Triphenylphosphine*.—Triphenylphosphine (66 mg, 0.25 mmol) was added to a solution of (2i) (167 mg, 0.25 mmol) in diethyl ether (20 cm^3). The yellow solution immediately turned orange. Solvent was removed *in vacuo* and the residue washed with light petroleum (2 × 10 cm^3) giving orange *microcrystals* of $[Pt_2(\mu\text{-}C_6Me_4O_2)(PPh_3)_2\{P(cyclo\text{-}C_6H_{11})_3\}_2]$ (4i) (175 mg, 85%), m.p. 128—134 °C (decomp.) (Found: C, 60.6; H, 6.9. $C_{82}H_{108}O_2P_4Pt_2$ requires C, 60.1; H, 6.6%); $\nu_{max.}$ (C=O), 1 592vs cm^{-1}; n.m.r. ($CDCl_3$), ^1H, τ 2.68 (m, 30 H, Ph), 7.84 [s, 6 H, Me, *J*(PH) 3, *J*(PtH) 16], 8.14 [s, 6 H, Me, *J*(PH) 4, *J*(PtH) 22 Hz], and 8.40—8.88 (m, 66 H, C_6H_{11}); ^{31}P, δ (p.p.m.) 26.6 [d, *J*(PP) 15, *J*(PtP) 3 699] and 23.9 [d, *J*(PP) 15, *J*(PtP) 3 630 Hz].

Crystal-structure Determination of $[Pt(\eta^2\text{-}C_6Me_4O_2)(C_2H_4)\text{-}\{P(cyclo\text{-}C_6H_{11})_3\}]$.—Crystals of (2i) grow from toluene as yellow plates; that for data collection was of dimensions 0.35 × 0.23 × 0.20 mm, and was sealed in a Lindemann glass capillary under nitrogen. Diffracted intensities were collected at 200 K on a Syntex $P2_1$ four-circle diffractometer.[11] Of the total of 6 807 intensities recorded in the range $2.9 \leqslant 2\theta \leqslant 55°$, 6 467 satisfied the criterion $I \geqslant 2\sigma(I)$ where $\sigma(I)$ is the standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure. Corrections were applied for Lorentz and polarisation effects and for *X*-ray absorption (numerical). Computations were carried out initially on the Syntex XTL system and later with the ' *X*-Ray ' system of programs [12] available for the CDC 7600 at the London Computing Centre.

Crystal data. $C_{30}H_{49}O_2PPt$, $M = 667.8$, Triclinic, $a = 9.818(3)$, $b = 10.489(3)$, $c = 14.486(3)$ Å, $\alpha = 97.27(2)$, $\beta = 97.93(2)$, $\gamma = 91.33(3)°$, $U = 1\,464.4$ Å^3, $D_m = 1.47$ (flotation), $Z = 2$, $D_c = 1.52$ g cm^{-3}, $F(000) = 676$, Mo-K_α *X*-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 49.7 cm^{-1}, space group $P\bar{1}$.

Structure solution and refinement. The platinum and phosphorus atoms were located by a Patterson synthesis, and all the remaining atoms (including hydrogen) by successive electron-density difference syntheses. The structure was refined by blocked-matrix least squares with anisotropic thermal parameters for all the non-hydrogen atoms. Refinement converged at *R* 0.027 (*R'* 0.033)* with a mean shift-to-error ratio in the last cycle of 0.1. A weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0015|F|^2]$, where $\sigma(F)$ is the estimated error in the observed structure factor based on counting statistics only, gave a satisfactory weight analysis with a maximum variation from the mean ($w|F_o - F_c|^2$) of 10%. The final electron-density difference synthesis showed no peaks >0.3 or < −0.3 e Å^{-3}. Scattering factors were from ref. 13 for C, O, and P, ref. 14 for H, and ref. 15 for Pt, including corrections for the effects of anomalous dispersion. The packing of the molecules in the unit

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* $R' = \Sigma[w^{\frac{1}{2}}(|F_o| - |F_c|)]/\Sigma w^{\frac{1}{2}}|F_o|$.

cell is shown in Figure 2. Atomic positional parameters are in Table 4, interatomic distances and angles in Table 5, and some least-squares planes in Table 6. Observed and calculated structure factors, all thermal parameters, and hydrogen-atom fractional co-ordinates are listed in Supplementary Publication No. SUP 22917 (32 pp.).*

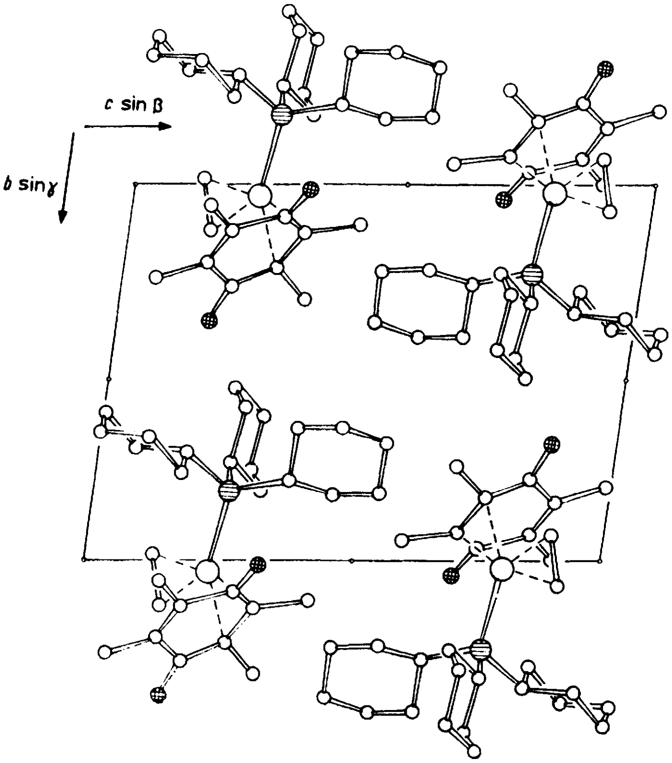

FIGURE 2 Contents of the triclinic unit cell seen in projection down *a* towards the origin

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

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