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

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A series of complexes $[Pt(\eta^2-quinone)(C_2H_4)\{P(cyclo-C_6H_{11})_3\}]$ has been prepared by treating $[Pt(C_2H_4)_2-\{P(cyclo-C_6H_{11})_3\}]$ 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 $[Pt(\eta^2-C_6Me_4O_2)(C_2H_4)\{P(cyclo-C_6H_{11})_3\}]$. Crystals are triclinic, space group $P\overline{1}$, 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 $\gamma = 91.33(3)^\circ$. The structure has been refined to R 0.027 (R' 0.033) for 6 467 independent reflections collected at 200 K for $2.9 \le 20 \le 55^\circ$ (Mo- $K_{\alpha}X$ -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

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-dit-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), ¹³C 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(C₂H₄)₂-(PR₃)],² in the expectation that a new type of platinumbenzo-1,4-quinone complex would be formed

RESULTS AND DISCUSSION

Addition of the quinone ligands (a)—(j) to a suspension of the compound $[Pt(C_2H_4)_2\{P(cyclo-C_6H_{11})_3\}]^2$ in diethyl ether afforded in good yield complexes $[Pt(quinone)-(C_2H_4)\{P(cyclo-C_6H_{11})_3\}]$ [(2a)—(2j)], characterised by microanalysis (Table 1), and by ¹H, ³¹P (Table 2), and ¹³C (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 ¹³C n.m.r. spectra of the compounds (Table 3) were very informative concerning the nature of the quinoneplatinum 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

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145 and 136 p.p.m. have no ¹⁹⁵Pt satellites confirming that the metal is not bonded to this CH=C(Me) group. In contrast, the other CH=C(Me) group gives rise to resonances at δ 69 p.p.m. (CMe) and 64 p.p.m. (CH),

> R^6 R^5 R^2 R^3 R (2a) Н н Н н C6H11 (25) Me Н Н C6H11 Н (2c) Me Me н Н C₆H₁₁ (2d) Me н Me н C6H11 (2e) Me H Н Me C 6H11 (2f) Bu^t н н Bu C6H11 (2g) Ph н Ph Н C₆H₁₁ (2h) СН CH Н н С₆Н₁₁ (2i) Me Me Me Me C 6H11 OMe (2j) н Н OMe C6H11 (3g) Ph н Ph н Ph (3h) СН Ph CH н н (3i) Me Me Me Ph Me

markedly shifted upfield from those in the free quinone and showing strong ¹⁹⁵Pt-¹³C 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 (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 C² and C⁶, and the C³ and C⁵ ring positions. Hence in the spectra of (2c), (2d), (2g), and (2h) the C₆H₁₁ rings show six resonances.

A further feature of the ¹³C 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 ethyleniccarbon atoms appear as one signal but with ¹⁹⁵Pt satellites. However, the ¹⁹⁵Pt-¹³C₂H₄ couplings in the spectra of (2c), (2d), (2g), and (2h) are smaller than the ¹⁹⁵Pt-¹³C (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 CH₂ 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 Xray 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 C₂F₄ ligand results in a lower barrier for C₂H₄ rotation than those found for the species [Pt- $(C_2H_4)_2(PR_3)$].² Similarly, in the $[Pt(quinone)(C_2H_4)-$

TABLE 1

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

Mne			u(C-O) d	Analysis (%)	
Compound b	$(\theta_c/^{\circ}C)$	Yield (%)	(cm^{-1})	c	H
(2a)	189-192	90	1 623 (sh), 1 610vs	51.6 (51.1)	6.7 (6.8)
(2b) °	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)	140146	85	1 619vs, 1 608vs	53.6 (54.0)	7.7 (7.3)
(2j) ^r	163 - 164	92	1 668s, 1 603s	50.3(50.1)	7.1 (6.8)
(2k) "		60	1 675w, 1 609m	57.1 (57.4)	6.8 (6.4)
(3g) A	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.

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 ¹³C spectrum of $[Pt\{\eta^4-C_6H_2O_2(Me_2-2,5)\}(cod)]$, the CMe and CH nuclei (δ 112 and 98 p.p.m.) have J(PtC) values of 40 and 50 Hz, respectively. (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.

An interesting feature of the ¹³C n.m.r. spectra of (2c),

The ¹³C n.m.r. spectra of the complexes (2e), (2f), (2i),

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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

atoms of a $CH=CBu^{t}$ group not bonded to platinum since in the spectrum of the free quinone these nuclei give resonances at δ 130.1 (CH) and 157.6 (CBu^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 CH

TABLE 2

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

			Phosph	orus-31 °
	Complex	Hydrogen-1 ^b	8	J(PtP)
(2a)	$[Pt(\eta^2 - C_6H_4O_2)(C_2H_4)\{P(C_6H_{11})_3\}]$	4.6-5.0 (m,br, 4 H, CH), 7.14 [s, 4 H, CH ₂ , <i>J</i> (PtH) 57], 8.0-8.8 (m, 33 H, C ₂ H ₁)	19.7	3 406
(2b)	$[Pt(\eta^2-C_6H_3O_2Me-2)(C_2H_4)\{P(C_6H_{11})_3\}]^{-d}$		24.6	3 502
			25.1	3 505
			19.3	$3 \ 415$
			19.8	3 412
(2c)	$[Pt\{\eta^2 - C_6H_2O_2(Me_2 - 2, 3)\}(C_2H_4)\{P(C_6H_{11})_3\}] \land$	5.70 [m, 1 H, CH, <i>f</i> (HH) 8, <i>f</i> (PH) 8, <i>f</i> (PtH) 54], 6.05 [m, 1 H, CH, <i>f</i> (HH) 8, <i>f</i> (PH) 3, <i>f</i> (PtH) 54], 6.94 [m, 2 H, CH ₂ , <i>N</i> (HH) 9.0, <i>f</i> (PtH) 56], 7.59 [m, 2 H, CH ₂ , <i>N</i> (HH) 10, <i>f</i> (PtH) 53], 7.5–9.0 (m, 33 H, C, H ₂) 8, 19 and 8, 23 (s, 6 H, Me)	24.5	3 508
(2d)	$[Pt\{\eta^2\text{-}C_6H_2O_2(\text{Me-}2,5)\}(C_2H_4)\{P(C_6H_{11})_3\}] \stackrel{\text{\tiny e}}{\to}$	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, $J(PtH)56], 7.45 [m, 2 H, CH2, N(HH) 8, J(PtH) 53],7.59.0 (m, 33 H, CH2), 8.20 8.26 (s, 3 H, Mc)$	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 ₆ H ₁₁), 8.23 (s, 6 H, Me)	24.7	3 413
(2f)	$[Pt\{\eta^2\text{-}C_6H_2O_2(But_2^-2,6)\}(C_2H_4)\{P(C_6H_{11})_3\}]$	4.96 [m, 2 H, CH, J (PtH) 23], 7.17 [s, 4 H, CH ₂ , J(PtH) 57], 7.558.9 (m, 33 H, C ₆ H ₁₁), 8.80 (s, 18 H, Bu [§])	22.8	3 373
(2g)	$[Pt\{\eta^{2}-C_{6}H_{2}O_{2}(Ph_{2}-2,5)\}(C_{2}H_{4})\{P(C_{6}H_{11})_{3}\}] \ $	2.4 – 2.9 (m, 10 H, Ph), 3.53 (s, 1 H, CH), 5.69 [d, 1 H, CH, f (PH) 3, f (PtH) 49], 6.93 [m, 2 H, CH ₂ , N(HH) 11, f (PtH) 56], 7.31 [m, 2 H, CH ₂ , N(HH) 11, f (PtH) 54], 7.56–8.95 (m, 33 H, C H)	23.9	3 512
(2h)	$[Pt(\eta^2 \text{-} C_{10}H_6O_2)(C_2H_4)\{P(C_6H_{11})_3\}] \prime$	$C_{6}^{(11_{11})}$ 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], 75–90 (m, 33 H, C.H.)	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, CH_2) 8 14 (s 6 H Me) 8 22 (s 6 H Me)	20.9	3569
(2j)	$[Pt\{\eta^2 - C_6H_2O_2[(OMc)_2 - 2, 6]\}(C_2H_4)\{P(C_6H_{11})_3\}]$	5.18 [s, 2 H, CH, J (PtH) 27], 6.43 (s, 6 H, OMe), 7.18 [s, 4 H, CH, J (PtH) 59], 7.45–8.8 (m, 33 H, C, H,)	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, $J(PtH)$ 59]	24.0	3 512
(3h)	$[\operatorname{Pt}(\eta^2\text{-}C_{10}H_6\mathrm{O}_2)(C_2H_4)(\operatorname{PPh}_3)]$	2.4-2.8 (m, 21 H, Ph and CH), 5.64 [s, 4 H, CH ₂ , $I(PtH)$ 56]	18.9	3 643
(3i)	$[\mathrm{Pt}(\eta^2\text{-}\mathrm{C_8Me_4O_2})(\mathrm{C_2H_4})(\mathrm{PPh_3})]$	2.7 (m, 15 H, Ph), 5.71 [s, 4 H, CH ₂ , <i>J</i> (PtH) 77], 7.79 [s, 6 H, Me, <i>J</i> (PtH) 19], 8.46 [d, 6 H, Me, <i>J</i> (PH) 2, <i>J</i> (PtH) 17]	29.1	3 883

^a Measured in $[{}^{2}H_{1}]$ 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% H₃PO₄ (external). ^d Isomeric mixture, see text. ^c N(AB) = |J(AB) + J(AB')| for an AA'BB' spin system of the co-ordinated C₂H₄.

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.

At room temperature, the ¹³C n.m.r. spectrum of (2f) (Table 3) did not show resonances due to the CH and CBu^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

(quinone) and CH_2 (C_2H_4) groups at τ 4.96 and 7.17, respectively, both with ¹⁹⁵Pt satellites, coalescence of the quinone CH peaks occurs at ca. -35 °C. At -100 °C (CCl₃F solution), the CH(quinone) protons give broad peaks at τ 4.10 and 6.26, only the latter showing ¹⁹⁵Pt-¹³C coupling (48 Hz). The $CH_2(C_2H_4)$ 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

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temperature (Table 2) the CH(quinone) protons give a resonance at τ 5.09. At -100 °C (CD₂Cl₂) the CH-(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 ¹³C n.m.r. measured at room temperature.

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.

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

TABLE 3

Carbon-13 n.m.r. data ^a for the complexes $[Pt(quinone)(C_2H_4)(PR_3)]$					
	Complex	86			
(2c)	$[Pt\{\eta^2-C_6H_2O_2(Me_2-2,3)\}(C_2H_4)\{P(C_6H_{11})_3\}]$	191 [C=O, J (PtC) 41], 189 [d, C=O, J (PC) 5, J (PtC) 35], 143, 142 (CMe), 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 ₆ H 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, H,) 12.9 [12.7 (Me)]			
(2d)	$[Pt\{\eta^2 - C_6H_2O_2(Mc_2 - 2, 5)\}(C_2H_4)\{P(C_6H_{11})_3\}]$	191 [C=O, J (PtC) 43], 187 [d, C=O, J (PC) 4, J (PtC) 35], 145 (CMe), 136 (CH), 69 [d, CMe, 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 ₆ H ₁), 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 ₆ H ₁), 18, 16 (Me)			
(2e)	$[Pt\{\eta^2 - C_6H_2O_2(Me - 2, 6)\}(C_2H_4)\{P(C_6H_{11})_3\}]$	191 (C=O), 190.5 (C=O), 99 [CH, J (PtC) 87], 54 [CH ₂ , J (PtC) 127], 34 [d, C(1)(C ₆ H ₁₁), J (PC) 23, J (PtC) 33], 30 [J (PtC) 18], 27.5 [d, J (PC) 11], 26.8 (C ₆ H ₁₁), 17 (Me)			
(2f)	$[Pt\{\eta^2\text{-}C_6H_2O_2(But_2^*\text{-}2,6)\}(C_2H_4)\{P(C_6H_{11})_3\}]$	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 (CMe ₃), 34 [d, C ¹ (C ₆ H ₁₁), J (PC) 23], 30.2 (Me), 30 [I (PtC) 18], 27.6 [d, J (PC) 11], 27 (C ₆ H ₁₁)			
(2g)	$[Pt\{\eta^2 - C_6H_2O_2(Ph_2 - 2, 5)\}(C_2H_4)\{P(C_6H_{11})_3\}]$	189 [C=O, f (PtC) 43], 184 [d, C=O, f (PC) 6, f (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), f(PC) 14, f (PtC) 170], 65 [d, CH, f (PC) 4, f (PtC) 200], 59 [CH ₂ , f(PtC) 116], 35 [d, C ¹ (C ₆ H ₁₁), f (PC) 23, f (PtC) 35], 30 [f (PtC) 15], 29 8 [f (PtC) 24] 27 4 [d, f (PC) 9] 27 [d, f (PtC) 11] 26 5 (C.H)			
(2h)	$[P_{4}(\eta^{2} - C_{10}H_{6}O_{2})(C_{2}H_{4})\{P(C_{6}H_{11})_{3}\}]$	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 ₆ H 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 ₆ H ₁₁)			
(2i)	$[Pt(\eta^2 - C_6 Mc_4 O_2)(C_2 H_4) \{ P(C_6 H_{11})_3 \}]$	188 [C=O, J(PtC) 50], 186 [d, C=O, J(PC) 5, J(PtC) 42], 105.6 [d, CMe, J(PC) 7, J(PtC) 68], 105.4 [CMe, J(PtC) 110], 56 [CH ₂ , J(PtC) 111], 35 [d, C ¹ (C ₆ H ₁₁), J(PC) 22, J(PtC) 33], 30 [J(PtC) 20], 27.4 [d, J(PC) 111 28 6 (C, H), 14 1 (Ma), 13 8 (Ma)			
(2j)	$[Pt\{\eta^2 - C_6H_2O_2[(OMe)_2 - 2, 6]\}(C_2H_4)\{P(C_6H_{11})_3\}]$	11, 26, C($_{6}$ (1,1), 14, (1,1), 15, (1,1), (2,1), (1,1)			
(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, CPh, J (PC) 15], 72 [CH, J (PtC) 125], 63 [CH ₂ , J (PtC) 117]			
(3h)	$[Pt(\eta^2 - C_{10}H_6O_2)(C_2H_4)(PPh_3)]$	184 [C=O, J(PtC) 35], 135–125 (Ph), 66 [CH, J(PtC) 171], 60 [CH ₂ , J(PtC)			
(3i)	$[Pt(7^2 - C_6 M c_4 O_2)(C_2 H_4)(PPh_3)]$	207 [C=O, $J(PtC)$ 31], 135—128 (Ph), 109 [CMe, $J(PtC)$ 35], 106 [CMe, $J(PtC)$ 35], 84 [CH ₂ , $J(PtC)$ 194], 14 (Me), 12 (Me)			

^a Measured in $[{}^{2}H_{1}]$ chloroform at room temperature. ^b Hydrogen-1 decoupled, chemical shifts in p.p.m. to high frequency of SiMe₄, coupling constants in Hz.

In contrast, the observation of 195 Pt $^{-13}$ C coupling of magnitude 171 Hz for the CH 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 lowenergy 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. 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 $[Pt(C_2H_4)(C_2F_4)]P(C_2C_6H_{11})_3]$,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

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TABLE 4

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

Atom	х	ν	Z
Pt	$0.087 \ 25(1)$	0.032[94(1)]	0.242.15(1)
P(1)	0.098(38(9))	-0.18284(8)	0.263.74(6)
Ethvlene			0.200 (1(0)
·(111)	-0.070.5(7)	0 192 1/6)	0 157 5(5)
S(111) E(1)	-0.0100(1)	0.1251(0) 0.126(7)	0.107 0(0)
H(9)	0.131(8)	0.130(7)	0.198(5) 0.194(5)
(1(-))	-0.042(0)	0.192(0)	0.134(3)
H(3)	-0.0337(3) 0.078(6)	-0.0100(3)	0.1555(4)
(1) (1)	-0.078(0)	-0.048(5)	0.000(4) 0.156(2)
(1(4)	-0.150(5)	-0.004(3)	0.156(5)
Cyclohexyl	groups		
2(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)	0.2084(4)	-0.2118(3)	0.3744(2)
C(202)	$0.266\ 3(5)$	-0.3464(4)	$0.376\ 7(3)$
C(203)	$0.363 \ 3(6)$	-0.3514(6)	0.467 4(4)
C(204)	$0.296\ 5(7)$	-0.3098(6)	$0.554 \ 8(4)$
C(205)	$0.238 \ 0(6)$	-0.177 9(5)	$0.552 \ 8(3)$
C(206)	$0.138 \ 4(4)$	-0.1745(4)	$0.461 \ 5(3)$
C(301)	-0.0749(4)	$-0.259\ 2(3)$	$0.259\ 2(2)$
C(302)	-0.168 9(4)	-0.1831(4)	0.3214(3)
2(303)	$-0.316 \ 3(4)$	-0.236 8(4)	0.298.6(3)
C(304)	-0.3244(5)	-0.380.6(5)	0.308.7(4)
2(305)	-0.229.9(5)	$-0.455\ 2(4)$	0.250.1(4)
C(306)	-0.0817(4)	$-0.401\ 2(4)$	$0.272\ 7(3)$
Juroquinor	ie		ζ,
$C(\mathbf{I})$	$0.214 \ 2(5)$	0.270.6(4)	0.209.5(3)
$\dot{\lambda}(\mathbf{I})$	0.158 9(4)	$0.365\ 6(3)$	0.180.0(3)
	0.1780(4)	0.220.5(3)	0.293 6(3)
2(21)	0.092.1(7)	0.307(3(5))	0.351.9(5)
$\overline{\mathcal{L}(3)}$	0.261.4(4)	0.126.9(3)	0.335.5(3)
(31)	0.275.2(7)	0.125 0(5)	0.441.1(3)
(4)	0.382.9(4)	0.084.3(4)	0.293.0(3)
(4)	0.468.9(3)	0.0010(1) 0.0171(3)	0.332.9(3)
(5)	0.404.9(4)	0.123 8(4)	0.199(7(3))
(51)	0.524.6(7)	0.064.1(8)	0.157 6(7)
(6)	0.3221(5)	0.0011(0)	0.160.2(3)
(6) (61)	0.338 9(9)	0.250 7(8)	0.100 2(5) 0.066 7/5)
(01)	0.000 2(8)	0.200 1(0)	0.000 7(0)

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			
$\begin{array}{c} Pt-P(1) \\ Pt-C(111) \\ Pt-C(112) \\ Pt-C(2) \\ Pt-C(3) \end{array}$	$\begin{array}{c} 2.326 \ 6(9) \\ 2.153(7) \\ 2.186(5) \\ 2.141(4) \\ 2.161(4) \end{array}$	C(111)-C(112) C(111)-H(1) C(111)-H(2) C(112)-H(3) C(112)-H(4)	$\begin{array}{c} 1.398(8)\\ 0.89(8)\\ 0.90(8)\\ 1.07(6)\\ 0.93(5) \end{array}$
Cyclohexyl groups P(1)-C(101) C(101)-C(102) C(102)-C(103) C(103)-C(104) C(104)-C(105) C(105)-C(106) C(106)-C(101)	$\begin{array}{c} 1.846(4) \\ 1.539(5) \\ 1.524(6) \\ 1.516(7) \\ 1.498(7) \\ 1.529(7) \\ 1.531(6) \end{array}$	$\begin{array}{c} P(1)-C(301)\\ C(301)-C(302)\\ C(302)-C(303)\\ C(303)-C(304)\\ C(304)-C(305)\\ C(304)-C(305)\\ C(306)-C(306)\\ C(306)-C(301) \end{array}$	$\begin{array}{c} 1.853(4)\\ 1.523(6)\\ 1.518(6)\\ 1.535(7)\\ 1.508(3)\\ 1.526(6)\\ 1.528(5)\end{array}$
$\begin{array}{l} P(1)-C(201)\\ C(201)-C(202)\\ C(202)-C(203)\\ C(203)-C(204)\\ C(204)-C(205)\\ C(205)-C(206)\\ C(206)-C(201) \end{array}$	$\begin{array}{c} 1.869(4) \\ 1.536(6) \\ 1.520(7) \\ 1.525(9) \\ 1.512(9) \\ 1.538(6) \\ 1.531(6) \end{array}$		
Duroquinone ligane C(1)-C(2) C(2)-C(3) C(2)-C(21) C(3)-C(31) C(3)-C(4) C(4)-C(5)	$\begin{array}{c} 1.470(7) \\ 1.432(6) \\ 1.514(8) \\ 1.521(6) \\ 1.469(6) \\ 1.505(7) \end{array}$	$\begin{array}{c} C(5)-C(6)\\ C(6)-C(61)\\ C(6)-C(1)\\ \end{array}$	$\begin{array}{c} 1.339(7) \\ 1.508(10) \\ 1.479(7) \\ 1.240(6) \\ 1.240(6) \end{array}$
C(5)-C(51) (b) Angles C(111)-Pt-C(112) H(3)-C(112)-C(111) H(4)-C(112)-C(111)	1.511(9) $37.6(2)$ $115(3)$ $129(3)$	H(1)-C(111)-C(112) H(2)-C(111)-C(112) H(1)-C(111)-H(2) H(3)-C(112)-H(4)	97(5) 142(5) 116(7) 109(4)
C(111,112)-Pt-P(1) C(2,3)-Pt-P(1) * C(111,112)-Pt-C(2, Cyclohexyl groups	(1) * 109.3(2) 124.0(1) (3) * 126.6(3)	C(2)-Pt-C(3)	38.9(1)
$\begin{array}{l} \mathrm{Pt-P(1)-C(101)}\\ \mathrm{Pt-P(1)-C(301)}\\ \mathrm{C(101)-P(1)-C(301)}\\ \mathrm{P(1)-C(101)-C(102)}\\ \mathrm{P(1)-C(101)-C(102)}\\ \mathrm{P(1)-C(101)-C(103)}\\ \mathrm{C(102)-C(103)-C(106)}\\ \mathrm{C(103)-C(104)-C(106)}\\ \mathrm{C(103)-C(106)-C(116)}\\ \mathrm{C(105)-C(106)-C(116)}\\ \mathrm{C(106)-C(101)-C(106)}\\ \mathrm{P(1)-C(301)-C(302)}\\ \mathrm{C(301)-C(302)-C(36)}\\ \mathrm{C(303)-C(306)-C(36)}\\ \mathrm{C(305)-C(306)-C(36)}\\ \end{array}$	$\begin{array}{c} 114.2(1)\\ 111.9(1)\\ 0 103.3(2)\\ 0 114.8(3)\\ 109.9(2)\\ 03)\\ 110.3(3)\\ 04)\\ 111.7(4)\\ 05)\\ 110.8(4)\\ 06)\\ 112.9(4)\\ 11)\\ 109.9(3)\\ 02)\\ 109.2(3)\\ 014.5(2)\\ 03)\\ 111.0(3)\\ 05)\\ 111.2(4)\\ 01)\\ 110.4(3)\\ \end{array}$	$\begin{array}{l} Pt-P(1)-C(201)\\ C(201)-P(1)-C(101)\\ C(201)-P(1)-C(301)\\ P(1)-C(201)-C(206)\\ P(1)-C(201)-C(202)\\ C(201)-C(202)-C(203)\\ C(202)-C(203)-C(204)\\ C(203)-C(204)-C(205)\\ C(205)-C(206)-C(206)\\ C(205)-C(206)-C(201)\\ C(205)-C(206)-C(201)\\ P(1)-C(301)-C(306)\\ C(302)-C(303)-C(306)\\ C(304)-C(305)-C(306)\\ C(306)-C(301)-C(302)\\ \end{array}$	$\begin{array}{c} 114.0(1)\\ 103.3(2)\\ 109.3(2)\\ 112.2(3)\\ 116.8(2)\\ 110.5(4)\\ 112.6(5)\\ 110.5(4)\\ 111.6(5)\\ 110.2(4)\\ 111.6(4)\\ 109.9(3)\\ 117.0(2)\\ 111.0(4)\\ 112.1(4)\\ 109.8(3) \end{array}$
Duroquinone ligand Pt-C(2)-C(3) Pt-C(2)-C(21) Pt-C(2)-C(1) C(1)-C(2)-C(21) C(3)-C(2)-C(21) C(3)-C(2)-C(21) C(2)-C(1)-C(3) C(2)-C(1)-C(6) C(2)-C(1)-O(1) C(6)-C(1)-O(1) C(1)-C(6)-C(5) C(1)-C(6)-C(61)	$1\\71.3(2)\\115.1(3)\\104.4(2)\\115.2(4)\\120.4(4)\\119.9(4)\\118.9(4)\\121.8(4)\\119.3(5)\\121.4(4)\\115.7(5)\\122.8(5)$	$\begin{array}{c} \mathrm{Pt-C(3)-C(2)}\\ \mathrm{Pt-C(3)-C(31)}\\ \mathrm{Pt-C(3)-C(4)}\\ \mathrm{C(4)-C(3)-C(31)}\\ \mathrm{C(2)-C(3)-C(31)}\\ \mathrm{C(2)-C(3)-C(4)}\\ \mathrm{C(3)-C(4)-C(5)}\\ \mathrm{C(3)-C(4)-C(5)}\\ \mathrm{C(3)-C(4)-C(5)}\\ \mathrm{C(4)-C(5)-C(6)}\\ \mathrm{C(4)-C(5)-C(51)}\\ \mathrm{C(6)-C(51)}\\ \mathrm{C(5)-C(51)} \end{array}$	$\begin{array}{c} 69.8(2)\\ 121.2(4)\\ 105.2(2)\\ 114.4(4)\\ 119.4(4)\\ 119.5(4)\\ 121.4(4)\\ 129.0(4)\\ 120.1(4)\\ 115.3(5)\\ 124.5(6)\end{array}$

* 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 metalcarbon distance in the latter case is attributable to the greater degree of metal-olefin back-bonding promoted by the two electron-donating PPh₃ groups. Indeed, this effect is probably responsible for significant asymmetry in the Pt-CH₂ separations observed in (2i). Thus C(111) which is *transoid* with respect to the P(cyclo-C₆H₁₁)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

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(4	5), C(6)		
	5.124x +	6.973y + 5	0.064z = 3	.966	
[C(1) 0.3	079, C(2) –	-0.030, C(3	-0.043	, C(4) 0.	.067, C(5)
-0.01	7, $C(6) = 0$	0.056, O(1)) 0.309, C	C(21) = 0.4	30, C(31)
0.549,	O(4) 0.241,	C(51) = 0.0	033, C(61)	-0.148]	
Plane (3): C	(21), C(2), C	(3), C(31)			
	7.135x +	6.820y = 0	0.389z = 2.	.630	
[C(21) -	0.014, C(2)	0.030, C(3)	-0.029, 0	C(31) 0.01	14]
Plane (4): C	(1), C(2), C(3), C(4)			
	4.579x +	6.867y + 6	0.102z = 4	118	
[C(5) - 0]	0.196, C(6) -	0.239, C(2	21) 0.561, 0	C(31) 0.69	92]
Plane (5): C	(1), C(6), C(61), C(5), C	(51), C(4)		•
1	5.428x + 7.	139v + 4.1	58z = 3.92	3	
[C(1) 0.0	43 C(6) 0	0.025 C(61)	-0.020.0	C(5) = 0.0	041. C(51)
0.038,	C(4) = 0.02	5, C(2) -0	161, C(3)	-0.203]	··· , , , ,
Plane (6) • * (T(11) = H(1)	C(112) H	(4)		
1 mile (0).	5 0582	9.780 + 0	084~ 0	815	
		2.100y + 0		.010	
Plane (7): * (C(111), H(2)	(112), H	.(3)		
	9.011x - 2	.289y + 3.4	440z = -0	0.364	
Plane (8): *	C(111), H(1), $H(2)$			
. ,	6.403x +	0.500v + 9	.324z = 1.	078	
Diana (0) . *	C(110) H(9) H (A)			
Plane (9). +	C(112), ri(a	(1, 11(4))	001. 0	070	
	7.098x =	0.241y + 0	0.021z = 0.021z	.078	
Dihedral ang	les (°)				
Plane	(1)	(3)	(4)	(5)	(6)
(2)	87.7	23.7	4.9	3.8	
(3) 1	11.1				
(4)	82.8	28.6			
(5)	91.3	8.7	8.7		
(6)	82.4				20.0
(7) 1	12.2				29.9



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 $[Pt(C_2H_4)-(C_2F_4)\{P(cyclo-C_6H_{11})_3\}]^3$ where the asymmetric $Pt-CH_2$ separations are 2.02(1) and 2.18(1) Å.

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 $H \cdot \cdot \cdot H$ contact is between hydrogen atoms on C(112) and C(302). However, with the relative uncertainty in the hydrogenatom 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-C₆H₁₁ 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 0.3and 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 C₆ 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 18electron η^4 bonded duroquinone intermediate.

Mention was made earlier of the formation of an isomeric mixture in the reaction of the quinone (b) with $[Pt(C_2H_4)_2{P(cyclo-C_6H_{11})_3}]$. This was most clearly demonstrated by the ³¹P n.m.r. spectrum (Table 2). Whereas all the other complexes $[Pt(quinone)(C_2H_4)-$ (PR₃)] showed the expected single resonance with ¹⁹⁵Pt-³¹P satellite peaks, after mixing (b) with $[Pt(C_2H_4)_2$ -{P(cyclo- 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 8 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 ¹³C 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-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(phenanthrene-quinone)(cod)].¹ In the ¹³C 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.

Reaction of compound (2i) with PPh₃ affords the diplatinum compound (4i) as a single isomer, as inferred from the ³¹P n.m.r. spectrum which showed only two resonances (Experimental section). The spectroscopic data do not establish whether the PPh₃ groups are *trans* as shown (4i) or *cis*. A related compound $[Pt_2(\mu-duroquinone)(PPh_3)_4]$ was first prepared ⁹ some years ago by reacting $[Pt(PPh_3)_3]$ with (i), and $[Pt_{\eta}^4-C_6H_2O_2(Me_2-2,6)](cod)]$ reacts with PPh₃ 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 $[Pt(C_2H_4)_2\{P(cyclo-C_6H_{11})_3\}]$ (531 mg, 1 mmol) in diethyl ether (20 cm³), 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 cm³). The washings were added to the mother-liquor and the solution was reduced in volume giving additional yellow solid. The combined yellow *microcrystals* of $[Pt(\eta^2-C_6M_4O_2)(C_2H_4)\{P(cyclo-C_6H_{11})_3\}]$ (2i) (580 mg, 85%) were washed with light petroleum (3 × 10 cm³).

(*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

dicthyl ether (10 cm³). 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 cm³) and dried *in vacuo* affording pale yellow *microcrystals of* [Pt(η^2 -C₁₀H₆O₂)(C₂H₄)(PPh₃)] (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 cm³). The yellow solution immediately turned orange. Solvent was removed *in vacuo* and the residue washed with light petroleum $(2 \times 10 \text{ cm}^3)$ giving orange *microcrystals* of $[Pt_2(\mu-C_6Me_4O_2)(PPh_3)_2\{P(cyclo-C_6H_{11})_3\}_2]$ (4i) (175 mg, 85%), m.p. 128—134 °C (decomp.) (Found: C, 60.6; H, 6.9. C₈₂H₁₀₈O₂P₄Pt₂ requires C, 60.1; H, 6.6%); $\nu_{\text{max},\cdot}$ (C=O), 1 592vs cm⁻¹; n.m.r. (CDCl₃), 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, C₆H₁₁); ³¹P, 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 $[Pt(\eta^2-C_6Me_4O_2)(C_2H_4) \{P(cyclo-C_6H_{11})_3\}$].—Crystals of (2i) grow from toluene as yellow plates; that for data collection was of dimensions $0.35 \times 0.23 \times 0.20$ 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 $2.9 \leq 2\theta \leq 55^{\circ}$, 6467 satisfied the criterion $I \geq$ $2\sigma(I)$ 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, $\alpha = 97.27(2)$. $\beta = 97.93(2)$, $\gamma = 91.33(3)^{\circ}$, U = 1.464.4 Å³, $D_m = 1.47$ (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, $\mu(Mo-K_{\alpha}) = 49.7$ cm⁻¹, space group PI.

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 $(w|F_0 F_{\rm c}|^2$) 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

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

cell is shown in Figure 2. Atomic positional parameters are in Table 4, interatomic distances and angles in Table 5, and

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

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.).*

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

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