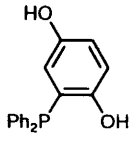
Palladium(II) 2-Diphenylphosphinohydroquinone (H_2pphq) Complexes: Preparation and Structures of a Novel Cluster, $[\{PdBr(Hpphq)\}_4]\cdot 2H_2O$, and a Phosphine–Phosphinite Complex, *cis*-$[PdBr_2\{C_6H_3(OH)$-1,PPh_2-3,PPh_2O-4$\}]\cdot 2H_2O$†

Seri Bima Sembiring, Stephen B. Colbran,* Donald. C. Craig and Marcia L. Scudder
Department of Inorganic and Nuclear Chemistry, University of New South Wales, Sydney, NSW 2052, Australia

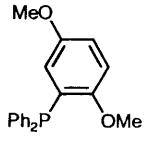
The complexes $[PdCl_2(PPh_3)L^2]$ (L^2 = 1,4-dimethoxy-2-diphenylphosphinobenzene), $[PdCl(bipy)L^2]^+$ (bipy = 2,2′-bipyridine) and $[PdCl_2(mpy)L^2]$ (mpy = 4-methylpyridine) have been prepared and their reactions with BBr_3 studied. The first two complexes afforded products resulting from protolytic cleavage of the phosphinohydroquinone ligand whereas reactions of the last with BBr_3 produced $[PdBr(mpy)(Hpphq$-*O*,*P*$)]$ (H_2pphq = H_2L^1 = 2-diphenylphosphinohydroquinone) when quenched with methanolic sodium carbonate or, when quenched with methanol alone, a mixture which contains the novel tetrameric cluster $[\{PdBr(HL^1)\}_4]$ and slowly deposits an unexpected phosphine–phosphinite complex, *cis*-$[PdBr_2\{C_6H_3(OH)$-1,PPh_2-3,PPh_2O-4$\}]\cdot H_2O$, on standing. The crystal structures of the last two complexes have been determined. The palladium tetramer was also formed when $[PdBr(mpy)(HL^1$-*O*,*P*$)]$ was treated with hydrobromic acid. The NMR spectra suggest that in solution the tetramer is in equilibrium with monomeric solvato complexes, $[PdBr(solv)(HL^1$-*O*,*P*$)]$ (solv = solvent).

Phosphinohydroquinones are intriguing ligands.[1–6] Nickel(II) complexes with a single *o*-*O*,*P*-chelated ligand, *e.g.*, $[NiPh(PPh_3)(Hpphq)]$ (H_2pphq = H_2L^1 = 2-diphenylphosphinohydroquinone) are efficient olefin oligomerisation catalysts.[1] Kaim and co-workers[2] have described 2,5-bis(diphenylphosphino)hydroquinone (H_2bpphq) and the diruthenium mixed-valent ion $[(bipy)_2Ru^{II}(bpphq)Ru^{III}(bipy)_2]^{3+}$ (bipy = 2,2′-bipyridine), in which the ruthenium atoms are bridged by the twice *O*,*P*-chelated hydroquinone dianion. Spectroelectrochemical investigations provided evidence for electronic delocalisation between the ruthenium centres, with the *p*-semiquinone tautomer of the bridging bpphq ligand being implicated in the mechanism of electronic coupling. We have recently described simple nickel(II), palladium(II) or platinum(II) complexes with two phosphinohydroquinone ligands[3–6] and have demonstrated that chelation (*o*-*O* and *P versus P* co-ordination) of these phosphine ligands can be reversibly controlled by adjustment of solution pH, chemistry also found for closely related *o*-phosphinophenol complexes.[7] However, the phosphinohydroquinone complexes are unique in that each ligand can also undergo chemically reversible, two-electron, two-proton oxidation to produce the corresponding *p*-phosphinoquinone complexes.[3] *p*-Quinones being poor nucleophiles are substitutionally labile ligands,[8] and thus complexes with phosphino-quinone or -hydroquinone ligands offer potential for electrochemical control of binding of the *o*-oxygen atom and, consequently, of the reactivity displayed by the metal centre.[3]

Our preliminary electrochemical studies of the complexes $[M(H_2L^1)X_2]$ (M = Pd or Pt; X = Cl, Br or I) and $[M(HL^1$-*O*,*P*$)_2]$ (M = Pd or Pt), each with two phosphinohydroquinone ligands, revealed complicated ligand-centred oxidation processes.[9] In order to simplify the electrochemistry,



H_2pphq, H_2L^1



L^2

we sought complexes with only a single such ligand. We had found that the preferred route to complexes of the type ML_2X_2 [M = Pd or Pt; L = H_2pphq or 2-diphenylphosphino-*p*-benzoquinone (ppq); X = Cl, Br or I] started with deprotection of the hydroquinone groups in the corresponding complex $[MCl_2(L^2)_2]$ [L^2 = $C_6H_3(OMe)_2$-1,4-PPh_2-2] using BBr_3 followed by methanol to destroy borate intermediates,[3,9,10] and so set out to prepare some palladium(II) complexes with a single $C_6H_3(OMe)_2(PPh_2)$ ligand for investigation of deprotection reactions with BBr_3.

Results and Discussion

The following three palladium(II) complexes were targeted: $[PdCl_2(mpy)L^2]$ (mpy = 4-methylpyridine), $[PdCl(bipy)L^2]^+$ and $[PdCl_2(PPh_3)L^2]$. Straightforward adaptations of established preparative routes to triphenylphosphine analogues were used to obtain them. Thus, following precedents set by Chatt and Vernazi,[11] and by Shaw and co-workers,[12] yellow-orange *trans*-$[PdCl_2(mpy)L^2]$ was obtained from mpy and $[PdCl_2(\mu\text{-}Cl)(L^2)_2]$ {available directly from $[PdCl_2(PhCN)_2]$ with equimolar amounts of L^2}. Dixon and co-workers[13] first reported the interesting complex ions $[PtL(PPh_3)_2X]^+$ (L = bipy or 1,10-phenanthroline, X = halide), which unusually have a monodentate heterocyclic ligand and a four-co-ordinate platinum centre, and their thermal conversion into the stable cations $[PtL(PPh_3)X]^+$. We found that direct reactions of $[Pd(bipy)Cl_2]$ with L^2 and an excess of ammonium hexafluorophosphate in boiling acetone–methanol (1:1) for 1 h gave

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.
Non-SI unit employed: mmHg ≈ 133 Pa.

yellow-orange $[PdCl(bipy)L^2][PF_6]$ in excellent yield (91%). Alternatively, *trans*-$[PdCl_2(L^2)_2]$, 2,2′-bipyridine and an excess of ammonium hexafluorophosphate in boiling acetone produced only a moderate yield (40%) even after 48 h. Nelson and co-workers[14] have demonstrated that phosphine-ligand redistribution reactions of palladium(II) phosphine complexes provide an excellent, high-yield route to palladium(II) 'mixed-phosphine' complexes [equation (1)]. We therefore expected

$$[Pd(PR_3)_2X_2] + [Pd(PR'_3)_2X_2] \longrightarrow 2[Pd(PR_3)(PR'_3)X_2] \quad (1)$$

that $[PdCl_2(PPh_3)L^2]$ would be directly available from reactions of a source of palladium(II) with an equivalent of each phosphine. However, reaction of an equimolar mixture of the phosphines, with *trans*-$[PdCl_2(PhCN)_2]$ in dichloromethane gave a 3:1:1 mixture of the 'mixed-phosphine' complex and $[PdCl_2(L^2)_2]$ and $[PdCl_2(PPh_3)_2]$. The composition of dichloromethane solutions of this mixture as ascertained by ^{31}P-$\{^1H\}$ NMR spectroscopy (see below) did not change on standing overnight.

The L^2 complexes were characterised by elemental analyses, and infrared, ^1H and ^{31}P-$\{^1H\}$ NMR spectroscopies. Full data are given in the Experimental section and are unexceptional and thus only a few brief comments will be made here. All elemental analyses were consistent with the given formulations. Infrared spectra showed two C–OMe stretching bands at *ca.* 1280 and 1230 cm^{-1}. The ^1H NMR spectrum of $[PdCl(bipy)L^2]^+$ was assigned with the aid of ^1H–^1H double quantum filtered correlation spectroscopy (DQF-COSY) and the ^1H NMR spectrum of $[PdCl_2(mpy)L^2]$ was readily assigned. Most revealing were the multiplets for the *o*-protons of the mpy ligand (H^2) which appeared at δ 8.80 as a 'filled-in' doublet of doublets because of virtual coupling to phosphorus, indicating *trans* phosphine and mpy ligands.[11] Minor peaks for a second species and for trace free mpy (≈5% from integrated peak intensities) were observed consistent with limited dissociation of mpy possibly to give *cis*-$[PdCl_2(L^2)]$ with an *O,P*-chelating ligand. The ^1H NMR spectrum of the 3:1:1 mixture of $[PdCl_2(PPh_3)L^2]$ and $[PdCl_2(L^2)_2]$ and $[PdCl_2(PPh_3)_2]$ showed easily assigned peaks for all three species. Fig. 1 shows the ^{31}P-$\{^1H\}$ NMR spectrum of the mixture with peaks at δ 23.36 and 16.30 for *trans*-$[PdCl_2(PPh_3)_2]$ and *trans*-$[PdCl_2(L^2)_2]$ respectively, and two AB doublets at δ 24.27 and 15.41 with $^2J(P–P)$ = 580 Hz for *trans*-$[PdCl_2(PPh_3)L^2]$ {for square-planar $[Pd(PR_3)(PR'_3)X_2]$ (PR_3 = phosphine, X = halide or pseudohalide) complexes typically $^2J(P–P)(cis)$ < 80 Hz whereas $^2J(P–P)(trans)$ > 500 Hz}.[15] The integrated peak intensities in the ^{31}P-$\{^1H\}$ NMR spectrum concur with the 3:1:1 ratio for the complexes.

Treatment of $[PdCl(bipy)L^2]^+$ or mixtures containing $[PdCl_2(PPh_3)L^2]$ with BBr_3 in dry dichloromethane followed by methanol to destroy the borate intermediates afforded good yields of $[PdBr_2(bipy)]$ (72%) or $[Pd(\mu\text{-}Br)_2Br_2(PPh_3)_2]$ (76%), respectively. In each reaction the phosphinohydroquinone ligand was lost. Its fate was not determined, but we note that H_2pphq (H_2L^1) is a strong Brönsted base; it has only been isolated as the hydrobromide, H_2L^1·HBr, which survives multiple recrystallisations.[3,7,9,16] This leads to a plausible explanation for the selective loss of the phosphinohydroquinone in these two reactions: the targeted complexes $[PdBr(bipy)(H_2L^1)]$ and $[PdBr_2(PPh_3)(H_2L^1)]$ form[17] but under the acidic conditions created when methanol is added (*e.g.* $ROBBr_2 + 3MeOH \longrightarrow ROH + B(OMe)_3 + 2HBr$) protolytic cleavage of the bulky, more labile and more basic H_2L^1 ligand occurs. It appears that protolytic-cleavage reactions may restrict the range of conditions under which phosphinohydroquinone complexes are stable.

Attempted deprotection of *trans*-$[PdBr_2(mpy)L^2]$ with BBr^3, followed by removal of all volatiles and a methanol quench to destroy borate intermediates, produced an orange powder. The ^1H NMR spectrum of the powder in $(CD_3)_2CO$ was complex and showed at least two components, the principal one giving sharp multiplets and the lesser broad peaks (see Fig. 2), the chemical shifts of which varied between samples from different preparations, possibly due to varying water content or sample acidity. Clearly a mixture had been isolated. The ^{31}P-$\{^1H\}$ NMR spectrum showed a broad singlet at *ca.* δ 50.5 and a second, more intense and sharp singlet at δ 46.32. As described in detail below, the principal component has been identified as the tetramer $[\{PdBr(HL^1)\}_4]$. The mpy ligand of the starting complex had been lost, most probably as the hydrobromide, mpy·HBr, from protolytic cleavage under the acidic conditions of the methanol quench (see below).

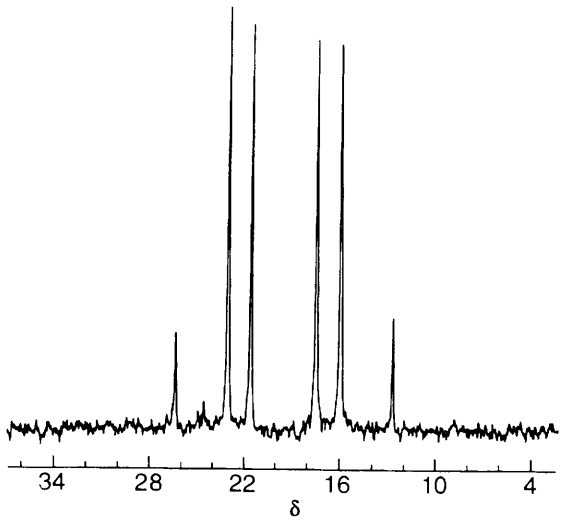


Fig. 1 The 121.49 MHz ^{31}P-$\{^1H\}$ NMR spectrum of the 3:1:1 mixture of $[PdCl_2(PPh_3)L^2]$, $[PdCl_2(PPh_3)_2]$ and $[PdCl_2(L^2)_2]$ in $CDCl_3$ solution

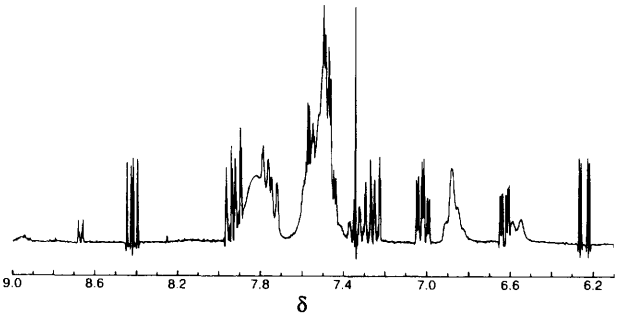
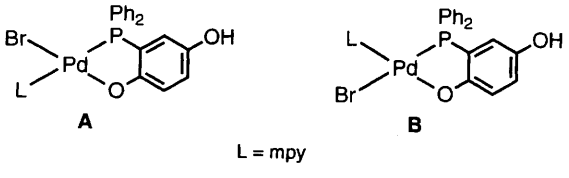


Fig. 2 The 300 MHz ^1H NMR spectrum of the crude product following treatment of *trans*-$[PdBr_2(mpy)L^2]$ with boron tribromide, removal of all volatiles, methanol quenching and precipitation with water; solvent $(CD_3)_2CO$

An attempt was made to quench the reaction of *trans*-$[PdBr(mpy)(H_2L^1)]$ with BBr_3 using basic conditions in order to ascertain whether or not the mpy ligand would be retained in the product(s). We had previously demonstrated that the complexes *trans*-$[MX_2(L^2)_2]$ (M = Pd or Pt, X = Cl or Br) are cleanly converted into the *O,P*-chelated phosphinohydroquinone complexes *cis*-$[M(HL^1\text{-}O,P)_2]$ when treated with BBr_3 followed by methanolic sodium carbonate.[3] In accord with expectations raised by these precedents, reaction of *trans*-$[PdBr(mpy)L^2]$ with BBr_3 followed by treatment with methanolic sodium carbonate gave yellow microcrystalline $[PdBr(mpy)(HL^1\text{-}O,P)]$ in 95% yield. This complex was readily soluble in dimethyl sulfoxide (dmso) and dimethylformamide and an elemental analysis agreed with its formulation. The infrared spectrum showed a broad hydroxy stretching band at 3200 cm^{-1}. Two singlets at δ 44.44 and 42.09 with a *ca.* 3:1

integrated peak-intensity ratio were observed in the $^{31}P-\{^1H\}$ NMR spectrum and the ^1H NMR spectrum revealed peaks for two species both with mpy and phosphinohydroquinone ligands. These observations are in accord with the two solution species being the two geometrical isomers of [PdBr(mpy)-(HL^1-*O*,*P*)], **A** and **B**. The solvato complex [PdBr{$(CD_3)_2SO$}-(HL^1-*O*,*P*)] arising from substitution of the mpy ligand, can be discounted; it is described below and shows different NMR parameters.

In order to confirm that the mpy ligand is lost from *trans*-[PdBr(mpy)(HL^1)] under acidic conditions, the complex was suspended in acetone and 48% aqueous hydrobromic acid slowly added until all solid dissolved. Addition of water at this point caused precipitation of an orange powder. The powder revealed the same ^1H and $^{31}P-\{^1H\}$ NMR spectra as those of the product obtained when *trans*-[$PdBr_2$(mpy)L^2] was treated with BBr_3, all volatiles removed, and the residue treated with methanol (see above). The orange powder was recrystallised from acetone–dichloromethane in air over a period of several weeks. The solution slowly darkened and produced a mixture of red rhombs, yellow needles and colourless crystals which were separated manually under a microscope. The yellow crystals were identified as 4-methylpyridine hydrobromide from comparison of their ^1H NMR spectral properties with those of an authentic sample. The red crystals gave an elemental analysis which suggested a 1:1:1:2 ratio for Pd, Br, H_2L^1 and 'extra' oxygen (O). The NMR properties of the compound are described below, but importantly the ^1H and $^{31}P-\{^1H\}$ spectra of the red crystals and of the orange powder from which they were obtained were almost identical. This suggests that the crystals represent the major product from the reactions of *trans*-[PdBr(mpy)(HL^1-*O*,*P*)] with aqueous hydrobromic acid, and of *trans*-[$PdBr_2$(mpy)L^2] with BBr_3 followed by methanol.



A single-crystal structure analysis was therefore undertaken on the red crystals unambiguously to establish the molecular identity and structure. It revealed that the novel cluster [{PdBr(HL^1)}$_4$], had been obtained and that it crystallised in the space group $P2_1/c$ with four molecules of tetramer and eight molecules of lattice water in the unit cell. The lattice water molecules were found to be well positioned for hydrogen bonding with the terminal *m*-hydroxyl groups and each other. Fig. 3 shows a view of the tetramer together with the atomic numbering scheme. Bond length and angle data and atomic parameters are given in Tables 1 and 2, respectively.

The tetramer consists of four 'PdBr(HL^1-*O*,*P*)' molecular fragments joined by bridging hydroquinone oxygen atoms to form a distorted cubic Pd_4O_4 core. The four fragments are similar and the tetramer exhibits approximate C_2 symmetry. Each palladium atom displays a distorted square-planar geometry and is co-ordinated by an *O*,*P*-chelated HL^1 ligand (average bite angle O–Pd–P 86.4°), the hydroquinone oxygen atom of an adjacent fragment and by one terminal bromide ligand. The Pd–P distances [2.166(6)–2.190(6) Å] are slightly shorter than those [2.227(1) Å] in [$Pd(HL^1-O,P)_2$]·H_2O·

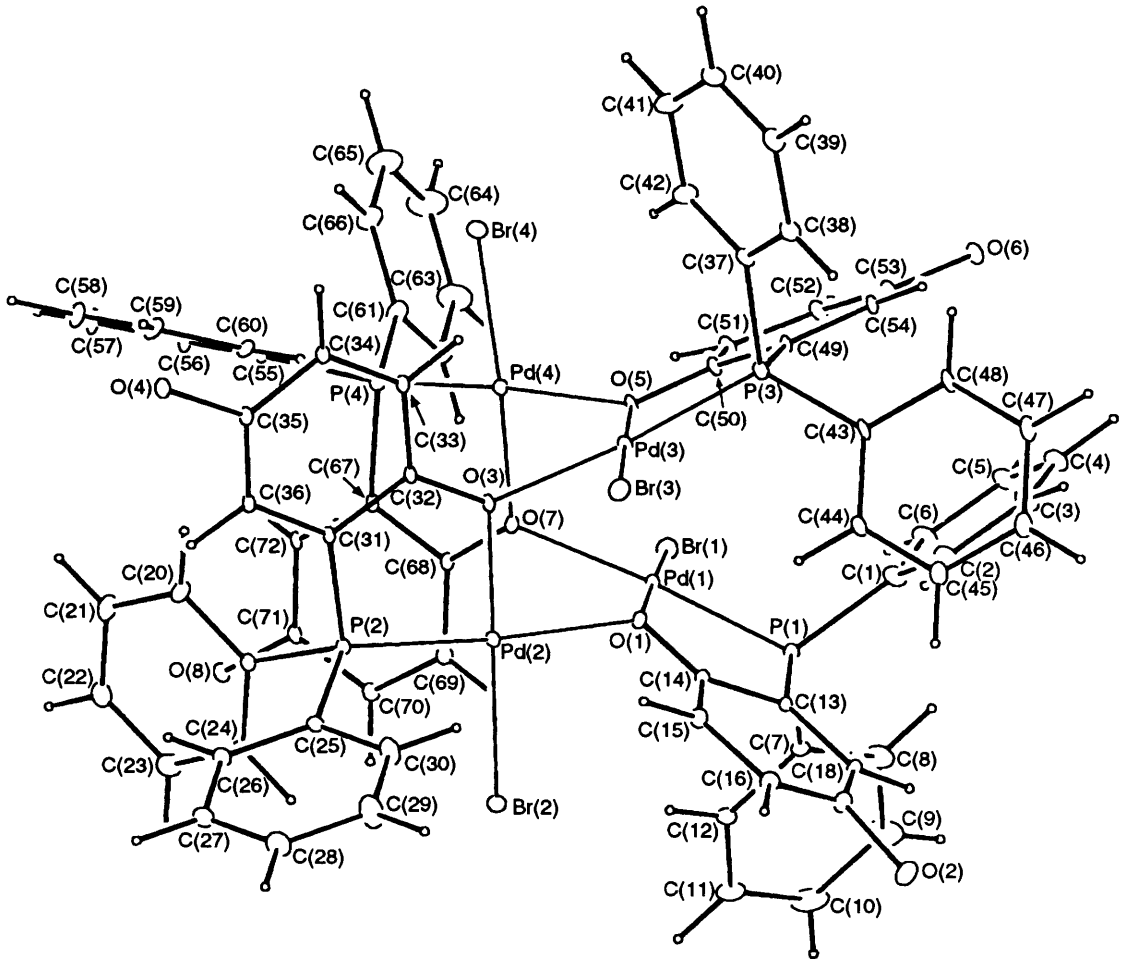
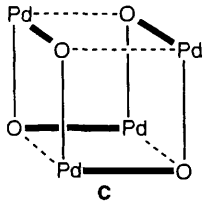


Fig. 3 An ORTEP diagram (20% thermal ellipsoids) showing the molecular structure of [{PdBr(HL^1)}$_4$] and the atom labelling scheme adopted

Table 1 Selected bond lengths (Å) and angles (°) for $[\{PdBr(HL^1)\}_4]\cdot 2H_2O$ with estimated standard deviations (e.s.d.s) in parentheses

Pd(1)–Br(1)	2.404(3)	Pd(3)–Br(3)	2.394(3)	P(1)–C(13)	1.826(19)	P(3)–C(49)	1.816(20)
Pd(2)–Br(2)	2.404(3)	Pd(4)–Br(4)	2.395(3)	P(2)–C(19)	1.794(6)	P(4)–C(55)	1.796(6)
Pd(1)–P(1)	2.170(6)	Pd(3)–P(3)	2.177(6)	P(2)–C(25)	1.793(6)	P(4)–C(61)	1.797(6)
Pd(2)–P(2)	2.190(6)	Pd(4)–P(4)	2.166(6)	P(2)–C(31)	1.770(20)	P(4)–C(67)	1.806(20)
Pd(1)–O(1)	2.055(13)	Pd(3)–O(3)	2.138(13)	O(1)–C(14)	1.319(20)	O(5)–C(50)	1.353(21)
Pd(1)–O(7)	2.128(13)	Pd(3)–O(5)	2.025(13)	O(2)–C(17)	1.431(23)	O(6)–C(53)	1.399(22)
Pd(2)–O(1)	2.135(12)	Pd(4)–O(5)	2.134(13)	O(3)–C(32)	1.317(20)	O(7)–C(68)	1.327(21)
Pd(2)–O(3)	2.039(13)	Pd(4)–O(7)	2.060(13)	O(4)–C(35)	1.400(22)	O(8)–C(71)	1.374(23)
P(1)–C(1)	1.795(6)	P(3)–C(37)	1.794(6)	Pd(1)···Pd(2)	3.460(2)	Pd(2)···Pd(3)	3.508(2)
P(1)–C(7)	1.794(6)	P(3)–C(43)	1.796(6)	Pd(1)···Pd(4)	3.578(2)	Pd(3)···Pd(4)	3.555(2)
Pd(2)–Pd(1)–Pd(4)	70.9(1)	Pd(2)–Pd(3)–Pd(4)	70.6(1)	Pd(1)–P(1)–C(7)	112.5(5)	Pd(3)–P(3)–C(43)	120.1(6)
Br(1)–Pd(1)–P(1)	92.4(2)	Br(3)–Pd(3)–P(3)	93.3(2)	Pd(2)–P(2)–C(31)	101.3(7)	Pd(4)–P(4)–C(67)	99.6(7)
Br(1)–Pd(1)–O(1)	177.0(4)	Br(3)–Pd(3)–O(3)	93.5(4)	Pd(2)–P(2)–C(19)	121.5(3)	Pd(4)–P(4)–C(55)	121.3(6)
Br(1)–Pd(1)–O(7)	90.8(4)	Br(3)–Pd(3)–O(5)	179.1(4)	Pd(2)–P(2)–C(25)	116.8(6)	Pd(4)–P(4)–C(61)	113.5(3)
P(1)–Pd(1)–O(1)	86.6(4)	P(3)–Pd(3)–O(3)	172.4(4)	C(13)–P(1)–C(1)	107.8(8)	C(49)–P(3)–C(37)	104.6(8)
P(1)–Pd(1)–O(7)	175.7(4)	P(3)–Pd(3)–O(5)	85.9(4)	C(13)–P(1)–C(7)	106.6(7)	C(49)–P(3)–C(43)	106.8(7)
O(1)–Pd(1)–O(7)	90.1(5)	O(3)–Pd(3)–O(5)	87.4(5)	C(1)–P(1)–C(7)	111.9(7)	C(37)–P(3)–C(43)	112.3(7)
Pd(1)–Pd(2)–Pd(3)	72.7(1)	Pd(1)–Pd(4)–Pd(3)	70.7(1)	C(31)–P(2)–C(19)	108.0(8)	C(67)–P(4)–C(55)	104.5(7)
Br(2)–Pd(2)–P(2)	93.4(2)	Br(4)–Pd(4)–P(4)	93.0(2)	C(31)–P(2)–C(25)	100.9(7)	C(67)–P(4)–C(61)	108.5(8)
Br(2)–Pd(2)–O(1)	92.0(4)	Br(4)–Pd(4)–O(5)	94.1(4)	C(19)–P(2)–C(25)	105.9(6)	C(55)–P(4)–C(61)	108.0(6)
Br(2)–Pd(2)–O(3)	177.7(4)	Br(4)–Pd(4)–O(7)	175.9(4)	Pd(1)–O(1)–Pd(2)	111.3(6)	Pd(3)–O(5)–Pd(4)	117.5(6)
P(2)–Pd(2)–O(1)	174.5(4)	P(4)–Pd(4)–O(5)	170.8(4)	Pd(1)–O(1)–C(14)	117.3(12)	Pd(3)–O(5)–C(50)	117.6(12)
P(2)–Pd(2)–O(3)	85.4(4)	P(4)–Pd(4)–O(7)	86.2(4)	Pd(2)–O(1)–C(14)	117.5(11)	Pd(4)–O(5)–C(50)	122.1(12)
O(1)–Pd(2)–O(3)	89.1(5)	O(5)–Pd(4)–O(7)	87.0(5)	Pd(2)–O(3)–Pd(3)	114.2(6)	Pd(1)–O(7)–Pd(4)	117.4(6)
Pd(1)–P(1)–C(13)	100.1(6)	Pd(3)–P(3)–C(49)	99.3(7)	Pd(2)–O(3)–C(32)	118.7(12)	Pd(1)–O(7)–C(68)	118.0(13)
Pd(1)–P(1)–C(1)	116.8(3)	Pd(3)–P(3)–C(37)	111.5(4)	Pd(3)–O(3)–C(32)	120.4(12)	Pd(4)–O(7)–C(68)	119.2(13)
Hydrogen bonds							
O(W1)···O(2)	2.897(19)	O(W2)···O(6)	2.982(21)	O(W1)···O(8)[a]	2.641(20)	O(W1)···O(W2)[b]	2.763(25)

[a] $1-x, -y, -z$. [b] $x, \frac{1}{2}-y, -\frac{1}{2}+z$.



C

2dmso,[9] and the Pd–Br distances [2.394(3)–2.404(3) Å] are comparable with those [2.435(1) Å] in $[PdBr_2(ppq)_2]\cdot Me_2CO$.[3] The Pd–O–Pd angles [111.3(6)–117.5(6)°] fall within the range of M–O–M angles in other alkoxide or phenoxide oxygen-atom bridged structures.[18] The two phenyl groups of each HL^1 ligand are inequivalent in the tetramer; one phenyl ring eclipses the chelating hydroquinone ring of the adjacent phosphine ligand while the other lies directed away from the cluster core.

The different Pd–O(bridge) bonds have different lengths: those within each 'PdBr(HL^1)' fragment [2.025(13)–2.060(13) Å] are shorter than those between different fragments [2.128(12)–2.138(12) Å].* These compare with the Pd–O bond lengths of 2.055(2) Å in $[Pd(HL^1\text{-}O,P)_2]\cdot H_2O\cdot 2dmso$.[9] The long Pd–O distances [Pd(1)···O(5), Pd(2)···O(7), Pd(3)···O(1) and Pd(4)···O(3)] within the distorted cube lie in the range 3.46–3.56 Å. Although sufficiently long to be considered 'non-bonding', these Pd···O interactions may be weakly attractive in nature and perhaps stabilise the overall tetrameric structure.[4,19] A schematic representation of the Pd_4O_4 core is shown in **C**, with the arrangement of the three discrete sets of Pd-to-O distances (heavy lines for the shorter Pd–O bonds, plain lines for the longer Pd–O bonds, and dashed lines for the longer Pd···O distances). The two pairs of opposite 'PdBr(HL^1)' fragments are not parallel in the structure but splayed. The Pd_4O_4 core structure resembles that recently found in the cluster tetrakis[(*R*)-*N*-α-methylbenzylsalicylideneaminato]tetrapalladium(II)[20] isolated when bis[(*R*)-*N*-α-methylbenzylsalicylideneaminato-*N*,*O*]palladium(II) was treated with acetic acid. In contrast, the latter complex and strong mineral acids (HX) are reported to produce *trans*-$[PdLX_2]$ (L = salicylideneaminate).[21] Protolytic loss of one ligand, followed by orthopalladation and aggregation of the resulting monomeric fragments, was suggested as a mechanism for formation of the tetrakis(salicylideneaminato)tetrapalladium cluster. Similarly, $[\{PdBr(HL^1)\}_4]$ is perhaps formed by protolytic loss of mpy from *trans*-[PdBr(mpy)(HL^1-*O*,*P*)] followed by aggregation of the resulting 'PdBr(HL^1)' monomeric fragments.

The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the red crystals of $[\{PdBr(HL^1)\}_4]\cdot 2H_2O$ in $(CD_3)_2CO$ (the least polar and poorest donor solvent in which the crystals dissolved) showed a broad singlet at δ 50.50 and a sharp singlet at δ 46.30 in a 1:3 ratio. Clearly there are two and perhaps more species in solution, with the broadness of the δ 50.50 peak suggestive of one or more species undergoing an exchange process. The ^1H NMR spectrum in $(CD_3)_2CO$ showed sharp peaks for a major species and a simpler set of broad peaks for a minor species. It was assigned using a ^1H–^1H DQF-COSY NMR spectrum, Fig. 4. The spectrum of the predominant species shows three multiplets for the three hydroquinone ring protons and two sets of multiplets for two inequivalent phenyl groups. The two HL^1 phenyl substituents are inequivalent in the tetramer but dimers such as $[\{PdBr(HL^1)\}_2]$ or $[\{Pd(\mu\text{-}Br)(HL^1)\}_2]$ would also have inequivalent phosphine phenyl groups provided they were hinged at the bridging atoms.[22] An isopiestic molecular-weight measurement of an acetone

* A referee suggested that since a phosphine is a ligand of high and a bromide one of low *trans* influence the difference in Pd–O distances in the tetramer is more or less as expected. We however suggest caution in concluding that the relative *trans* influences of the coligands result in the two sets of Pd–O distances in the tetramer: the shorter distances arise with transoid Br and O but are comparable to the distances in *cis*-$[Pd(HL^1)_2]\cdot 2H_2O$ which are 2.055(2) Å with O and P transoid.[9]

Table 2 Atomic parameters for $[\{PdBr(HL^1)\}_4]\cdot 2H_2O$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd(1)	0.5784(1)	0.1899(1)	0.1748(1)	C(28)	0.7891(11)	0.2177(10)	−0.0757(4)
Pd(2)	0.6909(1)	0.2092(1)	0.1025(1)	C(29)	0.7372(11)	0.2563(10)	−0.0596(6)
Pd(3)	0.7052(1)	0.3801(1)	0.1716(1)	C(30)	0.7411(9)	0.2423(9)	−0.0077(6)
Pd(4)	0.7864(1)	0.2324(1)	0.2711(1)	C(31)	0.8715(12)	0.2431(11)	0.1358(8)
Br(1)	0.5581(2)	0.1129(1)	0.2405(1)	C(32)	0.8420(12)	0.2934(11)	0.1649(8)
Br(2)	0.6025(2)	0.1210(2)	0.0335(1)	C(33)	0.8985(13)	0.3477(12)	0.1994(9)
Br(3)	0.7126(2)	0.4538(2)	0.0999(1)	C(34)	0.9757(13)	0.3559(12)	0.2061(9)
Br(4)	0.8873(2)	0.3162(2)	0.3361(1)	C(35)	1.0015(13)	0.3072(13)	0.1759(9)
P(1)	0.4494(3)	0.2193(3)	0.1306(2)	C(36)	0.9511(12)	0.2523(12)	0.1425(9)
P(2)	0.7993(4)	0.1743(3)	0.0946(2)	C(37)	0.7230(7)	0.5394(7)	0.2384(5)
P(3)	0.6487(3)	0.4706(3)	0.1961(2)	C(38)	0.7180(8)	0.6154(9)	0.2238(5)
P(4)	0.8602(3)	0.1335(3)	0.3089(2)	C(39)	0.7781(11)	0.6657(6)	0.2587(8)
O(1)	0.5925(8)	0.2516(7)	0.1155(5)	C(40)	0.8432(8)	0.6402(10)	0.3082(7)
O(2)	0.3070(10)	0.3371(10)	−0.0694(6)	C(41)	0.8481(8)	0.5641(11)	0.3227(5)
O(3)	0.7670(8)	0.2860(7)	0.1586(5)	C(42)	0.7880(10)	0.5138(7)	0.2878(7)
O(4)	1.0807(9)	0.3134(8)	0.1813(6)	C(43)	0.5551(4)	0.5130(7)	0.1456(5)
O(5)	0.6976(8)	0.3189(7)	0.2322(5)	C(44)	0.5144(8)	0.4821(6)	0.0922(6)
O(6)	0.5109(9)	0.4354(9)	0.3267(6)	C(45)	0.4414(8)	0.5144(9)	0.0526(4)
O(7)	0.7046(8)	0.1600(8)	0.2122(6)	C(46)	0.4093(6)	0.5776(9)	0.0663(6)
O(8)	0.8024(9)	−0.1350(8)	0.2193(6)	C(47)	0.4501(9)	0.6085(7)	0.1197(7)
C(1)	0.4127(4)	0.2860(7)	0.1638(5)	C(48)	0.5230(8)	0.5762(8)	0.1594(5)
C(2)	0.3997(9)	0.3608(8)	0.1458(5)	C(49)	0.6241(12)	0.4193(11)	0.2446(8)
C(3)	0.3711(10)	0.4128(6)	0.1715(8)	C(50)	0.6537(13)	0.3483(12)	0.2563(9)
C(4)	0.3556(8)	0.3901(9)	0.2151(7)	C(51)	0.6393(14)	0.3046(12)	0.2942(9)
C(5)	0.3686(10)	0.3153(11)	0.2331(6)	C(52)	0.5891(14)	0.3365(14)	0.3161(9)
C(6)	0.3971(9)	0.2632(7)	0.2074(6)	C(53)	0.5596(14)	0.4082(13)	0.3034(9)
C(7)	0.3844(7)	0.1380(5)	0.1063(4)	C(54)	0.5796(12)	0.4520(12)	0.2680(9)
C(8)	0.3170(11)	0.1284(10)	0.1162(7)	C(55)	0.9620(4)	0.1243(8)	0.3164(4)
C(9)	0.2682(10)	0.0642(13)	0.0967(9)	C(56)	1.0115(8)	0.0641(7)	0.3464(6)
C(10)	0.2868(12)	0.0094(8)	0.0672(7)	C(57)	1.0905(8)	0.0570(8)	0.3520(7)
C(11)	0.3542(13)	0.0191(8)	0.0572(7)	C(58)	1.1201(5)	0.1100(10)	0.3275(6)
C(12)	0.4030(8)	0.0833(9)	0.0768(7)	C(59)	1.0705(8)	0.1702(9)	0.2975(6)
C(13)	0.4463(12)	0.2646(11)	0.0690(8)	C(60)	0.9915(7)	0.1774(7)	0.2919(5)
C(14)	0.5253(12)	0.2729(11)	0.0712(9)	C(61)	0.8632(9)	0.1076(6)	0.3740(4)
C(15)	0.5239(13)	0.3076(12)	0.0245(9)	C(62)	0.8015(9)	0.0627(9)	0.3750(5)
C(16)	0.4490(15)	0.3310(13)	−0.0223(9)	C(63)	0.8043(11)	0.0429(10)	0.4258(8)
C(17)	0.3795(14)	0.3200(14)	−0.0190(9)	C(64)	0.8689(13)	0.0679(10)	0.4757(5)
C(18)	0.3728(12)	0.2853(13)	0.0226(8)	C(65)	0.9306(11)	0.1128(11)	0.4748(5)
C(19)	0.8448(9)	0.0833(5)	0.1175(5)	C(66)	0.9277(9)	0.1326(9)	0.4239(7)
C(20)	0.9226(9)	0.0740(7)	0.1625(6)	C(67)	0.8009(12)	0.0639(11)	0.2572(8)
C(21)	0.9553(7)	0.0019(10)	0.1785(6)	C(68)	0.7234(13)	0.0875(12)	0.2145(9)
C(22)	0.9101(11)	−0.0611(6)	0.1496(7)	C(69)	0.6761(13)	0.0362(12)	0.1739(9)
C(23)	0.8323(11)	−0.0518(6)	0.1046(7)	C(70)	0.7030(14)	−0.0361(12)	0.1757(9)
C(24)	0.7996(7)	0.0204(9)	0.0885(5)	C(71)	0.7778(14)	−0.0615(12)	0.2180(10)
C(25)	0.7969(8)	0.1897(7)	0.0283(3)	C(72)	0.8255(12)	−0.0124(12)	0.2591(9)
C(26)	0.8487(8)	0.1511(7)	0.0123(5)	O(W1)	0.3118(11)	0.2198(10)	−0.1424(7)
C(27)	0.8448(9)	0.1650(9)	−0.0397(6)	O(W2)	0.4714(11)	0.3292(11)	0.3963(7)

solution of the red crystals of $[\{PdBr(HL^1)\}_4]\cdot 2H_2O$ was made in order to help decide between these alternatives and gave a value of 1320 ± 300. This compares with molecular weights for $[\{PdBr(HL^1)\}_4]$, $[\{PdBr(HL^1)\}_2]$ and $[PdBr(Me_2CO)(HL^1)]$ of 1918, 959 and 538, respectively. The molecular-weight measurement is consistent with a mixture of the tetramer and lower-molecular-weight species in solution.

Before turning to the nature of the minor species in acetone solution, first it is best to note that the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the red crystals of $[\{PdBr(HL^1)\}_4]\cdot 2H_2O$ in $(CD_3)_2SO$ showed a sharp peak at δ 50.01 plus a very small, sharp peak at δ 54.86. The ^1H NMR spectrum in $(CD_3)_2SO$ is reproduced in Fig. 5, and shows peaks for three hydroquinone ring protons, for a hydroxyl proton, and for two equivalent phenyl groups. The pattern and the chemical shifts of the peaks are reminiscent of those for the major isomer of $[PdBr(mpy)(HL^1\text{-}O,P)]$ (see above), a result entirely consistent with break-up of the tetramer in dimethyl sulfoxide, which is a strong donor solvent, to give the monomeric solvato complex $[PdBr(dmso)(HL^1\text{-}O,P)]$, for which there are two possible isomers (**A**, **B**). The minor peaks in the NMR spectra may be from the other isomer. Assuming that cluster break-up occurs with the minimum possible rearrangement about the palladium centres, then the predominant isomer of $[PdBr(dmso)(HL^1)]$ would have cisoidal bromine and phosphorus atoms, *i.e.* isomer **A** with L = dmso. In the ^1H NMR spectrum of $[\{PdBr(HL^1)\}_4]\cdot 2H_2O$ in acetone solutions the minor species showed broad multiplets for two equivalent phenyl groups at δ 7.88–7.27 and for two hydroquinone ring protons at δ 6.80 (H^5) and 6.38 (H^3) (these peaks are identified by asterisks in Fig. 4). The multiplet for the third hydroquinone proton lies hidden under the peaks of the predominant species; with increasing acidity and water content, the ^1H NMR peaks of the minor species in acetone solutions move in chemical shift and the third hydroquinone proton becomes apparent (*e.g.* compare Fig. 4 with Fig. 2). The absence of couplings to the third hydroquinone proton in the $^1H\text{–}^1H$ DQF-COSY NMR spectrum, Fig. 4, suggests that the hidden peaks are broad (as expected given that the other peaks are also broad) and cross-peaks are not observed either because they have low intensities (plots at lower contour levels became very noisy) or because the linewidths are large compared to the coupling constants. The

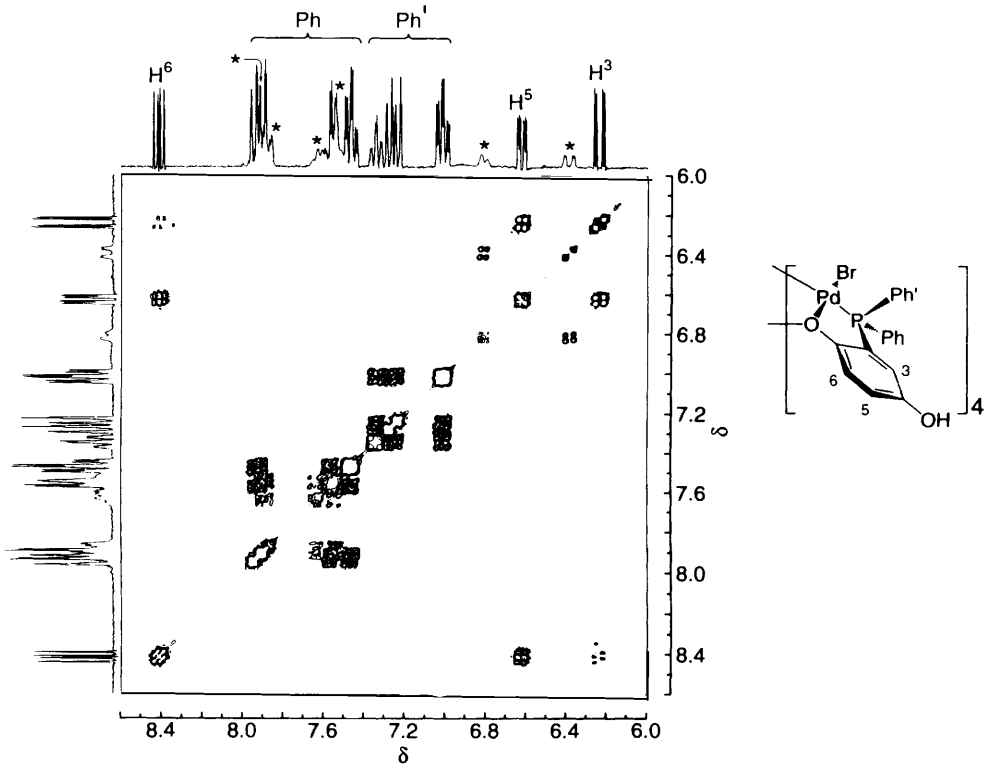


Fig. 4 The 300 MHz ^1H–^1H DQF-COSY NMR spectrum of crystals of $[\{PdBr(HL^1)\}_4]\cdot 2H_2O$ dissolved in $(CD_3)_2CO$

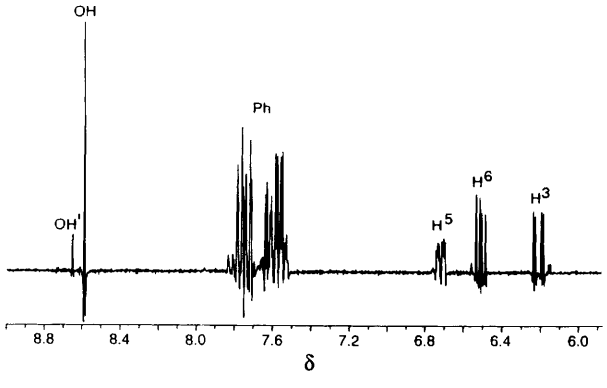
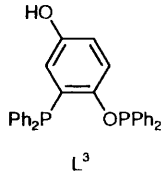


Fig. 5 The 300 MHz ^1H NMR spectrum of crystals of $[\{PdBr(HL^1)\}_4]\cdot 2H_2O$ dissolved in $(CD_3)_2SO$

hidden hydroquinone multiplet aside, the ^1H NMR spectrum of the minor species is very similar to those found for the monomeric complexes [PdBrL(HL^1-*O*,*P*)] (L = mpy or dmso), and based on this result we suggest that the minor species are the solvato complexes [PdBrL(HL^1-*O*,*P*)] [L = $(CD_3)_2CO$ or H_2O]. This would account for the broadness of the peaks (exchange on the NMR time-scale between these solvato complexes or between the geometrical isomers of these complexes or perhaps between these monomers and traces of dimeric species would lead to broad peaks) and the change in peak chemical shifts with water content. Presumably the fractions of acetone and aqua complexes would vary with water content.

As noted above, recrystallisation of the mixture obtained by treating [PdBr(mpy)(HL^1-*O*,*P*)] with concentrated aqueous hydrobromic acid also yielded colourless crystals. The IR spectrum of this product showed a broad O–H band centred at 3200 cm^{-1}, and the ^{31}P-{^1H} NMR spectrum exhibited doublets at δ 143.10 and 14.66, with a *J*(P–P) coupling constant of 22 Hz, indicative of the cisoid phosphinite and phosphine phosphorus atoms {for comparison, ^{31}P NMR data for *cis*-[$PdCl_2\{Ph_2PCH{=}C(Ph)OPPh_2\}$]: δ 129.5 (phosphinite) and −7.0 (phosphine) with *J*(P–P) = 6 Hz[23]}. The ^1H NMR spectrum revealed a hydroxyl singlet (one proton), phenyl multiplets (twenty protons), and three doublets of doublets for a substituted aryl [hydroquinone(?)] ring (three protons). In order fully to identify the compound its crystal structure was determined.



L^3

Colourless crystals of quality suitable for X-ray analysis were obtained by recrystallising the first batch of crystals a second time from acetone–dichloromethane solution. The X-ray analysis showed the complex to be *cis*-[$PdBr_2(L^3)$] [L^3 = C_6H_3-(OH)-1,PPh_2-3,PPh_2O-4] and that it crystallised in the space group $P\bar{1}$ with two molecules of complex and two molecules of water in the unit cell. Fig. 6 shows a view of the molecule along with the atomic numbering scheme. Relevant bond length and angle data are given in Table 3, and non-hydrogen atomic coordinates in Table 4.

The palladium atom displays distorted square-planar geometry and is co-ordinated by the bidentate L^3 ligand through both phosphorus atoms forming a distorted six-membered ring, and by two cisoid bromide ligands. The *m*-hydroxyl group hydrogen bonds to one water molecule [O(2) · · · O(W) 2.641(5) Å]. The molecular structure is closely related to that reported for *cis*-[$PdCl_2\{Ph_2PCH{=}C(Ph)OPPh_2\}$][23] except there appears to be less angular strain in the six-membered ring: the P–O–C angle [118.6(2)°] in *cis*-[$PdBr_2(L^3)$] is significantly smaller than in *cis*-[$PdCl_2\{Ph_2PCH{=}C(Ph)OPPh_2\}$] [P–O–C 131.1(4)°][23] and is comparable with that for the six-membered rings in [$Re(CO)_4(Ph_2POCH_2CMe_2CH_2)$] [121.2(6)°][24] and [$W(CO)_4\{Ph_2PCH{=}C(Ph)OPPh_2\}$]

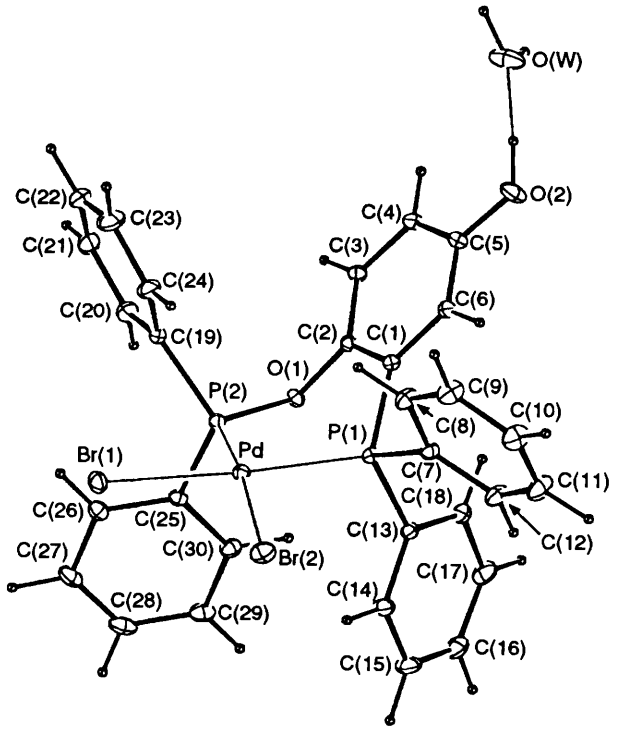


Fig. 6 An ORTEP diagram (20% thermal ellipsoids) of $[PdBr_2(L^3)]$ showing the atom labelling scheme adopted

Table 3 Selected bond lengths (Å) and angles (°) for *cis*-$[PdBr_2(L^3)]\cdot H_2O$ with e.s.d.s in parentheses

Pd–Br(1)	2.468(1)	C(5)–C(6)	1.378(5)
Pd–Br(2)	2.472(1)	C(6)–C(1)	1.394(5)
Pd–P(1)	2.251(1)	C(2)–O(1)	1.402(4)
Pd–P(2)	2.214(1)	C(5)–O(2)	1.355(5)
P(1)–C(1)	1.817(4)	P(2)–O(1)	1.640(3)
P(1)–C(7)	1.798(4)	P(2)–C(19)	1.793(4)
P(1)–C(13)	1.807(4)	P(2)–C(25)	1.803(4)
C(1)–C(2)	1.385(5)	O(2) · · · O(W)	2.641(5)
C(2)–C(3)	1.376(5)	Br(1) · · · O(W)[a]	3.369(3)
C(3)–C(4)	1.390(6)	Br(2) · · · O(W)[b]	3.336(3)
C(4)–C(5)	1.386(6)		
Br(1)–Pd–Br(2)	91.6(1)	C(4)–C(5)–C(6)	120.3(4)
Br(1)–Pd–P(1)	175.7(1)	C(4)–C(5)–O(2)	122.6(4)
Br(1)–Pd–P(2)	86.3(1)	C(6)–C(5)–O(2)	117.1(4)
Br(2)–Pd–P(1)	92.4(1)	C(5)–C(6)–C(1)	120.4(4)
Br(2)–Pd–P(2)	169.1(1)	P(1)–C(7)–C(8)	117.8(3)
P(1)–Pd–P(2)	90.1(1)	P(1)–C(7)–C(12)	122.9(3)
Pd–P(1)–C(1)	111.3(1)	P(1)–C(13)–C(14)	118.9(3)
Pd–P(1)–C(7)	115.0(1)	P(1)–C(13)–C(18)	121.7(3)
Pd–P(1)–C(13)	110.7(1)	Pd–P(2)–O(1)	114.4(1)
C(1)–P(1)–C(7)	104.6(2)	Pd–P(2)–C(19)	119.0(1)
C(1)–P(1)–C(13)	105.6(2)	Pd–P(2)–C(25)	109.1(1)
C(7)–P(1)–C(13)	109.0(2)	O(1)–P(2)–C(19)	103.1(2)
P(1)–C(1)–C(2)	119.3(3)	O(1)–P(2)–C(25)	99.3(1)
P(1)–C(1)–C(6)	122.1(3)	C(19)–P(2)–C(25)	110.1(2)
C(6)–C(1)–C(2)	118.6(3)	P(2)–O(1)–C(2)	118.6(2)
C(1)–C(2)–C(3)	121.5(3)	P(2)–C(19)–C(20)	120.7(3)
C(1)–C(2)–O(1)	119.8(3)	P(2)–C(19)–C(24)	118.7(3)
C(3)–C(2)–O(1)	118.7(3)	P(2)–C(25)–C(26)	120.6(3)
C(2)–C(3)–C(4)	119.4(3)	P(2)–C(25)–C(30)	118.1(3)
C(3)–C(4)–C(5)	119.8(3)		

[a] $x, -1 + y, z$; [b] $1 - x, 1 - y, 1 - z$.

[123.3(4)°].[25] The Pd–P(1) bond [2.251(1) Å] is noticeably longer than the Pd–P(2) bond [2.214(1) Å] reflecting the increase of s character in the latter bond due to the presence of the electronegative oxygen atom. The Pd–Br distances [2.468(1) and 2.472(1) Å] compare with 2.435(1) Å in $[PdBr_2(ppq)_2]\cdot Me_2CO$.[3]

That $[PdBr_2(L^3)]$ formed bears some comment. The ^{31}P NMR spectrum of the liquor from which the complex initially crystallised (and from which 4-methylpyridine hydrobromide and $[\{PdBr(HL^1)\}_4]$ also crystallised) was recorded intermittently over a period of several weeks and only showed the two peaks observed in spectra of solutions of the tetramer. From this observation we infer that no appreciable concentrations of intermediate complexes build up in solution, and that $[PdBr_2(L^3)]$ crystallised as it slowly formed under the rather harsh conditions (dioxygen, water, 4-methylpyridine hydrobromide, trace hydrobromic acid and presumably bromine from air oxidation of the hydrobromic acid are all present). What is remarkable is that the complex forms in a solution of species with one phosphine ligand per palladium atom, *e.g.* $[\{PdBr(HL^1)\}_4]$ or $[PdBr(L)(HL^1\text{-}O,P)]$ (L = mpy or solvent), and that the hydroquinone substituent is selectively lost from the phosphine ligand which ends up as the phosphinite group. We have previously observed clean elimination of the hydroquinone group also under acidic and oxidising conditions: treatment of $[PdI_2(L^2)_2]$ with CF_3SO_3H and tetraethylammonium iodide gave the dimer $[Pd_2(\mu\text{-}I)_2\{(PPh_2O)_2H\}_2]$ in up to 86% yield.[6] Complexes of phosphinohydroquinone ligands are susceptible to oxidation, yielding the corresponding phosphinoquinone complexes.[3] Our hypothesis for the loss of the hydroquinone group in these reactions, which is the basis for current work, is that it is oxidised thereby producing a phosphinoquinone complex which under the acidic reaction conditions eliminates *p*-benzoquinone.

Experimental

Materials and general techniques were as described in previous papers from our laboratories.[3-6,26] All reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk and cannula techniques, but the products were worked up and isolated in air. Solvents were routinely distilled from the appropriate drying agent under dinitrogen immediately prior to use: dichloromethane and acetonitrile from P_2O_5, acetone from anhydrous B_2O_3, hexanes and toluene from sodium wire, diethyl ether and tetrahydrofuran from sodium–benzophenone, dimethyl sulfoxide from $MgSO_4$ under reduced pressure (0.2 mmHg), and dimethylformamide from CaO under reduced pressure (0.2 mmHg). Boron tribromide was distilled before use. All other chemicals were from commercial sources (usually Aldrich) and used as obtained.

Proton NMR spectra were recorded on Bruker WM 500 (500 MHz) or AC-F 300 (300 MHz) spectrometers. Double-quantum-filtered phase-sensitive ^1H–^1H COSY spectra were acquired with a standard (Bruker) multiphase sequence. For spectra over the aryl proton region, 512 increments were routinely used, which were zero-filled to give 1 K data points in f_1. Apodisation was carried out using a shifted-sine function (shifted by $\pi/2$). The $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded on a Bruker AC-P 300 spectrometer operating at 121.49 MHz and were referenced relative to external 0.2% KH_2PO_4 in D_2O contained in a coaxial capillary [$\delta_{(KH_2PO_4)} = \delta_{(85\%\,H_3PO_4)} - 0.80$]. Isopiestic molecular-weight determinations were made following the method of Signer as adapted and described in detail by Burger and Bercaw[27] and utilised $[PdBr_2(L^2)]$[3,4,6] as the standard. The accuracy of this method is ± 10% at best.[27] Infrared spectra were recorded on Perkin-Elmer 500B or Hitachi 260-10 spectrometers. Elemental analyses for C, H and N were determined by the University of New South Wales microanalytical service.

Mixture of $[PdCl_2(PPh_3)(L^2)]$, $[PdCl_2(PPh_3)_2]$ *and* $[PdCl_2(L^2)_2]$.—A solution of $[PdCl_2(PhCN)_2]$ (0.10 g, 0.26 mmol) in dichloromethane (3 cm^3) was added to a stirred

Table 4 Atomic parameters for *cis*-[$PdBr_2(L^3)$]·H_2O with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd	0.664 55(3)	0.180 78(2)	0.252 17(2)	C(13)	0.969 5(4)	0.240 3(3)	0.124 5(3)
Br(1)	0.481 8(1)	0.093 12(4)	0.252 35(4)	C(14)	1.033 3(5)	0.128 3(4)	0.077 4(4)
Br(2)	0.797 5(1)	0.013 80(4)	0.332 30(4)	C(15)	1.143 0(5)	0.101 0(4)	−0.023 7(4)
P(1)	0.818 5(1)	0.273 7(1)	0.251 8(1)	C(16)	1.186 1(5)	0.185 4(5)	−0.078 6(4)
P(2)	0.567 0(1)	0.308 9(1)	0.151 3(1)	C(17)	1.126 1(5)	0.297 2(4)	−0.031 5(4)
O(1)	0.643 5(3)	0.407 1(2)	0.116 1(2)	C(18)	1.017 8(4)	0.325 1(4)	0.070 6(4)
O(2)	0.666 6(4)	0.682 8(3)	0.426 5(3)	C(19)	0.374 3(4)	0.392 3(3)	0.203 2(3)
C(1)	0.727 0(4)	0.428 8(3)	0.263 8(3)	C(20)	0.303 3(5)	0.454 8(4)	0.135 7(4)
C(2)	0.644 0(4)	0.476 8(3)	0.198 0(3)	C(21)	0.158 9(6)	0.527 4(4)	0.180 0(6)
C(3)	0.564 2(4)	0.592 7(3)	0.209 2(3)	C(22)	0.086 6(5)	0.537 3(5)	0.288 7(6)
C(4)	0.570 7(4)	0.664 2(3)	0.285 6(3)	C(23)	0.157 6(6)	0.476 1(5)	0.356 8(5)
C(5)	0.655 1(4)	0.617 8(3)	0.350 9(3)	C(24)	0.301 3(5)	0.402 4(4)	0.314 5(4)
C(6)	0.732 4(4)	0.501 3(3)	0.340 4(3)	C(25)	0.613 4(4)	0.239 9(3)	0.018 6(3)
C(7)	0.891 3(4)	0.247 3(3)	0.361 8(3)	C(26)	0.521 8(5)	0.191 0(4)	−0.002 9(3)
C(8)	0.792 3(5)	0.261 1(4)	0.466 8(3)	C(27)	0.570 8(6)	0.124 3(4)	−0.101 2(4)
C(9)	0.842 4(5)	0.244 1(5)	0.554 3(4)	C(28)	0.706 2(6)	0.110 6(4)	−0.175 2(4)
C(10)	0.988 9(6)	0.212 0(5)	0.537 7(4)	C(29)	0.796 8(5)	0.160 9(4)	−0.154 7(3)
C(11)	1.087 7(5)	0.199 3(5)	0.435 2(4)	C(30)	0.750 4(4)	0.225 9(4)	−0.056 8(3)
C(12)	1.039 6(4)	0.215 9(4)	0.346 2(4)	O(W)	0.485 1(5)	0.895 7(3)	0.435 8(3)

solution of L^2 (87 mg, 0.26 mmol) and triphenylphosphine (68 mg, 0.26 mmol) in dichloromethane (25 cm^3). The solution was stirred for 30 min and then the solvent volume was reduced to *ca.* 3 cm^3. The product was precipitated by adding diethyl ether (30 cm^3), and dried *in vacuo* to give a fine yellow solid (187 mg, 94%). Spectroscopic data indicated a 3:1:1 mixture of *trans*-[$PdCl_2(PPh_3)L^2$], *trans*-[$PdCl_2(L^2)_2$] and *trans*-[$PdCl_2(PPh_3)_2$]. M.p. 216 °C (decomp.). NMR ($CDCl_3$): ^1H, peaks for three species were observed, *trans*-[$PdCl_2(PPh_3)L^2$], δ 7.83–7.68, 7.52–7.35 {coincident with the Ph multiplets of *trans*-[$PdCl_2(L^2)_2$]}, 6.96 [dd, 1 H, ^3J(H–H) 9, ^4J(H–H) 3, C_6H_3], 6.88 [dd, 1 H, ^3J(H–H) 9, ^4J(P–H) 6, C_6H_3], 6.46 [dd, 1 H, ^3J(P–H) 10, ^4J(H–H) 3, C_6H_3], 3.81 (s, OCH_3) and 3.56 (s, OCH_3); *trans*-[$PdCl_2(L^2)_2$], δ 7.52–7.35, 6.93 [dd, 1 H, ^3J(H–H) 9, ^4J(H–H) 3, C_6H_3], 6.86 [dd, 1 H, ^3J(H–H) 9, ^4J(P–H) 6, C_6H_3], 6.50 [dd, 1 H, ^3J(P–H) 10, ^4J(H–H) 3, C_6H_3], 3.78 (s, OCH_3) and 3.56 (s, OCH_3); *trans*-[$PdCl_2(PPh_3)_2$], δ 7.50, 7.33 and 7.18 (Ph multiplets); ^{31}P-{^1H}, *trans*-[$PdCl_2(PPh_3)L^2$], δ 24.27 [d, *J*(P–P) 580, PPh_3] and 15.41 [d, *J*(P–P) 580 Hz, L^2]; *trans*-[$PdCl_2(L^2)_2$], δ 16.30 (s); *trans*-[$PdCl_2(PPh_3)_2$], δ 23.36 (s). IR (paraffin mull): 3055m, 1485s, 1439vs, 1411m, 1311m, 1277s, 1226s, 1184m, 1100s, 1052m, 1020m, 1001m, 817m, 747s, 723m, 708s, 695s, 571m, 513s and 356m cm^{-1} (Found: C, 54.85; H, 4.25. Calc. for $C_{38}H_{34}Cl_2O_2P_2Pd·CH_2Cl_2$: C, 55.30; H, 4.25%). The analytical data are consistent with a dichloromethane solvate of [$PdCl_2(PPh_3)L^2$] alone or of an equimolar mixture of [$PdCl_2(L^2)_2$] and [$PdCl_2(PPh_3)_2$] or of a mixture of [$PdCl_2(PPh_3)L^2$] and equimolar [$PdCl_2(L^2)_2$] and [$PdCl_2(PPh_3)_2$].

Reaction of *trans*-[$PdCl_2(PPh_3)L^2$] *with* BBr_3.—Boron tribromide (0.2 cm^3) was added to a precooled solution of the above mixture containing [$PdCl_2(PPh_3)L^2$] (0.10 g) in dichloromethane (15 cm^3). The yellow solution turned pale brown. The Schlenk flask was covered with aluminium foil and the reaction mixture stirred for 16 h. All volatiles were removed under reduced pressure and the resulting residue treated with methanol (10 cm^3). This gave a red solution from which a red solid crystallised on standing with analytical and spectroscopic data consistent for the known complex [$Pd_2Br_4(PPh_3)_2$][28] (50 mg, 72%). NMR [$(CD_3)_2SO$]: ^1H, δ 7.70–7.64 (m, 8 H, Ph) and 7.54–7.45 (m, 12 H, Ph); ^{31}P-{^1H}, δ 30.52 (s) (Found: C, 41.00; H, 2.75. Calc. for $C_{36}H_{30}Br_4P_2Pd_2$: C, 40.85; H, 2.50%).

[PdCl(bipy)L^2][PF_6].—*Method* 1. A mixture of L^2 (0.263 g, 0.81 mmol), [$PdCl_2$(bipy)] (0.270 g, 0.80 mmol) and ammonium hexafluorophosphate (0.130 g, 0.80 mmol) was refluxed in methanol–acetone (1:1, 50 cm^3) for 1 h. Removal of the solvent from the clear yellow solution gave a yellow-orange solid, which was extracted with dichloromethane. Removal of the solvent from the extracts and recrystallisation of the resulting solid from dichloromethane–diethyl ether yielded yellow-orange crystals (0.57 g, 91%), m.p. 182 °C (decomp.). NMR ($CDCl_3$): ^1H, δ 9.15 [t, 1 H, ^3J(H–H) 8, ^3J(H–H) 4, virtual coupling observed, bipy], 8.25 [d, 2 H, ^3J(H–H) 8, bipy], 8.03 [dd, 1 H, ^3J(H–H) 8, ^4J(H–H) 1.5, bipy], 7.55 (m, 4 H, Ph), 7.40 [d, 1 H, ^3J(H–H) 6, bipy], 7.38 [t, 1 H, ^3J(H–H) 7, ^3J(H–H) 6, bipy], 7.37 (m, 2 H, Ph), 7.23 (m, 4 H, Ph), 6.95 [dd, 1 H, ^3J(H–H) 9, ^4J(H–H) 3, C_6H_3], 6.85 [t, 1 H, ^3J(H–H) 7, ^3J(H–H) 6, bipy], 6.79 [dd, 1 H, ^4J(P–H) 6, ^3J(H–H) 9, C_6H_3], 6.59 [dd, 1 H, ^3J(P–H) 13, ^4J(H–H) 3, C_6H_3], 3.48 (s, 3 H, OCH_3) and 3.36 (s, 3 H, OCH_3); ^{31}P-{^1H}, δ 21.94 (s, L^2) and −144.26 [spt, *J*(P–F) 710 Hz, PF_6^-]. IR (paraffin mull): 1609m, 1577m, 1490vs, 1403m, 1318m, 1303m, 1279vs, 1250m, 1229vs, 1184s, 1165m, 1100s, 1073m, 1039s, 1019m, 878s, 843vs, 769s, 755s, 727s, 699s, 560vs and 513s cm^{-1} (Found: C, 47.35; H, 3.30; N, 3.50. Calc. for $C_{30}H_{27}ClF_6N_2O_2P_2Pd$: C, 47.05; H, 3.55; N, 3.65%).

Method 2. A mixture of *trans*-[$PdCl_2(L^2)_2$] (0.20 g, 0.24 mmol), ammonium hexafluorophosphate (0.10 g, 0.61 mmol) and 2,2′-bipyridine (0.10 g, 0.64 mmol) was refluxed in acetone (50 cm^3) for 48 h. The solvent was removed and the residue extracted with dichloromethane (3 × 20 cm^3). The volume of the dichloromethane solution was reduced to *ca.* 5 cm^3 and methanol (50 cm^3) added to precipitate an orange solid. Recrystallisation from dichloromethane–ether gave the product as an orange microcrystalline solid (70 mg, 40%). Spectroscopic data under Method 1.

Reaction of [PdCl(bipy)L^2][PF_6] *with* BBr_3.—Boron tribromide (0.10 cm^3, 1.06 mmol) was added to a solution of [PdCl(bipy)L^2][PF_6] (0.10 g, 0.13 mmol) in precooled dichloromethane (0 °C). An orange precipitate formed immediately. The Schlenk flask was covered with aluminium foil, and the reaction mixture warmed to room temperature and stirred for 16 h. The volatiles were removed using a water aspirator. Addition of methanol (15 cm^3) to the residue gave an orange suspension. The orange solid was filtered off, washed with diethyl ether and dried (40 mg). The analytical and spectroscopic data are entirely consistent with the formulation [$PdBr_2$(bipy)] for the product. ^1H NMR [$(CD_3)_2SO$]: δ 9.42 [dd, 2 H, ^3J(H–H) 6, ^4J(H–H) 1.5, bipy], 8.61 [dd, 2 H, ^3J(H–H) 8, ^4J(H–H) 1.5, bipy], 8.36 [dt, 1 H, *J*(H–H) 8, 1.5, bipy] and 7.81 [dt, 2 H, ^3J(H–H) 8, ^4J(H–H) 1.5 Hz, bipy] (Found: C, 28.50;

H, 2.25; N, 6.15. Calc. for $C_{10}H_8Br_2N_2Pd$: C, 28.40; H, 1.90; N, 6.15%).

$[Pd_2Cl_2(\mu\text{-}Cl)_2(L^2)_2]$.—A solution of L^2 (0.42 g, 1.30 mmol) in dichloromethane (20 cm^3) was added to a solution of $[PdCl_2(PhCN)_2]$ (0.50 g, 1.30 mmol) in dichloromethane (25 cm^3). A red-brown colour developed and the mixture was stirred for 30 min. The volume was reduced to *ca.* 5 cm^3 and then layered with diethyl ether (40 cm^3). A fine orange precipitate slowly formed and was collected and dried (0.62 g, 95%), m.p. 237 °C. NMR ($CDCl_3$): ^1H, δ 7.16 (m, 8 H, Ph), 6.92 (m, 4 H, Ph), 6.83 (m, 8 H, Ph), 6.46 [dd, 2 H, ^3J(H–H) 9, ^4J(H–H) 2.5, C_6H_3], 6.37 [dd, 2 H, ^3J(H–H) 9, ^4J(PH) 6, C_6H_3], 5.90 [dd, 2 H, ^3J(P–H) 15, ^4J(H–H) 2.5 Hz, C_6H_3], 3.18 (s, 3 H, OCH_3) and 3.02 (s, 3 H, OCH_3); ^{31}P-{^1H}, δ 23.46 (s) (Found: C, 47.85; H, 4.10. Calc. for $C_{40}H_{38}Cl_4O_4P_2Pd_2$: C, 48.05; H, 3.80%).

trans-$[PdCl_2(mpy)L^2]$.—4-Methylpyridine (0.5 cm^3) was slowly added to an orange suspension of $[Pd_2Cl_4(L^2)_2]$ (0.3 g, 0.30 mmol) in dichloromethane (30 cm^3). All the solid dissolved and a light yellow solution resulted. After 30 min the volume was reduced to *ca.* 5 cm^3, diethyl ether (40 cm^3) added, and the fine yellow microcrystalline solid filtered off and dried (0.306 g, 86%), m.p. 180 °C (decomp.). NMR ($CDCl_3$): ^1H, δ 8.80 (m, 2 H, mpy), 7.87 (m, 4 H, Ph), 7.46 (m, 2 H, Ph), 7.40 (m, 4 H, Ph), 7.15 [d, 2 H, ^3J(H–H) 5.8, mpy], 7.00 [dd, 1 H, ^3J(H–H) 9, ^4J(H–H) 3, C_6H_3], 6.90 [dd, 1 H, ^3J(H–H) 9, ^4J(P–H) 6, C_6H_3], 6.65 [dd, 1 H, ^3J(P–H) 13, ^4J(H–H) 3 Hz, C_6H_3], 3.80 (s, 3 H, OCH_3), 3.63 (s, 3 H, OCH_3) and 2.36 (s, 3 H, CH_3); weak multiplets for trace amounts (< 5%) of a second species, possibly the *cis* isomer, were apparent at δ 8.24, 7.80, 7.60, 7.24, 6.95, 6.75, 6.40, 4.07 (s, OCH_3), 3.58 (s, OCH_3) and 2.20 (s, CH_3); ^{31}P-{^1H}, δ 20.60 (s) plus minor peak δ 17.97 (s). IR (paraffin mull): 1481s, 1408m, 1272s, 1222s, 1100m, 1068m, 1048m, 1021m, 815m, 803m and 696m cm^{-1} (Found: C, 52.45; H, 4.70; N, 2.25%. Calc. for $C_{26}H_{26}Cl_2NO_2PPd$: C, 52.65; H, 4.40; N, 2.35%).

trans-$[PdBr_2(mpy)L^2]$.—An excess of sodium bromide (0.50 g) was added to a stirred acetone solution (20 cm^3) of *trans*-$[PdCl_2(mpy)L^2]$ (0.1 g, 0.17 mmol). The colour changed from light yellow to orange over 2 h. The undissolved solid was filtered off, the solvent removed from the filtrate, and the residue recrystallised from dichloromethane producing an orange microcrystalline solid (0.135 g, 85%), m.p. 186 °C (decomp.). NMR ($CDCl_3$): ^1H, δ 8.79 (m, 2 H, mpy), 7.88 (m, 4 H, Ph), 7.43 (m, 6 H, Ph), 7.15 [d, 2 H, ^3J(H–H) 5.8, mpy], 6.97 [dd, 1 H, ^3J(H–H) 9, ^4J(H–H) 3, C_6H_3], 6.88 [dd, 1 H, ^3J(H–H) 9, ^4J(P–H) 6, C_6H_3], 6.72 [dd, 1 H, ^3J(P–H) 13, ^4J(H–H) 3 Hz, C_6H_3], 3.81 (s, 3 H, OCH_3), 3.63 (s, 3 H, OCH_3) and 2.34 (s, 3 H, CH_3); ^{31}P-{^1H}, δ 12.38 (s). IR (paraffin mull): 1484s, 1272s, 1222s, 1179m, 1096m, 1067m, 1032m, 809m, 749m and 694m cm^{-1} (Found: C, 45.35; H, 3.35; N, 2.30. Calc. for $C_{26}H_{26}Br_2NO_2PPd$: C, 45.80; H, 3.85; N, 2.05%).

$[PdBr(mpy)(HL^1\text{-}O,P)]$.—Boron tribromide in hexane (5 cm^3, 5 mmol) was added *via* a syringe to a precooled (0 °C) dichloromethane solution of $[PdCl_2(mpy)L^2]$ (0.315 g, 0.52 mmol). The Schlenk flask was covered with aluminium foil, allowed to warm to room temperature and stirred for 16 h. The solvent was then removed using a water aspirator, and the resulting orange residue treated with a suspension of sodium carbonate (2.5 g) in methanol (25 cm^3). After 16 h the yellow-orange precipitate which had formed was filtered off and repeatedly washed with water to remove excess of sodium carbonate. It was then washed with diethyl ether and dried *in vacuo* (0.30 g, 95%). The product did not dissolve in dichloromethane, methanol or acetone but was soluble in dimethyl sulfoxide or in dimethylformamide. A 3:1 mixture of two isomers was revealed by NMR spectroscopy [$(CD_3)_2SO$]: ^1H, principal isomer, δ 8.86 [d, 2 H, ^3J(H–H) 5.5, mpy], 8.70 (s, 1 H, OH), 7.87 (m, Ph), 7.70 (m, Ph), 7.54 (m, 2 H, mpy), 6.83 [dd, 2 H, ^3J(H–H) 9, ^4J(H–H) 3, C_6H_3], 6.68 [dd, 2 H, ^3J(H–H) 9, ^4J(P–H) 6, C_6H_3], 6.37 [d, 2 H, ^3J(P–H) 12, C_6H_3] and 2.40 (s, 3 H, CH_3); minor isomer, δ 8.68 [d, 2 H, ^3J(H–H) 5.5, mpy], 8.45 (s, 1 H, OH), 7.44 (m, 2 H, mpy), 7.34 (m, Ph), 6.78 [dd, 2 H, ^3J(H–H) 9, ^4J(H–H) 3, C_6H_3], 6.59 [dd, 2 H, ^3J(H–H) 9, ^4J(P–H) 6 Hz, C_6H_3], 6.25 (m, 2 H, C_6H_3) and 2.37 (s, 1 H, CH_3); ^{31}P-{^1H}, δ 44.44 (s, principal isomer) and 42.09 (s, minor isomer). IR (paraffin mull): 3200 (br), 1620m, 1436s, 1272m, 1252m, 1232m, 1212m, 1182m, 1120m, 1101m, 1069m, 1030m, 812m, 745m, 710m and 692m cm^{-1} (Found: C, 49.00; H, 3.75; N, 2.15. Calc. for $C_{24}H_{21}BrNO_2PPd\cdot H_2O$: C, 48.90; H, 3.95; N, 2.40%).

Reaction of $[PdBr(mpy)(HL^1\text{-}O,P)]$ *with Aqueous Hydrobromic Acid.*—Concentrated aqueous hydrobromic acid (*ca.* 0.2 cm^3) was slowly added until a suspension of $[PdBr(mpy)(HL^1\text{-}O,P)]$ (0.1 g, 0.17 mmol) in acetone (25 cm^3) dissolved. The resulting solution was stirred for 30 min, the volume of the solution reduced to *ca.* 5 cm^3, and water (20 cm^3) added. The orange precipitate (0.1 g) was collected and recrystallised from acetone–dichloromethane solution. Over several weeks the solution darkened and a mixture of red, colourless and yellow crystals formed. These were manually separated under a microscope. The yellow crystals were identified as 4-methylpyridinehydrobomide (mpy·HBr) from comparison of their ^1H NMR spectrum with that of an authentic sample. X-Ray crystallographic analyses showed the red and colourless crystals to be $[\{PdBr(HL^1)\}_4]$ and $[PdBr_2(L^3)]$, respectively.

mpy·HBr. Yellow needles (10 mg). ^1H NMR [$(CD_3)_2CO$]: δ 9.12 [d, 2 H, ^3J(H–H) 6]), 7.18 [d, 2 H, ^3J(H–H) 6.5 Hz] and 2.40 (s, 3 H, CH_3).

$[\{PdBr(HL^1)\}_4]$. Red rhombs (60 mg) (Found: C, 44.35; H, 3.25. Calc. for $C_{72}H_{56}Br_4O_8P_4Pd_4\cdot 2H_2O$: C, 44.25; H, 3.10%). NMR [$(CO_3)_2CO$] showed peaks for two species: ^1H $[\{PdBr(HL^1)\}_4]$ (67%), δ 8.41 [dd, 1 H, ^3J(H–H) 9, ^4J(P–H) 6, C_6H_3], 7.93 (m, Ph), 7.54 (m, Ph), 7.47 (m, Ph), 7.37 (m, Ph'), 7.27 (m, Ph'), 7.01 (m, Ph'), 6.62 [dd, 1 H, ^3J(H–H) 9, ^4J(H–H) 3, C_6H_3] and 6.23 [dd, 1 H, ^3J(P–H) 12, ^4J(H–H) 3 Hz, C_6H_3]; $[PdBr(solv)(HL^1\text{-}O,P)]$, δ 7.88 (m, Ph), 7.64 (m, Ph), 7.56 (m, Ph), 6.80 (br d, 2 H, C_6H_3) and 6.38 (br dd, 1 H, C_6H_3); ^{31}P-{^1H}, $[\{PdBr(HL^1)\}_4]$, δ 46.30 (s); $[PdBr(solv)(HL^1\text{-}O,P)]$, δ 50.50 (s). NMR [$(CD_3)_2SO$] showed complete break up of the Pd_4 cluster and formation of the monomeric solvato complex, $[PdBr\{(CD_3)_2SO\}(HL^1\text{-}O,P)]$: ^1H, δ 8.59 (s, 1 H, OH), 7.73 (m, Ph), 7.56 (m, Ph), 6.70 (m, 1 H, C_6H_3), 6.52 [dd, 1 H, ^3J(H–H) 9, ^4J(P–H) 6, C_6H_3], 6.20 [dd, 1 H, ^3J(P–H) 12, ^4J(H–H) 3 Hz, C_6H_3], plus very weak peaks (< 5%), possibly for the other geometric isomer, δ 8.65 (s, 1 H, OH), 7.81 (m, Ph), 7.65 (m, Ph), 6.78 (m, C_6H_3), 6.57 (m, C_6H_3) and 6.17 (m, C_6H_3); ^{31}P-{^1H}, δ 50.01 (s) plus a very weak peak at 54.86 (s).

cis-$[PdBr_2(L^3)]$. Colourless crystals (20 mg). NMR [$(CD_3)_2SO$–$(CD_3)_2CO$ (1:2)]: δ 10.22 (s, 1 H, OH), 8.13 (m, 12 H, Ph), 7.95 (m, 8 H, Ph), 7.30 [dd, 1 H, ^3J(H–H) 9, ^4J(H–H) 3, C_6H_3], 7.21 [dd, 1 H, ^3J(H–H) 9, ^4J(P–H) 6, C_6H_3] and 6.60 [dd, 1 H, ^3J(P–H) 10, ^4J(H–H) 3, C_6H_3]; ^{31}P-{^1H}, δ 143.10 [d, 1 P, ^2J(P–P) 21.7, $OPPh_2$] and 14.66 [d, 1 P, ^2J(P–P) 21.7 Hz, PPh_2].

X-Ray Crystallography.—Crystal and refinement data for $[\{PdBr(HL^1)\}_4]\cdot 2H_2O$ and for *cis*-$[PdBr_2(L^3)]\cdot H_2O$ are given in Table 5. Reflection data were measured with an Enraf-Nonius CAD-4 diffractometer in θ–2θ scan mode using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). Data were corrected for absorption using the method of De Meulenaer and Tompa.[29] Reflections with $I > 3\sigma(I)$ were considered observed. The structures were determined by direct phasing (MULTAN 80[30]) and Fourier methods. Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) +$

Table 5 Crystal and refinement data *

Compound	$[\{PdBr(HL^1)\}_4]\cdot 2H_2O$	$[PdBr_2(L^3)]\cdot H_2O$
Formula	$C_{72}H_{56}Br_4O_8P_4Pd_4\cdot 2H_2O$	$C_{30}H_{24}Br_2O_2P_2Pd\cdot H_2O$
M	1954.4	762.7
Crystal description	{100}{001}{110}	{001}{110}(01$\bar{1}$)(2$\bar{7}$2)
Space group	$P2_1/c$	$P\bar{1}$
a/Å	18.40(1)	10.265(3)
b/Å	17.753(5)	12.407(4)
c/Å	27.04(1)	13.072(4)
α/°		88.07(2)
β/°	117.49(2)	70.93(2)
γ/°		70.06(2)
U/Å^3	7834(6)	1474(1)
Z	4	2
D_c/g cm^{-3}	1.65	1.72
μ/cm^{-1}	30.4	34.4
Crystal dimensions/mm	0.07 × 0.10 × 0.08	0.10 × 0.12 × 0.16
$2\theta_{max}$/°	40	50
ω Scan angle/°	0.45 + 0.35 tan θ	0.50 + 0.35 tan θ
No. intensity measurements	7915	5182
No. independent observed reflections	3528	3765
No. reflections (m) and variables (n) in final refinement	3528, 424	3765, 343
$R = \Sigma^m\|\Delta F\|/\Sigma^m\|F_o\|$	0.052	0.027
$R' = [\Sigma^m w\|\Delta F\|^2/\Sigma^m w\|F_o\|^2]^{\frac{1}{2}}$	0.061	0.034
$S = [\Sigma^m w\|\Delta F\|^2/(m-n)]^{\frac{1}{2}}$	1.60	1.21
Maximum, minimum transimission coefficients	0.81, 0.77	0.72, 0.51
R for multiple measurements	0.036	0.019

* Details in common: 21(1) °C; no crystal decay.

$(0.04I_o)^2]^{\frac{1}{2}}$. The weighted residual is defined as $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$. Atomic scattering factors and anomalous dispersion parameters were from ref. 31. The program ORTEP II [32] running on a Macintosh IIcx was used for the structural diagrams, and an IBM 3090 computer was used for calculations. The final atomic parameters are given in Tables 2 and 4, respectively.

cis-$[PdBr_2(L^3)]\cdot H_2O$. The hydroxyl and water hydrogen atoms were readily located in a Fourier difference synthesis, the others were included in calculated positions, and all were assigned thermal parameters equal to those of the atom to which they were bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined using full-matrix least squares (BLOCKLS, a local version of ORFLS [33]), and convergence was obtained with $R = 0.027$.

$[\{PdBr(HL^1)\}_4]\cdot 2H_2O$. The two largest peaks in a difference map were included as water molecules. They were well positioned to take part in hydrogen bonding to non-co-ordinated O(hydroquinone) atoms, and to each other. Positional and anisotropic thermal parameters for the non-hydrogen atoms were initially refined using full-matrix least squares (BLOCKLS). Phenyl and hydroquinone ring hydrogen atoms were included in calculated positions and were assigned thermal parameters equal to those of the atom to which they were bonded. Refinement converged with $R = 0.063$. The relatively poor quality and limited number of observed reflections made reduction of the number of refinable parameters desirable, so refinement was continued using a program with rigid-body capabilities (RAELS [34]). The eight phenyl rings were refined as rigid groups of *mm*2 symmetry. The P–C distances were slack constrained to be equal and the P–C vector was slack constrained to lie in the plane of the phenyl ring. The atoms of the hydroquinone rings were refined as individual atoms. The Pd, Br, P and the water oxygen atoms were refined anisotropically. Each ring was assigned a 12-parameter **TL** thermal model (where **T** is the translation tensor and **L** is the libration tensor). Refinement converged with $R = 0.052$. The largest peak in the final difference map was 3.1 e Å^{-3} located near the inversion centre at the origin. Attempts to model this residual electron density as a water or solvent acetone molecule did not lead to any improvement in R factor.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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