Complexes of New Electrochemically-Active *p*-Quinonyl-/*p*-Hydroquinonylphosphines: Multiple Electron/Proton Transfer Reactions and Electrochemical/pH Control of *o*-Oxygen Atom Coordination

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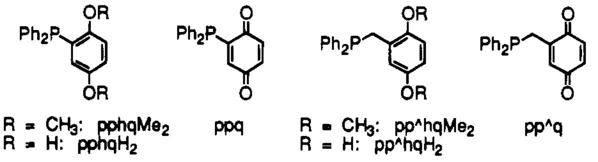
Received July 12, 1994

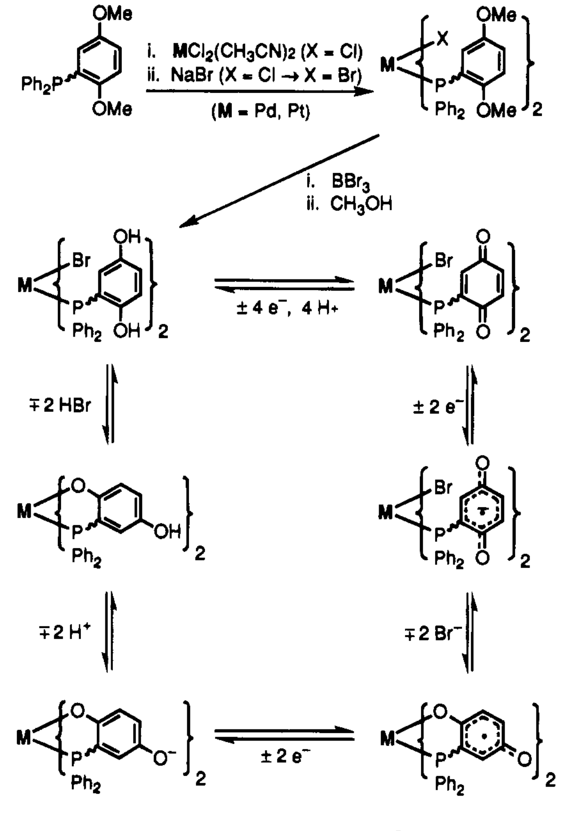
We report here palladium(II) and platinum(II) complexes of new *p*-quinonyl-substituted phosphine ligands, along with preliminary results demonstrating that these complexes can support multiple electron/proton transfer steps and that the coordination of the *p*-quinonyl/*p*-hydroquinonyl *o*-oxygen atom to the metal center can be electrochemically or pH controlled as outlined in Scheme 1.[1]

We anticipated that free *p*-quinonylphosphines, e.g., ppq and pp∧q, would be inaccessible due to either internal oxidation of the phosphine by the quinonyl moiety or Michael addition of the phosphine to the quinonyl moiety (Ramirez reactions).[2] Two "protected" phosphines, pphqMe$_2$ and pp∧hqMe$_2$,[3] provided the entry point. Straightforward reactions of these "protected" phosphines and MCl$_2$(PhCN)$_2$ (M = Pd, Pt) precusors in dichloromethane followed by metathesis with excess sodium bromide in acetone gave the square planar palladium(II) and platinum(II) complexes MBr$_2$(pphqMe$_2$)$_2$ and PtBr$_2$(pp∧hqMe$_2$)$_2$ (Scheme 1).[4] Deprotection with BBr$_3$ in dry dichloromethane, followed by methanol to destroy borate intermediates, afforded the corresponding hydroquinonylphosphine complexes *trans*-MBr$_2$(pphqH$_2$)$_2$ and *cis*-PtBr$_2$(pp∧hqH$_2$)$_2$, in excellent overall yields (always >80%).[4]



The hydroquinonylphosphine complexes, in common with complexes of simpler *o*-phenolphosphines,[5] exhibited reversible pH-controlled coordination of the *o*-oxygen atoms (Scheme 1). Thus, reactions of *trans*-MBr$_2$(pphqH$_2$)$_2$ and *cis*-PtBr$_2$(pp∧hqH$_2$)$_2$ with sodium carbonate in methanol afforded, in near quantitative yield, precipitates of the *O,P*-chelated hydroquinonylphosphine complexes *cis*-M(pphqH-*O,P*)$_2$ and *cis*-Pt(pp∧hqH-*O,P*)$_2$.[4] The latter complexes are presumably formed by two successive associative displacements of bromide ion by nucleophilic hydroquinonyl pendant anions[6] produced under the basic reaction conditions (pK_a(1) and pK_a(2) for *p*-hydroquinone are 9.9 and 12.9, respectively[7]). Suspensions of *cis*-M(pphqH-*O,P*)$_2$ and *cis*-Pt(pp∧hqH-*O,P*)$_2$ in acetone dissolved when a few drops of aqueous 48% hydrobromic acid were added and crystalline *trans*-MBr$_2$(pphqH)$_2$ and *cis*-PtBr$_2$(pp∧hqH)$_2$ slowly redeposited in moderate yields (typically 60–75%). Similar behavior was observed for other Brönsted acids, e.g., HCl, HI and CF$_3$CO$_2$H.[8]

Scheme 1



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(2) For a review: Ramirez, F. *Pure Appl. Chem.* **1964**, *9*, 337. See also: Ramirez, F; Rhum, D.; Smith, C. P. *Tetrahedron* **1965**, *21*, 1941.

(3) Details of the ligand preparations are given in the Supplementary Materials, but briefly: pphqMe$_2$ (Horner, L.; Simons, G. *Phosphorus Sulfur* **1983**, *14*, 189) was obtained in 76% yield by reaction of monolithiodimethoxybenzene in diethyl ether with diphenylphosphine chloride, and reaction of dimethoxybenzyl magnesium bromide (Baker, K. V.; Brown, J. M.; Hughes, N.; Skamulis, A. J.; Sexton, A. *J. Org. Chem.* **1991**, *56*, 698) with diphenylphosphine chloride in diethyl ether afforded pp∧hqMe$_2$ in 88% yield. The hydroquinonylphosphine hydrobromide, pphqH$_2$$\cdot$HBr, was obtained in 74% yield after treatment of pphqMe$_2$ with BBr$_3$ in dry dichloromethane, followed by methanolysis. Attempts to isolate free pphqH$_2$ or to oxidize pphqH$\cdot$HBr to either ppq or its hydrobromide were unsuccessful.

(4) All ligands and complexes gave satisfactory elemental analyses, and were characterized by FTIR, ^{1}H NMR, and ^{31}P{^{1}H} NMR spectroscopies (see Supplementary Materials), by cyclic voltammetry, and by X-ray single-crystal determinations of *trans*-PdBr$_2$(ppq)$_2$$\cdot$(CH$_3$)$_2$CO (communicated herein) and *trans*-PdCl$_2$(pphqMe$_2$)$_2$, *trans*-PdCl$_2$(pphqH$_2$)$_2$$\cdot$2(CH$_3$)$_2$CO, *trans*-PtCl$_2$(pphqH$_2$)$_2$$\cdot$4(CH$_3$)$_2$NCHO and *cis*-Pd(pphqH-*O,P*)$_2$$\cdot$H$_2O\cdot$2(CH$_3$)$_2$SO (to be reported elsewhere).

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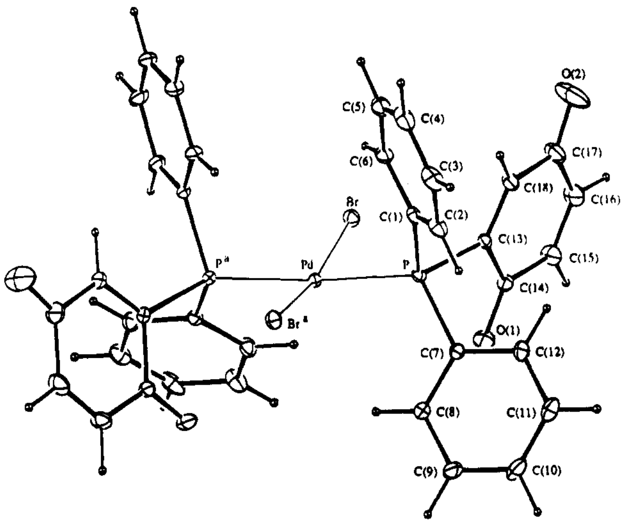

Figure 1. ORTEP plot showing the molecular structure and labelling scheme for *trans*-$PdBr_2(ppq)_2$ (20% probability elipsoids). Selected bond distances (Å) and angles (deg) are as follows: Br−Pd, 2.435(1); P−Pd, 2.318(1); C(13)−P, 1.831(5); C(14)−O(1), 1.221(6); C(14)−C(13), 1.491(7); C(15)−C(14), 1.462(8); C(16)−C(15), 1.314(9); C(17)−O(2), 1.211(8); C(17)−C(16), 1.450(10); C(18)−C(13), 1.318(7); C(18)−C(17), 1.489(8); Br−Pd−P, 92.4(0); Br−Pd−P^a; 87.1(0); Br−Pd−Br^a, 167.9(0); P−Pd−P^a, 175.9(1).

The *cis*-M(pphqH-*O*,*P*)$_2$ complexes were poorly soluble in most common solvents but dissolved in aqueous sodium hydroxide and other basic solutions such as triethylamine in methanol or acetonitrile. The *cis*-M(pphqH-*O*,*P*)$_2$ complexes reprecipitated when the solutions were neutralized. The basic solutions likely contain the anions, *cis*-[M(pphq-*O*,*P*)$_2$]$^{2-}$ or *cis*-[Pt(pp$\wedge$hq-*O*,*P*)$_2$]$^{2-}$ (Scheme 1), in which the noncoordinated hydroquinonyl oxygen atoms are also deprotonated.[8]

The quinonylphosphine complexes *trans*-$MBr_2(ppq)_2$ and *cis*-$PtBr_2(pp\wedge q)_2$,[4] cleanly formed when 2 equiv of 2,3-dichloro-5,6-dicyanoquinone were added to dichloromethane suspensions of *trans*-$MBr_2(pphqH_2)_2$ and *cis*-$PtBr_2(pp\wedge hqH_2)_2$. IR spectra of the ppq and pp$\wedge$q complexes show a strong quinonyl ν_{CO} band at 1665−1660 cm^{-1}. These 4e$^-$/4H$^+$ oxidations were chemically reversible: the hydroquinonylphosphine complex precipitated in near quantitative yield when chloroform solutions of each quinonylphosphine complex were treated with excess sodium dithionite in aqueous 0.1 M HBr and the mixtures vigorously agitated by sparging with nitrogen gas (Scheme 1). Crystals of *trans*-$PdBr_2(ppq)_2{\cdot}(CH_3)_2CO$ were obtained by cooling an acetone solution of the complex. The molecular structure and selected bond parameters of *trans*-$PdBr_2(ppq)_2$ are presented in Figure 1.[9] The metrical parameters are unambiguous for quinonyl substituents, and the phosphorus atom-to-quinone *ipso*-carbon atom distance, 1.818(5) Å, is comparable to the analogous phosphorus-to-hydroquinonyl *ipso*-carbon atom distances in $pphqH_2$ complexes which range 1.81−1.84 Å.[4,8] This suggests that there is little if any electronic delocalization (ylid character[2]) between the phosphorus atom and its quinone substituent.

Cyclic voltammograms at platinum working electrodes of *trans*-$PdBr_2(ppq)_2$ and *cis*-$PtBr_2(pp\wedge q)_2$ in dichloroethane with 0.1 M *n*-Bu_4NPF_6 showed chemically irreversible reduction processes at −0.90 and −0.89 V vs Fc$^+$/Fc, respectively, that can be confidently assigned as quinonyl-centered.[10] In the reverse scans, a coupled anodic peak was observed at ≅+0.2 V, the potential for the first oxidation displayed by free bromide ion under identical conditions. As the scan rate was increased for *trans*-$PtBr_2(ppq)_2$, the quinone/semiquinonyl couple at −0.84 V became more chemically reversible ($i_{pa}/i_{pc} \cong 0.4$ and 0.65 at 100 and 500 mV s^{-1}, respectively) and the height of the +0.2 V peak decreased, consistent with the initial electron transfer step being followed on the experimental time scale by dissociation of bromide ion.[11] Qualitatively similar electrochemical behavior was found in other solvents, e.g., dimethylformamide. A bulk electrolysis of $PtBr_2(ppq)_2$ at −1.2 V (Pt-mesh working electrode) in dimethylformamide with 0.4 M *n*-Bu_4NPF_6 consumed 4.2 electrons per molecule of complex and gave *cis*-Pt(pphqH-*O*,*P*)$_2$ as the only product (identifiable by $^{31}P\{^1H\}$ NMR spectroscopy after concentration of the solution *in vacuo*), confirming reduction of the quinonyl substituents was followed by displacement of the bromo ligands.

Scheme 1 shows a plausible mechanism for the observed electrochemistry. One-electron reduction of each electrochemically independent quinonyl substituent produces $[M(pp{\sim}sq^{\bullet})_2X_2]^{2-}$ dianions with nucleophilic semiquinonyl (sq$^\bullet$) substituents,[1,6,12,13] and is followed on by rapid associative displacement of the bromo ligands to give M(pp~sq$^\bullet$-*O*,*P*)$_2$ diradical species and bromide ions. The metal coordination in such species is well precedented, e.g., by the complexes *cis*-$M(PR_3)_2$(Cat) (M = Ni, Pd, Pt; PR_3 = phosphine ligand; Cat = *o*-catecholate ligand) which undergo reversible ligand-centered one-electron oxidations to the corresponding *o*-semiquinonyl complexes;[10,12] *o*-semiquinonyl diradical complexes of Pd(II) and Pt(II) are also known: e.g., M(*o*-dbsq$^\bullet$)$_2$ (M = Pd, Pt; *o*-dbsq$^\bullet$ = 3,5-di-*tert*-butyl-1,2-semiquinonate).[13] Then follows spontaneous one-electron reduction of each coordinated semiquinonyl moiety (σ-*O*-coordination to the electrophilic M(II) center will lower the potential of the semiquinonyl/hydroquinonyl couple[1,6,12,13]) to give the hydroquinonylphosphine dianions, [M(pp~hq-*O*,*P*)$_2$]$^{2-}$. Protonation gives the hydroquinonylphosphine complexes, M(*O*,*P*-pp~hqH-*O*,*P*)$_2$. Alternatively, rapid disproportionation of the diradical species and protonation could lead to the M(pp~hqH-*O*,*P*)$_2$ complexes.[1]

Supplementary Material Available: Text giving details of the ligand syntheses and listings of analytical and spectroscopic data for the ligands and complexes and tables of crystal and structure refinement parameters, atomic coordinates and thermal parameters, bond lengths and bond angles for *trans*-$PdBr_2(ppq)_2{\cdot}(CH_3)_2CO$ (11 pages). Ordering information is given on any current masthead page.

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(9) Crystal data for *trans*-$PdBr_2(ppq)_2{\cdot}(CH_3)_2CO$: $C_{39}H_{32}Br_2O_5P_2Pd$, monoclinic, *C*2/*c*, $a = 13.093(3)$ Å, $b = 14.950(2)$ Å, $c = 19.170(4)$ Å, $\beta = 90.21(1)°$, $V = 3752(1)$ Å^3, $Z = 4$, $M = 908.8$, $D_c = 1.61$ g cm^{-3}, Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). The structure was solved by direct phasing and Fourier methods, and refined using full-matrix least-squares methods to give $R = 0.032$, $R_w = 0.038$ for 2019 independent observed reflections [$3 \leq 2\theta \leq 50°$, $|F_o| > 3\sigma|(F_o)|$].

(10) The reversible *p*-benzoquinone/*p*-semiquinone couple occurs at −0.92 V vs Fc$^+$/Fc under identical conditions and no metal-centered redox processes are expected in the potential range scanned—the $pphqMe_2$ and PPh_3 analogues of the complexes are all electrochemically silent over the potential range +0.5 to −1.6 V (see: Amatore, C; Azzabi, M; Jutand, J. *J. Am. Chem. Soc.* **1991**, *113*, 8375. Chen, L; Davies, J. A.; Staples, R. *Inorg. Chem. Acta.* **1989**, *163*, 11. Reference 14).

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