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Crystal and Molecular Structure of the Oxidative Addition Product of Tetrachloro-1,2-benzoquinone to Tris(triphenylphosphine)palladium(0), $Pd(P(C_6H_5)_3)_2(O_2C_6Cl_4)$

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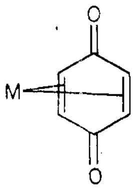
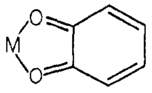
The crystal and molecular structure of $Pd(P(C_6H_5)_3)_2(O_2C_6Cl_4)$ has been determined from three-dimensional X-ray data collected by the θ–2θ scan technique. The structure was solved by standard heavy-atom methods and has been refined by least-squares procedures to a conventional R factor of 0.047 for 2976 reflections. The complex crystallizes in space group $P2_1/c$ of the monoclinic system in a cell of dimensions $a = 15.362$ (3), $b = 15.474$ (3), $c = 18.430$ (3) Å, $\beta = 121.09$ (5)°, and $V = 3748$ Å^3. There are four molecules per unit cell ($\rho_{\text{exptl}} = 1.54$ (1) g/cm^3, $\rho_{\text{calcd}} = 1.548$ g/cm^3). The quinone ligand is chelated to the metal through the oxygen donors with the $PdP_2(O_2C_6Cl_4)$ group forming a nearly perfect plane. Bonding parameters within the quinone ligand are consistent with a hydroquinone electronic structure.

Introduction

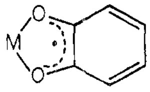
The addition of *o*-benzoquinone ligands to metals has been of considerable interest. While complexes of *p*-benzoquinones have been shown structurally to coordinate through localized ring olefin groups (I),[1] spectral properties of *o*-benzoquinone complexes indicate chelation through oxygen donors. Addition reactions of *o*-benzoquinones to a variety of nucleophilic group VIII metal complexes with d^8 and d^{10} electronic configurations have been studied.[2-7] Shifts of at least 200–300 cm^{-1} for the quinone carbonyl stretch indicate formal reduction on coordination to a catecholate with oxidation of the metal. Among the earliest reports of *o*-benzoquinone coordination are examples of complexes with metals of lower basicity.[8] Complexes of 9,10-phenanthrenequinone and 1,2-chrysenequinone with a range of metal ions have appeared which exhibit smaller shifts in $\nu(C{=}O)$ ($\sim$50 cm^{-1}) similar to *p*-quinones. Since olefin coordination is unlikely with many of the metals used (*i.e.*, Zn(II), Mo(VI)) these compounds probably contain oxygen-bonded, unreduced quinone ligands.[9] The intermediate possibility of radical anion coordination for *o*-benzoquinones has been demonstrated by the reversible chemical and electrochemical oxidation of reduced quinone complexes. Electron spin resonance spectra on these compounds (*i.e.*, $Pd(PPh_3)_2(O_2C_6Cl_4)^+$) indicate that the unpaired electron is localized on the semiquinone ligand.[10] Thus, three modes of coordination exist for *o*-benzoquinones (II) differing in formal oxidation state of the ligand with the relative importance of configurations IIa and IIc dependent on the basicity of the metal.



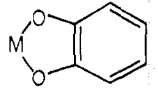
I



IIa

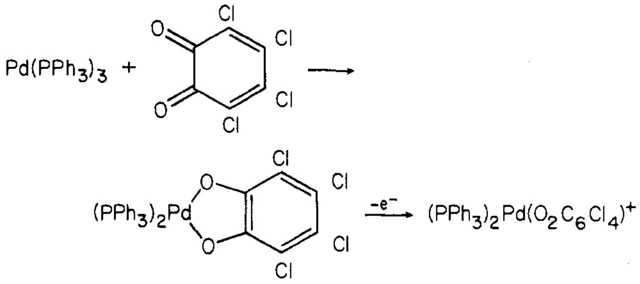


IIb



IIc

Representative of oxidative addition reactions of *o*-benzoquinones to basic metals is the addition of *o*-tetrachlorobenzoquinone to complexes of Pd(0). Balch has reported the formation of $Pd(PPh_3)_2(O_2C_6Cl_4)$ from $Pd(PPh_3)_3$ and found that the complex may be oxidized to the paramagnetic complex (IIb) $Pd(PPh_3)_2(O_2C_6Cl_4)$.[2,10] Ishii has found that addition of a variety of *o*-benzoquines to Pd(N-N)(DBA) (N-N = nitrogen donor ligand, DBA = dibenzylideneacetone) yields the respective amine-*o*-benzoquinone complex.[7] The complex $Pd(dipy)(O_2C_6Cl_4)$ may be formed in this manner and converted to $Pd(PPh_3)(O_2C_6Cl_4)$ by addition of PPh_3 to a suspension of the compound. Similarities in the infrared spectrum of the coordinated hydroquinone in each case suggest similar coordination geometries for the $Pd(O_2C_6Cl_4)$ group. A large band at 1425 cm^{-1} present in both the dipyridyl and phosphine complexes and also in $Pt(PPh_3)_2(O_2C_6Cl_4)$ has been assigned as $\nu(C{=}O)$.[3] This assignment is intriguing since it implies a considerable contribution from electronic structure IIa for the $Pd(O_2C_6Cl_4)$ group. From previous work on complexes with ligands capable of varying their formal oxidation state with that of the associated metal such a contribution may be expected to result in distortion of the square-planar geometry normally expected of Pd(II) with decrease in formal oxidation state of the metal.[11] To evaluate the structural significance of this effect in $Pd(PPh_3)_2(O_2C_6Cl_4)$ and to characterize further the coordination properties of *o*-benzoquinones the molecular structure of the complex has been determined crystallographically.



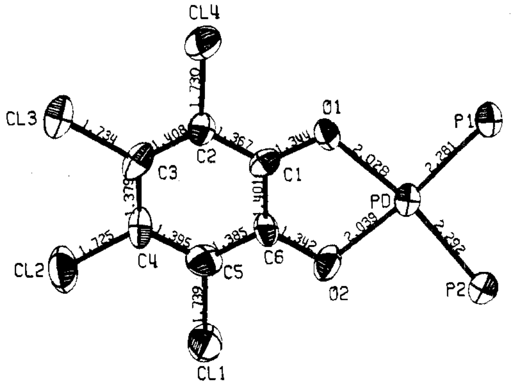


Figure 1. View of the inner coordination geometry of $Pd(P(C_6H_5)_3)_2(O_2C_6Cl_4)$ normal to the plane of the complex.

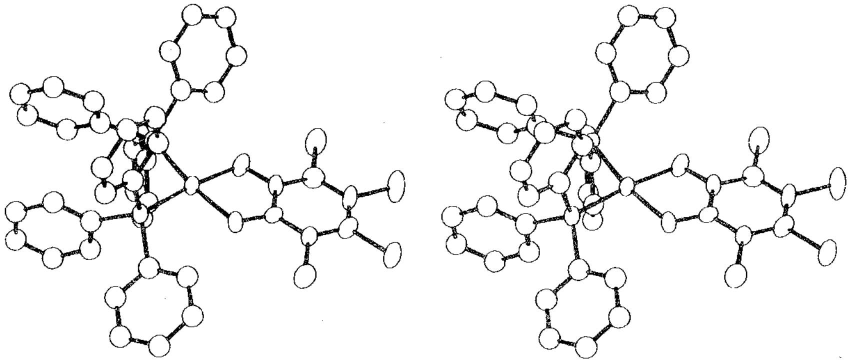


Figure 2. Stereoview of the entire $Pd(P(C_6H_5)_3)_2(O_2C_6Cl_4)$ molecule.

Table I. Final Structural Parameters for $Pd(P(C_6H_5)_3)_2(O_2C_6Cl_4)$

Atomic Positional and Thermal Parameters

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pd	−0.24014 (5)	−0.00524 (4)	0.20631 (4)	0.00379 (4)	0.00226 (3)	0.00256 (3)	−0.00023 (4)	0.00122 (3)	0.00015 (3)
P(1)	−0.24926 (18)	0.10403 (14)	0.28521 (15)	0.00400 (17)	0.00233 (10)	0.00299 (12)	0.00007 (11)	0.00121 (11)	0.00018 (10)
P(2)	−0.19881 (17)	0.07345 (14)	0.12281 (14)	0.00352 (16)	0.00290 (11)	0.00259 (11)	−0.00011 (11)	0.00118 (11)	0.00027 (9)
Cl(1)	−0.23757 (21)	−0.27448 (15)	0.05959 (15)	0.01195 (26)	0.00400 (14)	0.00448 (14)	−0.00142 (14)	0.00514 (17)	−0.00114 (11)
Cl(2)	−0.27940 (24)	−0.43793 (16)	0.13610 (18)	0.01504 (32)	0.00267 (12)	0.00623 (16)	−0.00085 (16)	0.00612 (20)	−0.00078 (12)
Cl(3)	−0.32791 (21)	−0.41715 (14)	0.28194 (17)	0.00844 (22)	0.00300 (12)	0.00553 (15)	−0.00038 (13)	0.00357 (16)	0.00105 (11)
Cl(4)	−0.33021 (20)	−0.23126 (15)	0.34872 (15)	0.00927 (21)	0.00441 (15)	0.00432 (12)	−0.00058 (14)	0.00448 (14)	0.00019 (10)
C(1)	−0.2752 (7)	−0.1739 (7)	0.2418 (6)	0.0034 (7)	0.0030 (5)	0.0023 (5)	−0.0001 (4)	0.0012 (5)	0.0005 (4)
C(2)	−0.2992 (6)	−0.2454 (8)	0.2715 (5)	0.0044 (5)	0.0027 (4)	0.0025 (4)	−0.0003 (6)	0.0013 (4)	0.0004 (5)
C(3)	−0.3007 (7)	−0.3284 (7)	0.2396 (6)	0.0047 (7)	0.0039 (6)	0.0024 (5)	−0.0007 (5)	0.0010 (5)	0.0012 (4)
C(4)	−0.2797 (8)	−0.3370 (6)	0.1757 (7)	0.0065 (9)	0.0022 (5)	0.0036 (6)	−0.006 (5)	0.0013 (6)	−0.0002 (4)
C(5)	−0.2600 (7)	−0.2636 (6)	0.1426 (5)	0.0063 (7)	0.0029 (7)	0.0028 (4)	−0.0009 (6)	0.0024 (5)	−0.0009 (4)
C(6)	−0.2571 (7)	−0.1822 (6)	0.1750 (6)	0.0045 (7)	0.0022 (4)	0.0025 (5)	−0.0002 (4)	0.0013 (5)	0.0004 (4)
O(1)	−0.2734 (4)	−0.0934 (4)	0.2700 (4)	0.0060 (5)	0.0023 (3)	0.0034 (3)	−0.0000 (3)	0.0026 (4)	−0.0003 (2)
O(2)	−0.2361 (4)	−0.1123 (4)	0.1436 (3)	0.0071 (5)	0.0029 (3)	0.0032 (3)	−0.0004 (3)	0.0028 (3)	0.0004 (3)

Group Positional Parameters

Group^c	x_c	y_c	z_c	ϕ	θ	ρ
P1R1	−0.3735	0.0779	0.3812	−2.766	−3.070	1.090
P1R2	−0.3492	0.2802	0.1844	2.120	2.930	−0.314
P1R3	−0.0305	0.1325	0.4512	0.497	−2.476	0.581
P2R1	−0.0383	−0.0328	0.0928	−0.859	−2.908	−0.630
P2R2	−0.1103	0.2679	0.1694	1.167	2.545	0.036
P2R3	−0.3907	0.0889	−0.0675	1.758	−2.245	−1.342

[a] Estimated standard deviations of the least significant figures are given in parentheses here and in succeeding tables. [b] Anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [c] x_c, y_c, and z_c are the fractional coordinates of the rigid group centers. The angles ϕ, θ, and ρ are in radians and have previously been defined by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

Table II. Derived Positional and Isotropic Thermal Parameters for Group Carbon Atoms

Atom	*x*	*y*	*z*	*B*, Å^2
		Ring R1		
R1C(1)	−0.4216 (9)	0.0680 (8)	0.4273 (7)	4.7 (2)
R1C(2)	−0.4311 (8)	0.1453 (9)	0.3851 (8)	4.4 (3)
R1C(3)	−0.3640 (8)	0.0007 (9)	0.4234 (9)	4.7 (3)
R1C(4)	−0.3254 (9)	0.0878 (8)	0.3352 (9)	2.7 (3)
R1C(5)	−0.3159 (8)	0.0107 (9)	0.3774 (8)	3.5 (3)
R1C(6)	−0.3830 (9)	0.1552 (8)	0.3391 (7)	3.9 (2)
		Ring R2		
R2C(1)	−0.3959 (10)	0.3562 (8)	0.1414 (8)	5.2 (3)
R2C(2)	−0.2961 (9)	0.3579 (9)	0.2097 (8)	5.6 (3)
R2C(3)	−0.4490 (9)	0.2785 (9)	0.1162 (7)	5.7 (3)
R2C(4)	−0.3025 (8)	0.2042 (7)	0.2274 (7)	2.9 (2)
R2C(5)	−0.4023 (8)	0.2024 (9)	0.1592 (7)	4.3 (2)
R2C(6)	−0.2494 (9)	0.2819 (8)	0.2526 (7)	3.4 (2)
		Ring R3		
R3C(1)	0.0645 (9)	0.1416 (8)	0.5248 (8)	5.4 (3)
R3C(2)	0.0514 (10)	0.0832 (9)	0.4625 (8)	5.3 (3)
R3C(3)	−0.0174 (10)	0.1909 (8)	0.5135 (7)	5.0 (3)
R3C(4)	−0.1254 (9)	0.1234 (9)	0.3777 (8)	2.9 (2)
R3C(5)	−0.1124 (8)	0.1818 (8)	0.4399 (9)	4.5 (3)
R3C(6)	−0.0436 (9)	0.0741 (8)	0.3889 (8)	3.8 (2)
		Ring R4		
R4C(1)	0.0285 (8)	−0.0798 (8)	0.0784 (7)	5.6 (3)
R4C(2)	−0.0724 (9)	−0.1058 (7)	0.0413 (6)	4.9 (3)
R4C(3)	0.0626 (8)	−0.0068 (9)	0.1298 (8)	4.9 (3)
R4C(4)	−0.1052 (8)	0.0142 (8)	0.1072 (6)	3.1 (2)
R4C(5)	−0.0042 (8)	0.0402 (9)	0.1443 (7)	4.4 (3)
R4C(6)	−0.1393 (9)	−0.0588 (7)	0.0557 (8)	4.1 (2)
		Ring R5		
R5C(1)	−0.0706 (9)	0.3513 (8)	0.1887 (7)	4.8 (3)
R5C(2)	−0.0207 (9)	0.2843 (9)	0.2459 (7)	4.5 (3)
R5C(3)	−0.1602 (9)	0.3350 (8)	0.1122 (7)	4.3 (3)
R5C(4)	−0.1499 (8)	0.1846 (7)	0.1500 (7)	3.1 (2)
R5C(5)	−0.1999 (8)	0.2516 (8)	0.0929 (6)	3.4 (2)
R5C(6)	−0.0604 (8)	0.2009 (8)	0.2265 (7)	3.5 (3)
		Ring R6		
R6C(1)	−0.4744 (8)	0.0962 (9)	−0.1495 (8)	4.7 (3)
R6C(2)	−0.3763 (8)	0.1016 (8)	−0.1353 (8)	3.8 (3)
R6C(3)	−0.4887 (8)	0.0835 (8)	−0.0817 (7)	5.5 (3)
R6C(4)	−0.3070 (7)	0.0816 (8)	0.0145 (7)	2.7 (2)
R6C(5)	−0.4057 (8)	0.0762 (9)	0.0003 (8)	4.1 (3)
R6C(6)	−0.2926 (8)	0.0943 (8)	−0.0533 (8)	3.6 (3)

Table III. Root-Mean-Square Amplitudes of Vibration for $Pd(P(C_6H_5)_3)_2(O_2C_6Cl_4)$

Atom	Min, Å	Intermed, Å	Max, Å
Pd	0.162 (1)	0.173 (1)	0.206 (1)
P(1)	0.166 (4)	0.181 (5)	0.222 (4)
P(2)	0.170 (4)	0.180 (4)	0.207 (4)
Cl(1)	0.184 (4)	0.224 (4)	0.328 (3)
Cl(2)	0.175 (4)	0.256 (4)	0.363 (3)
Cl(3)	0.169 (4)	0.269 (3)	0.279 (4)
Cl(4)	0.184 (4)	0.235 (4)	0.287 (3)
O(1)	0.163 (11)	0.201 (10)	0.229 (10)
O(2)	0.163 (12)	0.208 (10)	0.252 (9)
C(1)	0.157 (19)	0.174 (17)	0.209 (17)
C(2)	0.166 (20)	0.182 (17)	0.220 (16)
C(3)	0.146 (20)	0.190 (16)	0.269 (16)
C(4)	0.158 (19)	0.206 (17)	0.281 (15)
C(5)	0.155 (20)	0.200 (18)	0.242 (14)
C(6)	0.153 (19)	0.179 (16)	0.220 (16)

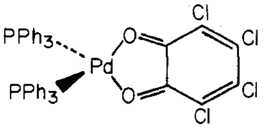
Experimental Section

Collection and Reduction of the X-Ray Data. A sample of the complex $Pd(PPh_3)_2(O_2C_6Cl_4)$ was prepared by the displacement of the dipyridyl ligand from $Pd(dipy)(O_2C_6Cl_4)$ in a methylene chloride solution containing an excess of triphenylphosphine. Crystals suitable for the crystallographic study were grown from methylene chloride. Optical examination of the crystals indicated the monoclinic system. Precession and Weissenberg photographs taken on crystals of the complex contained extinctions of $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, consistent with space group $P2_1/c$.[12] It was also observed that the crystals exhibited pleochroism appearing red approximately in the direction of the monoclinic axis and colorless in directions normal to b^*. A crystal was mounted and aligned along the monoclinic axis on a Picker four-circle automated diffractometer. The angular settings of 15 strong, independent reflections centered using Mo Kα radiation (λ 0.7107 Å) were used to give refined lattice constants of $a = 15.362$ (3) Å, $b = 15.474$ (3) Å, $c = 18.430$ (3) Å, $\beta = 121.09$ (5)°, and $V = 3748$ Å^3. An experimental density of 1.54 (1) g/cm^3 agrees with a calculated density of 1.548 g/cm^3 for four molecules per unit cell. The mosaic spread of the crystal was determined using the narrow-source open-counter ω-scan technique[13] and was found to be acceptable at 0.09°. An independent set of intensity data was collected by the θ–2θ scan technique using the Mo Kα peak with a Zr filter and allowances for the Kα_1–Kα_2 separation of higher 2θ values. The data set was collected within the angular range $4.5 \leq 2\theta \leq 50°$. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded 9000 counts/sec during the scan. During data collection the intensities of four standard reflections in different regions of reciprocal space were monitored after every 100 reflections measured. None of these standards deviated from its mean value by more than 3% during the time required to collect the data. Data were processed in the usual way with values of I and $\sigma(I)$ corrected for Lorentz and polarization effects. Since the crystal was approximately equidimensional in shape and the linear absorption coefficient small ($\mu = 8.90$ cm^{-1}), no correction was made for absorption effects. The intensities of a total of 4832 reflections were measured of which 2976 were observed to be greater than 2σ and have been included in the refinement.

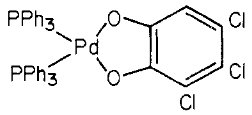
Solution and Refinement of the Structure. The position of the Pd atom was determined from a three-dimensional Patterson map. Two cycles of least-squares refinement of the Pd positional and thermal parameters and a scale factor gave discrepancy indices $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ of 0.474 and 0.570, respectively. From the Fourier map on this refinement the positions of all nonhydrogen atoms of the structure were obtained. Isotropic refinement of all atoms with phenyl rings of the triphenylphosphine ligands treated as rigid groups (d(C–C) = 1.392 Å) with a single group thermal parameter converged to discrepancy indices of $R_1 = 0.093$ and $R_2 = 0.108$. Further refinement with anisotropic thermal parameters for nongroup atoms and individual isotropic thermal parameters for atoms of the groups converted to $R_1 = 0.055$ and $R_2 = 0.061$. A final cycle of refinement was then performed including fixed contributions for phenyl hydrogens (d(C–H) = 0.98 Å). The final discrepancy indices for the structure were $R_1 = 0.047$ and $R_2 = 0.049$. At the completion of the refinement the standard deviation of an observation of unit weight was 1.26. During all cycles of refinement the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$. The standard deviations $\sigma(F^2)$ were estimated from counting statistics described previously.[14] In all calculations the atomic scattering factors for the nonhydrogen atoms were those of Cromer and Waber[15] while the hydrogen scattering factors were taken from the tabulation of Stewart, *et al.*[16] The effects of anomalous dispersion were included in the calculated structure factors with the appropriate values of $\Delta f'$ and $\Delta f''$ for the Pd, P, and Cl atoms taken from the report by Cromer and Liberman.[17] The final positional and thermal parameters of the structure are given in Table I. Derived positional and isotropic thermal parameters of the group carbon atoms are given in Table II. Table III contains root-mean-square vibrational amplitudes of atoms refined anisotropically. A table of the final F_o and $|F_c|$ values for the 2976 reflections used in the refinement is available.[18]

Description and Discussion of the Structure

Two limiting electronic structures (III) may be envisioned for $Pd(PPh_3)_2(O_2C_6Cl_4)$ differing in metal–ligand formal oxidation assignment and stereochemistry. A view of the



IIIa



IIIb

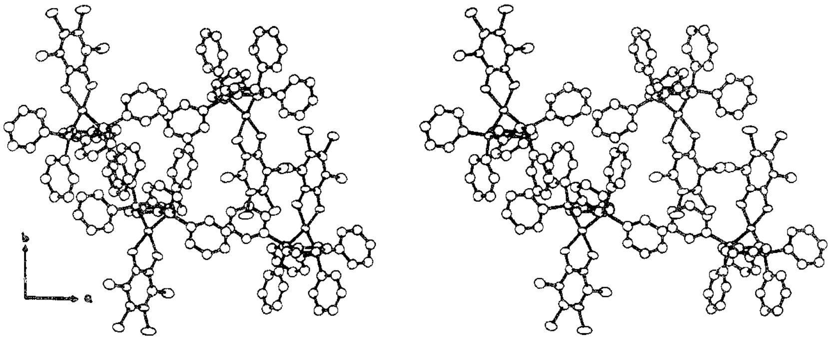
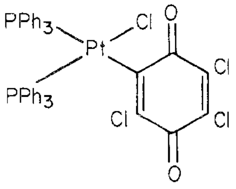


Figure 3. Stereoview of the contents of the unit cell. The quinone ligand is approximately in the crystallographic *ac* plane.

coordination geometry of the complex (Figure 1) is clearly consistent with IIIb and different from a third possibility resulting from metal insertion into a C–Cl bond as found in the addition of *p*-$O_2C_6Cl_4$ to $Pt(PPh_3)_4$ (IV).[3] Figure 2 contains a stereoview of the entire molecule with principal intramolecular bonding parameters presented in Table IV. A stereoview of the contents of the unit cell is presented in Figure 3 showing the orientation of the molecular plane approximately in the crystallographic *ab* plane. All nonbonding intra- and intermolecular contacts are normal.



IV

Bonding parameters within the $Pd(PPh_3)_2(O_2C_6Cl_4)$ molecule are most consistent with a planar palladium(II)–hydroquinone formulation. The dihedral angle between the PdP_2 and PdO_2 planes is 179.1 (6)° and none of the atoms of the $PdP_2(O_2C_6Cl_4)$ group are significantly off the PdP_2O_2 least-squares plane. While the C–O bond lengths of 1.345 (10) and 1.342 (10) Å are shorter than a normal single-bond length (~1.41 Å), they compare well with a value of 1.35 (1) Å found for *p*-tetrachlorohydroquinone[19] and are longer than 1.20 (1) Å for *p*-tetrachlorobenzoquinone.[20] The value is also longer than C–O distances reported for chelated carboxylate and acetylacetonate ligands with partial multiple C–O bonds and lengths of 1.25–1.28 Å. Further, carbon–carbon distances within the quinone benzene ring show no evidence of residual benzoquinone character. The Pd–O distances of 2.028 (5) and 2.038 (5) Å are within the range of values expected for a Pd(II) complex. Shorter values of 1.97 and 1.99 Å have been reported for bis complexes of acetylacetonate and acetate ligands;[21] longer values in excess of 2.10 Å have been observed for oxygen donors trans to strong acceptor ligands and in the presence of a strong trans effect.[22]

Table IV. Principal Intramolecular Bonding Parameters for $Pd(P(C_6H_5)_3)_2(O_2C_6Cl_4)$

Distances, Å

Pd–P(1)	2.280 (2)	C(5)–C(6)	1.384 (11)
Pd–P(2)	2.292 (2)	C(6)–C(1)	1.400 (11)
Pd–O(1)	2.028 (5)	Cl(1)–C(5)	1.739 (9)
Pd–O(2)	2.038 (5)	Cl(2)–C(4)	1.725 (9)
C(1)–O(1)	1.345 (10)	Cl(3)–C(3)	1.733 (9)
C(6)–O(2)	1.342 (10)	Cl(4)–C(2)	1.730 (8)
C(1)–C(2)	1.366 (11)	O(1)- - -O(2)	2.684 (8)
C(2)–C(3)	1.407 (11)	P(1)- - -P(2)	3.485 (3)
C(3)–C(4)	1.378 (12)	O(1)- - -P(1)	3.073 (6)
C(4)–C(5)	1.392 (12)	O(2)- - -P(2)	2.993 (6)

Angles, deg

P(1)–Pd–P(2)	99.34 (8)	C(1)–C(2)–C(3)	121.5 (8)
O(1)–Pd–O(2)	82.6 (2)	C(2)–C(3)–C(4)	118.9 (8)
P(1)–Pd–O(1)	90.8 (1)	C(3)–C(4)–C(5)	119.6 (9)
P(2)–Pd–O(2)	87.2 (1)	C(4)–C(5)–C(6)	121.3 (8)
P(1)–Pd–O(2)	173.4 (1)	C(5)–C(6)–C(1)	119.0 (8)
P(2)–Pd–O(1)	169.8 (1)	C(6)–C(1)–C(2)	119.6 (9)
Pd–O(1)–C(1)	111.2 (5)	Cl(1)–C(5)–C(6)	119.3 (7)
Pd–O(2)–C(6)	109.1 (5)	Cl(1)–C(5)–C(4)	119.4 (8)
Pd–O(1)–C(2)	139.6 (5)	Cl(2)–C(4)–C(5)	120.4 (8)
Pd–O(2)–C(5)	139.2 (5)	Cl(2)–C(4)–C(3)	120.0 (8)
O(1)–C(1)–C(2)	123.5 (8)	Cl(3)–C(3)–C(4)	121.6 (9)
O(1)–C(1)–C(6)	116.7 (9)	Cl(3)–C(3)–C(2)	119.4 (8)
O(2)–C(6)–C(1)	120.3 (8)	Cl(4)–C(2)–C(3)	120.4 (8)
O(2)–C(6)–C(5)	120.7 (8)	Cl(4)–C(2)–C(1)	118.1 (8)

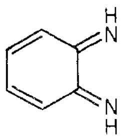
Dihedral Angle [Pd, P(1), P(2)] and [Pd, O(1), O(2)] = 179.1 (6)°

Distances from Least-Squares Plane[a] through PdP_2O_2 Group, Å
Eq of Plane: $11.12X - 1.79Y + 3.77Z = 1.88$

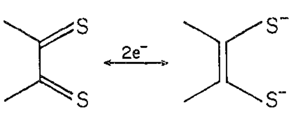
Pd	0.000 (1)	Cl(3)	0.045
P(1)	0.000 (2)	Cl(4)	−0.062
P(2)	0.004 (2)	C(1)	0.045
O(1)	0.028 (6)	C(2)	0.018
O(2)	0.000 (6)	C(3)	0.029
Cl(1)	−0.043[b]	C(4)	0.039
Cl(2)	0.072	C(5)	0.001
		C(6)	0.009

[a] Least-squares plane calculated according to W. C. Hamilton, *Acta Crystallgr.*, 14, 185 (1961). Equation given in monoclinic coordinates. [b] Not included in the calculations of the plane.

The Pd–O bond lengths are longer than would be expected if metal–ligand π bonding was a significant effect. Structural studies on complexes of *o*-benzoquinone diimine (V) with the ligand bonding as either a semiquinone in $Ni(C_6H_4(NH)_2)_2$[23] or a benzoquinone in $[Fe(CN)_4(C_6H_4(NH)_2)]^{2-}$ [24] have shown extremely short M–N distances, 1.83 and 1.91 Å, respectively, with ring C–C and C–N bond lengths reflecting the quinoid character of the ligand in each case. Bis(1,2-dithiolene) complexes show a similar trend with the neutral complex $Ni(S_2C_2Ph_2)_2$ having a short Ni–S distance of 2.101 (2) Å[25] and considerable multiple character to the C–S bond with a length of 1.71 (1) Å. When the character of the ligand changes from dithiolene (VIa) to dithiolate (VIb) as the complex undergoes reduction, the Ni–S distance increases with Ni–S distances of 2.146 (1) and 2.166 (6) Å reported for $[Ni(S_2C_2(CN)_2)_2]^-$ and $[Ni(S_2C_2(CN)_2)_2]^{2-}$ and metal–ligand



V



VIa VIb

π-bonding effects within the chelate ring decreasing in importance.[26,27] The quinone ligand in the oxidation product of the present complex $[Pd(PPh_3)_2(O_2C_6Cl_4)]^+$ is probably more similar in its electronic structure to the ligands in $Ni(C_6H_4(NH)_2)_2$ and $Ni(S_2C_2Ph_2)_2$. Shorter Pd–O distances and stronger metal–quinone π bonding would be expected. In the absence of intramolecular interligand delocalization present in the bis-dithiolene and -diimine complexes the geometry about the Pd atom in $[Pd(PPh_3)_2(O_2C_6Cl_4)]^+$ may be nonplanar, intermediate between IIIa and IIIb. A structure with the phosphine ligands out of the $PdO_2C_6Cl_4$ plane would be consistent with the small hyperfine coupling observed (<6 G) between the unpaired electron in the cationic complex and the phosphorus nuclei.[10]

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy of \$2.00 for microfiche, referring to code number AIC40519I.

Registry No. $Pd(P(C_6H_5)_3)_2(O_2C_6Cl_4)$, 31616-33-8.

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