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Preparation and Oxidation of Some Quinone Adducts of Transition Metal Complexes

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The additions of tetrachloro-1,2-benzoquinone and 9,10-phenanthrenequinone to $Ru(PPh_3)_3Cl_2$, of tetrachloro-1,2-benzoquinone and tetrabromo-1,2-benzoquinone to $Ru(CO)_3(PPh_3)_2$, of phenanthrenequinone imine to $Pt(PPh_3)_4$, and of tetrachloro-1,2-benzoquinone to $Pd(PPh_3)_3$ are described. The infrared spectra of the products indicate that the quinone has been reduced by adduct formation. 9,10-Phenanthroline-5,6-quinone reacts with $Pt(PPh_3)_4$ to yield $(Ph_3P)_2Pt(O_2C_{12}H_6N_2)$ which binds platinum through its oxygen donors while this quinone reacts with $(PhCN)_2PdCl_2$ to give $Pd(N_2C_{12}H_6O_2)Cl_2$ in which the α-diimine unit coordinates the metal. Cyclic voltammetry indicates that a number of the quinone adducts undergo reversible one-electron-transfer reactions. The one-electron oxidation products $Ru(1,2\text{-}O_2C_6X_4)(PPh_3)_2(CO)_2^+$ (X = Cl, Br) and $M(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2^+$ (M = Pd, Pt) have been generated in solution through chemical oxidation. These cations have been characterized by electronic, infrared, and electron spin resonance spectra. The phosphorus hyperfine structure which is observed in the ESR spectra of these cations is sensitive to the coordination geometry. It is concluded that these paramagnetic cations contain an unpaired electron which resides largely on a semiquinone ligand.

Introduction

The reactions of *o*-quinones with various transition metal complexes have recently attracted considerable attention. Although the scope of these reactions ranges from addition of a single quinone to coordinatively unsaturated complexes[1,2] through total substitution of all carbon monoxide ligands from certain metal carbonyls,[3,4] in all but a few cases[5] these reactions can be viewed as resulting in oxidation of the metal.

In this paper further examples of the addition of quinones to low-valent metal complexes are described, and the electron-transfer reactions of these and other quinone complexes are discussed. In general, the electron-transfer reactions of quinone–metal complexes have received scant attention, although the relation of these complexes to the dithiolenes,[6] whose electron-transfer behavior has been extensively explored, has been recognized. Portions of this work have been briefly communicated previously.[7–9]

Experimental Section

Preparation of Compounds. 1,10-Phenanthroline-5,6-quinone,[10] 1,2-naphthoquinone,[11] 9,10-phenanthrenequinone imine,[12] $Ru(CO)_3(PPh_3)_2$,[13] $RuCl_2(PPh_3)_3$,[14] $Pd(PPh_3)_3$,[15] and $(Ph_4As)[Rh(CO)_2Cl_2]$[16] were prepared by known procedures. Commercial 9,10-phenanthrenequinone was sublimed before use.

$Ru(1,2\text{-}O_2C_6Cl_4)(CO)_2[P(C_6H_5)_3]_2$. A solution containing 0.10 g (0.41 mmol) of tetrachloro-1,2-benzoquinone in 10 ml of dichloromethane was added to a solution of 0.30 g (0.42 mmol) of $Ru(CO)_3[P(C_6H_5)_3]_2$ in 30 ml of dichloromethane. The orange solution was filtered, 15 ml of heptane was added, and the solvent was removed by distillation until orange crystals formed. After cooling, the crystals were collected by filtration and recrystallized twice from dichloromethane–heptane. The product was vacuum-dried at 100° for 24 hr; mp 265–275° dec.

Anal. Calcd for $C_{44}H_{30}Cl_4O_4P_2Ru$: C, 56.98; H, 3.26; Cl, 15.29; mol wt 928. Found: C, 56.84; H, 3.20; Cl, 15.15; mol wt 890.

$Ru(1,2\text{-}O_2C_6Br_4)(CO)_2[P(C_6H_5)_3]_2$. This red-orange complex was prepared from tetrabromo-1,2-benzoquinone via the method outlined for the chlorinated analog; mp 240–250° dec.

Anal. Calcd for $C_{44}H_{30}Br_4O_4P_2Ru$: C, 47.81; H, 2.74; mol wt 1105. Found: C, 48.55; H, 2.77; mol wt 1100.

$Ru(1,2\text{-}O_2C_6Cl_4)[P(C_6H_5)_3]_2Cl_2$. A solution of 0.16 g (0.65 mmol) of tetrachloro-1,2-benzoquinone in 10 ml of acetone was added to a slurry of 0.48 g (0.50 mmol) of $(Ph_3P)_3RuCl_2$ in 30 ml of boiling acetone. The solution was filtered to remove any unreacted starting material and 10 ml of 2-propanol was added to the filtrate. The solvent was removed from the filtrate under reduced pressure until deep green crystals began to form. After collection by filtration the product was purified by recrystallization from acetone–2-propanol.

Anal. Calcd for $C_{42}H_{30}Cl_6O_2P_2Ru$: C, 53.53; H, 3.21; Cl, 22.57; P, 6.57. Found: C, 53.27; H, 3.15; Cl, 22.52; P, 6.29.

$Ru(9,10\text{-}O_2C_{14}H_8)[P(C_6H_5)_3]_2Cl_2$—Brown Isomer. A solution of 6.14 g (0.69 mmol) of 9,10-phenanthrenequinone dissolved in 20 ml of acetone was added to a slurry of 0.63 g (0.65 mmol) of $(Ph_3P)_3RuCl_2$ in 40 ml of boiling acetone. The solid dissolved to give a green solution which was immediately cooled. The brown crystalline product was collected by filtration and washed with acetone. Purification was achieved by dissolution of the product in cold dichloromethane, filtration of the solution, and addition of 2-propanol to the filtrate to precipitate the product. The complex dissolves to give yellow-brown solutions which slowly turn green; thin-layer chromatography (on silica gel with dichloromethane eluent) of a fresh solution indicates that a trace of the slower eluting blue isomer (vide infra) is present. The complex was obtained in 75% yield; it turns green above 180° and melts at 195–205°.

Anal. Calcd for $C_{50}H_{38}Cl_2O_2P_2Ru$: C, 66.38; H, 4.23; P, 6.85. Found: C, 66.33; H, 4.28; P, 6.41.

$Ru(9,10\text{-}O_2C_{14}H_8)[P(C_6H_5)_3]_2Cl_2$—Blue Isomer. A sample (0.3 g) of brown isomer was dissolved in 30 ml of a 1:1 v/v mixture of dichloromethane–1,2-dichloroethane. The solution was concentrated by boiling off solvent until blue-black crystals of the product began to separate. The solution was then cooled and the product (0.1 g, 33%) was collected by filtration and washed with dichloromethane; mp 204–208°. The mother liquor contained a green material which could not be induced to crystallize.

Anal. Found: C, 66.29; H, 4.47; P, 6.99.

$Ru(9,10\text{-}O_2C_{14}H_8)[P(C_6H_5)_3]_2Br_2$. A solution of 0.13 g (0.62 mmol) of phenanthrenequinone in 15 ml of acetone was added to a slurry of 0.50 g (0.45 mmol) of $(Ph_3P)_3RuBr_2$ in 40 ml of boiling acetone. The solution volume was reduced to 20 ml by distilling off the solvent. After cooling, the black, crystalline product was collected by filtration. The product (yield 0.18 g, 38%) was purified by recrystallization from dichloromethane–acetone; mp 187–189°.

Anal. Calcd for $C_{50}H_{38}Br_2O_2P_2Ru$: C, 60.43; H, 3.85. Found: C, 60.05; H, 3.92.

$Ru(1,2\text{-}O_2C_{10}H_6)[P(C_6H_5)_3]_2Br_2$. This complex was prepared from $(Ph_3P)_3RuBr_2$ using the method outlined above for the chloro analog; mp 184–185°.

Anal. Calcd for $C_{46}H_{36}Br_2O_2P_2Ru$: C, 58.56; H, 3.85. Found: C, 58.03; H, 4.13.

$Pt(5,6\text{-}O_2C_{12}H_6N_2)[P(C_6H_5)_3]_2$. Tetrakis(triphenylphosphine)platinum (0.61 g, 0.49 mmol) and 1,10-phenanthroline-5,6-quinone (0.12 g, 0.57 mmol) were added as solids to 30 ml of boiling dichloromethane. After filtration, 20 ml of *n*-hexane was added to the filtrate and the solvent was removed by distillation until crystals of the product began to appear. The red-brown product was removed by filtration and purified by recrystallization from dichloromethane–*n*-hexane; yield 0.40 g, 89%.

Anal. Calcd for $C_{48}H_{36}N_2O_2P_2Pt$: C, 62.00; H, 3.90; N, 3.01. Found: C, 62.20; H, 4.23; N, 2.64.

$Pt(9,10\text{-}HNOC_{14}H_8)[P(C_6H_5)_3]_2{\cdot}C_6H_{12}$. This compound was prepared from phenanthroquinone imine by the procedure described for $Pt(5,6\text{-}O_2C_{12}H_6N_2)[P(C_6H_5)_3]_2$ and recrystallized from dichloromethane–cyclohexane.

Anal. Calcd for $C_{50}H_{39}NOP_2Pt{\cdot}C_6H_{12}$: C, 66.52; H, 5.08; N, 1.38; P, 6.12. Found: C, 66.96; H, 4.17; N, 1.25; P, 6.36.

$Pd(5,6\text{-}O_2C_{12}H_6N_2)Cl_2$. A solution of 0.13 g (0.61 mmol) of 1,10-phenanthroline-5,6-quinone in 20 ml of dichloromethane was added to a solution of 0.26 g (0.68 mmol) of $(PhCN)_2PdCl_2$ in 20

Table I. Infrared Spectral Data[a]

Compd	ν(C≡O), cm^{-1}	Characteristic vibrations of the *o*-diolato or quinone ligand, cm^{-1}
$Ru(1,2\text{-}O_2C_6Cl_4)(CO)_2(PPh_3)_2$	2054 s, 1997 s	1525 w, 1261 s, 973 s, 808 s, 788 s
$Ru(1,2\text{-}O_2C_6Br_4)(CO)_2(PPh_3)_2$	2046 s, 1987 s	1495, 1264, 1240, 924
$Ru(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2Cl_2$		1515 w, 1224 s, 795 s, 790 s
$Ru(1,2\text{-}O_2C_{14}H_8)(PPh_3)_2Cl_2$		1600 s, 1590 sh, 1575 w, 1418 m, 1041 m, 948 w, 790 m, 770 s
$Pt(5,6\text{-}O_2C_{12}H_6N_2)(PPh_3)_2$		1597 s, 1588 sh, 1363 s, 1338 m, 1274 w, 1055 s, 1018 s, 940 w, 822 w, 807 m, 800 m
$Pt(9,10\text{-}HNOC_{14}H_8)(PPh_3)_2$		3525 w, 1611 s, 1589 s, 1520 m, 1398 s, 1379 s, 1280, 932, 790
$Pd(9,10\text{-}N_2C_{12}H_6O_2)(PPh_3)_2$		1710 w, 1705 s, 1605 w, 1575 s, 1480 m, 1375 s, 1295 s, 1200 m, 1155 m, 1090 m, 1060 w, 1030 w, 1020 m, 930 w, 820 s, 725 s
$Pd(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2$		1525 w, 1264 s, 972 s, 807 s, 793 s
$(Ph_4As)[Rh(1,2\text{-}O_2C_6Cl_4)(CO)_2]$	2050 s, 1980 s	1525 w, 1260 s, 970 s, 810 s
$(Ph_4As)[Rh(2,3\text{-}O_2C_{10}H_6)(CO)_2]$	2050 s, 1975 s	1505 w, 1280 s, 1170 m, 850 m, 845 m

[a] In hydrocarbon mull.

ml of dichloromethane. The yellow product, which precipitated in nearly quantitative yield, was collected by filtration, washed with dichloromethane, and vacuum-dried.

Anal. Calcd for $C_{12}H_6Cl_2N_2O_2Pd$: C, 37.19; H, 1.56. Found: C, 36.77; H, 1.64.

$Pd(1,2\text{-}O_2C_6Cl_4)[P(C_6H_5)_3]_2$. Method 1. A solution of 0.18 g (0.72 mmol) of tetrachloro-1,2-benzoquinone in 10 ml of dichloromethane was added to a solution of 0.72 g (0.62 mmol) of $(Ph_3P)_3Pd$ in 30 ml of dichloromethane. Upon addition of cyclohexane a small quantity of yellow solid precipitated. This was removed by filtration and discarded. Reduction of the volume of the filtrate caused a blue crystalline solid to form. This was collected and purified by recrystallization from dichloromethane–cyclohexane; mp 233–234°.

Method 2. A solution of 0.50 g of tetrachloropyrocatechol and 1.0 g of potassium hydroxide in 60 ml of methanol was added to a solution of 0.70 g of $(Ph_3P)_2PdCl_2$ in 60 ml of chloroform. After heating of the solution under reflux for 30 min, its volume was reduced to 20 ml and the solution was cooled. The precipitated complex was collected and purified by recrystallization from dichloromethane–methanol (yield 0.35 g).

Anal. Calcd for $C_{42}H_{30}Cl_4O_2P_2Pd$: C, 57.53; H, 3.45; Cl, 16.17. Found: C, 57.37; H, 3.28; Cl, 16.16.

$[(C_6H_5)_4As][Rh(1,2\text{-}O_2C_6Cl_4)(CO)_2]$. This preparation was carried out under a purified nitrogen atmosphere in dioxygen-free solvents. A solution of 0.55 g (0.90 mmol) of $[(C_6H_5)_4As][Rh(CO)_2Cl_2]$ in 30 ml of dichloromethane was added to a stirred solution of 0.12 g (2.1 mmol) of potassium hydroxide and 0.25 g (1.0 mmol) of tetrachlorocatechol in 30 ml of methanol. A white solid formed immediately. The resulting yellow solution was taken to dryness on a rotatory evaporator and then the remaining solid was extracted with chloroform. After the chloroform solution was filtered, cyclohexane was added to the filtrate, and chloroform was distilled off. Upon cooling, yellow crystals of the product (0.46 g 65%) were obtained; conductivity $\Lambda = 64$ cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for $C_{32}H_{20}AsCl_4O_4Rh$: C, 48.77; H, 2.56; Cl, 17.99. Found: C, 48.60; H, 2.52; Cl, 18.34.

$[(C_6H_5)_4As][Rh(2,3\text{-}O_2C_{10}H_6)(CO)_2]$. This complex was obtained by the procedure described for $[Ph_4As][Rh(1,2\text{-}O_2C_6Cl_4)(CO)_2]$ in 45% yield as yellow needles which were recrystallized from dichloromethane–cyclohexane; conductivity $\Lambda = 58$ cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for $C_{36}H_{26}AsO_4Rh$: C, 61.73; H, 3.74. Found: C, 61.58; H, 3.88.

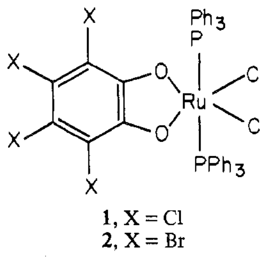
Oxidation Reactions. Solutions of the monocations $Ru(1,2\text{-}O_2C_6X_4)(CO)_2(PPh_3)_2^+$ (X = Cl, Br) and $M(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2^+$ (M = Pd, Pt) were prepared for spectroscopic observation by the following method. A solution of known concentration of the corresponding neutral complex was prepared in dichloromethane which has been previously distilled from phosphorus pentoxide. An excess of solid silver hexafluorophosphate was added to the solution and the mixture was vigorously shaken. In order to remove the remaining silver hexafluorophosphate and the silver metal which formed, the solution was filtered under a positive pressure of dry nitrogen gas. The solutions prepared in this fashion were stable for at least several hours. Spectroscopic properties of the oxidized solutions did not depend on the quantity of silver hexafluorophosphate used so long as it was in excess. For measurement of electron spin resonance spectra, $NiS_4C_4(CF_3)_4$[17] was also used as an oxidant. In this case, ESR resonances due to both the monocation and $NiS_4C_4(CF_3)_4^-$ were observed. The same ESR spectrum for each cation was obtained when either oxidant was used.

Physical Measurements. Electrochemical measurements were made on a Chemtrix SSP-2 polarograph using dichloromethane solutions with sample concentration of ca. 1 m*M*. The supporting electrolyte was 0.1 *M* tetra-*n*-butylammonium hexafluorophosphate. A saturated aqueous calomel electrode was utilized as the reference electrode and a platinum bead served as the working electrode. Conductivities were measured in 2×10^{-3} *M* solutions in nitromethane. Magnetic susceptibilities were measured on a Gouy balance with $HgCo(SCN)_4$ as the standard. Molecular weights were measured using a Mechrolab vapor pressure osmometer with chloroform as solvent and triphenylphosphine as standard.

Results and Discussion

Synthetic Studies. New complexes have been obtained by the addition of quinones to metal complexes with d^6, d^8, and d^{10} electronic configurations. Tetrachloro-1,2-benzoquinone, phenanthrenequinone, and 1,2-naphthoquinone react with the d^6 complex $Ru(PPh_3)_3Cl_2$ to yield six-coordinate complexes of the type $Ru(o\text{-diolato})(PPh_3)_2Cl_2$. Selected aspects of the infrared spectra of these and other complexes are set out in Table I. Upon adduct formation the quinone–carbonyl stretching vibration, which generally occurs at ca. 1700 cm^{-1}, is generally lost, an observation that is consistent with ligand reduction upon adduct formation. The vibrational bands which are assigned to the *o*-diolato ligands in Table I are those which are not obscured by bands due to triphenylphosphine or other entities present in the complexes. These assignments are consistent with the observations reported for similar compounds.[1] The magnetic moment of 2.7 BM found for $Ru(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2Cl_2$ is within the range found for some ruthenium(IV) hexahalide salts.[18] Due to the small amounts of material available, the magnetic susceptibilities of $Ru(9,10\text{-}O_2C_{14}H_8)(PPh_3)_2Cl_2$ and $Ru(1,2\text{-}O_2C_{10}H_6)(PPh_3)_2Cl_2$ were not measured. A brown and a blue form of $Ru(9,10\text{-}O_2C_{14}H_8)(PPh_3)_2Cl_2$ have been isolated. The infrared spectra of these two compounds are very similar except in the region where the Ru–Cl stretching vibration(s) should occur. The brown isomer exhibits two absorptions at 334 and 280 cm^{-1} while the blue isomer displays an absorption at 298 cm^{-1} with shoulders at 326 and 270 cm^{-1}. Consequently, it appears that these two forms are two of the three geometrical isomers expected for such a compound.

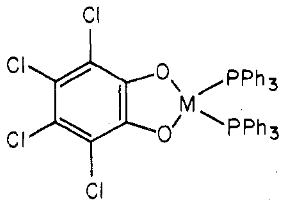
Tetrachloro-1,2-benzoquinone and tetrabromo-1,2-benzoquinone react readily with $Ru(CO)_3(PPh_3)_2$ to yield the orange complexes **1** and **2**. The lack of ν(C=O) in the infrared



1, X = Cl
2, X = Br

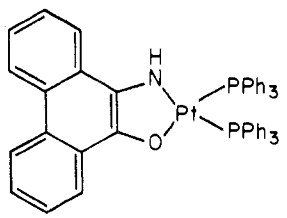
spectra of these two complexes is consistent with their formulation as ruthenium(II)–catecholato complexes. The observation of two carbon monoxide stretching frequencies in **1** and **2** indicates that these ligands occupy cis positions. The mutual trans location of the phosphine ligands has been inferred from the ESR spectra of the one-electron oxidation products of **1** and **2** (vida infra).

Tetrachloro-1,2-benzoquinone reacts with the d^{10} complex $Pd(PPh_3)_3$ to yield **3**. The analogous platinum complex as well



3, M = Pd
4, M = Pt

as platinum complexes with other quinones have been reported earlier.[19] Phenanthrenequinone imine also reacts with $Pt(PPh_3)_4$ to give red-brown **5**. The infrared spectrum of **5**



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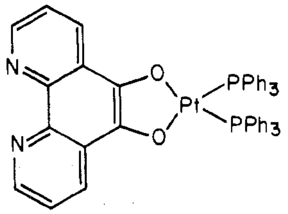
indicates that ν(N–H) has shifted from 3190 cm^{-1} in the free ligand to 3400 cm^{-1} in the adduct. Additionally, the infrared bands due to ν(C=O) and ν(C=N) at 1675 cm^{-1} of the quinone imine are absent in the adduct **5**. 1,10-Phenanthroline-5,6-quinone reacts with metal complexes either through the α-diimine fragment or through the α-dicarbonyl function. With the low-valent complex $Pt(PPh_3)_4$ this quinone undergoes oxidative addition to form red-brown **6**. The infrared spectrum of **6** is roughly similar to that of $Pt(9,10\text{-}O_2C_{14}H_8)(PPh_3)_2$.[19] In particular ν(C=O) of the parent quinone which occurs at 1705 and 1690 cm^{-1} is absent in the adduct **6**. In contrast 1,10-phenanthroline-5,6-quinone reacts with $(PhCN)_2PdCl_2$ to yield yellow **7** in which the α-diimine unit chelates palladium. The infrared spectrum of **7** shows only a small shift to higher energy of ν(C=O) which occurs at 1705 and 1690 cm^{-1} in the free ligand. Another complex, in which 1,10-phenanthroline-5,6-quinone bonds a metal through the α-diimine moiety, has been obtained by the nitration and oxidation of tris(1,10-phenanthroline)cobalt(III).[20]



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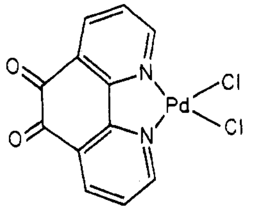

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The reaction of a metal halide complex with catechols in the presence of base offers an alternate method of preparation of some of these complexes. For example $(Ph_3P)_2PdCl_2$ reacts with 3,4,5,6-tetrachlorocatechol in the presence of potassium hydroxide to give **3**. Under similar conditions $(Ph_3P)_2Ru(CO)_2Cl_2$ reacts with 3,4,5,6-tetrachlorocatechol to give **1**. Other catecholato complexes may be prepared analogously. Treatment of $[Ph_4As][Rh(CO)_2Cl_2]$ with anions of 3,4,5,-6-tetrachlorocatechol or 2,3-naphthalenediol produces $[Ph_4As][Rh(1,2\text{-}O_2C_6Cl_4)(CO)_2]$ and $[Ph_4As][Rh(2,3\text{-}O_2C_{10}H_6)(CO)_2]$, respectively.

Table II. Data from Cyclic Voltammetry

Complexes	Couple	E_p^{ox}, V	i_p^{ox}, μA/mmol
$Ru(1,2\text{-}O_2C_6Cl_4)(CO)_2(PPh_3)_2$	$0 \rightleftarrows +1$	0.65	4.2
	$+1 \rightleftarrows +2$	1.76	3.9
$Ru(1,2\text{-}O_2C_6Br_4)(CO)_2(PPh_3)_2$	$0 \rightleftarrows +1$	0.66	3.9
	$+1 \rightleftarrows +2$	1.70	2.4
$Rh(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2(CO)Cl$	$0 \rightleftarrows +1$	0.92	4.3
$Ir(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2(CO)Cl$	$0 \rightleftarrows +1$	0.92	3.9
$Ir(1,2\text{-}O_2C_6Cl_4)(PPh_2Me)_2(CO)Cl$	$0 \rightleftarrows +1$	0.93	4.0
$Ir(1,2\text{-}O_2C_6Br_4)(PPh_3)_2(CO)Cl$	$0 \rightleftarrows +1$	0.96	3.9
$Pd(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2$	$0 \rightleftarrows +1$	0.72	4.1
$Pt(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2$	$0 \rightleftarrows +1$	0.89	3.8
$[Ph_4As][Rh(1,2\text{-}O_2C_6Cl_4)(CO)_2]$	$-1 \rightleftarrows 0$	0.63	2.4

Electron-Transfer Behavior. A number of the quinone adducts have been found to undergo reversible one-electron oxidation or reduction. The relevant polarographic data from cyclic voltammetric experiments are set out in Table II. All of the reactions reported are reversible one-electron processes. The observed peak currents are comparable to that found for the one-electron oxidation of $NiS_4C_4(CF_3)_4^{2-}$ to $NiS_4C_4(CF_3)_4^{-}$. The anodic and cathodic peak currents for each process are equal, and these peak currents are proportional to the square root of the scan rate as anticipated for reversible, one-electron transfers.[21]

Chemical oxidation of a number of the complexes to their monocations has been achieved through the use of either silver hexafluorophosphate or $NiS_4C_4(CF_3)_4$ as the oxidant. The oxidations of the ruthenium complexes **1** and **2**, the palladium complex **3**, and the platinum complex **4** have been examined in the greatest detail. Since the electrochemical data indicate that these cations will be readily reduced, no attempts have been made to isolate crystalline solids containing these cations; however, spectroscopic data have been obtained from relatively stable solutions of these cations. The electronic, infrared, and electron spin resonance spectroscopic data for these and some other cations are reported in Table III. The cations **1**$^+$–**4**$^+$ exhibit ESR spectra which are indicative of the presence of a compound with a doublet ground state, whereas the corresponding neutral complexes **1**–**4** are diamagnetic. The electronic spectra of the complexes display well-defined changes upon oxidation. The two carbonyl stretching frequencies of **1** and **2** occur at higher energies in the corresponding cations. This increase in ν(C≡O) is consistent with reduced metal–ligand back-bonding in the oxidized complexes. The observation of two carbon monoxide stretching frequencies in both **1**$^+$ and **2**$^+$ indicates that the cis arrangement of the carbon monoxide ligands is maintained upon oxidation.

The chemical formation of these cations is reversible. Oxidation of orange **2** in dichloromethane with silver hexafluorophosphate produces purple **2**$^+$; reduction of a solution of **2**$^+$ with clean zinc dust is accompanied by the quantitative regeneration of both the electronic and infrared spectra of **2**. Since it appears that the same geometrical isomer of **2** formed after oxidation to **2**$^+$ and rereduction to **2** and since both **2** and **2**$^+$ contain cis carbon monoxide ligands, it is very likely that **2** and **2**$^+$ exist as the same geometrical isomer. Similarly, the oxidation of yellow **4** to violet **4**$^+$ may be reversed (as evidenced by the quantitative recovery of the electronic spectrum of **4**) by the addition of hydrazine hydrate to **4**$^+$ in dichloromethane.

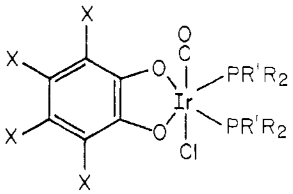
The observation of hyperfine structure due to the phosphorus ligands of the paramagnetic complexes of this type is useful in determining the coordination geometry. The observation

Table III. Spectroscopic Characterization Catecholato and Semiquinone Complexes

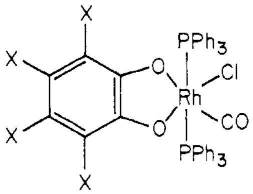
Compd	Electronic spectra,[a] λ_{max}, nm (ϵ)	Infrared spectra,[a] ν(C≡O), cm^{-1}	ESR spectra, $\langle g \rangle$ ($\langle A_{^{31}P} \rangle$)
$Ru(1,2\text{-}O_2C_6Cl_4)(CO)_2(PPh_3)_2$	440 (2.7×10^3), 340 sh (4.0×10^3)	2045, 1983	Diamagnetic
$Ru(1,2\text{-}O_2C_6Cl_4)(CO)_2(PPh_3)_2{}^+$	580 sh (2.3×10^3), 480 (3.2×10^3), 425 (3.4×10^3), 368 sh (3.2×10^3)	2072, 2022	2.004 (24.5 G)[b]
$Ru(1,2\text{-}O_2C_6Br_4)(CO)_2(PPh_3)_2$	440 (3.1×10^3), 330 sh (4.9×10^3)	2046, 1994	Diamagnetic
$Ru(1,2\text{-}O_2C_6Br_4)(CO)_2(PPh_3)_2{}^+$	595 (4.1×10^3), 518 (4.5×10^3), 415 (4.2×10^3), 385 (4.3×10^3), 335 sh (5.7×10^3)	2074, 2023	2.007 (24.7 G)[b]
$Pd(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2$	555 (2.8×10^2)		Diamagnetic
$Pd(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2{}^+$	458 (4.4×10^3), 437 (4.3×10^3), 372 (8.9×10^3)		2.006 (<6 G)[c]
$Pt(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2$	402 (2.9×10^2), 322 (1.1×10^4)		Diamagnetic
$Pt(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2{}^+$	600 (9×10^2), 470 (3.9×10^3), 323 (8.7×10^3)		2.004 (<8 G)[c]
$Rh(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2(CO)Cl^+$			2.003 (19.3 G)[b]
$Ir(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2(CO)Cl^+$			2.002 (<8 G)[c]
$Ir(1,2\text{-}O_2C_6Cl_4)(PMePh_2)_2(CO)Cl^+$			2.002 (<8 G)[c]

[a] Measured in dichloromethane solution. [b] Spectrum appears as a triplet with relative intensities 1:2:1 due to coupling to two equivalent phosphorus nuclei. [c] Peak to peak line width of the single-line spectrum.

of splitting in the ESR spectra of **1**$^+$ due to two equivalent phosphorus nucleii, along with the infrared observation of two carbon monoxide stretching frequencies, requires that **1**$^+$ have the geometry depicted above for **1**. Similar observations have been made for **2**$^+$. The magnitude of the phosphorus hyperfine splitting is correlated with the location of the phosphine ligands with respect to the semiquinone ligand. The square-planar complexes **3**$^+$ and **4**$^+$ as well as the six-coordinate complexes **8**$^+$ and **9**$^+$ display no detectable coupling to the phosphorus atoms. In these cases the phosphine ligands lie in the plane of the semiquinone ligand. In the complexes **1**$^+$, **2**$^+$, and **10**$^+$,[1] in which the phosphine ligands lie above and below the plane of the semiquinone ligand, a hyperfine coupling of ca. 18–25 G is observed for each phosphine.



8, R = R' = Ph
9, R' = CH$_3$, R = Ph



10

The cations **1**$^+$–**4**$^+$ and **8**$^+$–**10**$^+$ are formulated as complexes containing a semiquinone radical anion on the basis of the following observations. The ESR spectra of the cations reveal almost no dependence of the isotropic g values on the electronic configuration of the metal. In fact, the isotropic g values are quite similar to those reported for uncoordinated chlorosemiquinones.[22] Moreover, the g tensor anisotropy is quite small; **2**$^+$ exhibits an axially symmetric ESR spectrum in frozen dichloromethane solution at 77°K with $g_\perp = 2.02$ and $g_\parallel = 2.00$. In contrast, typical low-spin d^5 complexes of Ru(III) display pronounced rhombic symmetry in their ESR spectra with characteristic g values in the range 2.8, 2.0, 1.6.[23] Additionally, the ESR spectra of low-spin Ru(III) complexes are observed only at low temperature where line broadening due to spin–lattice relaxation is reduced.[19] The ESR spectra of the cations listed in Table III are readily observed in fluid solution at 25°. The pattern of hyperfine splitting due to ^{31}P of the phosphines is also consistent with the presence of a coordinated semiquinone radical. With complexes in which the phosphines lie trans to the semiquinone ligand the ^{31}P nuclei lie in a nodal plane of the π system which contains the odd electron. Consequently, no hyperfine splitting due to these ^{31}P nuclei is expected. However, in complexes in which the phosphines are arranged above and below the plane of the semiquinone ligand, spin density may be transferred from the semiquinone ligand to the ^{31}P nucleus either through a direct, through-space interaction or via a metal-mediated situation. In these cases a significant hyperfine coupling to ^{31}P is observed.

The d^8 complex $[Rh(1,2\text{-}O_2C_6Cl_4)(CO)_2]^-$ and its 2,3-naphthalenediolato analog were prepared to examine the possibility that these species might form dioxygen adducts which could react to produce oxidative cleavage of the aromatic catecholato nucleus. Additionally, these anions have a potential for one-electron ligand oxidation as well as oxidative addition to the metal. Unfortunately these anions do not form dioxygen adducts and it has not been possible to characterize any products of oxidative addition to rhodium. The electrochemical data indicate that $[Rh(1,2\text{-}O_2C_6Cl_4)(CO)_2]^-$ undergoes a reversible, one-electron oxidation. Oxidation of the yellow anion in dichloromethane solution with silver hexafluorophosphate yields unstable violet solutions which do not produce an ESR signal. Similarly, oxidation with $NiS_4C_4(CF_3)_4$ yields only the ESR signal due to $NiS_4C_4(CF_3)_4{}^-$. It appears that the various oxidation products of these rhodium anions are not stable.

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Registry No. $Ru(1,2\text{-}O_2C_6Cl_4)(CO)_2(PPh_3)_2$, 41326-30-1; $Ru(1,2\text{-}O_2C_6Br_4)(CO)_2(PPh_3)_2$, 41383-60-2; $Pd(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2$, 31616-33-8; $Pt(9,10\text{-}HNOC_{14}H_8)(PPh_3)_2$, 55401-34-8; $Pt(5,6\text{-}O_2C_{12}H_6N_2)(PPh_3)_2$, 55401-35-9; $Pd(5,6\text{-}O_2C_{12}H_6N_2)Cl_2$, 55401-36-0; $[Ph_4As][Rh(1,2\text{-}O_2C_6Cl_4)(CO)_2]$, 55401-38-2; $[Ph_4As][Rh(2,3\text{-}O_2C_{10}H_6)(CO)_2]$, 55401-40-6; $Ru(1,2\text{-}O_2C_6Cl_4)[PPh_3]_2Cl_2$, 55449-65-5; $Ru(9,10\text{-}O_2C_{14}H_8)[PPh_3]_2Cl_2$, 34417-14-6; $Ru(9,10\text{-}O_2C_{14}H_8)[PPh_3]_2Br_2$, 55401-41-7; $Ir(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2(CO)Cl$, 35794-39-9; $Ir(1,2\text{-}O_2C_6Cl_4)(PPh_2Me)_2(CO)Cl$, 35794-41-3; $Rh(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2(CO)Cl$, 35794-38-8; $Ir(1,2\text{-}O_2C_6Br_4)(PPh_3)_2(CO)Cl$, 35934-92-0; $Pt(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2$, 31616-32-7; $Ru(1,2\text{-}O_2C_6Cl_4)(CO)_2(PPh_3)_2{}^+$, 41383-62-4; $Ru(1,2\text{-}O_2C_6Br_4)(CO)_2(PPh_3)_2{}^+$, 41333-04-4; $Pd(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2{}^+$, 41021-90-3; $Pt(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2{}^+$, 41021-91-4; $Rh(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2(CO)Cl^+$, 41333-03-3; $Ir(1,2\text{-}O_2C_6Cl_4)(PPh_3)_2(CO)Cl^+$, 41383-61-3; $Ir(1,2\text{-}O_2C_6Cl_4)(PMePh_2)_2(CO)Cl^+$, 55428-37-0; $Ru(CO)_3[P(C_6H_5)_3]_2$, 14741-36-7; $(Ph_3P)_3RuCl_2$, 15529-49-4; $(Ph_3P)_3RuBr_2$, 15709-75-8; $(PhCN)_2PdCl_2$, 14220-64-5; $(Ph_3P)_3Pd$, 28516-49-6; $[(C_6H_5)_4As][Rh(CO)_2Cl_2]$, 13986-82-8; $Pd(9,10\text{-}N_2C_{12}H_6O_2)(PPh_3)_2$, 55428-38-1; tetrachloro-1,2-benzoquinone, 2435-53-2; tetrabromo-1,2-benzoquinone, 2435-54-3; 9,10-phenanthrenequinone, 84-11-7; 1,10-phenanthroline-5,6-quinone, 27318-90-7; phenanthrenequinone imine, 3942-85-6; $Pt(PPh_3)_4$, 14221-02-4; $(Ph_3P)_2PdCl_2$, 13965-03-2.

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Electron Transfer in Oxidized Biferrocene, Biferrocenylene, and [1.1]Ferrocenophane Systems

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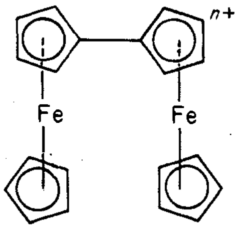
Oxidized salts of biferrocene, 1',6'-diiodobiferrocene, biferrocenylene, and 1,12-dimethyl[1.1]ferrocenophane are studied with ^{57}Fe Mössbauer spectroscopy, variable-temperature magnetic susceptibility, and X-band EPR, infrared, and electronic absorption spectroscopies with the objective of determining the "intervalence" electron-transfer rates in the singly oxidized species and relating the rates to the level of exchange-type interaction present. The compound biferricenium$^+$TCA$^-$·2TCAA shows ^{57}Fe Mössbauer spectra at 300 and 4.2°K that are interpretable in terms of a superposition of two quadrupole-split doublets (ΔE_Q = 2.176 and 0.392 mm/sec at 300°K) for a mixed-valence Fe^{II}Fe^{III} species and one lower intensity doublet (ΔE_Q = 0.903 mm/sec at 300°K) for an average-valence species. It is speculated that the flexibility of the singly fused, singly oxidized biferrocene ion appears to lead to some anion dependence in the electron-transfer rate. Singly oxidized 1',6'-diiodobiferrocene is a delocalized system (i.e., average valence) as characterized by Mössbauer spectroscopy (one doublet with ΔE_Q = 1.284 mm/sec at 300°K) and EPR (g_1 = 2.75, g_2 = 2.01, and g_3 = 1.97 for the solid at 12°K). A relatively isotropic g tensor ($g_1 \simeq 2.3$, $g_2 \simeq 2.0$, and $g_3 \simeq 1.9$) is also seen for the delocalized singly oxidized biferrocenylene ion in four salts and it is shown that for these fused ferrocene–ferricenium systems the conversion from mixed valence to average valence is characterized by a loss of orbital angular momentum (giving a relatively isotropic g tensor) as a result of the delocalization of the single unpaired electron onto two iron centers. The absence of the usual ferricenium $^2E_{1u} \leftarrow {}^2E_{2g}$ "hole" transition is explained for diamagnetic biferricenylenium(2+). The infrared spectra of biferrocenylene and biferricenylenium(n+) (n = 1, 2) are discussed. The unusual temperature dependence of the Mössbauer spectrum of 1,12-dimethyl[1.1]ferricenophanium$^+$I$_3^-$ is reinvestigated and data are presented for measurements at 300, 190, 140, 100, 80, and 4.2°K. It is suggested that the inner doublet for the Fe(III) site is tending to convert to a magnetic spectrum at the lowest temperatures. Finally and most importantly, evidence is presented to support the presence of direct Fe–Fe interaction in these systems by the reporting of *diamagnetism* for the DDQH$^-$ salt of dioxidized [Fe^{III}Fe^{III}] 1,12-dimethyl[1.1]ferrocenophane. A 4.2°K magnetically perturbed Mössbauer spectrum, which shows η = ~0.8, is also presented for this same compound.

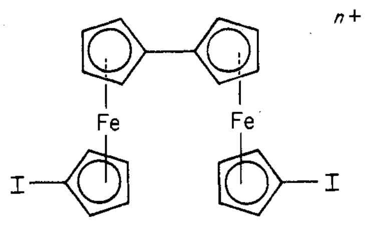
Introduction

The increased interest in mixed-valence compounds in recent years stems from attempts to make high-temperature superconducting materials and new semiconducting materials, increased interest in understanding biological mixed-valence compounds (most notably the ferredoxin systems), analogies between mixed-valence compounds and inner- and outer-sphere complexes formed during redox processes, and simply a renewed curiosity as to the intriguing characteristics of mixed-valence and analogous average-valence (i.e., delocalized) systems. The last is perhaps tempered by a feeling that an understanding of the mixed-valence phenomenon will in itself lead to a better understanding of the electronic structure of simpler systems. Results from a few concerted and continuing programs have appeared since the 1967 reviews[2-4] on mixed-valence compounds. Germane to this paper is the work[5-20] on mixed-valence biferrocene-type compounds; mixed-valence ferrocene polymers have also been reported.[21-24]

In this paper results will be reported on new biferricenium salts such as the trichloroacetate salt (TCA$^-$ stands for trichloroacetate and TCAA for trichloroacetic acid) of monooxidized biferrocene (I, n = 1) and the I$_3^-$ salt of monooxidized 1',6'-diiodobiferrocene (II, n = 1), and results will be presented for various biferrocenylene(III) and [1.1]ferrocenophane(IV) systems, most notably the magnetism and ^{57}Fe Mössbauer results for the 2,3-dichloro-5,6-dicyanobenzoquinone salt of dioxidized 1,12-dimethyl[1.1]ferrocenophane (IVb, n = 2).



I



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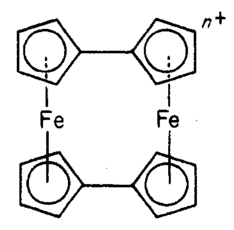
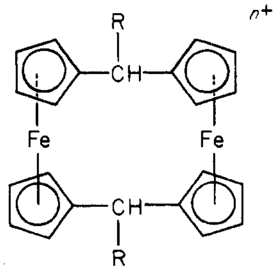


III



IV a, R = H
b, R = CH$_3$

Cowan and Kaufman[5] first prepared a salt of monooxidized biferrocene (I, n = 1) and reported that the cation was of the mixed-valence type, i.e., possessed both a low-spin Fe(II) and