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Comparative Bonding Properties of Semiquinonate and Iminosemiquinonate Radical Ligands in $Ru(CO)_2(3,6\text{-}DBSQ)_2$ and $Ru(CO)_2(PhenoxSQ)_2$

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Semiquinonate and iminosemiquiononate complexes of ruthenium have been prepared by treating $Ru_3(CO)_{12}$ with 3,6-di-*tert*-butyl-1,2-benzoquinone (3,6-DBBQ) and 2,4,6,8-tetra-*tert*-butylphenoxazin-1-one (PhenoxBQ). Crystallorgraphic characterization of $Ru(CO)_2(3,6\text{-}DBSQ)_2$ obtained as the 2-propanol solvate (tetragonal, $P\bar{4}2_1c$, $a = 19.066(2)$ Å, $c = 18.420(5)$ Å, $V = 6696(2)$ Å^3, $Z = 8$, $R = 0.041$) has shown that the carbonyl ligands are coordinated at *cis* sites. Structural characterization of $Ru(CO)_2(PhenoxSQ)_2$ carried out on crystals obtained as the dichloromethane solvate (orthorhombic, *Pbca*, $a = 31.215(6)$ Å, $b = 12.393(3)$Å, $c = 30.664(6)$Å, $V = 11862(5)$Å^3, $Z = 8$, $R = 0.069$) has shown that the carbonyl ligands bond at *cis* sites that are *trans* to the iminosemiquinone oxygen atoms. Radical ligands are antiferromagnetically coupled, resulting in diamagnetism and sharp NMR spectra for both complex molecules. Five-membered redox series consisting of two oxidations and two reductions, all ligand-based, appear in the electrochemistry. Potentials of iminoquinone couples are shifted negatively by approximately 0.5 V relative to corresponding quinone redox steps.

Introduction

Quinone complexes of the transition metals are of interest as systems that combine electrochemically active ligands with metals that typically have one or two readily accessible oxidation states.[2] Charge distribution within quinone complexes is directed by the balance of metal and quinone orbital energies. It is generally true that the complexes formed with quinone ligands have well-defined charges for both the metal and the quinone ligands and that delocalized electronic structures of the type associated with the 1,2-dithiolene and diimine complexes are not usually observed. This conclusion is based on observations on complexes that have spectroscopic and/or magnetic properties that point uniquely to a specific distribution of charge. The tris(quinone)iron complexes have structural features, magnetic properties, and Mössbauer spectra that indicate a tris(semiquinonato)iron(III) localized charge distribution.[3] Related complexes of ruthenium and osmium do not have specific features that point to a well-defined charge distribution, although the stereodynamic property of $Os(3,5\text{-}DBQ)_3$ relative to the rigidity of $Ru(3,5\text{-}DBQ)_3$ has been viewed as an indication of a higher degree of metal ion oxidation of $Os^{VI}(3,5\text{-}DBCat)_3$.[4] Shifts in charge distribution may result from the influence that coligands have on metal orbital energy in complexes of general formula $ML_2(Q)_2$.[5] Subtle changes in the bonding properties of nitrogen donor coligands have been used to induce shifts in charge distribution for the $Co^{III}(N\text{-}N)(SQ)(Cat)/Co^{II}(N\text{-}N)(SQ)_2$ series and the three-membered $Mn^{IV}(N\text{-}N)(Cat)_2/Mn^{III}(N\text{-}N)(SQ)(Cat)/Mn^{II}(N\text{-}N)(SQ)_2$ series.[6,7] With iron, related complexes appear to remain exclusively in the $Fe^{III}(N\text{-}N)(SQ)(Cat)$ form with no observable conversion to the $Fe^{II}(N\text{-}N)(SQ)_2$ charge distribution.[8] The low-spin metal centers of the related ruthenium and osmium complexes fail to show the dynamic shifts in charge distribution observed in solution and in the solid state for the complexes of Co and Mn, but changes in coligand have associated changes in structural features that reflect an internal transfer of charge.[5] The $Os^{IV}(bpy)(Cat)_2$ series shows the effects of a hard donor coligand and a 5d configuration, while for $Ru^{II}(PPh_3)_2(SQ)_2$, ligand features are more clearly those of semiquinones. Quinone substituent effects have also been investigated with the observation that complexes of the tetrachloroquinone ligand undergo ligand-based redox reactions at potentials that lie 0.5 V positive of corresponding 3,5-DBQ couples.

The present investigation has been carried out with iminoquinone ligands to study the effect of a shift in quinone redox potential in a direction that is substantially negative of the 3,5-DBQ couples. The complexes studied have carbonyl coligands that stabilize the metal in a reduced oxidation state and have been prepared by reaction with $Ru_3(CO)_{12}$. Reactions between metal carbonyl complexes and *o*-benzoquinones have proven to be a simple means of forming binary metal–quinone complexes, with displacement of CO upon metal oxidation. Bohle and Keister have observed that similar reactions carried out with $Ru_3(CO)_{12}$ and either 3,5-DBBQ or $H_2(3,5\text{-}DBCat)$ produce a complicated mixture of polynuclear ruthenium carbonyl quinone species.[9] We now describe the results of similar reactions carried out with 3,6-DBBQ.

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(2) (a) Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331. (b) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

(3) Cohn, M. J.; Xie, C.-L.; Tuchagues, J.-P. M.; Pierpont, C. G.; Hendrickson, D. N. *Inorg. Chem.* **1992**, *31*, 5028.

(4) Bhattacharya, S.; Boone, S. R.; Fox, G. A.; Pierpont, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 1088.

(5) (a) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1991**, *30*, 1511. (b) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1991**, *30*, 2906. (c) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 35. (d) Bag, N.; Lahiri, G. K.; Basu, P.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1992**, 113.

(6) (a) Jung, O.-S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 2227. (b) Adams, D. M.; Dei, A.; Rheingold, A. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 8221.

(7) Attia, A. S.; Pierpont, C. G. Submitted for publication.

(8) (a) Attia, A. S.; Jung, O.-S.; Pierpont, C. G. *Inorg. Chim. Acta* **1994**, *226*, 91. (b) Attia, A. S.; Pierpont, C. G. Submitted for publication.

(9) (a) Bohle, D. S.; Goodson, P. A. *J. Chem. Soc., Chem. Commun.* **1992**, 1205. (b) Bohle, D. S.; Christensen, A. N.; Goodson, P. A. *Inorg. Chem.* **1993**, *32*, 4173. (c) Churchill, M. R.; Lake, C. H.; Paw, W.; Keister, J. B. *Organometallics* **1994**, *13*, 8. (d) Bohle, D. S.; Carron, K. T.; Christensen, A. N.; Goodson, P. A.; Powell, A. K. *Organometallics* **1994**, *13*, 1355.

0020-1669/94/1333-6038$04.50/0

Table 1. Crystallographic Data for Ru(CO)$_2$(3,6-DBSQ)$_2$·C$_3$H$_7$OH and Ru(CO)$_2$(PhenoxSQ)$_2$·CH$_2$Cl$_2$[a]

	Ru(CO)$_2$(3,6-DBSQ)$_2$	Ru(CO)$_2$(PhenoxSQ)$_2$
formula	$C_{33}H_{48}O_7Ru$	$C_{59}H_{80}N_2O_6Cl_2Ru$
fw	657.7	1085.2
space group	$P\bar{4}2_1c$ (No. 114)	*Pbca* (No. 61)
a, Å	19.066(2)	31.215(6)
b, Å	19.066(2)	12.393(3)
c, Å	18.420(5)	30.664(6)
V, Å^3	6696(2)	11862(5)
Z	8	8
T, °C	24	24
λ(Mo Kα), Å	0.710 73	0.710 73
ϱ_{calcd}, ϱ_{obsd}, g cm^{-3}	1.305, 1.31	1.215, 1.21
μ, mm^{-1}	0.510	0.395
R, R_w	0.041, 0.053	0.069, 0.072

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

Experimental Section

Materials. Ru$_3$(CO)$_{12}$ was purchased from Strem Chemical Co., and 3,6-di-*tert*-butyl-1,2-benzoquinone (3,6-DBBQ) and 2,4,6,8-tetra-*tert*-butylphenoxazin-1-one (PhenoxBQ) were prepared according to literature procedures.[10,11]

Ru(CO)$_2$(3,6-DBSQ)$_2$. Toluene (50 mL) was added to a mixture of Ru$_3$(CO)$_{12}$ (0.100 g, 0.15 mmol) and 3,6-DBBQ (0.310 g, 1.41 mmol), and the resulting mixture was refluxed under N$_2$. The mixture became red-violet after 30 min. After 5 h the reaction mixture was cooled, solvent was removed under reduced pressure, and the residue was extracted with hexane. Hexane−soluble products were separated on a silica gel column using hexane as the eluant. The major product, Ru(CO)$_2$(3,6-DBSQ)$_2$, appeared first as a red-violet band; a purple band of Ru(3,6-DBSQ)$_3$ appeared next as a minor product. Further extraction with benzene produced a green band of unreacted 3,6-DBBQ. Ru(CO)$_2$(3,6-DBSQ)$_2$ was obtained in 60% yield, and Ru(3,6-DBSQ)$_3$ was obtained in 10% yield. Sample purity was determined spectroscopically; crystals of Ru(CO)$_2$(3,6-DBSQ)$_2$ were grown from a dichloromethane/2-propanol mixture.

Ru(CO)$_2$(PhenoxSQ)$_2$. Toluene (50 mL) was added to a mixture of Ru$_3$(CO)$_{12}$ (0.100 g, 0.15 mmol) and PhenoxBQ (0.600 g, 1.42 mmol), and the resulting mixture was refluxed under N$_2$. The mixture became brown after 30 min. After 6 h the reaction mixture was cooled, solvent was removed under reduced pressure, and the residue was extracted with benzene. Benzene-soluble products were separated on a silica gel column using benzene as the eluant. The major product, Ru(CO)$_2$(PhenoxSQ)$_2$, appeared first as a brown band. The fraction was collected, and the solvent was evaporated to give the crude product in 65% yield. The crude product was recrystallized from a dichloromethane/2-propanol mixture to give Ru(CO)$_2$(PhenoxSQ)$_2$ as the dichloromethane solvate.

Physical Measurements. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded on an IBM IR/30 FTIR spectrometer with samples prepared as KBr pellets. ^{1}H NMR spectra were recorded on a Varian VXR 300s spectrometer. Cyclic voltammograms were obtained with a Cypress CYSY-1 computer-controlled electroanalysis system. A Ag/Ag$^+$ reference electrode consisting of a CH$_3$CN solution of AgPF$_6$ in contact with a silver wire placed in glass tubing with a Vycor frit at one end was used to allow ion transport. Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte, and the Fc/Fc$^+$ couple was used as an internal standard. With this experimental arrangement the Fc/Fc$^+$ couple appeared at 0.191 V vs Ag/Ag$^+$ with ΔE = 146 mV.

Table 2. Selected Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Ru(CO)$_2$(3,6-DBSQ)$_2$

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Ru	8871(1)	3948(1)	9799(1)	43(1)
O1	8941(4)	4700(3)	9026(3)	47(2)
O2	8937(4)	3317(3)	8906(3)	47(2)
O3	8635(4)	3057(3)	10352(3)	49(3)
O4	7823(3)	3902(4)	9589(3)	53(3)
C29	9836(6)	3918(6)	10009(5)	57(4)
C30	8743(6)	4599(6)	10564(6)	55(4)
O5	10400(4)	3886(5)	10171(5)	94(4)
O6	8675(5)	5013(4)	10979(4)	82(4)
C1	8816(5)	4438(6)	8397(5)	46(4)
C2	8798(5)	3660(5)	8312(5)	33(3)
C3	8707(5)	3345(5)	7630(6)	38(3)
C4	8566(5)	3784(6)	7073(5)	53(4)
C5	8529(5)	4539(6)	7149(7)	60(5)
C6	8642(5)	4872(5)	7785(5)	44(4)
C15	8042(5)	2792(5)	10099(6)	50(4)
C16	7592(5)	3273(6)	9709(6)	51(4)
C17	6897(6)	3064(8)	9491(7)	64(5)
C18	6723(7)	2416(10)	9620(8)	96(7)
C19	7185(7)	1915(7)	9960(8)	94(7)
C20	7834(7)	2071(5)	10228(7)	69(5)

Crystallographic Structure Determination of Ru(CO)$_2$(3,6-DBSQ)$_2$. A red-violet needle of dimensions 0.54 × 0.24 × 0.24 mm^3 obtained by slow evaporation of a CH$_2$Cl$_2$/2-propanol solution was mounted and aligned on a Siemens P3/F diffractometer. Axial photographs indicated tetragonal symmetry, and the centered settings of 25 reflections gave the unit cell dimensions listed in Table 1. Data were collected by $\theta-2\theta$ scans within the angular range 3.0−45.0° over two redundant octants. Data were averaged with R_{int} = 0.026. The results of ψ scans indicated that absorption was negligible and no correction was applied. The structure was solved using a Patterson map. At the conclusion of preliminary refinement, the atom locations of a disordered 2-propanol molecule were obtained from a difference Fourier map and included in further refinement. Final cycles of refinement including fixed contributions for hydrogen atoms converged with disprepancy indices of $R = 0.041$ and $R_w = 0.053$. Selected atom positions are given in Table 2; tables containing complete listings of atom positions, anisotropic displacement parameters, hydrogen atom locations, bond lengths, and bond angles are available as supplementary material.

Crystallographic Structure Determination of Ru(CO)$_2$(PhenoxSQ)$_2$. A brown plate of dimensions 0.52 × 0.48 × 0.04 mm^3 obtained by slow evaporation of a CH$_2$Cl$_2$/2-propanol solution was mounted and aligned on a Siemens P3/F diffractometer. Axial photographs indicated orthorhombic symmetry, and the centered settings of 25 reflections gave the unit cell dimensions listed in Table 1. Data were collected by $\theta-2\theta$ scans within the angular range 3.0−45.0°. The structure was solved using a Patterson map. At the conclusion of preliminary refinement, a disordered dichloromethane solvate molecule was located and included in further refinement. Final cycles of refinement, including fixed contributions for hydrogen atoms, converged with discrepancy indices of $R = 0.069$ and $R_w = 0.072$. Selected atom positions are given in Table 3; tables containing complete listings of atom positions, anisotropic displacement parameters, hydrogen atom locations, bond lengths, and bond angles are available as supplementary material.

Results

o-Benzoquinones reacts oxidatively with metal carbonyl complexes to give either mixed carbonyl−quinone complexes as products or binary bis- and tris(quinone) complexes. These reactions may occur by thermal or photochemical pathways, and reactions of Mo, W, Mn, and Re have been extensively investigated.[2] Within the iron triad, Fe(CO)$_5$ has proven to be of use in the synthesis of semiquinone and catecholate complexes, but the extensive chemistry of the quinone complexes of ruthenium and osmium has been developed by using complexes of the oxidized metal ions as reagents.[5] Bridging interactions have been a complication in the chemistry of complexes formed with either the unsubstituted *o*-quinone ligand or complexes prepared with the 3,5-di-*tert*-butylquinone ligand. Reactions carried out with these ligands often lead to a mixture of products that require steps of chromatographic separation. Bohle and Keister have isolated and characterized the compli-

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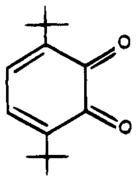
(10) Belostotskaya, I. S.; Komissarova, N. L.; Dzhuaryan, E. V.; Ershov, V. V. *Isv. Akad. Nauk SSSR* **1972**, 1594.

(11) Stegmann, H. B.; Scheffler, K. *Chem. Ber.* **1968**, *101*, 262.

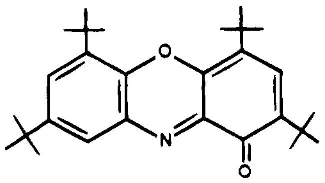
Table 3. Selected Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for $Ru(CO)_2(PhenoxSQ)_2$

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)
Ru	215(1)	695(1)	1445(1)	32(1)
O1	356(2)	833(7)	789(2)	39(3)
O2	1730(2)	1352(7)	1414(3)	42(3)
O3	238(3)	2348(6)	1413(3)	37(3)
O4	−1156(3)	1673(7)	875(3)	37(3)
O5	29(3)	761(10)	2410(3)	82(4)
O6	177(4)	−1719(8)	1389(4)	82(5)
N1	875(3)	721(8)	1464(3)	36(3)
N2	−410(3)	1033(8)	1301(3)	29(4)
C57	104(4)	729(12)	2044(5)	48(5)
C58	191(4)	−809(12)	1417(4)	45(4)
C1	1036(4)	1164(10)	1090(4)	32(5)
C2	749(4)	1192(9)	730(4)	32(5)
C3	899(4)	1557(10)	324(4)	37(5)
C4	1314(4)	1922(9)	320(4)	39(5)
C5	1613(4)	1913(10)	669(4)	40(5)
C6	1469(4)	1482(10)	1051(4)	37(5)
C7	1170(4)	385(9)	1778(4)	32(5)
C8	1591(3)	727(10)	1753(3)	31(4)
C9	1884(4)	405(9)	2077(4)	35(5)
C10	1732(4)	−325(10)	2391(4)	43(5)
C11	1316(4)	−697(11)	2411(4)	44(5)
C12	1027(4)	−325(9)	2105(4)	32(5)
C29	−446(4)	2023(10)	1113(3)	27(4)
C30	−88(4)	2716(10)	1178(4)	30(5)
C31	−119(5)	3773(10)	1018(4)	43(6)
C32	−469(5)	4041(10)	776(4)	44(6)
C33	−814(4)	3356(10)	695(4)	34(5)
C34	−810(4)	2371(10)	893(4)	32(5)
C35	−788(4)	434(9)	1346(3)	29(5)
C36	−1164(4)	763(11)	1133(4)	39(5)
C37	−1542(4)	175(11)	1189(4)	46(6)
C38	−1532(4)	−715(11)	1461(5)	57(5)
C39	−1164(4)	−1044(11)	1686(5)	54(6)
C40	−797(4)	−443(10)	1621(4)	44(5)

cated array of products obtained from reactions between catechol and 3,5-di-*tert*-butylcatechol with $Ru_3(CO)_{12}$.[9] The oligomeric products obtained from these reactions illustrate the various bridging interactions possible for the ligands, either through the quinone oxygen atoms or through the ring π-bonds. Related reactions carried out with the 3,6-di-*tert*-butyl-1,2-benzoquinone ligand have been investigated. The presence of bulky substituents at ring positions adjacent to the quinone oxygen atoms reduces the tendency for bridging interactions of both types and simplifies product isolation. *tert*-Butyl substituents of the iminoquinone 2,4,6,8-tetra-*tert*-butylphenoxazin-1-one (PhenoxBQ) may similarly block bridging interactions,[12] and with the availability of these two ligands, simple quinone and iminoquinone complexes of ruthenium have been formed, beginning with $Ru_3(CO)_{12}$, in relatively uncomplicated reactions.



3,6-DBBQ



PhenoxBQ

$Ru(CO)_2(3,6\text{-}DBSQ)_2$. The reaction between $Ru_3(CO)_{12}$ and 3,6-DBBQ produced two products that may be separated by column chromatography. The minor product has been identified as $Ru(3,6\text{-}DBQ)_3$. It has an electronic spectrum that is similar to the spectrum of $Ru(3,5\text{-}DBQ)_3$ and ^1H NMR resonances at 1.276 ppm for the *tert*-butyl protons and 7.084 ppm for the aromatic ring protons.[4] The formation of $Ru(3,6\text{-}DBQ)_3$ may be optimized with the use of excess 3,6-DBBQ and an extended reaction time. The major product of the reaction has carbonyl ν(CO) vibrations at 1981 and 2041 cm^{-1} and ^1H NMR resonances at 1.417 and 1.040 ppm for *tert*-butyl protons. Crystallographic characterization indicates that the molecule forms as the *cis* isomer of $Ru(CO)_2(3,6\text{-}DBSQ)_2$ shown in Figure 1. Bond distances and angles listed in Table 4 show that the Ru−C lengths for the carbonyl carbon atoms are relatively short and that the structural features of the quinone ligands are typical of semiquinones.[2,13] In particular, the average C−O length of 1.30 Å and slightly contracted C−C length of 1.35 Å at the C3−C4 and C5−C6 ring positions appear consistently and characteristically for semiquinone ligands. Electronic spectra recorded on $Ru(CO)_2(3,6\text{-}DBSQ)$ show intense bands at 970 nm (7300 M^{-1} cm^{-1}), 569 (4200), and 371 (4000) with a shoulder at 411 nm (Figure 2). Cyclic voltammograms (Figure 3) show the four couples associated with the five-membered

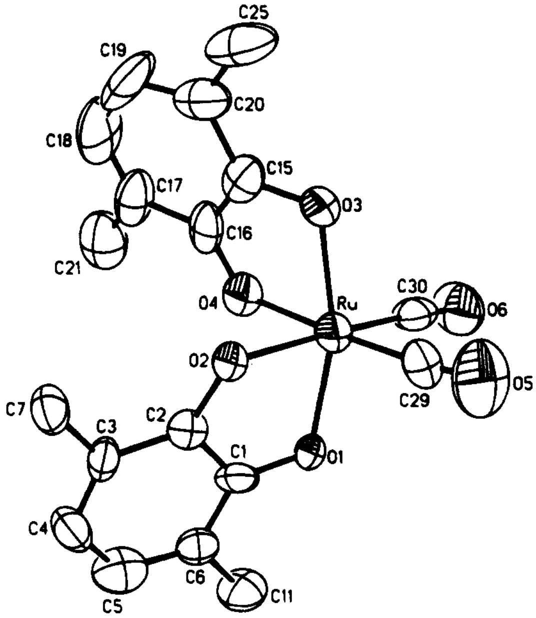


Figure 1. View of the $Ru(CO)_2(3,6\text{-}DBSQ)_2$ molecule. Methyl carbon atoms of *tert*-butyl groups have been omitted.

Table 4. Selected Bond Lengths and Angles for $Ru(CO)_2(3,6\text{-}DBSQ)_2$

	Bond Lengths (Å)		
Ru−O1	2.025(6)	C3−C4	1.352(14)
Ru−O2	2.042(6)	C4−C5	1.448(16)
Ru−O3	2.031(6)	C5−C6	1.349(15)
Ru−O4	2.037(6)	C1−C6	1.437(14)
Ru−C29	1.882(12)	O3−C15	1.324(12)
Ru−C30	1.893(11)	O4−C16	1.295(13)
C29−O5	1.118(14)	C15−C16	1.446(14)
C30−O6	1.106(13)	C16−C17	1.442(15)
O1−C1	1.284(11)	C17−C18	1.302(24)
O2−C2	1.302(10)	C18−C19	1.442(21)
C1−C2	1.493(14)	C19−C20	1.366(19)
C2−C3	1.403(13)	C15−C20	1.451(14)
	Angles (deg)		
O1−Ru−O2	81.2(2)	O1−Ru−O3	163.6(3)
O2−Ru−O3	85.7(2)	O1−Ru−O4	87.8(3)
O2−Ru−O4	83.2(3)	O3−Ru−O4	80.9(3)
O1−Ru−C29	95.8(4)	O2−Ru−C29	95.0(4)
O3−Ru−C29	95.1(4)	O4−Ru−C29	175.7(4)
O1−Ru−C30	93.9(4)	O2−Ru−C30	173.5(4)
O3−Ru−C30	98.5(4)	O4−Ru−C30	92.5(4)
C29−Ru−C30	89.6(5)		

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[12] Whalen, A. M.; Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 347.

[13] Carugo, O.; Castellani, C. B.; Djinovic, K.; Rizzi, M. *J. Chem. Soc., Dalton Trans* **1992**, 837.

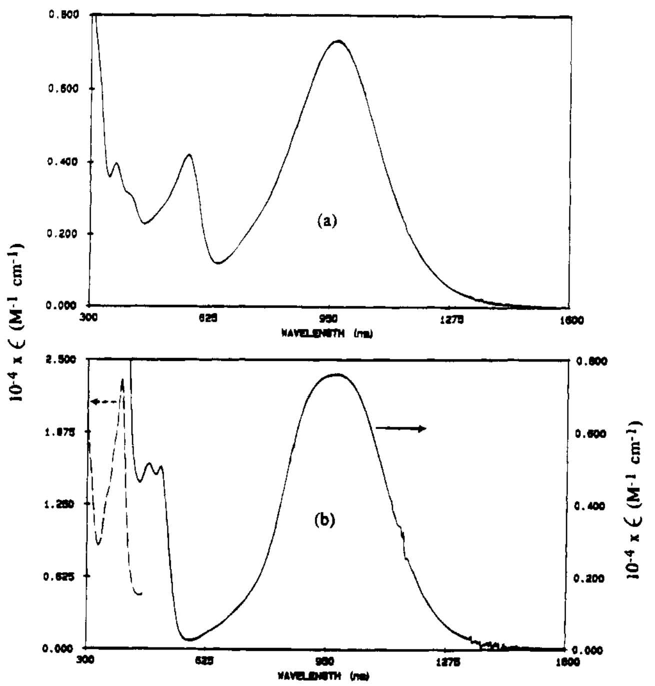

Figure 2. Electronic spectra recorded of $Ru(CO)_2(3,6\text{-}DBSQ)_2$ (a) and $Ru(CO)_2(PhenoxSQ)_2$ (b) in dichloromethane solution.

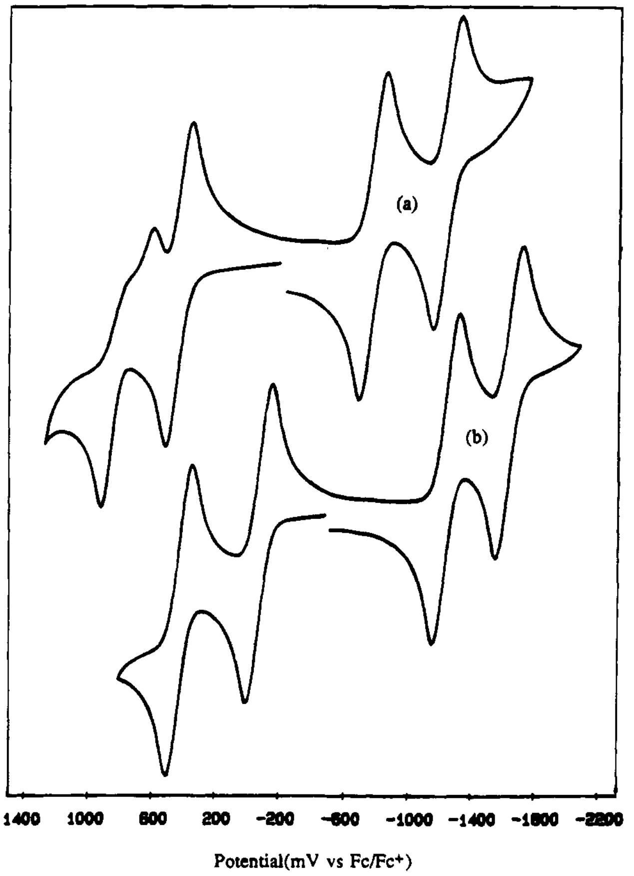

Figure 3. Cyclic voltammograms of $Ru(CO)_2(3,6\text{-}DBSQ)_2$ (a) and $Ru(CO)_2(PhenoxSQ)_2$ (b) in dichloromethane solution containing $NBu_4(PF_6)$ as electrolyte at a scan rate of 100 mV/s.

ligand-based redox series

$$[Ru^{II}(CO)_2(3,6\text{-}DBBQ)_2]^{2+} \rightleftarrows [Ru^{II}(CO)_2(3,6\text{-}DBBQ)(3,6\text{-}DBSQ)]^{+} \rightleftarrows Ru^{II}(CO)_2(3,6\text{-}DBSQ)_2 \rightleftarrows [Ru^{II}(CO)_2(3,6\text{-}DBSQ)(3,6\text{-}DBCat)]^{-} \rightleftarrows [Ru^{II}(CO)_2(3,6\text{-}DBCat)_2]^{2-}$$

The reduction step associated with the most positive oxidation shows evidence for a second reduction at nearly the same potential that is probably metal based.

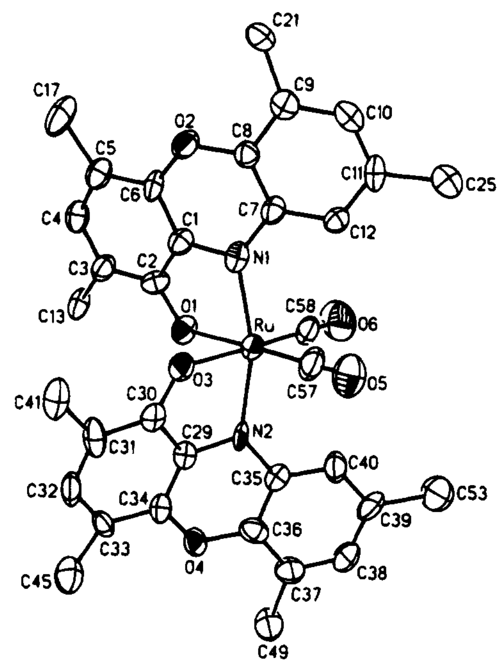

Figure 4. View of the $Ru(CO)_2(PhenoxSQ)_2$ molecule. Methyl carbon atoms of *tert*-butyl groups have been omitted.

Table 5. Selected Bond Lengths and Angles for $Ru(CO)_2(PhenoxSQ)_2$

	Bond Lengths (Å)		
Ru−O1	2.065(7)	C3−C4	1.374(17)
Ru−N1	2.058(8)	C4−C5	1.418(17)
Ru−O3	2.052(7)	C5−C6	1.365(17)
Ru−N2	2.045(9)	C1−C6	1.412(18)
Ru−C57	1.871(14)	N2−C29	1.360(15)
Ru−C58	1.867(15)	N2−C35	1.400(15)
C57−O5	1.147(16)	O3−C30	1.326(14)
C58−O6	1.132(18)	C29−C30	1.425(17)
N1−C1	1.367(15)	C30−C31	1.403(17)
N1−C7	1.396(15)	C31−C32	1.362(19)
O1−C2	1.320(14)	C32−C33	1.393(19)
C1−C2	1.423(17)	C33−C34	1.364(17)
C2−C3	1.405(17)	C29−C34	1.388(17)
	Angles (deg)		
O1−Ru−O3	82.2(3)	O1−Ru−N1	79.3(3)
O3−Ru−N1	87.2(4)	O1−Ru−N2	88.5(3)
O3−Ru−N2	79.5(4)	N1−Ru−N2	163.2(4)
O1−Ru−C57	173.8(5)	O3−Ru−C57	91.8(4)
N1−Ru−C57	99.0(5)	N2−Ru−C57	91.8(4)
O1−Ru−C58	92.6(5)	O3−Ru−C58	174.6(5)
N1−Ru−C58	93.3(5)	N2−Ru−C58	99.0(5)
C57−Ru−C58	93.4(6)		

$Ru(CO)_2(PhenoxSQ)_2$. Reactions carried out with $Ru_3(CO)_{12}$ and PhenoxBQ give *cis*-$Ru(CO)_2(PhenoxSQ)_2$ selectively as the isomer shown in Figure 4. ^1H NMR spectra recorded on the crude reaction product show the four *tert*-butyl resonances at 0.810, 1.333, 1.451, and 2.006 ppm associated with the *cis,trans* isomer characterized crystallographically. Infrared carbonyl vibrations at 1980 and 2039 cm^{-1} are nearly identical with those for $Ru(CO)_2(3,6\text{-}DBSQ)_2$, and to the extent that carbonyl bonding is sensitive to metal charge, the metal of $Ru(CO)_2(PhenoxSQ)_2$ is also divalent. Structural features of the PhenoxSQ ligands (Table 5) are in close agreement with the bond lengths of PhenoxSQ ligands of other structure determinations. PhenoxSQ C−O lengths are typically 1.32 Å, slightly longer than semiquinonate C−O lengths due to increased localization of negative charge on the more electronegative oxygen, and C−N lengths within the chelate ring (C1−N1) that

Table 6. Potentials ($E_{1/2}$, V vs Fc/Fc$^+$ (ΔE_p, mV)) for Steps in the Five-Membered Redox Series of the $ML_2(Q)_2^n$ Complexes of Ru and Os Recorded in Dichloromethane Solution

complex	Ox(II)	Ox(I)	Red(I)	Red(II)	ref
$Ru(CO)_2(3,6\text{-DBQ})_2$	0.95	0.456 (82)	−0.781 (86)	−1.256 (76)	
$Ru(bpy)(3,5\text{-DBQ})_2$	0.58	−0.11	−1.13	−1.84	14
$Os(bpy)(3,5\text{-DBQ})_2$	0.580 (72)	−0.034 (72)	−1.265 (74)	−2.023 (106)	5c
$Ru(PPh_3)_2(3,5\text{-DBQ})_2$	0.438 (126)	−0.220 (86)	−1.330 (118)	−1.791 (92)	5a
$Os(PPh_3)_2(3,5\text{-DBQ})_2$	0.505 (112)	−0.114 (98)	−1.335 (120)		5b
$Ru(PPh_3)_2(3,5\text{-DBQ})(Cl_4Q)$	0.739 (100)	0.155 (84)	−0.876 (110)	−1.437 (108)	5a
$Os(PPh_3)_2(3,5\text{-DBQ})(Cl_4Q)$	0.799 (103)	0.177 (87)	−0.943 (92)		5b
$Ru(bpy)(Cl_4Q)_2$	0.94	0.57	−0.31	−1.26	14
$Os(bpy)(Cl_4Q)_2$	1.114 (100)	0.630 (78)	−0.533 (72)	−1.469 (80)	5c
$Ru(PPh_3)_2(Cl_4Q)_2$	0.943 (87)	0.440 (82)	−0.383 (80)	−1.147 (108)	5a
$Os(PPh_3)_2(Cl_4Q)_2$	0.707 (103)	0.463 (90)	−0.494 (116)	−1.380 (144)	5b

Table 7. Potentials ($E_{1/2}$, V vs Fc/Fc$^+$ (ΔE_p, mV)) for Steps in the Five-Membered Redox Series of the $M(PhenoxSQ)_2$ Complexes

complex	Ox(II)	Ox(I)	Red(I)	Red(II)	ref
$Ru(CO)_2(PhenoxSQ)_2$	0.406 (96)	−0.081 (94)	−1.242 (98)	−1.672 (E_{pc})	
$Ru(PPh_3)Cl(PhenoxSQ)_2$	0.475 (92)	0.254 (102)	−1.426 (94)		20b
$FeCl(PhenoxSQ)_2$	0.803 (278)	0.115 (175)	−0.980 (183)	−1.489 (E_{pc})	12
$Cu(PhenoxSQ)_2$	0.800 (140)	−0.476 (154)	−1.104 (170)	−1.540 (196)	19
$Ni(PhenoxSQ)_2$	1.124 (147)	−0.032 (286)	−1.190 (126)	−1.611 (132)	12

are slightly shorter than outer lengths (C7−N1), showing that the primary center of iminoquinone redox activity is located within the chelated ring with little delocalization into the outer rings of PhenoxSQ.[12] Bands in the electronic spectrum of $Ru(CO)_2(PhenoxSQ)_2$, shown in Figure 2, have some similarity to those of $Ru(CO)_2(3,6\text{-DBSQ})_2$ with an intense transition at 973 nm (7600 M^{-1} cm^{-1}) and a series of higher energy bands at 501 nm (5000 (M^{-1} cm^{-1}), 468 (5100), and 393 (23 200). Electrochemical potentials of $Ru(CO)_2(Phenox)_2$ show an expected negative shift of approximately 0.5 V relative to the corresponding redox steps of $Ru(CO)_2(3,6\text{-DBSQ})_2$. Couples of the five-membered redox series are shown in Figure 3. All appear to be ligand-based, as with $Ru(CO)_2(3,6\text{-DBSQ})_2$, and a corresponding redox series exists for the iminoquinone ligands:

$$[Ru^{II}(CO)_2(PhenoxBQ)_2]^{2+} \rightleftarrows [Ru^{II}(CO)_2(PhenoxBQ)(PhenoxSQ)]^{+} \rightleftarrows Ru^{II}(CO)_2(PhenoxSQ)_2 \rightleftarrows [Ru^{II}(CO)_2(PhenoxSQ)(PhenoxCat)]^{-} \rightleftarrows [Ru^{II}(CO)_2(PhenoxCat)_2]^{2-}$$

Discussion

A striking feature of $Ru(CO)_2(3,6\text{-DBSQ})_2$, other members of the $RuL_2(Q)_2$ series, $Ru(CO)_2(PhenoxSQ)_2$, and members of the $ML_n(PhenoxSQ)_2$ series is that the primary centers of redox activity are the quinone ligands rather than the metal ions. Table 6 contains a list of redox potentials for the $RuL_2(Q)_2$ complexes, and Table 7 contains potentials for the redox series of the $ML_n(PhenoxSQ)_2$ complexes. Potentials of the $RuL_2(Q)_2$ series show a dependence upon ligand substituents with the potentials of the tetrachloroquinone complexes shifted positively relative to the oxidation potentials of the 3,5-DBQ series.[5,14,15] The redox properties of $Ru(CO)_2(3,6\text{-DBSQ})_2$ are most similar to those of the Cl_4Q complexes, an observation that was surprising, given the similarities between 3,5- and 3,6-DBBQ. Vlcek has noted that semiquinone ligands are π-donors of intermediate strength.[16] Synergistic bonding of the semiquinone ligands with the strong π-acceptor carbonyl ligands is, in part, responsible for the positive shift of the redox series. Further it is found that substitution at the ring 4- and 5-positions influences the redox properties of quinone ligands most strongly. Reduction potentials of Cl_4BQ appear at values that are approximately 0.5 V positive of 3,5-DBBQ, and the reductions of 3,6-DBBQ occur at potentials that are 0.3 V positive of 3,5-DBBQ.[17,18]

The redox chemistry of the $M(PhenoxSQ)_2$ complexes, summarized in Table 7, also consists of four one-electron couples, at potentials that are in the same general range as those of the redox steps of the ruthenium complexes listed in Table 6.[12,19,20] In general, iminoquinones undergo reduction at potentials that are approximately 0.5 V negative of related benzoquinone reductions, and diimines are shifted negatively by an additional 0.5 V. The redox steps of $Ru(CO)_2(PhenoxSQ)_2$ are correspondingly shifted by 0.5 V negatively from the related couples of $Ru(CO)_2(3,6\text{-DBSQ})_2$, a shift that would be anticipated from the electrochemistry of free PhenoxBQ.[20]

In an earlier report we described the oxidation of $Ru^{II}(PPh_3)Cl(PhenoxSQ)_2^-$ with dioxygen.[20] The complex was formed by the addition of PhenoxBQ to $Ru(PPh_3)_3Cl_2$, and the charge distribution within the $Ru^{II}(PhenoxSQ)_2$ unit is the same as that of $Ru(CO)_2(PhenoxSQ)_2$. The ligand oxidation reaction was proposed to proceed by the addition of O_2 at a vacant coordination site created at the nucleophilic metal by dissociation of the Cl^- ligand. In contrast, $Ru(CO)_2(PhenoxSQ)_2$ is air stable in solution, due in part to the kinetic stability of the carbonyl ligands. This provides further support for the view that the site of dioxygen addition is at the metal rather than at a radical PhenoxSQ ligand.

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Supplementary Material Available: Tables giving crystal data and details of the structure determinations, atomic coordinates, anisotropic thermal parameters, hydrogen atom locations, and bond lengths and angles for $Ru(CO)_2(3,6\text{-DBSQ})_2$ and $Ru(CO)_2(PhenoxSQ)_2$ (31 pages). Ordering information is given on any current masthead page.

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(14) Lever, A. B. P.; Auburn, P. R.; Dodsworth, E. S.; Haga, M.; Liu, W.; Melnik, M.; Nevin, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 8076.

(15) Auburn, P. R.; Dodsworth, E. S.; Haga, M.; Liu, W.; Nevin, W. A.; Lever, A. B. P. *Inorg. Chem.* **1991**, *30*, 3502.

(16) Hartl, F.; Stufkens, D. J.; Vlcek, A., Jr. *Inorg. Chem.* **1992**, *31*, 1687.

(17) Zirong, D.; Bhattacharya, S.; McCusker, J. K.; Hagen, P. M.; Hendrickson, D. N.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 870.

(18) Komissarova, N. L.; Belostotskaya, I. S.; Dzhuaryan, E. V.; Ershov, V. V. *Isv. Akad. Nauk SSSR* **1973**, 1340.

(19) Speier, G.; Whalen, A. M.; Csihony, J.; Pierpont, C. G. *Inorg. Chem.*, submitted for publication.

(20) (a) Bhattacharya, S.; Pierpont, C. G. *J. Am. Chem. Soc.* **1990**, *112*, 4561. (b) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 2020.