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Rhenium(I) Carbonyl Dioxolene Complexes: Electrochemical and Spectroelectrochemical (Resonance Raman, UV-Vis, IR) Study of $[\mathrm{Re(CO)_3L(Diox)}]^z$ and $[\mathrm{Re(CO)_2(PPh_3)_2(Diox)}]^z$ (L = CO, $\mathrm{PPh_3}$, *P*-dppe, THF, $\mathrm{Ph_3PO}$, $\mathrm{Me_2CO}$, py; $z = -1, 0, +1$) Redox Series

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The *fac*-$[\mathrm{Re^I(CO)_3L(DBSQ)}]$ (L = CO, THF, $\mathrm{PPh_3}$, $\mathrm{Ph_3PO}$, py, $\mathrm{Me_2CO}$, monodentate *P*-dppe) and $[\mathrm{Re^I(CO)_2(PPh_3)_2(DBSQ)}]$ complexes containing the 3,5-di-*tert*-butyl-1,2-benzosemiquinone radical anionic ligand (DBSQ) are electrochemically reduced and oxidized without a change in coordination number or stereochemistry to corresponding complexes of the catecholate (DBCat) and quinone (DBQ) ligand, respectively. The spectroelectrochemical study allowed the characterization of $[\mathrm{Re^I(CO)_3(PPh_3)(DBCat)}]^-$ and $[\mathrm{Re^I(CO)_2(PPh_3)_2(DBCat)}]^-$ by IR and UV-vis absorption spectroscopies. The $[\mathrm{Re^I(CO)_3L(DBCat)}]^-$ (L = CO, THF) complexes were generated chemically by the reaction between $\mathrm{Re(CO)_5^-}$ and DBQ in dry THF or by the reduction of $[\mathrm{Re(CO)_3(THF)(DBSQ)}]$ with $\mathrm{Cp_2Co}$ and were characterized by IR spectroscopy. The IR spectra of the oxidized $[\mathrm{Re^I(CO)_3(PPh_3)(DBQ)}]^+$ and $[\mathrm{Re^I(CO)_2(PPh_3)_2(DBQ)}]^+$ species were obtained spectroelectrochemically. The dicarbonyl complex $[\mathrm{Re^I(CO)_2(PPh_3)_2(DBQ)}]^+$ exhibits a very strong absorption band at 575 nm ($\epsilon = 18\,000\ \mathrm{M^{-1}\ cm^{-1}}$). A Raman peak corresponding to the Re—O stretching vibration at 568 cm^{-1} is very strongly intensity-enhanced by resonance with this electronic transition. The IR, UV-vis, and resonance Raman spectra of the radical $[\mathrm{Re^I(CO)_2(PPh_3)_2(DBSQ)}]$ complex are reported for the first time. A comparison of the substitution effects on redox potentials and spectra and, especially, the study of the UV-vis, resonance Raman, and IR spectra (average C≡O stretching force constants) as a function of the oxidation state of the dioxolene ligand along the $[\mathrm{Re^I(CO)_3L(DBDiox)}]^z$ and $[\mathrm{Re^I(CO)_2(PPh_3)_2(DBDiox)}]^z$ ($z = -1, 0, +1$; DBDiox = DBCat, DBSQ, DBQ, respectively) redox series allowed the characterization of the bonding properties of the DBDiox ligand in each of the three oxidation states. The DBCat ligand behaves as a strong σ-donor, and its Re complexes are unique examples of 6-coordinated carbonyls of a d^6-metal with a dianionic ligand in their coordination spheres. They exhibit LMCT transitions of relatively low intensity. The DBSQ radical anionic ligand is a weak π-acceptor. Spectra of its complexes show a typical MLCT transition. The DBQ ligand is a strong π-acceptor which forms a strongly stabilizing delocalized π-bond with the Re atom. The extent of this delocalization is very flexible and compensates for the substitution effects in the rest of the coordination sphere. The intense visible absorption is assigned to a transition between orbitals which are π-bonding and π-antibonding with respect to the Re—O bonds. $[\mathrm{Re^I(CO)_2(PPh_3)_2(DBQ)}]^+$ is one of the very few stable quinone complexes known.

Introduction

Increasing interest in the chemistry of transition-metal dioxolene[1] complexes stems from their very intriguing electrochemical,[2-17] spectroscopic,[12-21] structural,[2,22-24] and magnetochemical[2,13,14,25] properties, as well as from their abilities to activate small molecules,[4,8,29] namely, dioxygen, and to take part in catalytic[8,29] and enzymatic[26-29] reactions. This chemical and physical behavior arises from the coupling between redox properties of the dioxolene ligands and their coordinative ability. All three available oxidation states of the dioxolene ligands (i.e., catecholates, *o*-semiquinone anion radicals, and *o*-quinones) are good ligands, forming rather strong and kinetically stable bonds with suitable transition-metal-containing fragments, e.g.,[6,12,22] $\mathrm{Mn(CO)_3^+}$ or $\mathrm{Rubpy_2^{2+}}$. Moreover, the one-electron redox couples that are localized on the dioxolene ligand generally occur at potentials more positive than metal-localized reduction and more negative than metal-localized oxidation. The general picture of the electrochemistry of dioxolene complexes thus consists of two ligand-localized redox steps flanked with metal-localized ones. Hence, dioxolene complexes exist in several redox forms, each possessing low-lying electronic states which differ in the electron distribution between the metal and the dioxolene ligand(s). Spectroscopic and electrochemical studies of dioxolene complexes can thus uncover rather novel effects and may lead to applications as diverse as

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(1) The term "dioxolene" (Diox) is used for ligands derived from 1,2-dioxo-3,5-cyclohexadiene, irrespective of their oxidation state, i.e., catecholate dianion (Cat), *o*-semiquinone radical anion (SQ), or *o*-quinone (Q), without specifying the substituents on the benzene ring. The individual oxidation states of the 3,5-di-*tert*-butyl-1,2-dioxo-3,5-cyclohexadiene (DBDiox) are, in this study, denoted DBCat, DBSQ, and DBQ.

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optically induced bistability.[15] As far as the ability of dioxolene complexes to activate small molecules is concerned, a combination of an electron-rich redox-active catecholate ligand with a vacant site on the metal seems to play a special role.[8,25]

Recently,[22] we have synthesized and structurally characterized an unusual 5-coordinated Mn(I) complex, $[Mn(CO)_3(DBCat)]^-$. (See ref 1 for ligand name abbreviations.) This species, as well as its substitutional derivative $[Mn(CO)_2\{P(OEt)_3\}(DBCat)]^-$, possesses rather rich electrochemistry.[11] Stable 5-coordinated manganese(0) catecholate $[Mn(CO)_3(DBCat)]^{2-}$ as well as 6-coordinated semiquinone and quinone complexes $[Mn^I(CO)_3(L)(DBDiox)]^{0,+}$ and $[Mn^I(CO)_2\{P(OEt)_3\}_2(DBDiox)]^{0,+}$ were generated and studied in detail spectroscopically.[30] As far as the analogous Re chemistry is concerned, only complexes of the general type $[Re(CO)_{4-n}(L)_n(SQ)]$ (n = 0, 1, 2) containing semiquinone radical anionic ligand have been investigated so far.[23,24,31-35] Their electrochemistry has not been studied at all, except for the somewhat atypical dinuclear $[Re(CO)_7(PhenSQ)]$ species.[24] Hence, nothing is currently known about the existence, stability, and properties of rhenium carbonyl complexes of catecholate and quinone ligands. In principle, rather rich chemistry of rhenium carbonyl dioxolenes can be expected, especially in view of the strength and stability of the Re–CO bonds and the ability of the $Re(CO)_3^+$ fragment to coordinate and stabilize a wide variety of ligands.[36] Therefore, we have investigated rhenium carbonyl complexes containing the dioxolene ligand in oxidation states other than the semiquinone radical anion, aiming especially at their chemistry and spectroscopic properties and the effects of the changing oxidation state of the dioxolene.

Results

The rhenium(I) semiquinone complexes $[Re(CO)_3L(DBSQ)]$ and $[Re(CO)_2(PPh_3)_2(DBSQ)]$ were used as starting materials. The purities of their solutions were checked by EPR and IR spectroscopies. Unless stated otherwise, all experiments reported below were carried out in the presence of an excess of the free ligand L, except for L = CO. The IR and EPR spectra[32-35] as well as the crystal structure[23] of $[Re(CO)_3(PPh_3)(DBSQ)]$ show that the tricarbonyls are *fac* isomers, with the ligand L occupying the axial position perpendicular to the Re(DBSQ) chelate plane. The two PPh_3 ligands in $[Re(CO)_2(PPh_3)_2(DBSQ)]$ lie trans to each other and cis to the DBSQ ligand as indicated by the EPR spectrum.[33,34]

Electrochemistry of Semiquinone Complexes $[Re(CO)_3L(DBSQ)]$ and $[Re(CO)_2(PPh_3)_2(DBSQ)]$. Electrochemical experiments were conducted in CH_2Cl_2 solutions with the exception of $[Re(CO)_3(THF)(DBSQ)]$ for which THF was used. All these complexes exhibit one reduction and one oxidation peak during cyclic voltammetry, both corresponding to diffusion-controlled, one-electron processes as was established by[37] linear $i_p/v^{1/2}$ vs v dependence and by comparison of i_p/c values with those of well-known one-electron couples, e.g., Fc/Fc^+ and free DBQ/DBSQ (i_p is the peak current measured by cyclic voltammetry at scan rate v; c is the sample concentration). Redox potentials, listed in Table I, were measured against the Fc/Fc^+ couple which was used as an internal standard.[38]

Table I. Electrode Potentials of the Rhenium and Manganese[11,39] Carbonyl Dioxolene Complexes (V vs Fc/Fc^+)

compound	solv	DBCat/ DBSQ	DBSQ/ DBQ
$[Re(CO)_4(DBSQ)]$	$CH_2Cl_2{}^a$	-0.51^b	+0.43
$[Re(CO)_3(THF)(DBSQ)]$	THF	−0.63	+0.41
$[Re(CO)_3(PPh_3)(DBSQ)]$	$CH_2Cl_2{}^c$	−0.87	+0.24
$[Re(CO)_3(py)(DBSQ)]$	$CH_2Cl_2{}^d$	−0.71	+0.35
$[Re(CO)_3(Ph_3PO)(DBSQ)]$	CH_2Cl_2	-0.66^b	+0.30
$[Re(CO)_3(Me_2CO)(DBSQ)]$	$CH_2Cl_2{}^a$	-0.52^b	+0.35
$[Re(CO)_3(P\text{-dppe})(DBSQ)]$	CH_2Cl_2	−0.85	+0.27
$[Re(CO)_2(PPh_3)_2(DBSQ)]$	$CH_2Cl_2{}^c$	−1.14	−0.21
$[Mn(CO)_4(DBSQ)]$	$CH_2Cl_2{}^e$		+0.29
$[Mn(CO)_3(THF)(DBSQ)]$	THF^f	-0.70^g	+0.23
$[Mn(CO)_3(PPh_3)(DBSQ)]$	$CH_2Cl_2{}^{c,f}$	-0.92^g	+0.04
$[Mn(CO)_3(py)(DBSQ)]$	py^f	−0.90	+0.11
$[Mn(CO)_2\{P(OEt)_3\}_2(DBSQ)]$	$CH_2Cl_2{}^h$	-1.25^g	−0.37
$[Mn(CO)_2(PPh_3)_2(DBSQ)]$	$CH_2Cl_2{}^c$	-1.23^b	−0.46
DBSQ (free ligand)	THF	−1.70	−1.09

[a] −70 °C. [b] Electrochemically irreversible. [c] Excess free PPh_3 present. [d] 5% of pyridine present. [e] CO-saturated solution. [f] Solution of $[Mn(CO)_3(DBCat)]^-$. [g] Electrochemically quasireversible. [h] Solution of $[Mn(CO)_2(P(OEt)_3)_2(DBCat)]^-$, excess free $P(OEt)_3$ present.

The oxidation of all investigated $[Re(CO)_3L(DBSQ)]$ complexes (L = CO, THF, acetone, $P(OPh)_3$, Ph_3PO, PPh_3, pyridine, monodentate *P*-dppe) as well as the oxidation of $[Re(CO)_2(PPh_3)_2(DBSQ)]$ was found to be electrochemically reversible on the time scale of cyclic voltammetry (CV). The separation of the CV peaks was within the 60–90-mV range (at v = 50 or 100 mV/s) depending upon the experimental conditions. In each individual case, these values were equal to those obtained for the Fc/Fc^+ couple during the same experiment. (The Fc/Fc^+ couple[38] was used also as an internal reversibility standard.) The full electrochemical reversibility shows that the oxidation is a simple one-electron process that is not accompanied by any major structural reorganization of the molecule.[37] By analogy with the Mn complexes,[11,39,40] this process is ascribed to the oxidation of the coordinated DBSQ to DBQ, producing $[Re(CO)_3L(DBQ)]^+$ and $[Re(CO)_2(PPh_3)_2(DBQ)]^+$ complexes. The cathodic to anodic peak current ratio $i_p{}^c/i_p{}^a$ was found to be unity for L = CO, THF, PPh_3, $P(OPh)_3$, acetone, and Ph_3PO and for $[Re(CO)_2(PPh_3)_2(DBSQ)]$, pointing to chemical stability of corresponding cationic quinone complexes on the CV time scale (v = 50–100 mV/s). On the other hand, this ratio was much less than unity for L = pyridine and *P*-dppe, due to a follow-up chemical reaction of the quinone complexes which was not further investigated.

The reductions of $[Re(CO)_3L(DBSQ)]$ complexes (L = THF, PPh_3, py, *P*-dppe), as well as the reduction of $[Re(CO)_2(PPh_3)_2(DBSQ)]$, were found to be electrochemically reversible by both polarography and cyclic voltammetry in comparison with the Fc/Fc^+ couple.[38] The slopes of the log plots of the polarographic waves[37b] were in the range 63–77 mV whereas the separation of the CV peaks was within the 60–80-mV range at v = 50 or 100 mV/s. This electrochemical reversibility shows[37] that the reductions are simple one-electron processes not accompanied by any major structural reorganization. The products were thus formulated as 6-coordinated catecholate complexes $[Re(CO)_3L(DBCat)]^-$ and $[Re(CO)_2(PPh_3)_2(DBCat)]^-$, in contrast to their Mn counterparts $[Mn(CO)_3(DBCat)]^-$ and $[Mn(CO)_2\{P(OEt)_3\}(DBCat)]^-$, which are 5-coordinated,[11,22,39] and exhibit[11,39] electrochemically quasireversible DBSQ/DBCat redox couples. None of the investigated rhenium semiquinone complexes showed any further reduction steps at more negative potentials. The

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[40] The $3b_1$-orbital[7,14,41] is strongly π-antibonding with respect to the C–O bonds, weakly C_3–C_4 and C_5–C_6 π-antibonding, and weakly C_1–C_2 π-bonding. It is a frontier orbital of dioxolene ligands, being the LUMO of the quinone, SOMO of the semiquinone anion radical, and HOMO of the catecholate dianion. The symmetry label refers to the C_{2v} point group of an idealized ligand. Its energy decreases in the order from DBCat to DBSQ to DBQ.

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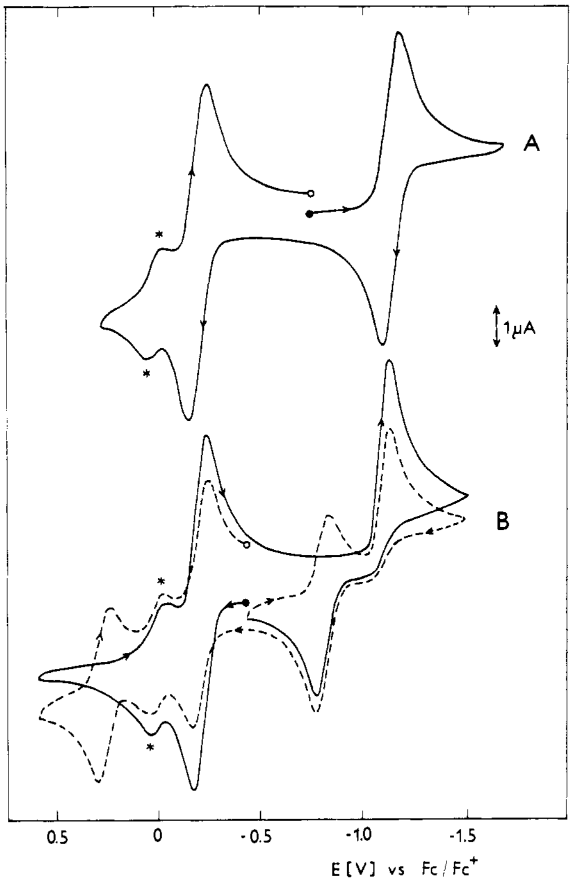

Figure 1. Cyclic voltammetry of [$Re(CO)_2(PPh_3)_2$(DBSQ)]: (A) under an Ar atmosphere; (B) in a CO-saturated solution. Conditions: 8×10^{-3} M solution in CH_2Cl_2 in the presence of 10^{-1} M Bu_4NPF_6 and excess PPh_3, Pt-disk electrode, +20 °C, 100 mV/s. Symbols: *, Fc/Fc$^+$ couple used as an internal standard; ●, start of the scan; ○, end of the scan; solid line, first scan starting in a positive direction; dashed line, second (successive) scan in the negative direction from the switching point.

reduced [$Re(CO)_2(PPh_3)_2$(DBCat)]$^-$ and [$Re(CO)_3$L(DBCat)]$^-$ complexes are stable on the time scale of cyclic voltammetry (v = 50–100 mV/s) for L = THF, PPh_3, *P*-dppe, and py as indicated by the $i_p^a/i_p^c = 1$. On the other hand, for L = CO and acetone, the peak current ratios were significantly less than unity and their shapes were distorted, suggesting the presence of an $\underline{E}C\underline{E}$ process. The redox potentials of these complexes (Table I) were thus measured at −70 °C where their reductions were chemically reversible but electrochemically irreversible: for L = CO, ΔE_p = 125 mV (Fc/Fc$^+$ 45 mV) whereas, for acetone, ΔE_p = 75 mV (Fc/Fc$^+$ 50 mV). Slight distortion of the CV peak and electrochemical irreversibility (ΔE_p = 140 mV) also occur for L = Ph_3PO.

The CV of [$Re(CO)_2(PPh_3)_2$(DBSQ)], measured in CH_2Cl_2 in the presence of an excess of PPh_3 under an argon atmosphere, exhibited a fully reversible reduction to [$Re(CO)_2(PPh_3)_2$(DBCat)]$^-$ and an oxidation to [$Re(CO)_2(PPh_3)_2$(DBQ)]$^+$ at −1.135 and −0.205 V, respectively (Figure 1A). This behavior was significantly altered in a solution saturated with CO (Figure 1B). Starting with the positive scan, the oxidation peak was unchanged, but the reduction to the catecholate became completely irreversible chemically, and the potential of the cathodic peak shifts from −1.175 to −1.125 V, owing to a fast follow-up reaction. This reaction produces a species that is reversibly oxidized in two steps at $E_{1/2}$ = −0.80 and +0.26 V, with ΔE_p = 75 and 65 mV, respectively; these couples appear on the second scan starting in the negative direction (Figure 2B, dashed curve). This behavior indicates the substitution of a PPh_3 ligand in the catecholate complex by CO:

$$[Re(CO)_2(PPh_3)_2(DBCat)]^- + CO \rightarrow [Re(CO)_3(PPh_3)(DBCat)]^- + PPh_3 \quad (1)$$

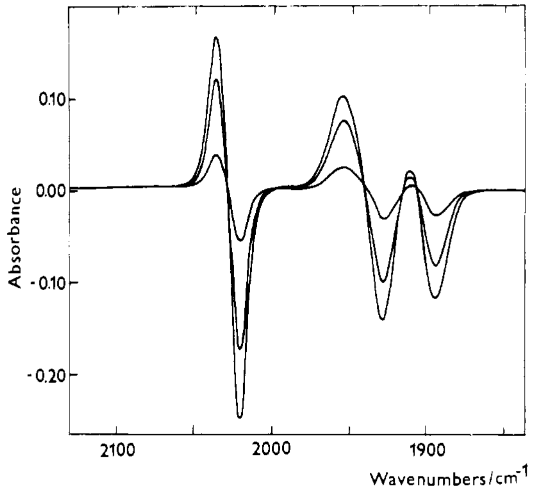

Figure 2. Electrochemical oxidation of [$Re(CO)_3(PPh_3)$(DBSQ)] to [$Re(CO)_3(PPh_3)$(DBQ)]$^+$, monitored by difference IR absorption spectroscopy. Conditions: IR-OTTLE cell,[42] Pt-mesh electrode, 8×10^{-3} M solution in CH_2Cl_2 in the presence of 10^{-1} M Bu_4NPF_6 and excess PPh_3. The negative absorption reflects the decreasing concentration of the parent [$Re(CO)_3(PPh_3)$(DBSQ)], whereas the positive peaks belong to the [$Re(CO)_3(PPh_3)$(DBQ)]$^+$ product. Its 1914-cm^{-1} band is somewhat obscured between the two low-frequency peaks of the DBSQ complex.

An authentic sample of [$Re(CO)_3(PPh_3)$(DBSQ)] affords two reversible couples at −0.87 and +0.24 V. The small positive shifts in the values obtained on the second negative potential scan for [$Re(CO)_2(PPh_3)_2$(DBCat)]$^-$ in the presence of excess CO are due to the kinetics of the substitution of the PPh_3 ligand.

Both of the one-electron redox couples found in the Re(DBSQ) complexes were assigned to changes in the oxidation state of the DBDiox ligand. Accordingly, the redox potentials (Table I) of the DBCat/DBSQ and DBSQ/DBQ couples of the tricarbonyl complexes [$Re(CO)_3$L(DBSQ)] vary within rather narrow potential ranges of 240 and 170 mV, respectively, when the ligand L is changed. In both redox steps, the change in the number of electrons occurs in the $3b_1$ orbital that is predominantly ligand-localized[40] and π-interacts with a lower-lying metal d_π-orbital. Increasing the donor strength of the ligand L raises the d_π-orbital energy. Consequently, the energy of the $3b_1$-orbital is raised as well, and both potentials are shifted slightly in a negative direction. The loss of π-back-bonding of the CO ligand going from [$Re(CO)_4$(DBSQ)] to substituted tricarbonyls has exactly the same effect. Surprisingly, the substitution of CO by a second PPh_3 ligand in [$Re(CO)_3(PPh_3)$(DBSQ)] shifts the potential of the DBCat/DBSQ couple by −260 mV, whereas the shift of the DBSQ/DBQ couple is much larger: 440 mV (Table I). This effect points to an additional stabilization of [$Re(CO)_2(PPh_3)_2$(DBQ)]$^+$ with respect to [$Re(CO)_3(PPh_3)$(DBQ)]$^+$ of about 0.18 eV, in addition to that caused by the simple increase in the d_π-orbital energy. In accordance with the results of the IR and resonance Raman studies, vide infra, a strong π-delocalization within the Re(DBQ)$^+$ chelate ring, typical for dicarbonyls, is proposed to be the source of this stabilization. Such a delocalization amounts to an extensive mixing between d_π- and $3b_1$-orbitals.

In summary, the electrochemical experiments described above have established the existence of a DBDiox ligand-based redox series

$$[Re(CO)_3L(DBCat)]^- \Leftrightarrow [Re(CO)_3L(DBSQ)] \Leftrightarrow [Re(CO)_3L(DBQ)]^+ \quad (2)$$

as well as the existence of an analogous [$Re(CO)_2(PPh_3)_2$(DBCat)]$^-$/[$Re(CO)_2(PPh_3)_2$(DBSQ)]/[$Re(CO)_2(PPh_3)_2$(DBQ)]$^+$ series.

Spectroelectrochemistry. Both the oxidations and reductions of [$Re(CO)_3$L(DBSQ)] complexes and of [$Re(CO)_2(PPh_3)_2$(DBSQ)] were investigated spectroelectrochemically in order to characterize the electrochemical products, and to confirm the

Table II. Infrared Frequencies of $\nu(C\equiv O)$ Vibrations of Rhenium and Manganese[19,39] Carbonyl Dioxolene Complexes

compound	solv	$\nu(C\equiv O)$, cm^{-1}	k^a	k_i^a
$[Re(CO)_4(DBSQ)]$	CH_2Cl_2	2110, 2012, 1984, 1942	16.36	
$[Re(CO)_4(DBCat)]^-$	THF	2080, 1970, 1962 (sh), 1908	15.85	
$[Re(CO)_3(THF)(DBSQ)]$	THF	2019, 1910, 1902	15.27	
$[Re(CO)_3(THF)(DBCat)]^-$	THF	1987, 1860, 1845	14.55	
$[Re(CO)_3(py)(DBSQ)]$	C_6H_6	2017, 1915, 1897	15.26	
$[Re(CO)_3(Ph_3PO)(DBSQ)]$	THF	2014, 1901, 1896	15.16	
$[Re(CO)_3(Me_2CO)(DBSQ)]$	*b*	2018, 1901 (br)		
$[Re(CO)_3(P\text{-dppe})(DBSQ)]$	C_6H_6	2022, 1931, 1893	15.35	
$[Re(CO)_3(PPh_3)(DBQ)]^+$	CH_2Cl_2	2035, 1952, 1914	15.63	
$[Re(CO)_3(PPh_3)(DBSQ)]$	CH_2Cl_2	2020, 1928, 1896	15.34	
$[Re(CO)_3(PPh_3)(DBCat)]^-$	CH_2Cl_2	1990, 1874, 1844	14.64	
$[Re(CO)_2(PPh_3)_2(DBQ)]^+$	CH_2Cl_2	1995, 1931	15.57	0.51
$[Re(CO)_2(PPh_3)_2(DBSQ)]$	CH_2Cl_2	1917, 1839	14.25	0.59
$[Re(CO)_2(PPh_3)_2(DBCat)]^-$	CH_2Cl_2	1875, 1786	13.54	0.66
$[Mn(CO)_4(DBSQ)]$	CH_2Cl_2	2105, 2029, 2004, 1960	16.56	
$[Mn(CO)_3(DBCat)]^-$	THF	1994, 1891	14.98	
$[Mn(CO)_3(DBCat)]^- \cdot PPh_3$	$CH_2Cl_2{}^c$	2001, 1904, 1867	14.96	
$[Mn(CO)_3(DBCat)]^- \cdot PCy_3$	$CH_2Cl_2{}^c$	1993, 1882, 1853	14.74	
$[Mn(CO)_3(DBCat)]^- \cdot py$	py	1995, 1885, 1862	14.81	
$[Mn(CO)_3(THF)(DBSQ)]$	THF	2030, 1934, 1923 (sh)	15.56	
$[Mn(CO)_3(PPh_3)(DBSQ)]$	CH_2Cl_2	2024, 1946, 1912	15.53	
$[Mn(CO)_2\{P(OEt)_3\}_2(DBQ)]^+$	CH_2Cl_2	2025, 1965	16.08	0.48
$[Mn(CO)_2\{P(OEt)_3\}_2(DBSQ)]$	CH_2Cl_2	1946, 1869	14.70	0.59
$[Mn(CO)_2\{P(OEt)_3\}(DBCat)]^-$	CH_2Cl_2	1909, 1821	14.05	0.66
$[Mn(CO)_2(PPh_3)_2(DBQ)]^+$	CH_2Cl_2	2003, 1943	15.72	0.48
$[Mn(CO)_2(PPh_3)_2(DBSQ)]$	CH_2Cl_2	1927, 1850	14.41	0.59

[a] Average ($\bar{k}$) and interaction force constants (k_i) (mdyn·Å^{-1}). [b] C_6H_6/Me_2CO (1/2, v/v). [c] −80 °C.

structures that were inferred from electrochemical data, vide supra. The IR, UV–vis, and resonance Raman spectroelectrochemical studies were carried out in situ on a Pt-minigrid electrode using an IR-OTTLE (optically transparent thin-layer electrochemical) cell.[42] Unless stated otherwise, CH_2Cl_2 solutions containing an excess of the ligand L (except for L = CO) were used.

Infrared spectra were investigated in the $\nu(C\equiv O)$ region, and the corresponding frequencies are summarized in Table II. Differential IR absorption spectra were obtained during the electrochemical oxidations of $[Re(CO)_3(PPh_3)(DBSQ)]$ (Figure 2) and $[Re(CO)_2(PPh_3)_2(DBSQ)]$. Clean isosbestic conversions were observed, giving $[Re(CO)_3(PPh_3)(DBQ)]^+$ and $[Re(CO)_2(PPh_3)_2(DBQ)]^+$ complexes which exhibit three and two $\nu(C\equiv O)$ bands, respectively.

Obviously, both the number of CO ligands and the stereochemistry of the complex molecules are retained upon oxidation; the shifts to higher wavenumbers (Table II) occur as a result of the oxidation of the DBSQ ligand.[30] Whereas $[Re(CO)_2(PPh_3)_2(DBQ)]^+$ is stable, the $[Re(CO)_3(PPh_3)(DBQ)]^+$ complex undergoes a slow decomposition manifested by the loss of the isosbestic points upon prolonged electrolysis. Although stable on the CV time scale, the oxidized $[Re(CO)_4(DBQ)]^+$ and $[Re(CO)_3(THF)(DBQ)]^+$ complexes decompose during electrolysis within the IR-OTTLE cell, precluding their spectral characterization. The oxidations of other rhenium semiquinone complexes were not followed spectroelectrochemically.

During the electrochemical reduction, the IR spectra of $[Re(CO)_3(PPh_3)(DBSQ)]$ (Figure 3) and $[Re(CO)_2(PPh_3)_2(DBSQ)]$ are isosbestically converted into those of corresponding catecholate anionic complexes. Their IR spectral patterns are identical with those of the parent semiquinone complexes, with the bands being shifted to lower frequencies (Table II). This shows that the number of CO ligands and composition and stereochemistry of the coordination sphere are not changed upon reduction. The reduction of the DBSQ ligand to DBCat causes the frequency shift.[30] Comparison of the IR spectra of Re and Mn complexes provides good evidence for the hexacoordination of the rhenium catecholate complexes: 6-coordinated complexes of the type $[M(CO)_3L(DBSQ)]$ (M = Mn, Re) as well as weak 6-coordinated adducts[39] $[Mn(CO)_3(DBCat)\cdot(L')]^-$ (L′ = py, PPh_3, PCy_3) exhibit a separation between the low-frequency $(A')_2$ and A″ $\nu(C\equiv O)$ IR bands in the range 8–37 cm^{-1}. On the other hand, these two vibrations are nearly degenerate in 5-coordinated $[Mn(CO)_3(Cat)]^-$, affording only a single broad IR band (Table II). The reduction of $[Re(CO)_3(PPh_3)(DBSQ)]$ to the catecholate complex leaves the $(A')_2$–A″ peak separation almost unchanged (32 vs 30 cm^{-1}). A separation of 15 cm^{-1} was found for the chemically prepared $[Re(CO)_3(THF)(DBCat)]^-$ complex. Evidently, the $\nu(C\equiv O)$ IR spectral patterns of the catecholate complexes are typical (see also data in ref 35) for compounds of the type $[M(CO)_3AB_2]$ (M = Re, Mn).

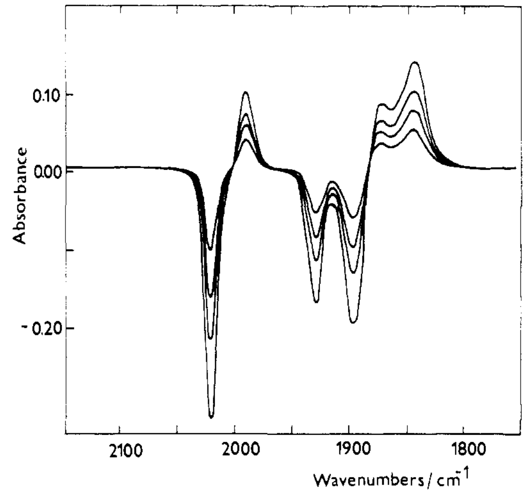

Figure 3. Electrochemical reduction of $[Re(CO)_3(PPh_3)(DBSQ)]$ to $[Re(CO)_3(PPh_3)(DBCat)]^-$, monitored by difference IR absorption spectroscopy. Conditions: IR-OTTLE cell,[42] Pt-mesh electrode, 7 × 10^{-3} M solution in CH_2Cl_2 in the presence of 10^{-1} M Bu_4NPF_6 and excess PPh_3. The negative absorption reflects the decreasing concentration of the parent $[Re(CO)_3(PPh_3)(DBSQ)]$, whereas the positive peaks belong to $[Re(CO)_3(PPh_3)(DBCat)]^-$ product.

The IR spectra show that both $[Re(CO)_3(PPh_3)(DBCat)]^-$ and $[Re(CO)_2(PPh_3)_2(DBCat)]^-$ are chemically stable in CH_2Cl_2 and THF solutions under an argon atmosphere. However, spectroelectrochemical reduction of $[Re(CO)_2(PPh_3)_2(DBSQ)]$ in a CO-saturated CH_2Cl_2 solution resulted in only a transient formation of $[Re(CO)_2(PPh_3)_2(DBCat)]^-$, characterized by IR bands at 1875 and 1786 cm^{-1}, which was followed by the appearance of bands

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characteristic of $[Re(CO)_3(PPh_3)(DBCat)]^-$ at 1990, 1874, and 1844 cm^{-1}, thus proving the substitution reaction (eq 1).

Attempts to prepare either $[Re(CO)_4(DBCat)]^-$ or $[Re(CO)_3(THF)(DBCat)]^-$ by the spectroelectrochemical reduction of the corresponding semiquinone complexes failed, producing another, as yet uncharacterized compound. However, these catecholate complexes can be generated in very dry THF by the dropwise addition of 1 equiv of DBQ to $Re(CO)_5^-$. The resulting yellow solution exhibits a $\nu(C{\equiv}O)$ spectral pattern that is typical of a tetracarbonyl complex (Table II), and was thus attributed to the 6-coordinated $[Re(CO)_4(DBCat)]^-$ species. This complex is not stable in THF: conversion to $[Re(CO)_3(THF)(DBCat)]^-$ takes place as manifested by the appearance of IR bands typical of tricarbonyls at 1987, 1860, and 1845 cm^{-1}. $[Re(CO)_3(THF)(DBCat)]^-$ was also obtained by the reduction of $[Re(CO)_3(THF)(DBSQ)]$ with Cp_2Co in 6/1 THF/C_6H_6 (v/v) solution; the product, characterized by IR bands at 1991, 1866, and 1845 cm^{-1}, was assigned to a $[Cp_2Co^+]\{[Re(CO)_3(THF)(DBCat)]^-\}$ ion pair.

The changes in $\nu(C{\equiv}O)$ frequencies and, especially, in C≡O force constants along the redox series are good indicators of the changing nature of the DBDiox ligand. The stretching force constants of the axial and equatorial carbonyls, and the interaction force constants k_i, may be calculated using the Cotton–Kraihanzel (CK) approximate force field[43-45] method. Such a calculation requires the correct assignment of the $\nu(C{\equiv}O)$ frequencies. In the case of tricarbonyls, it is very difficult[44,45] to unequivocally assign the two low-energy IR bands to the $(A')_2$ and A'' normal vibrational modes, unless the spectra of ^{13}CO-enriched isotopomers are known. Moreover, the two interaction force constants (k_{ax-eq} and k_{eq-eq}) could be different to such an extent that the CK approximation may break down.[45] Therefore, only the average force constants,[45] $\bar{k}$, were calculated (Table II) and employed in a qualitative discussion of electronic effects. (For dicarbonyls where only equatorial CO ligands are present, $k_2 = \bar{k}$ and $k_i = k_{eq-eq}$.) These force constants directly reflect the extent of the Re → CO π-back-bonding. The data in Table II show a significant increase in k_2 for $[Re(CO)_2(PPh_3)_2(DBDiox)]^z$ as the oxidation state of the DBDiox ligand increases: k_2 values increase in the order DBCat < DBSQ < DBQ, in accord with the previously proposed[30,35] π-donating, very weakly π-accepting, and strongly π-accepting nature of DBCat, DBSQ, and DBQ ligands, respectively. The interaction force constant, k_i, may be expected to increase with increasing Re → CO π-bonding.[43] Accordingly, the corresponding k_i values were found to increase in the order DBQ < DBSQ < DBCat. The trends in k_2 and k_i values within the $[Mn(CO)_2\{P(OEt)_3\}_2(DBDiox)]^z$ redox series[30] are analogous (Table II). The $\bar{k}$ values for the tricarbonyl $[Re(CO)_3(PPh_3)(DBDiox)]^z$ complexes follow the order DBCat ≪ DBSQ < DBQ. For the DBCat and DBSQ complexes, the $\bar{k}$ values decrease significantly when a CO ligand in $[Re(CO)_3(PPh_3)(DBDiox)]^z$ is interchanged for PPh_3, giving $[Re(CO)_2(PPh_3)_2(DBDiox)]^z$. Interestingly, almost no decrease in $\bar{k}$ occurs for DBQ complexes ($z = +1$). A significant decrease in $\bar{k}$ values also occurs upon the reduction of $[Re(CO)_3(THF)(DBSQ)]$ to $[Re(CO)_3(THF)(DBCat)]^-$.

In summary, the frequencies of the $\nu(C{\equiv}O)$ IR bands as well as the C≡O stretching force constants sensitively reflect changes in the π-bonding properties of the DBDiox ligand with its oxidation state. A significant decrease in Re → CO π-bonding on going from DBCat to DBSQ to DBQ ligand is apparent. It is important to note that all of the $\nu(C{\equiv}O)$ IR frequencies are well within the range typical of rhenium(I) carbonyl complexes,[47,51,52] indicating that changes in the formal oxidation states may be regarded as localized on the DBDiox ligand.

Electronic Absorption and Resonance Raman Spectra. Absorption and resonance Raman (RR) spectra of the semiquinone complexes $[Re(CO)_4(DBSQ)]$ and $[Re(CO)_3(PPh_3)(DBSQ)]$ were reported elsewhere.[46] Each exhibits a broad absorption band in the visible region, assigned to a MLCT (Re → DBSQ) transition[46] from a rhenium d_π-orbital to the $3b_1$-SOMO[40] of the DBSQ radical anionic ligand. An analogous absorption band of $[Re(CO)_2(PPh_3)_2(DBSQ)]$ is strongly red-shifted. It occurs at 702 nm (ϵ = 5300 M^{-1} cm^{-1}) with a shoulder at 630 nm (see Figures 5 and 7). The red shift is expected for a MLCT transition because of the increase in the d_π orbital energy that results from the increased electron density on the Re atom.

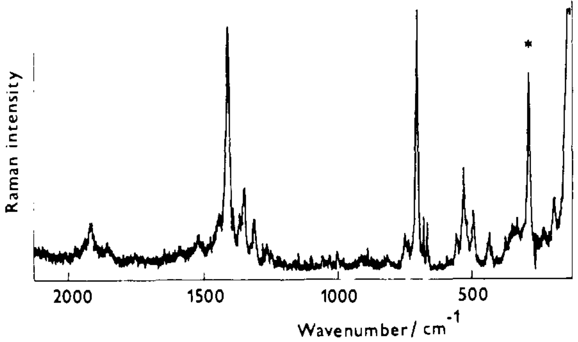

Figure 4. Resonance Raman spectrum of $[Re(CO)_2(PPh)_3(DBSQ)]$: excitation at 621 nm; *, peaks due to the CH_2Cl_2 solvent.

The RR spectra of $[Re(CO)_2(PPh_3)_2(DBSQ)]$ were measured using excitation into the onset of the absorption band at 566 nm and into its high-energy shoulder at 621 nm (Figure 4). The intensities of all Raman bands reported below (measured relatively to bands of the CH_2Cl_2 solvent) increased significantly on going from 566 to 621 nm excitation, thus proving their resonant enhancement. Assignments of the Raman bands to individual vibrations were based on comparisons with spectra of other Re,[46] Ru,[19] and Cr[21] semiquinone complexes. The most intense band in the RR spectrum is that assigned to the ν(C—O) vibration of the DBSQ ligand at 1414 cm^{-1}. A band due to a symmetrical vibration of the Re(DBSQ) chelate ring at 531 cm^{-1} is also intensity-enhanced. The corresponding vibration is denoted ν_s(Re—O). It is, in principle, a symmetrical Re—O stretching mode coupled to a C_1—C_2 vibration of the DBSQ ligand.[18,19] Importantly, the peak due to the $\nu_s(C{\equiv}O)$ vibration at 1918 cm^{-1} is also resonantly enhanced. Its frequency is identical with that of the $\nu(C{\equiv}O)$ IR band. Other weakly enhanced Raman bands correspond to internal vibrations of the DBSQ ligand: 1520 (vw), 1442 (vw), 1389 (vw), 1365 (vw), 1351, 1310, and 1261 (vw) cm^{-1}. Additional enhanced bands were found at 556, 494, and 433 cm^{-1}; these bands belong either to Re—O stretching vibrations coupled with the ring deformation, as in the oxalato complexes,[47] or to skeletal vibrations involving the Re—CO bonds. Both ν(Re—CO) and δ(Re—C—O) vibrations may occur in this frequency range.[45-47] The peak at 433 cm^{-1} may be tentatively assigned to a Re—CO stretch.[47-49]

Generally, the most strongly enhanced Raman bands belong to the vibrations of those bonds which are most affected by the resonant electronic transition.[53-55] The RR spectrum of the semiquinone complex clearly demonstrates the MLCT $d_\pi \rightarrow 3b_1$ character of the electronic transition involved. Increased population of the $3b_1$-orbital (i.e., the SOMO of the DBSQ ligand[40]), which is π-antibonding with respect to the C–O bonds of the DBSQ ligand, weakens these bonds and causes an intensity enhancement of those Raman peaks that correspond to their

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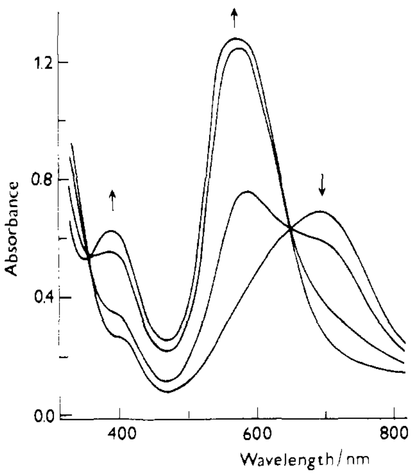

Figure 5. Electrochemical oxidation of $[Re(CO)_2(PPh_3)_2(DBSQ)]$ to $[Re(CO)_2(PPh_3)_2(DBQ)]^+$, monitored by visible absorption spectroscopy. Conditions: IR-OTTLE cell,[42] optical length 0.18 mm, Pt-mesh electrode, 7×10^{-3} M solution in CH_2Cl_2 in the presence of 10^{-1} M Bu_4NPF_6 and excess PPh_3.

stretching vibrations. However, the enhancement of the band that belongs to the skeletal ν(Re–O) vibration at 531 cm^{-1} shows that the $d_\pi \rightarrow 3b_1$ MLCT transition also affects the bonding within the Re(DBSQ) chelate ring. This suggests that mixing occurs between the d_π- and $3b_1$-orbitals, which thus acquire partially π-bonding and π-antibonding character with respect to the Re–DBSQ bonds. However, the fact that intensity enhancements of bands that correspond to the skeletal vibrations are much smaller than intensity enhancements of bands that are due to the DBSQ–intraligand vibrations shows that the extent of π-delocalization in the Re(DBSQ) chelate ring is rather limited.

The $d_\pi \rightarrow 3b_1$ transition depopulates the d_π-orbital, which is also involved in Re → CO π-bonding. The C≡O bonds are affected, and hence, the intensity of the Raman peak that corresponds to the symmetrical stretching vibration of equatorial CO ligands is resonantly enhanced as well. This is the first observation of the intensity enhancement of a Raman band that belongs to a vibration of CO ligands trans to the ligand involved in the resonant electronic MLCT transition. Except for the 5-coordinated $[Mn(CO)_3(DBCat)]^-$ complex,[30] the ν(C≡O) Raman bands known[51,52,56,57] to be enhanced through resonance with an electronic MLCT transition are those corresponding to a stretching vibration of axial CO ligands. This effect was usually explained[51,52,56,57] by a through-space interaction between the ligand π^*-orbitals (which are populated by the MLCT transition) and the π^*-orbitals of *cis*-CO. Such an interaction cannot occur in $[Re(CO)_2(PPh_3)_2(DBSQ)]$, because it has no axial CO ligands.

UV–vis spectra recorded during the electrochemical oxidation of a CH_2Cl_2 solution of $[Re(CO)_2(PPh_3)_2(DBSQ)]$ to $[Re(CO)_2(PPh_3)_2(DBQ)]^+$ within an OTTLE cell are shown in Figure 5. An isosbestic formation of absorption bands at 575 nm ($\epsilon \cong$ 18 000 M^{-1} cm^{-1}) and at 392 nm was observed. The band at 575 nm apparently encompasses at least two electronic transitions. The same compound was formed chemically, by oxidation with $[Cp_2Fe]BF_4$ in THF. The resulting dark blue solutions slowly decomposed, and partially regenerated the starting $[Re(CO)_2(PPh_3)_2(DBSQ)]$ complex, probably by a disproportionation reaction. To prevent this disproportionation from interfering with the spectroelectrochemical measurements, the working electrode was kept at constant potential (above −0.20 V) so that the disproportionation-produced $[Re(CO)_2(PPh_3)_2(DBSQ)]$ was immediately reoxidized.

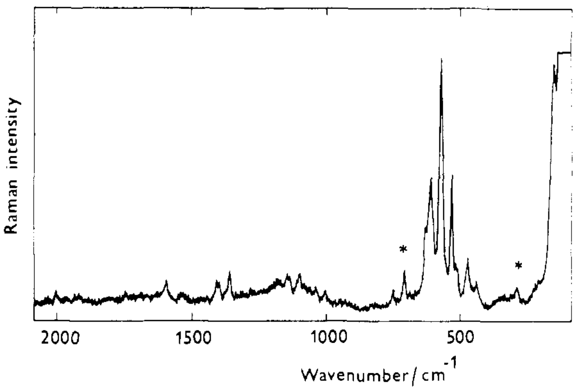

Figure 6. Resonance Raman spectrum of $[Re(CO)_2(PPh_3)_2(DBQ)]^+$: electrochemically generated in the IR-OTTLE cell[42] from $[Re(CO)_2(PPh_3)_2(DBSQ)]$, in the presence of 10^{-1} M Bu_4NPF_6 and excess PPh_3; excitation at 566 nm; *, peaks due to the CH_2Cl_2 solvent. Raman peaks of neither Bu_4NPF_6 nor PPh_3 are observable.

As in the $[Re(CO)_2(PPh_3)_2(DBSQ)]$ complex, the absorption band at 575 nm was assigned to the transition(s) of the $d_\pi \rightarrow 3b_1$ type, which should still be present, since the oxidation removes an electron from the singly occupied $3b_1$-orbital. However, the strong increase in the intensity of this band points to a significant difference in the character of the orbitals involved in the spectral transition(s) between the DBSQ and the oxidized DBQ complex. The nature of this electronic transition was therefore probed by RR spectroscopy.

The RR spectra of $[Re(CO)_2(PPh_3)_2(DBQ)]^+$ were measured following spectroelectrochemical generation. Excitations at 514.5, 541, 566, and 612 nm were employed. The relative intensities of all observed Raman bands increased as the excitation wavelength approached the absorption band maximum, indicating their resonant enhancement. The character of the RR spectrum of $[Re(CO)_2(PPh_3)_2(DBQ)]^+$, shown in Figure 6, is completely different from that of its DBSQ counterpart (Figure 4). The resonance effect is much stronger, and the spectrum is dominated by a group of greatly enhanced skeletal vibrations of the $Re(DBQ)^+$ chelate ring[19] at 606, 568, and 529 cm^{-1}, and by somewhat less intense bands at 510, 471, and 437 (vw) cm^{-1}. The most strongly enhanced band at 568 cm^{-1} has been assigned to the ν_s(Re—O) vibration. Those Raman bands corresponding to DBQ intraligand vibrations, at 1586, 1400, 1389, 1351, 1141, and 1098 cm^{-1}, as well as the band due the ν_s(C≡O) at 1997 cm^{-1} are only very weakly enhanced.

This very strong resonant enhancement of the Raman peaks belonging to the skeletal vibrations of the $Re(DBQ)^+$ chelate ring, together with a negligible RR effect on the DBQ and ν(C≡O) vibrations, indicates strong mixing between d_π- and $3b_1$-orbitals which, in the DBQ complex, lose their respective metal and ligand character. Instead, $(d_\pi + 3b_1)$- and $(d_\pi - 3b_1)$-orbitals are formed that are strongly delocalized over the $Re(DBQ)^+$ chelate ring. They are predominantly π-bonding (π_{ML}) and π-antibonding (π_{ML}^*) with respect to the Re—O bonds. The electronic transition may best be described as a delocalized $\pi_{ML} \rightarrow \pi_{ML}^*$ one. Such a transition does not change the population of the ligand orbitals but strongly influences the Re—DBQ bonding. Hence, the greatest enhancements occur for Raman peaks belonging to the ν(Re—O) vibrations. The presence of very weak bands that correspond to the intraligand DBQ and ν(C≡O) vibrations in the RR spectra shows, however, that this mixing is not complete, with the π_{ML}-orbital still having somewhat larger d_π-contribution, and the $3b_1$ orbital contributing a little more to the π_{ML}^*-orbital. The RR spectra thus show that there is delocalized π-bonding between Re and the DBQ ligand, which results in significant transfer of the metal d_π-electron density to the DBQ ligand. Despite this

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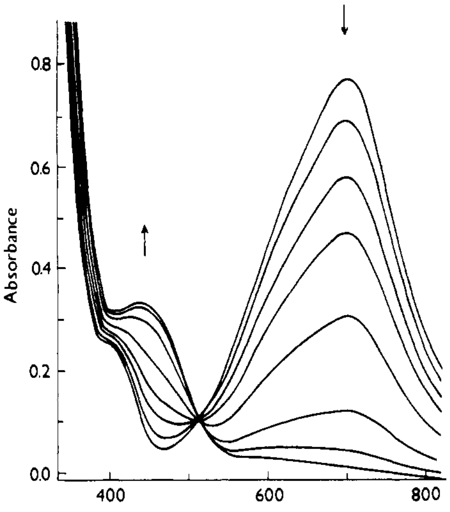

Figure 7. Electrochemical reduction of $[Re(CO)_2(PPh_3)_2(DBSQ)]$ to $[Re(CO)_2(PPh_3)_2(DBCat)]^-$, monitored by visible absorption spectroscopy. Conditions: IR-OTTLE cell.[42] optical length 0.18 mm, Pt-mesh electrode, 8×10^{-3} M solution in CH_2Cl_2 in the presence of 10^{-1} M Bu_4NPF_6 and excess PPh_3.

extensive orbital mixing, the concept of the formal oxidation states retains its meaning for both metal and ligand, which may still be regarded as Re(I) and DBQ, respectively. Interestingly, the same RR spectral pattern is exhibited by both of the other known stable *o*-quinone complexes $[Mn(CO)_2\{P(OEt)_3\}_2(DBQ)]^+$ [30] and $[Ru(bpy)_2(BQ)]^{2+}$,[19] suggesting a similar bonding pattern (BQ = unsubstituted 1,2-benzoquinone).

UV-vis spectroelectrochemical reduction of $[Re(CO)_3(PPh_3)(DBSQ)]$ to $[Re(CO)_3(PPh_3)(DBCat)]^-$ resulted in a weak absorption band at about 400 nm on the onset of a much more intense UV absorption band. Analogously, absorption spectra recorded during the reduction of $[Re(CO)_2(PPh_3)_2(DBSQ)]$ showed an isosbestic conversion of the spectrum of the parent compound to a spectrum exhibiting a band at 440 nm (ϵ = 1700 M^{-1} cm^{-1}), Figure 7. The absorption spectra of both of the rhenium catecholate complexes closely resemble those[30,39] of the 6-coordinated adducts $[Mn(CO)_3(DBCat)\cdot L]^-$ (L = py, PPh_3, PCy_3) and $[Mn(CO)_2\{P(OEt)_3\}(DBCat)\cdot P(OEt)_3]^-$, but are completely different from the 5-coordinated $[Mn(CO)_3(DBCat)]^-$ and $[Mn(CO)_2\{P(OEt)_3\}(DBCat)]^-$ species, which exhibit two intense bands in the visible spectral region.[30] The electronic absorption spectra thus provide very good evidence for 6-coordination in the rhenium catecholate complexes. The absorption band has been assigned, as in the case of the 6-coordinated manganese catecholate adducts, to a $3b_1 \rightarrow \sigma^*$ transition, $3b_1$ being the HOMO of the DBCat ligand. This assignment was corroborated by the rapid photochemical decomposition of $[Re(CO)_2(PPh_3)_2(DBCat)]^-$ under laser irradiation at 455 and 488.5 nm which prevents the measurement of the RR spectrum.

Discussion

As demonstrated by the IR spectroelectrochemistry of $[Re(CO)_3L(DBDiox)]^z$ and $[Re(CO)_2(PPh_3)_2(DBDiox)]^z$ complexes ($z = -1, 0, +1$), the coordination number, the composition of the coordination sphere, and its *fac* stereochemistry do not depend on the oxidation state of the DBDiox ligand.

The $[Re(CO)_3L(DBCat)]^-$ complexes represent a unique class of 6-coordinated carbonyl complexes possessing a dianionic chelating ligand. Because of the 6-coordination, the electron-rich DBCat ligand cannot behave as a π-donor, since no empty d_π-orbital is available.[58] Analogous complexes of Mn(I) were found[11,22,30,39] to be 5-coordinated with only a very weak tendency to reversibly bind the sixth ligand. Their preference for the 5-coordination has been explained[22,30,39] by the strong π-donation from the DBCat ligand to Mn(I). Several factors may account for this difference in preferred coordination number between manganese and rhenium catecholate complexes. First, the d-orbital energy is higher for Re than for Mn. Therefore, the energy gap between the empty d_π-orbital and the $3b_1$-HOMO[40] of the DBCat ligand in a hypothetical 5-coordinated rhenium catecholate complex would be higher than in the case of Mn; consequently, the π-bonding would be weaker, insufficient for stabilization of 5-coordinated geometry. The larger atomic radius of Re (1.37 Å compared with 1.27 Å for Mn) also favors 6-coordination, by reducing the steric crowding. Moreover, Re—CO bonds are generally stronger than Mn—CO ones. The CO ligands in the rhenium catecholate complexes can thus act as much stronger π-acceptors, and can compensate effectively for the increase in electron density on Re caused both by coordination of the sixth ligand and by the doubly negative charge on the DBCat ligand. This enhanced Re → CO π-back-bonding is an important stabilizing factor for 6-coordination. Experimentally, this effect can be seen in the values of the average C≡O force constants, $\bar{k}$, which are smaller for 6-coordinated complexes of Re than they are for 5-coordinated manganese catecholate complexes and their adducts (Table II). In conclusion, the DBCat ligand in a 6-coordinated complex of a d^6-metal can be regarded mainly as a strong σ-donor. Such complexes are rather unusual, since the catecholate ligand generally prefers high-valent metals with a lower number of d-electrons,[1] where it can exert its π-donating properties. For the same reason, the most stable catecholate complexes of d^6-metals are usually 5-coordinated, as demonstrated for Mn(I)[22] as well as for the triphosphine catecholate complexes of Co(III), Rh(III), and Ir(III).[7,8]

The semiquinone complexes possess an unpaired electron in the $3b_1$ SOMO of the DBSQ ligand. The low a_{Re} splitting constant values observed by EPR,[33-35,50] together with the RR spectra,[46] suggest the predominant localization of the unpaired electron on the DBSQ ligand as well as a rather limited extent of mixing between the doubly occupied d_π- and singly occupied $3b_1$-orbitals, amounting to very weak π-back-bonding within the Re(DBSQ) chelate ring. The extent of this interaction appears to be determined by the magnitude of the $d_\pi - 3b_1$ energy gap. The sequential substitution of the CO ligands in a $[Re(CO)_4(DBSQ)]$ complex by PPh_3 raises the d_π-orbital energy, decreasing the energy gap and increasing the orbital interaction. Consequently, the a_{Re} splitting constant increases from 28.2 G, for $[Re(CO)_4(DBSQ)]$, to 38.2 and 58.8 G, for $[Re(CO)_3(PPh_3)(DBSQ)]$ and $[Re(CO)_2(PPh_3)_2(DBSQ)]$, respectively. The intensity enhancement of the ν(Re–O) Raman band increases in the same direction, indicating increasing π-delocalization within the Re(DBSQ) chelate ring. Generally, the DBSQ ligand may be regarded as a good σ-donor and a very weak π-acceptor, in accord with previous observations.[30,35]

The oxidation of the DBSQ ligand to DBQ stabilizes the ligand $3b_1$-orbital. Consequently, the energy gap with the occupied rhenium d_π-orbital diminishes, and very delocalized bonding within the $Re(DBQ)^+$ chelate ring appears. The chemical stability of the described $Re(DBQ)^+$ complexes is exceptional, and is comparable only with Mn analogues,[30] $[Rubpy_2Q]^{2+}$ and $[Rupy_4Q]^{2+}$ complexes.[6,19] DBQ is a rather weak σ-donor because of the ketone-like character of its oxygen donor atoms. Therefore, the extent of π-bonding within the $Re(DBQ)^+$ chelate ring must be the crucial factor that determines the stability of the DBQ complexes. This conclusion is supported by a comparison of the visible absorption spectra and, especially, the RR spectra of all three known, chemically stable, transition-metal quinone complexes, i.e., $[Re(CO)_2(PPh_3)_2(DBQ)]^+$, $[Mn(CO)_2\{P(OEt)_3\}_2(DBQ)]^+$,[30] and $[Ru(bpy)_2(BQ)]^{2+}$.[19] The spectroscopic studies discussed above point to a common bonding pattern in these complexes, i.e., an extensive π-delocalization within the M(DBQ) chelate ring, which appears to be the most important factor in determining the chemical stability of the quinone complexes. The availability of occupied d_π-orbitals that are energetically close to the $3b_1$-LUMO of the DBQ ligand is a necessary prerequisite for π-delocalization, and therefore chemical stability. Hence, the stability of the

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[58] Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985.

manganese and rhenium carbonyl quinone complexes is highest for the dicarbonyl species, where the d_π-orbital energy is increased, compared with tri- and, especially, tetracarbonyls. On the other hand, quinone complexes of more electropositive transition metals or of metals in higher oxidation states with low-lying or empty d_π-orbitals readily decompose on the CV time scale,[7,9,13,15] often by substitution of a DBQ ligand with a solvent molecule.

Interestingly, changing the number of CO ligands from three to two has little effect on the C≡O force constants in $[Re(CO)_{4-n}(PPh_3)_n(DBQ)]^+$ complexes ($n = 1, 2$). On the other hand, the redox potential of the ligand-localized DBSQ/DBQ couple is dramatically shifted in a negative direction. For $[Re(CO)_3(PPh_3)(DBQ)]^+$, $\bar{k} = 15.63$ mdyn/Å and $E_{1/2} = +0.27$ V whereas, for $[Re(CO)_2(PPh_3)_2(DBQ)]^+$, $\bar{k} = 15.57$ mdyn/Å and $E_{1/2} = -0.21$ V). Neither the compensating effect on $\bar{k}$ nor the large $E_{1/2}$ shift was observed with lower oxidation states of the dioxolene ligand. Whereas $\bar{k}$ values reflect the d_π-electron density, the $E_{1/2}$ values are determined by the energy of the $d_\pi - 3b_1$, i.e., $\pi_{ML}{}^*$, LUMO of the quinone complexes. Going from the tricarbonyl to the dicarbonyl complex, the increase in the d_π-electron density is effectively compensated for by the increased extent of interaction between the d_π- and $3b_1$-orbitals which, in turn, means increased Re → DBQ π-back-bonding. The DBQ ligand thus behaves as a rather flexible π-acceptor, and effectively competes with CO ligand for d_π-electron density, compensating for the substitutional effects on the C≡O force constants. However, such an increase in the orbital interaction raises the LUMO orbital energy; this is manifested as a strong negative shift in the reduction potential.

Experimental Section

Materials. 3,5-Di-*tert*-butyl-1,2-benzoquinone, DBQ (Aldrich), was recrystallized from *n*-heptane. Bu_4NPF_6 (Fluka) was dried in vacuo at 80 °C for 10 h. $Re_2(CO)_{10}$ and PPh_3 were used as obtained from Strem and Merck, respectively. $[Cp_2Fe]BF_4$ was prepared according to ref 59. All solutions for spectroscopic studies were freeze–pump–thaw degassed and handled under high vacuum. Solvents (all of spectroscopic grade) were freshly distilled under an argon atmosphere and degassed on a vacuum line. THF (Fluka) was distilled from a sodium–benzophenone mixture, and CH_2Cl_2 (Fluka) was distilled from P_2O_5. Benzene (Fluka) was distilled under nitrogen from sodium wire. Pyridine (Merck) was dried by refluxing with KOH, followed by fractional distillation.

An improved synthetic procedure was developed to generate $Na[Re(CO)_5]$. Addition of a THF solution containing sodium anthracenide to an equimolar amount of $Re_2(CO)_{10}$ in THF instantaneously produced $[Re(CO)_5]^-$ (IR bands: 1910 (s), 1862 (vs), 1833 (w) cm^{-1}). Contrary to previously published synthetic procedures, no undesired byproducts are formed. $[Re(CO)_4(DBSQ)]$ was generated by photolysis of a freeze–pump–thaw degassed benzene or CH_2Cl_2 solution of 10^{-2} M DBQ and 5×10^{-3} M $Re_2(CO)_{10}$. For irradiation, either a 125-W medium-pressure or a 200-W high-pressure mercury lamp was used for 4 and 3 h, respectively. The 300–370-nm photolysis spectral region was selected by a combination of the Pyrex glass of the reaction vessel and a UG11 band-pass spectral filter (Oriel) to minimize absorption by free DBQ. The solution was well-stirred during irradiation. Over 90% conversion was achieved, as indicated by IR. The $[Re(CO)_3L(DBSQ)]$ complexes were prepared by the addition of a 100-fold molar excess of free ligand L to the $[Re(CO)_4(DBSQ)]$ solution under an inert atmosphere. An analogous procedure was employed to prepare the $[Re(CO)_2(PPh_3)_2(DBSQ)]$ complex; however, the reaction mixture containing PPh_3 was further photolyzed for 3 h under vacuum. Alternatively, the solution containing $Re_2(CO)_{10}$ and DBQ in equimolar quantities and a 100-fold excess of PPh_3 was photolyzed for 6–7 h. The purity of the resulting solutions was checked by EPR and IR spectroscopies, which showed the presence of no other radical and no other carbonyl complex, except for traces of unreacted $Re_2(CO)_{10}$. EPR, IR, and visible absorption spectra were in agreement with the published data.[32-35] The most convenient way to prepare rhenium catecholate complexes is through reduction of the corresponding semiquinone complexes either spectroelectrochemically or, in less polar solvents, using Cp_2Co as a reducing agent. Oxidative substitution of $[Re(CO)_5]^-$ and $[Re(CO)_4(PPh_3)]^-$ by DBQ can be used to generate $[Re(CO)_4(DBCat)]^-$ and $[Re(CO)_3(PPh_3)(DBCat)]^-$, respectively (vide supra). In these experiments, 1 molar equiv of DBQ in THF was added dropwise to THF solutions of the Re anions. The rhenium quinone complexes were generated by spectroelectrochemical oxidation of the corresponding semiquinone species within the OTTLE cell. $[Re(CO)_2(PPh_3)_2(DBQ)]^+$ can also be generated by chemical oxidation of $[Re(CO)_2(PPh_3)_2(DBSQ)]$ with $[Cp_2Fe]BF_4$ in a THF solution.

Instrumentation. Hewlett-Packard 8452A diode array and Carl-Zeiss-Jena M40 spectrophotometers were used to measure electronic absorption spectra. The IR spectra were recorded on Philips PU9800 FTIR and Nicolet 7199B FTIR spectrometers at a resolution of 4 and 1 cm^{-1}, respectively. EPR spectra were measured using a Varian E4 X-band spectrometer. The resonance Raman spectra were measured with a Dilor XY spectrometer, with excitation by the lines of a SP 2016 Ar^+ laser, or by a CR-590 dye laser employing Coumarine 6 or Rhodamine 6G dyes pumped by the Ar^+ laser. The sample solutions were placed in an IR-OTTLE cell[42] equipped with a Pt-minigrid working electrode (6 × 5 mm rectangle, 32 wires/cm) and NaCl windows. The laser beam was directed at the surface of the working electrode, and the back-scattered light was detected. The same infrared OTTLE cell was also employed to measure the IR (with KBr windows) and UV–vis (with CaF_2 windows) spectra of the spectroelectrochemically generated DBSQ and DBQ complexes. Controlled-potential electrolyses within the OTTLE cell were carried out using a Polarographic analyzer PA4 (Laboratorní přístroje, Prague) or a PAR Model 173 potentiostat. These instruments were also used for CV experiments. All potentials are reported with respect to the Fc/Fc$^+$ couple.[38]

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