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Reduction of (η^5-C_5Ph_4q)Ru(CO)$_2$Br (q = 2,5-Benzoquinonyl): Evidence for an 18 − δ Metalate Anion with a Reduced (Semiquinone) Substituent

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Summary: Three-electron reduction of the cyclopentadienyl complex (C_5Ph_4q)Ru(CO)$_2$Br (q = 2,5-quinone) produces metalate and bromide anions. The metalate anion is best described as an 18 − δ complex with a reduced (semiquinone) substituent, i.e., it is (C_5Ph_4sq)Ru(CO)$_2^{2-}$ (sq = 2,5-semiquinone) or (C_5Ph_4sqH)Ru(CO)$_2^-$ (sqH = protonated 2,5-semiquinone). A semiquinone substituent for the metalate anion is required by electron accounting, and delocalization between the semiquinone and metalate centers explains the higher ν(C≡O) frequencies and lower nucleophilicity of the metalate anion compared to (C_5Ph_4Ar)Ru(CO)$_2^-$ (Ar = 2,5-dimethoxyphenyl), which has the same primary coordination sphere.

Basicity[1] and nucleophilicity[2] are fundamental and much-studied properties of metal carbonylate anions that govern their reactivity. In this communication, we consider the effect of a quinone substituent on the reactivity of a cyclopentadienyl metal cabonylate anion produced by reduction of (η^5-C_5Ph_4q)Ru(CO)$_2$Br (q = 2,5-benzoquinonyl). Usually organometallic complexes with ligands having reduced, radical centers display activated reactivities compared to analogues with exactly 18 valence electrons, for example, toward substitution.[3b,d,e] The term "18 + δ" has been introduced to describe the valence electron count in these paramagnetic organometallic complexes where the metal centers receive a small amount of electron density (δ) from the reduced, radical ligands.[3] However, the radical anion/dianion couple remains accessible for many radical anion ligands.[3a] In species with reducing, electron-rich metal and ligand radical centers, therefore, it is possible that the direction of electron delocalization is from the metal to the radical center. Such species formally would be "18 − δ" complexes. This work tests this idea and provides evidence for a 18 − δ complex with a reduced, radical substituent.

The quinone-substituted cyclopentadienyl complex, (C_5Ph_4q)Ru(CO)$_2$Br,[4] was obtained in 72% overall yield following deprotection of the hydroquinone moiety in ($C_5Ph_4hqMe_2$)Ru(CO)$_2$Br[5] (hqMe$_2$ = 2,5-dimethoxyphenyl) with BBr$_3$ and then oxidation of the intermediate complex, ($C_5Ph_4hqH_2$)Ru(CO)$_2$Br (hqH$_2$ = 2,5-hydroquinonyl), with 1 equiv of 2,3-dichloro-5,6-dicyanoquinone.

Cyclic voltammograms of (C_5Ph_4q)Ru(CO)$_2$Br in 1,2-dichloroethane (DCE) with 0.1 M [Bu$_4$N][PF$_6$][6] show a reversible quinone/semiquinone anion (q/sq$^{\bullet-}$) couple at −0.83 V[7] and a quasi-reversible semiquinone anion/hydroquinone dianion (sq$^{\bullet-}$/hq^{2-}) couple with smaller peak currents at −1.33 V (see Figure 1S in the Supporting Information), eqs 1 and 2, respectively. For

$$(C_5Ph_4q)Ru(CO)_2Br + e^- \leftrightarrows (C_5Ph_4sq^{\bullet})Ru(CO)_2Br^- \quad (1)$$

$$(C_5Ph_4sq^{\bullet})Ru(CO)_2Br^- + e^- \leftrightarrows (C_5Ph_4hq)Ru(CO)_2Br^{2-} \quad (2)$$

comparison, ($C_5Ph_4hqMe_2$)Ru(CO)$_2$Br is electrochemically silent between +0.8 and −1.9 V (the two-electron reduction to the metalate and bromide ions occurs at −1.92 V),[5] and *p*-benzoquinone under identical conditions shows a reversible q/sq$^{\bullet-}$ couple at −0.96 V and a quasi-reversible sq$^{\bullet-}$/hq^{2-} couple, again with smaller peak currents, at −1.56 V. Other benzoquinones behave similarly.[8] However, the results do not discount reactions such as protonation or loss of bromide ion from (C_5Ph_4hq)Ru(CO)$_2$Br^{2-} as contributing to the voltammetric response observed for the second (sq$^{\bullet-}$/hq^{2-}) couple.

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(1) (a) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255. (b) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (c) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257. (d) Kristjansdottir, S. S.; Moody, A. E.; Werberg, R. T.; Norton, J. R. *Organometallics* **1988**, *7*, 1983. (e) Tiset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711. (f) Skagestad, V.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 5077. (g) Kramarz, K. W.; Norton, J. R. *Prog. Inorg. Chem.* **1994**, *42*, 1.

(2) (a) Dessy, R. E.; Weissman, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 5121. (b) Dessy, R. E.; Weissman, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 5124. (c) Pearson, R. G.; Figmore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541. (d) Lai, C.-K.; Feighery, W. G.; Zhen, Y.; Atwood, J. D. *J. Am. Chem. Soc.* **1989**, *28*, 3929. (e) Corraine, M. S.; Atwood, J. D. *Organometallics* **1991**, *10*, 2315. (f) Niecke, E.; Metternich, H. J.; Nieger, M.; Gudat, D.; Wenderoth, P.; Malisch, W.; Hahner, C.; Reich, W. *Chem. Ber.* **1993**, *126*, 1299. (g) Striejewske, W. S.; Churchill, M. R.; Atwood, J. D. *Organometallics* **1993**, *12*, 4413. (h) Mayr, H.; Patz, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938. (i) Sykhrannova, M. I.; Khorshev, S. Y.; Tatarnikov, A. N.; Gladyshev, E. N. *Russ. Chem. Bull.* **1994**, *43*, 1405. (j) Atwood, J. D.; Corrainepandolfino, M. S.; Zhen, Y. Q.; Striejewske, W. S.; Ang, P. *J. Coord. Chem.* **1994**, *32*, 65.

(3) (a) Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187. (b) Brown, T. L. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; Chapter 3. (c) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325. (d) Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1995**, *14*, 2387. (e) van Outersterp, J. W. M.; Hartl, F.; Stufkens, D. J. *Organometallics* **1995**, *14*, 3303. (f) Avey, A.; Nieckarz, G. F.; Keana, K.; Tyler, D. R. *Organometallics* **1995**, *14*, 2790. (g) Schut, D. M.; Keanna, K. J.; Tyler, D. R.; Rieger, P. H. *J. Am. Chem. Soc.* **1995**, *117*, 8939. (h) Klein, A.; Vogler, C.; Kaim, W. *Organometallics* **1996**, *15*, 236.

(4) Anal. Calcd for $C_{37}H_{23}O_4BrRu$: C, 62.37; H 3.25. Found: C, 61.93; H, 3.62. IR (CH$_2$Cl$_2$), ν(C≡O): 2053 (vs), 2008 (vs), 1662 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.25−6.99 (m, *Ph* and 2,5-C$_6$*H*$_3$O$_2$, 21 H), 6.71 (dd, *J* 10.3, 2.6 Hz, 2,5-C$_6$*H*$_3$O$_2$, 1 H), 6.60 (d, *J* = 10.3 Hz, 2,5-C$_6$*H*$_3$O$_2$, 1 H). EI−MS: *m/z* 714 (M$^+$, 2), 656 (M$^+$ − 2CO, 18), 303 (100).

(5) Colbran, S. B.; Harrison, W. M.; Saadeh, C. *Organometallics* **1994**, *13*, 1061.

(6) The same (spectro)electrochemistry is observed for (C_5Ph_4q)Ru(CO)$_2$Br in 1,2-dimethoxyethane (DME) with 0.4 M [Bu$_4$N][PF$_6$]; ν(C≡O) = 1904, 1825 cm^{-1} for the metalate anion in DME with 0.4 M [Bu$_4$N][PF$_6$].

(7) All electrochemical experiments used a BAS100B Electrochemical Analyzer; potentials are quoted relative to the ferrocenium−ferrocene couple.

(8) (a) Gupta, N; Linschitz, H. *J. Am. Chem. Soc.* **1997**, *119*, 6384. (b) Chambers, J. Q. In *Chemistry of the Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley, New York, 1988; Vol. II, Chapter 12.

S0276-7333(97)00669-9 CCC: $14.00

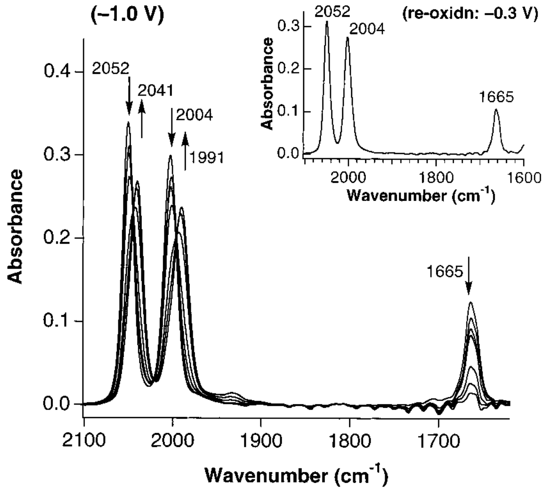

Figure 1. IR spectra recorded during the first reduction of $(C_5Ph_4q)Ru(CO)_2Br$ at a Pt gauze electrode in DCE with 0.4 M $[Bu_4N][PF_6]$. Inset: IR spectrum after re-oxidation of the final electrolysis product.

EPR spectra recorded after scanning the potential of the Pt wire working electrode of an EPR spectroelectrochemical cell[9] once through the first reduction process of $(C_5Ph_4q)Ru(CO)_2Br$ showed a doublet of triplets (g = 2.013; a_H = 2.835 (1H), 2.151 (2H) G; Figure 2S, Supporting Information), confirming that the ligand-centered semiquinone anion is formed, eq 1.

FTIR spectra collected during electroreduction with the platinum mesh working electrode of an optically transparent, thin-layer electrochemical (OTTLE) cell poised just negative of the potential for the first reduction process are presented in Figure 1 and show isosbestic replacement of all carbonyl bands of $(C_5Ph_4q)Ru(CO)_2Br$ ($\nu(C\equiv O) = 2052, 2004\ cm^{-1}$) by those of the reduction product ($\nu(C\equiv O) = 2041, 1991\ cm^{-1}$). The loss of the quinone C=O band at 1665 cm^{-1} and the small shift in the carbonyl ligand bands to lower wavenumber by ~12 cm^{-1} in the reduction product are consistent with a ligand centered reduction to give 18 + δ $(C_5Ph_4sq)Ru(CO)_2Br^-$ (compare with 2048 and 1999 cm^{-1} for $\nu(C\equiv O)$ of the hydroquinone complex, $(C_5Ph_4hqH_2)Ru(CO)_2Br$, in DCE with 0.4 M $[Bu_4N][PF_6]$). The reduction process was fully reversible—re-oxidation of $(C_5Ph_4sq)Ru(CO)_2Br^-$ regenerated $(C_5Ph_4q)Ru(CO)_2Br$ (see the inset to Figure 1).

The coulometry experiments were also in accord with $(C_5Ph_4sq)Ru(CO)_2Br^-$ being the product of the first reduction, i.e., eq 1; 0.99 ± 0.1 faraday/mol were consumed on bulk electrolysis (using a conventional three-compartment cell with large Pt gauze working and auxiliary electrodes and an Ag wire pseudoreference electrode). However, 2.03 ± 0.1 faraday/mol were passed during the second reduction revealing the process to be more complicated than eq 2 on the longer timescale of the bulk electrolyses. Cyclic voltammograms recorded after the second electrolysis revealed anodic peaks at −0.51 and +0.25 V for irreversible oxidations of the reduction product and bromide ion, respectively.

Figure 2 presents FTIR spectra accumulated during the electroreduction of $(C_5Ph_4sq)Ru(CO)_2Br^-$ in the OTTLE cell at the potential of the second reduction process. Clearly evident is an initial small shift in the carbonyl peak frequencies by ~5 cm^{-1} to lower energy, consistent with a ligand-centered reduction to give the hydroquinone dianion, eq 2. Concomitantly, the carbonyl peaks of this reduction product ($\nu(C\equiv O) = 2036, 1986\ cm^{-1}$), likely $(C_5Ph_4hq)Ru(CO)_2Br^{2-}$, are cleanly replaced by those of the ultimate, second reduction product ($\nu(C\equiv O) = 1900, 1819\ cm^{-1}$). The large shift in the C≡O ligand bands to lower energy identify this reduction product as a metalate anion (for comparison, $\nu(C\equiv O)$ for $(C_5Ph_4hqMe_2)Ru(CO)_2^-$ 1885, 1804 cm^{-1} in 1,2-dimethoxyethane (DME) with 0.4 M $[Bu_4N][PF_6]$). That the reduction consumes 2 charge equiv (three overall from $(C_5Ph_4q)Ru(CO)_2Br$) and that a bromide ion is lost on the longer timescale of the electrolyses, suggests that the product has semiquinone and metalate centers, i.e., it is either $(C_5Ph_4sq)Ru(CO)_2^{2-}$ or $(C_5Ph_4sqH)Ru(CO)_2^-$. Generally, semiquinones rapidly disproportionate when protonated.[10] This would suggest that $(C_5Ph_4sq)Ru(CO)_2^{2-}$ is the more likely product,[11] but, as described below, the semiquinone and metalate centers may be stabilized by electronic delocalization between them. EPR spectra recorded on solutions of $(C_5Ph_4q)Ru(CO)_2Br$ with the Pt wire electrode of the EPR spectroelectrochemical cell poised at the second reduction potential showed only the signal for $(C_5Ph_4sq)Ru(CO)_2Br^-$. The result is expected and follows because loss of a bromide ion from $(C_5Ph_4hq)Ru(CO)_2Br^{2-}$ is comparatively slow (as shown by the IR spectroelectrochemical experiments). As this dianion diffuses from the Pt wire working electrode into the bulk solution, comproportionation with the parent complex will give $(C_5Ph_4sq)Ru(CO)_2Br^-$, eq 3. Equations 2 and 4 summarize the overall second reduction process. The $sq^{\bullet -}/hq^{2-}$ couple of the quinone substituent mediates[3h,12] the two-electron reduction at the metal center to form

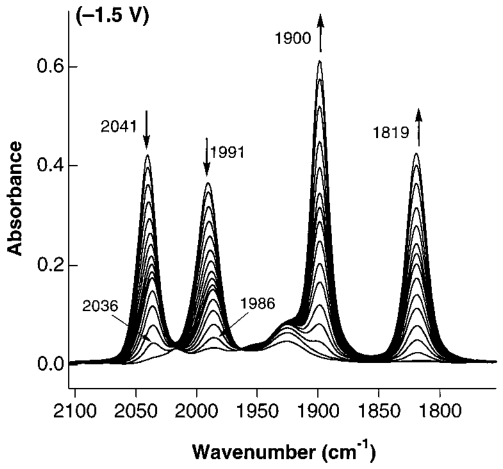

Figure 2. IR spectra recorded during the second reduction of $(C_5Ph_4q)Ru(CO)_2Br$ at a Pt gauze electrode in DCE with 0.4 M $[Bu_4N][PF_6]$.

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[9] Fernando, K. R.; McQuillan, A. J.; Peake, B. M.; Wells, J. *J. Magn. Reson.* **1986**, *68*, 551.

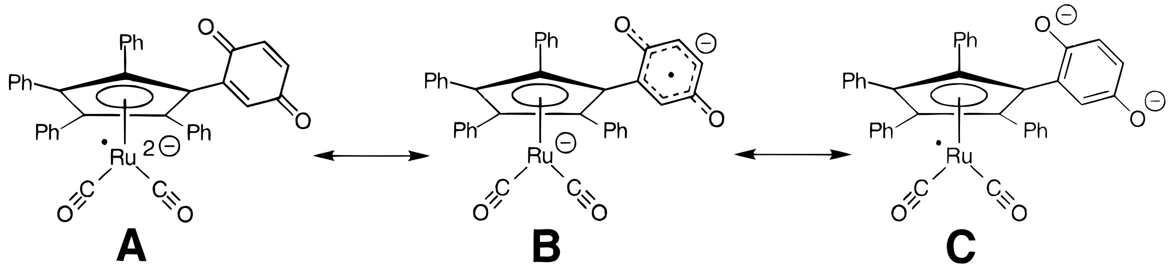
[10] Denisov, E. T.; Khudyakov, I. V. *Chem. Rev.* **1987**, *87*, 1313.

[11] In support of this argument, electrochemical reduction of $(C_5Ph_4q)Ru(CO)_2Br$ at the potential of the $q/sq^{\bullet -}$ couple with 5 equiv of pyridinium *p*-toluenesulfonate cleanly produced $(C_5Ph_4hqH_2)Ru(CO)_2Br$ revealing the semiquinone anion, $(C_5Ph_4sq)Ru(CO)_2Br^-$, to disproportionate in the presence of proton sources.

[12] Pugh, J. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 3784.

[13] The assignment as $(C_5Ph_4hqH_2)Ru(CO)_2Br$ is made on the exact coincidence of the $\nu(C\equiv O)$ values of the product with those of an authentic sample of $(C_5Ph_4hqH_2)Ru(CO)_2Br$ in the same medium. Diffusion of oxidizing materials produced at the counter-electrode into the working compartment of the OTTLE cell probably accounts for the slow oxidation of the metalate anion observed in the experiment, although slow leakage of adventitious oxygen cannot be discounted.

Scheme 1



$$(C_5Ph_4q)Ru(CO)_2Br + (C_5Ph_4hq)Ru(CO)_2Br^{2-} \rightarrow 2(C_5Ph_4sq^{\bullet})Ru(CO)_2Br^{-} \quad (3)$$

$$(C_5Ph_4hq)Ru(CO)_2Br^{2-} + e^{-} + xH^{+} \rightarrow (C_5Ph_4sqH_x^{\bullet})Ru(CO)_2^{(2-x)-}\ (x = 0 \text{ or } 1) + Br^{-} \quad (4)$$

bromide and metalate ions (the process occurs ~600 mV positive of the analogous reduction of $(C_5Ph_4hqMe_2)Ru(CO)_2Br$[5]).

The IR spectrum and the reactivity displayed by the metalate anion produced by the second reduction process is also in accord with it being either $(C_5Ph_4sq)Ru(CO)_2^{2-}$ or $(C_5Ph_4sqH)Ru(CO)_2^{-}$. First, the C≡O band energies of the metalate anion are significantly higher than those of $(C_5Ph_4hqMe_2)Ru(CO)_2^{-}$ (by 19 and 21 cm^{-1} for the a and b modes, respectively, in 1,2-dimethoxyethane with 0.4 M $[Bu_4N][PF_6]$[5,6]), a result inconsistent with a donor hydroquinone substituent but consistent with a semiquinone substituent. In the latter case, i.e., for $(C_5Ph_4sq)Ru(CO)_2^{2-}$ or $(C_5Ph_4sqH)Ru(CO)_2^{-}$, delocalization of electron density from the electron-rich metalate center to the directly-linked semiquinone would decrease $d\pi(Ru) \rightarrow \pi^*(CO)$ back-bonding and raise the ν(C≡O) frequencies.

Second, the product metalate anion is considerably less basic and less nucleophilic than $(C_5Ph_4hqMe_2)Ru(CO)_2^{-}$, a result consistent with it being $(C_5Ph_4sq)Ru(CO)_2^{2-}$ or $(C_5Ph_4sqH)Ru(CO)_2^{-}$ (but inconsistent with the hydroquinone-substituted species $(C_5Ph_4hqH_y)Ru(CO)_2^{(3-y)-}$ ($y = 0-2$) which should be at least as reactive as $(C_5Ph_4hqMe_2)Ru(CO)_2^{-}$). The product metalate anion was produced in DCE solution and was apparent for 350 min after the electrolysis was ceased (over this time slow conversion to the hydroquinone complex $(C_5Ph_4hqH_2)Ru(CO)_2Br$ (ν(C≡O) = 2048, 1999 cm^{-1}) was observed;[13] no products from nucleophilic substitution reactions with DCE were observed). In contrast, whereas reductive electrolyses of $(C_5Ph_4hqMe_2)Ru(CO)_2Br$ in DME produced the metalate anion $(C_5Ph_4hqMe_2)Ru(CO)_2^{-}$, in DCE the only products observed by FTIR spectroscopy as the electrolyses proceeded were the hydride $(C_5Ph_4hqMe_2)Ru(CO)_2H$ (minor product, from proton abstraction by intermediary $(C_5Ph_4hqMe_2)Ru(CO)_2^{-}$) and the ethylene-bridged dimer $\{(C_5Ph_4hqMe_2)Ru(CO)_2CH_2\}_2$ (major product, from the reaction of 2 equiv of the strongly nucleophilic intermediate, $(C_5Ph_4hqMe_2)Ru(CO)_2^{-}$, with DCE).[5]

From the IR spectroelectrochemical experiments, the half-life of $(C_5Ph_4hqMe_2)Ru(CO)_2^{-}$ in DCE is less than ~60 s (otherwise it would have been observed). The experiments, thus, place a *lower* limit of 350 for the relative difference in the nucleophilicities (as indicated by the relative rates of the nucleophilic displacement reactions with DCE) of $(C_5Ph_4hqMe_2)Ru(CO)_2^{-}$ and the product metalate anion, either $(C_5Ph_4sq)Ru(CO)_2^{2-}$ or $(C_5Ph_4sqH)Ru(CO)_2^{-}$. The latter result is related to recent, elegant demonstrations of control over the stoichiometric and catalytic reactivity of transition metal centers by switching the state-of-charge of a ligand with a "remote", redox-active center.[14]

Switching from a hydroquinone ($hqMe_2$) to a semiquinone (sq or sqH) pendant to the metalate anion center has a remarkable influence on reactivity at the ruthenium center, with the change being understandable in terms of the direction of delocalization between the semiquinone and metalate redox centers. In simple valence bond terms, **A**−**C** are limiting canonical forms for the dianion, $(C_5Ph_4sq)Ru(CO)_2^{2-}$ (protonation gives the canonical structures for $(C_5Ph_4sqH)Ru(CO)_2^{-}$), Scheme 1. Structure **B** with its 18-electron, d^8 Ru(0) metalate center will clearly be the major contributor to the structure of the metalate anion. For an $18 + \delta$ metalate ion **A** (with 19-electron, d^9 Ru(−I) and quinone centers) would contribute significantly; conversely if **C** (with 17-electron, d^7 Ru(I) and hydroquinone centers) is a significant contributor, then an $18 - \delta$ metalate anion results. The higher ν(C≡O) frequencies and lower nucleophilicity in the metalate anion, either $(C_5Ph_4sq)Ru(CO)_2^{2-}$ or $(C_5Ph_4sqH)Ru(CO)_2^{-}$, compared to $(C_5Ph_4hqMe_2)Ru(CO)_2^{-}$ are consistent with a significant contribution from **C**, not **A**. The metalate anion is best formulated as an $18 - \delta$ complex with a semiquinone substituent.

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Supporting Information Available: Figures showing the cyclic voltammogram of $(C_5Ph_4q)Ru(CO)_2Br$ and the EPR spectrum of $(C_5Ph_4sq)Ru(CO)_2Br^{-}$ (2 pages). Ordering information is given on any current masthead page.

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[14] (a) Lorkovic, I. M.; Wrighton, M. S.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6220. (b) Wolf, M. O.; Wrighton, M. S. *Chem. Mater.* **1994**, *6*,1526. (c) Lorkovic, I. M.; Duff, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 3617.