Reduction Chemistry of Organometallic Molybdenum, Tungsten, and Ruthenium Bromo Complexes of the Bulky, Perarylated Cyclopentadienyl Ligand η^5-$C_5Ph_4hqMe_2$: Evidence for the Intermediacy of Metal-Centered Radicals and Nucleophilic Reactions of Product Metalate Anions with Chlorinated Solvent

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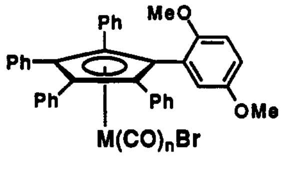
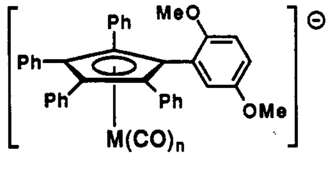
Summary: The bromo complexes $(C_5Ph_4hqMe_2)M(CO)_nBr$ (1, M = Mo, n = 3; 2, M = W, n = 3; 3, M = Ru, n = 2) have been prepared and are reduced via the $(C_5Ph_4hqMe_2)M(CO)_n^{\bullet}$ radicals in a two-electron (ECE) process to the corresponding metalate $(C_5Ph_4hqMe_2)M(CO)_n^-$ (4–6) and bromide anions at −1.76 V (Mo), −1.84 V (W) and −1.92 V (Ru). Reduction of 3 with cobaltocene in THF affords the dimer $\{(C_5Ph_4hqMe_2)Ru(CO)_2\}_2$ (7). Anions 4 and 5 and dimer 7 show electrochemically quasi-reversible $(C_5Ph_4hqMe_2)M(CO)_n^{\bullet}/(C_5Ph_4hqMe_2)M(CO)_n^-$ couples at −0.54 V (Mo), −0.52 V (W), and −1.30 V (Ru). Anion 4 does not react with 1,2-dichloroethane on the bulk electrolysis time scale (3–10 min); 5 reacts slightly, and 6 reacts completely, in accord with the anticipated nucleophilicities of these metalate anions.

The electrochemistries of the organometallic halides $M(\eta\text{-}C_5R_5)_m(CO)_nX$ (X = halogen atom) have received relatively little attention,[1] whereas the electrochemical reactivities of the organometallic dimers $\{M(\eta\text{-}C_5R_5)_m(CO)_n\}_2$ (R = H, Me)[2] and organic halides[3] have been active areas of research. We wish to report preliminary results from cyclic voltammetric and FTIR spectroelectrochemical studies aimed at determining the redox chemistries of some organo-transition-metal bromo complexes (1–3) of the bulky perarylated cyclopentadienyl ligand $C_5Ph_4hqMe_2$,[4] and of the metalate anions (4–6) derived from these bromo complexes. $C_5Ph_4hqMe_2$ was chosen as the cyclopentadienyl ligand for the following reasons. (i) Perarylated cyclopentadienyl ligands (C_5Ph_5 is the most studied[5]) stabilize complexes in unusual oxidation states; e.g., 17-electron C_5Ph_5 metal-centered radicals are very much less reactive (even isolable)[6] than their C_5H_5 or C_5Me_5 congeners (for which recombination rates have been photochemically estimated to exceed $10^9\ M^{-1}\ s^{-1}$ [7]). We expected, therefore, to find evidence for stabilized 17-electron metal-centered radicals in the electrochemistry of the $C_5Ph_4hqMe_2$ complexes. (ii) The hydroquinone dimethyl ether ($hqMe_2$) pendant renders $C_5Ph_4hqMe_2$ complexes more soluble and tractable than their C_5Ph_5 counterparts,[8,9] provides a convenient NMR "handle" for characterization,[8,9] and can be elaborated to provide complexes with electrochemically active hydroquinonyl or quinonyl pendants.[9] Mo, W, and Ru complexes were studied in order to probe for effects due to the nucleophilicity of the metalate anions (e.g. the nucleophilicities (k_2 for reaction with MeI in THF) of the analogous C_5H_5 metalate anions are $(C_5H_5)Mo(CO)_3^-$ ($67\ M^{-1}\ s^{-1}$) < $(C_5H_5)W(CO)_3^-$ (~500 $M^{-1}\ s^{-1}$) ≪ $(C_5H_5)Ru(CO)_2^-$ ($7.5 \times 10^6\ M^{-1}\ s^{-1}$)[10]).

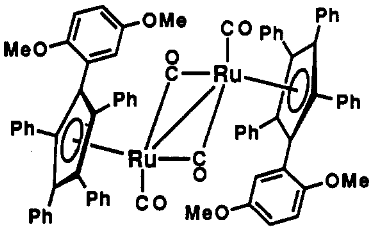
Chart 1





1 M = Mo, n = 3
2 M = W, n = 3
3 M = Ru, n = 2

4 M = Mo, n = 3
5 M = W, n = 3
6 M = Ru, n = 2



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Complexes 1–5 and 7 were obtained from syntheses analogous to those reported for the corresponding

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(4) Abbreviations: $C_5Ph_4hqMe_2$ = η-(2,5-dimethoxyphenyl)tetraphenylcyclopentadienyl; C_5Ph_5 = η-pentaphenylcyclopentadienyl; THF = tetrahydrofuran.

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Table 1. Electrochemical Data[a]

	$MBr + 2e^- \rightarrow M^- + Br^-$				$M^- \rightleftharpoons M^\bullet + e^-$			
M	E_p, V	$\lvert E_p - E_{p/2}\rvert$, mV	$\lvert\Delta E_p(Fc^+/Fc)\rvert$, mV	E_p^{anodic},[b] V	$E_{1/2}$, V	i^c/i^a	$\lvert\Delta E_p\rvert$, mV	$\lvert\Delta E_p(Fc^+/Fc)\rvert$, mV
$(C_5Ph_4hqMe_2)Mo(CO)_3$	−1.70	120	65	−0.46	−0.54	0.8	110	80
$(C_5Ph_4hqMe_2)W(CO)_3$	−1.84	130	70	−0.50	−0.52	0.8	90	60
$(C_5Ph_4hqMe_2)Ru(CO)_2$	−1.92	110	65	−1.04 (0.28)	−1.30	1.1	120	85

[a] Data taken from cyclic voltammograms (0.8-mm-diameter Pt-disk working electrode; scan rate 100 mV s^{-1}) of ~10^{-3} M complex in 1,2-dichloroethane with 0.1 M *n*-Bu_4NPF_6 at 25 °C. Potentials are quoted relative to the ferrocenium/ferrocene couple ($E_{1/2}(Fc^+/Fc) = 0$ V). [b] Associated anodic peak(s) in reverse positive scan (e.g. see Figure 1).

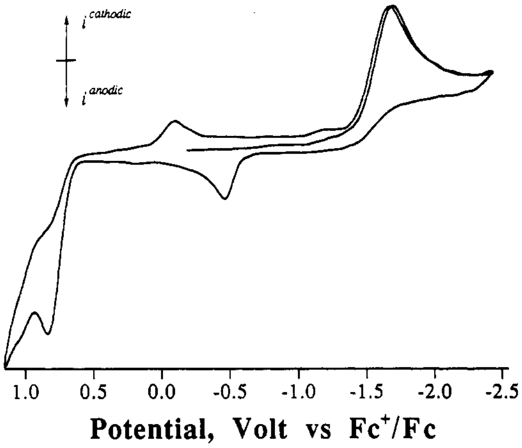

Figure 1. Cyclic voltammogram (0.8-mm-diameter Pt-disk working electrode; scan rate 100 mV s^{-1}) of ~10^{-3} M $(C_5Ph_4hqMe_2)Mo(CO)_3Br$ in 1,2-dichloroethane with 0.1 M *n*-Bu_4NPF_6 at 25 °C.

Mo,[6b,c,8,11] W,[11] or Ru[9,12] η-C_5Ph_5 complex and were fully characterized by elemental analysis and mass, FTIR, ^1H NMR, and ^{13}C NMR spectroscopies (details are given in the Supplementary Material). The metalate anion **6** was not isolated, but solutions of **6** (ν_{CO}(THF): 1885, 1784 cm^{-1}) were prepared by reduction of **3** or **7** with sodium amalgam.

The voltammetric responses of **1**–**3** were similar to each other and were the same irrespective of whether the solvent was 1,2-dichloroethane or 1,2-dimethoxyethane (both with 0.1 M *n*-Bu_4NPF_6). Figure 1 shows a typical cyclic voltammogram[13] (of **1**). Each complex showed a broad, electrochemically irreversible reduction process ($\lvert E_{p/2} - E_p\rvert > \lvert\Delta E_p(Fc^+/Fc)\rvert$) and an associated anodic process after scan inversion (data are listed in Table 1). The reduction behavior is indicative of a slow, rate-controlling electron-transfer reaction.[14] Chemically irreversible oxidation waves ($\lvert E_{p/2} - E_p\rvert \approx \lvert\Delta E_p(Fc^+/Fc)\rvert$, but $i^c/i^a = 0$) were also observed for each complex at positive potentials (>0.8 V). These oxidation processes lead to complete decomposition of the complexes, evidenced by the complete loss of all ν_{CO} bands from IR spectra of the oxidation product(s), and will not be discussed further here.

Bulk electrolyses of **1**–**3** at ambient temperature were carried out at the Pt-gauze working electrode of a thin-layer, transmission IR spectroelectrochemical cell of conventional design. The electroreductions in 1,2-dichloroethane consumed $2e^-$ per molecule of complex, and the IR spectra recorded during the electrolyses showed that **1** gave **4**, **2** gave **5**, and **3** gave $(C_5Ph_4hqMe_2)Ru(CO)_2CH_2CH_2Cl$[15] and $\{(C_5Ph_4hqMe_2)Ru(CO)_2CH_2\}_2$[15] (Figure 2). **1** was the only product of the reoxidation of fully reduced solutions of **1** (i.e. of **4** and Br^- ion). Reoxidation of solutions of fully reduced **2** (i.e. of **5** and Br^- ion) produced **2** (*ca.* 75% by ν_{CO} peak intensity) and $(C_5Ph_4hqMe_2)W(CO)_2CH_2CH_2Cl$,[15] plus a single ν_{CO} peak from an unknown species (Figure 2d and inset). Careful subtraction of the ν_{CO} peaks for **2** and **5** from the IR spectra collected during the reduction of **2** also reveals small ν_{CO} peaks for $(C_5Ph_4hqMe_2)W(CO)_2CH_2CH_2Cl$.[15] In contrast, chemical reduction of **1**–**3** with sodium amalgam in 1,2-dimethoxyethane cleanly gave the corresponding metalate anion (**4**–**6**) as the only product detectable by IR spectroscopy, and chemical reduction of **3** with 1 equiv of cobaltocene in tetrahydrofuran afforded orange-red, microcrystalline **7** in moderately good yield (~60% after recrystallization).[16]

Cyclic voltammograms[13] of metalate anions **4** and **5** and dimer **7** showed electrochemically quasi-reversible $(C_5Ph_4hqMe_2)M(CO)_n^\bullet/(C_5Ph_4hqMe_2)M(CO)_n^-$ couples (Table 1). These observations parallel those recently described for $C_5Ph_5Cr(CO)_3^-$ [6a] and for the dimers $\{(\eta\text{-}C_5R_5)Cr(CO)_3\}_2$ (R = H, CH_3)[17] and point to 17-electron $(C_5Ph_4hqMe_2)M(CO)_n^\bullet$ radicals stabilized by the steric bulk of the $C_5Ph_4hqMe_2$ ligand (C_5H_5 and C_5Me_5 analogues of **4**–**6** show only irreversible oxidation processes because of rapid recombination of the electrochemically produced 17-electron radicals[2]). The electrochemical results are indicative for a rapid equilibrium between **7** and $(C_5Ph_4hqMe_2)Ru(CO)_n^\bullet$.[6b,17] The $(C_5Ph_4hqMe_2)M(CO)_n^\bullet/(C_5Ph_4hqMe_2)M(CO)_n^-$ couples are not completely chemically reversible (see the i^a/i^c values listed in Table 1), and peaks for new electroactive products are observed after the couples are traversed. The results suggest that the $(C_5Ph_4hqMe_2)M(CO)_n^\bullet$ radicals undergo further processes within the cyclic voltammetry time scale, and experiments are underway to fully characterize these.

An ECE mechanism (Scheme 1, eqs 1–3; **M** = $(C_5Ph_4hqMe_2)W(CO)_3$, $(C_5Ph_4hqMe_2)Mo(CO)_3$, $(C_5Ph_4hqMe_2)Ru(CO)_2$) accounts for the cyclic voltammetry of **1**–**3**.[14] All steps are well precedented. The first step in the reduction (eq 1) produces 19-electron bromo radicals, $(\mathbf{M}\text{–}Br)^{\bullet-}$.[1,18–21] The closely related radicals $(C_5H_5)Mo(CO)_3I^{\bullet-}$, $(C_5H_5)W(CO)_3I^{\bullet-}$, and $(C_5H_5)Fe(CO)_2X^{\bullet-}$ (X = Cl, I) have been stabilized and spectroscopically characterized at 77

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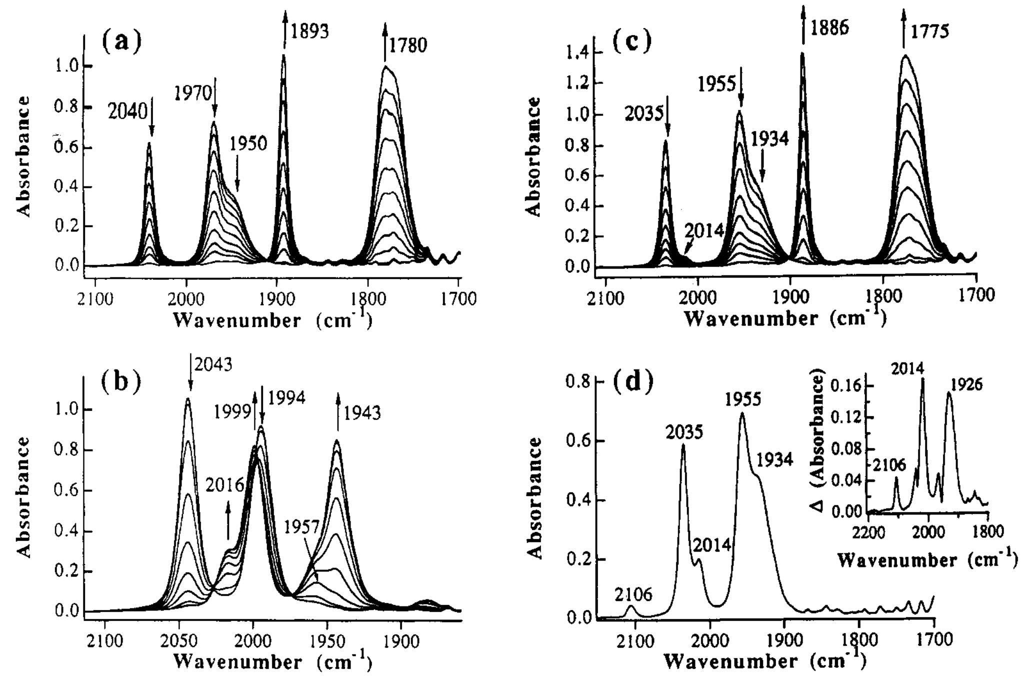

Figure 2. FTIR spectra recorded in 1,2-dichloroethane with 0.4 M *n*-Bu_4NPF_6 at 25 °C: (a) for electroreduction of $(C_5Ph_4hqMe_2)(CO)_3Br$, $(C_5Ph_4hqMe_2)Mo(CO)_3^-$ being the product; (b) for electroreduction of $(C_5Ph_4hqMe_2)Ru(CO)_2Br$, $(C_5Ph_4hqMe_2)Ru(CO)_2CH_2CH_2Cl$ (ν_{CO}: 2016 and 1957 cm^{-1}) and $\{(C_5Ph_4hqMe_2)Ru(CO)_2CH_2CH_2\}_2$ (ν_{CO}: 1999 and 1943 cm^{-1}) being the products; (c) for electroreduction of $(C_5Ph_4hqMe_2)W(CO)_3Br$, the major product being $(C_5Ph_4hqMe_2)W(CO)_3^-$ (ν_{CO}: 1886 and 1775 cm^{-1}); (d) after reoxidation of the fully reduced solution from (c). Inset: difference spectrum, obtained after subtraction of the spectrum of $(C_5Ph_4hqMe_2)W(CO)_3Br$ from spectrum d, showing IR peaks for $(C_5Ph_4hqMe_2)W(CO)_3CH_2CH_2Cl$ (ν_{CO}: 2014 and 1926 cm^{-1}).

Scheme 1

$\text{M-Br} + e^- \rightleftharpoons (\text{M-Br})^{\bullet-}$ (1)

$(\text{M-Br})^{\bullet-} \rightleftharpoons \text{M}^\bullet + \text{Br}^-$ (2)

$\text{M}^\bullet + e^- \rightleftharpoons \text{M}^-$ (3)

$2\,\text{M}^\bullet \rightleftharpoons \text{M}_2$ (4)

$\text{M}^- + \text{M-Br} \rightarrow \text{M}_2 + \text{Br}^-$ (5)

$\text{M}^- + \text{RCl} \rightarrow \text{M-R} + \text{Cl}^-$ (6)

K.[20] Nineteen-electron radicals such as $(\mathbf{M}\text{–Br})^{\bullet-}$ are generally labile, and the equilibrium with $\mathbf{M}^\bullet$ and free bromide ion (eq 2) is anticipated.[19,21] The equilibrium constants for eq 2 are expected to be small (e.g., the photochemical estimate of $K_{eq} \geq 65$ for $(C_5H_5)Mo(CO)_3^\bullet + Br^- \rightleftharpoons (C_5H_5)Mo(CO)_3Br^{\bullet-}$ [21]), and the reaction direction will be dictated by the other reactions of $\mathbf{M}^\bullet$ and $(\mathbf{M}\text{–Br})^{\bullet-}$. Finally, the $\mathbf{M}^\bullet/\mathbf{M}^-$ couple (eq 3) is quite positive of the potential of the first electron transfer (Table 1), and thus spontaneous reduction of the 17-electron radical $\mathbf{M}^\bullet$ will occur, either at the electrode or in a solution electron-transfer reaction with $(\mathbf{M}\text{–Br})^{\bullet-}$.[2c] The overall reduction mechanism is very similar to those proposed for the reductions of organometallic dimers $\{M(\eta\text{-}C_5R_5)_m(CO)_n\}_2$ (R = H, Me).[2] Cobaltocene ($E_{1/2}((C_5H_5)_2Co^+/(C_5H_5)_2Co) = -1.34$ V) presumably catalyzes the reduction of **3**.[2a] Our results are consistent with two mechanisms for the formation of **7**: either reduction of **3** to $(C_5Ph_4hqMe_2)Ru(CO)_2^\bullet$ (eqs 1 and 2) and then dimerization of the 17-electron radical (eq 4) to **7** or reduction of **3** to **6** (eqs 1–3) followed by attack of strongly nucleophilic **6** on **3** (eq 5).[10,22]

Finally, we turn our attention to the bulk electrolysis results, e.g. Figure 2. Here, 1,2-dichloroethane was deliberately chosen as a reactive solvent. On the longer time scale of the electrolyses (3–10 min), reaction of the electrogenerated metalate anion with this chlorinated solvent occurs (eq 6): totally for $\mathbf{M} = (C_5Ph_4hqMe_2)Ru(CO)_2$, slightly for $\mathbf{M} = (C_5Ph_4hqMe_2)W(CO)_3$, and not at all for $\mathbf{M} = (C_5Ph_4hqMe_2)Mo(CO)_3$.[23] This is in very good accord with expectations raised by the anticipated nucleophilicities of the metalate anions (i.e. Mo < W ≪ Ru;[10] see above). The reactions are precedented: e.g., $(C_5H_5)Ru(CO)_2\{(CH_2)_nX\}$ (n = 3–5; X = Cl, Br, I) and $\{(C_5H_5)Ru(CO)_2(CH_2)_{n/2}\}_2$ have been prepared from reactions of $X(CH_2)_nX$ with $(C_5H_5)Ru(CO)_2^-$,[24] and $(C_5H_5)Ru(CO)_2^-$ and 1,2-dichloroethane afford $\{(C_5H_5)Ru(CO)_2CH_2\}_2$.[25]

Acknowledgment. C.S. and W.M.H. acknowledge Australian Postgraduate Research Awards, and we thank Prof. Brynn Hibbert, UNSW, for access to the BAS 100B electrochemical analyzer.

Supplementary Material Available: Text giving analytical and spectroscopic data for compounds **1–5** and **7** (3 pages). Ordering information is given on any current masthead page.

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[18] Note, however, that our results do not strictly determine between sequential electron transfer and metal–halogen bond breaking, and the concerted process: M–Br + e^- → $M^\bullet$ + Br^-. See ref 3 for detailed discussions of concerted versus sequential electron transfer and bond breaking in organic halides.

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