On the Question of Redox-Induced Haptotropic Rearrangements in the Electrochemical Reduction of η^6-Triolefin Chromium Complexes Having Nonaromatic Ligands

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The electrochemical reduction of two types of Cr(η^6-triolefin)(CO)$_3$ complexes has been studied by voltammetry and by electrolysis. In contrast to Cr(η^6-arene)(CO)$_3$ compounds, the bicyclic ligand in Cr(η^4:η^2-C$_9$H$_8$Ph$_2$)(CO)$_3$ (**1a**) and the fulvene-type ligand in Cr(η^6-C$_5$H$_4$CPh$_2$)(CO)$_3$ (**2**) are nonaromatic and display two *separate* one-electron reductions to the nominally 19e and 20e complexes: $E_{1/2}(1) = -2.00$ V and $E_{1/2}(2) = -2.20$ V for **1a**, $E_{1/2}(1) = -1.40$ V and $E_{1/2}(2) = -2.10$ V for **2** in THF/0.1 M [NBu$_4$][PF$_6$] (potentials vs ferrocene/ferrocenium). On the basis of the IR and ESR data of **1a**$^-$ and on the redox behavior when one or more phenyl groups in **1a** are replaced by a SiMe$_3$ group, **1a**$^-$ is viewed as a delocalized metal−ligand radical that is likely to retain the η^4:η^2 hapticity of the bicyclic ligand. In contrast, an η^6/η^5 haptotropic rearrangement is very fast and perhaps concomitant with the **2**/**2**$^-$ electron-transfer process. The rearrangement lends thermodynamic stability to the monoanion **2**$^-$, manifested as an increased separation of the two one-electron potentials ($\Delta E_{1/2} = E_{1/2}(1) - E_{1/2}(2)$) to +700 mV for **2**, compared to +200 mV for **1a** and the *negative* values previously reported for Cr(arene) complexes. The dianions **1a**$^{2-}$ and **2**$^{2-}$ undergo facile protonation reactions. Whereas the protonation product **1aH**$^-$ is reoxidized with loss of H$^+$ to regenerate **1a**, the protonation product **2aH**$^-$ is a stable 18-electron cyclopentadienyl-substituted compound which, when oxidized, retains its chromium−Cp character. The results are evaluated in light of the redox-induced haptotropic rearrangements previously identified for relevant metal−arene complexes.

Introduction

Given the fundamentally important role of ligand hapticity in determining the structures and reactivities of transition-metal π complexes, electron-transfer-initiated haptotropic rearrangements (often referred to as "ring slippage") are of intense interest in organometallic redox chemistry.[1] Prototypical candidates for inquiry are Cr(η^6-arene)(CO)$_3$ compounds, for which reduced arene hapticities are held to be a key property of intermediates formed in their thermal, photochemical, or electrochemical reactions.[2,3] Cathodic reduction of Cr(η^6-benzene)(CO)$_3$ occurs in a single two-electron process,[4] yielding a dianion, short-lived at room temperature, which has been assigned the η^4 structure [Cr(η^4-benzene)(CO)$_3$]$^{2-}$.[5] The analogous reduced naphthalene (naph) complex was more resilient, and by recording NMR spectra of the dianion [Cr(naph)(CO)$_3$]$^{2-}$, Rieke and co-workers confirmed the occurrence of a haptotropic rearrangement wherein the naphthalene ligand takes on an essentially η^4-bonding mode in the reduced complex.[4c] These dianions are strong nucleophiles and react readily with protons and other electrophiles.[4,5] Similar rearrangements proposed[6] to accompany the reduction of isoelectronic Mn complexes, e.g. [Mn(η^6-arene)(CO)$_3$]$^{+/-}$, have largely been confirmed in a recent paper.[1d] Although the favored structures of reduced chromium arene complexes are more difficult to precisely categorize, calculations show that lower ligand hapticities are clearly necessary to avoid a hypervalent 20-electron metal center.[7] The single two-electron voltammetry waves of these systems reflect the thermodynamic instability of the 19-electron radical intermediate, which causes an "inversion" [8] of the formal potentials, with $E°_2$ (eq 1) being

$$\mathrm{Cr}(\eta^6\text{-arene})(\mathrm{CO})_3 \underset{}{\overset{E°_1}{\rightleftharpoons}} [\mathrm{Cr}(\eta^?\text{-arene})(\mathrm{CO})_3]^- \overset{E°_2}{\rightleftharpoons} [\mathrm{Cr}(\eta^4\text{-arene})(\mathrm{CO})_3]^{2-} \quad (1)$$

positive of $E°_1$. The resulting strong tendency toward disproportionation of the monoanion makes it difficult to obtain structural or even spectroscopic information about the one-

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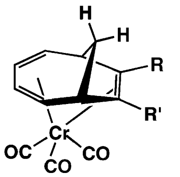
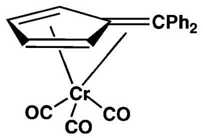
electron intermediate. In fact, ring slippage was assigned as occurring in the first one-electron reduction of Cr(η^6-arene)(CO)$_3$[4] but in the second one-electron reduction of [Mn(η^6-arene)(CO)$_3$]$^+$.[6]

We were interested in investigating the reduction of systems in which the η^6-triolefin ligand is nonaromatic, thereby allowing a different approach to probing the electron count/structure relationship for this general class of molecules. One of the models chosen for this study, Cr(η^4:η^2-C$_9$H$_8$RR′)(CO$_3$) (**1**), has a bicyclo[4.2.1]nonatriene ligand[9,10] in which a Cr(CO)$_3$ moiety is coordinated to an η^4-diene group as well as to a third, nonconjugated η^2-C=C bond. The rigidity of the bicyclic ligand imposes restrictions on possible haptotropic rearrangements. Complexes having R = R′ = Ph (**1a**), R = Ph, R′ = SiMe$_3$ (**1b**), and R = R′ = SiMe$_3$ (**1c**) were investigated by cyclic voltammetry, and **1a** was submitted to a more thorough electrochemical study.



1a R,R' = Ph
1b R = Ph R' = SiMe$_3$
1c R,R' = SiMe$_3$



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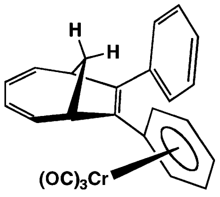

1a'

A second model system was the fulvene complex **2**, in which the third chromium−olefin bond includes the α-carbon. It was expected that the rather weak Cr−C$_\alpha$ bond[11] in **2** might be easily cleaved in a one-electron reduction, and, if so, result in a haptotropic rearrangement based on a *one-electron* transfer. Both η^6-triolefin compounds were judged to be more likely than their η^6-arene counterparts to support thermodynamically accessible one-electron intermediates.

We found that both compounds **1a** and **2** do, indeed, undergo sequential one-electron reductions to the corresponding monoanions and dianions, which were detected by cyclic voltammetry (CV), allowing characterization of electron-transfer kinetics and measurement of the $\Delta E_{1/2}$ values[12] ($\Delta E_{1/2} = E_{1/2}(1) - E_{1/2}(2)$). The monoanions were sufficiently stable to permit their spectral characterization, which supports the assignment of a haptotropic (η^6/η^5) rearrangement in the one-electron reduction of **2** but not in the reduction of the more rigid **1a**.

Experimental Section

All experiments were carried out under an atmosphere of dry nitrogen. Solvents were dried and distilled from appropriate drying agents, and other synthetic aspects followed standard Schlenk techniques. Microanalyses were performed by Robertson Microlit (Madison, NJ). Photolyses were performed through Pyrex glassware spaced approximately 5 cm from a 450 W Hanovia medium-pressure Hg broadband UV lamp. X-band ESR spectra were measured on a Bruker ESP 300E spectrometer, IR spectra were obtained on a Mattson FTIR spectrometer operating at 4 cm^{-1} resolution, and NMR spectra were recorded on a Varian VXR-400S (400 MHz) or Varian Unity Inova (500 MHz) spectrometer. Alkynes were purchased from GFS Chemicals, and complexes **1a**[9,10] **1b**,[9,10] **1c**,[13] and **2**[14] were prepared by the literature methods.

Electrochemistry. A standard three-electrode configuration was employed for voltammetry and electrolysis experiments. A PARC 273A potentiostat was used in conjunction with homemade software linking the potentiostat to a personal computer. All electrochemical experiments were conducted inside a Vacuum Atmospheres drybox under nitrogen. The drybox was outfitted with a cooling bath capable of controlling solution temperatures to better than 1 °C. Oxygen levels in the drybox were typically 1−5 ppm during the course of an experiment. THF was first distilled from potassium under Schlenk conditions and then from a purple potassium−benzophenone mixture under bulb-to-bulb vacuum conditions. The collection bulb was transferred to and opened in the drybox. Glassware was heated overnight at 120 °C and then transferred directly to the drybox antechamber.

All potentials given in this paper are referenced to the ferrocene/ferrocenium reference couple, as recommended elsewhere.[15] The experimental reference electrode at the University of Vermont was a homemade AgCl-coated Ag wire. At Rutgers, Ag/Ag$^+$ in acetonitrile performed this function. In both laboratories, at an appropriate time in the experiment, a small amount of ferrocene was added to the analyte solution and the ferrocene/ferrocenium potential was recorded. To convert the potentials listed in this paper to an SCE reference potential, 0.55 V must be added. A Pt wire was used as the auxiliary electrode, and the supporting electrolyte was 0.1 M [NBu$_4$][PF$_6$] (prepared by metathesis of K[PF$_6$] and [NBu$_4$]I, recrystallized twice from 95% EtOH, and vacuum-dried).

Glassy-carbon (GC) electrodes gave the most consistent behavior for the compounds studied, which were prone to exhibit electrode history effects on Pt or Au electrodes, especially when scanning through the second reduction waves. These effects apparently arise from a tendency of the product dianions to adsorb onto the electrode. GC electrodes were cleaned frequently using alumina or diamond polishing compounds of 10−0.25 μm diameter. Bulk electrolyses were carried out using a platinum-mesh cylindrical working electrode separated from the auxiliary compartment by a fine frit and required 20−30 min for completion. Samples of the electrolysis solutions were taken by syringe for IR and ESR analysis. Digital simulations were performed on background-subtracted CV scans using DIGISIM (Bioanalytical Systems). Analyte concentrations were generally about 1 mM or less for CV experiments and 2−6 mM for bulk electrolysis experiments. Concentration changes did not appear to have an effect on the shapes or positions of CV curves, indicating that second-order processes, such as a homogeneous disproportionation reaction, were not important.[16] This finding was particularly important in the case of **1a**, which has a relatively small $\Delta E_{1/2}$ value. The interested reader can find a good treatment of homogeneous effects on electrochemical responses in a review by

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(7) Calculations have shown that a number of different hapticities, from η^1 to η^6, are possible under different conditions. See ref 3 for leading references.

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(16) Except for the expected proportional change between current and concentration, no change in CV behavior was observed for concentrations of **1a** ranging from 0.3 to 1.2 mM. There was, however, an effect on the height and breadth of the second wave, in which **1a**$^-$ is reduced to **1a**$^{2-}$, in differential pulse voltammograms. This is attributed to the adsorption of the dianion on the electrode, which has the effect of reducing the current height and increasing the peak width. The fact that a similar effect is not seen in CV curves arises from the fact that the CV time scale is much faster, thereby minimizing the amount of adsorbed analyte.

Table 1. Electrochemical Potentials Measured for Cr Compounds in THF/0.1 M [NBu_4][PF_6] in V vs Ferrocene/Ferrocenium

compd	temp (K)	$E°_1$	$E°_2$	comments
1a	283	−2.00	−2.20	quasi-Nernstian waves
1a′	room temp	−2.63		irrev; $E_{p,c}$ at 0.2 V s^{-1} given
1b	room temp	−2.16	−2.34	both chemically rev
1c	room temp	−2.3		irrev; second redn not obsd
2	268	−1.40	−2.10	second wave chemically irrev at low scan rates

Evans.[17] Diagnostic criteria for electrochemical mechanisms relied on current and potential measurements over a range of scan rates, using the procedures described elsewhere.[18]

Results

Bicyclo[4.2.1] Complexes (1a−c). No cathodic processes were observed for the free ligand itself, 7,8-diphenylbicyclo-[4.2.1]nona-2,4,7-triene, out to the background at −3.2 V. The bicyclic Cr(CO)$_3$ complexes all exhibited at least a single one-electron reduction. Compounds **1b**,**c** were investigated only by cyclic voltammetry, for the main purpose of comparison with the more thoroughly studied bis(phenyl) derivative **1a**. As the two phenyl substituents of **1a** are replaced by trimethylsilyl groups (one in **1b**, two in **1c**), the first reduction of the Cr complexes shifts more negative by about 150 mV for each substitution (see Table 1), in keeping with the comparatively stronger donor character of the SiMe$_3$ group. Most importantly, two chemically reversible reductions are seen as long as there is at least one phenyl substituent (**1a**,**b**), but only an irreversible one-electron wave is seen for **1c**. As shown below, this finding was relevant to our interpretation of the cathodic properties of **1a**.

An important control experiment involved checking the voltammetric behavior of the η^6-arene complex **1a′**, a known[9] isomer of **1a** in which the Cr(CO)$_3$ group has thermally migrated to an arene. This isomer displayed only a single irreversible reduction at a potential considerably negative of those observed for the first and second reductions of **1a** (Table 1). There was no evidence, therefore, that reduction of **1a** causes migration of the metal to one of the arenes on either the voltammetric or electrosynthetic time scale.

Cr(η^4:η^2-$C_9H_8Ph_2$)(CO)$_3$ (1a). (a) Voltammetry. Compound **1a** displays two well-behaved one-electron reductions at $E_{1/2}(1) = -2.00$ V and $E_{1/2}(2) = -2.20$ V, with $\Delta E_{1/2} = 200$ mV (Figure 1a). Cyclic voltammetry over scan rates of 0.1−1 V s^{-1} gave a current function ($i_{p,c}$/(scan rate)$^{1/2}$) that was constant to within 10%, showing that both waves were diffusion-controlled. The observed CV peak separations of the first wave, ca. 90 mV at 0.1 V s^{-1}, were similar to those measured for the ferrocene/ferrocenium couple under similar conditions, implying that the increase in ΔE_p over the theoretical value of 60 mV was due to uncompensated ohmic loss. In the time scale of our measurements, the process **1a** $\rightleftharpoons$ **1a**$^-$ can be considered to be quasi-Nernstian: i.e., exhibiting fast charge transfer. The charge-transfer kinetic behavior of the second one-electron process, which exhibits somewhat larger ΔE_p values (e.g., 120 mV at 0.1 V s^{-1}), is less well defined. Although the larger ΔE_p values could be interpreted as evidence of a slower charge transfer for **1a**$^-$ $\rightleftharpoons$ **1a**$^{2-}$, other voltammetric data raise doubts about such an interpretation. Specifically, ΔE_p for the second wave increases slightly with replicate scans unless the electrode surface is repolished between scans. This "electrode history" makes us hesitant to describe the couple **1a**$^-$ $\rightleftharpoons$ **1a**$^{2-}$ as anything but a quasi-reversible couple. Weak adsorption of the dianion **1a**$^{2-}$, resulting in a partially passivating film, is likely to be responsible for the increases in ΔE_p. This notion is boosted by differential pulse voltammetry (DPV) data. Whereas DPV scans of **1a** at a concentration of 0.6 mM displayed two cathodic peaks of equal height, the second wave was considerably smaller and broader when the analyte concentration was increased to 1.2 mM. The dominance of the adsorption effect in these scans is ascribed to the longer scan time (and, thus, deposition time) for DPV[19] compared to cyclic voltammetry.

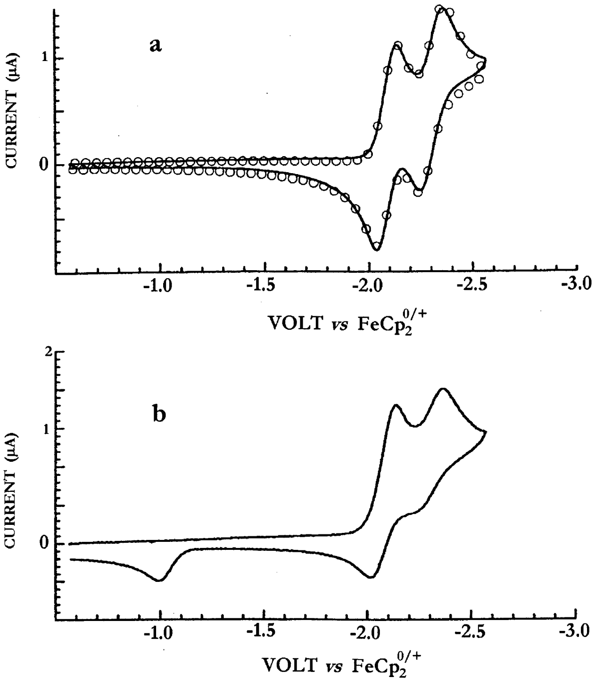

Figure 1. (a) CV scans of 0.86 mM **1a** in THF/0.1 M[NBu_4][PF_6] at 283 K, at a scan rate of 0.2 V s^{-1}, with digital simulation of the EE mechanism given as rings (b) CV scans of the solution in (a) after addition of 1 equiv of trimethylphenol.

In terms of chemical reversibility, reduced temperatures or higher scan rates were necessary to completely outrun the follow-up chemical reaction of **1a**$^{2-}$. For example, at room temperature and a scan rate of 0.2 V s^{-1}, reversing the scan after formation of the dianion shows a small anodic product wave (shown to be reversible by multiple scans) at $E_{1/2} = -1.0$ V. This is barely observable in Figure 1a. The fact that this follow-up product increased markedly when a proton donor was added to the solution (Figure 1b) argues that it arises from the protonation of **1a**$^{2-}$.[20] It was also shown to be the major product following two-electron bulk electrolysis of **1a** (vide infra). Assuming a single-step protonation of the dianion,[21] the overall cathodic mechanism of **1a** is therefore the EEC$_{H^+}$ process of eq 2.

$$\mathbf{1a} \xrightleftharpoons{-2.00\text{ V}} \mathbf{1a}^{-} \xrightleftharpoons{-2.20\text{ V}} \mathbf{1a}^{2-} \xrightleftharpoons{\text{H}^+\text{ (slow)}} \mathbf{1aH}^{-}$$

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Table 2. Carbonyl-Region IR Bands for Relevant Compounds and Ions

compd	medium	ν_{CO} (cm^{-1})	av $\Delta\nu_{CO}$ (cm^{-1})[a]	ref
1a	THF	1967, 1895, 1867	n.a.	this work
1a$^-$	THF	1888, 1805, 1767	−90	this work
2	THF	1985, 1906[b]	n.a.	this work
2$^-$	THF	1888, 1793, 1773	−114	this work
2H$^-$	THF	1888, 1781, 1762	not measd	this work
$[Cr(C_5H_5)(CO)_3]Na$	THF	1897, 1793, 1743	−123	*c*
$[Cr(C_5H_5)(CO)_3][Na(hmpa)]$[d]		1895, 1778[b]	−117	*c*
$Cr(C_5H_5)(CO)_3$	toluene	2013, 1895[b]	n.a.	*e*
$Cr(C_5Ph_5)(CO)_3$	THF	2005, 1897[b]	n.a.	*f*
$[Cr(C_5Ph_5)(CO)_3][PPN]$[g]	THF	1895, 1792[b]	−108	*f*
$Fe(C_5Ph_5)(CO)_2$	benzene	1990, 1921	n.a.	*h*
$[Fe(C_5Ph_5)(CO)_2][Na(hmpa)]$[d]		1872, 1807	−116	*h*

[a] The average of the spectral shift for ν_{CO} bands that accompanies the one-electron reduction. [b] For the purpose of calculating an average spectral shift, the degenerate ν_{asym} band is counted twice. [c] Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521. [d] hmpa = hexamethylphosphoramide. [e] McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643. [f] Hoobler, R. J.; Hutton, M. A.; Dillard, M. M.; Castellani, M. P.; Rheingold, A. L.; Rieger, A. L.; Rieger, P. H.; Richards, T. C.; Geiger, W. E. *Organometallics* **1993**, *12*, 116. [g] PPN = bis(triphenylphosphine)nitrogen(1+). [h] Kuksis, I.; Baird, M. C. *Organometallics* **1996**, *15*, 4755.

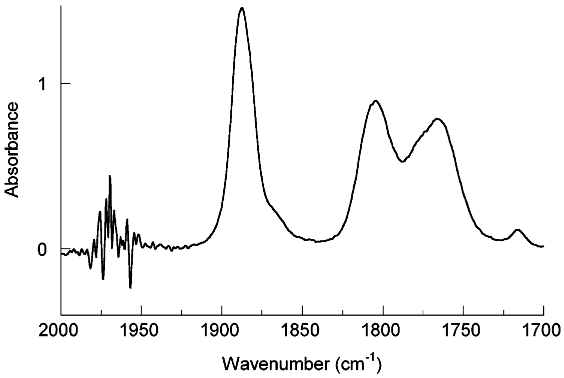

Figure 2. IR spectrum of **1a**$^-$ in THF following bulk electrolysis of 1.9 mM **1**. The residual contribution from unelectrolyzed **1** has been subtracted.

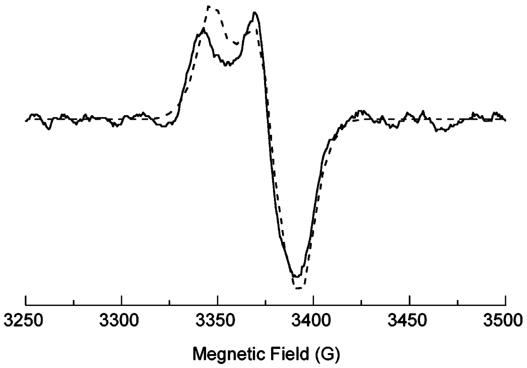

Figure 3. Experimental (solid line) and simulated (dashed line) ESR spectra of **1a**$^-$ in frozen THF at 135 K using $g_1 = 2.024$, $g_2 = 2.004$, and $g_3 = 1.996$.

Digital simulations of CVs at different scan rates (Figure 1a) are consistent with this model.

(b) Electrolysis of 1a and Spectral Characterization of 1a$^-$. Bulk electrolysis to the monoanion was carried out at 268 K on a 2 mM solution of **1a** with $E_{appl} = -2.1$ V. In two different experiments, the electrolysis was interrupted after passage of either 0.7 or 0.9 F/equiv and linear scan voltammograms (LSV) were recorded which showed that either 75% or 90%, respectively, of **1a** had been converted to the monoanion **1a**$^-$, confirming the one-electron stoichiometry of the reaction and showing no evidence of the protonation product. The IR spectra of samples taken from these solutions showed three dominant bands in the metal−carbonyl range at 1888, 1805, and 1767 cm^{-1}, along with residual bands for the unelectrolyzed starting material at 1967, 1895, and 1867 cm^{-1} (IR results are collected in Table 2). With the latter three peaks for **1a** subtracted from the raw spectrum[22] (as a 10% contribution), Figure 2 displays the carbonyl-range IR absorption of the monoanion **1a**$^-$. The average shift in ν_{CO} was −90 cm^{-1} on going from **1a** to **1a**$^-$. Treatment of the electrolysis solution with 1 equiv of cobaltocenium ion as an oxidizing agent gave quantitative regeneration of neutral **1a**, as shown by both LSV and IR data. Taken together, these data confirm that the radical anion **1a**$^-$ is persistent.

The ESR spectrum of **1a**$^-$ was also recorded. A frozen solution at 135 K gave a nearly axial spectrum, with a simulation allowing an estimate of the small difference in the pseudo-$g_\perp$ values ($g_1 = 2.025$, $g_2 = 2.004$, $g_3 = 1.996$) (Figure 3).

Reduction of **1a** to the dianion was achieved by bulk electrolysis at $E_{appl} = -2.8$ V ($T = 283$ K). After about 85% electrolysis (based on LSV scans), 1.5 F/equiv had been passed, roughly consistent with an overall two-electron process. The major electrolysis product had a reversible oxidation at the same potential ($E_{1/2} = -1.0$ V), as seen for the follow-up product from the second reduction in slow scan CVs.[23] When this fully reduced solution was back-electrolyzed at $E_{appl} = -0.55$ V, 1.2 F/equiv of charge was released and the starting material **1a** was regenerated at about 60% of its initial concentration. These results are consistent with the sequence of eq 2, wherein slow protonation of **1a**$^{2-}$ gives **1aH**$^-$, and reoxidation of **1aH**$^-$ to **1aH** is followed by proton loss, resulting in regeneration of **1a**. We assume that protonation occurs at the butadiene-like fragment of the ligand. Figure SM1 (Supporting Information) gives representative CV figures from the electrolysis experiments.

Cr(η^6-$C_5H_4CPh_2$) (2). The fulvene complex **2** also displays two one-electron reductions (Figure 4) having a large potential separation, at $E_{1/2}(1) = -1.40$ V and $E_{1/2}(2) = -2.10$ V, with

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(21) No change in reversibility was apparent in the first reduction wave when a phenol was added, implying that the monoanion **1a**$^-$ is not readily protonated under these conditions.

(22) Because IR signal to noise is poor in THF in the spectral range of ca. 1980−1960 cm^{-1} owing to solvent absorption, the spectrum of **1a** was best measured in a more concentrated (6 mM) solution. In the less concentrated electrolysis solutions, only the two lower energy bands at 1895 and 1867 cm^{-1} were monitored for **1a**.

(23) The fact that the peak current of the second wave ($E_{p,a} = -0.2$ V, scan rate 0.2 V s^{-1}) arising from follow-up product(s) was equal to that of the follow-up product at $E_{1/2} = -1.0$ V suggests that they arise from sequential oxidation of the same species, namely protonated **1a**$^{2-}$.

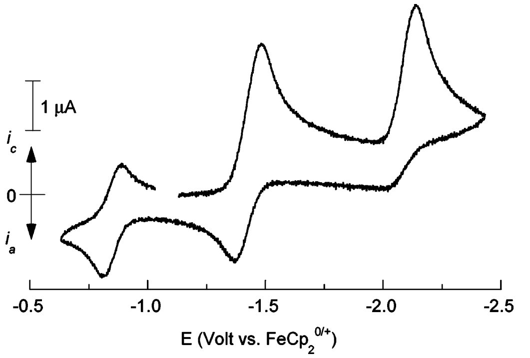
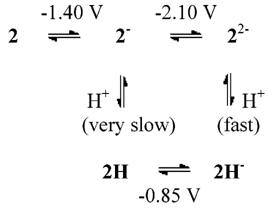


Figure 4. CV scan of 0.06 mM **2** in THF/[NBu$_4$][PF$_6$] at 268 K, at a scan rate of 0.2 V s^{-1}.

Scheme 1



$\Delta E_{1/2}$ = 700 mV. The first reduction follows Nernstian diagnostics[24] over a scan rate range of 0.1−4 V s^{-1}, demonstrating that the electron-transfer reaction **2**/**2**$^-$ is fast and that **2**$^-$ is stable. The half-life of the dianion **2**$^{2-}$ is only about 0.3 s at 268 K, considerably shorter than that of **1a**$^{2-}$, which is estimated as about 10 s at this temperature.[25] A reversible product wave ($E_{1/2} = -0.85$ V) was again observed arising from a follow-up reaction of the dianion. That this reaction was a protonation was demonstrated by the fact that formation of the product was complete, even at fast CV scan rates, if 1 equiv of phenol was added to the solution. The reversibility of the first wave was unaffected by addition of up to 140 equiv of phenol. The reduction of **2** was modeled successfully by digital simulations as an EEC process with a first-order chemical reaction having a rate constant of 1.5 s^{-1} (see Figure SM2 in the Supporting Information). There are obvious parallels in the cathodic mechanisms of **2** and **1a**, which also undergoes an EEC$_{\mathrm{H+}}$ process. On the basis of bulk electrolysis data (vide infra) in which a small amount of the protonation product was detected after electrolysis of **2** to **2**$^-$, it appears that the monoanion may react with weak acids, but at a rate that is orders of magnitude slower than that of the dianion (see Scheme 1).

(a) Electrolysis of 2 and Spectral Characterization of 2$^-$. The one-electron electrolysis of **2** to **2**$^-$ proceeded without complication at 268 K ($E_{\mathrm{appl}} = -1.77$ V, 0.96 F/equiv) as the solution went through a nondescript color change from dark brown to a lighter brown. LSV scans showed that the yield of **2**$^-$ was virtually quantitative. A very small amount (<5%) of the secondary product was formed, as shown by a very minor wave at −0.85 V. Samples of this solution were taken for ESR and IR spectroscopy.

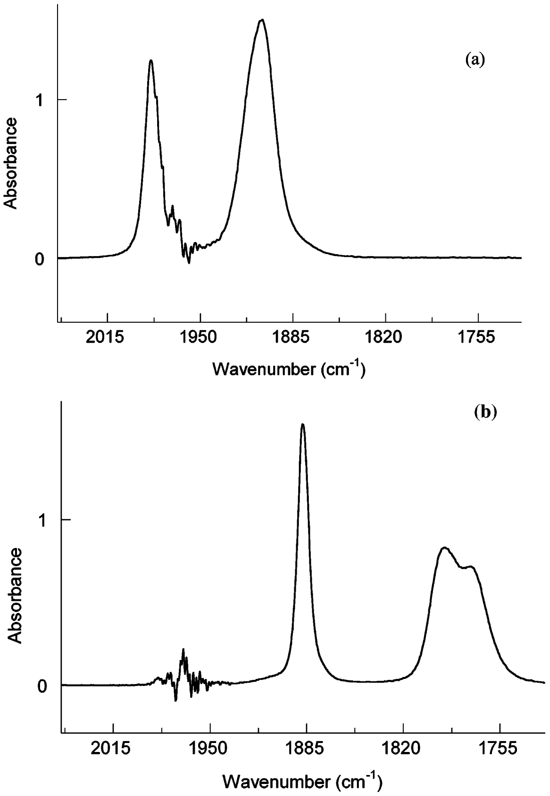


Figure 5. IR spectra of (a) 1.86 mM **2** and (b) **2**$^-$ produced by bulk electrolysis in THF/[NBu$_4$][PF$_6$] at $E_{\mathrm{appl}} = -1.7$ V.

As shown in Figure 5, the carbonyl region of the IR spectrum went cleanly from a pair of bands for **2** (ν_{sym} 1985 cm^{-1}, ν_{asym} 1906 cm^{-1}) to three bands for **2**$^-$ (1888, 1793, 1773 cm^{-1}), a weighted average shift of −114 cm^{-1}. The spectrum of **2**$^-$ did not change when phenol was added, but complete regeneration of neutral **2** occurred with addition of 1 equiv of ferrocenium ion as oxidant.

Although a shift of this magnitude in ν_{CO} frequencies is generally viewed as indicating a one-unit lowering of the metal oxidation state,[26] the ESR spectra of **2**$^-$ showed that its SOMO has virtually no metal character. The frozen spectrum at 135 K consisted of a single intense and symmetrical line at $g = 2.005$ with about a 9 G peak-to-peak width. When this solution was melted, a narrow-line spectrum rich in hyperfine splittings and diagnostic of an organic radical was obtained (Figure 6).[27] The general pattern of lines in the fluid spectrum is reminiscent of that reported for the free ligand radical $C_5H_4CPh_2^{\bullet}$,[28] but lacking the same degree of overall spread in signal, from the lowest field to the highest field features. A number of attempts were made to simulate the spectrum of **2**$^-$, which in principle contains 225 overlapped lines, but a perfect match was not obtained.

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[24] ΔE_{p} values for **2**/**2**$^-$ were within 10 mV of the values measured for the ferrocene/ferrocenium couple under the same conditions, which included: glassy-carbon electrode, room temperature, concentration of analyte 0.5 mM. Ohmic errors are essentially the same under these conditions owing to the virtually identical diffusion coefficients for ferrocene and for **2** (measured by chronoamperometry as 1.4 × 10^{-5} and 1.3 × 10^{-5} cm^2 s^{-1}, respectively). Representative values for ΔE_{p}, e.g. 115 mV at 0.2 V s^{-1} and 250 mV at 2 V s^{-1}, manifest the comparatively high resistivity of THF electrolyte solutions. For suggestions on how to minimize this experimental difficulty, see: LeSuer, R. J.; Buttolph, C.; Geiger, W. E. *Anal. Chem.* **2004**, *76*, 6395.

[25] The half-life of **2**$^{2-}$ was measured directly from the chemical reversibility of the **2**$^-$/**2**$^{2-}$ couple at scan rates of 0.2−2.0 V s^{-1}. That of **1a**$^{2-}$ was too slow to accurately measure on the CV time scale and was estimated from the lowest scan rate (0.1 V s^{-1}) at which some evidence of the follow-up reaction product was observed at −1.0 V. A reaction that is first order in dianion was assumed.

[26] (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; pp 291−295. (b) Willner, H.; Aubke, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2403. (c) Goldman, A. S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1996**, *118*, 12159.

[27] Careful inspection of the spectrum near 3355 G ($g = 2.016$) shows that a small secondary signal grows slowly over time and at higher temperatures. This is ascribed to a minor Cr-based decomposition product.

[28] Camaggi, C. M.; Perkins, M. J.; Ward, P. *J. Chem. Soc.* **1971**, 2416.

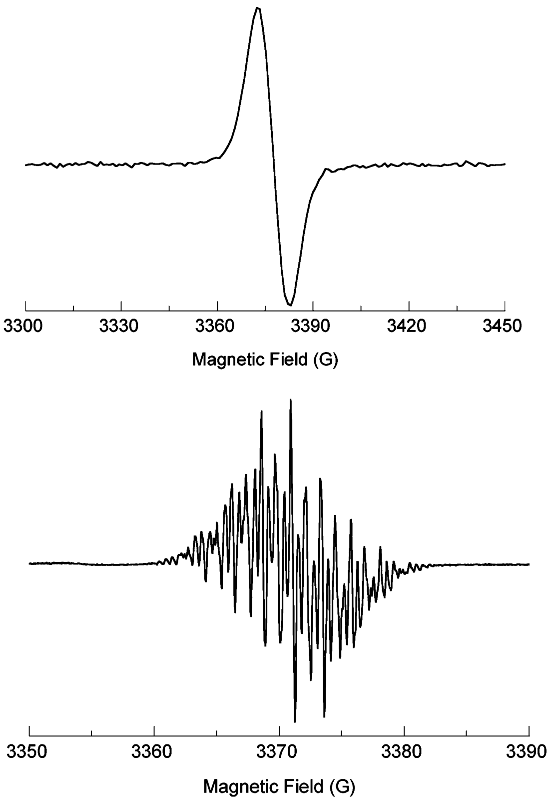


Figure 6. ESR spectra of $\mathbf{2}^-$ obtained after one-electron electrolytic reduction of **2**, at sample temperatures of 135 K (top) and 225 K (bottom).

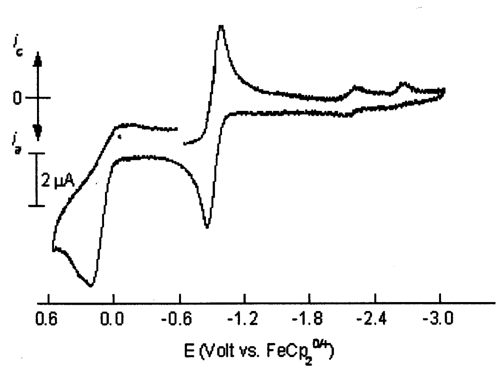


Figure 7. CV scan after two-electron reduction of **2** ($E_{\mathrm{appl}} = -2.2$ V) in THF/$[NBu_4][PF_6]$ at room temperature, at a scan rate of 0.2 V s^{-1}.

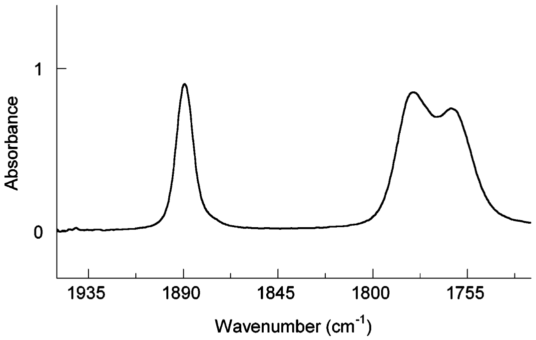
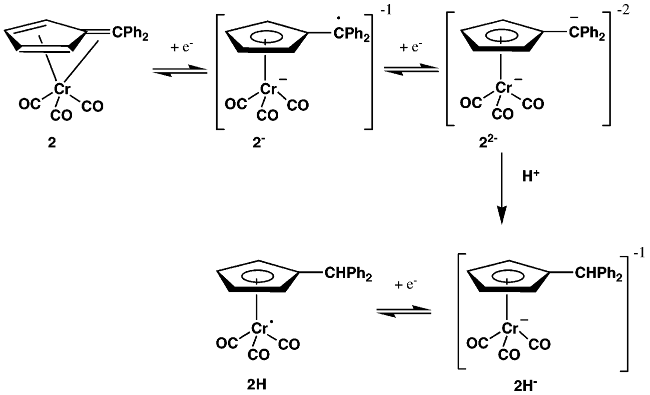


Figure 8. IR spectrum of the follow-up product produced by electrolysis of 1.86 mM **2** in THF/$[NBu_4][PF_6]$ at $E_{\mathrm{appl}} = -2.2$ V.

Scheme 2



However, reasonably good fits were obtained with proton hyperfine splittings that were about 90% as large in $\mathbf{2}^-$ as in the carbo radical $C_5H_4CPh_2^{\bullet}$.[29] The SOMO of $\mathbf{2}^-$ is therefore assigned as largely localized on the diphenylfulvenyl ligand, with the majority of the spin density being on the carbon that is α to the five-membered ring.

We were particularly concerned that the fluid spectrum might be arising from a small amount of free ligand radical produced through a decomposition of $\mathbf{2}^-$. Several facts argue against this. First, the bulk electrolysis experiment showed that the monoanion $\mathbf{2}^-$ and the neutral compound **2** could be quantitatively generated and regenerated, one from the other, within the accuracy of our measurements. Second, the ESR signal was very strong, suggesting that it did not arise from a minor product. Third, if the anion $\mathbf{2}^-$ was *not* responsible for the narrow-line signal, there should be a major superimposed metal-based signal of significantly different g value, at least in the frozen spectrum. This was not observed. Fourth, the observed fluid spectrum is not *exactly* the same as that reported[28] (and reproduced in our laboratory) for $C_5H_4CPh_2^{\bullet}$. Furthermore, as shown in the Discussion, the IR and ESR results are not incompatible, since the IR shifts are *charge* sensitive and the ESR hyperfine splittings are *spin* sensitive.

(b) Electrochemical and IR Characterization of $\mathbf{2H}^-$. If the electrolyses were carried out at $E_{\mathrm{appl}} = -2.2$ V, a potential sufficient to reduce **2** to the dianion, 1.9 F/ equiv, was taken up and the resulting yellow solution exhibited two pairs of product waves. The major pair was composed of a reversible oxidation at $E_{1/2} = -0.85$ V and an irreversible oxidation at $E_{\mathrm{p,a}} = 0.20$ V. The minor pair ($E_{1/2} = -2.14$ V and $E_{\mathrm{p,c}} = -2.6$ V; see Figure 7), responsible for only about 10% of the product distribution, arises from the free ligand, diphenylfulvene, which increased the sizes of the minor pair when added to the solution.

The major long-term product is $\mathbf{2H}^-$, formed by reaction of the dianion $\mathbf{2}^{2-}$ with an unknown proton donor, possibly the supporting electrolyte cation, $[NBu_4]^+$, or an adventitious agent. This assignment is based in part on the $E_{1/2}$ value of $\mathbf{2H}^-$ (−0.85 V), which was identical with that of the product formed by deliberate protonation of $\mathbf{2}^{2-}$ with phenol (see above). The IR spectrum of this solution showed three strong lines at 1888, 1781, and 1762 cm^{-1} (Figure 8). Exhaustive reoxidation of $\mathbf{2H}^-$ by one electron did not cause proton loss from $\mathbf{2H}^-$, as it had from $\mathbf{1aH}^-$. Rather, a persistent product, **2H**, was formed.

Taken together, these facts allow us to identify $\mathbf{2H}^-$ as being the monosubstituted cyclopentadienyl complex shown in Scheme 2. The observed $E_{1/2}$ value of −0.85 V for the couple $\mathbf{2H}/\mathbf{2H}^-$ compares favorably with the value of −0.69 V reported for the pentaphenylcyclopentadienyl analogue $[Cr(C_5Ph_5)(CO)_3]^{0/-}$.[30a] The observed chemically reversible oxidation to **2H** is in concert

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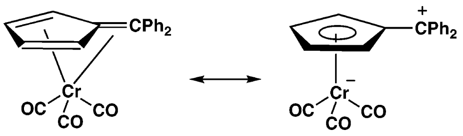
[29] For one of these simulations, see Figure SM2 in the Supporting Information.

with the known stability of the 17-electron compounds $Cr(C_5R_5)(CO)_3$.[30] The IR bands of **2H**$^-$ compare well with those of $[Cr(C_5H_5)(CO)_3]^-$ (see Table 2).

Discussion

We first address the reduction of **2**, for which a one-electron-induced haptotropic rearrangement explains the body of electrochemical and spectral evidence. Scheme 2 describes our conclusions in structural form, with the key step being the η^6 to η^5 rearrangement of the fulvene ring, wherein the anion **2**$^-$ adopts the character of an α-radical-substituted cyclopentadienyl complex. This accounts for the two important spectral features of **2**$^-$, namely the highly ligand-based SOMO (based on ESR spectra) and the strong downfield shift in ν_{CO} (IR spectra). It is noteworthy that the IR shift (-114 cm^{-1}) is the same as those reported for other half-sandwich metal carbonyls measured both as neutral compounds and as monoanions in THF (average shift of -115 cm^{-1}; see Table 2). This concordance is indicative of a full negative charge on the Cr(cyclopentadienyl) tricarbonyl moiety in **2**$^-$. A further inference is that neutral **2** has a rather small contribution from the zwitterionic resonance structure



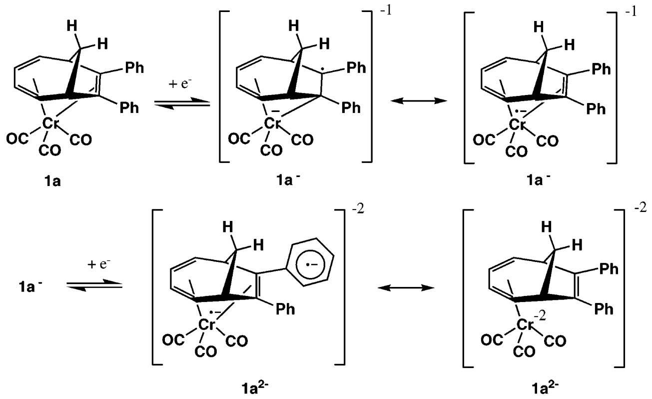
sometimes used to describe the electronic structures of metal-fulvene compounds.

The structural rearrangement in the reduction of **2** to **2**$^-$ may, in principle, be either concerted with the electron-transfer step or after it.[31] In the present case there is no evidence for a nonrearranged isomer of **2**$^-$, at least under these (CV) experiment times, and we favor the model of a structural rearrangement that is concerted with electron transfer. The fast charge transfer is rationalized by the expected facility of making and breaking the rather weak bond[32] of the metal to the α-carbon atom. To reiterate, however, a stepwise (EC-type) process cannot be ruled out.

The reduction of **2**$^-$ to the dianion is viewed as the reduction of a carbo radical, bonded to an 18-electron cyclopentadienylchromium tricarbonyl anion, to the corresponding (and easily protonated) carbanion **2**$^{2-}$. The protonation product **2H**$^-$ is then a simple 18-electron complex having a $CHPh_2$-substituted Cp ring. As such, it is expected to be easily and reversibly oxidized to the corresponding 17e radical **2H**, as are other anions of this type.[30] All of the electrochemical and spectroscopic data appear to be consistent with Scheme 2.

Turning to **1a**, we first address whether its reductions should be viewed as "phenyl-based" or metal-based. Certainly the fact that an *absence* of phenyl groups in the bicyclic ligand makes the reduction strongly negative and chemically irreversible (see **1c**) suggests that the phenyl group plays an important role in the one-electron reduction. However, the ν_{CO} shift of -90 cm^{-1} for **1a**/**1a**$^-$ is almost as large as expected for a metal-based reduction. The ESR spectrum of **1a**$^-$ also sends mixed signals, in that it clearly indicates some metal character in the SOMO, but it has a very small spread of *g* values. Furthermore, $E_{1/2}(1)$, at -2.00 V, is quite positive of that expected for a substituted arene (cf. -2.65 V vs ferrocene for $Cr(toluene)(CO)_3$).[4a,33]

Scheme 3



The experimental findings are consistent with Scheme 3, in which the original one-electron reduction is seen as involving the phenylethylene group. Analogous reductions are well-known for stilbene and a wide range of other diphenylethylene derivatives.[34] Resonance forms for **1a**$^-$ would include a phenyl-based radical anion (not shown in the scheme) having an 18-electron neutral metal, a 19-electron metal center,[1a,b,35,36] (third entry in Scheme 3), and an ethynyl-type radical with a negatively charged 18-electron metal (second entry). The metal−ligand hapticity is η^6 in all structural forms except in the ethynyl radical, for which η^5 hapticity is likely. The electronic structure of the dianion **1a**$^{2-}$ likely involves an extension of this reasoning involving charge on the phenyl rings, the C−C moiety, and the metal center. Although there may be some measure of structure change involving the Cr−olefin bond in the redox reactions, we find no evidence suggesting a formal cleavage of that bond to give an η^4 bicyclic ligand.

There is a striking difference in the $\Delta E_{1/2}$ values of **1a** (200 mV) and **2** (700 mV). The unexpectedly large value for **2** is interpreted as originating in the facile haptotropic rearrangement in **2**/**2**$^-$ that lowers the free energy of the monoanion and results in a positive shift of $E_{1/2}(1)$. We have previously noted that thermodynamic factors are more difficult to interpret than are kinetic factors when considering redox-linked haptotropic rearrangements.[1c] With that counsel in mind, we comment on the possible relevance of the present results to the question of η^6/η^4 rearrangements in one-step, two-electron reductions of Cr(arene) complexes.[4] There is certainly a dramatic difference between the $\Delta E_{1/2}$ value of **2** (+700 mV) and that of Cr(η^6-

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[30] (a) Hoobler, R. J.; Hutton, M. A.; Dillard, M. M.; Castellani, M. P.; Rheingold, A. L.; Rieger, A. L.; Rieger, P. H.; Richards, T. C.; Geiger, W. E. *Organometallics* **1993**, *12*, 116. (b) Hoff, C. D. *Coord. Chem. Rev.* **2000**, *206−207*, 451.

[31] This comment refers to the now classic arguments over single-step vs double-step electron-transfer processes when a significant structural change occurs in the transition between Ox and Red. For an introduction to this problem see: Evans, D. H.; O'Connell, K. M. In *Electoanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1986; Vol. 14, pp 113−207.

[32] The Cr to exo carbon bond length is 2.548 Å in neutral **2**. See: (a) Andrianov, V. G.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1977**, *18*, 318. (b) Watts, W. E. *J. Organomet. Chem.* **1981**, *220*, 165.

[33] The potential reported in ref 4a was -1.66 V vs SCE. Conversion to ferrocene/ferrocenium requires subtraction of 0.40 V for $CH_3CN/[NEt_4][ClO_4]$. The potential for $[Cr(naph)(CO)_3]^{0/2-}$ is -2.06 V vs ferrocene/ferrocenium using this conversion.

[34] For more recent work on the reductions of multiphenylated ethylenes, as well as leading references to earlier work, see: (a) Geraldo, M. D.; Montenegro, M. I.; Slevin, L.; Pletcher, D. *J. Phys. Chem. B* **2001**, *105*, 3182. (b) Muzyka, J. L.; Fox, M. A. *J. Org. Chem.* **1991**, *56*, 4550.

[35] Tyler, D. R. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; pp 338−364. This monograph is Volume 22 of the *Journal of Organometallic Chemistry Library*.

[36] For an excellent account of a 19e system ($[CoCp_2]^-$) having unexpectedly large metal−ligand delocalization, see: Braden, D. A.; Tyler, D. R. *J. Am. Chem. Soc.* **1998**, *120*, 942.

arene)(CO)$_3$ (for which *negative* values of $\Delta E_{1/2}$ are required).[2,37] However, in both systems the major structural change is assigned as occurring in the *first* one-electron step. In the case of [Cr(η^4−naphthalene)(CO)$_3$]$^-$, the monoanion was thereby seen as having a 17-electron metal center.[2] Direct experimental evidence of the one-electron intermediate in that case is, of course, difficult to obtain owing to its strongly favored disproportionation. A recent DFT study[3] of arene hapticity in singlet- or triplet-state Cr(benzene)(CO)$_n$ ($n = 1-5$) complexes showed that a number of lower hapticity structures are possible, at least in even-electron systems. Analogous computational studies on the nominally Cr(1−) and Cr(2−) reduced Cr(η-arene)(CO)$_3$ complexes would be welcome.

Conclusions

Cr(η^4:η^2-$C_9H_8Ph_2$)(CO)$_3$ (**1a**) undergoes two rather facile one-electron reductions in which the negative charges are metal−ligand delocalized and explicable in terms of no more than slight structural changes accompanying the electron-transfer processes.

The apparent lack of an η^6/η^4 haptotropic rearrangement originates in the rigidity of the bicyclic triolefin ligand and in the ability of the phenyl ethylene moiety to accept negative charges, obviating the requirement of a 20-electron metal in the dianion. The fulvene complex **2** also undergoes two one-electron reductions. In this case a fast and reversible η^6/η^5 haptotropic rearrangement is shown to be coupled to the **2**/**2**$^-$ couple, facilitated by the formation of a carbo radical substituted cyclopentadienyl structure in the monoanion. The fact that the hapticity change is coupled to the first reduction leads to a greatly increased $\Delta E_{1/2}$ value for this compound compared to the values for other Cr(η^6-triolefin)(CO)$_3$ compounds. These results should prove to be relevant to the broader question of the circumstances under which Cr(triolefin)-containing complexes may undergo haptotropic rearrangements. The dianions of both **1a** and **2** undergo facile protonation reactions.

Acknowledgment. We are grateful to the National Science Foundation for support of this work both at Vermont (Grant Nos. NSF-CHE 0092702 and CHE 0411703) and at Rutgers (Grant No. MRI 01106066).

Supporting Information Available: Two figures showing (i) voltammograms after the bulk cathodic reduction of **1a** and (ii) CV digital simulation of the EEC mechanism for reduction of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) This requirement is clearest in the case of Cr(naphthalene)(CO)$_3$, which has the voltammetric behavior of a quasi-Nernstian two-electron process.[4] $\Delta E°$ is likely to be ca. ≤ -120 mV in such a case. See: Polcyn, D. S.; Shain, I. *Anal. Chem.* **1966**, *38*, 370.