In-Situ IR Spectroelectrochemistry Study of One-Electron Oxidations of Bis(cyclopentadienyl) Molybdenum(II)−Alkyne or −Alkene Compounds

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Anodic oxidations of the bis-cyclopentadienyl alkyne compound $MoCp_2(\eta^2\text{-}C_2Ph_2)$, **1**, and three metal−alkene analogues $MCp_2(\eta^2\text{-}C_2H_2\ \textit{trans}\text{-}R_2)$ (M = Mo, R = CO_2Me, **2**; M = Mo, R = H, **3**; M = W, R = H, **4**) have been studied by a combination of electrochemistry and in-situ IR spectroelectrochemistry. The primary redox process for all compounds is a reversible one-electron oxidation at very facile potentials (from −0.30 V vs $FeCp_2^{0/+}$ for **2** to −0.80 V for **4**). The ν_{CC} alkyne stretch in the IR spectrum of 17-electron Mo−alkyne ion $\mathbf{1}^+$ (1824 cm^{-1}) was shifted 50 cm^{-1} to higher energy than the same band in **1**, consistent with a decrease in the metal−alkyne interaction in the Mo(III) cation. Compounds **2**−**4** all gave Mo(III) cations that were stable on the cyclic voltammetry (CV) time scale. In bulk electrolyses monitored by a combination of voltammetric and in-situ IR spectroelectrochemical analyses, the Mo(III) cation $\mathbf{2}^+$ was shown to undergo some loss of alkene. The fiber-optic in-situ IR technique is a powerful method for characterizing organometallic redox processes in which slow chemical reactions are coupled to the electron-transfer step.

Introduction

The redox chemistry of d^4 M(II) π-complexes (M = Mo, W) having alkyne or alkene ligands has not been broadly addressed.[1] Connelly and co-workers showed that the d^4 system $[MoTp^{Me2}(CO)_2(\eta\text{-}C_2Ph_2)]^+$ (Tp^{Me2} = tris(3,5-dimethylpyrazolyl)borate) could be reversibly reduced to the d^5 neutral complex[2a,b] and that $WTp^{Me2}X(CO)(\eta\text{-}C_2Me_2)$ was oxidized reversibly to the d^3 cation.[2c] In these cases X-ray structures of single crystals were obtained on both members of the redox pair, permitting valuable information to be obtained about the effect of electron transfer on the nature of the metal−alkyne bond. Studies of alkyne compounds are of particular interest owing to the electronic flexibility of the ligand in being able to function as either a two-electron or four-electron donor.[3−5]

The present work adds to this area with an investigation of the oxidation of the bis-cyclopentadienyl alkyne compound $MoCp_2(\eta^2\text{-}C_2Ph_2)$, **1**, and three metal−alkene analogues $MCp_2(\eta^2\text{-}C_2H_2\ \textit{trans}\text{-}R_2)$: M = Mo, R = CO_2Me, **2**; M = Mo, R = H, **3**; M = W, R = H, **4**. Our motivation came in part from the desire to test in-situ IR spectroelectrochemistry as a convenient method of identifying redox products that are stable on the time scale of cyclic voltammetry (CV, up to ca. 10−15 s) but not on that of conventional bulk electrolysis (ca. 10−30 min). Using the simple fiber-optic transmission method previously reported,[6,7] a spectral window of ca. 1500−2200 cm^{-1} is available in $CH_2Cl_2/[NBu_4][A]$, A = PF_6 or BF_4. This allows monitoring of the spectral region anticipated for the relatively intense C−C stretch of the alkyne complex **1**.[8a] Metal−alkene complexes, on the other hand, usually have rather weak ν_{CC} features, which are difficult to assign.[8b] For this reason, IR spectroelectrochemical study of the metal alkenes was limited to the dimethylfumarate complex **2**, for which ν_{CO} was followed. An important advantage of the in-situ IR method is that the spectral measurement is largely independent of the electrochemical methodology used to generate the electrolysis product(s). The in-situ method has an important advantage over the widely used thin-layer spectroelectrochemical method.[9,10] The

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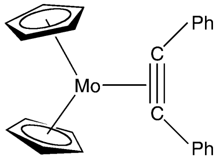
former allows for monitoring of reaction products under synthetic-level bulk electrolysis conditions in which standard voltammetric product analysis (e.g., by CV and steady-state scans) may still be employed. It promises to be valuable for the quantitative characterization of reactions that are complicated by chemical follow-up reactions that accompany electron-transfer processes. As shown below for the oxidation of **2**, combining the spectral and voltammetric data allows the qualitative identification and the quantitation of ligand cleavage reactions that are slow on the CV time scale but sufficiently rapid to affect the product stability on the synthetic time scale.



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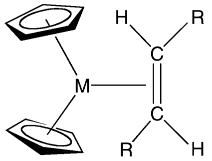

2: M = Mo, R = CO_2Me
3: M = Mo, R = H
4: M = W, R = H

Experimental Section

All experimental work required strict anaerobic and anhydrous conditions under an inert atmosphere. Electrochemical experiments were carried out within a Vacuum Atmospheres drybox. All other experiments utilized traditional Schlenk techniques. Reagent-grade dichloromethane and dichloroethane were twice distilled from CaH_2, first under nitrogen and then bulb-to-bulb under static high vacuum. Spectro-grade acetonitrile was predried by storage over 3 Å molecular sieves and then distilled under nitrogen from CaH_2, followed by freeze−pump−thaw cycles before electrochemical experiments. Elemental analysis was carried out at Robertson Laboratories.

Chemicals. Compounds **3** and **4** were gifts from Prof. Russell Hughes of Dartmouth College. $[FeCp_2][BF_4]$ was prepared from sublimed ferrocene by the literature procedure.[11] Diphenylacetylene (Aldrich) was sublimed under vacuum at 315 K. $MoCp_2H_2$ was prepared in ca. 4 g quantities using literature methods[12,13] through the reaction of $MoCl_5$ (Strem) with $Na[BH_4]$ (Aldrich) and freshly prepared NaCp. Pure $MoCp_2H_2$ was obtained by treating it with acid (3 M HCl) to extract the compound as the trihydride, followed by treatment with 2 M NaOH until a yellow precipitate formed. After collection, this solid was dissolved in ether, filtered, and vacuum-dried. $MoCp_2(\eta\text{-}C_2Ph_2)$, **1**, was prepared in ca. 50% yield by the reaction[14] of $MoCp_2H_2$ with C_2Ph_2 and checked for purity by melting point (163−165 °C), ^1H NMR and IR spectroscopies, and elemental (C,H) analysis. $MoCp_2(\eta^2\text{-}C_2H_2(CO_2CH_3)_2)$, **2**, was prepared in 65% yield by the reaction of dimethylfumarate (Aldrich) with $MoCp_2H_2$,[15] recrystallized as small red needles from CH_2Cl_2/toluene, and checked by ^1H NMR. Full experimental details of the preparation and purification of the Mo compounds are available elsewhere.[16]

$[MoCp_2(\eta\text{-}C_2Ph_2)][BF_4]$, 1[BF$_4$]. **1** (75 mg, 18.6 mmol) in 20 mL of CH_2Cl_2 was cannulated into a solution of 49 mg (17.9 mmol) of $[FeCp_2][BF_4]$ in 20 mL of CH_2Cl_2. The resulting green solution was stirred for 5 min and then evaporated. Ferrocene was removed by washing the residue with ether until the filtrate was colorless. The green residue was taken up in minimal CH_2Cl_2, filter-cannulated, and evaporated, leaving a dark green solid with an oily consistency. Several triturations with ether followed by vacuum-drying gave the green powder **1**$[BF_4]$ in 40−50% yield. Despite the washings, ca. 5% ferrocene (determined by voltammetry) remained in the isolated solids. Anal. Calcd for **1**$[BF_4]$: C, 57.09, H 4.15. Found: C, 58.69; H, 4.10.

Electrochemistry. Electrochemical experiments carried out in the drybox employed a PARC Model 270 potentiostat interfaced to a personal computer. In-situ IR spectroelectrochemical experiments employed drybox or Schlenk-type techniques, and a PARC Model 173 potentiostat was operated using in-house software. All potentials reported in this paper are given vs the ferrocene/ferrocenium couple[17] and may be converted to SCE values by addition of 0.46 V (CH_2Cl_2), 0.56 V (THF), or 0.40 V (CH_3CN).[11] The experimental reference electrode was a homemade Ag/AgCl electrode separated from the test solution by a fine glass frit. Working electrodes for voltammetry experiments were either homemade Pt electrodes (diameter 0.125, 0.25, or 0.50 mm) or commercial Pt disks (diameter 2 mm, Bioanalytical Systems; 5 mm, Beckman). The area of the 5 mm electrode was determined to be 0.248 cm^2 by chronoamperometry data on ferrocene in CH_3CN/0.1 M $[NEt_4][ClO_4]$ ($D_o = 2.4 \times 10^{-5}$ cm^2 s^{-1}).[18] This electrode was used for the determination of the diffusion coefficient for **1** in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ ($D_o = 7.50 \times 10^{-6}$ cm^2 s^{-1}). Glassy carbon electrodes were also suitable for studying the oxidations of these compounds, which gave no indications of adsorption or electrode history effects. Unless otherwise noted the supporting electrolyte was 0.1 M $[NBu_4][PF_6]$. Because of the mechanistic simplicity of CV scans of compounds **1**−**4**, digital simulations of CV curves were not carried out.

Bulk electrolyses were conducted in an H-type cell using a Pt basket working electrode in a compartment separated from the auxiliary compartment by one or two vertically positioned fine glass frits. The working compartment volume was about 20 mL, and analyte concentrations were in the millimolar range. Immersion of the cell in a temperature-controlled 2,2,4-trimethylpentane solution fixed the electrolysis temperature.

Spectroscopy. Optical spectra were recorded with an OLIS-modified Cary 14 spectrometer. EPR spectra were obtained using a Bruker ESP 300E spectrometer equipped with a Bruker B-VT temperature controller, and NMR spectra were recorded with a 250 MHz Bruker spectrometer. IR spectra of electrolysis solutions were obtained by the in-situ method first described by Shaw.[6] In this method a “dip” probe is connected to an FTIR (Mattson Polaris) spectrometer through a 1 m fiber-optic cable (Remspec Corporation) and operated in an external reflectance mode at a gold surface. The probe was inserted into the working compartment of a solution in an H-cell of the type described previously. Bulk electrolysis was then carried out at a platinum basket electrode, while the extent of the electrolysis was followed by coulometry. The electrolysis was periodically halted and an IR spectrum of the solution recorded. To enhance the signal-

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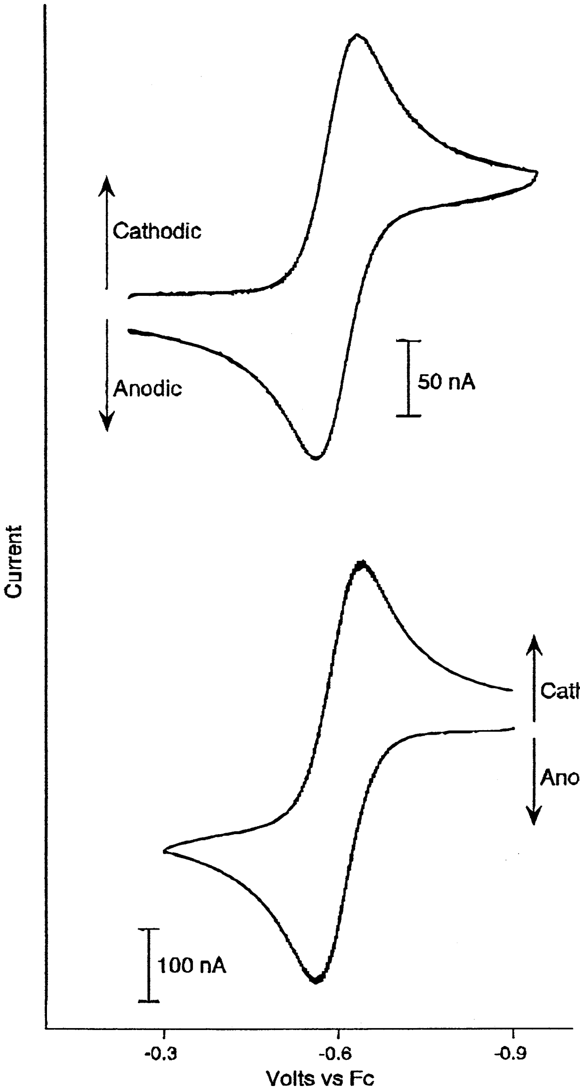

Figure 1. CV scans of 0.65 mM **1**[BF_4] (top) at 0.25 mm Pt disk and 0.42 mM **1** (bottom) at 0.5 mm Pt disk in CH_2Cl_2/0.1 M [NBu_4][PF_6] at 0.2 V/s and room temperature.

to-noise ratio, 64 scans at 4 cm^{-1} resolution were usually employed, requiring a sampling time of about 2 min. A liquid nitrogen-cooled HgCdTe detector (Graseby Infrared Model 1640115) was employed.

Results and Discussion

General Electrochemical Approach. The anodic reactions of compounds **1** and **2** were characterized by a number of electrochemical methods including cyclic voltammetry (CV), linear scan voltammetry (LSV), square wave voltammetry (SWV), and bulk electrolysis. Fiber-optic in situ IR spectroscopy[6] was employed to monitor the electrolysis products for the oxidation of **2**. Less extensive investigations were done on the ethylene compounds **3** and **4**, which were available to us in smaller amounts. In all cases the oxidations were shown to be diffusion-controlled one-electron processes that are fully reversible (i.e., Nernstian) on the voltammetric time scale. The diagnostic criteria for mechanistic analyses were used as previously described,[19] and full experimental details are available elsewhere.[16]

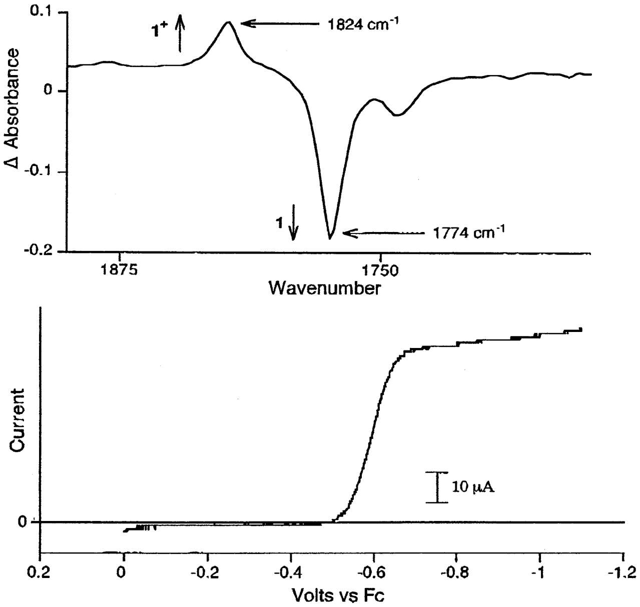

Figure 2. (top) IR difference spectrum in the ν_{CO} region for oxidation of 4.1 mM **1** in CH_2Cl_2/0.1 M [NBu_4][PF_6] at 273 K. (bottom) Steady-state voltammogram, scan rate 5 mV s^{-1}, 1 mm Pt disk electrode, after completion of anodic oxidation to $\mathbf{1}^+$.

MoCp$_2$(η-C$_2$Ph$_2$), 1. Oxidation of **1** is thermodynamically facile ($E_{1/2} = -0.60$ V) and gives a 17-electron cation $\mathbf{1}^+$ that is quite stable. CV scans of **1** (Figure 1, bottom) are fully reversible even in donor solvents such as THF and CH_3CN. Bulk electrolysis of 0.42 mM **1** in CH_2Cl_2/0.1 M [NBu_4][PF_6] at 290 K ($E_{appl} = -0.4$ V) passed one electron (measured: 1.0 F/equiv) as the solution changed from maroon to the lime green of $\mathbf{1}^+$, the presence of which was confirmed by CV and LSV scans. A back-electrolysis at $E_{appl} = -0.9$ V resulted in at least 90% regeneration of the starting material. The electrolysis experiment was repeated at a higher concentration (4.1 mM **1**) while employing the fiber-optic IR probe to monitor the alkyne absorption band. After about 95% anodic electrolysis as indicated by coulometry and by LSV (Figure 2, bottom), difference spectra showed that the ν_{CC} alkyne band at 1774 cm^{-1} for **1** had been replaced by an 1824 cm^{-1} band in $\mathbf{1}^+$ (Figure 2, top). Back-electrolysis regenerated the original band of neutral **1**.

Bulk anodic oxidations were also used to generate samples of $\mathbf{1}^+$ for other types of spectral analysis. Relatively weak visible bands characterize this redox pair through an incompletely resolved absorption at ca. 525 nm for **1** (ϵ = 70 cm^{-1} M^{-1}) and a red-shifted absorption at $\lambda_{max} = 660$ nm for $\mathbf{1}^+$ (ϵ = 50 cm^{-1} M^{-1}). EPR spectra of $\mathbf{1}^+$ were also recorded. A single line with $g_{iso} = 2.049$ was observed in CH_2Cl_2 at ambient temperature, and a rhombic spectrum was seen at 120 K in a 1:1 CH_2Cl_2/$C_2H_4Cl_2$ glass (Figure 3), $g_1 = 2.142$, $g_2 = 2.009$, $g_3 = 1.996$, $g_{av} = 2.049$. A single hyperfine splitting is observed, assigned as A_3(Mo) ca. 20 G.

The oxidized Mo complex was finally isolated as the [BF_4]$^-$ salt using [$FeCp_2$][BF_4] as an oxidizing agent. As detailed in the Experimental Section, oily green solids were obtained, which were difficult to rid of small amounts of residual ferrocene. Reasonable elemental analyses, spectroscopy, and electrochemistry (Figure 1,

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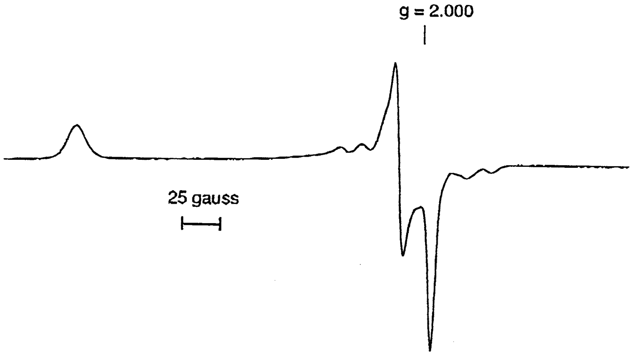

Figure 3. Frozen solution ESR spectrum of ca. 1 mM $\mathbf{1}^+$, from previous chemical oxidation of **1** with Fc[BF$_4$], in 1:1 vol:vol CH$_2$Cl$_2$/1,2-C$_2$H$_4$Cl$_2$ at 120 K.

top) were ultimately obtained on green powders of **1**[BF$_4$], but X-ray quality crystals were not obtained. To our knowledge, this is the first time a bent molybdenocene in the formal +3 oxidation state has been isolated. Compound $\mathbf{1}^+$ did not appear to undergo the type of nucleophilic attacks observed[20] for Mo(II) analogues when treated with either PPh$_3$, Ph$_2$NH (no reaction) or NaOMe, NEt$_3$, and HSnBu$_3$ (simple regeneration of **1**). The very facile one-electron reduction of $\mathbf{1}^+$ seems to dominate its reaction chemistry.

The most informative spectral characteristic of $\mathbf{1}^+$ is its 1824 cm^{-1} ν_{CC} band, increased by 50 cm^{-1} over that of **1**, implying a considerably stronger alkyne C−C bond in the radical. This may be surprising in light of the fact that the SOMO of $\mathbf{1}^+$ is largely metal-based, derived predominantly from the nonbonding 1a$_1$ (d$_{z^2}$) metal orbital.[21] The strongest interaction between the metal and the diphenylacetylene ligand is, however, derived from the metal b$_2$/ligand $\pi_{\|}^*$ interaction, which gives the metal−C$_2$ bond its metallocyclopropyl character. Shrinking of the metal center and the concomitant decrease in metal−ligand orbital overlap likely leads to decreased back-bonding contribution to the $\pi_{\|}^*$ orbital and therefore a stronger C−C bond.

Another important aspect to consider in metal−alkyne bonding is the possible influence from the π-perpendicular ligand orbitals, $\pi_\perp$ and $\pi_\perp^*$.[3] While the $\pi_\perp$ orbitals can play an important role in the bonding of certain complexes, the diphenylacetylene ligand in **1** is a formal two-electron donor having minimal interaction between the metal orbitals and ligand $\pi_\perp$ orbitals. In **1** the difference in energy between the metal b$_1$(d$_{xz}$) orbital and the $\pi_\perp$ ligand orbital is great enough to inhibit substantial interaction. There is a possibility that upon oxidation of **1** to $\mathbf{1}^+$ the $\pi_\perp$ to b$_1$(d$_{xz}$) interaction could increase in magnitude to compensate for the electron-deficient 17-e$^-$ metal center, but the spectroscopic data do not provide insight into this change. Additionally it would be difficult to measure changes in $\pi_\perp$/b$_1$(xy) bonding against the decrease in the metal b$_2$/ligand $\pi_{\|}^*$ back-bonding interaction and possible increase in ligand $\pi_{\|}$/metal 2a$_1$ interaction in the absence of detailed theoretical calculations. Any increase in the $\pi_\perp$/b$_1$(xy) bonding is masked by the more substantial decrease in metal b$_2$/ligand $\pi_{\|}^*$ interaction.

MoCp$_2$(η^2−C$_2$H$_2$(CO$_2$CH$_3$)$_2$), 2. The dimethylfumarate complex **2** is oxidized to the corresponding 17-electron cation $\mathbf{2}^+$ at $E_{1/2} = -0.30$ V in a process that is chemically reversible by CV scans but subject to partial decomposition of $\mathbf{2}^+$ during a bulk electrolysis. Oxidation at $E_{\text{appl}} = -0.1$ V at 295 K released 0.92 C/equiv as the solution went from the reddish color of **2** to the light

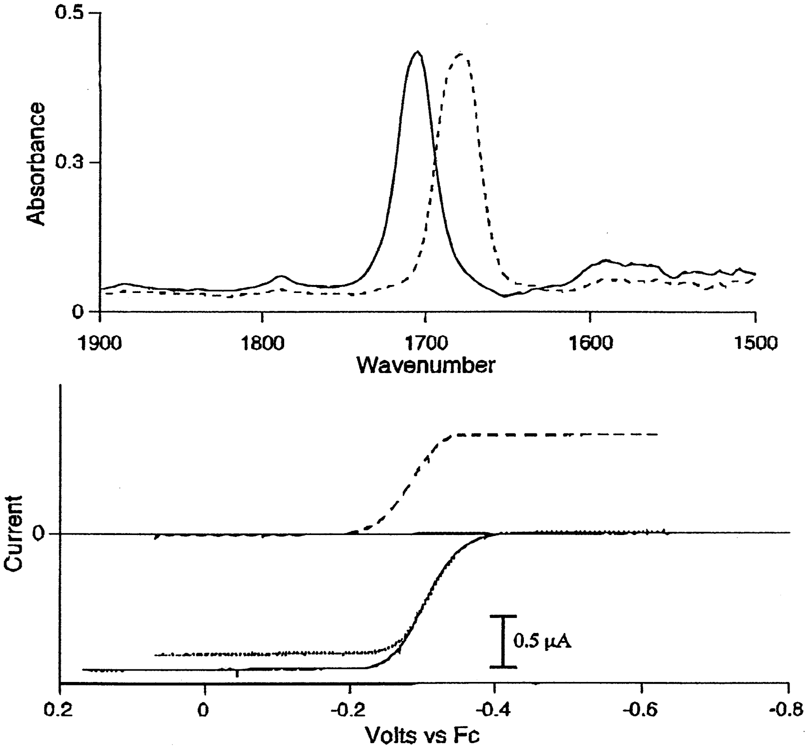

Figure 4. Results of IR spectroelectrochemistry experiment on 3.3 mM **2** in CH$_2$Cl$_2$/0.1 M [NBu$_4$][PF$_6$] at 273 K. (Top) IR spectrum of **2** before anodic electrolysis (dashed line) and of $\mathbf{2}^+$ after electrolysis (solid line). (Bottom) Steady-state voltammograms before electrolysis (solid line), after anodic electrolysis at $E_{\text{appl}} = -0.1$ V (dashed line), and after cathodic re-electrolysis at $E_{\text{appl}} = -0.6$ V (dotted line).

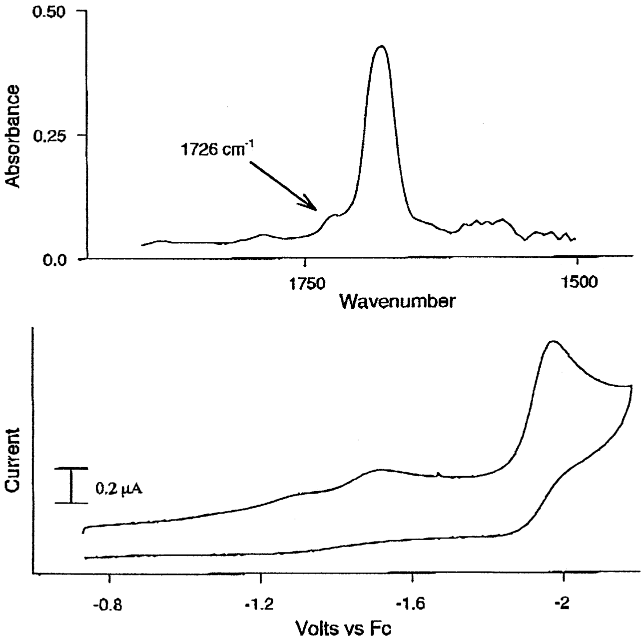

Figure 5. IR spectrum (top) of solution from spectroelectrochemistry of **2** after re-electrolysis showing evidence for the presence of free dimethylfumarate with a peak at 1726 cm^{-1} and CV (bottom) of the same solution displaying an irreversible reduction peak at −1.99 V corresponding to the free dimethylfumarate ligand. Conditions are as described in Figure 4.

yellow of $\mathbf{2}^+$. Only about 75% of the starting material was regenerated when $\mathbf{2}^+$ was reduced in a back-electrolysis at $E_{appl} = -0.6$ V. After the initial anodic electrolysis, CV scans showed, in addition to the reversible wave for $\mathbf{2}^{+/0}$, a chemically irreversible cathodic wave at $E_p = -1.99$ V, which was ascribed to a decomposition product. Its peak current was about half of that observed for $\mathbf{2}^{+/0}$ and fell at the same potential as that of free dimethylfumarate, measured in a separate experiment. This allowed a tentative assignment of the decomposition reaction as one in which there is cleavage of the Mo−olefin bond through an EC mechanism (eq 1):

$$\mathbf{2} - e^- \rightarrow \mathbf{2}^+ + \text{dimethylfumarate} + \text{unknown Mo cmpd} \quad (1)$$

When the anodic electrolysis of **2** was repeated at 273 K, the reaction was followed by fiber-optic spectroscopy. LSV scans in the region of the $\mathbf{2}^{+/0}$ wave (Figure 4, bottom) showed that about 90% of the original compound was regenerated when the original bulk oxidation was followed by a back-reduction. IR spectra in the carbonyl region showed that the ν_{CO} band at 1679 cm^{-1} of **2** was replaced, apparently cleanly, by the ν_{CO} band at 1706 cm^{-1} of $\mathbf{2}^+$ (Figure 4, top). The band at 1726 cm^{-1} expected for any free dimethylfumarate is not observed owing to spectral interference by the 1706 cm^{-1} band of $\mathbf{2}^+$. CV scans to more negative potentials did, in fact, confirm the presence of about 10% of an equivalent of free dimethylfumarate by a cathodic peak at −1.99 V. When the electrolysis solution was back-electrolyzed, removing $\mathbf{2}^+$, the small IR absorption of the free olefin was indeed observed (Figure 5). The complementary nature of the electrochemical and in-situ IR methods is demonstrated by this sequence of measurements.

Table 1. $E_{1/2}$ Potentials vs $Cp_2Fe^{0/+}$ for 0/1+ Redox Reactions of Bis(η^5-cyclopentadienyl)metal− Alkene or −Alkyne Complexes[a]

compound	$E_{1/2}$ (V)
$MoCp_2(\eta$-$C_2Ph_2)$, **1**	−0.60
1	−0.61 (THF)
1	−0.60 (CH_3CN)
$MoCp_2(\eta^2$-$C_2H_2(CO_2CH_3)_2)$, **2**	−0.30
$MoCp_2(\eta$-$C_2H_4)$, **3**	−0.79
$WCp_2(\eta$-$C_2H_4)$, **4**	−0.80

[a] Solvent was CH_2Cl_2 except where noted. Supporting electrolyte was 0.1 M $[NBu_4][PF_6]$.

Table 2. Selected IR Bands for Reduced and Oxidized Forms of 1 and 2 in CH_2Cl_2/ 0.1 M $[NBu_4][PF_6]$

compound	frequency (cm^{-1})	assignment
$MoCp_2(\eta$-$C_2Ph_2)$, **1**	1774	ν_{CC}
$\mathbf{1}^+$	1824	ν_{CC}
$MoCp_2(\eta^2$-$C_2H_2(CO_2CH_3)_2)$, **2**	1679	ν_{CO}
$\mathbf{2}^+$	1706	ν_{CO}
trans-$C_2H_2(CO_2CH_3)_2$	1726	ν_{CO}

Several attempts to isolate $\mathbf{2}^+$ through oxidation of **2** by ferrocenium salts were thwarted by the extreme air sensitivity of $\mathbf{2}^+$ in concert with the presence of the reaction byproducts. When treated with 1 equiv of $[FeCp_2][B(C_6F_5)_4]$ in CH_2Cl_2 at 230 K, **2** gave a yellow solution that yielded a light green solid after further cooling, filtration, and washing with hexane. A portion of the solid, dissolved in 1:1 $CH_2Cl_2/C_2H_4Cl_2$, gave an EPR signal at 150 K having an axial *g*-tensor with $g_{\parallel} = 2.134$, $g_{\perp} = 2.001$ that is attributed to $\mathbf{2}^+$.

$MCp_2(C_2H_4)$, M = Mo (3), M = W (4). The two ethylene complexes **3** and **4** undergo Nernstian one-electron oxidations at potentials ($E_{1/2} = -0.79$ V for **3**; −0.80 V for **4**) that are about 0.5 V negative of the same process for the dimethylfumarate compound **2**, bringing attention to the effect of the strongly electron-withdrawing carboxymethyl groups in **2**. Bulk electrolysis of either **3** or **4** at room temperature in CH_2Cl_2 confirmed the one-electron nature of the oxidations and showed that about half of the neutral compound was regenerated in a back-electrolysis.

Conclusions

By combining electrochemical, in-situ IR spectroscopic, and synthetic procedures the one-electron oxidation of the d^4 M(II) complexes **1**−**4** have been studied. Each of the compounds undergoes a thermodynamically accessible, essentially Nernstian, one-electron oxidation process at potentials that are similar to those reported for the M(IV) compounds MCp_2Me_2.[22] The similarity of redox potentials of the Mo(II) and Mo(IV) systems supports the idea that bonding between the metal and the alkynes or alkenes is well represented by a metal-

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locyclic structure.[23] The alkyne C−C stretching frequency of **1**$^+$ was shifted 50 cm^{-1} to higher frequency compared to **1**, indicating a likely decrease in the metal−CC interaction in the Mo(III) complex.

The Mo(III) complex **1**$^+$ was sufficiently long-lived to allow its isolation as a $[PF_6]^-$ or $[BF_4]^-$ salt. This was not the case for the Mo−alkene complex **2**$^+$, which underwent some decomposition over about 20 min. Combined use of voltammetry and in-situ IR spectroscopy, which enabled both the characterization of **2**$^+$ and detection of its slow loss of alkene, is an attractive method for studying organometallic redox reactions in which the original electron-transfer product undergoes reactions on a time scale of minutes or longer.

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