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Direct Electrochemical Investigations of 17-Electron Complexes of CpM(CO)$_3^{\bullet}$ (M = Mo, W, and Cr)

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Photolysis of complexes of the type M$_2$(CO)$_6$(RC$_5$H$_4$)$_2$ (where M = W, Mo, Cr and R = H (Cp) or CH$_3$ (Cp′)) leads to the production of short lived 17-electron radicals. Direct electrochemical characterization of these intermediates has been achieved using a technique known as photomodulated voltammetry (PMV). The results from PMV analysis are in excellent agreement with literature estimates for CpMo(CO)$_3^{\bullet}$ and CpCr(CO)$_3^{\bullet}$. However, CpW(CO)$_3^{\bullet}$ is found to be shifted oxidatively 115 mV relative to previous literature estimates. The change in the value for the tungsten complex changes previous estimates to the bond dissociation energy for tungsten metal hydrides by 3.0 ± 0.9 kcal/mol. Lifetime information on the radicals is also reported based on the phase shift of the electrochemical signal observed by PMV under limiting current conditions.

Introduction

The existence of organometallic radicals that deviate from the conventional 18-electron rule is now well established.[1−3] In particular, the 17-electron complexes of chromium, molybdenum, and tungsten have received considerable attention.[4,5] Intermediates of the form CpM(CO)$_3^{\bullet}$ can be readily generated by visible photolysis of the metal−metal bond in precursor dimer complexes,[6] eq 1. The 17-electron complexes that are

$$M_2(Cp)_2(CO)_6 + h\nu \rightarrow 2CpM(CO)_3^{\bullet} \qquad (1)$$

generated in this fashion subsequently recombine by second-order kinetics to form the parent dimers on time scales of microseconds to milliseconds.[7] Due to the reactive nature of these radical intermediates, a variety of reactions have also been studied including ligand substitution, halide/proton abstraction, and electron transfer.[8]

The majority of the information that has been gathered in the past decade has focused on mechanistic aspects of 17-electron chemistry. Intermolecular reactions have been investigated extensively and provide basic information on the potential role these intermediates may play in catalytic cycles. Mechanistic characterization has been facilitated by advances in time-resolved spectroscopies, that have been developed in the past decade.[9,10] Structural information has also recently been obtained with the use of time-resolved infrared spectroscopy.[11]

Thermodynamic data is also crucial to the understanding of chemical reactivity. Several groups have attempted to provide additional thermodynamic data in these systems through electrochemical analysis.[12] On the basis of cyclic voltammetry of the dimeric precursors to the 17-electron complexes, Kadish et al. first reported that an ECE mechanism was most likely involved. The results show that electrolysis of the dimer at reductive potentials leads to the formation of the dimer anion. In this form the anion is unstable and undergoes metal−metal bond homolysis resulting in the anion, [M(Cp)(CO)$_3$]$^-$ and radical, CpM(CO)$_3^{\bullet}$. At this potential, the radical is immediately reduced to the corresponding anion, [M(Cp)(CO)$_3$]$^-$, setting an upper limit for the reduction potential of the radical. The oxidation observed following reduction has been assigned to the dimerization process of the anion [CpM(CO)$_3$]$^-$.

At least three methods of determining the electrochemical potentials of the transient odd-electron complexes have been used.[13−16] As early as 1981, Wrighton and co-workers established that intermolecular electron transfer reactions involving the ferrocene$^{+/0}$ couple could be initiated with 17-electron intermediates.[13] Though this was later extended to a series of electron transfer quenchers, the estimates that resulted were limited and did not provide information as to the nature of the electron transfer agent. Fast scan electrochemistry has also been used to infer the electrochemical potentials as described by Pugh and Meyer.[14] By far the most common method has been modification of the ligand sphere or the metal in order to increase the lifetime of the intermediate. For example, substitution of Cp by tris(pyrazolyl)borate (Tpb) or Cr for Mo or W

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results in relatively stable 17-electron complexes of the form (Tpb)M(CO)$_3^\bullet$ or CpCr(CO)$_3^\bullet$, respectively, for which the electrochemistry has been observed.[15] Tilset and Parker have also reported the electrochemistry of the radical anion prepared directly as a salt.[16] By application of relatively straightforward kinetic corrections they were able to assign $E_{1/2}$ values to the [CpM(CO)$_3$]$^{-/\bullet}$ couple. While thermodynamic data on transient intermediates (e.g. CpW(CO)$_3^\bullet$ and CpMo(CO)$_3^\bullet$) can be inferred from these results, direct observation of the electrochemical potentials would be far more valuable.

In addition, the nature of the electron transfer agent in the dimer photolysis needs to be addressed. While the 17-electron species is one possibility, it is known that the solvento species is also generated.[1] On the basis of careful cyclic voltammetry studies and digital simulations, Tilset[16b] has recently suggested that the 19-electron radical CpM(CO)$_3$(NCMe)$^\bullet$ is the most likely species being oxidized in the cyclic voltammetry studies of the dimer Cp$_2$M$_2$(CO)$_6$. This result is certainly consistent with the estimates of the electrochemical potentials known to date.

We describe here the results of direct electrochemical investigations of 17-electron complexes using a recent electrochemical technique known as photomodulated voltammetry (PMV). This technique has been shown to be well suited to electrochemical investigations of organic radicals[17] and, more recently, for short-lived excited states.[18b] Given the recombination rates ($\sim 10^9$ M^{-1} s^{-1}) of the odd-electron transition metal complexes being described here, the electrochemical potentials of CpM(CO)$_3^\bullet$ (M = Mo, W) are readily accessible. We also have the opportunity to look at more stable odd-electron complexes such as CpCr(CO)$_3^\bullet$ by both cyclic voltammetry and PMV to confirm the validity of our transient measurements. The frequency domain nature of PMV also provides access to information on the kinetics of the intermediate being interrogated. Analysis of the observed electrochemical potentials combined with preliminary kinetic information can be used to help elucidate the nature of the electroactive species.

Experimental Section

Materials. The cyclopentadienyl ligand was prepared by fractional distillation from dicyclopentadiene followed by degassing (Aldrich). The methylcyclopentadienyl ligand was prepared by vacuum distillation from the methylcyclopentadiene dimer (Aldrich). The oxidized surface of sodium (Fisher) was removed prior to use. The metal hexacarbonyls, M(CO)$_6$, where M = Mo (Strem), and W (Aldrich), were recrystallized in acetone prior to use. Cr(CO)$_6$ (Aldrich) was used as received and stored under nitrogen. Tetrabutylammonium hexafluorophosphate (TBAH) (Sachem) used in all electrochemical experiments was used as received. The spectrograde solvents acetonitrile, dimethyl formamide (DMF), methylene chloride, and tetrahydrofuran (THF) (Burdick and Jackson), used in all spectroscopic and electrochemical measurements, were stored under an inert atmosphere and used as received.

Synthesis. The preparation of the precursor dimers (η^5-RC$_5$H$_4$)$_2$M$_2$(CO)$_6$ (M = Mo, W, Cr; R = H, CH$_3$) has been previously reported.[19−24] All reactions were carried out under nitrogen with dried, N$_2$-bubble-deoxygenated solvents. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 2s UV−vis spectrometer with 1 cm matching quartz cells. Infrared spectra were recorded on a Nicolet 20SXC FTIR spectrometer with a 1.0 mm path length NaCl solution cell.

Electrochemistry. An EG&G PAR 273A potentiostat coupled to a personal computer performed all conventional electrochemical measurements. A typical electrochemical experiment was performed on a N$_2$-degassed, 0.001 M solution of dimer in 0.1−0.2 M TBAH/(CH$_3$CN, DMF, CH$_2$Cl$_2$, THF) solution. In the case of the chromium dimer, cyclic voltammetry was performed in a Vacuum Atmospheres N$_2$ glovebox. A platinum button working electrode (BAS), a coiled platinum wire (20 gauge) counter electrode, and a freshly prepared silver/silver chloride (22 gauge) reference electrode comprised the three electrode system used in all electrochemical experiments. Scan rates for cyclic voltammetry ranged from 50 to 500 mV/s.

Photomodulated Voltammetry. For PMV the 488 nm continuous wave line from an argon ion laser (Spectra Physics 171) was modulated by a low voltage electrooptic light modulator (Lasermetric AF1). The power supply/amplifier (Lasermetric) for the light modulator was driven by a sine wave from a variable 10 MHz function generator (Tektronix Model CFG250). The sinusoidally modulated light is then incident upon the electrochemical flow cell.[18,25] The ac component of electrochemical signals received by a PAR 273A potentiostat is compared to the reference signal of the function generator within an EG&G PAR 5210 lock in amplifier. Determination of the phase shift for lifetime analysis was corrected by measuring the signal from a fast photodiode assembly (EG&G FFD-100) against the signal of the function generator on a Tektronix digitizing oscilloscope (Model TDS 540). All potentials are reported versus the saturated calomel electrode (SCE).

For typical PMV experiments, the argon ion laser was tuned to 488 nm with a power, incident at the cell, of 0.250−0.350 W as measured by an Ophir 30A-P power meter. The modulation frequency was set and measured at a specific frequency from 100 Hz to 10 kHz. The observed potentials were independent of the excitation frequency over a range of several kHz. In each experiment, a solvent solution of analyte (100−150 mL, 0.001 M) and supporting electrolyte (0.1−0.2 M) was N$_2$ degassed for 15 min within a closed system. In the case of the chromium dimer, the solution was prepared in a glovebox with Aldrich Sure Seal solvents and kept within a sealed system and shielded from light. The solution is delivered through an electrochemical flow cell by applying a positive pressure of N$_2$ gas to achieve a rate of $\sim$5 mL/min.[18] In order to maintain a voltammetric steady state, scan rates of 4−10 mV/s were utilized. For each experiment, cyclic voltammetry was performed on an internal ferrocene standard to determine the actual potentials observed versus the silver/silver chloride reference electrode.

Results

Dimer Electrochemistry. Electrochemical measurements of the dimeric precursors to the 17-electron photoproducts demonstrate the purity of the materials used. In the cases of (η^5-C$_5$H$_5$)$_2$W$_2$(CO)$_6$, (η^5-C$_5$H$_5$)$_2$Mo$_2$(CO)$_6$, and (η^5-C$_5$H$_5$)$_2$Cr$_2$(CO)$_6$, the results of cyclic voltammetry have been previously reported in acetonitrile.[12,16b] Each reduction/oxidation process, eqs 2−5, follows an ECE mechanism as described previously. The results

$$2e^- + M_2(Cp)_2(CO)_6 \rightarrow 2M(Cp)(CO)_3^- \text{ (I)} \qquad (2)$$

$$2M(Cp)(CO)_3^- \rightarrow M_2(Cp)_2(CO)_6 + 2e^- \text{ (II)} \qquad (3)$$

$$M_2(Cp)_2(CO)_6 \rightarrow 2M(Cp)(CO)_3^+ + 2e^- \text{ (III)} \qquad (4)$$

$$2M(Cp)(CO)_3(\text{solvent})^+ + 2e^- \rightarrow M_2(Cp)_2(CO)_6 \text{ (IV)} \qquad (5)$$

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Table 1. Room Temperature Cyclic Voltammetry of the Dimer Precursors to the 17-Electron Complexes vs SCE (V)[a]

compound	solvent	(I)[b]	(II)[b]	(III)[b]	(IV)[b]
$(\eta^5\text{-}C_5H_5)_2W_2(CO)_6$	CH_3CN	−1.28	−0.06	1.03	−0.67
	DMF	−1.34	−0.05	1.07	−0.61
$(\eta^5\text{-}MeC_5H_4)_2W_2(CO)_6$	CH_3CN	−1.42	−0.09	1.03	−0.74
	DMF	−1.39	−0.06	1.06	−0.62
$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$	CH_3CN	−1.13	−0.09	1.00	−0.60
	DMF	−1.05	−0.02	1.10	−0.39
$(\eta^5\text{-}MeC_5H_4)_2Mo_2(CO)_6$	CH_3CN	−1.12	−0.09	0.98	−0.55
	DMF	−1.10	−0.06	0.95	−0.44

[a] Reported as peak potentials (±0.03 V) vs SCE at a scan rate of 100 mV/s. All solutions were 0.001 M analyte in 0.2 M TBAH/solvent and were bubble deoxygenated for 10 min by N_2. [b] Reactions I−IV correspond to eqs 2−5 and the peaks labeled in Figure 1.

Table 2. Electrochemical Potentials vs SCE (v) for $(\eta^5\text{-}C_5H_4R)Cr(CO)_3^{\bullet/-}$ Couples Determined by Cyclic Voltammetry[a]

couple	$E_{1/2}$
$(\eta^5\text{-}C_5H_5)Cr(CO)_3^{\bullet/-}$	−0.28
$(\eta^5\text{-}C_5H_4CH_3)Cr(CO)_3^{\bullet/-}$	−0.34

[a] Solutions with 0.001 M analyte were prepared in acetonitrile (0.1 M TBAH) in an inert atmosphere glovebox. Electrochemical measurements were made in an inert atmosphere glovebox at 100 mV/s.

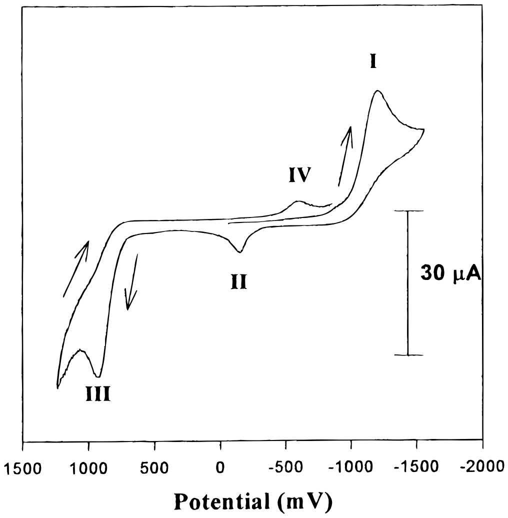

Figure 1. Ground state cyclic voltammogram for $Cp'_2W_2(CO)_6$ in DMF with 0.1 M TBAH. Scan rate = 0.100 V/s.

determined here, reported as peak current potentials in Tables 1 and 2, are in excellent agreement with previous reports.

The cyclic voltammetry of the methylated dimers (e.g. $(\eta^5\text{-}C_5H_4CH_3)_2M_2(CO)_6$) have not been reported previously. A cyclic voltammogram of $(\eta^5\text{-}C_5H_4CH_3)_2W_2(CO)_6$ is shown in Figure 1. The results of cyclic voltammetry of the dimers $(\eta^5\text{-}C_5H_4CH_3)_2W_2(CO)_6$ and $(\eta^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_6$ in polar organic solvents are reported in Table 1. Four irreversible electrochemical waves were observed in a 0.2 M TBAH/CH_3CN solution of $(C_5H_4CH_3)_2W_2(CO)_6$. A two-electron irreversible reduction occurs at $E_p^c = -1.42$ V vs SCE, followed by an irreversible oxidation at $E_p^a = -0.09$ V. A two-electron irreversible oxidation occurs at $E_p^a = 1.03$ V and, on the return scan, an irreversible reduction at $E_p^c = -0.74$ V.

The same pattern of waves is observed in the cyclic voltammogram of $(C_5H_4CH_3)_2Mo_2(CO)_6$ and occur at $E_p^c = -1.12$ V, $E_p^a = 0.98$ V, $E_p^a = -0.09$ V, and $E_p^c = -0.55$ V, respectively. These processes are observed regardless of the initial direction of the potential sweep. For both the Mo and W dimer electrochemistry the potentials are shifted 50−100 mV more negative upon monomethylation.

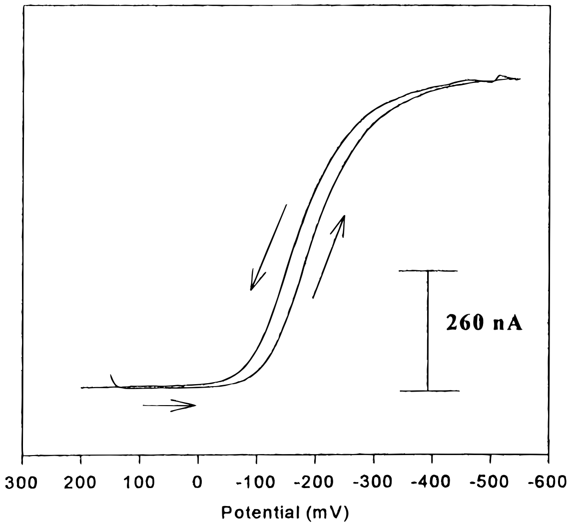

Figure 2. PMV vs Ag/AgCl trace of $CpW(CO)_3^\bullet$ in DMF with 0.1 M TBAH. Scan rate = 0.005 V/s.

Room temperature solutions of the M = Cr system have been shown to contain substantial steady state concentrations of the 17-electron radical $(\eta^5\text{-}C_5H_5)Cr(CO)_3^\bullet$.[4,26] The 1−10% concentrations are sufficient for direct observation by electrochemical methods and can provide for measurement of dimerization rate constants.[27a] The potentials determined for the reduction of $(\eta^5\text{-}C_5H_5)Cr(CO)_3^\bullet$ here are in excellent agreement with literature results.[26] The monomethylated dimers studied also show appreciable concentrations of $(\eta^5\text{-}C_5H_4CH_3)Cr(CO)_3^\bullet$. The reversible couple at $E_{1/2} = -0.34$ V, Table 2, is assigned to the reduction of the $[(\eta^5\text{-}C_5H_4CH_3)Cr(CO)_3]^{\bullet/-}$. At more negative potentials, reduction of the anion occurs.

17-Electron Electrochemistry. $(\eta^5\text{-}C_5H_4R)W(CO)_3^\bullet$. Phase-modulated voltammetry of $(\eta^5\text{-}C_5H_5)W(CO)_3^\bullet$ and $(\eta^5\text{-}C_5H_4CH_3)W(CO)_3^\bullet$ in DMF/0.2 M TBAH solution is shown in Figures 2 and 3. In both cases the modulation frequency was calibrated at 1 kHz and the electrochemical signals were referenced to the ferrocene/ferrocenium couple using a freshly prepared Ag/AgCl reference electrode in the cell. By taking the first derivative of the sigmoidal *i*/*E* curve, the electrochemical potential of the $[(\eta^5\text{-}C_5H_5)W(CO)_3]^{\bullet/-}$ one electron reduction was measured to be $E_{red} = +0.04$ V vs SCE in DMF. The average between the forward and reverse scans in each experiment, Figure 2, was used to assign the potential. Upon methyl substitution of the Cp ligand, the reduction potential for $(\eta^5\text{-}C_5H_4CH_3)W(CO)_3^\bullet$ shifts reductively to $E_{red} = -0.11$ vs SCE, Figure 3a. Table 3 shows the results of phase-modulated voltammetry for $(\eta^5\text{-}C_5H_5)W(CO)_3^\bullet$ and $(\eta^5\text{-}C_5H_4CH_3)W(CO)_3^\bullet$. When the potential was scanned from −0.9 to +0.8 V there was no evidence of additional electrochemical signals from the 17-electron complexes.

$(\eta^5\text{-}C_5H_4R)Mo(CO)_3^\bullet$. Upon substitution of Mo for W a similar pattern is observed to the results described above. The reduction potentials shift with methylation from −0.08 V vs SCE for $(\eta^5\text{-}C_5H_5)Mo(CO)_3^\bullet$ to −0.16 V vs SCE for $(\eta^5\text{-}C_5H_4CH_3)Mo(CO)_3^\bullet$. The phase-modulated voltammogram for $(\eta^5\text{-}C_5H_4CH_3)Mo(CO)_3^\bullet$ is shown in Figure 3b. Under the same experimental conditions, the reduction shifts to more negative potentials for both $(\eta^5\text{-}C_5H_5)Mo(CO)_3^\bullet$ and $(\eta^5\text{-}C_5H_4CH_3)$Mo-

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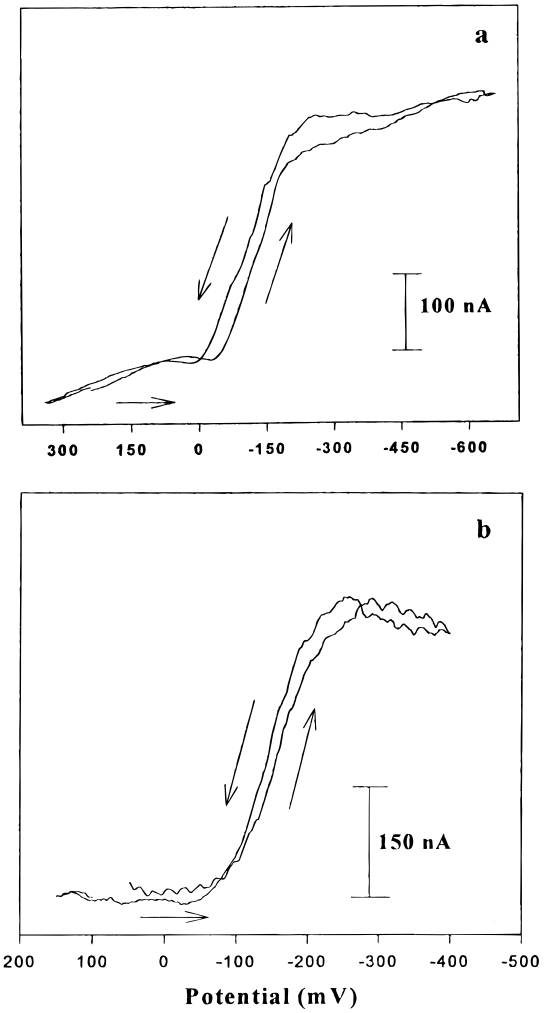

Figure 3. PMV traces: (a) $Cp'W(CO)_3^{\bullet}$ in CH_2Cl_2 with 0.1 M TBAH: (b) $Cp'Mo(CO)_3^{\bullet}$ in DMF with 0.1 M TBAH. Scan rate = 0.005 V/s.

Table 3. Electrochemical Potentials vs SCE (v) of the 17-Electron Complexes Determined by Room Temperature PMV at 488 nm[a]

couple	solvent	electrochemical potential	lit. value
$(\eta^5\text{-}C_5H_5)W(CO)_3^{\bullet/-}$	DMF	0.04 ± 0.02	0.021 (CH_3CN)[a]
$(\eta^5\text{-}C_5H_4CH_3)W(CO)_3^{\bullet/-}$	DMF	−0.11 ± 0.05	
$(\eta^5\text{-}C_5H_5)Mo(CO)_3^{\bullet/-}$	DMF	−0.08 ± 0.04	0.015 (CH_3CN)[b] −0.08 (CH_3CN)[c]
$(\eta^5\text{-}C_5H_4CH_3)Mo(CO)_3^{\bullet/-}$	DMF	−0.16 ± 0.06	
$(\eta^5\text{-}C_5H_5)Cr(CO)_3^{\bullet/-}$ [d]	CH_3CN	−0.30 ± 0.05	−0.26 (CH_2Cl_2)[e] −0.037 (benzonitrile)[f] −0.28 (CH_3CN)[g] −0.298 (CH_3CN)[b]

[a] Background measurements were made by performing PMV on a 0.2 M TBAH solution. All solutions were degassed for ten minutes prior to the experiment. [b] As reported by Tilset and Parker, ref 16a, Table 1. [c] As reported by Pugh and Meyer.[14] Value corrected to SCE by subtracting 0.05 V. [d] Solution was first prepared in the VAC drybox and kept under nitrogen throughout the experiment. [e] As reported by Baird and co-workers.[30] Value corrected to SCE by subtracting 0.045 V. [f] As reported by Madach and Vahrenkamp.[29] Value corrected to SCE by subtracting 0.20 V. [g] As reported by Tilset.[16b] Value corrected to SCE by addition of 0.40 V.

$(CO)_3^{\bullet}$ relative to the corresponding tungsten radicals. The results are reported in Table 3.

$(\eta^5\text{-}C_5H_5)Cr(CO)_3^{\bullet}$. The result of photomodulated voltammetry for $(\eta^5\text{-}C_5H_5)Cr(CO)_3^{\bullet}$ is listed in Table 3. The reduction of the $(\eta^5\text{-}C_5H_5)Cr(CO)_3^{\bullet}$ radical occurs at −0.30 V vs SCE. As in the case of both the Mo and W samples, no additional signals that could be attributed to the 17-electron species were observed. This result is identical to those obtained by cyclic voltammetry as described above.

Lifetime Measurements. Additional information is available from the frequency dependent measurements of the 17-electron complexes. Careful determination of the phase shift, ϕ, in the ac electrochemical signal provides information concerning the lifetime of the intermediate under investigation. For first-order or pseudo-first-order decay processes, eq 6 can be used where f is the frequency of the modulation and τ is the lifetime of the transient.[18] For bimolecular processes, it has been shown that the relationship between the phase shift and the recombination rate is more accurately described by eq 7.[17b] In eq 7, k_{rec} is the recombination rate of the radicals to form the initial dimer and $[R^{\bullet}]$ is the maximum steady state concentration of the 17-electron radical.

$$\tan(2\phi) = 2\pi f\tau \tag{6}$$

$$\phi \propto \log(2k_{rec}[R^{\bullet}]/f) \tag{7}$$

While an in-depth study of a series of 17-electron radicals is currently underway, we report here initial attempts to study the kinetics of the M = W system by PMV. The W radicals formed by photolysis recombine by second-order kinetics.[6,7,11] The phase shift determined by PMV was measured under diffusion limited current conditions to minimize any phase shifts due to electron transfer at the electrode.[17b] The measurements described here were obtained at a potential 150 mV more negative than the observed reduction potential.

The phase shift was determined at a series of frequencies from 100 to 1000 Hz and related directly to k_2 in eq 7 by simulation.[28] A correction must be applied in each phase shift determination for the RC time constant of the electrochemical cell which introduced an additional shift of −5 to −12°. The variability of the phase shift requires that it be measured following each experiment. The cell RC time-constant also limited the frequency range of our measurements to a maximum of 1000 Hz (the majority of our data was collected below 500 Hz).

The recombination rate constants determined by PMV for $(\eta^5\text{-}C_5H_5)W(CO)_3^{\bullet}$ and $(\eta^5\text{-}C_5H_4CH_3)W(CO)_3^{\bullet}$ are $2 \pm 1 \times 10^9$ M^{-1} s^{-1} based on phase shifts of −30 to −40°. Within experimental error, these data are in good agreement with second-order rate constants determined by time-resolved infrared spectroscopy[11] and transient absorption.[7a,14] Further evaluation of PMV-based kinetic analysis is ongoing in our laboratory.

Discussion

Ground State Electrochemistry. While the dimer electrochemistry is now well established,[12] the effect of ligand substitution on the electrochemistry has not been reported. The Cp′ data reported here are consistent with respect to the effect of methylation on the electrochemical potentials. On the basis of previous investigations[27] of substituted Cp's in the Fc/Fc^+ system, a reductive shift upon methylation is anticipated. This is observed for both the W and Mo complexes, Table 1. However, the peak potentials reported are also very susceptible

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(28) The simulated data in Figure 8 of ref 17b was used for this analysis. This simulation uses an electron transfer rate $k_s = 1 \times 10^5$, a transfer coefficient $\alpha = 0.5$, and a ratio of the diffusion coefficient of the radical to the anion, D, equal to 1. These estimates are reasonable based on comparison to organic radical studies by PMV[17] and, in some cases, comparison to dimer electrochemical results.[12]

to the chemical kinetics (recombination rates) in the ECE mechanism. This limits further analysis without simulation of the voltammograms.

A more effective use of the dimer electrochemistry is in the determination of the electrochemical window appropriate to run PMV. The usable window for the PMV experiments was limited to be within $E_{p,c}$ and $E_{p,a}$ of the dimer precursors, Table 1 and Figure 1. There are two reasons for this limitation. It is necessary to minimize the "background" faradaic currents generated by the dimer. Though the lock-in amplifier effectively removes relatively low frequency background currents as the potential is scanned, large background currents limit the dynamic range that can be monitored effectively. Signals for background electrolyte measurements ranged from 10 to 60 nA, while analyte signals ranged from 100 nA to 1μA. The second reason for the limitation of the potential window was to ensure that only the dimer was being excited by the modulated laser beam. The monomer anions $[CpM(CO)_3]^-$ and cations $[CpM(CO)_3]^+$ generated during cyclic voltammetry, eqs 2 and 4, have absorptions in the visible region of the spectrum and could also be excited by the modulated laser source. This would introduce additional photocurrents at the excitation frequency that are difficult to discriminate against using the lock-in amplifier.

A closer examination of the ground state electrochemistry provides some information concerning the radical reduction and oxidation. In the seminal paper by Kadish et al.,[12] oxidation of the monomer anion, $[CpM(CO)_3]^-$, is reported to lead directly to the formation of both the dimer and the monomer cation, $[CpM(CO)_3]^+$. Likewise, reduction of the monomer cation, $[CpM(CO)_3]^+$, leads directly to the formation of the dimer and the monomer anion, $[CpM(CO)_3]^-$. Direct competition between metal−metal bond formation and a slow reduction/oxidation of the radical is the cause for the observation of both products. However, observation of the cation at the oxidation potential of the anion indicates that the intermediate product, the radical, is also oxidized at this potential and represents an upper limit for the oxidation of the radical, $[CpM(CO)_3]^{\bullet/+}$. In the case of the cation reduction, observation of the anion at the reduction potential of the cation indicates that the radical also undergoes reduction at this potential. This provides the lower limit for the reduction of the radical, $[CpM(CO)_3]^{\bullet/-}$.

17-Electron Intermediate Electrochemistry. While PMV has been established for organic systems,[17] this represents the first direct observation of electrochemistry from transition metal odd-electron complexes of W and Mo. To help validate the approach, the $[CpCr(CO)_3]^{\bullet/-}$ couple was crucial. The steady state concentration of $[CpCr(CO)_3]^\bullet$ is sufficient for direct electrochemical determination of $E_{1/2}$ by cyclic voltammetry. The results from PMV analysis were in excellent agreement with both our own cyclic voltammetry on the same system and previous cyclic voltammetry investigations.[16b,29,30]

Within the window of the dimer redox potentials, there was no evidence for additional electrochemical signals. We had anticipated that additional information would be acquired concerning the oxidation of the 17-electron radicals. The limit of the oxidation potentials that we could scan, 0.8 V vs SCE, is therefore assigned as the minimum value for this potential. In an earlier investigation it was suggested that the oxidation potential must sit at least 1.0 V more positive than the reduction potential.[16b] Our "negative" result is consistent with this observation, though work is continuing to try to observe the oxidation potentials directly.

The direct electrochemical determinations reported here for the 17-electron radicals are well within the limits set by the cyclic voltammetry as described above. They also compare favorably to previous estimates, Table 3, given the relatively large error bars associated with many of those estimates and the differences in solvents used. A common problem in the literature is the assignment of different reference potentials.[31] For the purpose of this discussion, we have adjusted all of the literature data in Table 3 relative to SCE. The actual values are given in the table footnotes[32] and are based on established corrections published previously by Geiger for ferrocene electrochemistry in different solvents[27] or Bard.[32]

The electrochemical potentials of the Cr system are in excellent agreement with literature reports as mentioned above.[16] For the Mo and W complexes, a discrepancy occurs between our direct measurements and some of the literature values, Table 3. It is possible that the difference arises due to the different solvents used previously. We were unable to achieve PMV analysis in CH_3CN solutions of the W and Mo complexes due to limited solubility.

Prior to this study, the most direct measure of the 17-electron electrochemistry was reported by Parker and Tilset in a study where the Cr, W, and Mo anions were prepared synthetically as stable salts. In that study, cyclic voltammetry was run in CH_3CN to determine the oxidation potential of the anions, Table 3. They reported their electrochemical potentials corrected for the recombination rate of the radical. One concern with respect to their data is the fact that different solvents were used in estimating the recombination rates for the radical. Recombination rates are known to be very solvent dependent based on spectroscopic determinations.[6] In addition their potentials are corrected based on the activities of the solutions in order to estimate a potential vs NHE. It is the NHE referenced data that Meyer and Pugh later assign to the $CpM(CO)_3{}^{\bullet/-}$ couple.[14] The value reported by Pugh and Meyer is in good agreement with our results despite the difficulties described above in the recombination rate.

Applications of Electrochemical Results. One use of the electrochemical potentials of the 17-electron radicals is in the estimation of the bond dissociation energies (BDE) of metal hydrides.[16a] The differences observed between the anion oxidation and the results by PMV have a direct impact on the current estimates to the M−H bond dissociation energies in $CpM(CO)_3(H)$ with M = W and Mo. Using established thermodynamic cycles, we calculate that the BDE of $CpM(CO)_3(H)$ (where M = Mo and W) are 62 and 68 kcal/mol, respectively. The molybdenum data is unchanged if we use the activities reported by Norton and co-workers.[33] The tungsten data show an increase of 3 kcal/mol over the previous estimates when handled in the same fashion. The increase in the BDE is consistent with earlier data that suggested a BDE of 80.7 kcal/mol for $CpW(CO)_3(H)$.[34]

The intermolecular electron transfer chemistry of $CpM(CO)_3{}^\bullet$ where M is Cr, Mo, and W has been investigated previously. A key question in the electron transfer reactions is the role that the solvento complex $CpM(CO)_3(solvent)^\bullet$ plays in this chemistry. An equilibrium exists between the radical initially formed

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and the substituted solvento complex, eq 8. The kinetics of

$$\mathrm{CpM(CO)_3^{\bullet} + solvent \rightleftharpoons CpM(CO)_3(solvent)^{\bullet}} \qquad (8)$$

this equilibrium have recently been described for the Cr complex by Richards, Geiger, and Baird using electrochemistry.[35]

The literature suggests that the equilibrium in eq 8 sits to the left for Mo and W. Espenson *et al.*, have discussed two issues which support the stability of $\mathrm{CpM(CO)_3^{\bullet}}$.[36] The first is that k_{rec} for Mo and W approaches the diffusion limit. In addition, a theoretical kinetic treatment of electron transfer from the coordinated radical versus the bare radical points out the improbability of a coordinated radical. Alternatively, Tilset recently presented electrochemical simulation data that suggest intermolecular electron transfer reactions in acetonitrile may involve the solvento complex for molybdenum and tungsten.[16b] This is consistent with earlier observations concerning the dimer electrochemistry and the fact that the solvent coordinated cation can be observed directly.

If the solvento complex plays a significant role in the electron transfer chemistry, PMV would indicate this in two ways. A shift in the observed recombination rate would be expected. The recombination rate constants are expected to be larger for open-shell complexes compared to expanded-shell solvento complexes. The lifetime values reported here in DMF are similar to those reported from spectroscopy in CH_3CN.[7a] On the basis of literature assignment of the spectroscopic measurements to the bare radical, we could conclude that the bare radical is also involved in these measurements. However, the shift in recombination rate upon varying solvent from cyclohexane (no coordination) to tetrahydrofuran (strongly coordinating 2-electron donor) is less than a factor of 3 for both Mo and W.[7] Given the error in the preliminary analysis of the recombination rates by PMV, we cannot draw a firm conclusion as to the role of the solvento complex based on this kinetic information.

The magnitude of the reduction potential would also be affected by formation of the solvento complex. Coordination of a 2-electron-donating solvent forms a 19-electron ($18 + \delta$) complex.[2] A shift in the reduction potential to significantly more negative values is expected based on the electron-rich nature of the 19-electron radical. The limited electrochemical data on established, stable 19-electron complexes of Mo, W, and Cr however make this assignment difficult. Nonetheless, based on the relatively weak reduction potentials observed here (<-0.30 V vs SCE), the data obtained by PMV appear to be consistent with earlier results that suggest the equilibrium in eq 8 sits far to the left.[36]

Conclusion

The assignment of accurate electrochemical potentials to odd-electron complexes is critical to a complete understanding and application of their dynamic reactivity. The results presented here demonstrate for the first time the applicability of photomodulated voltammetry to the study of inorganic radicals. The electrochemical results provide direct support of the quality of many of the previous estimates to these potentials and create an opportunity for more in depth investigations of similar intermediates. The lifetime information obtained, though crude in comparison to more established spectroscopic determinations, can provide insight into the nature of the electroactive species in intermolecular electron transfer reactions studied previously. More work is necessary to further evaluate the utility of PMV for kinetic measurements.

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