

# Synthesis and Characterization of Tetrahydrofurfurylcyclopentadienyl Molybdenum Tricarbonyl Dimer: Evidence for 19-Electron Intramolecular “Solvento” Interactions

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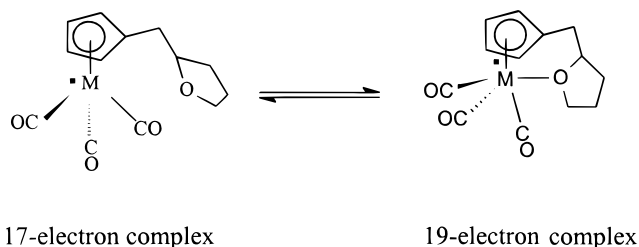
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The synthesis and characterization of a THF pendant, dimeric Mo cyclopentadienyl complex is reported and the structure characterized by NMR, FTIR, and UV–vis spectroscopies. The dimer was found to undergo metal–metal bond homolysis under either photochemical or electrochemical conditions to yield an odd-electron complex. Cyclic voltammetry under varying scan rate conditions from 25 to 10 000 mV/s demonstrates a dynamic equilibrium process that we assign to the formation of either an intramolecular 19-electron ( $18 + \delta$ ) complex or a bare 17-electron complex. Photolysis of the dimer in room temperature solution could be monitored as a loss of the  $d\pi-d\sigma^*$  transition at 503 nm by transient absorption spectroscopy. The recovery of the transient absorption signal at 410 nm follows first-order kinetics at a rate of  $5 \times 10^3 \text{ s}^{-1}$ .

## Introduction

Unsaturated organometallic complexes have received noteworthy attention for over two decades based on their utility in catalysis and polymerization.<sup>1,2</sup> Reactive, odd-electron transition metal complexes represent key intermediates that can be generated photochemically or electrochemically and have been characterized by numerous spectroscopic, electrochemical, and mechanistic techniques.<sup>3–5</sup> A key area that is currently being investigated involves the generation of electron rich odd-electron complexes by coordination of a Lewis base solvent species to a 17-electron unsaturated complex. The result is an electron rich complex that is highly reactive.

There are two interpretations concerning these electron rich solvento intermediates. Previous studies have suggested that bimolecular, solvent coordination results in a dynamic equilibrium between the 17-electron, uncoordinated species and a 19-electron solvent-coordinated species.<sup>6,7</sup> Alternatively, it has been postulated that the formation of the electron rich complex with two-electron-donating solvents should be described on the basis of orbital energy considerations.<sup>8,9</sup> In this case, the definition



17-electron complex

19-electron complex

**Figure 1.** Intramolecular 19-electron complex formation in the pendant Cp dimer.

of a 19-electron complex is described more accurately as  $18 + \delta$  in which the additional electron density is pushed onto the Cp ligand. This has been demonstrated for stable complexes using two-electron donating ligands such as triphenylphosphine.<sup>6</sup> The direct investigation of the solvento intermediates involving tetrahydrofuran (THF), pyridines, and ethers has been hampered by the reactive nature and the dynamic equilibrium that is established with the 17-electron precursor.

We have now prepared a novel solvent pendant complex, tetrahydrofurfurylcyclopentadienyl molybdenum tricarbonyl dimer,  $[\text{Cp}^{\text{P}}\text{Mo}(\text{CO})_3]_2$ , designed to provide more direct insight into the ground and excited state electrochemical properties of solvent-coordinated odd-electron complexes of group 6 metals. This complex is a member of a unique family of cyclopentadienyl dimers that contain pendant solvent molecules such as tetrahydrofuran, thiophene, and pyridine. Metal–metal bonded dimeric complexes of this type produce 17-electron odd-electron complexes upon photolysis with the ability to coordinate electron-donating solvents.<sup>5</sup> The incorporation of a tethered THF or pyridine molecule to the cyclopentadiene ligand provides for facile intramolecular rearrangement in solution, Figure 1, to yield the 19-electron complex.

## Experimental Section

Standard drybox or Schlenk techniques were used for all manipulations of air-sensitive materials. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY. Proton NMR spectra

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were obtained at 360 MHz with a Bruker AM-360 spectrophotometer and referenced to the residual protons of  $\text{CDCl}_3$  ( $\delta = 7.24$ ) or  $\text{THF}-d_8$  ( $\delta = 3.58$ ). Carbon ( $^{13}\text{C}$ ) NMR spectra were obtained at 90.5 MHz with a Bruker 200 and referenced to the residual  $^{13}\text{C}$  resonances of  $\text{CDCl}_3$  ( $\delta = 77.0$ ). Infrared data were obtained on a Bruker Equinox 55 spectrometer with a 1.00 mm path length NaCl solution cell ( $\text{CHCl}_3$ ). UV-vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with 1 cm matching quartz cells.

**Materials.** Molybdenum hexacarbonyl purchased from Aldrich was opened and handled under nitrogen. Solvents were dried and degassed by standard methods or purchased as Sureseal reagents from Aldrich. All other commercially available reagents were used without further purification.

**Synthesis of Tetrahydrofurfurylcyclopentadiene (HCp<sup>P</sup>).** Although the HCp<sup>P</sup> ligand is known, there are few reports in the literature of its use.<sup>10–12</sup> The ligand is readily synthesized through a metathesis reaction of tetrahydrofurfuryl chloride and sodium cyclopentadienide in THF.<sup>10</sup> The ligand was purified and isolated through vacuum distillation at 55 °C (0.30 mmHg) with low yields of pure ligand (7.03%).

**Synthesis of Potassium Tetrahydrofurfurylcyclopentadienide (KCp<sup>P</sup>).** Molecular sieves were added to the tetrahydrofurfurylcyclopentadiene and the ligand was freeze-pump-thawed. An apparatus consisting of a 100 mL three-neck round-bottom flask, two stoppers, condenser, gas inlet, and a stir bar was brought into the nitrogen drybox and assembled. KH (Acros, 1.173 g, 0.0292 mol) was then added to the flask. THF (approximately 50 mL) was also added to the flask and stirred. The ligand (HCp<sup>P</sup>, 4.37 g, 0.0291 mol) was then added to the flask slowly with a pipet. The color of the solution changed from colorless to yellow to brown. Hydrogen gas could be seen evolving. The reaction mixture was stirred overnight. The mixture was transferred from the flask to a 125 mL Erlenmeyer flask equipped with a gas inlet. This flask was then removed from the drybox, and the THF was removed by vacuum. A brown solid (5.084 g, 0.0270 mol, 92.96%) was isolated. Proton NMR characterization of this was consistent with analogous compounds reported by Bitterwolf.<sup>8</sup>

**Synthesis of  $[\text{Cp}^{\text{P}}\text{Mo}(\text{CO})_3]_2$ .** The dimer was synthesized and characterized through a modification of several preparations reported previously.<sup>13–15</sup> An apparatus consisting of a 250 mL three-neck round-bottom flask equipped with two stoppers, condenser, gas inlet, and stir bar was assembled in the drybox. KCp<sup>P</sup> (2.386 g, 0.0127 mol) was added to the flask. The apparatus was then brought out of the drybox and connected to the vacuum line. The line was purged three times, and nitrogen was introduced to the entire apparatus. Under a positive pressure of nitrogen, one stopper was replaced with a septum. Diglyme (Aldrich, 75 mL) was added to the flask with a nitrogen-purged syringe, and gas evolution was observed.  $\text{Mo}(\text{CO})_6$  (3.336 g, 0.0126 mol) was added to the reaction mixture. The mixture was heated to reflux for 1½ h. The color of the reaction mixture was red and gradually became a yellow/orange color.  $\text{Mo}(\text{CO})_6$  could be seen subliming on the walls of the flask. The reaction mixture was allowed to come to room temperature. Methanol (2.5 mL) followed by distilled water (2.5 mL) was slowly added afterward. Nitrogen was bubbled through both of these solutions prior to their additions. A nitrogen-purged filtered solution consisting of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$  (8.61 g, 0.0182 mol), distilled water (125 mL), and glacial acetic acid (7.5 mL) was then added to the reaction mixture with a nitrogen-purged syringe. The mixture became deep red and was cooled in ice to precipitate crystals. The mixture was then filtered using a fritted funnel and washed with distilled water, and a red solid (4.165 g, 0.006 326 mol, 50.2%) was isolated.

Vacuum sublimation was used to remove unreacted  $\text{Mo}(\text{CO})_6$  from the reaction mixture. The product was recrystallized from hot acetone, resulting in fine red crystals: dec 112–115 °C. Anal. Calcd for  $\text{C}_{26}\text{H}_{26}\text{Mo}_2\text{O}_8$ : C, 47.4; H, 3.98. Found (average): C, 47.02; H, 4.07. Repeated elemental analyses did not provide any two duplicate results.  $^1\text{H}$  NMR (Bruker 360 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.30 (s, 2H, Cp ring H), 5.14 (s, 2H, Cp ring H), 3.85 (m, 2H, H-7, H-10), 3.72 (m, 1H, H-10), 2.56 (m, 2H, H-6), 1.99 (m, 1H, H-8), 1.85 (m, 2H, H-9), 1.54 (m, 1H, H-8). Assignments were made by COSY and numbered as referenced by Bitterwolf.<sup>8</sup>  $^{13}\text{C}$  NMR (Bruker,  $\text{CDCl}_3$ ):  $\delta$  94.2 (Cp ring C), 94.0 (Cp ring C), 92.0 (Cp ring C), 91.8 (Cp ring C), 80.0 (C-7), 68.0 (C-10), 36.0 (C-6), 31.0 (C-8), 26.0 (C-9). Assignments were made with C–H correlation. There was no evidence for the carbonyl carbons. IR  $\nu$  (CO) (Bruker Equinox 55,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 1954.3 s, 1913.7 s, 1895.7 sh. UV-vis (DMF):  $\lambda_{\text{max}}$  (nm) ( $\epsilon$ ) 386 (12 900  $\text{M}^{-1}\text{cm}^{-1}$ ), 503 (1 530  $\text{M}^{-1}\text{cm}^{-1}$ ).

**Electrochemistry.** An EG&G PAR 273A potentiostat coupled to a personal computer performed all conventional electrochemical experiments. The typical electrochemical experiment was performed on either a  $\text{N}_2$ - or an argon-deoxygenated, ~1.0 mM solution of dimer in 0.1–0.2 M TBAH/ $(\text{CH}_3\text{CN}, \text{DMF}, \text{THF}, \text{CH}_2\text{Cl}_2)$  solution. Background experiments were performed on the solvent/salt solution prior to the addition of dimer. The electrode configuration was as follows for all electrochemical experiments: a platinum button working electrode (BAS), a coiled platinum wire (20 gauge) counter electrode, and a fresh silver/silver chloride reference electrode (22 gauge). All electrochemical half-wave potentials are reported with reference to the ferrocene standard couple versus SCE. Scan rates utilized during cyclic voltammetry experiments ranged from 25 to 10 000 mV/s.

**Laser Flash Photolysis.** Transient absorption was performed at the Center for Photoinduced Charge Transfer at the University of Rochester on a system described elsewhere.<sup>16</sup>

The solutions were bubbled through with argon gas, and typical concentrations were 0.01–0.10 mM. The samples were irradiated at 500 nm by an excimer-pumped dye laser with a coumarin dye. Excitation at 500 nm into the low-energy band leads to the loss of both the high- and low-energy absorptions. Typical flash photolysis experiments monitored the recovery of absorption at 410 nm. A spectrum of wavelengths were collected between 350 and 800 nm at 15 nm intervals. No new absorptions were observed following flash photolysis. Monitoring at 410 nm is possible due to the high extinction coefficient. Due to the low extinction coefficient of the low-energy band centered at 503 nm, no change in absorption was observed in the 500 nm region. This is also observed for the analogous  $[\text{CpMo}(\text{CO})_3]_2$  dimer. Changes in absorption following excitation did not reversibly return to the base line in all experiments.

## Results

Although tetrahydrofurfurylcyclopentadiene was easily synthesized through a metathetical reaction of tetrahydrofurfuryl chloride and sodium cyclopentadienide in THF using established procedures,<sup>8a</sup> its isolation through vacuum distillation (55 °C, 0.30 mmHg) proved challenging. Pure ligand was obtained in low yield (7.03%). Potassium tetrahydrofurfurylcyclopentadienide was synthesized through a metalation reaction using KH and HCp<sup>P</sup>. The potassium salt was minimally characterized using low-field proton NMR. KCp<sup>P</sup> was then used to synthesize the tetrahydrofurfurylcyclopentadienyl tricarbonyl molybdenum dimer (50.2% yield) using established methods.<sup>14,15</sup> The red, air-stable  $[\text{Cp}^{\text{P}}\text{Mo}(\text{CO})_3]_2$  was fully characterized with  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, FTIR spectroscopy, UV-vis spectroscopy, and electrochemistry. All characterization could be assigned definitively to the title compound. The proton NMR spectrum was assigned definitively using H,H-COSY and is consistent with those reported by Bitterwolf.<sup>8a</sup> The carbons, with the exception of the carbonyls, were subsequently assigned using

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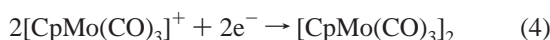
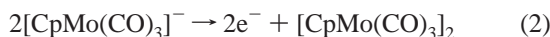
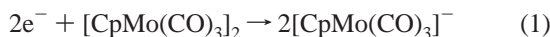
**Table 1.** Infrared, UV-Vis, and Electrochemical Data of Representative Complexes of the Type  $[\text{CpMo}(\text{CO})_3]_2$ 

complex <sup>a</sup>	IR <sup>b</sup> carbonyl stretching $\nu$			electrochemical results <sup>c,d</sup>				
	1	2	3	1	2	3	4	5
$[\text{CpMo}(\text{CO})_3]_2$	1959 s <sup>e</sup>	1916 s	1905 sh	-1.13	-0.09	1.00	-0.60	
$[\text{Cp}'\text{Mo}(\text{CO})_3]_2$	1953 s	1912 s	1897 sh	-1.12	-0.09	0.98	-0.55	
$[\text{Cp}^{\text{P}}\text{Mo}(\text{CO})_3]_2$	1954 s	1914 s	1895 sh	-1.32	-0.16	0.93	-0.34	-0.68
$[\text{Cp}^{\text{3i}}\text{Mo}(\text{CO})_3]_2$	1938 s	1905 s	1882 sh	-1.39	-0.16	0.92	-0.76	

<sup>a</sup> Cp = C<sub>5</sub>H<sub>5</sub>, Cp' = C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>, Cp<sup>3i</sup> = 1,2,4-triisopropylcyclopentadiene, Cp<sup>P</sup> = tetrahydrofurfurylcyclopentadiene. <sup>b</sup> IR data collected in complex dissolved in CHCl<sub>3</sub> and reported as cm<sup>-1</sup>. <sup>c</sup> Electrochemical data collected in 0.1 M TBAH/DMF solutions with peak potentials reported versus SCE at scan rates of 100 or 250 (for Cp<sup>P</sup>) mV s<sup>-1</sup>. <sup>d</sup> Electrochemical processes refer to eqs 1–4. <sup>e</sup> Manning, A. R.; Hacket, P.; Birdwhistell, R.; Soye, P. *Inorg. Synth.* **1990**, 28, 148.

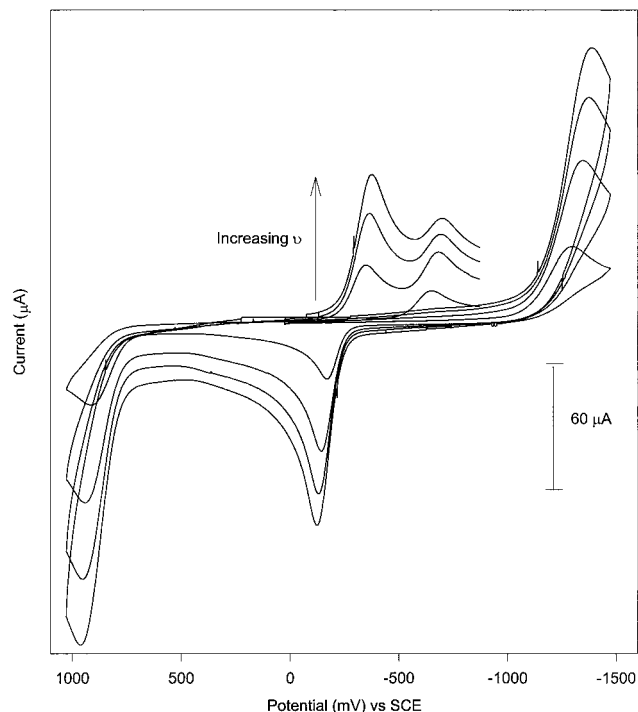
C–H correlation. The elemental analysis for the compound was inconclusive due to lack of internal consistency in duplicate analyses as observed previously for related complexes where sodium mineral oil dispersions were used in the preparation.<sup>8a</sup>

The UV-vis spectra for the dimer show two absorption bands, a higher energy band at  $\lambda = 386$  nm ( $\epsilon = 12\,900$  M<sup>-1</sup> cm<sup>-1</sup>) and a broad low-energy band at  $\lambda = 503$  nm ( $\epsilon = 1530$  M<sup>-1</sup> cm<sup>-1</sup>) in DMF. By comparison to literature data,<sup>5</sup> we assign the high-energy peak to a  $\sigma \rightarrow \sigma^*$  transition leading to carbonyl expulsion. The absorption into the low-energy band is a ligand field transition with  $d\pi \rightarrow d\sigma^*$  character that results in metal–metal bond homolysis.<sup>1,2</sup> Shown in Table 1 are the IR and electrochemical results for the pendant Cp dimer, **I**, along with related data for analogous dimers. A comparison of infrared data and electrochemical data indicates the typical pattern expected for a monosubstituted cyclopentadienyl ligand including a set of two irreversible oxidations (eqs 2, 3) and two irreversible reductions (eqs 1, 4), Table 1.

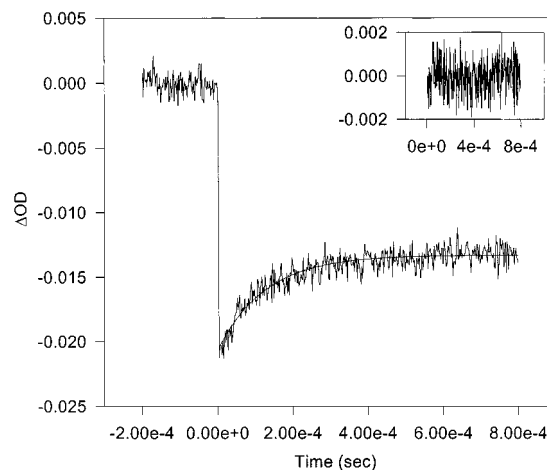


The cyclic voltammetry (CV) of dimer **I** in DMF as shown in Figure 2 is highly scan rate dependent. This CV result is notably different from previous reports in the literature.<sup>2,7</sup> On the basis of earlier work, the peaks at slow scan rates (<100 mV/s) could be assigned according to eqs 1–4. The unstable dimeric anion is formed initially at reductive potentials. It undergoes metal–metal bond homolysis to form the 17-electron radical, CpMo(CO)<sub>3</sub>, and the anion, [CpMo(CO)<sub>3</sub>]<sup>-</sup>. The radical is immediately reduced to the anion, **IV**, setting an upper limit to the reduction potential. Likewise, an unstable dimeric cation is formed upon initial oxidation. After metal–metal bond homolysis of **I** and subsequent oxidation of the 17-electron radical, two 16-electron cations are formed, **II**.

As the cyclic voltammetric scan rate is increased from 100 to 1500 mV/s, an additional reduction appears at -0.34 V vs SCE. The increase in intensity of this new reduction is coupled to the decrease in intensity of the original cation reduction -0.68 V. The additional reduction is not present for any other substituted or unsubstituted cyclopentadienyl group 6 dimer complexes even at scan rates exceeding 10 V/s. These earlier experiments were typically conducted in less coordinating solvents such as acetonitrile and DMF. However, it was demonstrated that even coordinating solvents such as THF do not show the additional reduction in the absence of the pendant ligand.



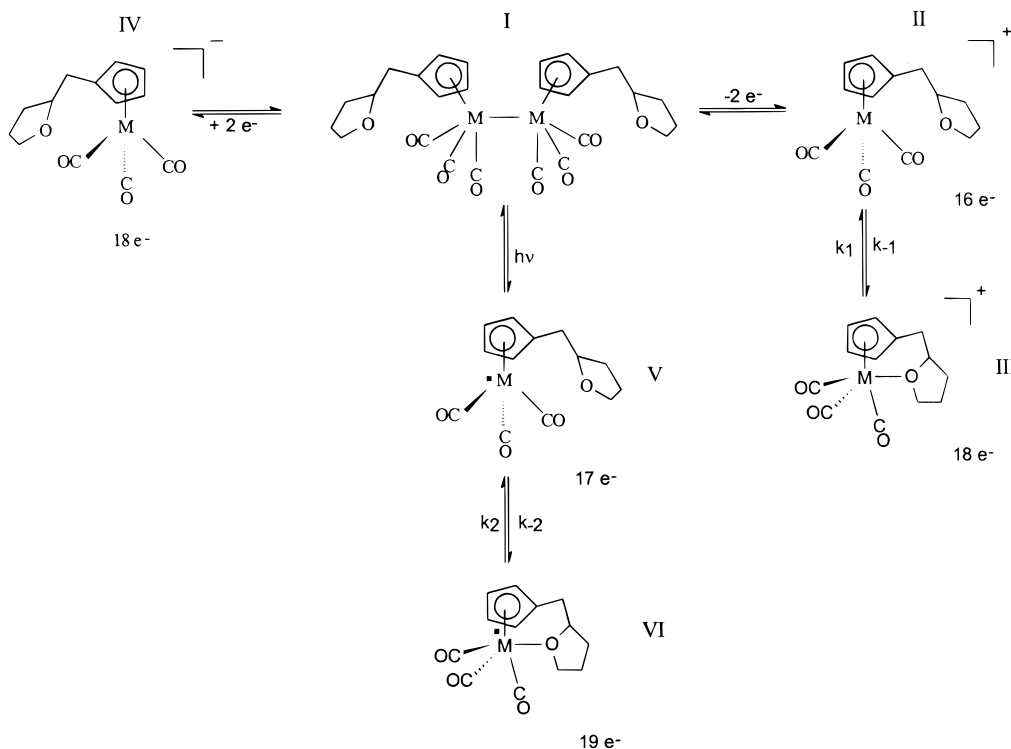
**Figure 2.** Electrochemistry of  $[\text{Cp}^{\text{P}}\text{Mo}(\text{CO})_3]_2$  in 0.1 M TBAH/CH<sub>3</sub>CN solution. Cyclic voltammogram of  $9.1 \times 10^{-4}$  M of  $[\text{Cp}^{\text{P}}\text{Mo}(\text{CO})_3]_2$  in 0.1 M TBAH/CH<sub>3</sub>CN at scan rates of 100, 500, 1000, and 1500 mV s<sup>-1</sup>. Initial negative scan. All potentials are reported versus SCE.



**Figure 3.** Transient absorption trace of  $[\text{Cp}^{\text{P}}\text{Mo}(\text{CO})_3]_2$  in DMF with residuals and curve fit.

## Discussion

There are a few reports in the literature of the use of tetrahydrofurfurylcyclopentadiene.<sup>8a,10–13</sup> This may be attributed to the fact that the ligand was isolated in relatively low yield through a challenging vacuum distillation. It can be seen in the

**Scheme 1.** Proposed Mechanism for Electrochemical and Photochemical Processes of the  $[\text{Cp}^{\text{P}}\text{Mo}(\text{CO})_3]_2$  Dimer

H,H-COSY of the final product that there was a small amount of hydrocarbon contamination in the  $\text{HCp}^{\text{P}}$  sample. The contamination persisted through numerous redistillations under varying dynamic vacuum conditions. It is due to the sodium mineral oil dispersion used in the preparation. This contamination did not interfere with subsequent reactions and has been reported previously.<sup>8a</sup>

Sodium and potassium tetrahydrofurfurylcyclopentadienide have both been reported in the literature.<sup>10,11</sup> These syntheses were accomplished with metallic sodium and potassium rather than potassium hydride. As in this report, the metalated ligand is generally used for subsequent syntheses with only minimal characterization. This report represents the first preparation of a dimeric complex containing a THF pendant Cp group.

The electrochemical experiments establish that two different species exist at early times following dimer oxidation, eq 3. We assign these species as the bare Cp cation, **II**, and the intramolecularly coordinated, THF-substituted cation, **III**. By comparison with the observed peak potential for reduction of  $[\text{Cp}^{\text{P}}\text{Mo}(\text{CO})_3]^+$  in THF, we assign the reduction at  $-0.68$  V vs SCE to the intramolecularly coordinated solvento cation. The additional reduction peak that exists at fast scan rates can be assigned to the reduction of the bare cation, eq 4. These assignments are also consistent with the more electron rich nature of the coordinated solvento complex, **III**. The electrochemical system was observed to be chemically reversible, reforming the dimer following cyclic voltammetry, indicating that if the solvento cation were involved it must be in dynamic equilibrium with the bare cation.

Earlier studies have shown that facile rearrangement of a tethered ligand around a metal center results in formation of a more stable intermediate.<sup>17</sup> Transient absorption measurements of the dimer, **I**, in room temperature DMF solution were used to directly explore the stability of the intermediates formed following photolysis. There was a decrease in the low-energy

visible absorption at  $\lambda_{\text{max}} = 503$  nm following laser photolysis at 500 nm. This has previously been assigned to a metal–metal bond homolysis in which two identical 17-electron radicals are formed, **V** in Scheme 1.<sup>1–3</sup> The loss of absorption monitored at 410 nm does not return to base line on a time scale of seconds, indicating partial irreversibility of the photochemical process (Figure 3). A kinetic analysis of the return of the absorption at 410 nm is best fit by the function  $y = A \exp^{-kt} + C$ , where  $C$  is a constant equal to the new base line that is established after 5 ms. This result is consistent with a first-order kinetic process with a rate of  $5 \times 10^3 \text{ s}^{-1}$ . This rate is substantially slower than the bimolecular recombination rate observed for the  $[\text{CpMo}(\text{CO})_3]_2$  dimer previously.<sup>2</sup> The decreased rate constant and apparent unimolecular kinetics are consistent with formation of an intramolecularly coordinated solvento, odd-electron complex, **VI**. By inference, this provides additional support for the involvement of the coordinated solvent ligand in the electrochemical results above.

Previous work in this area has concentrated on intermolecular interactions in group 6, 17-electron radical intermediates of the form  $\text{CpM}(\text{CO})_3$ .<sup>1–3</sup> This result is the first direct observation and characterization that we are aware of involving an intramolecularly coordinated solvent species to generate an odd-electron transition metal radical. This type of interaction gives rise to electronic and physical properties not observed or characterized previously which may prove useful in catalysis and electron transfer. Further, the new series of complexes can help to shed new light on the dynamic equilibrium that is established between 17-electron complexes and electron rich solvents.

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