

# New General Synthetic Strategy of Fulvalene Homodinuclear Zwitterions. Electrochemical Behavior of $(\eta^5\text{-}\eta^5\text{-(C}_5\text{H}_3\text{CO}_2\text{Me)}_2\text{)Mo}_2\text{(CO)}_6\text{R}_2$ (R = I, Me)

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The reaction of  $\text{Li}_2[(\eta^5\text{-}\eta^5\text{-(C}_5\text{H}_3\text{CO}_2\text{Me)}_2\text{)Mo}_2\text{(CO)}_6]$  (from *trans*- $(\eta^5\text{-}\eta^5\text{-(C}_5\text{H}_3\text{CO}_2\text{Me)}_2\text{)Mo}_2\text{(CO)}_6$ ) (**1**) with MeI yields  $(\eta^5\text{-}\eta^5\text{-(C}_5\text{H}_3\text{CO}_2\text{Me)}_2\text{)Mo}_2\text{(CO)}_6\text{Me}_2$  (**3**). The reaction of *cis*- $(\eta^5\text{-}\eta^5\text{-(C}_5\text{H}_3\text{CO}_2\text{Me)}_2\text{)Mo}_2\text{(CO)}_6$  (**2**) with I<sub>2</sub> leads to the formation of  $(\eta^5\text{-}\eta^5\text{-(C}_5\text{H}_3\text{CO}_2\text{Me)}_2\text{)Mo}_2\text{(CO)}_6\text{I}_2$  (**4**). The X-ray structure of **4** has been determined. The reactions of **1** with P-donor nucleophiles (PPhMe<sub>2</sub>, PPh<sub>2</sub>Me, P(n-Bu)<sub>3</sub>, and PMe<sub>3</sub>) and  $(\eta^5\text{-}\eta^5\text{-(C}_{10}\text{H}_8\text{)M}_2\text{(CO)}_6$  (M = Mo and W) with PMe<sub>3</sub>, in the presence of 1 equiv of Me<sub>3</sub>NO, produce CO labilization and formation of the dinuclear zwitterions  $(\eta^5\text{-}\eta^5\text{-(C}_5\text{H}_3\text{CO}_2\text{Me)}_2\text{)Mo}_2\text{(CO)}_5\text{L}_2$  and  $(\eta^5\text{-}\eta^5\text{-(C}_{10}\text{H}_8\text{)-M}_2\text{(CO)}_5\text{(PMe}_3\text{)}_2$  (M = Mo and W) **5**, **6**, **7**, **8**, **9**, and **10**, respectively). The dimer  $[(\eta^5\text{-C}_5\text{H}_4\text{-CO}_2\text{Me)Mo(CO)}_3]_2$  (**11**) was obtained by reaction of Mo(CO)<sub>6</sub> with sodium carbomethoxy cyclopentadienide in THF followed by oxidation with ferric sulfate. The reaction of **11** with PPh<sub>2</sub>Me in the presence of 1 equiv of Me<sub>3</sub>NO gives the disproportionation species  $[(\eta^5\text{-C}_5\text{H}_4\text{-CO}_2\text{Me)Mo(CO)}_2\text{(PPh}_2\text{Me)}_2]^+[(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{Me)Mo(CO)}_3]^-$  (**12**). The electrochemical study of **3** and **4** is reported. Two distinct cathodic waves are observed in the voltammetric reduction of **4**, the less negative one with a coupled anodic peak at high sweep rates in PC.

## Introduction

Organometallic compounds that incorporate two or more reactive metal sites in close proximity might provide access to reaction pathways not available to mononuclear systems as a result of cooperative electronic and/or steric effects.<sup>1</sup> A known ready access to dinuclear complexes is using the fulvalene ligand (Fv), in which the Cp moieties are directly attached to each other without intervening bridging groups. The high yield syntheses have facilitated the exploration of the chemistry of such species in detail.<sup>2</sup>

In contrast to the well-studied cyclopentadienylmetal carbonyl dimers, the fulvalene-bridged analogues are expected to show, and have shown in several cases, enhanced reactivity. This is due, in part, to the ability of the fulvalene ligand to allow for metal–metal bond cleavage while inhibiting fragmentation to mononuclear

complexes; metal–metal cooperativity can be maintained through relative proximity and possibly by communication through the  $\pi$ -bond system of the fulvalene ligand.<sup>3</sup> The presence of significant electronic communication is supported by the report that FvRh<sub>2</sub>(CO)<sub>2</sub>-(PPh<sub>3</sub>)<sub>2</sub> underwent a reversible, two-electron oxidation at 0.01 V vs SCE, whereas CpRh(CO)(PPh<sub>3</sub>) underwent a one-electron oxidation at 0.43 V.<sup>4</sup> The large difference in oxidation potentials suggests that special stabilization is provided to the cation in the former case. Additional evidence for electronic communication through the Fv ligand was provided by the observation<sup>3</sup> that the radical cation FvFe<sub>2</sub>(HMB)<sub>2</sub><sup>2+</sup> (HMB = hexamethylbenzene), in which the Fe atoms may safely be assumed to be located anti with respect to the Fv ligand, had only one type of Fe atom, as found by Mössbauer spectroscopy even at 4.2 K (time scale of experiment: ca. 10<sup>-9</sup> s), and FvFe<sub>2</sub>(HMB)<sub>2</sub> exists as a diradical,<sup>3</sup> demonstrating that while there may be electronic communication between the metal centers, this does not necessarily lead to spin pairing of electrons. Finally, it was shown that the cation radical of FvMn<sub>2</sub>(CO)<sub>4</sub>( $\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) had a delocalized charge on the ESR time scale (10<sup>-8</sup> s) but not on the IR spectroscopy time scale (10<sup>-12</sup> s),<sup>5</sup> and it has recently been reported that the zwitterionic complex

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FvMo<sub>2</sub>(CO)<sub>5</sub>(PMe<sub>3</sub>)<sub>2</sub> undergoes a decomplexation reaction in the presence of excess PMe<sub>3</sub>, yielding FvMo(CO)<sub>2</sub>-(PMe<sub>3</sub>)<sub>2</sub>. This clearly demonstrates the occurrence of electronic communication through the  $\pi$  system of the Fv ligand.<sup>6</sup>

There is currently considerable interest in the chemistry of 17-electron organotransition-metal radicals.<sup>7</sup> In the fulvalene compounds, a potential route to prepare biradicals could involve abstraction of hydrogen atoms from substituted hydrides, an approach that has been extensively utilized for the synthesis of simple 17-electron compounds<sup>8</sup> and has been shown to be of general utility. In this way, complexes of the type *trans*-FvM<sub>2</sub>(CO)<sub>4</sub>L<sub>2</sub> (M = Mo, Cr; L = PPh<sub>3</sub>, PCy<sub>3</sub>, PMe<sub>2</sub>Ph)<sup>2c,9</sup> have been prepared.

The synthesis of ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> has been recently reported.<sup>10</sup> Two pure isomers *trans* (**1**) and *cis* (**2**) were easily isolated by thin-layer chromatography (TLC), and each of them has been well characterized. In contrast, the purification of FvMo<sub>2</sub>(CO)<sub>6</sub> is rather difficult. For this reason, in this paper we report the reactions of ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> (isomers *cis* and *trans*) with I<sub>2</sub> and MeI. The electrochemical behavior of the fulvalene complexes has been studied in different solvents in order to evaluate the possibility of electronic communication via the  $\pi$  system of the fulvalene ligand. A comparative study of the effect of the substituent on the fulvalene ring (H, Me, CO<sub>2</sub>Me) on the electrochemical behavior of related compounds has recently been published.<sup>11</sup>

Direct substitution of the carbonyl ligands in FvM<sub>2</sub>(CO)<sub>6</sub> (M = Cr, Mo, W) with tertiary phosphines does not generally occur.<sup>6,12</sup> In addition, with very few exceptions, no fulvalene complexes are known with ligands larger than the relatively small PMe<sub>3</sub>,<sup>12b</sup> and recently the preparation of FvMo<sub>2</sub>(CO)<sub>4</sub>L<sub>2</sub> (L = PPh<sub>3</sub>, PCy<sub>3</sub>, PXy<sub>3</sub>) by reduction of the fulvalene halomolybdenum compounds FvMo<sub>2</sub>(CO)<sub>4</sub>L<sub>2</sub>X<sub>2</sub> (X = Cl, Br, I)<sup>13</sup> has been described.

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Trimethylamine *N*-oxide has been shown to be a valuable synthetic reagent in the preparation of substituted metal carbonyl complexes. For example, the reaction of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)M(CO)<sub>3</sub>X (M = Mo, W; X = halide) with phosphines proceeds rapidly at room temperature in the presence of Me<sub>3</sub>NO to yield *cis*- $\eta^5$ -C<sub>5</sub>H<sub>5</sub>M(CO)<sub>2</sub>-LX,<sup>14</sup> and recently it has been reported that the reaction of FvMo<sub>2</sub>(CO)<sub>6</sub> with alkynes in the presence of Me<sub>3</sub>NO gives alkyne–dimolybdenum tetrahedral clusters FvMo<sub>2</sub>(CO)<sub>4</sub>(RC(CCR<sub>2</sub>(OMe)).<sup>2d</sup>

In this work, we describe a new general strategy of synthesis of substituted carbonyl fulvalene dimolybdenum compounds by direct substitution of carbonyl ligands in ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> [isolated as isomers **1** (*trans*) and **2** (*cis*)]<sup>10</sup> and ( $\eta^5$ : $\eta^5$ -C<sub>10</sub>H<sub>8</sub>)M<sub>2</sub>(CO)<sub>6</sub> (M = Mo and W) with phosphines of different electronic and steric properties in the presence of Me<sub>3</sub>NO to give the dinuclear *zwitterions* ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>5</sub>L<sub>2</sub> (L = PPhMe<sub>2</sub>, PPh<sub>2</sub>Me, P(*n*-Bu)<sub>3</sub>, and PMe<sub>3</sub>). With phosphines of larger steric demand, such as PPh<sub>3</sub> and PCy<sub>3</sub>, no reactions occur. The reactivity of ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>5</sub>(PMe<sub>3</sub>)<sub>2</sub> with CF<sub>3</sub>COOH clearly reflects the zwitterionic nature of this system.

## Experimental Section

**Materials.** All manipulations were carried out by using standard Schlenk vacuum-line and syringe techniques under an atmosphere of oxygen-free Ar. All solvents for synthetic use were reagent grade. 1,2-Dimethoxyethane (DME), hexane, and tetrahydrofuran (THF) were dried and distilled over sodium in the presence of benzophenone ketyl under an Ar atmosphere; dichloromethane and 1,2-dichloroethane (DCE) were dried and distilled over CaH<sub>2</sub> under an Ar atmosphere. Also under an Ar atmosphere acetone was dried and distilled over CaCl<sub>2</sub> and propylene carbonate (PC) was stored over molecular sieves (5 Å). Acetonitrile (AN) anhydrous was used as received (Aldrich). All solvents were bubbled with Ar for 1 h after distillation and then stored under Ar or degassed by means of at least three freeze–pump–thaw cycles after distillation and before use. Column chromatography was performed by using Alfa neutral alumina at activity II. Methyl iodide, Li(Et)<sub>3</sub>BH, trifluoroacetic acid (TFA), PPhMe<sub>2</sub>, PPh<sub>2</sub>Me, and PMe<sub>3</sub> were used as received (Aldrich). P(*n*-Bu)<sub>3</sub> was purified by distillation under reduced pressure of argon immediately before use. Me<sub>3</sub>NO was sublimed prior to use and stored under argon. The compounds *trans*- and *cis*-( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> (**1** and **2**), Li<sub>2</sub>( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>-Mo<sub>2</sub>(CO)<sub>6</sub>, Na( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>Me), ( $\eta^5$ : $\eta^5$ -C<sub>10</sub>H<sub>8</sub>)Mo<sub>2</sub>(CO)<sub>6</sub>, and ( $\eta^5$ : $\eta^5$ -C<sub>10</sub>H<sub>8</sub>)W<sub>2</sub>(CO)<sub>6</sub> were prepared according to literature procedures,<sup>10,15,16</sup> and all reagents were used without further purification unless otherwise noted.

( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub>Me<sub>2</sub> (**3**). A solution of 0.14 g (0.23 mmol) of Li<sub>2</sub>( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> [obtained from ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> *trans* isomer (**1**)] in 20 mL of THF at 0 °C was prepared, and then 0.030 mL (1:1) of MeI was added by syringe. The reaction was monitored by IR spectroscopy. The solvent was removed under vacuum, and the product was purified by TLC using acetone/hexane (1:1) as eluent. A yellow-brownish solid was obtained (92% yield). IR (THF):  $\nu_{\text{CO}}$  2020 (s), 1971 (vs), 1732 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  5.99 (dd, 2H), 5.71 (t, 2H), 5.56 (dd, 2H),

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3.69 (s, 6H), 0.51 (s, 6H). UV (THF):  $\lambda_{\max}$  368 nm. Anal. Calcd for  $C_{22}H_{18}Mo_2O_{10}$ : C, 41.66; H, 2.86. Found: C, 41.5; H, 2.9.

**( $\eta^5$ : $\eta^5$ - $C_5H_3CO_2Me$ ) $_2Mo_2(CO)_6I_2$  (**4**).** A solution of 0.7 g (1.2 mmol) of ( $\eta^5$ : $\eta^5$ - $C_5H_3CO_2Me$ ) $_2Mo_2(CO)_6$  (cis isomer, **2**) in 20 mL of THF was prepared, and then 0.29 g (1.2 mmol) of  $I_2$  was added dropwise by transfer with constant stirring. The color immediately turned from purple to red. The reaction was monitored by IR spectroscopy. The solvent was removed under vacuum. Purification by thin-layer chromatography (TLC) using  $CH_2Cl_2$ /hexane (1:1) as eluent gave ( $\eta^5$ : $\eta^5$ - $C_5H_3CO_2Me$ ) $_2Mo_2(CO)_6I_2$  as the major product in 90% yield. IR (THF):  $\nu_{CO}$  2046 (vs), 1979 (vs), 1734 (m)  $cm^{-1}$ .  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  6.45 (dd, 2H), 5.97 (dd, 2H), 5.57 (t, 2H), 3.87 (s, 6H). UV (THF):  $\lambda_{\max}$  498 nm. Anal. Calcd for  $C_{20}H_{12}Mo_2I_2O_{10}$ : C, 28.00; H, 1.41. Found: C, 27.8; H, 1.5.

**( $\eta^5$ : $\eta^5$ - $C_5H_3CO_2Me$ ) $_2Mo_2(CO)_5(PPhMe_2)_2$  (**5**).** Trimethylamine *N*-oxide is utilized to chemically oxidize and remove one CO molecule. The same general procedure was followed in the preparation of all dinuclear zwitterions. A solution of 0.15 g (0.25 mmol) of ( $\eta^5$ : $\eta^5$ - $C_5H_3CO_2Me$ ) $_2Mo_2(CO)_6$  (trans isomer, **1**) and 0.069 g (0.50 mmol) of  $PPhMe_2$  in 25 mL of THF was prepared. Trimethylamine *N*-oxide (0.019 g, 0.25 mmol) was added with vigorous magnetic stirring. The color immediately turned from purple to yellow. The solution was stirred until the reaction was seen to be completed by IR spectroscopy. After 10 min, no starting material remained. Solvent removal followed by recrystallization ( $CH_2Cl_2$ -hexane, at  $-20^\circ C$ ) afforded 0.20 g of yellow-brown crystalline product (95% yield). UV (THF)  $\lambda_{\max}$  460 nm. Anal. Calcd for  $C_{35}H_{34}Mo_2O_9P_2$ : C, 49.31; H, 4.02. Found: C, 49.0; H, 4.1.

**( $\eta^5$ : $\eta^5$ - $C_5H_3CO_2Me$ ) $_2Mo_2(CO)_5(PPh_2Me)_2$  (**6**):** from 0.10 g (0.50 mmol) of  $PPh_2Me$  and 0.019 g (0.25 mmol) of  $Me_3NO$ ; yellow-brown needles (98% yield). MS:  $m/e$  976.6 ( $M^+$ ), 776.4 ( $-PPh_2Me$ ), 548.2 ( $-PPh_2Me$ ). UV (THF)  $\lambda_{\max}$  484 nm. Anal. Calcd for  $C_{45}H_{38}Mo_2O_9P_2$ : C, 55.34; H, 3.92. Found: C, 55.0; H, 4.0.

**( $\eta^5$ : $\eta^5$ - $C_5H_3CO_2Me$ ) $_2Mo_2(CO)_5[P(n-Bu)_3]_2$  (**7**):** from 0.10 g (0.50 mmol) of  $P(n-Bu)_3$  and 0.019 g (0.25 mmol) of  $Me_3NO$ ; yellow needles (92% yield). MS:  $m/e$  782 ( $M^+ - P(n-Bu)_3$ ). UV (THF)  $\lambda_{\max}$  448 nm. Anal. Calcd for  $C_{43}H_{66}Mo_2O_9P_2$ : C, 52.66; H, 6.78. Found: C, 52.4; H, 6.9.

**( $\eta^5$ : $\eta^5$ - $C_5H_3CO_2Me$ ) $_2Mo_2(CO)_5(PMe_3)_2$  (**8**):** from 0.038 g (0.50 mmol) of  $PMe_3$  and 0.019 g (0.25 mmol) of  $Me_3NO$ ; yellow-brown needles (80% yield). UV (THF)  $\lambda_{\max}$  445 nm. Anal. Calcd for  $C_{25}H_{30}Mo_2O_9P_2$ : C, 41.23; H, 4.18. Found: C, 41.2; H, 4.2.

**( $\eta^5$ : $\eta^5$ - $C_{10}H_8$ ) $Mo_2(CO)_5(PMe_3)_2$  (**9**):** from 0.122 g (0.25 mmol) of ( $\eta^5$ : $\eta^5$ - $C_{10}H_8$ ) $Mo_2(CO)_6$ , 0.038 g (0.50 mmol) of  $PMe_3$  and 0.019 g (0.25 mmol) of  $Me_3NO$ ; yellow-brown needles (95% yield). The product was identified by comparing their FTIR,  $^1H$  and  $^{31}P$  NMR, and FAB-MS spectra data with those previously reported.<sup>6</sup>

**( $\eta^5$ : $\eta^5$ - $C_{10}H_8$ ) $W_2(CO)_5(PMe_3)_2$  (**10**):** from 0.166 g (0.25 mmol) of ( $\eta^5$ : $\eta^5$ - $C_{10}H_8$ ) $W_2(CO)_6$ , 0.038 g (0.50 mmol) of  $PMe_3$ , and 0.019 g (0.25 mmol) of  $Me_3NO$ ; yellow-brown needles (90% yield). The product was identified by comparing their FTIR,  $^1H$  and  $^{31}P$  NMR, and FAB-MS spectra data with those previously reported.<sup>6</sup>

**[( $\eta^5$ - $C_5H_4CO_2Me$ ) $Mo(CO)_3]_2$  (**11**).** Using one of the general methods for the synthesis of  $[CpMo(CO)_3]_2$ ,<sup>17</sup> a solution of 2.68 g (0.018 mol) of  $Na(\eta^5-C_5H_4CO_2Me)$  and 4.85 g (0.018 mol) of  $Mo(CO)_6$  in THF was refluxed for 18 h to obtain  $Na[(\eta^5-C_5H_4CO_2Me)Mo(CO)_3]$ . The solution was cooled to room temperature, and a mixture of ferric sulfate (7.72 g) and acetic acid (13 mL) in water was added over a period of 30 min. The color changed from yellow-reddish to red, and dark red crystals of the dimer precipitated. These were filtered off, washed with water, methanol, and hexane, and dried in vacuo (95% yield).

IR (THF):  $\nu_{CO}$  2018 (s), 1972 (s), 1924 (vs), 1731 (s)  $cm^{-1}$ .  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  5.85 (m, 4H), 5.28 (m, 4H), 3.84 (s, 6H). UV (THF)  $\lambda_{\max}$  508, 387 nm. Anal. Calcd for  $C_{20}H_{14}Mo_2O_{10}$ : C, 39.63; H, 2.33. Found: C, 39.4; H, 2.4.

**( $\eta^5$ - $C_5H_4CO_2Me$ ) $Mo(CO)_2(PPh_2Me)_2^+[(\eta^5-C_5H_4CO_2Me)Mo(CO)_3^-]$  (**12**).** To a solution of 0.5 g (0.82 mmol) of  $[(\eta^5-C_5H_4CO_2Me)Mo(CO)_3]_2$  and 0.33 g (1.65 mmol) of  $PPh_2Me$  in THF (50 mL) was added  $Me_3NO$  (0.062 g, 0.82 mmol) with stirring. The color turned from dark red to yellow instantly. The solution was stirred for 15 min, after which a yellow precipitate formed. The volatiles were removed by vacuum, and the residue was washed with hexane and dried in vacuo (95% yield). UV (THF)  $\lambda_{\max}$  489 nm. Anal. Calcd for  $C_{45}H_{40}Mo_2O_9P_2$ : C, 55.23; H, 4.12. Found: C, 55.1; H, 4.3.

**Instruments.** The  $^1H$  NMR spectra were recorded on a Bruker AMX-300 instrument. Chemical shifts were measured relative either to an internal reference of tetramethylsilane or to residual protons of the solvents. FTIR spectra were obtained by using a Perkin-Elmer 1650 infrared spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the University Autónoma de Madrid on a Perkin-Elmer 240 B microanalyzer. Electronic spectra were recorded on a Pye Unicam SP 8-100 UV-visible spectrophotometer. Mass spectra were measured on a VG-Autospec mass spectrometer for FAB or AIE by the Mass Laboratory of the University Autónoma de Madrid.

**X-ray Crystallography.** Orange, block-shaped crystals of ( $\eta^5$ : $\eta^5$ - $(C_5H_3CO_2Me)_2$ ) $Mo_2(CO)_6I_2$ , **4**, are obtained by recrystallization of the complex from  $CH_2Cl_2$ /hexane mixtures. Intensity data were collected on a Siemens P4 diffractometer using graphite-monochromated Mo  $K\alpha$  radiation. The unit cell dimensions were determined and refined using the positions of 45 high-angle reflections ( $19^\circ < 2\theta < 40^\circ$ ). The intensities of three standard reflections measured every 97 reflections showed no decay during data collection. The cell unit parameters and intensity data provided strong evidence for the centric space group  $P\bar{1}$ . The structure was successfully solved and refined in this space group. Lorentz, polarization, and background corrections were applied to the data using the Siemens P4 software.<sup>18</sup> The position of the Mo atom was solved by the Patterson method, and the remaining non-H atoms were located by successive difference Fourier syntheses. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques on  $F^2$ . The H-atom positions were calculated and the atoms were constrained as riding atoms with  $U$  isotropic 20% larger than the corresponding C atom. No secondary extinction correction was applied to the data. All calculations were performed using SHELXTL Version 5 on a personal computer.<sup>18</sup>

Selected experimental details of the X-ray determination are given in Table 1. Final positional parameters, anisotropic thermal parameters, hydrogen atom parameters, and structure amplitudes are available as Supporting Information. Table 2 contains selected bond distances and angles. Figure 1 presents a molecular diagram of **4**.

**Electrochemical Measurements.** A computer-driven PAR model 273 electrochemistry system with positive feedback *iR* compensation was employed. Measurements were carried out in a three-electrode cell under  $N_2$  atmosphere in anhydrous deoxygenated solvent (PC, AN, DCE, and THF) containing 0.2 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as supporting electrolyte. Temperature was maintained constant at  $25^\circ C$ .

Cyclic voltammetry studies were made on a pc-Pt working electrode (0.05  $cm^2$  real surface area, as calculated in a separate experiment through the H adatom charge in 0.5 M  $H_2SO_4$  solution<sup>19</sup>). The counter electrode was a Pt gauze. The reference electrode was an Ag wire quasi-reference electrode

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**Table 1. Crystal Data and Structure Refinement for 4**

empirical formula	C <sub>20</sub> H <sub>12</sub> I <sub>2</sub> Mo <sub>2</sub> O <sub>10</sub>	
fw	857.98	
temp	173(2) K	
wavelength	0.71073 Å	
cryst syst	triclinic	
space group	P $\bar{1}$	
unit cell dimens	$a = 7.3610(10)$ Å	$\alpha = 115.80^\circ$
	$b = 9.504(2)$ Å	$\beta = 98.17^\circ$
	$c = 10.485(2)$ Å	$\gamma = 103.95^\circ$
vol, Z	614.8(2) Å <sup>3</sup> , 1	
density (calcd)	2.317 Mg/m <sup>3</sup>	
abs coeff	3.582 mm <sup>-1</sup>	
F(000)	402	
cryst size	0.10 × 0.05 × 0.08 mm	
$\theta$ range for data collection	2.53–26.00°	
limiting indices	0 ≤ $h$ ≤ 9, -10 ≤ $k$ ≤ 9, -12 ≤ $l$ ≤ 12	
no. of reflns collected	2443	
no. of independent reflns	2262 [ $R(\text{int}) = 0.0406$ ]	
refinement method	full-matrix least-squares on $F^2$	
no. of data/restraints/param	2262/0/155	
goodness-of-fit on $F^2$	0.772	
final $R$ indices [ $I > 2(I)$ ]	$R1 = 0.0407$ , $wR2 = 0.0710$	
$R$ indices (all data)	$R1 = 0.0884$ , $wR2 = 0.0816$	
largest diff peak and hole	0.675 and -0.693 e Å <sup>-3</sup>	

**Table 2. Bond Lengths [Å] and Angles [deg] for 4<sup>a</sup>**

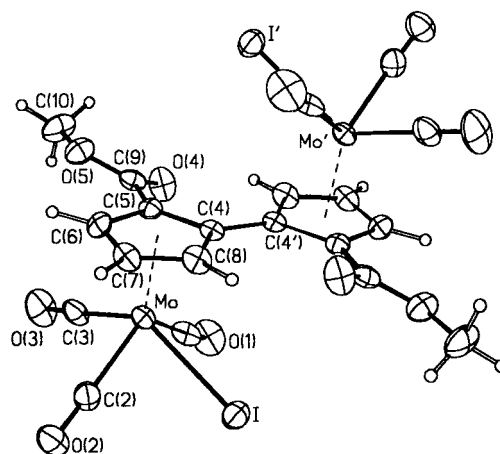
Mo–C(1)	2.019(10)	C(3)–O(3)	1.152(10)
Mo–C(2)	2.038(9)	C(4)–C(4')	1.45(2)
Mo–C(3)	1.999(10)	C(4)–C(8)	1.456(11)
Mo–C(4)	2.345(8)	C(4)–C(5)	1.465(11)
Mo–C(5)	2.287(8)	C(5)–C(6)	1.434(11)
Mo–C(6)	2.297(8)	C(5)–C(9)	1.520(11)
Mo–C(7)	2.371(8)	C(6)–C(7)	1.416(11)
Mo–C(8)	2.386(8)	C(7)–C(8)	1.393(12)
Mo–I	2.8384(11)	C(9)–O(4)	1.207(10)
C(1)–O(1)	1.137(10)	C(9)–O(5)	1.322(11)
C(2)–O(2)	1.146(10)	O(5)–C(10)	1.462(9)
C(3)–Mo–C(1)	77.2(4)	C(8)–C(4)–C(5)	104.4(7)
C(3)–Mo–C(2)	80.3(3)	C(6)–C(5)–C(4)	108.0(7)
C(1)–Mo–C(2)	111.7(4)	C(6)–C(5)–C(9)	118.7(7)
C(1)–Mo–I	75.7(3)	C(4)–C(5)–C(9)	133.3(7)
C(2)–Mo–I	75.9(3)	C(7)–C(6)–C(5)	109.0(7)
C(3)–Mo–I	133.6(3)	C(8)–C(7)–C(6)	107.8(7)
O(1)–C(1)–Mo	174.9(8)	C(7)–C(8)–C(4)	110.9(7)
O(2)–C(2)–Mo	176.4(9)	O(4)–C(9)–O(5)	125.7(8)
O(3)–C(3)–Mo	176.6(8)	O(4)–C(9)–C(5)	124.6(8)
C(4)–C(4)–C(8)	125.7(9)	O(5)–C(9)–C(5)	109.7(8)
C(4)–C(4)–C(5)	129.6(9)	C(9)–O(5)–C(10)	115.1(7)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms:  $-x+1, -y+1, -z$ .

(QRE), pretreated by immersion in 10 M HNO<sub>3</sub> for 5 min before use. After a series of experiments, the QRE potential was calibrated by adding ferrocene (Fc) to the solution and taking voltammograms of the Fc<sup>+</sup>/Fc system. All potentials in this paper were then referred to the Fc<sup>+</sup>/Fc couple, which IUPAC recommends as an internal standard.<sup>20,21</sup> Controlled potential coulometry studies were made on a large area Pt working electrode.

## Results and Discussion

**Diiodide and Dimethyl Complexes ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub>X<sub>2</sub> (X = I, Me).** The diiodide complex ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub>I<sub>2</sub> (**4**) has been prepared in a quantitative yield from ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>-Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub><sup>10</sup> (isomer **2**, CO<sub>2</sub>Me groups in cis) and I<sub>2</sub>



**Figure 1.** A view of molecule **1** with 25% probability ellipsoids. For clarity, H atoms are represented as open spheres.

in THF. The IR spectrum exhibits two absorption bands at 2046 and 1799 cm<sup>-1</sup> associated with terminal Mo–CO stretching ( $\nu_{\text{CO}}$ ) modes and a third at 1734 cm<sup>-1</sup> associated with  $\nu_{\text{CO}}$  of the CO<sub>2</sub>Me group. The <sup>1</sup>H NMR spectrum shows three Fv signals at  $\delta$  6.45, 5.97, and 5.57 and a singlet signal at 3.87 arising from the methyl protons of the CO<sub>2</sub>Me group. These results are in agreement with the analogous previously reported FvMo<sub>2</sub>(CO)<sub>6</sub>I<sub>2</sub> complex.<sup>22</sup>

The treatment of Li<sub>2</sub>[( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub>] (from isomer **1**, CO<sub>2</sub>Me groups in trans) with MeI produced the methylated complex ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>-Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub>Me<sub>2</sub> (**3**) in high yield. In the IR spectrum there are two terminal carbonyl stretching absorptions at 2020 and 1971 cm<sup>-1</sup>, which are indicative of C<sub>s</sub> symmetry for each metal atom. The <sup>1</sup>H NMR spectrum shows three resonances (ABX system) at 5.56, 5.71, and 5.99 due to the Fv ligand and two singlets at 3.69 and 0.51 due to the methyl protons of CO<sub>2</sub>Me and Me groups, respectively. These data are consistent with the expected structure for **3** based on the comparison with ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub>I<sub>2</sub>, whose molecular structure is reported in this paper.

**Description of the Crystal and Molecular Structure of ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub>I<sub>2</sub> (**4**).** The crystal structure consists of one discrete molecule of **4** per unit cell. Complex **4** possesses a crystallographically imposed center of inversion. The two Mo(CO)<sub>3</sub>I units are on opposite sides of a carbomethoxy-substituted Fv ligand, as shown in Figure 1. The Fv ligand adopts the 1,1'-( $\eta^5$ : $\eta^5$ ) binding mode, and the Mo centers have a four-legged piano stool structure (square pyramidal). The Fv ligands have –CO<sub>2</sub>Me groups trans with respect to the bridgehead C–C bond.

The molecular structure determination of **4** shows that the Mo(CO)<sub>3</sub>I units are on opposite sides of the Fv ligand. In the parent molecule ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub>, **2**, both Mo(CO)<sub>3</sub>I units are on the same side of the Fv ligand.<sup>10</sup> Some structural differences between **1**, **2**, and **4** arise as a result of the new orientation of the Mo(CO)<sub>3</sub>I units. As presented in Table 3, the most dramatic change is observed in the bend angle  $\theta$  (the

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**Table 3. Comparison of Structural Data in 1,1'-( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub>, Isomers 1 and 2, and ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub>I<sub>2</sub>, 4**

	1	2	4
Mo–Cp <sup>a,b</sup>	1.995(10)	2.000(2), 1.997(2)	1.99(2)
C–C bridgehead <sup>a</sup>	1.474(12)	1.465(3)	1.45(2) <sup>c</sup>
average C=O distance <sup>a</sup>	1.134(1)	1.144(2)	1.145(7)
bend angle (dihedral angle between Cp rings) $\theta$ <sup>d</sup>	32.2	32.3	0

<sup>a</sup> In Angstroms, Å. <sup>b</sup> Refers to metal-to-Cp ring centroid distance. <sup>c</sup> Refers to C(4)–C(4') distance. <sup>d</sup> In deg.

dihedral angle between the two Cp planes of the fulvalene ligand) which is 0° (symmetry imposed) in 4 and much larger in 1 and 2. In 4, the C–C bridgehead distance, C(4)–C(4') (1.45(2) Å), and the mean C=O bond length (1.145(7) Å) are normal.<sup>23</sup> The Mo–Cp ring carbon distances range from 2.287(8) to 2.386(8) Å; these values are consistent with Mo–Cp ring carbon distances seen in other dimolybdenum compounds.<sup>23</sup> The Mo–I distance, 2.8384(11) Å, also is normal.<sup>23</sup>

**Reactions of ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> and ( $\eta^5$ : $\eta^5$ -C<sub>10</sub>H<sub>8</sub>)M<sub>2</sub>(CO)<sub>6</sub> (M = Mo and W) with Phosphines: Synthesis of Dinuclear Organometallic Zwitterions.** The reactions of Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> with PR<sub>3</sub> may yield phosphine-substituted Mo–Mo-bonded dimers Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6-x</sub>(PR<sub>3</sub>)<sub>x</sub> (x = 1, 2)<sup>24</sup> or disproportionation products [CpMo(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>]<sup>+</sup>[CpMo(CO)<sub>3</sub>]<sup>-</sup><sup>25,26</sup> depending on reaction conditions and the electronic and steric properties of PR<sub>3</sub>. Disproportionation is favored over phosphine-substituted dimers when electron-rich sterically undemanding and/or chelating phosphines are used. The mechanism of this process has been studied in detail by Tyler and co-workers and takes place by a photochemically induced radical chain process involving 17- and 19-electron intermediates.<sup>27</sup>

The preparation of zwitterionic fulvalene complexes are of interest in the context of nonlinear optics.<sup>28–31</sup> The reaction of FvMo<sub>2</sub>(CO)<sub>6</sub> with PPh<sub>3</sub>, Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, or Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> under thermal or photochemical conditions gave no isolable products. However, when strongly electron-donating phosphines were used (PMe<sub>3</sub> and dmpm), the zwitterionic fulvalene complexes were obtained.<sup>6a</sup> Recently, the electron-reservoir complexes

[Fe<sup>I</sup>Cp(C<sub>6</sub>H<sub>6</sub>)], [Fe<sup>I</sup>CpC<sub>6</sub>Me<sub>6</sub>], and [Fe<sup>I</sup>Cp\*(C<sub>6</sub>Me<sub>6</sub>)] (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>; Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>) have been used as initiators for the electron-transfer chain-catalyzed (electrocatalyzed) synthesis of the homobimetallic zwitterions [(CO)<sub>3</sub>M–FvM<sup>+</sup>(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] (M = Mo, W; Fv =  $\mu_2$ - $\eta^{10}$ -fulvalene; R = Me, OMe) from FvM<sub>2</sub>(CO)<sub>6</sub> and PR<sub>3</sub>.<sup>6b,32</sup>

The reactions of ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> (isomer 1) with PPhMe<sub>2</sub>, PPh<sub>2</sub>Me, P(n-Bu)<sub>3</sub>, or PMe<sub>3</sub> in THF solution in the presence of 1 equiv of Me<sub>3</sub>NO lead in high yield to the formation of yellow-brown analytically pure products of composition ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>5</sub>L<sub>2</sub> (5–8). IR monitoring of these reactions shows the formation of two isosbestic points at 2003 and 1980 cm<sup>-1</sup>, which is indicative of a clean reaction without the formation of detectable intermediates and secondary products. 5–8 are partially soluble in THF, CH<sub>2</sub>Cl<sub>2</sub>, and AN. These reactions do not take place thermally without Me<sub>3</sub>NO being present. When we use P-donor ligands with cone angle  $\theta \geq 145^\circ$ , such as PPh<sub>3</sub> or PCy<sub>3</sub>, the reactions gave no isolable products even in the presence of Me<sub>3</sub>NO.

IR and NMR spectroscopic data for 5–8 are listed in Tables 4 and 5. The IR spectra of 5–8 closely resemble those of CpMo(CO)<sub>3</sub><sup>-</sup> (1770–1780 and 1890–1900 cm<sup>-1</sup>) and CpMo(CO)<sub>2</sub>L<sub>2</sub><sup>+</sup> (1900–1920 and 1990–2000 cm<sup>-1</sup>).<sup>24a,33</sup> The close match of the IR  $\nu_{CO}$  bands of ( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>5</sub>(PPh<sub>2</sub>Me)<sub>2</sub> (6) with those of [( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>Me)Mo(CO)<sub>3</sub>]<sup>-</sup>[( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>Me)Mo(CO)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub>]<sup>+</sup> (12) prepared by us from [( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>Me)Mo(CO)<sub>3</sub>]<sub>2</sub> and PPh<sub>2</sub>Me in the presence of Me<sub>3</sub>NO (1976, 1948, 1898, 1798 cm<sup>-1</sup>) is noteworthy. 6 and 12 show stretching modes at higher frequencies than the analogous unsubstituted species, which is due to the electron-withdrawing properties of the carbomethoxy substituent in the Fv and Cp rings, respectively. On the other hand, the bands observed at 1905 and 1848 cm<sup>-1</sup> in the IR spectra of 5–8 are very similar to those shown by the lithium salt Li<sub>2</sub>[( $\eta^5$ : $\eta^5$ -C<sub>5</sub>H<sub>3</sub>CO<sub>2</sub>Me)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub>],<sup>10</sup> which supports their ionic nature.

The cationic half of zwitterionic molecules 5–8 displayed two CO absorptions with intensity ratios consistent with the cis geometry<sup>34</sup> (high-energy band more intense), while in the disproportionation compound 12 the cationic half [( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CO<sub>2</sub>Me)Mo(CO)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub>]<sup>+</sup> is consistent with trans geometry (low-energy band more intense), similar to that found previously for analogous compounds.<sup>24c,33a</sup> Only cis isomers are also observed for the FvMo<sub>2</sub>(CO)<sub>4</sub>L<sub>2</sub>X<sub>2</sub> (L = PPh<sub>3</sub>, PCy<sub>3</sub>, PXY<sub>3</sub>; X = Cl, Br) compounds.<sup>13</sup>

The presence of five fulvalene resonances in the <sup>1</sup>H NMR spectra shows that 5–8 are less symmetrical than their substrates. Decoupling <sup>1</sup>H–<sup>1</sup>H experiments show that only the signal of the broad multiplet (ca. 5.53, 5.26, 5.56, and 5.59 for 5, 6, 7, and 8, respectively) is coupled, so that it corresponds to two protons of the same ring. These experiments made possible the assignment of the two halves of the fulvalene systems (Table 5) and showed that both phosphines were attached to the same metal.

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**Table 4. IR ( $\nu_{\text{CO}}$ ) Data for Zwitterionic Compounds in THF Solution**

compound	$\nu_{\text{CO}}$ ( $\text{cm}^{-1}$ )		$\nu_{\text{CO}}$ ( $\text{CO}_2\text{Me}$ ) ( $\text{cm}^{-1}$ )
	cationic fragment	anionic fragment	
$\text{Fv}(\text{Mo}_2(\text{CO})_5(\text{PMe}_3)_2)^a$	1986 vs, 1922 s	1902 vs, 1835 s	1726 m
$\text{Fv}(\text{Mo}_2(\text{CO})_5(\text{PPh}_2\text{Me})_2)$	1988 vs, 1925 m	1905 vs, 1848 m	1726 m
$\text{Fv}(\text{Mo}_2(\text{CO})_5(\text{PPhMe}_2)_2)$	1988 vs, 1923 m	1904 vs, 1846 m	1729 m
$\text{Fv}(\text{Mo}_2(\text{CO})_5(\text{P}^i\text{Bu}_3)_2)$	1986 vs, 1921 m	1904 vs, 1844 m	1727 m
$(\text{Cp}^*\text{Mo}(\text{CO})_2(\text{PPh}_2\text{Me})_2^+)^b$ $[\text{Cp}^*\text{Mo}(\text{CO})_3^-]$	1976 m, 1948 vs	1898 vs, 1798 vs	1726 m, 1717 m

<sup>a</sup>  $\text{Fv}' = (\eta^5:\eta^5\text{-C}_5\text{H}_3\text{CO}_2\text{Me})_2$ . <sup>b</sup>  $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{Me}$ .

**Table 5.  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR Data for Zwitterionic Compounds in  $\text{CDCl}_3$  Solution**

compound	$^1\text{H}$ NMR, $\delta$				$^{31}\text{P}\{^1\text{H}\}$ NMR, $\delta$
	fulvalene ligand			others	
	cationic fragment	anionic fragment			
$\text{Fv}(\text{Mo}_2(\text{CO})_5(\text{PMe}_3)_2)^a$	6.05 (m, 1H), 4.65 (m, 1H), 4.42 (m, 1H)	5.59 (m, br, 2H), 4.80 (t, 1H)	3.75 (s), 3.71 (s), 1.51 (d)		31.13 (s)
$\text{Fv}(\text{Mo}_2(\text{CO})_5(\text{PPh}_2\text{Me})_2)$	6.06 (dd, 1H), 4.73 (dd, 1H), 4.44 (dd, 1H)	5.26 (m, br, 2H), 4.85 (t, 1H)	7.70 (m), 7.52 (m), 3.70 (s), 3.68 (s), 1.62 (d)		50.50 (s)
$\text{Fv}(\text{Mo}_2(\text{CO})_5(\text{PPhMe}_2)_2)$	5.94 (m, 1H), 4.70 (m, 1H), 4.34 (m, 1H)	5.53 (m, br, 2H), 5.05 (t, 1H)	7.54 (m), 3.60 (s), 3.56 (s), 1.29 (d)		35.20 (s)
$\text{Fv}(\text{Mo}_2(\text{CO})_5(\text{P}^i\text{Bu}_3)_2)$	6.02 (m, 1H), 4.72 (m, 1H), 4.45 (m, 1H)	5.56 (m, br, 2H), 4.82 (t, 1H)	3.74 (s), 3.71 (s), 1.51 (m), 0.98 (m)		49.11 (s)
$(\text{Cp}'\text{Mo}(\text{CO})_2(\text{PPh}_2\text{Me})_2^+)^b$ $[\text{Cp}'\text{Mo}(\text{CO})_3^-]$	5.86 (t, 2H), 5.20 (t, 2H)	5.48 (t, 2H), 5.16 (t, 2H)	7.51 (m), 3.64 (s), 3.55 (s), 1.62 (d)		30.32 (s)

<sup>a</sup>  $\text{Fv}' = (\eta^5:\eta^5\text{-C}_5\text{H}_3\text{CO}_2\text{Me})_2$ . <sup>b</sup>  $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{Me}$ .

The ionic nature of **5–8** is in accordance with the two signals observed (triplet and multiplet) at ca. 4.80 and 5.50 ppm attributable to the anionic half, by analogy with the lithium salt previously prepared.<sup>10</sup> The  $^{31}\text{P}$  NMR spectra show a single signal for all compounds in the characteristic range of the cis isomer.<sup>13,35</sup>

The zwitterionic character is also demonstrated by the reaction between the anionic half of  $[(\eta^5:\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{Me})_2\text{Mo}_2(\text{CO})_5(\text{PMe}_3)_2]$  (**8**) and an electrophile as  $\text{CF}_3\text{-COOH}$  to yield the hydride salt  $[(\eta^5:\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{Me})_2\text{Mo}_2(\text{CO})_5(\text{PMe}_3)_2\text{H}^+][\text{CF}_3\text{COO}^-]$ , which could not be isolated, but was characterized by its IR spectrum. During the reaction, the disappearance of the two bands due to the anionic half and the appearance of two new bands (2020, 1990 (sh)  $\text{cm}^{-1}$ ) attributable to the protonated fragment are observed. The IR  $\nu_{\text{CO}}$  data for the product show that the CO stretching frequencies for the unreacted cationic half remained virtually unchanged at ca. 1980 and 1921  $\text{cm}^{-1}$ .

The preparation of the known  $\text{FvM}_2(\text{CO})_5(\text{PMe}_3)_2$  ( $\text{M} = \text{Mo}$  and  $\text{W}$ )<sup>6a</sup> (**9** and **10**) zwitterion complexes using  $\text{Me}_3\text{NO}$  takes place under mild conditions, short reaction times, and higher yields and does not require a large excess of ligand. Both compounds were readily identified by comparison of their spectral data with those previously reported.<sup>6</sup> Only zwitterion products were obtained.

To compare the efficiency of this method (using  $\text{Me}_3\text{NO}$ ) and of the electrocatalytic process (using electron-reservoir  $\text{Fe}^{\text{I}}$  complexes) performed by Astruc and al.,<sup>32</sup> we have gathered the yields, conditions, and ligand concentration of both methods in Table 6.

Preliminary results carried out in our laboratory have revealed that the tungsten species  $(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{W}_2(\text{CO})_6\text{I}_2$  is stable with respect to CO loss in the presence of  $\text{PR}_3$  ligand under thermal conditions, but in the presence of  $\text{Me}_3\text{NO}$  the compound loses CO rapidly and

**Table 6. Comparison of  $\text{Me}_3\text{NO}$  (A) and Electrocatalysis (B) Methods in the Homobimetallic Zwitterions Syntheses**

compound	method	time (min)	ligand (equiv)	yield (%)
<b>9</b>	A	10	2	95
<b>9</b>	B <sup>a</sup>	20	10	70
<b>10</b>	A	5	2	90
<b>10</b>	B <sup>a</sup>	15	20	56

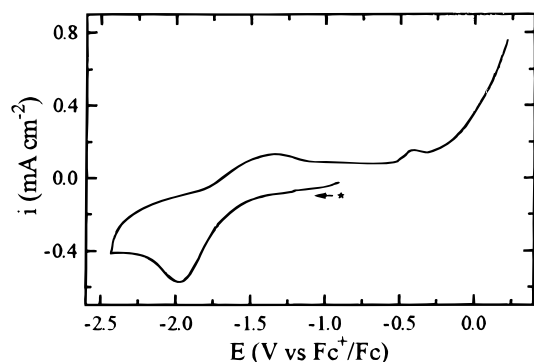
<sup>a</sup> Values from ref 31.

substituted species  $[\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{W}_2(\text{CO})_4(\text{PR}_3)_2\text{I}_2]$  are cleanly formed according to IR data in a short time.<sup>11</sup>

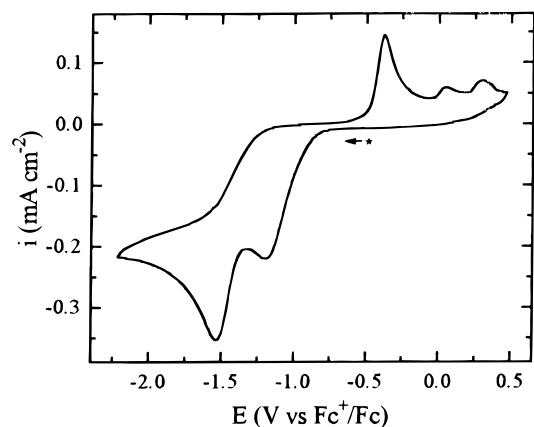
We believe that the examples chosen here, involving CO loss in fulvalene complexes using the  $\text{Me}_3\text{NO}$  to remove a ligated CO molecule can be extended to other homo- or heteronuclear bimetallic fulvalenes, making this method a very efficient and general way to perform CO substitution reactions.

**Electrochemical Studies of 3 and 4.** The voltammetric behavior of **3** was investigated in PC and AN. A reduction wave at ca.  $-2.0$  V ( $\nu = 0.1$  V  $\text{s}^{-1}$ ) is observed in AN solution (Figure 2). A small coupled anodic peak appears at ca.  $-1.4$  V upon scan reversal. If the positive sweep is further extended, another small peak at ca.  $-0.4$  V is observed, but just after it, the current suddenly increases, and any attempt to reproduce results with the same electrode fails. The Pt working electrode has to be taken out of the solution and repolished. Thus, it seems that a severe poisoning of the electrode has taken place.

On the other hand, when working in a PC solution, the reduction process is poorly resolved. A wide reduction wave is obtained at ca.  $-1.9$  V. However, the anodic sweep following reduction can be extended until ca.  $0.5$  V without any observable change in the voltammetric characteristics. When the cell is switched at  $-1.2$  V and the potential is swept in the positive direction, an oxidation wave is observed at  $+0.12$  V ( $\nu = 0.1$  V  $\text{s}^{-1}$ ). No coupled cathodic peak appears even



**Figure 2.** Cyclic voltammogram for the reduction of a  $1.9 \times 10^{-3}$  M solution of **3** in AN containing 0.2 M TBAPF<sub>6</sub> at  $0.1 \text{ V s}^{-1}$  and  $25 \text{ }^\circ\text{C}$ . Scan started at  $-0.9 \text{ V}$  in the cathodic direction.



**Figure 3.** Cyclic voltammogram for the reduction of a  $5 \times 10^{-4}$  M solution of **4** in AN containing 0.2 M TBAPF<sub>6</sub> at  $0.1 \text{ V s}^{-1}$  and  $25 \text{ }^\circ\text{C}$ . Scan started at  $-0.6 \text{ V}$  in the cathodic direction.

at a sweep rate as high as  $20 \text{ V s}^{-1}$ . All attempts to determine by controlled potential electrolysis the overall number of electrons transferred in the reduction process of **3** failed (both in AN and PC), with currents decaying to the background value when less than 0.5 F/mol had been consumed.

The reduction of cyclopentadienyl-substituted compounds related to **3** that contain only one M–CH<sub>3</sub> bond are known to follow EC-type mechanisms in which the charge transfer is followed by the breakage of the M–C bond, yielding the anion  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3^-$  and CH<sub>3</sub> radicals.<sup>11,36</sup> The latter further evolve to form ethane or methane. In the same way,  $(\eta^5:\eta^5\text{-}(\text{C}_5\text{H}_3\text{CO}_2\text{Me})_2)\text{Mo}_2(\text{CO})_6^{2-}$  and CH<sub>3</sub> could well be the products of the reduction of **3**, but the poor reproducibility and failed coulometric determination of the overall number of electrons transferred also suggest a more complicated process in which adsorption of species on the electrode could be involved.

The voltammetric reduction of **4** was studied in four different solvents: PC, AN, THF, and DCE. Two cathodic waves of nearly equal height at low sweep rates are observed in all the media (Figure 3). The solvent-dependent peak potentials,  $E_{r1}$  and  $E_{r2}$ , are assembled in Table 7. In the overall reduction process, a reduced species is formed which reoxidizes upon scan reversal

**Table 7. Electrochemical Data for 4 in the Different Solvents**

	PC	AN	THF	DCE
$E_{r1}$ (V vs Fc <sup>+</sup> /Fc) <sup>a</sup>	-1.20	-1.22	-1.26	-1.28
$E_{r2}$ (V vs Fc <sup>+</sup> /Fc) <sup>a</sup>	-1.50	-1.53	-1.54	-1.55
$i_p/C$ (mA cm <sup>-2</sup> M <sup>-1</sup> ) <sup>a,b</sup>	130	422	310	204
$E_{\text{reox}}$ (V vs Fc <sup>+</sup> /Fc) <sup>a</sup>	-0.37	-0.38	-0.67	-0.42
$i_{\text{reox}}/C$ (mA cm <sup>-2</sup> M <sup>-1</sup> ) <sup>a,c</sup>	105	262	190	116
$E_{\text{ox}}$ (V vs Fc <sup>+</sup> /Fc) <sup>a</sup>	0.83	0.77; 1.07	0.77	0.86
$i_{\text{ox}}/C$ (mA cm <sup>-2</sup> M <sup>-1</sup> ) <sup>a,d</sup>	230	472	ca. 350 <sup>e</sup>	245
solvent viscosity (cP)	2.53	0.343	0.46	0.785
solvent dipole moment (D)	4.94	4.1	1.75	
solvent dielectric constant	64.9	36.0	7.6	10.42

<sup>a</sup> Data at  $\nu = 0.1 \text{ V s}^{-1}$ . <sup>b</sup> Peak current density/C of the first cathodic peak assumed to be equal to that of the second one for  $\nu \leq 0.1 \text{ V s}^{-1}$ . <sup>c</sup> Reoxidation peak current density/C. <sup>d</sup> Oxidation peak current density/C. <sup>e</sup> The oxidation peak is too close to the positive limit of the solvent system to accurately determine  $i_{\text{ox}}$ ; the given value is an estimation.

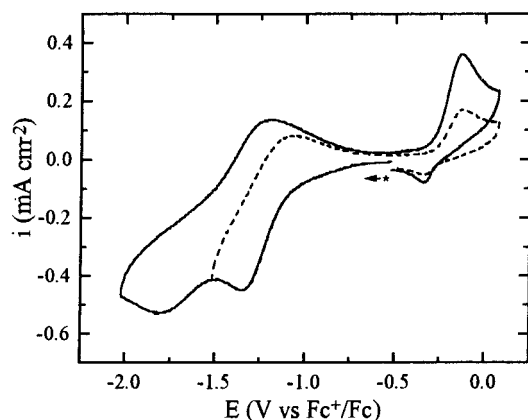
at a much more positive potential,  $E_{\text{reox}}$  (Figure 3, Table 7). Additional anodic peaks corresponding to the oxidation of I<sup>-</sup> (as confirmed by addition of authentic samples of KI to the solutions) are also observed when the positive scan following the reduction of **4** is extended until  $0.5 \text{ V vs Fc}^+/\text{Fc}$ .

The overall number of electrons transferred in the reduction process was determined by controlled potential coulometry in AN solution. Thus, a weighted amount of **4** was dissolved (yielding an orange solution) and reduced at  $-2.0 \text{ V vs Fc}^+/\text{Fc}$ , a potential well within the diffusion-limited region of the most negative reduction wave. The amount of electricity consumed when the current decayed to background (after ca. 1 h) indicated that the overall reduction was a four-electron process. The color of the reduced solution was yellow. The almost equal height of the two cathodic peaks at low sweep rates ( $\nu \leq 0.1 \text{ V s}^{-1}$ ) indicates that each of them involves a two-electron process. Coulometry was also attempted in a PC solution, but the current intensity decayed to the background value when less than 1 F/mol had been consumed and the color of the solution had not changed, indicating that a passivation of the electrode had probably taken place. However, the general similarity of the reduction waves and the values of the peak current densities in PC and the other solvents (Table 7) seem to indicate that the same number of electrons as in AN are involved, when the different viscosities,  $\eta$ , of the media are taken into account. According to Walden's rule ( $D\eta = D'\eta'$ ), the higher the viscosity, the smaller the diffusion coefficient,  $D$ , and, consequently, a smaller current density,  $i$ , is expected.

$(\eta^5:\eta^5\text{-}(\text{C}_5\text{H}_3\text{CO}_2\text{Me})_2)\text{Mo}_2(\text{CO})_6^{2-}$  together with I<sup>-</sup> are very probably the final products of the overall reduction process. The same dianion results from the voltammetric reduction of the metal–metal-bonded species **1** and **2**, which were studied in a previous work,<sup>10</sup> where it was found that the dianion reoxidized at  $-0.39 \text{ V}$  in PC and at  $-0.70 \text{ V}$  in THF. These potential values are in very good agreement with those found in the present study for  $E_{\text{reox}}$  (Table 7).

The voltammetric study at different sweep rates ( $\nu$ ) reveals that, in all the media, the peak current density





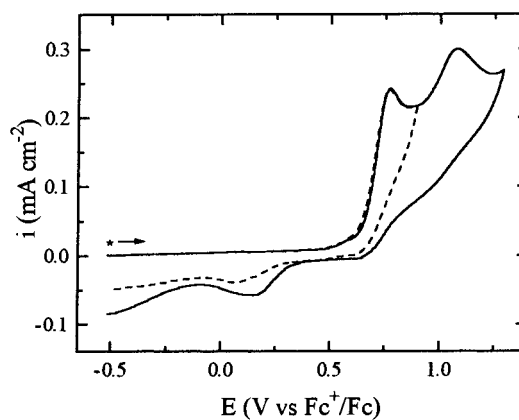
**Figure 4.** Cyclic voltammograms for the reduction of a  $5 \times 10^{-4}$  M solution of **4** in PC containing 0.2 M TBAPF<sub>6</sub> at  $5 \text{ V s}^{-1}$  and  $25 \text{ }^\circ\text{C}$  with different cathodic switching potentials. Scans started at  $-0.5 \text{ V}$  in the cathodic direction.

of the least negative reduction peak,  $i_{r1}$ , is a linear function of  $\nu^{1/2}$  in the range  $0.01 \text{ V s}^{-1} < \nu < 2 \text{ V s}^{-1}$ . This observation can only be an estimation in DCE because, in this solvent, the first cathodic peak is not well-resolved and appears as a “shoulder” of the second one, thus making the evaluation of  $i_{r1}$  rather imprecise.

In AN, DCE, and THF solutions, no sign of coupled anodic peaks for any of the cathodic waves is shown with sweep rates as high as  $80 \text{ V s}^{-1}$ . This behavior significantly differs from that observed in PC. In the latter solvent, a return anodic peak coupled to the least cathodic reduction wave can be observed for  $\nu \geq 0.5 \text{ V s}^{-1}$ , with  $i_{\text{anod}}/i_{\text{cath}}$  approaching 1 as  $\nu$  increases (Figure 4). Correspondingly, the ratio  $i_{r2}/i_{r1}$  diminishes with increasing  $\nu$ . The difference between the anodic and cathodic peak potentials is larger than that of ferrocene under the same conditions, indicating quasi-reversible electrochemical behavior. Experiments carried out in our laboratory have revealed that other related compounds such as  $(\eta^5:\eta^5\text{-C}_5\text{H}_3\text{Me})_2\text{Mo}_2(\text{CO})_6\text{I}_2$  and  $(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{W}_2(\text{CO})_6\text{I}_2$  show the same qualitative behavior in PC solution.<sup>11</sup>

The electrochemical oxidation of **4** was also studied. A completely irreversible peak is observed in all the media at a potential value of around  $0.8 \text{ V}$  ( $\nu = 0.1 \text{ V s}^{-1}$ ; see Table 7 and Figure 5). In AN solution, where the anodic range is larger, a second peak, also irreversible, appears at  $1.07 \text{ V}$ . No coupled cathodic peaks are observed in any of the solvents for sweep rates as high as  $80 \text{ V s}^{-1}$ , which is in agreement with the existence of fast follow-up chemical reactions.

Moulton et al.<sup>37</sup> explored the electrochemical behavior of a number of dihalide compounds closely related to **4**.  $(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{Ru}_2(\text{CO})_6\text{Br}_2$  and  $(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{Cr}_2(\text{CO})_6\text{I}_2$  were found to be reduced at a potential positive of the metal–metal-bonded compounds  $(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{Ru}_2(\text{CO})_6$  and  $(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{Cr}_2(\text{CO})_6$ , respectively. The latter complexes were proposed as products of such reductions, as a second cathodic wave was observed at the potentials at which authentic samples of  $(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{Ru}_2(\text{CO})_6$  and  $(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{Cr}_2(\text{CO})_6$  are re-



**Figure 5.** Cyclic voltammogram for the oxidation of a  $5 \times 10^{-4}$  M solution of **4** in AN containing 0.2 M TBAPF<sub>6</sub> at  $0.1 \text{ V s}^{-1}$  and  $25 \text{ }^\circ\text{C}$ . Scan started at  $-0.5 \text{ V}$  in the anodic direction.

duced to the corresponding dianions. Thus, the possibility of an analogous reductive scheme was checked for **4**, and its reduction potentials were compared with that of the Mo–Mo-bonded species **2**. **2** is reduced to  $(\eta^5:\eta^5\text{-C}_5\text{H}_3\text{CO}_2\text{Me})_2\text{Mo}_2(\text{CO})_6^{2-}$  at  $-1.20$  and  $-1.37 \text{ V}$  in PC and THF solutions, respectively.<sup>10</sup> On the other hand, the reduction peak potentials of **4** are  $-1.20$  and  $-1.50 \text{ V}$  in PC and  $-1.26$  and  $-1.54 \text{ V}$  in THF (Table 7). Thus, **2** is not the product of the first reduction wave of **4**, and a more complicated mechanism is taking place.

The reduction behavior of **4** can be compared with those of the halocyclopentadienyl derivatives  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}; \text{M} = \text{Mo}, \text{W}$ ). It is well-established<sup>38</sup> that the latter kind of compounds are reduced in a single two-electron cathodic wave to the anions  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3^-$  and  $\text{I}^-$ . No coupled anodic peaks, at least until  $\nu = 80 \text{ V s}^{-1}$ , are found. In the case that the two redox centers in **4** were completely noninteracting and independent of each other, it could be expected that each of them would be reduced in the same way as  $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{X}$  and that a single cathodic wave would be observed in the voltammogram<sup>39</sup> (a very small  $E$  separation of the two redox centers due to statistical factors would not be resolvable). This is however definitively not the case, and two clearly distinct well-separated peaks are observed in all the solvents, with  $\Delta E$  about  $0.3 \text{ V}$ . This could be indicative of some sort of interaction between the two redox sites, so that electronic communication between the two metal centers could be taking place via the planar fulvalene ligand.<sup>39</sup>

The sequence of steps constituting the reduction mechanism is still unclear, as the information from the mostly irreversible cyclic voltammograms is limited. In particular, the possibility of tetranuclear species such as reported by Astruc and co-workers<sup>40</sup> being involved in the reduction mechanism cannot be ruled out. Some general considerations can however be made. The presence of an anodic peak coupled to the first cathodic wave at fast sweep rates in PC but not in the other

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solvents (at least up to  $80 \text{ V s}^{-1}$ ) seems to indicate that the product of the electron transfers involved in the first wave,  $P_1$ , undergoes a follow-up chemical reaction to yield a species that can be further reduced at the second cathodic wave and that the rate of the chemical step is strongly solvent-dependent. Thus, in PC it is not too fast, and at high  $v$ , a considerable amount of  $P_1$  remains unchanged and can be reoxidized when the sweep is reversed. In the other three solvents, the chemical reaction is much faster; that is,  $P_1$  is less stable. It seems that the highly polar and bulky propylene carbonate molecules exert a strong stabilizing effect on  $P_1$ .

### Conclusion

The reactions of  $(\eta^5:\eta^5\text{-}(\text{C}_5\text{H}_3\text{CO}_2\text{Me})_2)\text{Mo}_2(\text{CO})_6$  with P-donor nucleophiles, in the presence of 1 equiv of  $\text{Me}_3\text{-NO}$ , yield the dinuclear zwitterions  $(\eta^5:\eta^5\text{-}(\text{C}_5\text{H}_3\text{CO}_2\text{-Me})_2)\text{Mo}_2(\text{CO})_5\text{L}_2$ . The preparation of these complexes takes place under mild conditions, short reaction times, and higher yields and does not require large excess of ligand. This synthetic strategy can be extended to

heteronuclear bimetallic fulvalenes, making this method a general way to perform CO substitution reactions.

The electrochemical study of **4** in different solvents is reported. Two distinct cathodic waves appear in the cyclic voltammetry reduction of **4**, and this behavior is markedly different from that of related halocyclopentadienyl derivatives.

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**Supporting Information Available:** Tables of crystallographic parameters, positional and thermal parameters, and complete bond distances and angles of **4** (6 pages) Ordering information is given on any current masthead page.

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