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## Bridging Ligands in Organometallic Chemistry. 1. $\eta^5:\eta^5$ -Fulvalene Complexes of Molybdenum Carbonyl

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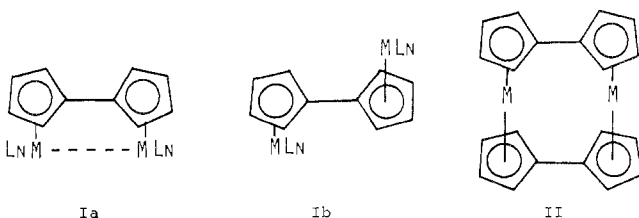
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The isolation of sodium cyclopentadienide as a crystalline 1,2-dimethoxyethane adduct has led to an efficient in situ synthesis of the bicyclopentadienyl or fulvalene dianion. This bridging ligand reacts with molybdenum hexacarbonyl to yield the ( $\eta^5:\eta^5$ -fulvalene)hexacarbonyldimolybdenum dianion which was alkylated to yield a dimethyl derivative, oxidized to a metal-metal bonded dimer, and metathesized to a mercury(II)-bridged polymer.

### Introduction

In an effort to develop general synthetic routes to dinuclear organometallic compounds with new electronic structures and novel catalytic properties, we are exploring the chemistry of metallofulvalene complexes. Three different synthetic routes have yielded metal compounds containing a bridging bicyclopentadienyl or fulvalene ligand.

Reduction of bis(cyclopentadienyl)titanium(IV) complexes has led to well-characterized compounds of structural type Ia



that contain additional bridging ligands ( $L_nMML_n = [(C_5H_5)_2Ti]_2-\mu-H_2$ ,<sup>1,2</sup>  $[(C_5H_5)_2Ti]_2-\mu-H-\mu-H_2AlEt_2$ ,<sup>3</sup>  $[(C_5H_5)_2Ti]_2-\mu-(OH)_2$ ,<sup>4</sup>).

Formation of the bridging fulvalene ligand is thought to involve dimerization of a reactive titanium(II) species, by oxidative addition of a ring C-H bond to yield a  $[(\eta^1:\eta^5-C_5H_4)TiH]_2$  moiety, followed by reductive coupling to form the  $\eta^5:\eta^5-C_{10}H_8$  fulvalene ligand and bridging hydrides. Although we have very recently found a similar transformation in the preparation of "molybdenocene",<sup>5,6</sup> this route to metallofulvalene complexes remains virtually unexplored.

Ullmann coupling reactions of iodocymantrene,  $\eta^5$ -iodocyclopentadiene- $\eta^4$ -tetraphenylcyclobutadienecobalt, iodoferecenes, and iodoruthenocenes have yielded complexes of type Ib ( $M L_n = Mn(CO)_3$ ,<sup>7</sup>  $Co(\eta^4-C_4(C_6H_5)_4)$ ,<sup>8</sup>  $Fe(C_5H_5)$ ,<sup>9</sup>  $Ru(C_5H_5)$ <sup>10</sup>) and type II ( $M = Fe$ ,<sup>7,11</sup>  $Ru$ <sup>12</sup>). This synthetic approach is limited by the availability of appropriately substituted cyclopentadienylmetal complexes. The mercury-substituted precursors to these halo-substituted derivatives have only been prepared in stable organometallic systems that undergo electrophilic ring substitutions.<sup>13</sup>

This work describes a more general and versatile route to metallofulvalene complexes of type Ia ( $L_nMML_n = [Mo(CO)_3]_2$ ) and type Ib ( $M L_n = Mo(CO)_3^-$ ,  $[Mo(CO)_3Hg]_n$ ,  $Mo(CO)_3CH_3$ ,  $Mo(CO)_3Br$ ), from an in situ preparation of the fulvalene dianion<sup>14</sup> followed by nucleophilic substitution of molybdenum hexacarbonyl. The utility of this approach has been demonstrated by the efficient synthesis of complexes of type II ( $M = Ni$ ,<sup>15</sup>  $Co$ ,<sup>16</sup>  $Fe$ ,<sup>17</sup>  $Cr$ ,<sup>18</sup>  $Mo$ <sup>19</sup>).

### Experimental Section

**General Data.** Reagent grade tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were predried over KOH pellets. Benzene, toluene, THF, and DME were purified by distillation from sodium benzophenone ketyl and stored under nitrogen. Cyclopentadiene was obtained by "cracking" dicyclopentadiene (MCB chemicals 98%) over carborundum boiling chips and distillation through a Vigreux column (1.5 × 45 cm) at 40 °C, into a receiving flask cooled to -78 °C (Dry

Ice/2-propanol). Cyclopentadiene can be stored in the absence of air as the solid monomer at -196 °C (liquid nitrogen) and it can be conveniently syringed at -78 °C. Sodium dispersion (40% in mineral oil, Ventron Corp.) was used without removing the oil. Molybdenum hexacarbonyl (Pressure Chemical Co.) was used without further purification. All other chemicals and solvents were reagent grade and were used without further purification.

Air-sensitive solids were stored and manipulated in a Vacuum Atmospheres glovebox with a modified dry train. Deoxygenated solvents and air-sensitive solutions were transferred via 18-gauge stainless steel cannulae connected with polyethylene tubing (Clay Adams, Intramedic, Fischer Scientific Co.), using standard inert-atmosphere and Schlenk-tube techniques.

Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer as Nujol or halocarbon mulls and calibrated with polystyrene. Proton NMR spectra were obtained with a Varian Associates Model T-60 spectrometer and with a modified Bruker HX-360 spectrometer operating in the pulsed Fourier-transform mode. Mass spectra were obtained with an AEI MS12 mass spectrometer equipped with a direct-inlet system. Selected ions with relative abundances greater than 1% for the isotope <sup>96</sup>Mo are reported. Elemental analyses were performed by the microanalytical laboratory of the University of California, Berkeley, Calif.

**Sodium (1,2-Dimethoxyethane)cyclopentadienide, Na(DME)C<sub>5</sub>H<sub>5</sub>.** To a dry 1-L three-necked round-bottom flask was added 86.3 g (1.5 g-atom) of sodium dispersion (40% in mineral oil). The flask was fitted with a reflux condenser with stopcock and two stoppers and then evacuated to degas the oil. It was then refilled with nitrogen and, under a counter stream of nitrogen, the stoppers were replaced with a mechanical stirrer and a rubber septum. The flask was immersed in a dry ice/2-propanol bath and dry, oxygen-free DME (600 mL) was added via a cannula. Stirring of the mixture was delayed until the DME had cooled sufficiently to prevent aggregation of the dispersed sodium. By using a counter stream of nitrogen, the flask was then fitted with a pressure-equalizing dropping funnel containing cyclopentadiene (124 mL, 1.65 mol, 10% excess). The cooling bath was then removed, 20 mL of cyclopentadiene added to the rapidly stirred suspension, and the reaction allowed to warm to room temperature. When the hydrogen evolution slowed, cyclopentadiene was added carefully at a rate sufficient to maintain a steady evolution of gas without allowing the reaction mixture to foam into the reflux condenser. After the addition was complete (ca. 1 h), the slurry of white crystalline Na(DME)C<sub>5</sub>H<sub>5</sub> was heated to reflux to ensure complete reaction, the heating and stirring were stopped, and the stirrer and dropping funnel were removed under a counter stream of nitrogen and replaced by stoppers. The hot solution was allowed to cool to room temperature to yield a large mass of crystalline product and a supernatant solution that was colorless to deep red, depending upon the degree of air oxidation. The reflux condenser was removed and quickly replaced with a stopper, all three joints were sealed (Manostat § joint clamps, Metro Scientific, Inc.), and the flask was passed into a drybox. The white crystalline product was removed by filtration (medium-porosity fritted disk), washed with dry, oxygen-free hexane (3 × 100 mL), and dried in vacuo (0.1 mm) to yield 223 g (1.25 mol, 83.5%). The equivalent weight was determined by hydrolysis of three samples of crystalline material, followed by titration with standard acid: calcd for C<sub>9</sub>H<sub>15</sub>NaO<sub>2</sub>, 178.2; found, 178.6 ± 0.5. <sup>1</sup>H NMR (THF-*d*<sub>8</sub>): δ 5.60 (s, 5 H), 3.42 (s, 4 H), 3.28 (s, 6 H).

**Preparation of the Fulvalene Dianion, C<sub>10</sub>H<sub>8</sub><sup>2-</sup>.** In a drybox, Na(DME)C<sub>5</sub>H<sub>5</sub> (3.56 g, 20.0 mmol) was added to a 250-mL round-bottomed flask, equipped with a side-arm stopcock and magnetic

stir bar. The flask was sealed with a rubber septum and passed out of the drybox. Dry, oxygen-free THF (125 mL) was added via a cannula, the resulting solution cooled to  $-78^\circ\text{C}$ . Iodine (2.66 g, 10.5 mmol, 5% excess) was added against a counter stream of nitrogen and the reaction mixture was allowed to warm until it began to darken (ca. 20 min). It was then cooled to  $-78^\circ\text{C}$  and butyllithium (8.8 mL, 2.4 M in hexane, 21.0 mmol, 5% excess) was added via syringe. The resulting solution was allowed to warm, to room temperature, with formation of a small amount of white precipitate. Solutions of the fulvalene dianion prepared in this manner are pale yellow to purple, depending on the degree of air oxidation.  $^1\text{H}$  NMR (THF- $d_6$ , 60 MHz):  $\delta$  5.20 (4 H, t), 5.38 (4 H, t).

**Reaction of  $\text{C}_{10}\text{H}_8^{2-}$  with  $\text{Mo}(\text{CO})_6$ .** By using the procedure described above, a solution of the fulvalene dianion in THF (10 mmol in 125 mL) was prepared. Molybdenum hexacarbonyl (5.28 g, 20.0 mmol) was added to this solution against a counter stream of nitrogen. The flask was then fitted with a nitrogen-filled condenser and the dark yellow reaction mixture was heated at reflux for 24 h to yield a brown solution of  $(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)[\text{Mo}(\text{CO})_3]_2^{2-}$  used in subsequent reactions.

**Preparation of (Fulvalene)hexacarbonyldimethylmolybdenum,  $(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)[(\text{CO})_3\text{CH}_3\text{Mo}]_2$ .** By using the procedure described above, a solution of  $(\text{C}_{10}\text{H}_8)\text{Mo}_2(\text{CO})_6^{2-}$  (10 mmol) in THF (125 mL) was prepared and cooled to  $-78^\circ\text{C}$ . Degassed dimethyl sulfate (1.90 mL, 2.52 g, 20.0 mmol) was added via syringe and the reaction mixture was allowed to warm and stir for 7 h. The solvent was removed in vacuo and the resulting brown material was extracted with toluene (200 mL), filtered under nitrogen, and further extracted with toluene ( $2 \times 50$  mL); the remaining brown solid was discarded. The combined bright yellow filtrate was washed with degassed water ( $3 \times 150$  mL) and dried ( $\text{MgSO}_4$ ). The volume was reduced under vacuum at  $40^\circ\text{C}$  until the solution became cloudy. Cooling to  $-15^\circ\text{C}$  yielded yellow-brown crystals which were collected by filtration, washed with ethanol ( $3 \times 15$  mL), and dried in vacuo. A second crop was obtained by the same procedure to give a combined yield of 3.32 g (64% based on  $\text{Na}(\text{DME})\text{C}_5\text{H}_5$ ). An analytical sample was obtained by recrystallization from hot, oxygen-free acetone. Anal. Calcd for  $\text{C}_{18}\text{H}_{14}\text{Mo}_2\text{O}_6$ : C, 41.72; H, 2.72. Found: C, 41.61; H, 2.88.  $^1\text{H}$  NMR (acetone- $d_6$ , 60 MHz):  $\delta$  0.23 (6 H, s), 5.43 (4 H, t,  $J = 2.0$  Hz), 5.78 (4 H, t,  $J = 2.0$  Hz). Infrared: 3110 (w), 2980 (w), 2900 (w), 2010 (vs), 1925 (vs, b) (2010 (vs), 1935 (vs) in  $\text{CCl}_4$  solution), 1445 (w), 1405 (w), 1168 (m), 1061 (m), 1042 (m), 1008 (m), 878 (w), 850 (sh), 832 (s), 620 (w), 590 (s), 565 (s), 491 (s), 451 (m)  $\text{cm}^{-1}$ . Mass spectrum (70 eV) [ $m/e$  (relative abundance)]:  $(\text{C}_{10}\text{H}_8)^{96}\text{Mo}_2(\text{CH}_3)_{2-m}(\text{CO})_{6-n}^+$ ,  $m = 0$ ,  $n = 0-6$ , 518 (4), 490 (0), 462 (11), 434 (19), 406 (16), 378 (33), 350 (23);  $m = 1$ ,  $n = 0-6$ , 503 (0), 475 (0), 447 (2), 419 (10), 391 (29), 363 (38), 335 (83), 334 (100);  $m = 2$ ,  $n = 0-6$ , 488 (0), 460 (10), 432 (23), 404 (16), 376 (37), 348 (33), 320 (26);  $^{96}\text{Mo}_2^+$ , 192 (23);  $\text{C}_{10}\text{H}_8^+$ , 128 (12);  $\text{Mo}_2^{2+}$ , 96 (9).

**Preparation of (Fulvalene)hexacarbonyldimolybdenum,  $(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)(\text{CO})_6\text{Mo}_2$ .** A yellow-brown solution of (fulvalene)hexacarbonyldimolybdenum dianion (10.0 mmol) obtained by the preparation above was cooled to  $-78^\circ\text{C}$  to yield a thick yellow suspension. Bromine (0.52 mL, 1.60 g, 10.0 mmol) was added via syringe, and the mixture was allowed to warm to room temperature. The resulting red-brown solution was stirred for 12 h and the solvent was removed in vacuo. The resulting maroon oil was extracted with hot toluene (200 mL) and filtered. The filtrate was reduced to ca. 100 mL by heating under a stream of nitrogen and then cooled to  $-15^\circ\text{C}$  to yield maroon crystals. These were collected by filtration, washed with ethanol ( $4 \times 15$  mL), and dried in vacuo to give 3.01 g of moderately pure product (62% based on  $\text{Na}(\text{DME})\text{C}_5\text{H}_5$ ).

An analytical sample was prepared by passing a saturated solution of the complex (0.1 g in 25 mL of THF) through a column of alumina (activity grade III) and eluting with benzene. Reduction of the eluent volume followed by cooling yielded pure, crystalline product. These manipulations must be performed with minimum exposure of the solutions to light and air. Anal. Calcd for  $\text{C}_{16}\text{H}_8\text{Mo}_2\text{O}_6$ : C, 39.37; H, 1.65. Found: C, 39.58; H, 1.83.  $^1\text{H}$  NMR (toluene- $d_6$ , 360 MHz):  $\delta$  3.40 (4 H, t,  $J = 2.4$  Hz); 4.32 (4 H, t,  $J = 2.4$  Hz). Infrared: 3125 (m), 1990 (vs), 1915 (vs), 1865 (vs) (2010 (vs), 1960 (vs), 1925 (vs), 1905 (sh), 1880 (sh) in THF solution), 1460 (m), 1450 (m), 1316 (w), 1191 (w), 1080 (w), 1060 (m), 1051 (m), 886 (m), 832 (s), 813 (sh), 588 (s), 554 (s), 493 (s), 451 (s)  $\text{cm}^{-1}$ . Mass spectrum (70 eV) [ $m/e$  (relative abundance)]:  $(\text{C}_{10}\text{H}_8)^{96}\text{Mo}_2(\text{CO})_{6-n}^+$ ,  $n = 0-6$ , 488 (9), 460 (12), 432 (12), 404 (12), 376 (63), 348 (53), 320 (70);  $\text{Mo}_2^+$ ,

192 (32);  $\text{C}_{10}\text{H}_8^+$ , 128 (21);  $\text{Mo}_2^{2+}$ , 96 (9);  $\text{C}_7\text{H}_7^+$ , 91 (100).

## Discussion

The preparation of the 1,2-dimethoxyethane adduct of sodium cyclopentadienide represents convenient, large-scale synthesis and isolation of this widely used organometallic ligand. An equivalent weight determination and integrated  $^1\text{H}$  NMR spectrum clearly establish its formulation as a mono(dimethoxyethane) adduct. The isolation of the pure, crystalline  $\text{Na}(\text{DME})\text{C}_5\text{H}_5$  is particularly useful in maintaining good control of stoichiometry in the reaction with iodine to yield 5-iodocyclopentadiene,<sup>20</sup> which undergoes nucleophilic substitution by cyclopentadienide to yield solutions of 9,10-dihydrofulvalene. This hydrocarbon is stable in solution at low temperature and has been shown to convert to the 1,5 isomer on warming.<sup>21,22</sup> An in situ deprotonation with *n*-butyllithium generates the bicyclopentadienide or fulvalene dianion in good overall yield. The reaction of this ligand with molybdenum hexacarbonyl to yield the  $(\eta^5:\eta^5\text{-fulvalene})\text{-hexacarbonyldimolybdenum}$  dianion (**1**) parallels the early work of Fischer et al.<sup>23</sup> in the synthesis of the  $\eta^5\text{-cyclopentadienylmolybdenum tricarbonyl anion}$ , which they isolated as a soluble mercury(II) complex. The reaction of the (fulvalene)hexacarbonyldimolybdenum dianion (**1**) with mercuric acetate in THF yielded a dark red solution and a small amount of uncharacterized yellow material ( $\nu_{\text{CO}}$  2000 (sh), 1970 (m), 1910 (sh), 1880 (m),  $\nu_{\text{O}_2\text{CCH}_3}$  1580 (s), 1445 (s)  $\text{cm}^{-1}$ ). The addition of hexane to the red THF solution yielded a yellow precipitate that would not redissolve in THF. Removal of solvent from the remaining solution and extraction of the residue with ether removed trace amounts of a soluble compound whose  $^1\text{H}$  NMR ( $\text{CDCl}_3$   $\delta$  5.41 (s), 5.26 (t), 4.27 (t),  $J = 2.0$  Hz) and infrared spectra ( $\nu_{\text{CO}}$  2020 (sh), 1965 (m), 1880 (s, b)  $\text{cm}^{-1}$ , as halocarbon null) are consistent with the formulation of a tetramer  $(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)\text{Mo}_2(\text{CO})_6\text{-}\mu\text{-}[\text{Hg}(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ . Further solvent extraction gave evidence for the presence of trace amounts of higher oligomers. The insoluble material is presumably a polymer linked by molybdenum-mercury bonds and bridging fulvalene ligands, with the unsubstituted cyclopentadienyl end groups originating from trace amounts of uncoupled cyclopentadienide ion.

The reaction of **1** with dimethyl sulfate gave good overall yields of the dimethyl derivative. Cleavage of the methyl-molybdenum bond with bromine yielded the slightly soluble dibromo derivative ( $\nu_{\text{CO}}$  2050 (s), 1975 (s, b)  $\text{cm}^{-1}$ , in THF solution). Attempts to prepare the dihydride complex by protonation of **1** with acetic acid resulted in formation of the metal-metal bonded derivative  $(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)[\text{Mo}(\text{CO})_3]_2$  (**2**) in low yield. It appears that the dihydride derivative in the fulvalene system is distinctly less stable to loss of hydrogen than the "parent"  $\eta^5\text{-cyclopentadienylmolybdenum tricarbonyl hydride}$ .<sup>24</sup> Oxidation of **1** with 1 equiv of bromine gave good yields of the slightly soluble **2**. This compound is somewhat light sensitive in both the solid and the solution, and samples that were not chromatographed in the dark consistently gave low carbon and hydrogen analysis.

The mass spectra of both the dimethyl and the metal-metal bonded derivatives exhibit a parent ion envelope with an isotope distribution characteristic of two molybdenum atoms. The metal-metal bonded derivative exhibited a sequential loss of all carbonyls with relatively more abundant ions corresponding to the loss of four and six carbonyls. The mass spectrum of the dimethyl derivative is complicated by the overlay of three fragmentation patterns corresponding to the concurrent loss of carbonyl and methyl groups. Interestingly, no ions corresponding to the loss of one carbonyl and/or one methyl group were observed. The most intense ion envelope, with a maximum at  $m/e$  334, is of a  $(\text{C}_{10}\text{H}_8)\text{Mo}_2(\text{CH}_3)^+$  ion, with some loss of hydrogen. Both derivatives exhibited relatively

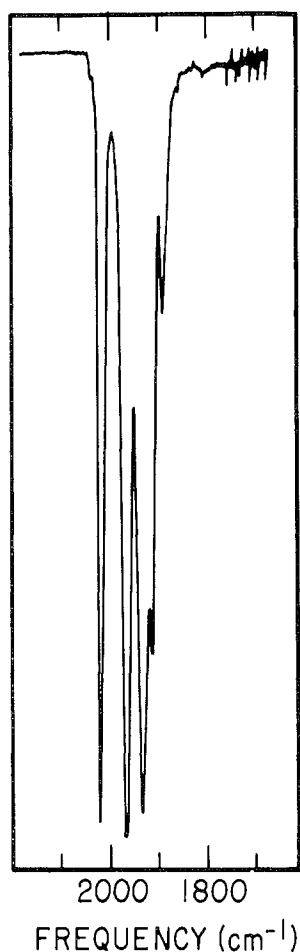


Figure 1. Infrared spectrum of  $(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)(\text{CO})_6\text{Mo}_2$  in tetrahydrofuran.

abundant  $\text{C}_{10}\text{H}_8^+$ ,  $\text{Mo}_2^+$ , and  $\text{Mo}_2^{2+}$  ions.

The infrared spectra of the dimethyl and dibromo derivatives exhibit carbonyl stretching frequencies that are very similar to those of the parent compounds and indicate that the two  $\text{Mo}(\text{CO})_3$  moieties are not vibrationally coupled. The spectrum of metal-metal bonded **2** in Figure 1 exhibits five well-resolved terminal carbonyl stretching bands. This is consistent with the presence of a completely coupled  $\text{Mo}_2(\text{CO})_6$  moiety of local  $C_{2v}$  point group symmetry. The "parent" dimer exhibited two bands at somewhat lower frequency, consistent with  $C_{2h}$  symmetry of a trans conformation.<sup>25</sup>

The  $^1\text{H}$  NMR spectrum of the dimethyl derivative exhibits a closely spaced pair of symmetrical triplets of the fulvalene ligand and a sharp methyl resonance at higher field. Both ring resonances are deshielded with respect to  $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_3$ . The  $^1\text{H}$  NMR spectrum of **2** exhibits a widely spaced, three-line pattern of approximately equal intensity, in which the inner line of each pattern is relatively broad. Homonuclear decoupling experiments confirm the assignment of an  $\text{AA}'\text{BB}'$  spin system, in which  $J_{\text{AB}} \neq J_{\text{A'B'}}$  and are ca. 2.4 Hz while  $J_{\text{AA}'}$ ,  $J_{\text{BB}'}$  are ca. zero. The large chemical shift difference between the protons  $\alpha$  and  $\beta$  to the bridge is consistent with that observed for complexes of type II, compared to those of type Ib, and seems to be associated with a relatively coplanar disposition of five-membered rings in the bridging ligand. Both resonances of **2** are more strongly

shielded than those of the fulvalene dianion and the dimethyl derivative of **1**, as well as that of the "parent"  $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_3$  ( $\delta$  5.33 in  $\text{DCCl}_3$ ).

We attribute this shielding and the larger chemical shift difference of the protons of **2** to the magnetic anisotropy induced by the metal-metal bond. This effect has been shown to be a function of the position of the proton with respect to the metal-metal bond and the longitudinal and transverse magnetic susceptibilities of the bond.<sup>26</sup> While the exact geometry of **2** has not been determined, it appears that the  $\beta$  protons lie in a position to be more shielded by this effect. This suggests that resonances at higher and lower field can be assigned to the  $\alpha$  and  $\beta$  protons. Similar assignments (for different reasons) have been suggested for complexes of types Ib and II. If the correlation of  $^1\text{H}$  NMR spectra with structural features can be well established, it may serve to differentiate complexes of types Ia and Ib and metal-metal bonding in complexes of type II.

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**Registry No.** **1**, 62228-17-5; **2**, 62228-18-6;  $(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)[(\text{CO})_3\text{CH}_3\text{Mo}]_2$ , 62228-19-7;  $\text{Na}(\text{DME})\text{C}_5\text{H}_5$ , 62228-16-4;  $\text{C}_{10}\text{H}_8^{2-}$ , 62228-12-0;  $\text{Mo}(\text{CO})_6$ , 13939-06-5; DME, 25154-53-4; cyclopentadiene, 542-92-7; dimethyl sulfate, 77-78-1;  $(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)\text{Mo}_2(\text{CO})_6\text{-}\mu\text{-}[\text{Hg}(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ , 62279-98-5.

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