

# Syntheses, Properties, and X-ray Crystal Structures of the Molybdenum Dimers [ $\eta^5\text{-Cp}_2\text{Mo}_2\text{Br}_2(\text{CO})_2$ ] and [ $\eta^5\text{-Cp}_2\text{Mo}_2\text{Br}_4$ ] ( $\eta^5\text{-1-(2,5-Dimethoxyphenyl)-2,3,4,5-tetraphenylcyclopentadienyl}$ )

Charles Saadeh, Stephen B. Colbran,\* Donald C. Craig, and A. David Rae

Department of Inorganic and Nuclear Chemistry, University of New South Wales,  
P.O. Box 1, Kensington, Australia 2033

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The  $d^4\text{-}d^4$  [ $\eta^5\text{-CpMo}(\mu\text{-Br})(\mu\text{-CO})$ ] $_2$  (Mo=Mo bond: 2.641 (2) Å) and  $d^3\text{-}d^3$  [ $\eta^5\text{-CpMo}(\mu\text{-Br})_2$ ] $_2$  (Mo-Mo bond: 2.691 (4) Å) dimers have been prepared and their X-ray crystal structures elucidated ([ $\eta^5\text{-Cp}_2\text{Mo}_2\text{Br}_2(\text{CO})_2$ ] $\cdot 2\text{C}_8\text{H}_{10}$ ,  $P\bar{1}$ ,  $a = 10.433$  (12) Å,  $b = 11.857$  (14) Å,  $c = 16.054$  (17) Å,  $\alpha = 86.44$  (8) $^\circ$ ,  $\beta = 76.81$  (9) $^\circ$ ,  $\gamma = 75.44$  (9) $^\circ$ ,  $V = 1871$  (4) Å $^3$ ,  $Z = 1$ ,  $R = 0.069$ ,  $R_w = 0.087$ ; [ $\eta^5\text{-Cp}_2\text{Mo}_2\text{Br}_4$ ] $\cdot 2\text{CH}_2\text{Cl}_2$ ,  $P\bar{1}$ ,  $a = 11.234$  (15) Å,  $b = 13.453$  (20) Å,  $c = 14.612$  (14) Å,  $\alpha = 74.37$  (8) $^\circ$ ,  $\beta = 70.27$  (9) $^\circ$ ,  $\gamma = 89.43$  (7) $^\circ$ ,  $V = 1994$  (5) Å $^3$ ,  $Z = 1$ ,  $R = 0.063$ ,  $R_w = 0.075$ ). Dynamic behavior observed in variable-temperature  $^1\text{H}$  NMR spectra (260–400 K) of the molybdenum dimers is discussed, and the electrochemistries and chemical oxidations of the dimers are described.

The recent resurgence of interest in transition metal complexes of the pentaphenylcyclopentadienyl ( $\eta\text{-C}_5\text{Ph}_5$ ) ligand has been largely fueled by the discovery that these complexes have enhanced kinetic stabilities and redox chemistries compared to  $\eta^5\text{-C}_5\text{R}_5$  ( $R = \text{H}$ , alkyl) analogues.<sup>1-3</sup> The stability of these complexes arises from the steric bulk of the  $\eta\text{-C}_5\text{Ph}_5$  ligand whereas their rich redox chemistries presumably indicate some electronic interaction between the cyclopentadienyl ring and its phenyl substituents. We have reported the preparation of 1-(2,4-dimethoxyphenyl)-2,3,4,5-tetraphenylcyclopentadienyl ( $\eta^5\text{-Cp}$ ) ruthenium(II) complexes and have shown that the dimethoxyphenyl group can be further elaborated to produce electrochemically-active complexes with pendant hydroquinones or quinones.<sup>2</sup> In an extension of this chemistry, we have developed routes to  $\eta^5\text{-CpMo}$  complexes. There are few reports of molybdenum complexes of the analogous  $\text{C}_5\text{Ph}_5$  ligand,<sup>3</sup> and to the best of our knowledge, [ $\eta\text{-C}_5\text{Ph}_5$ ] $_2\text{Pd}_2(\mu\text{-PhC}\equiv\text{CPh})$  is the single crystallographically characterized metal-metal bonded dimer in which both metals are bonded by the bulky  $\text{C}_5\text{Ph}_5$  ligand.<sup>4</sup> Herein, we report the syntheses, properties, and X-ray structures of the dimeric complexes [ $\eta^5\text{-Cp}_2\text{Mo}_2(\mu\text{-Br})_2(\mu\text{-CO})_2$ ] and [ $\eta^5\text{-Cp}_2\text{Mo}_2(\mu\text{-Br})_4$ ].

## Results and Discussion

**Syntheses and Spectroscopic Data.** Reaction of [ $\text{Mo}(\text{CO})_6$ ] with  $\text{Na}^+\text{Cp}^{5-}$  (produced in situ from  $\eta^5\text{-CpBr}^2$  and excess sodium amalgam (1%)) in tetrahydrofuran heated at reflux gave  $\text{Na}^+[\eta^5\text{-CpMo}(\text{CO})_3]$ , which following metathesis with  $\text{PPh}_4\text{Br}$  was obtained as its  $\text{PPh}_4^+$  salt,  $\text{PPh}_4^+[\eta^5\text{-CpMo}(\text{CO})_3]$  (1), as a pale yellow microcrystalline powder in 86% overall yield (see the Experimental Section for analytical and spectroscopic data). Metalate anion 1 has two peaks at 1896 and 1781  $\text{cm}^{-1}$  in its carbonyl IR spectrum, and its  $^1\text{H}$  NMR spectrum in *d*-chloroform revealed aryl resonances and two methoxy peaks at  $\delta$  3.46, 2.99. The methoxy peaks remained sharp from 200 to 350 K whereas changes were observed in the phenyl proton multiplets over this temperature range that are consistent with freezing phenyl ring rotation.<sup>6-8</sup> Treatment of 1 with glacial acetic acid followed by 1 equiv of *N*-bromosuccinimide provided a facile high yield (82%) route to the orange crystalline Mo(II) bromide complex [ $\eta^5\text{-CpMo}(\text{CO})_3\text{Br}$ ] (2). The expected shift to higher carbonyl

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(8) Accumulated evidence from  $\eta^5\text{-Cp}$  complexes suggests that the dimethoxyphenyl substituent lies almost perpendicular to the cyclopentadienyl ring with the *o*-methoxy group orientated away from the molybdenum atom,<sup>7</sup> e.g.: (i) fluxional processes are never observed for the methoxy groups in  $\eta^5\text{-Cp}$  complexes where the other ligands that bond the metal are equivalent, e.g. 1 and 4; (ii) all five crystal structures of  $\eta^5\text{-Cp}$  complexes solved to date show this orientation for the dimethoxyphenyl substituent; (iii) modeling studies (using BIOSYM DISCOVERY molecular mechanics package) of the ligand anion  $\eta^5\text{-Cp}^-$  suggest that the flanking phenyl rings severely restrict the rotation of the dimethoxyphenyl ring from one side of the cyclopentadienyl ring to the other (Colbran, S. B.; Saadeh, C.; Scudder, M. Unpublished results); (iv) the routes established to  $\eta^5\text{-Cp}$  complexes fail for metal complexes of the analogous 1-(2,4,6-trimethoxyphenyl)-2,3,4,5-tetraphenylcyclopentadienyl anion which would necessarily have an *o*-methoxy group pointing toward the metal atom (Colbran, S. B.; Saadeh, C. Unpublished results).

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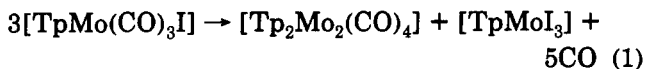
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frequencies (found at 2047, 1979, and 1960  $\text{cm}^{-1}$ ) was observed in the IR spectrum of **2**. In the ambient-temperature  $^1\text{H}$  NMR spectrum of **2** recorded in *d*-chloroform, the methoxy proton resonances were noticeably broad. On cooling, these sharpen to give two sets of methoxy peaks at  $\delta$  3.66, 3.13 and  $\delta$  3.15, 3.02, which we attribute to the two rotamers that arise from the dimethoxyphenyl group either lying between two carbonyl ligands or between a carbonyl and a bromide ligand.<sup>3a-c,8</sup> Concomitant changes in the phenyl region, again consistent with freezing the phenyl ring rotation, were also seen as the temperature was lowered.<sup>6</sup> A detailed description of fluxional processes in complexes of the type  $[\#\text{CpM}(\text{CO})_n\text{X}]$  will be given elsewhere.<sup>7</sup>

Heating **2** in xylenes at reflux with slow nitrogen sparging cleanly gave the orange-red  $d^4-d^4$  dimer  $[\#\text{Cp}_2\text{Mo}_2\text{Br}_2(\text{CO})_2]$  (**3**) in 93% yield. The formation of **3** is unprecedented. Only dimers of the type  $[(\eta\text{-C}_5\text{R}_5)_2\text{Mo}_2(\text{CO})_4\text{X}_2]$  (R = H, alkyl; X = Cl, Br, I) have been isolated from thermal or photolytic decarbonylation reactions of  $[(\eta\text{-C}_5\text{R}_5)\text{Mo}(\text{CO})_3\text{X}]$  or from the reactions of  $[(\eta\text{-C}_5\text{R}_5)_2\text{Mo}_2(\text{CO})_4]$  with halogens.<sup>9</sup> Also a hydridotris(pyrazolyl)borate (Tp) analogue of **2**,  $[\text{TpMo}(\text{CO})_3\text{I}]$ , disproportionates rather than dimerizes when heated (eq 1).<sup>10</sup> IR spectra



of **3** in the carbonyl region show three bands at 1940, 1888, and 1853  $\text{cm}^{-1}$  in dichloromethane solution and at 1939, 1891, and 1856  $\text{cm}^{-1}$  in the solid state. It follows that **3** has equivalent solution- and solid-state structures. The lower  $\nu(\text{CO})$  frequencies of **3** compared to **2** are consistent with bridging (or semibringing) carbonyl ligands in **3**. An X-ray crystal analysis of **3** revealed that all four bromide and carbonyl ligands are bridging but disordered (vide infra). Both *cis* and *trans* arrangements of these bridging ligands are possible.  $^1\text{H}$  NMR spectra of **3** provide conclusive evidence that the dimer was in fact isolated as a mixture of *cis* and *trans* isomers. The ambient-temperature  $^1\text{H}$  NMR spectrum recorded in *d*-chloroform revealed sharp methoxy peaks at  $\delta$  3.59, 3.31 flanked by two lower intensity pairs of broad methoxy peaks at  $\delta$  3.61, 3.58 and  $\delta$  3.29, 2.98, as well as the expected aryl multiplets. The broad low intensity methoxy resonances suggested exchange processes were occurring.

A variable-temperature 500-MHz  $^1\text{H}$  NMR study of **3** in *d*<sub>5</sub>-chlorobenzene was undertaken to characterize the fluxional processes in this dimer. Expansions over the methoxy region of the  $^1\text{H}$  NMR spectra are reproduced in Figure 1. Our accumulated evidence suggests that in all  $\#\text{Cp}$  complexes the dimethoxyphenyl substituent lies almost perpendicular to the cyclopentadienyl ring with the *o*-methoxy group orientated away from the molybdenum atom.<sup>8</sup> The spectra are readily interpreted provided that the two  $\#\text{Cp}$  ligands rotate independently of each other.<sup>11</sup> Chart I shows representations of the *trans*-**3**

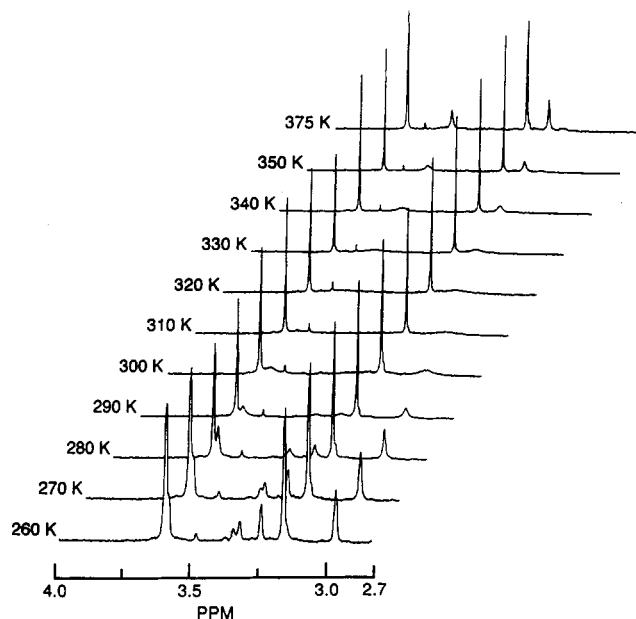
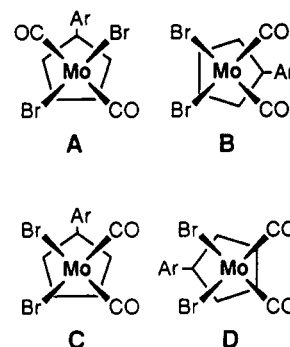


Figure 1. Temperature-dependent 500-MHz  $^1\text{H}$ -NMR spectra (methoxy region) of  $[\#\text{Cp}_2\text{Mo}_2\text{Br}_2(\text{CO})_2]$  in *d*<sub>5</sub>-chlorobenzene. (The small peak at  $\delta \sim 3.49$  is due to an impurity.)

Chart I

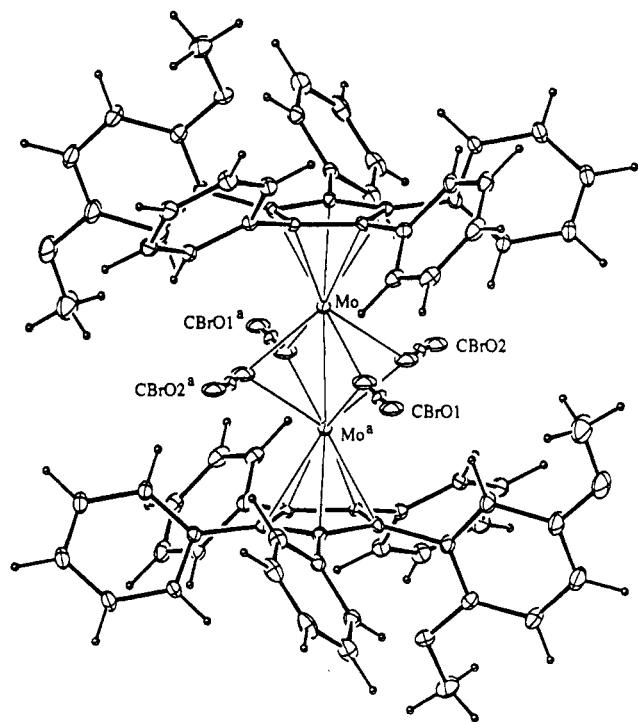


(A) and *cis*-**3** (B–D) drawn looking down the Mo–Mo axis from one molybdenum atom toward the other so as to emphasize the possible positions for the dimethoxyphenyl substituent (Ar). For *trans*-**3** only structure A is possible, and thus the two highest intensity methoxy peaks at  $\delta$  3.59 and 3.14 (in the 260 K spectrum) which remain sharp over the temperature range 260–400 K must arise from this isomer. For *cis*-**3** three rotamers, B–D, are possible. Six methoxy peaks, one pair for each rotamer, are thus expected in the limiting low-temperature spectrum of *cis*-**3** and are observed at  $\delta$  3.57, 3.34, 3.31, 3.24, and 2.96 in the 260 K spectrum. The coalescences observed for the methoxy peaks of *cis*-**3**, one each at  $T_c \sim 315$  K for the  $\#\text{Cp}$  *o*- and *m*-methoxy groups, are indicative of rapid exchange between rotamers B–D. From the integrated intensities of the methoxy peaks the ratio of *cis*-**3** to *trans*-**3** is  $\sim 1:2$ . Changes in the aryl region of  $^1\text{H}$  NMR spectra recorded over the temperature range 260–375 K were also observed; the multiplets of the *meso*-phenyl protons coalesced and split in two as the temperature was lowered. This behavior is analogous to that observed in tetraphenylcyclopentadienyl ( $\eta^5\text{-C}_5\text{Ph}_4\text{H}$ ) complexes and is indicative of hindered phenyl substituent rotation.<sup>6</sup> In contrast, no coalescence was observed for the dimethoxyphenyl multiplets providing further evidence for static dimethoxyphenyl groups in **3**.<sup>8</sup>

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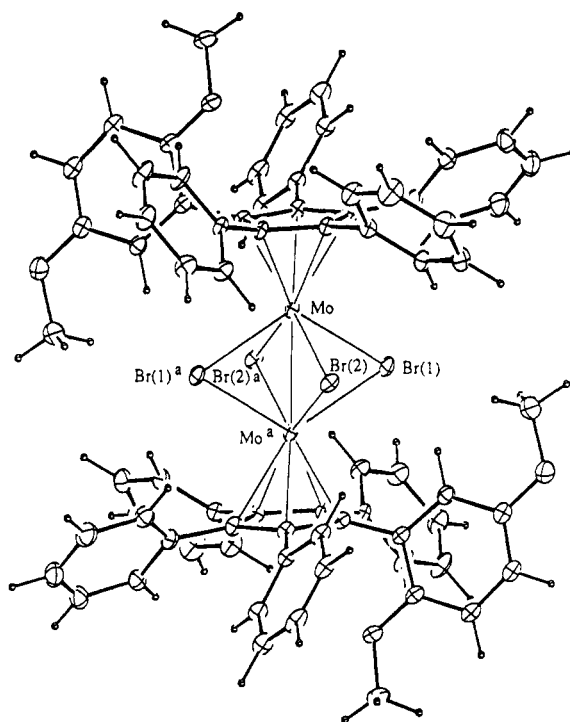
(11) The observation of two sharp methoxy peaks for *trans*-**3** from 260–400 K in the  $^1\text{H}$  NMR spectra provides confirmation that the dimethoxyphenyl groups do not rotate and that rotation of the two  $\#\text{Cp}$  ligands is not correlated and also indicates that no interconversion of *cis*-**3** and *trans*-**3** occurs.



**Figure 2.** ORTEP plot of  $[\text{Cp}_2\text{Mo}_2\text{Br}_2(\text{CO})_2]$ . The bridging Br and CO ligands are disordered—each bridging position was modeled as a half-occupancy Br and two quarter-occupancy semibringing CO ligands (see text). For clarity the two semibringing CO ligands per bridging position are shown as an averaged (i.e. symmetrically bridging) CO ligand.

The orange  $d^3-d^3$  dimer  $[\text{Cp}_2\text{Mo}_2\text{Br}_4]$  (4) is readily accessible (86% yield) from the reaction of 2 with excess allylbromide in octane heated at reflux. This synthesis contrasts with the reactions of allylhalides with the complexes  $[(\eta\text{-C}_5\text{R}_5)\text{Mo}(\text{CO})_3\text{X}]$  (R = H, alkyl; X = Cl, Br, I), which yield  $\eta$ -allyl-substituted products,<sup>12</sup> but parallels the preparations of the chromium dimers  $[(\eta\text{-Cp})_2\text{Cr}_2\text{X}_4]$  (X = Br, I) first described by Fischer et al. in 1963.<sup>13</sup> However,  $[(\eta\text{-C}_5\text{R}_5)_2\text{Mo}_2\text{X}_4]$  (R = H, alkyl; X = Cl, Br) analogues of 4 have been prepared by reduction of the respective  $[(\eta\text{-C}_5\text{R}_5)\text{MoX}_4]$  monomers<sup>14</sup> or by treating the fulvene-arene complexes  $[\text{Mo}(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{-}\mu\text{-CR}_2)(\eta\text{-arene})]$  with HCl.<sup>15</sup> The  $^1\text{H}$  NMR spectrum of 4 showed the requisite aryl proton resonances and two methoxy peaks (at  $\delta$  3.59 and 3.31 in *d*-chloroform). In variable-temperature 500-MHz  $^1\text{H}$  NMR spectra of 4 recorded in *d*<sub>5</sub>-chlorobenzene from 260 to 400 K, exchange processes were apparent for the phenyl protons but not for the dimethoxyphenyl aryl or methoxy protons which remained sharp over the whole temperature range. This, again, is indicative of hindered phenyl substituent rotation<sup>6</sup> but fixed dimethoxyphenyl substituents in the coordinated #Cp ligands of, in this case, 4.

**X-ray Structures of 3 and 4.** The molecular structures of 3 and 4 are shown in Figures 2 and 3 with selected



**Figure 3.** ORTEP plot of  $[\text{Cp}_2\text{Mo}_2\text{Br}_4]$ .

bond lengths and angles listed in Tables I and II, respectively. The structures of both compounds consist of a centrosymmetric dimolybdenum unit with each molybdenum atom bound by an axially coordinated  $\eta^5$ -#Cp ligand and with the Mo-Mo axis spanned by four bridging ligands (two carbonyl and two bromide ligands in 3 and four bromide ligands in 4). The bromide and carbonyl bridging ligands in 3 are completely disordered over the four bridging positions. Therefore, information about the cis/trans geometrical isomerization in 3 cannot be ascertained. Each of the two independent bridging positions was modeled to comprise a half-occupancy Br atom and two quarter-occupancy semibringing CO ligands<sup>16</sup> (see Experimental Section). The Mo-C and Mo-O distances were restrained to maintain a consistency between sites and refined to a short Mo-C distance of 2.098 (16) Å and a long Mo-C distance of 2.303 (17) Å for each semibringing CO ligand. The Mo-C-Mo(a) angles were all 73.6 (4)° and the Mo-C-O angles were all in the range 135–141 (2)° for the short Mo-C distance, while Mo-C-O angles in a range 115–118 (2)° were obtained for the long Mo-C distance. These distances and angles are typical for semibringing CO ligands.<sup>16</sup> Dimer 3 is the only crystallographically characterized transition metal dimer spanned by two bridging or semibringing carbonyl ligands and by two bridging halide ligands. The geometry of 4 is common to other early transition metal monocyclopentadienyl halides<sup>17</sup> (crystallographically characterized examples:  $d^2-d^2$   $[(\eta^5\text{-C}_5\text{Me}_5\text{Et})\text{VBr}_2]_2$ <sup>18</sup> and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{TaBr}_2]_2$ ,<sup>19</sup>  $d^3-d^3$   $[(\eta^5\text{-C}_5\text{H}_4\text{-Pr}^i)\text{MoCl}_2]_2$ <sup>15</sup> and  $[(\eta^5-$

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**Table I.** Selected Bond Distances (Å) and Interbond Angles (deg) for [ $\eta^5\text{Cp}_2\text{Mo}_2(\text{CO})_2\text{Br}_2$ ]<sup>a</sup>

Bond Distances					
Mo-Moa	2.641 (2)	Mo-Br(1)	2.532 (2)	Mo-Br(1)a	2.641 (2)
Mo-Br(2)	2.633 (2)	Mo-Br(2)a	2.514 (2)	Mo-CC(1)a	2.099 (16)
Mo-CC(2)a	2.098 (16)	Mo-CC(1)'	2.098 (16)	Mo-CC(2)'	2.098 (16)
Mo-CC(1)'a	2.303 (17)	Mo-CC(2)'a	2.303 (17)	Mo-CC(1)	2.303 (17)
Mo-CC(2)	2.303 (17)	Mo-C(1)	2.243 (9)	Mo-C(2)	2.351 (8)
Mo-C(3)	2.421 (8)	Mo-C(4)	2.372 (9)	Mo-C(5)	2.264 (9)
OC(1)-CC(1)	1.133 (11)	OC(2)-CC(2)	1.139 (9)	OC(1)'-CC(1)'	1.155 (12)
OC(2)'-CC(2)'	1.140 (10)	C(2)-C(1)	1.431 (7)	C(3)-C(2)	1.431 (8)
C(4)-C(3)	1.428 (8)	C(5)-C(1)	1.434 (7)	C(5)-C(4)	1.434 (8)
C(6)-C(1)	1.534 (15)	C(14)-C(2)	1.478 (9)	C(20)-C(3)	1.478 (9)
C(26)-C(4)	1.478 (9)	C(32)-C(5)	1.478 (9)		

Interbond Angles			
Br(1)-Mo-Br(2)	75.1 (1)	Br(1)a-Mo-Br(2)a	75.2 (1)
Br(1)-Mo-Br(2)a	76.5 (1)	Br(2)-Mo-Br(1)a	72.6 (1)
Br(1)-Mo-Br(1)a	118.6 (1)	Br(2)-Mo-Br(2)a	118.3 (1)
#Cp-Mo-Br(1)	120.1 (5)	#Cp-Mo-Br(2)	118.2 (5)
#Cp-Mo-Br(1)a	121.0 (5)	#Cp-Mo-Br(2)a	123.4 (5)
Mo-Br(1)-Moa	61.4 (1)	Mo-Br(2)-Moa	61.7 (1)
Mo-CC(1)-OC(1)	118.4 (18)	OC(2)'-CC(2)'-Moa	114.5 (17)
Mo-CC(2)-OC(2)	114.7 (17)	OC(1)'-CC(1)'-Moa	117.2 (17)
Mo-CC(1)'-OC(1)'	138.4 (23)	OC(2)-CC(2)-Moa	135.4 (19)
Mo-CC(2)'-OC(2)'	135.2 (19)	OC(1)-CC(1)-Moa	140.8 (24)
Mo-CC(1)-Moa	73.6 (4)	Mo-CC(2)-Moa	73.6 (4)
Mo-CC(1)'-Moa	73.6 (4)	Mo-CC(2)'-Moa	73.6 (4)

<sup>a</sup> "a" refers to the equivalent position 1 - x, -y, -z; #Cp is the centroid of the cyclopentadienyl (C<sub>5</sub>) ring.

**Table II.** Selected Bond Distances (Å) and Interbond Angles (deg) for [ $\eta^5\text{Cp}_2\text{Mo}_2\text{Br}_4$ ]<sup>a</sup>

Bond Distances					
Mo-Moa	2.691 (4)	Br(1)-Mo	2.614 (3)	Br(1)-Moa	2.629 (3)
Br(2)-Mo	2.608 (3)	Br(2)-Moa	2.623 (3)	C(1)-Mo	2.238 (19)
C(2)-Mo	2.233 (15)	C(3)-Mo	2.355 (16)	C(4)-Mo	2.434 (16)
C(5)-Mo	2.351 (16)	C(2)-C(1)	1.466 (14)	C(3)-C(2)	1.463 (15)
C(4)-C(3)	1.456 (15)	C(5)-C(4)	1.454 (15)	C(5)-C(1)	1.461 (14)
C(6)-C(1)	1.439 (31)	C(14)-C(2)	1.482 (16)	C(20)-C(3)	1.481 (16)
C(26)-C(4)	1.482 (16)	C(32)-C(5)	1.482 (16)		

Interbond Angles			
Br(1)-Mo-Br(2)	75.2 (1)	Br(1)a-Mo-Br(2)a	74.7 (1)
Br(1)-Mo-Br(2)a	74.4 (1)	Br(2)-Mo-Br(1)a	74.4 (1)
Br(1)-Mo-Br(1)a	118.2 (1)	Br(2)-Mo-Br(2)a	118.1 (1)
#Cp-Mo-Br(1)	120.1 (5)	#Cp-Mo-Br(2)	118.6 (5)
#Cp-Mo-Br(1)a	121.6 (5)	#Cp-Mo-Br(2)a	123.4 (5)
Mo-Br(1)-Moa	61.8 (1)	Mo-Br(2)-Moa	61.9 (1)

<sup>a</sup> "a" refers to the equivalent position 1 - x, 1 - y, -z; #Cp is the centroid of the cyclopentadienyl (C<sub>5</sub>) ring.

C<sub>5</sub>Me<sub>5</sub>WCl<sub>2</sub>]<sub>2</sub>,<sup>20</sup> and d<sup>2</sup>-d<sup>3</sup> [( $\eta^5\text{-C}_5\text{Me}_5$ )MoI<sub>2</sub>]<sub>2</sub>I<sub>3</sub>]<sup>21</sup>).

The #Cp cyclopentadienyl C-Mo distances in both dimers are unremarkable averaging 2.33 Å in **3** and 2.36 Å in **4**. The angles between the C<sub>5</sub> ring and the phenyl groups attached via atoms C(1)-C(5) are 75.3, 45.4, 48.1, 48.3, and 53.6°, respectively, for **3** and 76.8, 55.8, 47.8, 48.0, and 55.4°, respectively, for **4**. The Br-Mo distances average 2.580 Å in **3** and 2.618 Å in **4**. More importantly, the acute Mo-Br-Mo angles which are remarkably similar in **3** and **4** (averaging 61.5° in **3** and 61.9° in **4**) are indicative of strong metal-metal interaction in both compounds. According to the EAN formalism there should be a Mo=Mo double bond in **3** and a Mo-Mo single bond in **4**. The Mo-Mo separation is 2.641 (2) Å in **3** and 2.691 (4) Å in **4**, a difference of only 0.050 Å. The small difference probably reflects the fact that with four bridging groups the Mo-Mo bond distances in **3** and **4** are highly constrained—lengthening the Mo-Mo distance would lead

to unreasonable contacts between the bridgehead atoms, while shortening the Mo-Mo distance would cause excessive contacts between the bulky #Cp and bridging ligands.<sup>22</sup> The dimers [( $\eta\text{-Cp}$ )Mo( $\mu\text{-PPh}_2$ )(CO)]<sub>2</sub><sup>23</sup> and [( $\eta\text{-Cp}$ )Mo( $\mu\text{-SBU}^t$ )(CO)]<sub>2</sub>,<sup>24</sup> which are isoelectronic with **3** and provide the most relevant comparison with **3**, display Mo=Mo distances of 2.712 (2) and 2.616 (2) Å, respectively. Interestingly these dimers adopt a different structure compared to **3**—in both dimers the carbonyl ligands are terminal and disposed in a trans arrangement about the Mo-Mo axis, as are the Cp ligands.<sup>23,24</sup> Models suggest that the steric bulk of the #Cp ligand would prevent such a ligand arrangement being adopted by **3**.

**Cyclic Voltammetry and Chemical Oxidations.** The major features observed in the cyclic voltammogram of **3** are a reversible oxidation process at 0.01 V ( $\Delta E_p = 68$  mV; cf.  $\Delta E_p = 70$  mV for the Fc<sup>+0</sup> couple suggesting a one-electron process), an irreversible reduction at -1.79 V which gives rise to four waves at -1.41, -0.76, -0.14, and 0.24 V in the reverse anodic scan, and a quasireversible reduction at -1.92 V ( $\Delta E_p = 130$  mV) which follows the irreversible reduction (Figure 4a). At more positive potentials three irreversible oxidation processes at 0.61, 1.05, and 1.30 V were also observed before the solvent discharge (not shown). Assignment of the reversible oxidation process is complicated because of the following: (i) accurate coulometry could not be undertaken—attempts to oxidize **3** either by electrolysis or by chemical oxidation using Ag(I) salts caused complete degradation of **3** as evidenced by the complete loss of all carbonyl bands from the IR spectrum; (ii) **3** is a mixture of cis and trans isomers—thus the stereochemistry of the species giving rise to the observed reversible couple cannot be definitively established (e.g., is oxidation of cis-**3** or trans-**3** or both

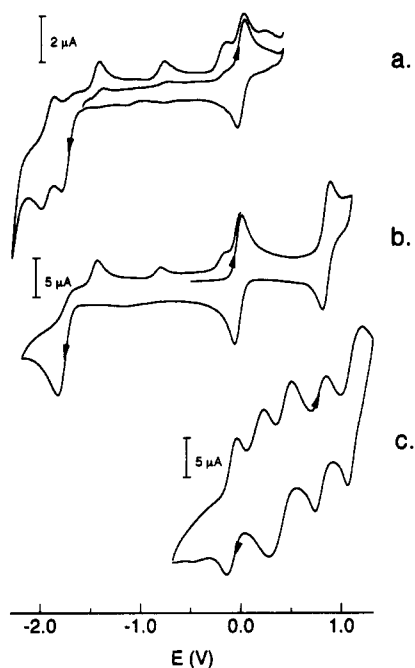
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**Figure 4.** Cyclic voltammograms at a platinum disk electrode in 1,2-dichloroethane (0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>) at 25 °C with a scan rate of 100 mV s<sup>-1</sup> for (a) [ $\eta$ -C<sub>5</sub>Me<sub>5</sub>]<sub>2</sub>Mo<sub>2</sub>Br<sub>2</sub>(CO)<sub>2</sub>, (b) [ $\eta$ -C<sub>5</sub>Me<sub>5</sub>]<sub>2</sub>Mo<sub>2</sub>Br<sub>4</sub>, and (c) [ $\eta$ -C<sub>5</sub>Me<sub>5</sub>]<sub>2</sub>Mo<sub>2</sub>Br<sub>4</sub>(Br<sub>3</sub>).

species observed?). Likewise, the reduction behavior is clearly complex and has not been assigned.

Cyclic voltammograms of 4 showed a reversible one-electron oxidation at -0.03 V ( $\Delta E_p = 68$  mV; cf.  $\Delta E_p = 68$  mV for the Fc<sup>+0</sup> couple), a second quasireversible one-electron oxidation at 0.85 V ( $i^c/i^a = 0.9$ ,  $\Delta E_p = 80$  mV), and an irreversible reduction process at -1.83 V which gives rise to three waves at -1.44, -0.80, and -0.18 V in the return anodic scan (Figure 4b). These results concur with the recent theoretical analyses of Green et al. which would place the six molybdenum d-electrons of 4 in a strongly bonding  $\sigma$ -orbital and in higher-lying, largely nonbonding  $\delta$ ,  $\delta^*$  orbitals.<sup>22</sup> Oxidation thus corresponds to removal of nonbonding  $\delta$  or  $\delta^*$  electrons and will only be accompanied by minor perturbations of the parent structure (i.e. small bond length and angle changes at most). Fast, reversible oxidation(s) are therefore expected for 4. On the other hand, reduction of 4 to [ $\eta$ -C<sub>5</sub>Me<sub>5</sub>]<sub>2</sub>Mo<sub>2</sub>( $\mu$ -Br)<sub>4</sub>]<sup>*n*-</sup> (*n* = 1, 2) places extra electrons in a M-Br antibonding orbital and alternative structures such as [ $\eta$ -C<sub>5</sub>Me<sub>5</sub>]<sub>2</sub>Mo<sub>2</sub>( $\mu$ -Br)<sub>2</sub>Br<sub>2</sub>]<sup>*n*-</sup> (i.e. the same structure as found for d<sup>4</sup>-d<sup>4</sup> [( $\eta$ -C<sub>5</sub>Me<sub>4</sub>Et)<sub>2</sub>Re<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>Cl<sub>2</sub>]<sup>25</sup>) are expected to become energetically favored.<sup>22</sup> A molecular rearrangement, following the initial electron transfer, to a new product with its own distinctive electrochemistry<sup>26</sup> would account for the observed reductive electrochemistry of 4. It is interesting to note that the reverse anodic scan after the irreversible reduction of 4 is very similar to the reverse anodic scan after the first reduction of 3 is traversed. This suggests that the irreversible reductions of 3 and 4 generate common unidentified species.

As expected from the above voltammetry, dimer 4 was easily oxidized yielding its paramagnetic d<sup>2</sup>.d<sup>3</sup> dimolybdenum mixed-valence ion: green crystalline [ $\eta$ -C<sub>5</sub>Me<sub>5</sub>]<sub>2</sub>Mo<sub>2</sub>Br<sub>4</sub>]SbF<sub>6</sub>, ([4<sup>+</sup>]SbF<sub>6</sub>) was obtained from the

reaction mixture of 4 with 1/2 equiv of AgSbF<sub>6</sub>, and green crystalline [ $\eta$ -C<sub>5</sub>Me<sub>5</sub>]<sub>2</sub>Mo<sub>2</sub>Br<sub>4</sub>]Br<sub>3</sub> ([4<sup>+</sup>]Br<sub>3</sub>) was isolated after treating 4 with 1/2 equiv of bromine in dichloromethane. Poli and co-workers have very recently reported the preparation of [( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>L<sub>4</sub>]I<sub>3</sub> (analogous to [4<sup>+</sup>]Br<sub>3</sub>) by thermolysis of [( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)Mo(CO)<sub>2</sub>I<sub>3</sub>].<sup>21</sup> In their respective <sup>1</sup>H NMR spectrum both [4<sup>+</sup>]SbF<sub>6</sub> and [4<sup>+</sup>]Br<sub>3</sub> show four broad phenyl resonances and two broad methoxy peaks at  $\delta$  3.9 and 3.4. Solutions of [4<sup>+</sup>]SbF<sub>6</sub> and [4<sup>+</sup>]Br<sub>3</sub> were EPR silent at room temperature,<sup>27</sup> but in frozen dichloromethane solution at 77 K both complexes showed a broad line at  $g = 2.05$  with no evidence of hyperfine coupling. In contrast, under the same conditions [( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>L<sub>4</sub>]I<sub>3</sub> is reported to display a tetragonal  $g$  tensor with  $g_{\perp} = 2.14$  and  $g_{\parallel} = 2.35$ , which gives  $g_{av} = 2.21$ .<sup>21</sup> The divergent  $g$  values suggest significant electronic differences for the [( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>L<sub>4</sub>]<sup>+</sup> and [ $\eta$ -C<sub>5</sub>Me<sub>5</sub>]<sub>2</sub>Mo<sub>2</sub>Br<sub>4</sub>]<sup>+</sup> mixed-valent cations. Cyclic voltammograms of [4<sup>+</sup>]SbF<sub>6</sub> and [4<sup>+</sup>]Br<sub>3</sub> were also recorded: the voltammogram of [4<sup>+</sup>]SbF<sub>6</sub> was exactly the same as that of 4, thus confirming complete reversibility for the 4<sup>+</sup>/4 couple, whereas the voltammogram of [4<sup>+</sup>]Br<sub>3</sub> was considerably complicated by extra electrochemical processes. The peaks at 0.23 and 0.50 V in the anodic scan and at 0.28 and -0.44 V in the cathodic scan are attributable to the Br<sub>3</sub><sup>-</sup> anion<sup>28</sup> (Figure 4c) in much the same way as the I<sub>3</sub><sup>-</sup> anion was found to complicate the electrochemistry of [( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Mo<sub>2</sub>L<sub>4</sub>]I<sub>3</sub>.<sup>21</sup>

## Experimental Section

Reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk and cannula techniques. Solvents were routinely distilled from an appropriate drying agent under dinitrogen immediately prior to use: dichloromethane from P<sub>2</sub>O<sub>5</sub>; acetone from anhydrous B<sub>2</sub>O<sub>3</sub>; hexanes, toluene, and xylenes from sodium wire; diethyl ether and dimethoxyethane from sodium benzoquinone ketyl. The ligand 1-(2,4-dimethoxyphenyl)-2,3,4,5-tetraphenylcyclopentadienyl bromide ( $\eta$ -CpBr) was prepared according to the published method.<sup>2</sup> All other chemicals were used as obtained from commercial sources (usually Aldrich).

**Physical Measurements.** Infrared spectra were recorded on a Perkin-Elmer 500B infrared spectrometer. <sup>1</sup>H NMR spectra were recorded on Bruker AM500 and CXP300 spectrometers. X-band EPR spectra were recorded on a Bruker ESP300 instrument, using dpph as external calibrant. Melting points are uncorrected. Elemental analyses were determined by the University of NSW microanalytical service. Cyclic voltammograms were recorded with a BAS 100B electrochemical analyzer interfaced to an AT personal computer. A standard three-electrode configuration was used with a Ag/AgCl reference electrode (BAS), a freshly polished platinum working electrode (BAS), and a single Pt wire as the auxiliary electrode. All potentials are quoted relative to the ferrocenium/ferrocene couple, which was measured in situ as an internal calibrant. Solutions were degassed by sparging with high-purity nitrogen (presaturated with solvent) and then blanketed with a cover of nitrogen for the duration of the experiment. An electrochemical scan of the solvent electrolyte system was always recorded before the addition of the compound to ensure that there were no spurious signals.

**Preparation of [PPh<sub>4</sub>][ $\eta$ -CpMo(CO)<sub>2</sub>].** A solution of  $\eta$ -CpBr (2.0 g, 3.4 mmol) in tetrahydrofuran (40 mL) was stirred with 1% sodium amalgam (~4 mL) for 1 h. The resulting yellow solution

(27) The observation of <sup>1</sup>H-NMR spectra implies that the relaxation times must be inappropriate for observation of EPR spectra, see: LaMar, G. N.; Horrocks, W., DeW., Jr., Holm, R. H., Eds.; *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

(28) For comparison, the cyclic voltammogram of [Me<sub>3</sub>NCH<sub>2</sub>Ph]Br<sub>3</sub> recorded in 1,2-dichloroethane (0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>) showed peaks at 0.17 and 0.50 V in the anodic scan and at 0.24 and -0.40 V in the reverse cathodic scan (scan rate = 100 mV s<sup>-1</sup>).

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of Na<sup>\*</sup>Cp was filtered into a Schlenk flask containing [Mo(CO)<sub>6</sub>] (0.9 g, 3.4 mmol) and the mixture heated at reflux for 24 h. The solvent was removed giving crude Na[\*CpMo(CO)<sub>3</sub>] as a yellow powder, which was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and treated with Ph<sub>4</sub>PBr (1.4 g, 3.3 mmol). Recrystallization from hot MeOH-CH<sub>2</sub>Cl<sub>2</sub> gave the yellow, crystalline product: yield 3.0 g (86%); mp 130–132 °C. Anal. Calcd for C<sub>67</sub>H<sub>58</sub>MoO<sub>6</sub>P: C, 75.2; H, 5.5. Found: C, 74.8, H, 5.2. IR (paraffin mull): 1894 vs, 1770 vs, 1381 s, 1224 m, 1112 s, 726 s, 695 s, 531 s cm<sup>-1</sup>. ν<sub>CO</sub> (CH<sub>2</sub>Cl<sub>2</sub>): 1896 vs, 1781 vs cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.82–7.53 (m, PPh<sub>4</sub><sup>+</sup>, 20H), 7.16–6.82 (m, Ph and (MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 21H), 6.54 (dd, <sup>3</sup>J 8.9 Hz, <sup>4</sup>J 3.0 Hz, (MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 1H), 6.48 (d, <sup>3</sup>J 8.9 Hz, (MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 1H), 3.46 (s, MeO, 3H), 2.99 (s, MeO, 3H).

**Preparation of [\*CpMo(CO)<sub>3</sub>Br].** Glacial acetic acid (2 mL) was added dropwise to a solution of Na[\*CpMo(CO)<sub>3</sub>] (3.4 mmol, prepared from \*CpBr and [Mo(CO)<sub>6</sub>] as above) in tetrahydrofuran. After being stirred for 0.5 h, the solution was cooled to -10 °C (ethanol/ice bath) and *N*-bromosuccinamide (0.6 g, 3.3 mmol) added in small portions. Bubbles of gas evolved, and an orange solution formed. Removal of the volatiles in vacuo gave a brown solid, which was extracted with CH<sub>2</sub>Cl<sub>2</sub> and filtered through a 4 × 2 cm plug of silica gel. Recrystallization of the residue from CH<sub>2</sub>Cl<sub>2</sub>-MeOH gave orange crystals of the product: yield 2.8 g (82%); mp 170–172 °C. Anal. Calcd for C<sub>43</sub>H<sub>38</sub>BrMoO<sub>3</sub>: C, 62.8; H, 3.8. Found: C, 62.5, H, 3.7. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.19–6.93 (m, Ph and (MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 21H), 6.75 (dd, <sup>3</sup>J 9.2 Hz, <sup>4</sup>J 3.1 Hz, (MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 1H), 6.57 (d, <sup>3</sup>J 9.2 Hz, (MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 1H), 3.63 (br s, MeO, 3H), 3.19 (s, MeO, 3H). IR (paraffin mull): 2046 vs, 1987 vs, 1950 vs, 1274 vs, 1218 s, 1042 m, 1019 w, 729 m, 704 m, 566 w, 412 w, 387 m cm<sup>-1</sup>. ν<sub>CO</sub>(CH<sub>2</sub>Cl<sub>2</sub>): 2047 vs, 1979 vs, 1960 (sh) cm<sup>-1</sup>.

**Preparation of [\*Cp<sub>2</sub>Mo<sub>2</sub>Br<sub>2</sub>(CO)<sub>2</sub>].** A solution of [\*CpMo(CO)<sub>3</sub>Br] (0.1 g, 0.13 mmol) in *o*-xylene (10 mL) was heated at reflux, while a fine stream of nitrogen gas was passed through the solution for a period of 2 h. The solution was reduced to a third of the original volume and cooled to 0 °C. Dark orange crystals precipitated. These were isolated by filtration, washed with hexane, and dried under vacuum to give the product: yield 0.09 g (93%); mp 234–236 °C. Anal. Calcd for C<sub>78</sub>H<sub>58</sub>Br<sub>2</sub>Mo<sub>2</sub>O<sub>6</sub>: C, 64.3; H, 4.1. Found: C, 64.5; H, 4.3. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.15–6.80 (m, Ph and (MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 21H), 6.63 (m, (MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3H), 3.59 (s, MeO, 3H), 3.31 (s, MeO, 3H). IR (paraffin mull): 1939 w, 1891 s, 1856 s, 1225 vs, 1182 m, 1044 s, 725 m, 703 s, 561 w, 537 w cm<sup>-1</sup>. ν<sub>CO</sub> (CH<sub>2</sub>Cl<sub>3</sub>): 1940 w, 1888 s, 1853 s cm<sup>-1</sup>.

**Preparation of [\*Cp<sub>2</sub>Mo<sub>2</sub>Br<sub>4</sub>].** Allyl bromide (1.5 mL) was added to a suspension of [\*CpMo(CO)<sub>3</sub>Br] (0.50 g, 6.53 mmol) in octane and the resulting mixture heated at reflux for 1 h. The orange powder which precipitated as the solution cooled was collected by filtration, washed with hexane, and then dried in vacuo. Recrystallization from saturated chloroform solution layered with hexane gave the orange crystalline product which was dried in vacuo: yield 0.43 g (86%); mp 234–235 °C. Anal. Calcd for C<sub>74</sub>H<sub>58</sub>Br<sub>4</sub>Mo<sub>2</sub>O<sub>4</sub>: C, 58.3; H, 3.8. Found: C, 58.4; H, 3.8. IR (KBr disk): 3062 vs, 2936 s, 2837 s, 1606 s, 1505 vs, 1469 s, 1430 s, 1280 s, 1229 vs, 1085 s, 1046 s, 931 s, 898 s, 776 s, 727 vs, 702 vs, 540 m cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.10–6.80 (m, Ph, 20H), 6.68–6.59 (m, (MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3H), 3.59 (s, MeO, 3H), 3.31 (s, MeO, 3H).

**Preparation of [\*Cp<sub>2</sub>Mo<sub>2</sub>Br<sub>4</sub>]SbF<sub>6</sub>.** AgSbF<sub>6</sub> (0.023 g, 0.066 mmol) was added to [\*Cp<sub>2</sub>Mo<sub>2</sub>Br<sub>4</sub>] (100 mg, 0.066 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (25 mL). A dark precipitate immediately formed, and the solution turned green. The solution was filtered to remove the solid, and then reduced to a ca. 10-mL volume, layered with 10 mL of *n*-hexane, and left to crystallize at -5 °C. The resulting green crystalline solid was collected by filtration, washed with hexane, and dried in vacuo: yield 98 mg (84%); mp 232–233 °C. Anal. Calcd for C<sub>74</sub>H<sub>58</sub>Br<sub>4</sub>F<sub>6</sub>Mo<sub>2</sub>O<sub>4</sub>Sb: C, 50.5; H, 3.3. Found: C, 50.4; H, 3.2. IR (paraffin mull): 3056 s, 2836 s, 1963 w, 1903 w, 1813 w, 1720 m, 1579 m, 1495 s, 1275 s, 1221 s, 1024 m cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.2 (fwhh = 125 Hz), 7.4 (fwhh = 60 Hz),

6.9 (fwhh = 50 Hz), 6.6 (fwhh = 40 Hz), 3.9 (fwhh = 85 Hz), 3.4 (fwhh = 50 Hz). EPR (CH<sub>2</sub>Cl<sub>2</sub>, 77 K): *g* = 2.05 (80 G peak-to-peak).

**Preparation of [\*Cp<sub>2</sub>Mo<sub>2</sub>Br<sub>4</sub>]Br<sub>3</sub>.** A cooled solution of [\*Cp<sub>2</sub>Mo<sub>2</sub>Br<sub>4</sub>] (0.10 g, 0.066 mmol) in CHCl<sub>3</sub> (10 mL, 0 °C) was treated with a solution of bromine in CHCl<sub>3</sub> (0.75 mL, 0.13 M, 0.099 mmol). A dark green solution immediately resulted. The volatiles were removed under reduced pressure. The dark green residue was extracted with dichloromethane and filtered. An equal volume of hexane was added. Dark green crystals of the product precipitated on cooling the solution overnight at -20 °C: yield 100 mg (85%); mp 225 °C. Anal. Calcd for C<sub>74</sub>H<sub>58</sub>Br<sub>7</sub>O<sub>4</sub>Mo<sub>2</sub>C<sub>6</sub>H<sub>14</sub>: C, 52.0; H, 3.9. Found: C, 51.8; H, 3.7. IR (paraffin mull): 3055 s, 2835 s, 1963 w, 1903 w, 1813 w, 1579 m, 1495 s, 1275 s, 1275 s, 1223 s, 1044 m, 1026 m, 926 w cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.1 (fwhh = 115 Hz), 7.4 (fwhh = 100 Hz), 6.9 (fwhh = 50 Hz), 6.6 (fwhh = 40 Hz), 3.9 (fwhh = 80 Hz), 3.4 (fwhh = 70 Hz); plus peaks for hexane, δ 1.24 (m, CH<sub>2</sub>), 0.86 (t, CH<sub>3</sub>). EPR (CH<sub>2</sub>Cl<sub>2</sub>, 77 K): *g* = 2.05 (65 G peak-to-peak).

**X-ray Crystallography.** [\*Cp<sub>2</sub>Mo<sub>2</sub>Br<sub>2</sub>(CO)<sub>2</sub>]-2C<sub>6</sub>H<sub>10</sub>. **Crystal Data:** *a* = 10.433 (12) Å, *b* = 11.857 (14) Å, *c* = 16.054 (17) Å, α = 86.44 (8)°, β = 76.81 (9)°, γ = 75.44 (9)°, *V* = 1871 (4) Å<sup>3</sup>, *M<sub>r</sub>* = 1631.3, *P*<sub>1</sub>, *Z* = 1, *D<sub>c</sub>* = 1.45 g cm<sup>-3</sup>, λ(Mo Kα) = 0.7107 Å, and μ = 14.37 cm<sup>-1</sup>. Maximum and minimum transmission coefficients: 0.94 and 0.79. Reflections measured: ±*h*, ±*k*, *l*. Final residuals *R*, *R<sub>w</sub>* were 0.069, 0.087 for the 2505 of 4864 independent, measured reflections with 2θ < 45° that had *I*(*h*) < 3σ(*I*(*h*)) and were used for refinement.

**Structure Determination.** Dark orange crystals were obtained by slowly cooling an *o*-xylene solution of the complex. The crystals, which contained molecules of *o*-xylene, were put in a capillary to prevent decomposition during data collection. Reflection data were measured with an Enraf-Nonius CAD-4 diffractometer in θ/2θ scan mode using graphite-monochromatized molybdenum radiation (λ = 0.7107 Å). Spot shape was poor. Data were corrected for absorption using Gaussian integration on a 12 × 12 × 12 grid. Constrained refinement using RAELS89<sup>9</sup> employed 221 variables to describe the 58 non-hydrogen atom sites in the crystal. Hydrogen atoms were incorporated at chemically sensible positions in each cycle and were not refined. The four phenyl groups had common refineable local coordinates and were constrained to maintain planarity and local *mm*2 symmetry. The six phenyl C atoms of the 2,5-dimethoxyphenyl ring and the eight C atoms of the *o*-xylene solvent molecule were also constrained to maintain local planar *mm*2 symmetries. Restraints were used to impose planarity on the five-membered ring C(1)-C(5) coordinated to the Mo atom. The \*Cp ligand was subdivided into five rigid groups to describe the thermal motion. The *l*th (*l* = 1–5) rigid group comprised the atom C(*l*) and the ring system attached. Each system was then described with a refineable 12-parameter TL rigid body thermal parameter model where the center of libration was fixed on the atom C(*l*). Each of the two independent bridging positions was modeled to comprise a half-occupancy Br atom and two quarter-occupancy CO groups. The other two positions are related by inversion symmetry. A disordered semibridging model for the CO groups with respect to the centrosymmetrically related Mo atoms was necessary in order to obtain satisfactory CO bond lengths (a half-occupancy CO model gave C–O distances of about 0.8 Å). There are 3 degrees of freedom associated with the six occupancy parameters describing the Br and CO ligands. These occupancy parameters were allowed to vary while chemical composition was maintained but did not significantly alter the disorder model. The Mo–C and Mo–O distances were restrained to maintain a consistency between sites. The C–O distances were restrained to approach 1.15 Å, and the range 1.133–1.155 (10) Å was obtained. The *o*-xylene solvent molecule was refined using a 15-parameter TLS model in which the center of libration was

Table III. Positional Parameters for [<sup>#</sup>Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>2</sub>Br<sub>2</sub>]-2C<sub>8</sub>H<sub>10</sub>

atom	x	y	z
Mo	0.4296 (1)	0.0465 (1)	0.0743 (1)
Br(1)	0.5374 (2)	0.1746 (2)	-0.0379 (1)
Br(2)	0.3201 (2)	0.0416 (2)	-0.0574 (1)
CC(1)	0.5704 (26)	0.1195 (14)	-0.0360 (15)
CC(2)	0.3704 (16)	0.0559 (21)	-0.0561 (13)
OC(1)	0.5385 (27)	0.2148 (15)	-0.0539 (17)
OC(2)	0.2671 (17)	0.0386 (25)	-0.0536 (16)
CC(1)'	0.5027 (26)	0.1449 (14)	-0.0307 (14)
CC(2)'	0.3509 (16)	0.0651 (21)	-0.0363 (13)
OC(1)'	0.5817 (26)	0.2003 (16)	-0.0496 (17)
OC(2)'	0.2727 (18)	0.0295 (25)	-0.0588 (16)
O(1)	0.2874 (9)	0.0604 (8)	0.3975 (6)
O(2)	0.6487 (13)	-0.3542 (10)	0.2865 (11)
C(1)	0.3625 (9)	0.0268 (8)	0.2164 (6)
C(2)	0.4054 (9)	0.1334 (7)	0.2065 (5)
C(3)	0.3145 (8)	0.2148 (6)	0.1640 (6)
C(4)	0.2164 (8)	0.1591 (6)	0.1477 (6)
C(5)	0.2456 (8)	0.0423 (6)	0.1802 (6)
C(6)	0.4144 (11)	-0.0682 (10)	0.2783 (8)
C(7)	0.3782 (11)	-0.0442 (11)	0.3640 (8)
C(8)	0.4302 (15)	-0.1206 (14)	0.4217 (9)
C(9)	0.5213 (17)	-0.2247 (16)	0.3940 (12)
C(10)	0.5586 (13)	-0.2506 (13)	0.3104 (12)
C(11)	0.5046 (12)	-0.1704 (11)	0.2469 (9)
C(12)	0.2741 (22)	0.1032 (18)	0.4702 (10)
C(13)	0.6803 (34)	-0.3876 (19)	0.2057 (19)
C(14)	0.5001 (8)	0.1623 (7)	0.2529 (5)
C(15)	0.6250 (9)	0.0870 (7)	0.2576 (6)
C(16)	0.7070 (8)	0.1145 (8)	0.3056 (6)
C(17)	0.6657 (9)	0.2180 (8)	0.3498 (6)
C(18)	0.5433 (10)	0.2941 (7)	0.3464 (6)
C(19)	0.4613 (8)	0.2666 (7)	0.2985 (6)
C(20)	0.3138 (8)	0.3391 (6)	0.1481 (6)
C(21)	0.4299 (8)	0.3804 (8)	0.1161 (6)
C(22)	0.4237 (10)	0.4982 (8)	0.1122 (7)
C(23)	0.3014 (12)	0.5770 (8)	0.1403 (7)
C(24)	0.1852 (10)	0.5392 (7)	0.1721 (7)
C(25)	0.1913 (8)	0.4214 (7)	0.1760 (6)
C(26)	0.1017 (8)	0.2177 (7)	0.1083 (5)
C(27)	0.1167 (8)	0.2878 (7)	0.0352 (5)
C(28)	0.0057 (10)	0.3489 (8)	0.0045 (5)
C(29)	-0.1226 (9)	0.3411 (8)	0.0463 (6)
C(30)	-0.1410 (7)	0.2729 (9)	0.1185 (6)
C(31)	-0.0299 (8)	0.2118 (8)	0.1492 (5)
C(32)	0.1538 (9)	-0.0369 (7)	0.1912 (5)
C(23)	0.1016 (10)	-0.0650 (8)	0.1245 (5)
C(34)	0.0063 (10)	-0.1304 (9)	0.1391 (7)
C(35)	-0.0387 (10)	-0.1691 (8)	0.2205 (8)
C(36)	0.0107 (10)	-0.1430 (9)	0.2876 (6)
C(37)	0.1060 (10)	-0.0776 (8)	0.2731 (5)
C1X	0.8696 (24)	0.4140 (21)	0.4641 (19)
C6X	0.8292 (18)	0.3231 (29)	0.5311 (13)
C5X	0.8841 (26)	0.2227 (29)	0.5072 (19)
C4X	0.9669 (24)	0.1771 (21)	0.4394 (19)
C3X	1.0055 (19)	0.2640 (30)	0.3753 (13)
C2X	0.9491 (26)	0.3689 (30)	0.3994 (18)
C7X	0.7930 (39)	0.5259 (28)	0.5059 (34)
C8X	0.7351 (24)	0.3958 (45)	0.6018 (19)

refineable.<sup>30</sup> Table III lists the atomic positions for the non-hydrogen atoms.

[<sup>#</sup>Cp<sub>2</sub>Mo<sub>2</sub>Br<sub>2</sub>]-2CH<sub>2</sub>Cl<sub>2</sub>. Crystal Data:  $a = 11.234$  (15) Å,  $b = 13.453$  (20) Å,  $c = 14.612$  (14) Å,  $\alpha = 74.37$  (8)°,  $\beta = 70.27$  (9)°,  $\gamma = 89.43$  (7)°,  $V = 1994$  (5) Å<sup>3</sup>,  $M_r = 1862.5$  P1,  $Z = 1$ ,  $D_c = 1.55$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.7107$  Å, and  $\mu = 26.07$  cm<sup>-1</sup>. Maximum and minimum transmission coefficients: 0.84 and 0.74. Reflections measured:  $\pm h, \pm k, l$ . Final residuals  $R, R_w$  were 0.063, 0.075 for the 1355 of 3412 independent, measured reflections with  $2\theta < 40^\circ$  that had  $I(h) < 3\sigma(I(h))$  and were used for refinement.

**Structure Determination.** Orange crystals, obtained from a dichloromethane/hexane mixture, were placed in a capillary to minimize crystal decomposition due to dichloromethane loss.

(30) Rae, A. D. *Acta Crystallogr.* 1975, *A31*, 560. Rae, A. D. *Ibid.* 1975, *A31*, 570.

Table IV. Positional Parameters for [<sup>#</sup>Cp<sub>2</sub>Mo<sub>2</sub>Br<sub>4</sub>]

atom	x	y	z
Mo	0.4367 (2)	0.4290 (2)	0.0882 (2)
Br(1)	0.6668 (2)	0.4037 (2)	-0.0210 (2)
Br(2)	0.4187 (2)	0.4153 (2)	-0.0814 (2)
O(1)	0.1827 (13)	0.3133 (13)	0.4471 (12)
O(2)	0.2322 (16)	0.7389 (16)	0.3151 (16)
C(1)	0.3074 (15)	0.3964 (15)	0.2497 (14)
C(2)	0.2471 (13)	0.3505 (12)	0.1940 (13)
C(3)	0.3200 (14)	0.2657 (12)	0.1666 (12)
C(4)	0.4252 (16)	0.2585 (12)	0.2044 (13)
C(5)	0.4168 (16)	0.3388 (13)	0.2554 (12)
C(7)	0.1987 (14)	0.4185 (22)	0.4157 (19)
C(8)	0.1544 (16)	0.4804 (24)	0.4830 (20)
C(9)	0.1680 (17)	0.5837 (25)	0.4460 (21)
C(10)	0.2213 (16)	0.6333 (24)	0.3484 (23)
C(11)	0.2654 (16)	0.5717 (20)	0.2814 (19)
C(12)	0.1439 (32)	0.2600 (24)	0.5535 (21)
C(13)	0.3037 (42)	0.7902 (25)	0.2101 (29)
C(14)	0.1166 (14)	0.3649 (14)	0.1928 (13)
C(15)	0.0181 (17)	0.3572 (16)	0.2831 (12)
C(16)	-0.1059 (15)	0.3682 (19)	0.2837 (14)
C(17)	-0.1299 (16)	0.3868 (18)	0.1941 (16)
C(18)	-0.0319 (18)	0.3945 (17)	0.1039 (13)
C(19)	0.0921 (15)	0.3835 (16)	0.1033 (12)
C(20)	0.2932 (16)	0.1891 (12)	0.1183 (13)
C(21)	0.1705 (15)	0.1428 (15)	0.1539 (13)
C(22)	0.1413 (16)	0.0670 (16)	0.1138 (18)
C(23)	0.2352 (21)	0.0384 (15)	0.0384 (17)
C(24)	0.3578 (19)	0.0844 (15)	0.0026 (13)
C(25)	0.3870 (14)	0.1602 (14)	0.0427 (13)
C(26)	0.5162 (17)	0.1779 (13)	0.2026 (14)
C(27)	0.4688 (16)	0.0750 (15)	0.2329 (15)
C(28)	0.5499 (25)	-0.0036 (12)	0.2413 (16)
C(29)	0.6774 (22)	0.0214 (17)	0.2193 (18)
C(30)	0.7251 (15)	0.1239 (20)	0.1890 (18)
C(31)	0.6441 (19)	0.2026 (13)	0.1806 (15)
C(32)	0.4819 (16)	0.3450 (14)	0.3268 (13)
C(33)	0.4768 (17)	0.2537 (12)	0.4004 (15)
C(34)	0.5212 (19)	0.2542 (15)	0.4788 (13)
C(35)	0.5703 (17)	0.3462 (18)	0.4827 (14)
C(36)	0.5756 (16)	0.4376 (15)	0.4094 (16)
C(37)	0.5312 (16)	0.4370 (13)	0.3310 (13)

Reflection data were measured with an Enraf-Nonius CAD-4 diffractometer in  $\theta/2\theta$  scan model using graphite-monochromatized molybdenum radiation ( $\lambda = 0.7107$  Å). Spot shape was poor. Data were corrected for absorption using Gaussian integration on a  $12 \times 12 \times 12$  grid. Intensity measurements of standard reflections decreased 40% during data collection. The shortage of quality data necessitated the use of constrained refinement, and RAELS89<sup>29</sup> was used for this purpose. A total of 156 variables were used to describe the 42 non-hydrogen atom sites in the crystal. The constraints and restraints imposed on the <sup>#</sup>Cp moiety were as described for the previous structure. Hydrogen atoms were incorporated at chemically sensible positions in each cycle and were not refined. The atoms of the dichloromethane molecules were not well determined, and the solvent region could not be simply parametrized. Rather this region was modeled using back Fourier transform techniques.<sup>31</sup> The dichloromethane molecules occupy a region near the center of inversion at 0, 0, 1/2. The atomic positions for the non-hydrogen atoms are listed in Table IV.

**Supplementary Material Available:** For 3 and 4, figures showing a view of the asymmetric unit with atom labeling and tables of bond lengths, bond angles, torsional angles, hydrogen atom fractional coordinates, and anisotropic thermal parameters (19 pages). Ordering information is given on any current masthead page.

OM920360Y

(31) Baker, A. T.; Rae, A. D. *Acta Crystallogr.* 1984, *A40* (suppl.), 17.4-4.