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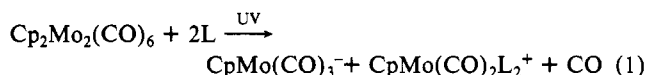
# Mechanism of the Low-Energy Photochemical Disproportionation Reactions of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$

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Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received February 22, 1983

**Abstract:** The photochemical disproportionation reactions of the  $(\text{RCp})_2\text{Mo}_2(\text{CO})_6$  ( $\text{R} = \text{H}$  or  $\text{CH}_3$ ;  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) complexes were investigated. The general disproportionation reaction can be written  $(\text{RCp})_2\text{Mo}_2(\text{CO})_6 + 2\text{L} \xrightarrow{h\nu} (\text{RCp})\text{Mo}(\text{CO})_3^- + (\text{RCp})\text{Mo}(\text{CO})_2\text{L}_2^+ + \text{CO}$ . Control experiments showed that the previously reported analogous thermal disproportionation reactions are actually photochemical reactions. The properties of the ligand  $\text{L}$  are important in determining whether or not the  $(\text{RCp})_2\text{Mo}_2(\text{CO})_6$  complex will disproportionate; the ligands cannot be sterically bulky and they must be good electron-donating ligands if disproportionation is to occur. If either of these criteria is not met, then irradiation of the  $(\text{RCp})_2\text{Mo}_2(\text{CO})_6$  complex in the presence of the ligand leads only to substitution products of the type  $(\text{RCp})_2\text{Mo}_2(\text{CO})_5\text{L}$  and/or  $(\text{RCp})_2\text{Mo}_2(\text{CO})_4\text{L}_2$ . The disproportionation reaction is wavelength dependent. For example,  $\text{PPh}_3$  will disproportionate the  $(\text{RCp})_2\text{Mo}_2(\text{CO})_6$  complex upon 290-nm irradiation but not upon 405-nm irradiation. Smaller ligands will disproportionate the dimer with 405-nm irradiation. The mechanism of the lower energy pathway was investigated in detail, and it is proposed to be a radical chain pathway: (1)  $(\text{RCp})_2\text{Mo}_2(\text{CO})_6 \xrightarrow{h\nu} 2(\text{RCp})\text{Mo}(\text{CO})_3$ , (2)  $(\text{RCp})\text{Mo}(\text{CO})_3 + \text{L} \rightarrow (\text{RCp})\text{Mo}(\text{CO})_2\text{L} + \text{CO}$ , (3)  $(\text{RCp})\text{Mo}(\text{CO})_2\text{L} + \text{L} \rightarrow (\text{RCp})\text{Mo}(\text{CO})_2\text{L}_2$ , (4)  $(\text{RCp})\text{Mo}(\text{CO})_2\text{L}_2 + (\text{RCp})_2\text{Mo}_2(\text{CO})_6 \rightarrow (\text{RCp})\text{Mo}(\text{CO})_2\text{L}_2^+ + (\text{RCp})_2\text{Mo}_2(\text{CO})_6^-$ , (5)  $(\text{RCp})_2\text{Mo}_2(\text{CO})_6^- \rightarrow (\text{RCp})_2\text{Mo}(\text{CO})_3^- + (\text{RCp})\text{Mo}(\text{CO})_3$ . The quantum yield data support this chain pathway; the quantum yields are greater than 1 and they are not reproducible from trial to trial. The key intermediate  $(\text{CH}_3\text{Cp})_2\text{Mo}_2(\text{CO})_6^-$  was generated by reacting  $(\text{CH}_3\text{Cp})_2\text{Mo}_2(\text{CO})_6$  with  $\text{Na}$ ; in the presence of appropriate  $\text{L}$  disproportionation resulted. The key to the mechanism is the formation of the 19-electron intermediate  $(\text{RCp})\text{Mo}(\text{CO})_2\text{L}_2$ . Electron transfer from this electron-rich species is the driving force for the reaction. Evidence is presented for the formation of this intermediate.

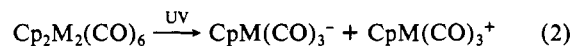
Very little is known about the mechanism of the photochemically induced disproportionation reactions of metal-metal bonded dimers. For this reason we have been investigating the photochemical disproportionation reactions of the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) complex, a general example of which is shown in eq 1.<sup>1,2</sup>



The disproportionation reactions and their ionic products are something of an anomaly in the field of metal-metal bond photochemistry. Generally, the photochemical reactions of the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  ( $\text{M} = \text{Mo}, \text{W}$ ) complexes do not give ionic (i.e., electron-transfer) products.<sup>3</sup> The reason for this is that irradiation of the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  complexes generally results in homolytic cleavage of the metal-metal bond with the subsequent formation of metal radical intermediates. The photochemistry is thus typical of the chemistry of metal-centered radicals. Common photochemical reactions in nonpolar solvents include halogen atom abstraction from halocarbon molecules, metal-metal cross coupling reactions, and substitution reactions.<sup>3</sup> The products of all these reactions are neutral species, and no intermetal electron transfer has occurred.

Allen, Cox, Kemp, Sultana, and Pitts were the first to ponder the intimate mechanism of the photochemical disproportionation of the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  complexes.<sup>4</sup> They found that when these complexes were irradiated (broad-band irradiation) in polar, coordinating solvents, disproportionation sometimes occurred (eq

1). Why should photochemical disproportionation (i.e., electron transfer) occur in polar solvents but not in nonpolar solvents? Allen and co-workers suggested that the primary photoprocess was different in the two types of solvent systems.<sup>4</sup> They suggested that disproportionation was a consequence of direct photochemical heterolysis of the  $\text{M-M}$  bond; i.e., homolysis was not the primary photoprocess in polar, coordinating solvents. The disproportionation mechanism shown in eq 2 and 3 was proposed. No evidence was given to support this mechanism, however, nor was the wavelength dependence of the disproportionation discussed.



$\text{S} = \text{solvent}$

In a preliminary communication of our results,<sup>1</sup> we presented evidence to show that the disproportionation reaction is not the result of a solvent effect but rather is a consequence of the ligand. (In the reactions reported by Allen and co-workers,<sup>4</sup> the polar, coordinating solvent was simply acting as a ligand.) Nevertheless, the suggestion by Allen et al. that a different primary photoprocess is responsible for the disproportionation may have some validity: we were able to show a marked wavelength dependence for the disproportionation of the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  complexes in the presence of certain ligands. Further investigation of the wavelength dependence of the disproportionation reactions was one of the aims of our research and the results are reported herein.

Having established that disproportionation is not a solvent but a ligand effect, we were faced with another interesting feature of these reactions: disproportionation occurs for some ligands but not for others. For example,  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  will disproportionate when the ligand is  $\text{PPh}_3$  or pyridine but not when the ligand is  $\text{P}(\text{O}i\text{-Pr})_3$  or  $\text{P}(i\text{-Pr})_3$  ( $i\text{-Pr}$  is isopropyl). Why should this be? Furthermore, it was reported that some phosphines and phosphites disproportionated the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  complexes in *thermal* reactions at room temperature.<sup>5</sup> As in the photochemical reactions, it was noted that not all phosphines and phosphites reacted in

(1) (a) Stiegman, A. E.; Tyler, D. R. *J. Am. Chem. Soc.* **1982**, *104*, 2944-2945. (b) McCullen, S. B.; Brown, T. L. *Inorg. Chem.* **1981**, *20*, 3528-3533.

(2) Our study utilized both the Mo and W complexes. Both complexes appear always to react identically. We report only the results for the Mo complex in this paper because all of the quantum yield measurements were made with this complex. Qualitatively, however, the  $\text{Cp}_2\text{W}_2(\text{CO})_6$  complex can be substituted for  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  wherever the latter appears in this paper. ( $\text{MeCp}$ ) $_2\text{Mo}_2(\text{CO})_6$  was generally used instead of  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  because the former complex is more soluble in the solvents employed in this study.

(3) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(4) Allen, D. M.; Cox, A.; Kemp, T. J.; Sultana, Q. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1189-1193.

(5) (a) Haines, R. J.; Nolte, C. R. *J. Organomet. Chem.* **1970**, *24*, 725-736. (b) Haines, R. J.; DuPreez, A. L.; Marais, I. L. *Ibid.* **1971**, *28*, 97-104.

thermal disproportionation reactions; some did thermally substitute the dimers, however.<sup>5</sup> The confusing thing was that there was no apparent pattern as to which phosphines or phosphites reacted photochemically and which reacted thermally, nor was there a pattern as to which ligands led to substitution and which led to disproportionation.

We thought that if we could understand the reasons why some ligands lead to disproportionation and others do not, then we might learn something about the mechanism of the disproportionation reactions. Thus, we undertook a systematic study of the disproportionation reactions using various ligands under varying conditions. This paper reports the results of our study and discusses the mechanistic implications of those results.

### Experimental Section

$(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ ,<sup>6</sup>  $\text{Cp}_2\text{Mo}_2(\text{CO})_2\text{PPh}_3$ ,<sup>7</sup>  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{P}(\text{OCH}_3)_3)_2$ ,<sup>8a</sup> and  $[\text{CpMo}(\text{CO})_2(\text{dppe})][\text{PF}_6]$ <sup>8</sup> were prepared by literature methods.  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$  was recrystallized from cyclohexane, and  $\text{Cp}_2\text{Mo}_2(\text{CO})_2\text{PPh}_3$  was purified by overnight extraction under argon with petroleum ether to remove unreacted starting material.  $\text{Mo}(\text{CO})_6$  was obtained from Pressure Chemical Co. and used as received.

$\text{P}(\text{OCH}_3)_3$ ,  $\text{P}(\text{O}-i\text{-Pr})_3$ ,  $\text{P}(\text{O}-n\text{-Bu})_3$ ,  $\text{PPh}_3$ ,  $\text{AsPh}_3$ ,  $\text{P}(n\text{-Bu})_3$ ,  $\text{P}(\text{OPh})_3$ ,  $\text{dppe}$  (1,2-bis(diphenylphosphino)ethane), and  $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{CH}_3$  were obtained from Aldrich (*i*-Pr = isopropyl; *n*-Bu = *n*-butyl).  $\text{P}(\text{OCH}_3)_3$  and  $\text{P}(\text{O}-i\text{-Pr})_3$  were stirred overnight with sodium and distilled under argon through a 10-cm distillation column filled with glass beads.<sup>9</sup>  $\text{P}(\text{OCH}_3)_3$  and  $\text{P}(\text{O}-i\text{-Pr})_3$  were stirred overnight with sodium and distilled under argon through a 10-cm distillation column filled with glass beads.<sup>9</sup>  $\text{PPh}_3$  was recrystallized from ethanol before use.  $\text{PPh}_2(\text{CH}_3)$ ,  $\text{PPh}_2(\text{Bu})$ ,  $\text{P}(i\text{-Pr})_3$ ,  $\text{P}(c\text{-Hx})_3$ , and  $\text{PPh}_2(i\text{-Pr})$  (*c*-Hx = cyclohexyl) were purchased from Strem Chemicals and used without further purification.  $\text{P}(\text{O}-\text{tol})_3$  (tol = tolyl) was obtained from Pfaltz & Bauer and used as received.  $\text{P}(\text{O}-\text{C}_6\text{H}_4\text{-OCH}_3)_3$  was synthesized by standard techniques.<sup>10</sup> Sodium suspension in mineral oils (40% by weight) was obtained from Aldrich. Reagent grade triethylamine was obtained from MCB, then dried, and distilled from calcium hydride.<sup>9</sup> Pyridine and aniline (Fisher) were distilled and stored over Linde 4A molecular sieves.

Reagent grade cyclohexane was passed through a column of freshly heated silica gel and distilled over calcium hydride under an argon atmosphere.<sup>9</sup> Ultrapure benzene was obtained from Burdick and Jackson and used without further purification.

All IR spectra were obtained by using a Perkin-Elmer 621 spectrophotometer. Electronic spectra were obtained with a Cary 17 spectrophotometer.

All photochemical reactions were carried out under argon in Schlenk flasks or tubes. The light source was a 200-W Oriel high-pressure mercury lamp or a Viceroy electronic flash. Wavelengths at 405 and 505 nm were isolated by using interference filters obtained from Edmund Scientific; 290-nm radiation was isolated by using an interference filter obtained from Corion Co. When photolyses were monitored by infrared spectroscopy, silicon wafers were taped over the windows of the infrared cells to prevent photolysis by the instrument beam.

Absolute quantum yield measurements were made with a Beckman DU spectrophotometer using matched quartz 1.00-cm cells fitted with rubber septum caps. All solutions were stirred during irradiation, and the disappearance of  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$  was monitored at 508 nm. The lamp intensity was measured by ferrioxalate actinometry; lamp intensities at 405 nm were typically  $5 \times 10^{-8}$  einstein/min.<sup>11</sup>

Relative quantum yields were measured in thoroughly degassed cyclohexane solution by monitoring the rate of product growth in the carbonyl region of the infrared spectrum.  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{P}(\text{OCH}_3)_3)_2$ ,  $\text{Cp}_2\text{Mo}_2(\text{CO})_2\text{PPh}_3$ ,  $(\text{MeCp})\text{Mo}(\text{CO})_3^-$ ,  $\text{CpMo}(\text{CO})_3^-$ , and  $\text{CpMo}(\text{CO})_2(\text{dppe})^+$  were monitored by their characteristic carbonyl stretches at 1817 ( $\epsilon = 460 \text{ M}^{-1} \text{ cm}^{-1}$ ), 1854 (35), 1765 (170), 1765 (170), and 1980  $\text{cm}^{-1}$  (160), respectively.<sup>12</sup> The rate of product growth was calculated by a least-squares fit of the concentration as a function of the number of flashes. A typical flash delivered  $1 \times 10^{-8}$  einstein.<sup>13</sup>

Table I.  $A_1$  Mode CO Stretching Frequencies for  $\text{Mo}(\text{CO})_5\text{L}$

ligand	$\nu(\text{C}\equiv\text{O})$ , $\text{cm}^{-1}$	does disproportionation occur? (broad-band irradiation)
$\text{NEt}_3$	1915	yes
$\text{C}_5\text{H}_5\text{N}$	1917	yes
$\text{NH}_2\text{Ph}$	1917	yes
$\text{CH}_3\text{CN}$	1924	yes
$\text{P}(i\text{-Pr})_3$	1933	no
$\text{P}(c\text{-Hx})_3$	1937	no
$\text{P}(n\text{-Bu})_3$	1940	yes
$\text{AsPh}_3$	1948	yes
$\text{PPh}_3$	1950	yes
$\text{PPh}_2(i\text{-Pr})$	1951	no
$\text{P}(\text{O}-i\text{-Pr})_3$	1960	yes
$\text{P}(\text{OCH}_3)_3$	1964	yes
$\text{P}(\text{O}-n\text{-Bu})_3$	1964	yes
$\text{P}(\text{O}-\text{C}_6\text{H}_4\text{-OCH}_3)_3$	1966	no
$\text{P}(\text{O}-\text{C}_6\text{H}_4\text{-CH}_3)_3$	1969	no
$\text{P}(\text{OPh})_3$	1970	no

culated by a least-squares fit of the concentration as a function of the number of flashes. A typical flash delivered  $1 \times 10^{-8}$  einstein.<sup>13</sup>

The IR spectra of the monosubstituted hexacarbonyls  $\text{Mo}(\text{CO})_5\text{L}$  were obtained by irradiation ( $\lambda > 340 \text{ nm}$ ) of  $\text{Mo}(\text{CO})_6$  in cyclohexane in the presence of ligand, thus generating  $\text{Mo}(\text{CO})_5\text{L}$  in situ.<sup>3</sup> The  $A_1$  stretching mode was identified by reference to published work.<sup>14</sup>

It occurred to us that perhaps the electron transfer in the disproportionation reactions was being catalyzed or initiated by trace impurities. For this reason, we thoroughly purified the solvents, metal complexes, and the most frequently used phosphines and phosphites. As a check on the possibility that a reaction was occurring with phosphine oxides or phosphonates (the most common impurities in phosphines and phosphites, respectively<sup>9</sup>), we irradiated ( $\lambda > 400$  and 290 nm)  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$  (0.052 g) in cyclohexane (10 mL) in the presence of  $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{CH}_3$  and  $\text{OPPh}_3$ ; no reactions occurred. From these control experiments we conclude that phosphine oxide or phosphonate impurities are probably not responsible for the observed disproportionation photochemistry.

### Results and Discussion

**Dark Reactions.** One of the problems we expected to face in our investigation of the disproportionation reactions was that of the thermal reactions of the ligands with the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  complexes.<sup>5</sup> It had been reported that various ligands disproportionated the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  complexes at room temperature in benzene solution. The presence of a thermal reaction is undesirable because it complicates quantum yield measurements and makes analysis of the data more difficult in general. Fortunately, we were able to show that the reported thermal reactions are actually photochemical reactions caused by ambient laboratory light. Control experiments showed that rigorous exclusion of light from the reaction cell prevented the "thermal" reaction. For example, in the complete absence of light 0.039 g of  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  in 10 mL of benzene containing 2.5 mL of  $\text{P}(\text{OCH}_3)_3$  underwent no reaction in 85 mins. When the covering was removed from the same solution and the cell was put on a laboratory bench top and exposed to the overhead fluorescent lighting, 34% of the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  disappeared in 5 min.

**Ligand Properties Required for Disproportionation.** One of the most important ligand properties in an electron-transfer reaction is expected to be the electron-donating ability of the ligand. For this reason we decided to measure the electron-donating ability of a series of ligands and then to see if there was a correlation between the electron-donating ability and whether or not a ligand induced disproportionation. The electron-donating abilities of the ligands were measured by examining the trans CO stretching

(13) The output of electronic flash guns varies in intensity from flash to flash, thereby making them unsuitable for absolute quantum yield determinations. For the relative quantum yields reported here, the intensity of the flash cancels in the ratio, thus negating this inconsistency.

(14) Dobson, G. R.; Stolz, I. W.; Sheline, R. K. *Adv. Inorg. Radiochem.* **1966**, *8*, 1-82. We are aware of the argument that the higher energy  $A_1$  band may be a forbidden B band.

(6) Birdwhistle, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239-241.

(7) Barnett, K. W.; Treichel, P. M. *Inorg. Chem.* **1967**, *6*, 294-299.

(8) King, R. B.; Pannell, K. H.; Eggers, C. A.; Houk, L. W. *Inorg. Chem.* **1968**, *7*, 2353-2356.

(9) Perrin, D. D.; Armarego, W. L.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Oxford, 1966.

(10) Jarvis, B. B.; Marien, B. A. *J. Org. Chem.* **1976**, *41*, 2182-2187.

(11) (a) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966. (b) Bowman, W. D.; Demas, J. N. *J. Phys. Chem.* **1976**, *80*, 2434.

(12) With some counteranions, the  $\text{CpMo}(\text{CO})_3^-$  and  $(\text{MeCp})\text{Mo}(\text{CO})_3^-$  anions showed two peaks near 1775 and 1755  $\text{cm}^{-1}$ . As an example, two peaks are present when the cation is  $(\text{MeCp})\text{Mo}(\text{CO})_2(\text{py})_2^+$  (py = pyridine).

**Table II.** Wavelength Dependence of Disproportionation as a Function of the Cone Angle of the Entering Ligand

ligand	cone angle, deg	does disproportionation occur?	
		405 nm <sup>b</sup>	290 nm
P(OCH <sub>3</sub> ) <sub>3</sub>	107	yes	yes
P(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	109	yes	yes
P(O- <i>i</i> -Pr) <sub>3</sub>	130	yes	yes
P( <i>n</i> -Bu) <sub>3</sub>	132	yes	yes
PPh <sub>2</sub> (CH <sub>3</sub> )	136	yes	yes
PPh <sub>2</sub> ( <i>n</i> -Bu) <sup>a</sup>	140	yes	yes
P( <i>i</i> -Bu) <sub>3</sub>	143	slight	yes
PPh <sub>3</sub>	145	no	yes
PPh <sub>2</sub> ( <i>i</i> -Pr)	150	no	no
P( <i>i</i> -Pr) <sub>3</sub>	160	no	no
P( <i>c</i> -Hx) <sub>3</sub>	170	no	no

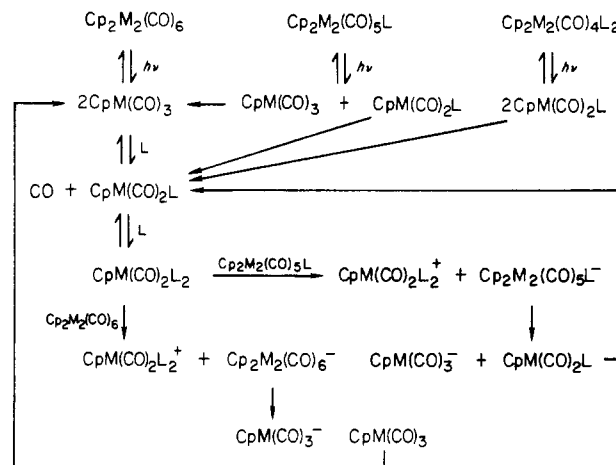
<sup>a</sup> This cone angle estimated as  $2/3$  of the value between P(*n*-butyl)<sub>3</sub> and PPh<sub>3</sub>. See ref 15, p 315. <sup>b</sup> A 505-nm excitation gave identical results.

frequency (A<sub>1</sub> mode) of the Mo(CO)<sub>5</sub>L complexes.<sup>14</sup>  $\pi$ -Back-bonding arguments allow one to conclude that the lower the frequency of this mode, the better the electron-donating ability of the ligand. The frequencies of the trans CO stretches of the Mo(CO)<sub>5</sub>L complexes are shown in Table I. Our ordering is essentially the same as the one obtained by Tolman using the Ni(CO)<sub>3</sub>L complexes.<sup>15</sup> Included in Table I is a column telling whether or not disproportionation occurs with that ligand (broad-band irradiation,  $\lambda > 254$  nm). As Table I shows, there is an electronic cutoff point in the list of ligands. With only three exceptions, ligands above the cutoff (the good donors) lead to disproportionation while those below the cutoff (the poorer donors) do not.

Interestingly, the three ligands that lie above the cutoff but that do not lead to disproportionation are bulky ligands;<sup>15</sup> thus, not unexpectedly, steric factors are important in determining whether or not a ligand will lead to disproportionation. To quantify the steric dependence of the disproportionation reactions, the ligands above the electronic cutoff were ranked according to their size. The commonly accepted parameter of ligand size is the cone angle.<sup>15</sup> Table II is a listing of the ligands above the electronic cutoff in order of increasing cone angle. Notice that ligands with cone angles greater than about 145° will not induce disproportionation, whereas those with smaller cone angles do induce disproportionation. Also note that the three ligands with cone angles greater than 145° are the three ligands in Table I that should have led to disproportionation based only on their electron-donating ability but that did not. From the results presented thus far, we can conclude that in order to induce disproportionation, ligands must be able to donate sufficient electron density to the metal and they must also be smaller than a certain critical size.

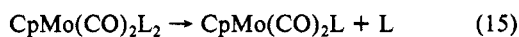
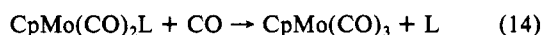
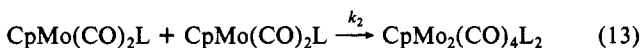
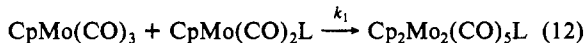
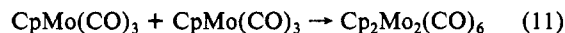
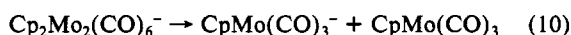
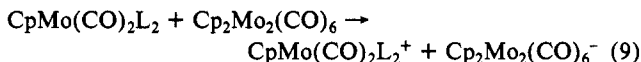
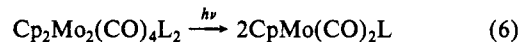
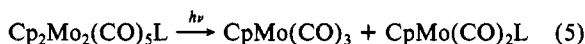
**Wavelength Dependence.** The data and results presented up to this point have all been obtained by using the broad-band radiation output from a 200-W high-pressure Hg arc lamp. As we reported in a preliminary communication, however, there is a marked wavelength dependence of the disproportionation reaction. Some ligands will induce disproportionation upon low-energy excitation (505, 405, or 366 nm; identical photochemical results are obtained at these wavelengths) of the (MeCp)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> dimer, but other ligands participate in the disproportionation only when the (MeCp)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> dimer is irradiated at higher energy ( $\lambda < 300$  nm). A list of ligands used in this study and the wavelength dependence of the disproportionation reaction are shown in Table II.

It seems clear that two different pathways are operating in the disproportionation of the Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> dimer: a high-energy pathway and a low-energy pathway. As shown in Table II, the steric requirements of the ligands are about the same for each pathway. The difference in the steric requirements for the two

**Scheme I**

pathways is that phosphine ligands larger than P(*i*-Bu)<sub>3</sub> (cone angle = 143°) will not induce disproportionation by the low-energy method, while the steric cutoff point for the high-energy pathway is somewhere between a cone angle of 145° and 150° (between PPh<sub>3</sub> and PPh<sub>2</sub>(*i*-Pr)). The remainder of this paper will be concerned only with the low-energy disproportionation mechanism.

**Mechanism of the Reaction.** We propose that the low-energy disproportionation reactions follow the radical chain pathway in Scheme I. For convenience in referring to specific reactions later in the paper, the individual reactions in Scheme I, as well as several additional (termination) steps, are numbered as eq 4–15.



The pathway in Scheme I is similar to the one proposed by Brown and McCullen for the disproportionation reactions of Mn<sub>2</sub>(CO)<sub>10</sub> with pyridine and various substituted pyridines.<sup>1b</sup> However, as will be pointed out, Scheme I differs from the Brown–McCullen mechanism in a few very important aspects.

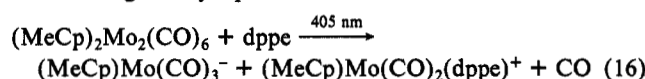
The quantum yields of the disproportionation reactions are consistent with the pathway in Scheme I. Unfortunately there is a problem in measuring the disproportionation quantum yields: the ionic disproportionation products are not the only products formed when the (MeCp)<sub>2</sub>Mo<sub>2</sub>(CO)<sub>6</sub> complex is irradiated in the presence of phosphine or phosphite ligands. Monosubstituted and disubstituted dimers also form. Thus, for most ligands it was impossible to measure absolutely the quantum yields for disproportionation because of the competing side reactions. However, we found that disproportionation was the only reaction when 1,2-bis(diphenylphosphino)ethane (dppe) was the entering ligand. This is an expected result of the pathway in Scheme I. The rate constant for attack by the second ligand (eq 8) is expected to be

Table III. Quantum Yields for the Disproportionation of  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ <sup>a</sup> with dppe<sup>b</sup> upon 405-nm Irradiation in Benzene

[dppe], M	$\phi^c$
0.010	3.30, 7.79, 11.83, 6.62
0.005	3.34, 2.70, 1.92, 5.14, 3.00
0.004	3.74, 3.04, 5.33, 5.21
0.003	2.14, 3.19, 4.09
0.002	2.68, 2.51, 5.86
0.001	1.63

<sup>a</sup>  $[(\text{MeCp})_2\text{Mo}_2(\text{CO})_6] = 1.5 \times 10^{-3}$  M. <sup>b</sup> dppe = bis(1,2-diphenylphosphino)ethane. <sup>c</sup> Each number for a given concentration represents an independent quantum yield measurement at that concentration.

faster<sup>16</sup> than the initial substitution (eq 7) because this is a ring closure step when  $L = \text{dppe}$ . The ring closure and subsequent electron transfer (eq 9) thus occur before recombination of two 17-electron fragments (eq 11, 12, or 13). As a consequence, there are no competing substitution reactions when  $L$  is dppe. The sole reaction is given by eq 16.



The quantum yields for the disproportionation reaction in eq 16 are given in Table III. Three points concerning these quantum yields immediately stand out. First, all of the quantum yields are greater than 1. A quantum yield greater than 1 is consistent with the chain process<sup>17</sup> in Scheme I. Second, the quantum yields at a given concentration of dppe are nonreproducible. Nonreproducible quantum yields are generally a characteristic of radical chain mechanisms. Third, although it is difficult to draw any conclusions with certainty because of the wide scatter of the quantum yields, there appears to be a rough trend of increasing quantum yield with increasing dppe concentration. This trend reflects the increasing ability of the disproportionation reaction to compete with reaction 11 (a chain-terminating reaction) as the concentration of the dppe increases.

The results of other experiments are also consistent with the pathway in Scheme I. One of the key intermediates in the disproportionation pathway is the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6^-$  (or  $\text{Cp}_2\text{Mo}_2(\text{CO})_5\text{L}^-$ ) complex. We devised the following experiment to test for the intermediacy of this dimer anion in the disproportionation reactions. With the rigorous exclusion of all light, 10 mL of degassed cyclohexane was added to 0.052 g of  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ . To this solution was added 0.4 mL of  $\text{PPh}_2(\text{CH}_3)$ , and the combined solutions were mixed. An aliquot of this solution was withdrawn by syringe and used to fill an infrared cell. This cell served as the control experiment. A silicon wafer was taped to the window of the cell to prevent photolysis by stray light or by the infrared spectrophotometer beam. To the remaining portion of the solution was added 0.2 mL of sodium dispersed in mineral oil (40% Na by weight). After the solution was mixed for several seconds, an aliquot was withdrawn by syringe and injected into a second infrared cell. (This cell also had silicon wafers taped to its windows.) The infrared spectrum (Figure 1) of the sodium-treated solution was run immediately (within 2 min of adding the sodium), and it showed that disproportionation (but no substitution) had occurred ( $\nu(\text{C}\equiv\text{O}) = 1881$  and  $1758 \text{ cm}^{-1}$ , the other product bands were obscured by unreacted starting material). No disproportionation occurred in the sodium-free control cell. (Note that disproportionation did occur when the Si wafers were removed; the visible light in the IR beam is sufficient to photolyze the solution.) Further control experiments showed that the phosphine, in this case  $\text{PPh}_2(\text{CH}_3)$ , must be present in order for disproportionation to occur. When the sodium dispersion was added to a cyclohexane solution containing  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ , only a very small amount of  $(\text{MeCp})\text{Mo}(\text{CO})_3^-$  was detected by

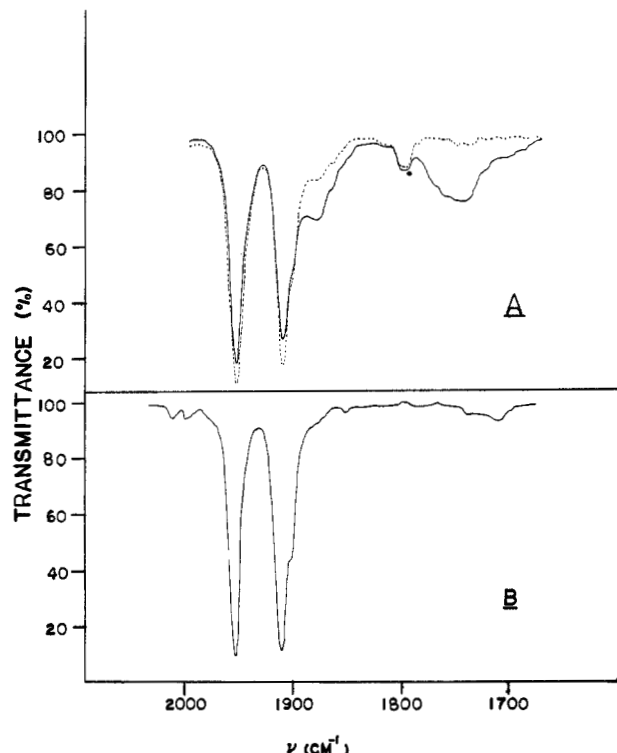


Figure 1. (A) Spectral changes accompanying the dark reaction of  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$  with Na in the presence of  $\text{PPh}_2(\text{CH}_3)$  in cyclohexane (---, before reaction; —, after 2 min). (B) The same reaction as in (A), but no  $\text{PPh}_2(\text{CH}_3)$  was present. The spectrum shown was obtained 4 min after the Na was added to the cyclohexane solution of  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ . The peak with the asterisk (\*) is a  $\text{PPh}_2(\text{CH}_3)$  absorption band.

IR. The above experiments were all repeated by using dppe as the ligand, and identical results were obtained.

Our interpretation of the experiments above is as follows. We propose that sodium is reducing the  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$  complex and generating the  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6^-$  anion. Once the  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6^-$  anion is generated, it decomposes according to eq 10 and the disproportionation chain reaction is started. Finally, to point out the obvious, the control experiments show that sodium is not just simply reducing the  $(\text{MeCp})\text{Mo}_2(\text{CO})_6$  dimer. If this were the case, then no cation would form.<sup>18</sup>

Note that there is some precedence for reaction 10, the decomposition of the anionic dimer to a monomeric anion and a metal radical. It has been observed that electrochemical reduction of  $(\text{CO})_5\text{Mn}-\text{Fe}(\text{CO})_2\text{Cp}$  results in the cleavage of the metal-metal bond to form  $\text{Mn}(\text{CO})_5^-$  and  $\text{CpFe}(\text{CO})_2$ .<sup>19</sup>

A key feature of the mechanism in Scheme I is the sequence of steps in eq 8 and 9. Note that according to this reaction sequence, the second  $L$  bonds to  $\text{CpM}(\text{CO})_2\text{L}$  to give  $\text{CpM}(\text{CO})_2\text{L}_2$  (a 19-electron species) before electron transfer takes place. (The species  $\text{CpM}(\text{CO})_2\text{L}_2$  might not be a 19-electron complex if the cyclopentadienyl ring is bonded in a  $\eta^3$  fashion;

(18) It might be argued that the sodium-induced disproportionation pathway above is not the same as the photochemically induced disproportionation pathway. To check this possibility, we repeated the sodium experiment using  $\text{PPh}_3$  as the ligand. Recall that 290-nm excitation is required for  $\text{PPh}_3$  to induce disproportionation of the  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$  complex (lower energy excitation simply results in substitution.) This result tells us that the radical chain mechanism cannot be operable when  $\text{PPh}_3$  is the ligand. If this is the case and if the sodium-induced pathway is the same as the photochemical pathway, then no disproportionation should occur when sodium is added to a solution containing  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$  and  $\text{PPh}_3$ . Experimentally, no disproportionation occurs when sodium (0.2 mL of dispersed in mineral oil) is added to a cyclohexane solution (10 mL) of  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$  (0.052 g) and  $\text{PPh}_3$  (0.06 g). Thus, while not proving that the photochemical and sodium-induced pathways are the same, this experiment result is consistent with the notion that both pathways are the same.

(19) Dessy, R. E.; Weissman, P. M.; Pohl, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5117–5121.

(16) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Chemistry*; Wiley: New York, 1958; p 223.

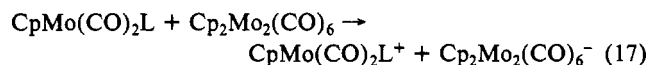
(17) Hoffman, N. W.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 613–617.

**Table IV.** Quantum Yields for the Disproportionation of  $\text{Cp}_2\text{Mo}_2(\text{CO})_5(\text{PPh}_3)^a$  in the Presence of Various Ligands upon Irradiation at 405 nm in Benzene

ligand	cone angle, deg	concn, <sup>b</sup> M	$\phi$
$\text{PPh}_2(n\text{-Bu})$	141	1.0	0.21
$\text{PPh}_2(\text{CH}_3)$	136	1.0	0.45
$\text{P}(\text{OCH}_3)_3$	107	1.0	1.40

<sup>a</sup>  $[\text{Cp}_2\text{Mo}_2(\text{CO})_5(\text{PPh}_3)] = 1.5 \times 10^{-3}$  M. <sup>b</sup> These measurements were taken at a ligand concentration such that no substitution products were observed (see text).

this would make it a 17-electron species. Whatever the structure, the point is that the complex is electron rich—so rich that it transfers an electron to the dimer.) It is arguable that the sequence of steps in eq 8 and 9 is reversed; i.e., electron transfer occurs before addition of the second L, although it is not obvious why the electron-deficient 17-electron species should want to transfer an electron to become an even more electron-deficient 16-electron species (eq 17 and 18).



Although this latter sequence of reactions is more orthodox<sup>20</sup> than the sequence in eq 8 and 9 (in the former sequence the Mo atom in the  $\text{CpMo}(\text{CO})\text{L}$  complex begins with 17 electrons, goes to 19,<sup>21</sup> and then to 18, while in the latter sequence a 17–16–18 route is followed), we believe that the sequence of reactions in eq 8 and 9 is correct for the reasons outlined below.

The following observations are consistent with the reaction sequence in eq 8 and 9. Recall that  $\text{PPh}_3$  does not disproportionate the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  complexes upon low-energy excitation. The lack of reactivity is easily explained by the sequence in eq 8 and 9 but not by the sequence in eq 17 and 18. According to the latter sequence, the coordinatively unsaturated species  $\text{CpMo}(\text{CO})_2\text{L}^+$  is generated by electron transfer and then a second L bonds to fill the vacant coordination site. For the case of  $\text{PPh}_3$ , there should be no impediment to this sequence of events because there is no reason that  $\text{PPh}_3$  cannot bond to  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)^+$ ; after all,  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)_2^+$  is a known complex<sup>22</sup> (it forms upon 290-nm irradiation of the same reaction solution). Obviously,  $\text{PPh}_3$  does not react for kinetic reasons and not because of the instability of the products. The point is that there should not necessarily be a large kinetic barrier for the reaction of  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)^+$  with  $\text{PPh}_3$ . On the other hand, one can imagine several kinetic barriers that might prevent the disproportionation of  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  by  $\text{PPh}_3$  according to the sequence of reactions in eq 8 and 9. First, the 17-electron intermediate  $\text{CpMo}(\text{CO})_2\text{PPh}_3$  might be too sterically crowded to undergo a bimolecular reaction with  $\text{PPh}_3$ .<sup>23</sup> Second, assuming that the 19-electron intermediate  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)_2$  did form, it is certainly a very bulky species and it might not be able to get close enough to  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  to transfer an electron in an outersphere reaction,<sup>24</sup> in which case it simply decomposes to  $\text{CpMo}(\text{CO})_2\text{PPh}_3$  and  $\text{PPh}_3$  (eq 15).

The quantum yield data in Table IV are also consistent with the reaction sequence in eq 8 and 9. Table IV shows the quantum yields for the disproportionation of  $\text{Cp}_2\text{Mo}_2(\text{CO})_5(\text{PPh}_3)$  by P-

**Table V.** Quantum Yields for the Disproportionation of  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6^a$  in the Presence of  $\text{P}(\text{OCH}_3)_3$  or  $\text{PPh}_2(\text{CH}_3)$  upon Irradiation at 405 nm in Benzene

ligand	concn, <sup>b</sup> M	$\phi$
$\text{PPh}_2(\text{CH}_3)$	0.20	2.0
$\text{PPh}_2(\text{CH}_3)$	0.60	6.0
$\text{P}(\text{OCH}_3)_3$	2.00	1.2

<sup>a</sup>  $[(\text{MeCp})_2\text{Mo}_2(\text{CO})_6] = 1.5 \times 10^{-3}$  M. <sup>b</sup> These measurements were taken at a ligand concentration such that no substitution products were observed (see text).

$(\text{OCH}_3)_3$  ( $\theta = 107^\circ$ ),  $\text{PPh}_2(\text{CH}_3)$  ( $\theta = 136^\circ$ ), and  $\text{PPh}_2(n\text{-Bu})$  ( $\theta = 140^\circ$ ). The important trend in Table IV is that the quantum yield for the disproportionation decreases as the size of the phosphine increases (at constant phosphine concentration). This trend is easily explained by the sequence in eq 8 and 9; the rate of the bimolecular reaction in eq 8 will be dependent on the size of the phosphine. On the other hand, in order for the sequence of events of eq 17 and 18 to explain the trend in Table IV, it is necessary to postulate that the rate of eq 18 is ligand dependent. This possibility seems unlikely because the ligand is simply filling a vacant coordination site in the  $\text{CpMo}(\text{CO})_2\text{L}^+$  complex; the rate constants for such processes are usually ligand independent.<sup>25,26</sup>

Not unexpectedly, the results of cyclic voltammetry experiments confirm that the proposed 19-electron intermediates are powerful reducing agents. In an attempt to obtain  $\text{CpMo}(\text{CO})_2(\text{dppe})$ , a  $10^{-3}$  M THF solution of  $\text{CpMo}(\text{CO})_2(\text{dppe})^+$  was scanned from +1.0 to -3.5 V (vs. a standard  $\text{Ag}^+/\text{Ag}$  reference electrode). The  $\text{CpMo}(\text{CO})_2(\text{dppe})^+$  complex could not be reduced. From this result we conclude that the  $\text{CpMo}(\text{CO})_2(\text{dppe})$  complex is a strong reducing agent. (Potentials lower than -3.5 V were unattainable because the THF begins to reduce at this potential.<sup>27</sup>)

Finally, in regard to the pathway in Scheme I, it is worth pointing out that the electronic and steric cutoffs discussed earlier are entirely consistent with the proposed mechanism. The steric properties of the ligands should be important because of the associative nature of the substitution of the 17-electron intermediate<sup>28a</sup> (eq 7) and because the 19-electron species is formed in a bimolecular reaction (eq 8). The electron-donating ability of the ligands will be important because increased electron density on the metal should increase the rate of the electron-transfer reaction<sup>24</sup> (eq 9) and because the electron-donating ability is indirectly related to the nucleophilicity of the ligand.<sup>29</sup> (The nucleophilicity will be important in the associative reactions mentioned above.) Which property, steric size, or electron-donating ability dominates in the disproportionation reaction? From the data in Table IV and the discussion thereof, it might seem that it is the size of the ligand that ultimately controls the quantum yield of the reaction. This is not always the case, however. Quantum yield data are presented in Table V for the disproportionation ( $\lambda = 405$  nm) of the  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$  complex by  $\text{PPh}_2(\text{CH}_3)$  ( $\theta = 136^\circ$ ) and  $\text{P}(\text{OCH}_3)_3$  ( $\theta = 107^\circ$ ). Clearly, if the size alone determined the quantum yields, then the quantum yield for the reaction with  $\text{P}(\text{OCH}_3)_3$  would be much larger than the quantum yields with  $\text{PPh}_2(\text{CH}_3)$ . But  $\text{PPh}_2(\text{CH}_3)$  is a much better electron donor than  $\text{P}(\text{OCH}_3)_3$ , and it is obviously this

(20) See ref 16, p 527.

(21) Summers, D. P.; Luong, J. C.; Weighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 5238–5241. Hepp and Wrighton have also shown that the rates of oxidation of photogenerated 17-electron metal radicals is higher in a donor solvent ( $\text{CH}_3\text{CN}$ ) than in nondonor solvents, a fact that may be attributable to the intermediate formation of 19-electron species in  $\text{CH}_3\text{CN}$ . See: Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258–1261.

(22) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 43–46.

(23) Our scale models of the molecules involved suggest this is a real possibility.

(24) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966–978. (b) Zwolinski, B. J.; Marcus, R. J.; Eyring, H. *Chem. Rev.* **1955**, *55*, 157–180.

(25) Wilkins, R. G. "The Study of the Kinetics and Mechanism of Reactions of Transition Metal Complexes"; Allyn and Bacon: Boston, 1974.

(26) An interesting point in Table IV is that several of the quantum yields are less than unity. This can be attributed to the  $\text{PPh}_3$  ligand. Recall that because of its size,  $\text{PPh}_3$  by itself will not disproportionate the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  dimer ( $\lambda > 290$  nm) because the 19-electron intermediate  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)_2$  cannot form. In the disproportionation reactions summarized by Table IV, the 19-electron intermediate will be  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{L}$  [ $\text{L} = \text{PPh}_2(\text{CH}_3)$ ,  $\text{PPh}_2(n\text{-Bu})$ ,  $\text{P}(\text{OCH}_3)_3$ ]. Apparently, this intermediate can form in these reactions, but the efficiency with which it does form is much lower than normal because of the bulky  $\text{PPh}_3$  ligand and, hence, the quantum yields are lower.

(27) Jaun, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741–5748.

(28) (a) Shi, Q.; Richmond, T. G.; Troglor, W. C.; Basolo, F.; *J. Am. Chem. Soc.* **1982**, *104*, 4032–4034. (b) McCullen, S. B.; Walker, H. W.; Brown, T. L. *Ibid.* **1982**, *104*, 4007–4008.

(29) (a) Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**, *60*, 716–722. (b) Derencsenyi, T. T. *Inorg. Chem.* **1981**, *20*, 665–670.

**Table VI.** The Relationship of the Cone Angle to the Substitution Products That Form upon Irradiation ( $\lambda = 405$  nm) of  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$  in Cyclohexane

ligand	cone angle, deg	does $(\text{MeCp})_2\text{Mo}_2(\text{CO})_5\text{L}$ form?	does $(\text{MeCp})_2\text{Mo}_2(\text{CO})_4\text{L}_2$ form?
$\text{P}(\text{OCH}_3)_3$	107	yes	yes
$\text{P}(\text{OC}_2\text{H}_5)_3$	109	yes	yes
$\text{P}(\text{O-}i\text{-Pr})_3$	130	yes	yes
$\text{P}(n\text{-Bu})_3$	132	yes	yes
$\text{PPh}_2(\text{CH}_3)$	136	yes	yes
$\text{PPh}_2(n\text{-Bu})^a$	140	yes	slight
$\text{P}(i\text{-Bu})_3$	143	yes	no
$\text{PPh}_3$	145	yes	no
$\text{PPh}_2(i\text{-Pr})$	150	yes	no
$\text{P}(i\text{-Pr})_3$	160	yes	no
$\text{P}(c\text{-Hx})_3$	170	yes	no

<sup>a</sup> This cone angle estimated as  $2/3$  of the value between  $\text{P}(n\text{-Bu})_3$  and  $\text{PPh}_3$ . See ref 15, p 315.

property that makes the quantum yield for the reaction with  $\text{PPh}_2(\text{CH}_3)$  greater than the  $\text{P}(\text{OCH}_3)_3$  quantum yield. The point is that in comparing ligands with different sizes and with different electron-donating abilities, it is not always possible to predict the relative rates (efficiencies) of the reactions. Note that Table V also shows the point illustrated by the data in Table III: the quantum yield of disproportionation increases as the concentration of the ligand increases.

**Substitution vs. Disproportionation.** As mentioned above, in addition to disproportionation, substitution of the  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  complex occurs when the dimers are irradiated in the presence of a ligand.<sup>30</sup> The monosubstituted dimers always form, but the disubstituted dimers form only with certain ligands. Both the monosubstituted dimers  $\text{Cp}_2\text{Mo}_2(\text{CO})_5\text{L}$  and the disubstituted dimers  $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{L}_2$  will photochemically react further to give the ionic disproportionation products, provided that L is present and also that additional  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  is present in the case of the disubstituted dimers.

Table VI summarizes the products that form when  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$  is irradiated (405 nm) in the presence of various ligands. The ratio of substitution to disproportionation products that form is dependent on the size of the ligand and on the concentration of the ligand. We have observed that as the ligand increases in size, the monosubstituted dimer is formed preferentially to the disubstituted dimer. Also, as the concentration of the ligand increases, the amount of substitution products decrease and the amount of disproportionation products increase. These results are illustrated by the data in Table VII. Thus, small ligands (e.g.,  $\text{P}(\text{OCH}_3)_3$ ) at low concentrations yield predominantly

**Table VII.** Ratios of the Quantum Yields for the Formation of Substituted Products to Disproportionation Products from  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$  as a Function of Ligand Concentration upon Irradiation at 405 nm in Cyclohexane

$[\text{P}(\text{OCH}_3)_3], \text{M}$	$\phi_{\text{disub}}/\phi_{\text{dispro}}$	$[\text{P}(\text{OCH}_3)_3], \text{M}$	$\phi_{\text{disub}}/\phi_{\text{dispro}}$
0.25	0.55	1.02	0.06
0.48	0.45	2.00	0.00
0.76	0.23		
$[\text{PPh}_2(n\text{-Bu})], \text{M}$	$\phi_{\text{disub}}/\phi_{\text{dispro}}$	$[\text{PPh}_2(n\text{-Bu})], \text{M}$	$\phi_{\text{disub}}/\phi_{\text{dispro}}$
0.02	13.3	0.16	2.0
0.04	5.8	0.50	0.0
0.12	2.4		

<sup>a</sup>  $[(\text{MeCp})_2\text{Mo}_2(\text{CO})_6] = 1.5 \times 10^{-3} \text{ M}$ .

disubstituted products and some disproportionation products; very little monosubstituted dimer is seen even at very low concentrations. At high concentrations of small ligands the amount of substitution products decrease and only ionic products are observed. For large ligands (e.g.,  $\text{PPh}_2(n\text{-Bu})$ ) the formation of monosubstituted dimer dominates at low concentration and the parent dimer is almost completely converted to monosubstituted dimer before any disproportionation products are observed. As the concentration of the large ligands increases, the relative yield of disproportionation products increase (Table VII).

Once again, the results above are entirely consistent with the pathway in Scheme I. The ratio of monosubstituted dimer to disubstituted dimer is controlled by the ratio of the rate constants  $k_1$  and  $k_2$ . As L increase in size,  $k_2$  becomes smaller because the coupling of two  $\text{CpMo}(\text{CO})_2\text{L}$  fragments is sterically less favorable. The dependence of the  $\phi_{\text{sub}}/\phi_{\text{dispro}}$  ratio on the concentration of the ligand is also easily explained by Scheme I. Obviously, as the concentration of the ligand increases, the rate of reaction 8 will increase and more disproportionation products will form relative to the substitution product.

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**Registry No.**  $\text{Mo}(\text{CO})_5\text{NEt}_3$ , 33846-95-6;  $\text{Mo}(\text{CO})_5\text{CH}_3\text{N}$ , 14324-76-6;  $\text{Mo}(\text{CO})_5\text{NH}_2\text{Ph}$ , 83455-05-4;  $\text{Mo}(\text{CO})_5\text{CH}_3\text{CN}$ , 17594-16-0;  $\text{Mo}(\text{CO})_5\text{P}(i\text{-Pr})_3$ , 65774-62-1;  $\text{Mo}(\text{CO})_5\text{P}(c\text{-Hx})_3$ , 15603-94-8;  $\text{Mo}(\text{CO})_5\text{P}(n\text{-Bu})_3$ , 15680-62-3;  $\text{Mo}(\text{CO})_5\text{AsPh}_3$ , 19212-22-7;  $\text{Mo}(\text{CO})_5\text{PPh}_3$ , 14971-42-7;  $\text{Mo}(\text{CO})_5\text{PPh}_2(i\text{-Pr})$ , 18534-30-0;  $\text{Mo}(\text{CO})_5\text{P}(\text{O-}i\text{-Pr})_3$ , 34369-19-2;  $\text{Mo}(\text{CO})_5\text{P}(\text{OCH}_3)_3$ , 15631-20-6;  $\text{Mo}(\text{CO})_5\text{P}(\text{O-}n\text{-Bu})_3$ , 21485-22-3;  $\text{Mo}(\text{CO})_5\text{P}(\text{O-C}_6\text{H}_4\text{-OCH}_3)_3$ , 86497-23-6;  $\text{Mo}(\text{CO})_5\text{P}(\text{O-C}_6\text{H}_4\text{-CH}_3)_3$ , 36491-10-8;  $\text{Mo}(\text{CO})_5\text{P}(\text{OPh})_3$ , 15711-66-7;  $\text{P}(\text{OCH}_3)_3$ , 121-45-9;  $\text{P}(\text{OC}_2\text{H}_5)_3$ , 122-52-1;  $\text{P}(\text{O-}i\text{-Pr})_3$ , 116-17-6;  $\text{P}(n\text{-Bu})_3$ , 102-85-2;  $\text{PPh}_2(\text{CH}_3)$ , 1486-28-8;  $\text{PPh}_2(n\text{-Bu})$ , 6372-41-4;  $\text{P}(i\text{-Bu})_3$ , 4125-25-1;  $\text{PPh}_3$ , 603-35-0;  $\text{PPh}_2(i\text{-Pr})$ , 6372-40-3;  $\text{P}(i\text{-Pr})_3$ , 6476-36-4;  $\text{P}(c\text{-Hx})_3$ , 2622-14-2;  $(\text{MeCp})_2\text{Mo}_2(\text{CO})_6$ , 33056-03-0;  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ , 12091-64-4;  $\text{Cp}_2\text{Mo}_2(\text{CO})_5(\text{PPh}_3)$ , 12119-01-6;  $\text{Cp}_2\text{W}_2(\text{CO})_6$ , 12091-65-5; Na, 7440-23-5; dppe, 1663-45-2.

(30) The various  $\text{Cp}_2\text{Mo}_2(\text{CO})_5\text{L}$  and  $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{L}_2$  complexes (or the MeCp analogues) were identified by infrared spectroscopy. All of the  $\text{Cp}_2\text{Mo}_2(\text{CO})_5\text{L}$  or  $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{L}_2$  complexes have essentially the same infrared spectra so identification was made by comparison with  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{P}(\text{OMe})_3)_2$  or  $\text{Cp}_2\text{Mo}_2(\text{CO})_5\text{PPh}_3$ . See also ref 5a.