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Back-Reactions in the Photochemical Disproportionation of $Cp_2Mo_2(CO)_6$ (Cp = $C_5H_4CH_3$) and the Wavelength-Dependent Photochemistry of the $Cp_2Mo_2(CO)_6$ Complex with PPh_3

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Irradiation ($\lambda > 525$ nm) of $Cp_2Mo_2(CO)_6$ (Cp = η^5-C_5H_5, η^5-$C_5H_4CH_3$) with PPh_3 in CH_2Cl_2 proceeds as follows: $Cp_2Mo_2(CO)_6 + PPh_3 \xrightarrow{h\nu} CpMo(CO)_3PPh_3^+ + CpMo(CO)_3^-$. A similar disproportionation reaction does not occur in benzene or other nonpolar solvents for $\lambda > 525$ nm but does occur for $\lambda = 290$ nm. (The cationic product in this case is $CpMo(CO)_2(PPh_3)_2^+$.) The dependence of the disproportionation reaction on solvent and radiation wavelength is shown to be a consequence of a facile back-reaction: $CpMo(CO)_3PPh_3^+ + CpMo(CO)_3^- \rightarrow Cp_2Mo_2(CO)_6 + PPh_3$. Thus, irradiation of $Cp_2Mo_2(CO)_6$ with PPh_3 at 525 nm in nonpolar solvents does disproportionate the dimer but the back-reaction occurs and there is no net disproportionation. The back-reaction is considerably slower in CH_2Cl_2, and net disproportionation is therefore observed in this solvent. Net disproportionation does occur at 290 nm in benzene because a secondary photochemical reaction of the initially formed $CpMo(CO)_3PPh_3^+$ product occurs: $CpMo(CO)_3PPh_3^+ + PPh_3 \xrightarrow{h\nu} CpMo(CO)_2(PPh_3)_2^+$; this disubstituted cation and $CpMo(CO)_3^-$ do not back-react. Several other unexplained observations from our previous studies of the disproportionation reactions can also be interpreted in terms of the occurrence of a back-reaction. The back-reactions can be prevented in several ways: a more polar solvent can be used; the cationic or anionic products can be reacted further; the disproportionation reaction can be done at low temperature. Each of these methods is discussed and demonstrated.

In a recent paper, we demonstrated that irradiation of $Cp_2Fe_2(CO)_4$ in the presence of tertiary phosphorus ligands results in disproportionation of the $Cp_2Fe_2(CO)_4$:[1]

$$Cp_2Fe_2(CO)_4 + 2L \xrightarrow{h\nu} CpFe(CO)L_2^+ + CpFe(CO)_2^- + CO \quad (1)$$

L = a phosphine or phosphite

However, the back-reaction of the ionic products to re-form $Cp_2Fe_2(CO)_4$ is usually so facile that no net reaction is observed. The occurrence of a similar back-reaction in the disproportionation reactions of the $Cp_2Mo_2(CO)_6$ complex would explain many of the puzzling and unexplained results we have noted in our studies of this complex.[2,3] In particular, the wavelength-dependent disproportionation photochemistry of the $Cp_2Mo_2(CO)_6$ complex[2] (eq 2 and 3) could be explained by a back-reaction of the type

$$Cp_2Mo_2(CO)_6 \xrightarrow[PPh_3]{\lambda = 290\text{ nm}} CpMo(CO)_2(PPh_3)_2^+ + CpMo(CO)_3^- + CO \quad (2)$$

$$Cp_2Mo_2(CO)_6 \xrightarrow[PPh_3]{\lambda > 366\text{ nm}} \text{no disproportionation, only } Cp_2Mo_2(CO)_5PPh_3 \quad (3)$$

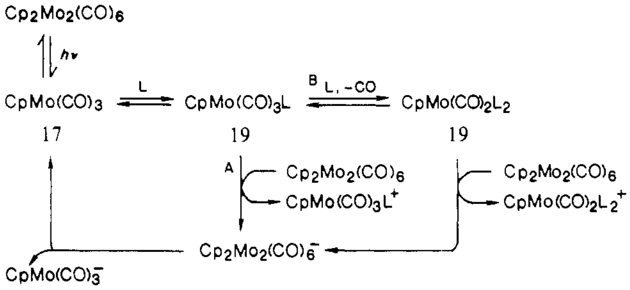
observed for reaction 1. In this paper, we report on our investigation of back-reactions of the $Cp_2Mo_2(CO)_6$ disproportionation reactions and we use the results to interpret several previously unexplained effects.

Experimental Section

$Cp_2Mo_2(CO)_6$ (Cp = η^5-C_5H_5, η^5-$C_5H_4CH_3$),[4] $[CpMo(CO)_3PPh_3][PF_6]$,[5] and $[NEt_4][CpMo(CO)_3]$[6] were prepared by literature methods. All other materials were obtained commercially and used as received. CH_2Cl_2 was Aldrich "Anhydrous Gold Label".

All reactions were carried out under an argon atmosphere as previously described.[2,3] All irradiations were performed in an IR spectroscopy cell and monitored in the ν_{CO} region, 2200-1600 cm^{-1}. Products were identified by comparison of their spectra to the spectra of previously reported complexes.[7] The light source used was a 200-W Oriel Co. high-pressure mercury arc lamp. Identical results were obtained for irradiations at 405, 505, and >525 nm. Edmund Scientific Co. interference filters were used for irradiations at 405 and 505 nm. A Corning Glass CS 3-68 filter was used for irradiations with $\lambda > 525$ nm. An interference filter was used for $\lambda = 290$ nm. IR spectra were obtained with a Perkin-Elmer 983, Beckman 4240, or Nicolet 5DXB FT-IR spectrophotometer. Lamp intensities were measured with use of Aberchrome 540 actinometry.[8]

Scheme I



Results and Discussion

Wavelength-Dependent Photochemistry with PPh_3. Irradiation ($\lambda > 525$ nm) of a CH_2Cl_2 solution of $Cp_2Mo_2(CO)_6$ (15 mM) and PPh_3 (0.2 M) results in disproportionation of the $Cp_2Mo_2(CO)_6$ complex (eq 4) and, to a lesser extent, substitution (eq 5).

$$Cp_2Mo_2(CO)_6 + PPh_3 \xrightarrow[CH_2Cl_2]{\lambda > 525\text{ nm}} CpMo(CO)_3PPh_3^+ + CpMo(CO)_3^- \quad (4)$$

$$Cp_2Mo_2(CO)_6 + PPh_3 \xrightarrow[CH_2Cl_2]{\lambda > 525\text{ nm}} Cp_2Mo_2(CO)_5PPh_3 + CO \quad (5)$$

Under the conditions of irradiation, the reaction proceeds to about 85% disappearance of $Cp_2Mo_2(CO)_6$ when Cp = η^5-C_5H_4Me.[9] Upon standing in the dark for 1 h, 90% of the ionic products formed in eq 4 undergo recombination to form $Cp_2Mo_2(CO)_6$:

$$CpMo(CO)_3PPh_3^+ + CpMo(CO)_3^- \rightarrow Cp_2Mo_2(CO)_6 + PPh_3 \quad (6)$$

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(1) Goldman, A. S.; Tyler, D. R. *Inorg. Chem.*, in press.
(2) Stiegman, A. E.; Tyler, D. R. *J. Am. Chem. Soc.* **1982**, *104*, 2944-2945.
(3) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032-6037.
(4) Birdwhistle, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239-241.
(5) Nolte, M. J.; Reimann, R. H. *J. Chem. Soc., Dalton Trans.* **1978**, 932-937.
(6) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263-268.
(7) (a) Suenkel, K.; Ernst, H.; Beck, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 474-481. (b) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 43-46.
(8) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 1* **1981**, 341-343.
(9) With Cp = η^5-C_5H_5, the dominant (net) reaction is eq 5 accompanied by reaction 4 to a lesser extent. The back-reaction of the ionic products is qualitatively much faster for Cp = η^5-C_5H_5 than with Cp = η^5-$C_5H_4CH_3$ complexes.

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Table I. Selected Infrared Data in CH_2Cl_2

complex	$\nu(C{\equiv}O)$, cm^{-1}
$[CpMo(CO)_3PPh_3^+][CpMo(CO)_3^-]$[a]	2055 (m), 1995 (sh), 1975 (m), 1894 (s), 1774 (s)
$[CpMo(CO)_2(PPh_3)_2^+][PF_6^-]$[a]	1974 (m), 1897 (s)
$[CpMo(CO)_3PPh_3^+][PF_6^-]$[a]	2057 (m), 1995 (sh), 1973 (m)
$Cp_2Mo_2(CO)_6$[a]	2012 (w), 1956 (s), 1911 (s)
$Cp_2Mo_2(CO)_5PPh_3$[b]	1967 (s), 1893 (s), 1881 (s), 1813 (m)
$[NEt_4][CpMo(CO)_3^-]$[b]	1894 (s), 1774 (s)
$CpMo(CO)_3H$[b]	2025 (s), 1938 (s)

[a] $Cp = \eta^5\text{-}C_5H_4CH_3$. [b] $Cp = \eta^5\text{-}C_5H_5$.

For future reference, we note that the mechanism of the disproportionation reactions has been studied in nonpolar solvents and the reactions proceed via the chain pathway in Scheme I.[3] The reactions in CH_2Cl_2 undoubtedly follow the same route. Consistent with this proposal is our finding that the quantum yield for disproportionation of $Cp_2Mo_2(CO)_6$ with dppe in CH_2Cl_2 is 80.[10] (The cationic product in this reaction is $CpMo(CO)_2dppe^+$, as identified by IR spectroscopy.[11])

The recombination of the ionic products in eq 4 is an important observation because it accounts for several unexplained observations we made in earlier studies.[2,3] Of most importance, we propose that it explains the wavelength-dependent disproportionation photochemistry[2] of the $Cp_2Mo_2(CO)_6$ complex with PPh_3 in nonpolar solvents (eq 2 and 3). Note that in nonpolar solvents, unlike the case in CH_2Cl_2,[12] disproportionation of the $Cp_2Mo_2(CO)_6$ complex does not occur with low-energy irradiation. In addition, note that, with higher energy radiation (eq 2), the cationic product is the disubstituted $CpMo(CO)_2(PPh_3)_2^+$ complex and not the monosubstituted $CpMo(CO)_3PPh_3^+$ complex as in eq 4. Our proposed explanation for these results is as follows. We propose that reaction 1 does occur with low-energy irradiation in nonpolar solvents but that no *net* disproportionation occurs because the back-reaction of the $CpMo(CO)_3PPh_3^+$ cation with $CpMo(CO)_3^-$ is too fast to allow observation of the ions. These products, however, are stable in CH_2Cl_2 because a polar solvent will stabilize the ions with respect to the back-reaction.[13] Furthermore, we propose that the formation of $CpMo(CO)_2(PPh_3)_2^+$ in reaction 2 is the result of reaction 1, followed by a secondary photochemical reaction of the initially formed $CpMo(CO)_3PPh_3^+$ cation:

$$CpMo(CO)_3PPh_3^+ + PPh_3 \xrightarrow{\lambda = 290\ nm} CpMo(CO)_2(PPh_3)_2^+ + CO \quad (7)$$

Finally, we propose that the failure of reaction 2 to proceed with long-wavelength light is explained by the fact that $CpMo(CO)_3PPh_3^+$ does not absorb at long wavelengths ($\lambda > 400$ nm).[14]

Table II. Results from Irradiating $Cp_2Mo_2(CO)_6$ with Various Phosphine and Phosphite Ligands in CH_2Cl_2 and Nonpolar Solvents

ligand	cone angle, deg[a]	disproportionation?[b,c] nonpolar solvents[d] 525 nm[e]	nonpolar solvents[d] 290 nm	CH_2Cl_2 525 nm[c]	CH_2Cl_2 290 nm
$P(OMe)_3$	107	di	di	di[f]	di[f]
$P(OEt)_3$	109	di	di		
$P(O\text{-}n\text{-}Bu)_3$	109[g]			di + mono	di + mono
$P(OPh)_3$[h]	128	di	di	yes[i]	yes[i]
$P(O\text{-}i\text{-}Pr)_3$	130	di	di	di + mono	di + mono
PEt_3	132			di[f]	di[f]
$P(n\text{-}Bu)_3$	132	di	di	di[f]	di[f]
PPh_2Me	136	di	di	di[f]	di[f]
$PPh_2(n\text{-}Bu)$	140	di	di	di + mono	di + mono
$P(i\text{-}Bu)_3$	143	slight, di	di		
PPh_3	145	no	di	mono	mono + very small amt of di
$PPh_2(i\text{-}Pr)$	150	no	no	mono	mono
$P(i\text{-}Pr)_3$	160	no	no	mono	mono
$P(chx)_3$	170	no	no	mono	mono

[a] See ref 16. [b] Substitution also occurs in many cases; see text. [c] Di indicates formation of the disubstituted $CpMo(CO)_2L_2^+$ product; mono indicates formation of the monosubstituted $CpMo(CO)_3L^+$ product in the disproportionation reaction. The cations were identified with use of infrared spectroscopy by comparison to the spectra reported in ref 7 and Table I. [d] Many of the results in nonpolar solvents have been reported previously; see ref 3. [e] Similar results were obtained with 405- and 505-nm irradiation. [f] $CpMo(CO)_3L^+$ (mono) can be made to form in these reactions; see ref 18. [g] Value taken as identical with that of $P(OEt)_3$. [h] Includes $P(O\text{-}p\text{-}C_6H_4\text{-}OCH_3)_3$ and $P(O\text{-}p\text{-}C_6H_4\text{-}CH_3)_3$. [i] Yes indicates that disproportionation has occurred (as indicated by formation of $CpMo(CO)_3^-$) but the cation IR bands were not identified.

To test for the occurrence of reaction 7, a CH_2Cl_2 solution of $[CpMo(CO)_3PPh_3][PF_6]$ (10 mM) and PPh_3 (0.2 M) was irradiated ($\lambda = 290$ nm). The product was $CpMo(CO)_2(PPh_3)_2^+$, as identified by infrared spectroscopy (Table I). A control experiment showed that no reaction occurred for $\lambda > 525$ nm. Another test for reaction 7 was performed as follows. A CH_2Cl_2 solution of $[CpMo(CO)_3PPh_3^+][CpMo(CO)_3^-]$ was generated by irradiating ($\lambda > 525$ nm) a mixture of $Cp_2Mo_2(CO)_6$ (10 mM) with PPh_3 (0.2 M). Subsequent irradiation of the reaction solution with 290-nm irradiation led to the disappearance of the $CpMo(CO)_3PPh_3^+$ and the appearance of $CpMo(CO)_2(PPh_3)_2^+$ as monitored by infrared spectroscopy.[15]

A second part of the hypothesis presented above is that the back-reaction of $CpMo(CO)_3PPh_3^+$ with $CpMo(CO)_3^-$ is fast in nonpolar solvents. To check this idea, $[CpMo(CO)_3PPh_3][PF_6]$ (13.3 mg) and $[NEt_4][CpMo(CO)_3]$ (6.9 mg) were dissolved in 0.1 mL of CH_2Cl_2 and then 1.9 mL of benzene was added. An infrared spectrum of the solution, taken immediately after the benzene was added, showed the complete disappearance of the ionic reactants and the formation of the $Cp_2Mo_2(CO)_6$ complex. A control experiment showed that, for an identical experiment in neat CH_2Cl_2 solution, the reaction of the ionic species to form $Cp_2Mo_2(CO)_6$ was not complete after 12 h. At intermediate ratios of benzene:$CHCl_2$, we qualitatively observed that the rate of the back-reaction increased as the proportion of CH_2Cl_2 increased.[16]

Results with Other Phosphines. The results of irradiating mixtures of $Cp_2Mo_2(CO)_6$ with other phosphines in both polar and nonpolar solvents are shown in Table II. The phosphine and phosphite ligands are listed in order of increasing cone angle.[17] The results in nonpolar solvents have been reported and explained

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(10) Although the quantum yields with L = PPh_3 are also qualitatively quite high, we were unable to get quantitative data with PPh_3 because photochemical substitution is also occurring. The overlapping absorption bands of $Cp_2Mo_2(CO)_6$ and $Cp_2Mo_2(CO)_5PPh_3$ prevented an accurate measurement of the disappearance quantum yield.

(11) King, R. B.; Parnell, K. H.; Eggens, C. A.; Houk, L. W. *Inorg. Chem.* **1968**, *7*, 2353–2356.

(12) We were restricted in our choice of polar solvents because most other polar solvents led to disproportionation of the $Cp_2Mo_2(CO)_6$ complex, a result attributable to the coordinating ability of these solvents. Note that no photochemical Cl atom abstraction reactions were observed in CH_2Cl_2; i.e.

$$Cp_2Mo_2(CO)_6 \not\xrightarrow[CH_2Cl_2]{h\nu} 2CpMo(CO)_3Cl$$

under the conditions of our experiments.

(13) Reichardt has reviewed the ability of polar solvents to stabilize ionic reactants. In general, for a reaction between oppositely charged ions giving a neutral product, the rate will slow as the solvent polarity (and dielectric constant) increases. See: Reichardt, A. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29–40.

(14) The yellow $[CpMo(CO)_3PPh_3^+][PF_6^-]$ complex has an absorption band maximum at 228 nm with a shoulder at 364 nm. This shoulder has a tail trailing into the visible region of the spectrum but there is no significant absorption for wavelengths longer than 400 nm.

(15) In view of the fact that small amounts of dimer are necessarily still present in the reaction mixture, the monosubstituted cation is not necessarily the source of the disubstituted cation. However, the disappearance of the $CpMo(CO)_3PPh_3^+$ is consistent with the notion that it can be converted to $CpMo(CO)_2(PPh_3)_2^+$ under these conditions.

(16) A pertinent question we cannot answer yet in detail is why the back-reaction does not take place with $CpMo(CO)_2(PPh_3)_2^+$. We are presently studying the mechanism of the back-reactions.

(17) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

before.[3] Note that, at any irradiation wavelength in nonpolar solvents, if disproportionation occurs, then only the disubstituted cation forms. This result is consistent with the results obtained above for PPh_3; i.e., the monosubstituted cation and the anion will back-react quickly. Also note that there is an apparent steric cutoff in the size of the ligands that promote disproportionation: ligands with cone angles larger than 145° are too bulky to form a disubstituted cationic product via the (low energy) mechanism in Scheme I. However, in the case of PPh_3, the disubstituted cation can form via the secondary photochemical reaction in eq 7. Apparently, even reaction 7 is not possible at high energy with the three largest phosphines in Table II so no net disproportionation occurs with these ligands.

Both mono- and disubstituted cations form in CH_2Cl_2 solution[12,18] for ligands smaller than PPh_3. The mechanism in Scheme I explains this result. However, as discussed previously for PPh_3, only the monosubstituted cation forms with PPh_3 and larger ligands;[3] steric crowding apparently prevents the reactions in route B in Scheme I from occurring. As discussed previously, the ionic products are stable to back-reaction in CH_2Cl_2 solution and thus net disproportionation occurs with these ligands even with low-energy radiation. Similar results are obtained at 290 nm in CH_2Cl_2 solution except that some disubstituted cation is obtained with PPh_3, probably via reaction 7. As in the nonpolar solvents, note that reaction 7 is not possible with $PPh_2(i\text{-}Pr)$, $P(i\text{-}Pr)_3$, and $P(chx)_3$ (chx = cyclohexyl) and thus the monosubstituted cation is the only cationic product that forms.

From Table II we conclude that irradiation of $Cp_2Mo_2(CO)_6$ with any phosphine or phosphite ligand of reasonable size will lead to disproportionation of the dimer. The failure of certain large ligands to give a net disproportionation reaction in nonpolar solvents can be attributed to the back-reaction in eq 6 and the inability of these ligands to form disubstituted cation products, either via route B in Scheme I or via the secondary photolysis in eq 7.

Just as ligand size is not important in determining whether disproportionation of the $Cp_2Mo_2(CO)_6$ dimer will occur, we found that the electron-donating ability of the ligand is also not important. Previously, we had reported that poor electron donors such as $P(OPh)_3$, $P(O\text{-}p\text{-}C_6H_4\text{-}CH_3)_3$, and $P(O\text{-}p\text{-}C_6H_4\text{-}OCH_3)_3$ failed to react photochemically (at any wavelength) with $Cp_2Mo_2(CO)_6$ in benzene according to eq 2. However, disproportionation does occur when $Cp_2Mo_2(CO)_6$ (10 mM) and $P(OPh)_3$ (0.2 M) are irradiated ($\lambda > 525$ nm) in CH_2Cl_2, as evidenced by the formation of a peak at 1774 cm^{-1} in the infrared spectrum attributable to $CpMo(CO)_3^-$. The inability of $P(OPh)_3$ and the related ligands above to give $Cp_2Mo_2(CO)_6$ disproportionation products in benzene can probably be attributed to the poor nucleophilicity of these strongly electron-withdrawing phosphites and their consequent inability to form a disubstituted cationic product via route B in Scheme I.

Interpretation of Other Unexplained Results. In a previous paper we discussed the photochemical disproportionation of the $Cp_2Mo_2(CO)_6$ complex with halides:[19]

$$Cp_2Mo_2(CO)_6 + X^- \xrightarrow{h\nu} CpMo(CO)_3X + CpMo(CO)_3^- \qquad (8)$$

In THF,[20] the reaction was shown to follow the pathway in Scheme I (route A; L = X^-) and it seemed logical that a similar pathway should hold in benzene solution. However, no reaction was observed in benzene. Although puzzling at the time, the reason is now obvious: in benzene, the back-reaction of the anion and the halide complex is facile and there is no net reaction. Consistent with this interpretation is our observation that irradiation ($\lambda >$ 525 nm) of $Cp_2Mo_2(CO)_6$ in benzene containing HCl proceeded as shown in eq 9. The products were identified by infrared

$$Cp_2Mo_2(CO)_6 + HCl \xrightarrow{\lambda > 525\ \text{nm}} CpMo(CO)_3Cl + CpMo(CO)_3H \qquad (9)$$

spectroscopy (Table I). We suggest that disproportionation of the $Cp_2Mo_2(CO)_6$ occurs with Cl^- but that a back-reaction of the products is prevented because the $CpMo(CO)_3^-$ is trapped by the proton to give the hydride complex, $CpMo(CO)_3H$. Reaction 9 is thus a further illustration of the principle that the back-reactions of the disproportionation reactions can be prevented by reacting further one of the disproportionation products. This principle was first delineated in our study of the $Cp_2Fe_2(CO)_4$ dimer. We observed that monodentate phosphine ligands will not disproportionate the $Cp_2Fe_2(CO)_4$ dimer in THF, acetone, or benzene solution. However, in CH_2Cl_2 solution, net disproportionation (eq 10) with the same monodentate phosphines is observed because the $CpFe(CO)_2^-$ anion formed in the disproportionation reaction reacts with CH_2Cl_2 to form $CpFe(CO)_2CH_2Cl$.

$$Cp_2Fe_2(CO)_4 + 2L \xrightarrow[CH_2Cl_2]{h\nu} CpFe(CO)L_2^+ + CpFe(CO)_2CH_2Cl + Cl^- \qquad (10)$$

Finally, note that in some cases the back-reaction can be prevented by carrying out the reaction at low temperature. Reactions 11 and 12, previously reported,[19] demonstrate this technique.

$$Cp_2Mo_2(CO)_6 \xrightarrow[\text{acetone}]{\lambda = 405\ \text{nm, room temp}} \text{no reaction} \qquad (11)$$

$$Cp_2Mo_2(CO)_6 \xrightarrow[\text{acetone}]{\lambda = 405\ \text{nm, }-78\ ^\circ\text{C}} CpMo(CO)_3^- + CpMo(CO)_3((CH_3)_2CO)^+ \qquad (12)$$

Conclusion. This paper demonstrated that in many cases the cationic and anionic products formed in the disproportionation reactions of the $Cp_2Mo_2(CO)_6$ complex will quickly back-react. This back-reaction gives rise to the wavelength-dependent disproportionation photochemistry observed with the PPh_3 ligand. In addition, the $Cp_2Mo_2(CO)_6$ dimer will disproportionate with nearly all phosphine and phosphite ligands (although a back-reaction may occur, of course); there appear to be no special steric and electronic requirements for the ligands. The back-reactions can be prevented in several ways: (1) a more polar solvent can be used (compare eq 3 and 4); (2) the cationic or anionic products can be reacted further (eq 7, 9, and 10); (3) the reaction can be done at low temperature (compare eq 11 and 12).[18]

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(18) In several of the reactions in CH_2Cl_2 solution under N_2, the formation of the $CpMo(CO)_3L^+$ product was not observed. However, this cation was formed under a CO atmosphere. For example, when a solution of $Cp_2Mo_2(CO)_6$ (15 mM) and PBu_3 (0.1 M) in CH_2Cl_2 is irradiated under N_2, disproportionation results to give $CpMo(CO)_3^-$ and a mixture of mono- and disubstituted cation. Under an atmosphere of CO, the same solution affords only the monosubstituted cation. These results follow logically from Scheme I. Under N_2, both pathways A and B in Scheme I are operative. Under a CO atmosphere, however, pathway B is prevented (i.e. the equilibrium $CpMo(CO)_3L + L \rightleftharpoons CpMo(CO)_2L_2 + CO$ is pushed to the left) and then only $CpMo(CO)_3L^+$ can form (via pathway A).

(19) Stiegman, A. E.; Tyler, D. R. *J. Am. Chem. Soc.* **1985**, *107*, 967–971.

(20) Note that irradiation of $Cp_2Mo_2(CO)_6$ in THF (and no added ligand) will not disproportionate the $Cp_2Mo_2(CO)_6$ complex.