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# Supramolecular Photochemistry of the $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ Complex. Chemical Ramifications of a Tentacle Ligand Covalently Bonded Nearby to a Reactive Metal Center

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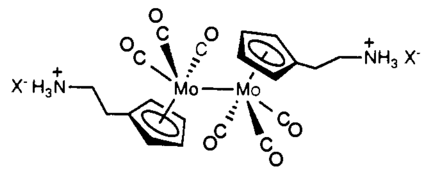
**Abstract**: The photochemistry of the $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ complex is described. Because of the tentacle group on the Cp ligand, the photochemistry of the complex is considerably different from that of the $Cp_2Mo_2(CO)_6$ parent complex. Thus, visible irradiation of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ in THF in the absence of added ligands leads to metal–metal bond disproportionation. For comparison, no net reaction occurs when the $(MeCp)_2Mo_2(CO)_6$ dimer is irradiated in the presence of an excess of $[C_6H_5CH_2CH_2NH_3^+][PF_6^-]$. Mechanistic work established that the different reactivities can be ascribed to a supramolecular effect of the tentacle ligand; specifically, the tentacle ligand inhibits a back-reaction of the initial photochemical products in the case of the $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ complex. The following pathway is proposed: Irradiation of either dimer complex leads to photolysis of the metal–metal bond. The photogenerated 17-electron complexes then react with THF (the solvent) to form 19-electron adducts; disproportionation then follows, likely by the standard chain pathway previously reported. The initial disproportionation products are $Cp^xMo(CO)_3(THF)^+$ and $Cp^xMo(CO)_3^-$ ($Cp^x$ = $CpCH_2CH_2NH_3^+$, MeCp). In the case of the $(MeCp)_2Mo_2(CO)_6$ dimer, a facile back-reaction of these products ensues, and the result is no net reaction. In the case of the tentacle dimer, proton transfer yields $[(CpCH_2CH_2NH_3^+)Mo(CO)_3H]$ and $[(CpCH_2CH_2NH_2)\text{-}Mo(CO)_3THF]^+$, and then facile coordination of the free amine effectively blocks the back-reaction by forming $[(CpCH_2CH_2\overline{NH_2)Mo}(CO)_3]^+$. This cooperative reactivity between the tentacle ligands and the unstable initial products of disproportionation to yield stable products is an example of supramolecular reactivity. Reaction of the free amine with a CO group also yields the carbamoyl complex $[(CpCH_2CH_2\overline{NHCO)Mo}(CO)_2PPh_3]$ .

We recently began a research program to explore the reactivity of 19-electron organometallic complexes in aqueous solution.[1,2] Metal–metal bonded dimers are a convenient precursor to 19-electron complexes,[3,7] and for that reason the synthesis of aqueous-soluble dimers was a necessary preliminary goal. In an initial paper, we demonstrated that functionalizing the cyclopentadienyl rings of the $Cp_2W_2(CO)_6$ complex with a carboxylic acid group rendered the dimer soluble in neutral to basic solution.[1a] More recently, we reported the reactivity of the $[(CpCH_2CH_2NH_3^+)_2\text{-}Mo_2(CO)_6][NO_3^-]_2$ complex in acidic aqueous solution.[1b]

The $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6]$ complex is among the growing class of complexes known as "tentacle ligand complexes."[8] These are complexes in which extended chain ligands are appended to molecules for the purpose of imparting some new property to the complex. The tentacle ligand in the $[(CpCH_2CH_2NH_3^+)_2\text{-}Mo_2(CO)_6]$ complex was intended only to impart aqueous solubility to the complex and not to impart new reactivity to the photogenerated radical. However, preliminary experiments in nonaqueous solvents showed considerable reactivity differences between the $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ complex (**1**) and the unsubstituted Cp analog. In order to understand fully these reactivity differences, a complete photochemical study of the $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ complex in nonaqueous solution was undertaken. The specific goal was to understand the ramifications of having a potentially reactive substituent attached to the Cp ring. A long-term goal was to understand the nonaqueous photochemistry of the molecule so that, coupled with our knowledge of the aqueous chemistry,[1b] the catalytic chemistry in biphasic solutions could be properly interpreted.[9,10] In this paper we report the photochemistry of the $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ dimer in nonaqueous solvents.



**1** X = $PF_6^-$

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[1] (1) For the preceding papers in this series, see: (a) Avey, A.; Tenhaeff, S. C.; Weakley, T. J. R.; Tyler, D. R. *Organometallics* **1991**, *10*, 3607–3613. (b) Avey, A.; Tyler, D. R. *Organometallics* **1992**, *11*, 3856–3863. (c) MacKenzie, V.; Tyler, D. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1783–1784.

[2] (2) For a recent review of aqueous organometallic chemistry, see: Barton, M.; Atwood J. M. *J. Coord. Chem.* **1991**, *24*, 43–67. For other leading references, see ref 2 in ref 1b above.

[3] (3) The adducts that form in the reactions of 17-electron species with ligands are known in the literature as "19-electron adducts" (or "19-electron complexes") simply because the sum of 17 valence electrons from the metal radical and the two electrons from the ligand is 19. No implication about the electronic or geometric structures of these complexes is necessarily implied by this name. See refs 4–6 for a complete discussion of the possibility that the adducts need not necessarily have a "19-electron" configuration; slipped Cp rings, bent CO ligands (i.e., CO acting as a one-electron donor), and phosphoranyl radical-type structures are all possible and would result in an 18- or 17-electron configuration at the metal center.

[4] (4) Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* **1986**, *5*, 215–245.

[5] (5) Tyler, D. R. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; pp 338–364.

[6] (6) Tyler, D. R.; Mao, F. *Coord. Chem. Rev.* **1990**, *97*, 119–140.

[7] (7) Nineteen-electron complexes have several features that make them ideal photogenerated reducing agents,[4–6] and one of our long-range goals is to exploit the 19-electron complexes as electron-transfer initiators and relays in aqueous catalytic cycles (e.g., in photochemical water-splitting schemes for solar energy conversion). For further discussion of the reducing properties of 19-electron complexes, see ref 8 in ref 1b.

[8] (8) Siemeling, U. *J. Chem. Soc., Chem. Commun.* **1992**, 1335–1336.

[9] (9) Kuntz, E. G. *CHEMTECH* **1983**, *17*, 570.

0002-7863/93/1515-7706$04.00/0

Table I. Electronic Spectroscopic Data

| complex[a] | $\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$) | ref |
|---|---|---|
| $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$[b,e] | 503 (2100), 388 (18 000) | 1b |
| $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$[c] | 505 (2080), 389 (20 100) | 1b |
| $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$[f] | 503 (1700), 387 (16 000) | this work |
| $(MeCp)_2Mo_2(CO)_6$[c] | 506 (2400), 390 (20 000) | 11 |
| $Cp_2Mo_2(CO)_6$[d] | 505 (1610), 385 (17 400) | 12 |

[a] Cp = ($\eta^5$-$C_5H_5$); MeCp = ($\eta^5$-$C_5H_4CH_3$); $CpCH_2CH_2NH_3^+$ = ($\eta^5$-$C_5H_4CH_2CH_2NH_3^+$). [b] $H_2O$ pH 2 buffer. [c] MeOH. [d] $CH_2Cl_2$. [e] $H_2O$ pH 7 buffer. [f] THF.

## Results

**Electronic Spectrum of Dimer 1.** The electronic absorption spectrum of dimer **1** in THF is similar to that of the previously reported nitrate salt in methanol.[1b] The spectrum exhibits two bands in the visible/near-UV region (Table I). There is a weak band at 503 nm ($\epsilon$ = 1700 $M^{-1}$ $cm^{-1}$) and an intense band at 387 nm (16 000 $M^{-1}$ $cm^{-1}$). This spectrum is essentially identical to the spectra of $Cp_2Mo_2(CO)_6$ and $(MeCp)_2Mo_2(CO)_6$ in nonaqueous solvents (Table I), and similar band assignments are therefore proposed.[11-16] Thus, the band at 387 nm is assigned to the metal–metal $\sigma \rightarrow \sigma^*$ transition and the band at 503 nm to a $d\pi \rightarrow \sigma^*$ transition. All of the photochemical irradiations in this paper were carried out by irradiating into the low-energy tail of the $d\pi \rightarrow \sigma^*$ transition ($\lambda > 525$ nm for general irradiations or $\lambda = 550$ nm for quantum yields).

**Reaction Chemistry of Dimer 1.** The reactions of dimer **1** are summarized in Scheme I. What follows is an elaboration of these reactions along with some discussion pertaining to the characterizations of the products. Mechanistic discussions concerning these reactions are postponed to the Discussion section.

**Photolysis of the Mo–Mo Bond.**[17] Irradiation of the dimer in $CCl_4$/THF led to the quantitative formation of metal chloride **14** (eq 7, Scheme I). The formation of metal chloride species in reactions with $CCl_4$ is taken as evidence of metal–metal bond homolysis in analogous systems, and homolysis is undoubtedly also occurring here (Table II).[14]

The quantum yield for disappearance of the dimer in the 1.0 M $CCl_4$/THF solvent system is considerably smaller than the quantum yield for the disappearance of the $(MeCp)_2Mo_2(CO)_6$ dimer under identical conditions (0.39 ± 0.04 vs 0.55 ± 0.05, respectively; Table III). In THF, the cationic dimer and its $PF_6^-$ counterions probably exist as a closely associated ion pair. This may slow the rate of diffusion of the geminate pair out of the cage, due to increased mass and bulk of the diffusing species.[1b,19] Slower diffusion of the geminate pair will favor recombination, resulting in lower quantum yields for nonaqueous systems.

**Formation of 19-Electron Complexes.** Our previous studies showed that 19-electron complexes are key intermediates in the photochemical disproportionation reactions of the metal–metal-bonded carbonyl dimers.[20-22] Therefore, if disproportionation of dimer **1** occurred, it would strongly suggest the intermediate formation of 19-electron complexes (formed by reaction of photogenerated $[(CpCH_2CH_2NH_3^+)Mo(CO)_3]$ radicals with a ligand). In fact, disproportionation did occur: irradiation of complex **1** in the presence of $PPh_3$ in THF gave the disproportionation products shown in eq 1 in Scheme I.

Note that cation **8** and cation **9** both form in the disproportionation reaction. Analogous mono- and disubstituted cationic products also form in the disproportionation reactions of the $Cp_2Mo_2(CO)_6$ complexes in nonaqueous solvents.[20-22] The disproportionation chain mechanism[21,22] accounts for both products, so the formation of both products in eq 1 should not be construed as unusual. Complexes **8–11** exhibit subsequent thermal chemistry of a type not observed with the Cp or MeCp analogs. These thermal reactions are discussed later.

**Disproportionation of Dimer 1 in THF without Added Ligand.** Irradiation of dimer **1** in THF without added ligand results in the formation of cation **2** and hydride **3**, as evidenced by IR and NMR spectroscopy (eq 2 in Scheme I). The proposed structure of **2** is strongly suggested by the close similarity of its NMR spectrum to that of the "chelated" compound **4** (for which a crystal structure was obtained; see below). In particular, one of the most notable features in the $^1H$ NMR spectrum of **2** is the large difference in the chemical shifts of the Cp protons at 6.41 and 5.41 ppm. The large difference is a result of the ethylamine arm locking the Cp ring into a rigid conformation, one in which the ring protons are in different environments.[23,24] As Figure 1a shows, the protons farthest away from the amine tether ($H_b$) are situated out and away from the carbonyls that lie cis to the nitrogen, whereas the protons nearest the tether ($H_a$) are situated almost directly above the carbonyls that lie cis to the nitrogen. The peaks show an AA'BB' splitting pattern common to similar compounds, such as **4**.[23,24] The similarity in the IR spectra between the tethered compounds **2** and **4** lends further support to the structure of **2**. Complex **2** has the same symmetry about the metal atom as complex **4**, and as a result the NH stretches are identical for the two compounds: 3310 and 3135 $cm^{-1}$.

The identity of **2** was confirmed by independently synthesizing it via the same route (eqs 7 and 8) that was used to synthesize the analogous $[CpMo(CO)_3NH_3^+]Cl^-$ species.[25] Thus, photochemical generation of $[(CpCH_2CH_2NH_3^+)Mo(CO)_3Cl][PF_6^-]$, **14** (eq 7), followed by reaction with Proton Sponge (eq 8) gave a product with spectroscopic properties identical to those of compound **2** formed via the route in eq 2 in Scheme I.

The formation of hydride **3** in reaction 2 was confirmed by comparison of its infrared and NMR spectra with those of $CpMo(CO)_3H$ and $Cp'Mo(CO)_3H$ (Table I).[25] Hydride **3** was also independently synthesized in quantitative yield by reduction of **1** with $NaK_{2.8}$ to form anion **12** (eq 9),[26] followed by protonation with $CF_3COOH$ (eq 10).[27] The IR and $^1H$ NMR spectra of **3** formed in the photochemical disproportionation (eq 2) were identical to that of **3** made by this independent route.

**Reactions of Compounds 2 and 3 with PPh₃.** Addition of $PPh_3$ to a photochemically generated solution of **2** and **3** results in slow

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(10) Kuntz, E. G. Fr. Patent 2314910, 1975.

(11) Goldman A. S.; Tyler D. R. *Organometallics* **1984**, *3*, 449–456.

(12) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*. 4246–4251.

(13) Smith D. W.; Williams J. P. *Struct. Bonding* **1970**, *7*, 8–39.

(14) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187–218.

(15) Watanabe T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617–2619.

(16) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979; p 62.

(17) This section is not meant to imply that Mo–Mo photolysis is the only primary photoprocess. Abrahamson showed[18] that W–W homolysis and W–CO bond dissociation both occurred as primary photoprocesses when the $Cp_2W_2(CO)_6$ complex (Cp = $\eta^5$-$C_5H_5$) is irradiated with visible light. It is therefore logical to assume that Mo–CO bond dissociation also occurs when the $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ complex is irradiated. One ostensible outcome of Mo–CO dissociation would be the formation of substitution products; e.g., $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_5(L)][PF_6^-]_2$ would form when $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ is irradiated in the presence of a ligand, as was indeed observed. Note however that this product can photochemically disproportionate.

(18) Van Vlierberge, B. A.; Abrahamson H. B. *J. Photochem. Photobiol., A* **1990**, *52*, 69-81.

(19) Covert, K. C.; Askew, E. F.; Grunkemeier, J.; Koenig, T.; Tyler, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 10446–10448.

(20) Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1987**, *26*, 253–258.

(21) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032–6037.

(22) Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217–140.

(23) (a) Coolbaugh, T. S.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 6310–6318. (b) Wang, T.; Lee, T.; Chou J.; Ong, C. *J. Organomet. Chem.* **1992**, *423*. 31–38.

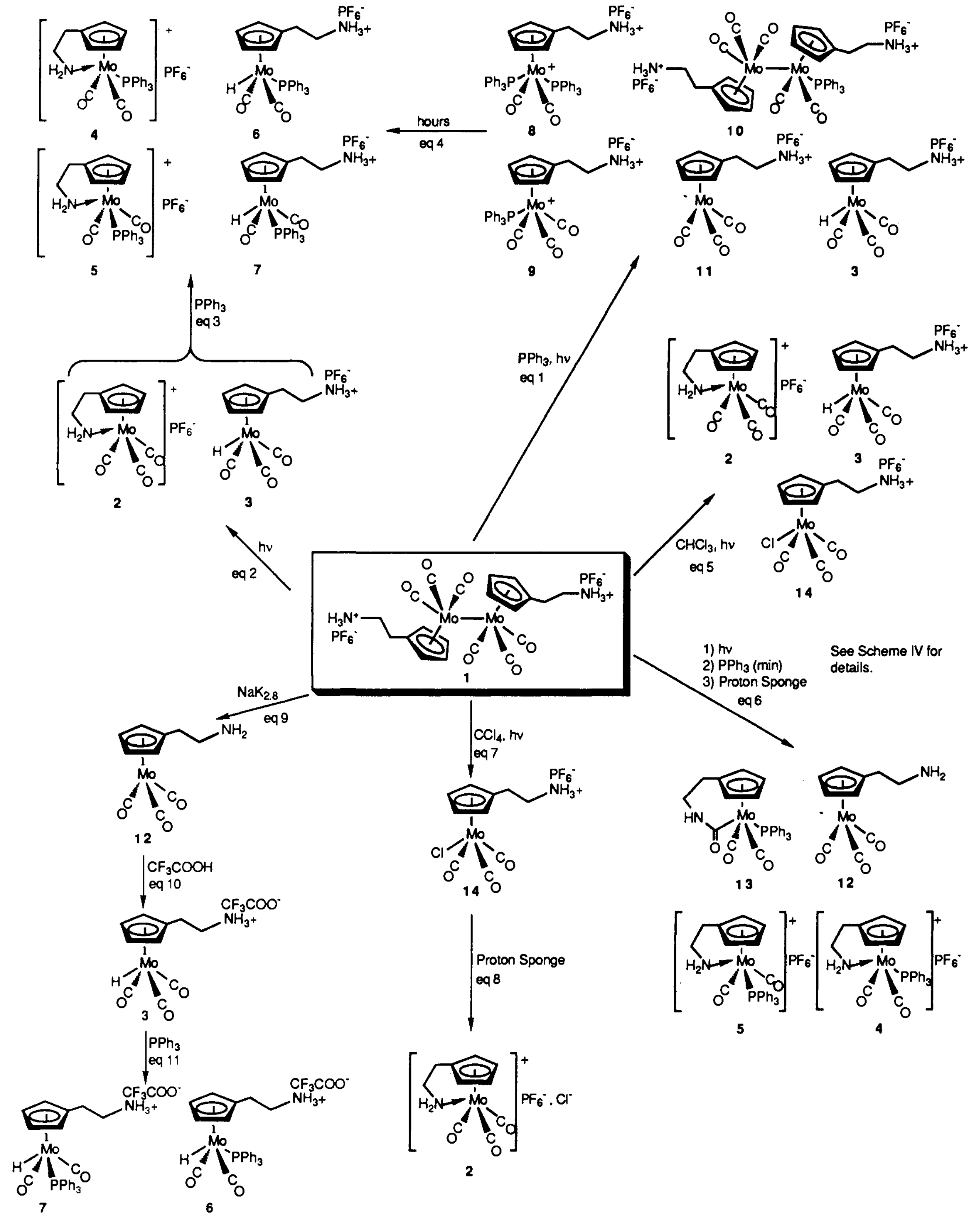
(24) (a) Omae, I. *Coord. Chem. Rev.* **1988**, *83*, 137–167. (b) Omae, I. *Coord. Chem. Rev.* **1982**, *42*, 31–54 (and references therein).

(25) Fischer, E. O.; Moser, E. *J. Organomet. Chem.* **1964**, *2*, 230–235.

(26) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263–268.

(27) King, R. B. *Organometallic Syntheses*; Academic: New York, 1965; Vol. 1, p 156.

**Scheme I**



(several hours) substitution of the complexes, as indicated in eq 3 in Scheme I. The reaction was monitored by infrared spectroscopy, which showed the disappearance of the characteristic IR bands of hydride **3** and cation **2**, accompanied by the appearance of bands assigned to **4**–**7**.[28] The substituted hydrides **6** and **7** were independently synthesized by reacting species **3** (synthesized via eqs 9 and 10) with $PPh_3$ for 5 h (eq 11). The IR and NMR spectra of the products were identical to those of the complexes formed from hydride **3** in eq 3.

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[28] Alt, H. G.; Eichner M. E. *J. Organomet. Chem.* **1981**, *212*, 397–403. Alt, H. G.; Engelhardt, H. E.; Klaui, W.; Muller, A. *J. Organomet. Chem.* **1987**, *331*, 317–327.

**Table II.** Summary of Spectroscopic Data

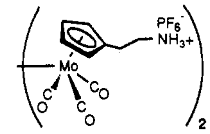
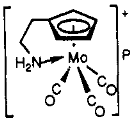
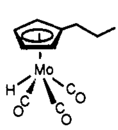
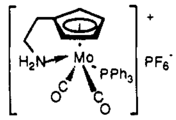
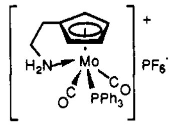
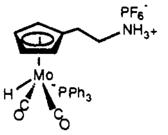
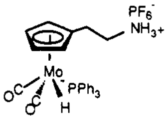
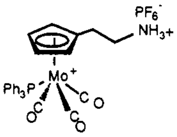
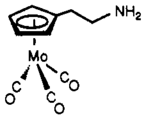
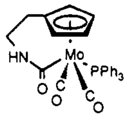
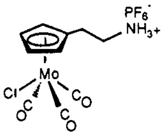
| no. | complex[a] | NMR (THF-$d_8$), $\delta$ | $\nu$(CO), cm$^{-1}$ | ref |
|---|---|---|---|---|
| **1** |  | 7.26 (s (br), 6H, $CpCH_2CH_2N\mathit{H}_3^+$), 5.53 (m, 8H, $\mathit{Cp}CH_2CH_2NH_3^+$), 3.23 (m, 2H, $CpCH_2C\mathit{H}_2NH_3^+$), 2.82 (m, 2H, $CpC\mathit{H}_2CH_2NH_3^+$) | 2010 (m), 1953 (8000), 1913 (s) | this work |
| **2** |  | 6.41 (d, $J_{H\text{-}H}$ = 1.8 Hz, 2H, $\mathit{Cp}CH_2CH_2NH_2$), 5.41 (d, $J_{H\text{-}H}$ = 1.8 Hz, 2H, $\mathit{Cp}CH_2CH_2NH_2$), 4.65 (s (br), 2H, $CpCH_2CH_2N\mathit{H}_2$), 3.59 (m, 2H, $CpCH_2C\mathit{H}_2NH_2$), 2.49 (t, $J_{H\text{-}H}$ = 6.4 Hz, 2H, $CpC\mathit{H}_2CH_2NH_2$) | 2060 (s), 1987 (vs), 1958 (vs) | this work |
| **3** |  | 7.27 (s (br), 3H, $CpCH_2CH_2N\mathit{H}_3^+$), 5.50 (s, 2H, $\mathit{Cp}CH_2CH_2NH_3^+$), 5.64 (s, 2H, $\mathit{Cp}CH_2CH_2NH_3^+$), 3.04 (t, $J_{H\text{-}H}$ = 6.3 Hz, 2H, $CpCH_2C\mathit{H}_2NH_3^+$), 2.65 (t, $J_{H\text{-}H}$ = 6.3 Hz, 2H, $CpC\mathit{H}_2CH_2NH_3^+$), −5.48 (d, 1H, M–H) | 2022 (vs), 1933 (vs), 1914 (sh) | this work |
| **4** |  | 6.24 (m, 2H, $\mathit{Cp}CH_2CH_2NH_2$), 4.64 (s (br), 2H, $CpCH_2CH_2N\mathit{H}_2$), 4.17 (m (br), 2H, $\mathit{Cp}CH_2CH_2NH_2$), 3.56 (m, 2H, $CpCH_2C\mathit{H}_2NH_2$), 2.36 (t, $J_{H\text{-}\mathit{H}}$ = 6.3 Hz, 2H, $CpC\mathit{H}_2CH_2NH_2$) | 1982 (s), 1899 (vs) | this work |
| **5** |  | 6.30 (s, 1H, $\mathit{Cp}CH_2CH_2NH_2$), 6.25 (s, 1H, $\mathit{Cp}CH_2CH_2NH_2$), 5.05 (s, 1H, $\mathit{Cp}CH_2CH_2NH_2$), 4.97 (s, 1H, $\mathit{Cp}CH_2CH_2NH_2$), 4.66 (d br, 2H, $CpCH_2CH_2N\mathit{H}_2$), 3.22 (m, 2H, $CpCH_2C\mathit{H}_2NH_2$), 2.36 (t, $J_{H\text{-}H}$ = 6.3 Hz, 2H, $CpC\mathit{H}_2CH_2NH_2$) | 1982 (s), 1899 (s) | this work |
| **6** |  | 7.82 (s (br), 3H, $CpCH_2CH_2N\mathit{H}_3^+$), 7.6 $PPh_3$ (approx obscured by excess $PPh_3$), 5.21 (s, 2H, $\mathit{Cp}CH_2$-$CH_2NH_3^+$), 4.85 (s, 2H, $\mathit{Cp}CH_2CH_2NH_3^+$), 3.18 (s (br), 2H, $CpCH_2C\mathit{H}_2NH_3^+$), 2.64 (m, 2H, $CpC\mathit{H}_2CH_2NH_3^+$), −5.50 trans (s (br), 1H, Mo–*H*) | 1939 (s), 1864 (s) | this work |
| **7** |  | 7.82 (s (br), 3H, $CpCH_2CH_2N\mathit{H}_3^+$), 7.6 $PPh_3$ (approx obscured by excess $PPh_3$), 5.21 (s, 2H, $\mathit{Cp}CH_2$-$CH_2NH_3^+$), 4.85 (s, 2H, $\mathit{Cp}CH_2CH_2NH_3^+$), 3.18 (s (br), 2H, $CpCH_2C\mathit{H}_2NH_3^+$), 2.64 (m, 2H, $CpC\mathit{H}_2CH_2NH_3^+$), −5.36 cis (s (br), 1H, Mo–*H*) | 1939 (s), 1864 (s) | this work |
| **9** |  | *7.3* ($CpCH_2CH_2N\mathit{H}_3^+$), *7.5* ($PPh_3$), 6.18 (s, 2H, $\mathit{Cp}CH_2CH_2NH_2$), 5.67 (s, 2H, $\mathit{Cp}CH_2CH_2NH_2$), *3.15* ($CpCH_2C\mathit{H}_2NH_2$), 2.83 ($CpC\mathit{H}_2CH_2NH_2$) | 2059 (s), 1987 (m), 1965 (s) | this work |
| **12** |  | 4.94 (d, 2H, $J$ = 2.1 Hz, $\mathit{Cp}CH_2CH_2NH_2$), 4.85 (d, 2H, $J$ = 2.1 Hz, $\mathit{Cp}CH_2CH_2NH_2$), 2.66 (pent, 2H, $J$ = 7.0 Hz, $CpCH_2C\mathit{H}_2NH_2$), 2.33 (m, 2H, $J$ = 6.9 Hz, $CpC\mathit{H}_2CH_2NH_2$), 1.23 (t, $J$ = 6.9 Hz, 2H, $CpCH_2CH_2N\mathit{H}_2$) | 1908 (s), 1813 (s), 1786 (s) | this work |
| **13** |  | 5.65 (AA′BB′, 2H, $\mathit{Cp}CH_2CH_2NHCO$), 4.39 (m, 2H, $\mathit{Cp}CH_2CH_2NHCO$), 3.84 (m, 2H, $CpCH_2C\mathit{H}_2NHCO$), 2.39 (m, 2H, $CpC\mathit{H}_2CH_2NHCO$), ($CpCH_2CH_2N\mathit{H}CO$, obscured by other resonances) | 1939 (m), 1862 (m), 1578 (vs) | this work |
| **14** |  | 7.90 (s (br), 3H, $CpCH_2CH_2N\mathit{H}_3^+$), 5.99 (s, 2H, $\mathit{Cp}CH_2CH_2NH_3^+$), 5.40 (s, 2H, $\mathit{Cp}CH_2CH_2NH_3^+$), 3.07 (s (br), 2H, $CpCH_2C\mathit{H}_2NH_3^+$), 2.61 (t, $J_{H\text{-}H}$ = 7.2 Hz, 2H, $CpC\mathit{H}_2CH_2NH_3^+$) | 2050 (m), 1971 (s), 1956 (sh) | this work |
|  | $(MeCp)_2Mo_2(CO)_6$[b] |  | 2012 (m), 1956 (s), 1912 (s) | 11 |
|  | $(MeCp)Mo(CO)_3Cl$[f] |  | 2051, 1981 (3300),[g] 1957 | 11, this work |
|  | $[CpMo^{II}(CO)_3PPh_3^+][BF_4^-]$[e] |  | 2062, 2001, 1975 | 47 |
|  | $[CpMo^{II}(CO)_3(PEt_3)^+][BF_4^-]$[e] |  | 2056 (s), 1993 (m), 1966 (vs) | 47 |
|  | $[CpMo^{II}(CO)_2(PPh_3)_2^+][BF_4^-]$[e] |  | 1978 (s), 1901 (vs) | 47 |
|  | $[CpMo^{II}(CO)_2(PEt_3)_2^+][BF_4^-]$[e] |  | 1963 (s), 1884 (vs) | 47 |
| **16** | $[(CpCH_2CH_2NH_3^+)Mo^I(CO)_3(THF)]^{2+}$ |  | 2072, 1979 | this work |
|  | $[(Cp)Mo^I(CO)_3(THF)]^+[BF_4^-]$ |  | 2070, 1980 | 48 |
| **16** | $[(CpCH_2CH_2NH_3^+)Mo^I(CO)_3\text{-}(NCCH_3)]^{2+}$ |  | 2077, 1993 | this work |
|  | $[(Cp)Mo^I(CO)_3(NCCH_3)]^+[BF_4^-]$ |  | 2076, 1997 | 48 |

Table II (Continued)

| no. | complex[a] | NMR (THF-$d_8$), δ | ν(CO), cm⁻¹ | ref |
|---|---|---|---|---|
| **8** | $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(PPh_3)_2]^{2+}$ [c,d] | | 1965 (s), 1900 (s) | this work |
| | $CpMo^{II}(CO)_3H$ [c] | | 2030 (vs), 1949 (vs), 1913 (w) | 49 |
| | $K^+[CpMo(CO)_3^-]$ [c] | | 1898 (s), 1790 (s), 1750 (s) | 26 |
| **11** | $[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3]$ [c] | | 1908 (s), 1813 (s), 1786 (s) | this work |
| | $Cp_2Mo_2(CO)_5PPh_3$ [b] | | 1968 (s), 1900 (s), 1827 (m) | 50 |
| **10** | $[(CpCH_2CH_2NH_3^+)_2Mo^I_2(CO)_5(PPh_3)]^{2+}$ [c,d] | | 1939 (s), 1913 (s), 1863 (s) | this work |

[a] Cp = ($\eta^5$-$C_5H_5$); MeCp = ($\eta^5$-$C_5H_4CH_3$); $CpCH_2CH_2NH_3^+$ = ($\eta^5$-$C_5H_4CH_2CH_2NH_3^+$). [b] $CCl_4$. [c] THF. [d] $PF_6^-$ counterion. [e] $CH_2Cl_2$. [f] $CS_2$. [g] ε; $M^{-1}$ $cm^{-1}$.

**Table III.** Disappearance Quantum Yields[a] for the Reactions of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$, $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$, and $(MeCp)_2Mo_2(CO)_6$ with Various Substrates

| conditions | eq in Scheme I | Φ | ref |
|---|---|---|---|
| 1 M $CCl_4$ in THF | 7 | 0.39 ± 0.04 | 1b |
| 0.050 M $CCl_3CH_2OH$ in $H_2O$[b] | na | 0.78 ± 0.15 | 1b |
| PTA in $H_2O$[b] | na | 0.32 ± 0.05 | 1b |
| $H_2O$[b] | na | 0.16 ± 0.01 | 1b |
| THF | 2 | 0.36 ± 0.05 | this work |
| 1 M $CCl_4$ in THF[c] | na | 0.55 ± 0.05 | 1b |

[a] λ = 550; $I \approx 1 \times 10^{-9}$ einstein/s. [b] pH 7. [c] $(MeCp)_2Mo_2(CO)_6$.

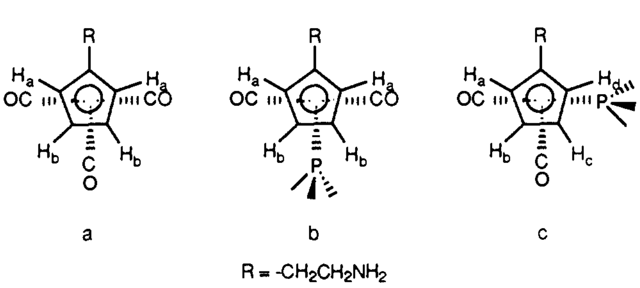


**Figure 1.** Projections along the Cp-centroid molybdenum axis showing the different environments of the Cp ring protons: (a) complex **2**; (b) complex **4**; (c) complex **5**.

The Cp rings in **6** and **7** are untethered, as shown by the similar NMR shifts for the ring protons (5.50 and 5.64 ppm) and by the existence of the ammonium resonances in the ¹H NMR (Table I). The two compounds are formed in approximately the same cis to trans ratio (1:2) as form when $CpMo(CO)_3H$ is substituted by $PPh_3$ under the same conditions. (The cis to trans ratio was determined by the integration of the hydride resonances in the NMR.[28])

Crystals of the products from the reaction of **2** with $PPh_3$ (eq 3) were grown by layering hexane on top of the THF reaction solution and allowing slow diffusion of the two solvents. Crystals of yellow **4** and orange **5** were obtained, but the substituted hydrides **6** and **7** did not crystallize. Separation of the yellow and orange crystals was accomplished by hand under a microscope on the basis of color. The X-ray crystal structures of **4** and **5** are discussed in a later section.

The NMR spectra of **4** and **5** reflect the difference in symmetry of the two species. The trans isomer, **4**, with a mirror plane of symmetry containing the phosphorus, molybdenum, and nitrogen atoms gives rise to two sets of symmetry-equivalent Cp protons at 6.24 and 4.17 ppm. The large difference in shifts is once again attributed to the rigid tethering of the ring, which places the two protons ($H_b$) farthest from the tether very close to the phenyl rings on the $PPh_3$ (Figure 1b). The result is a large upfield shift to 4.17 ppm.[23a] The protons closest to the tether ($H_a$) are positioned over the carbonyls that lie cis to the nitrogen and are seen at 6.22 ppm. The resonance at 6.22 ppm is a pseudotriplet (AA'BB') due to coupling to the other Cp ring protons. The complex pattern of resonances at 4.17 ppm is a pseudopentet, which arises from coupling to the phosphorus (doublet) as well as to the other Cp ring protons (pseudotriplet AA'BB'). The coupling to the phosphorus is clearly observed in a series of decoupling experiments. When the 6.24 ppm resonance is selectively irradiated, the 4.17 ppm resonance becomes a doublet with $J_{P-H}$ = 4.5 Hz. Coupling of this type has been reported previously in several trans intramolecular metaloester tethered complexes (Figure 2a)[23,24,29] and has been attributed to through-space coupling between the ring protons and the phosphorus.[23,29,31]

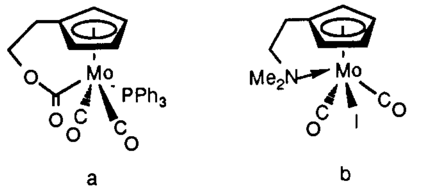


**Figure 2.** Two previously reported tethered compounds: (a) ref 23a; (b) ref 23b.

The NMR spectrum of cation **5** showed four singlets with unresolvable coupling in the Cp region (Table II).[32] The lack of resolvable coupling was also observed in the analogous tethered complex with cis geometry shown in Figure 2b.[23] The four Cp proton resonances arise from the fact that in the cis conformation all of the protons on the tethered Cp ring are inequivalent (Figure 1c). The resonance at 4.66 ppm (two broad singlets) is attributed to the coordinated amine N–H protons. This pattern is a result of the protons being in a different orientation with respect to the $PPh_3$ group, one proton pointing toward the phosphorus atom and the other away.[23] Cation **5** is unstable in THF solution and cleanly converts to the trans cation **4** over a period of 2 weeks at room temperature (eq 12).

(12)

**Disproportionation of Dimer 1 in THF in the Presence of $PPh_3$ and Subsequent Thermal Chemistry.** Irradiation of dimer **1** in THF in the presence of $PPh_3$ for 75 s in an IR cell results in the

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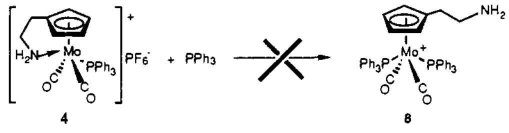
(29) The IR spectrum of **4** clearly shows N–H stretches at 3310 and 3135 $cm^{-1}$, which are similar to **2**. The CO stretches are consistant with a trans geometry for **4** because the high-energy stretch is less intense than the lower energy stretch.[30]

(30) Craig, P. J.; Edwards, J. *J. Less-Common Met.* **1974**, *36*, 193–202.

(31) Cation **4** does not react with $PPh_3$ to make the cation **8**, even after several weeks under roomlight in the drybox (eq 12).



Attempts to substitute the cation by an electron-transfer-catalyzed pathway[5] using photogenerated 19-electron complexes (formed by adding dimer to the reaction solution and irradiating with visible light) also failed.

(32) The IR spectrum of cis disubstituted cation **5** shows two interesting features: (1) There are two very sharp NH stretches of medium intensity at 3332 and 3275 $cm^{-1}$. (2) The ν(CO) bands are consistent with the cis geometry,[35] exhibiting two stretches of near equal intensity at 1982 and 1898 $cm^{-1}$.

formation of cation **9**, anion **11**, hydride **3**, substituted dimer **10**, and the disubstituted cation **8** (eq 1). The cation **9** and anion **11** products are a result of standard disproportionation chemistry, as discussed above and in previous publications.[21] The substituted dimer **10** is likely a product of photochemical CO loss from dimer **1**, or it is a back-reaction product of cation **9** and anion **11**. (Both types of reactivity have previously been shown to give $Cp_2Mo_2(CO)_5L$-type products.[18,33]) Hydride **3** is attributed to protonation of anion **11** with a proton from the ammonium group on cation **9**. The latter species subsequently reacts to form the cations **4** and **5**. Cation **8** is also a product from the disproportionation of **1**,[31] but it was unstable and reacted further to form cations **4** and **5**. Cation **8** is spectroscopically observable because its thermal reactions are slow; the reactions to form **4** and **5** take several hours, whereas the photochemical generation of the products in eq 1 is over in 75 s under our conditions.

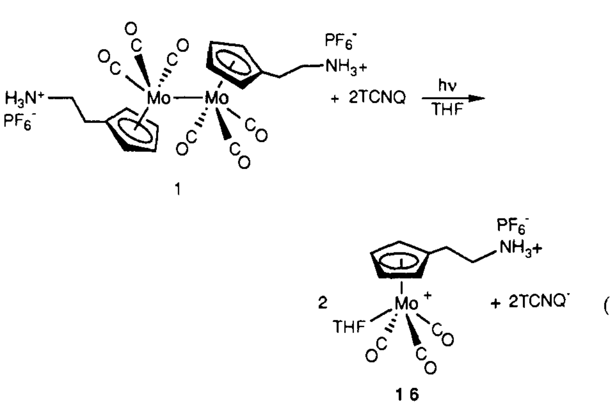
The formation of all the products in reaction **1** can be monitored conveniently by NMR. At the earliest time, 20 min, the NMR spectrum showed the presence of cation **9** (22%), anion **11** (28%), hydride **3** (22%), **5** (4%), **6** (2%), and cation **2** (22%). After 24 h in the dark in the drybox, the solution contained cation **9** (15%), anion **11** (17%), hydride **3** (10%), **5** (18%), **4** (14%), cation **2** (2%), and cis- and trans-substituted hydrides **7** and **6** (24%). After 2 weeks in the dark, the only products remaining were **4** (80%), hydrides **6** and **7** (16%), and $[(CpCH_2CH_2NH_3^+)Mo^0(CO)(PPh_3)_2H]^+$ (4%).[28] The only species detectable by NMR after 3 weeks was cation **4**.

**Photochemical Reaction of Dimer 1 with $CHCl_3$.** Because the disproportionation of dimer **1** is "built in" by having a potential ligand attached to the Cp ring, the choice of reactants is paramount in controlling the reactivity of the dimer. This feature is illustrated in the photochemical formation of metal chloride species **14** using different organic chlorides as radical traps. When $CCl_4$ is used as a radical trap, the only product formed is the metal chloride species **14**. However, when $CHCl_3$ is used, the products are a mixture of disproportionation products **2** and **3** and the metal chloride **14**, in a ratio of 1.9 to 1, respectively. The occurrence of both reactions can be attributed to the fact that metal radical trapping by $CHCl_3$ is approximately 1000 times slower than with $CCl_4$.[34] The decrease in the rate of trapping with $CHCl_3$ thus allows disproportionation to occur competitively.

**Disproportionation of Dimer 1 in $CH_3CN$.** In the Discussion section, evidence is presented that THF is the disproportionating ligand in eq 2. The proposed disproportionation mechanism, analogous to the previously published disproportionation mechanism of $Cp_2Mo_2(CO)_6$,[21,22] is shown in Scheme II. In order to observe the solvent-coordinated species **16** in Scheme II, $CH_3CN$, a stronger coordinating solvent, was chosen to slow the rate of amine chelation. For this reaction, dimer **1** was irradiated for 60 s in an infrared cell, after which time no starting material was left. The products were identified by IR spectroscopy as cation **16** (where the solvent is $CH_3CN$) and anion **11** (Table II). Following irradiation, the bands for **16** and **11** disappeared and the bands of **2** and **3** grew in over a period of 10 min.[35]

**Photochemical Reduction of TCNQ by Dimer 1.** In order to eliminate the possibility that the ammonium group or a small amount of free amine is acting as the disproportionating ligand, a solution of TCNQ and the dimer was irradiated. The reaction was monitored by IR and showed the formation of $[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3THF]^+$ and $TCNQ^-$ (eq 13). No cation **2** was observed. The implications of this experiment are discussed in the Discussion section.

**Intramolecular Nucleophilic Attack on Bound CO.** The CO stretching frequencies of the cationic compounds formed in this



(13)

study are in the range reported for those complexes that react with amines to give carbamoyl complexes.[36] In fact, as shown in eq 6 of Scheme I, the reaction of the disproportionation products **2** and **3** with $PPh_3$, followed by addition of Proton Sponge, resulted in the formation of the carbamoyl compound **13**, compound **12** (in quantitative yield based on the amount of hydride **3** present before the addition of base), and a small amount of **4** and **5**. That the carbamoyl reaction is intramolecular is suggested by the lack of an amide II stretch in the IR spectrum. (In a 6-membered cyclic lactam, the amide II band is not IR active.[37]) The tethering of the Cp ring is also suggested by the NMR spectrum: the Cp proton chemical shifts are 5.65 and 4.39 ppm. As discussed above, large differences in the chemical shifts such as this are indicative of a tethered Cp ring.[24] The carbamoyl group, as formed in reaction 6, is trans to the $PPh_3$. The formation of the trans isomer is indicated by the IR spectrum of the solution, which shows that the high energy $\nu$(CO) band is much less intense than the low energy stretch.[30] Likewise, the NMR spectrum (Table II) is similar to the trans substituted cation **4** and to the previously reported intramolecular metaloester shown in Figure 2a.[30] A discussion of the mechanism for carbamoyl formation is postponed to the Discussion section.

**Molecular Structure of 4.** The molecular structure of **4** was determined by X-ray crystallography (Figure 3). One of the most interesting features is that the cyclopentadienyl ring is unsymmetrically bonded to the molybdenum. It appears that the ring is being pulled by the tether and pushed by the $PPh_3$. The sum of these effects results in long Mo–C3 and Mo–C4 bonds of 2.354 and 2.350 Å, respectively, and an unusually short Mo–C6 bond of 2.275 Å [Mo–C(Cp) bond lengths are typically $\approx$2.32 Å].[38] The ring C–C bond distances are symmetric, and there is no evidence of a "diene" or "allylene" type bonding of the ring.[38,39] The strain on the tether can be seen in the P–Mo–N bond angle of 145.4°. This angle is 7° larger than in an analogous intramolecular metaloester complex (Figure 2a), which has a six-membered tether.[23] The larger angle is indicative of more strain on a five-membered tether, which is not surprising. Further evidence for the strain can be seen in displacement of C8 from the Cp plane by 7.0° (measured from the C3 carbon). The other bond distances and bond angles of the $CH_2CH_2NH_2$ tethering arm are all normal. The C1–Mo–C2 bond angle of 107° is similar to other four-legged piano stool compounds, as are the C–Mo–P bond angles (78.7 and 77.6°).[23] Finally, the C–O bond distances are unremarkable.

**Molecular Structure of 5.** The molecular structure of compound **5** (Figure 4) shows the same type of structural features as **4**.

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[33] For a discussion of the back-reaction problem and ways to prevent it, see: Philbin, C. E.; Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 4434–4436.

[34] Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1986**, *16*, 388–391.

[35] Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257–2263.

[36] Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335–341.

[37] Silverstein, R. M.; Bassler, G. C., Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 120.

[38] Many of these data are compiled in the references listed in ref 39.

[39] (a) Bennett, M. J.; Chuchill, M. R.; Gerloch, M.; Mason, R. *Nature (London)* **1964**, *201*, 1318–1320. (b) Teller, R. G.; Williams, J. M. *Inorg. Chem.* **1980**, *19*, 2770–2773. (c) Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277–284. (d) Wheatley, P. J. In *Perspectives in Structural Chemistry*; Dunitz, J. D., Ibers, J. A., Eds.; Wiley: New York, 1967; Vol. 1, pp 1–40.

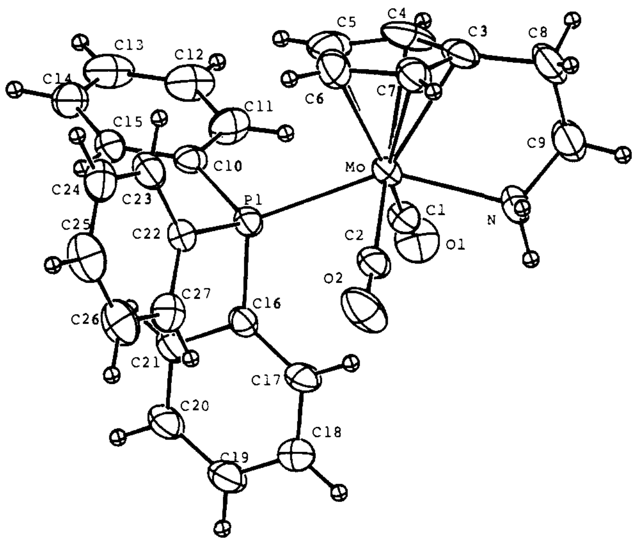


Figure 3. Molecular structure of compound **4**.

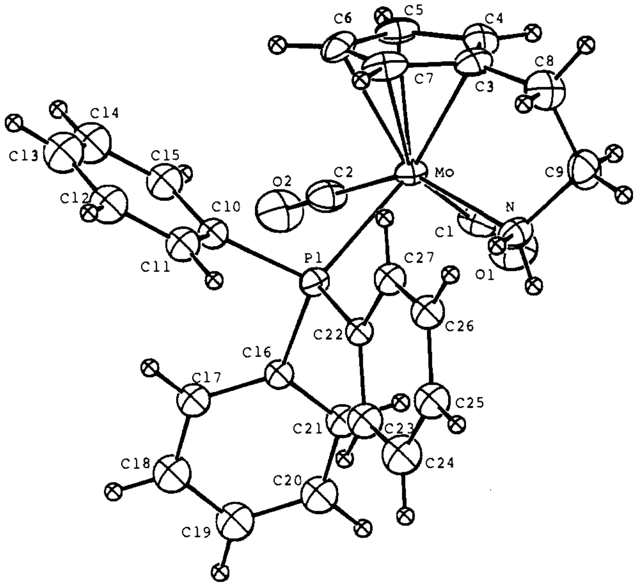
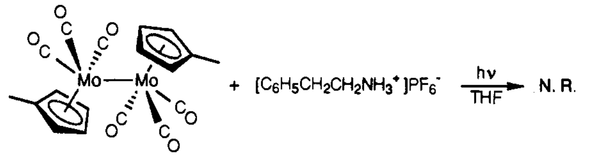


Figure 4. Molecular structure of compound **5**.

Again, one of the most interesting features is that the cyclopentadienyl ring is unsymmetrically bonded to the Mo atom. It appears that the ring is being pulled by the tether and tipped up and away from the $PPh_3$. The sum of these effects results in long Mo–C3 and Mo–C7 bonds of 2.351 and 2.337 Å, respectively, and an unusually short Mo–C5 bond of 2.269 Å. The ring C–C bond distances are symmetric, and again there is no evidence of a "diene" or "allylene" type bonding of the ring.[39] The strain on the tether can be seen in the C2–Mo–N bond angle of 143°. As mentioned above, this angle is 5° larger than in the intramolecular metaloester compound in Figure 4a.[23] The larger angle again indicates more strain on the five-membered tether. The C8 carbon of the tether is displaced 7.2° from the Cp plane, similar to cation **4**. The other bond distances and bond angles of the $CH_2CH_2NH_2$ tethering arm are all as expected. All of the other ligand–ligand bond angles are similar to other four-legged piano stool compounds. Finally, the C–O bond distances are very similar to compound **4** and to other four-legged piano stool compounds.

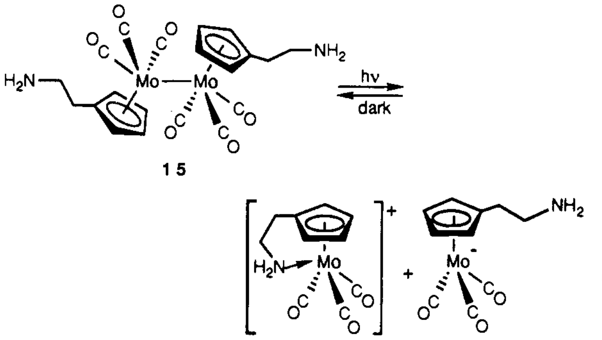
## Discussion

**Mechanism of Reaction 2.** The most remarkable feature in the photochemistry of dimer **1** is that metal–metal bond disproportionation occurs in THF solution when no added ligand is present (eq 2). This feature becomes even more interesting in light of the fact that the bimolecular analog of the disproportionation reaction does not occur. Thus, irradiation of $(MeCp)_2Mo_2(CO)_6$ in THF in the presence of a 10-fold excess of $[C_6H_5CH_2CH_2NH_3^+][PF_6^-]$ resulted in no reaction, even after 20 min of irradiation (eq 14).



(14)

The key to understanding why disproportionation occurs when **1** is irradiated but not when $(MeCp)_2Mo_2(CO)_6/(C_6H_5CH_2CH_2NH_3^+)$ is irradiated is provided by the analogous disproportionation reactivity of dimer **15**. (This latter species is formed by deprotonation of **1** using $NEt_3$.) Irradiation of **15** gives the disproportionation products shown in eq 15 (as detected by IR spectroscopy). However, the key observation is that in a matter of minutes these products back-react in the dark to re-form **15**.



**15** **2** **12**

(15)

Back-reactions are common in the disproportionation reactions of metal-metal-bonded dimers.[33] However, they can be suppressed by further reacting the cationic or anionic products so as to prevent them from participating in the back-reactions. It is suggested that net disproportionation occurs in eq 2, but not in eqs 14 or 15, because two reactions occur subsequent to disproportionation in eq 2: (1) proton transfer from the ammonium group of the cation to the anion and (2) chelation of the free amine arm (see Scheme II). Proton transfer effectively prevents a rapid back-reaction from occurring because the hydride species is less nucleophilic and does not back-react at an appreciable rate. However, because the proton transfer is reversible,[40] this step alone is not enough to ensure that no back-reaction occurs in eq 2. For that, coordination of the amine is required. Once the amine is coordinated, it is removed from any equilibrium involving the proton, and the disproportionation reaction becomes irreversible. Control experiments showed that reaction 2 did not back-react even after 24 h in the dark. Note that reaction 2 is a supramolecular reaction[42] in that one component of a molecule (the tentacle ligand) changes the reactivity in another component (proton transfer to the anion prevents an immediate back-reaction), which in turn changes the reactivity of the first

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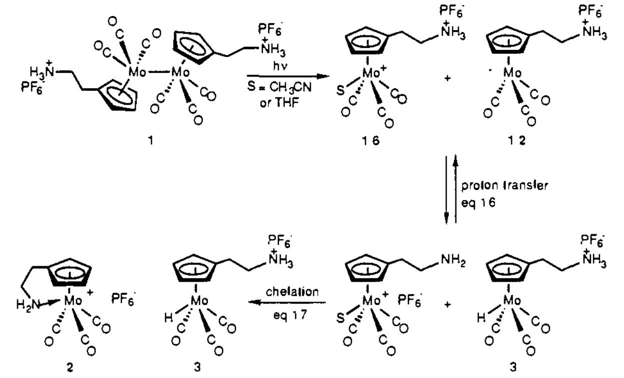
(40) Norton, for example, showed that acid–base reactions analogous to the proton transfer proposed here are equilibria.[41]

$$CpMo(CO)_3H + ArNH_2 \rightleftharpoons CpMo(CO)_3^- + ArNH_3^+$$

(41) (a) Ediden, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945–3953. (b) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255–1263.

(42) Balzani V. In *Supramolecular Photochemistry*; Balzani, V., Ed.; Reidel: Dordrecht, The Netherlands, 1987; Vol. 214, pp 1–28.

**Scheme II.** Proposed Mechanism for Photochemical Disproportionation of Dimer 1



**Scheme III.** Chain Mechanism for Substitution of $CpMo(CO)_3H$-type Complexes

$$CpMo(CO)_3H + R\cdot \longrightarrow CpMo(CO)_3\cdot + RH$$

$$CpMo(CO)_3\cdot + PPh_3 \longrightarrow CpMo(CO)_2PPh_3\cdot + CO$$

$$CpMo(CO)_2PPh_3\cdot + CpMo(CO)_3H \longrightarrow CpMo(CO)_2PPh_3H + CpMo(CO)_3\cdot$$

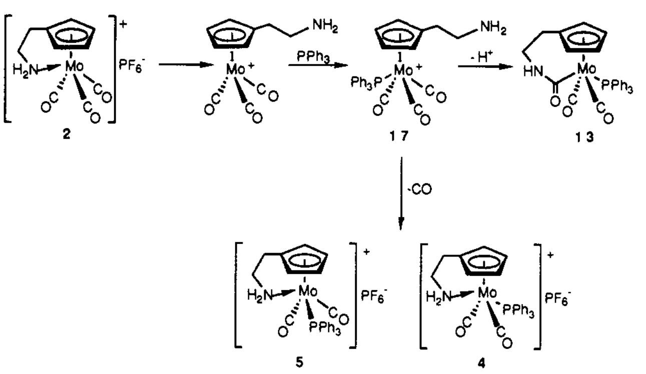
component (the tentacle ligand is now a free amine and coordination occurs).[43]

**Role of THF.** THF is the proposed disproportionating ligand in the pathway shown in Scheme II. Two experimental results support this assertion. (1) Irradiation of 1 in $CH_3CN$ shows the initial formation of $[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3NCCH_3]^{2+}$ and anion **11**. Subsequent monitoring of the reaction solution (kept in the dark) showed the conversion of these species to cation **2** and hydride **3**. (2) Irradiation of **1** in the presence of TCNQ gives $[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3(THF)]^{2+}$ and $TCNQ^-$ (eq 12). As discussed in previous papers, the 19-electron intermediates formed by irradiation of metal-metal-bonded dimers are excellent reducing agents.[4-7] If the ammonium group were somehow acting as the ligand in reaction 2, the expected 18-electron cationic product formed after 19-electron complex reduction of TCNQ would be cation **2**. Cation **2**, however, was not observed, and it is unlikely therefore that the ammonium group is involved in the initial disproportionation process.

**Mechanism of Reaction 3.** With regard to reactions 3 and 11, hydride **3** most likely converts to the cis- and trans-substituted hydrides **6** and **7** by the standard chain mechanism established by Brown and Hoffman[44] for the substitution of the non-functionalized $CpMo(CO)_3H$ compounds (Scheme III). This mechanism explains the apparent inconsistency in the observed rate of substitution between the IR and NMR experiments. Whereas the substitution reaction was over in a few minutes in the IR cell, it took several hours in the NMR tube. Brown and Hoffman discovered that the salt plates of the IR cell initiated the radical chain substitution and therefore enhanced the rate. There is no evidence of the ammonium functionality playing a role in the substitution of hydride **3**.

Two reasonable mechanisms for the substitution of cation **2** with $PPh_3$ are (1) direct CO loss from cation **2** followed by coordination of $PPh_3$ to the vacant coordination site or (2) decoordination of the amine followed by association of $PPh_3$ and then loss of CO followed by recoordination of the amine (Scheme IV). The substitution of cation **2** is proposed to follow the latter pathway. This proposal is supported by the observation that a very small amount of the deprotonated cation **9** (complex **17**) forms initially in reaction 3, as detected by NMR spectroscopy. Continued spectroscopic monitoring then shows the disappearance of **17**, followed by the appearance of compounds **4** and **5**. Also consistent with the mechanism in Scheme IV is the observation that the intramolecular carbamoyl complex **13** forms if Proton Sponge is added to the solution containing $PPh_3$ (eq 6; see also Scheme IV). Formation of the carbamoyl complex implies a nucleophilic attack of the non-coordinated amine ligand on a bound CO, so the substitution mechanism involving direct loss of CO is ruled out.

**Scheme IV.** Proposed Mechanism for the Reaction of **2** With $PPh_3$ to Form the Cations **4** and **5** and with $PPh_3$ and Base to Form the Carbamoyl **13**



## Conclusion

Attachment of a $-CH_2CH_2NH_3^+$ tentacle to the Cp rings of the $Cp_2Mo_2(CO)_6$ molecule does not alter the photochemistry of the metal-metal unit; thus, visible irradiation of the tentacle molecule leads to metal-metal bond homolysis. In THF solution, the photogenerated 17-electron fragments react with the solvent to form 19-electron complexes, which, in turn, lead to metal-metal bond disproportionation. In the case of $(MeCp)_2Mo_2(CO)_6$, there is no net disproportionation reaction in THF (even in the presence of ammonium salts) because the disproportionation products back-react to re-form the metal-metal-bonded dimer. In the case of the tentacle-ligand-containing disproportionation products, the back-reaction is prevented by proton transfer from the ammonium group, followed by facile coordination of the free amine to form products **2** and **3**. The cooperative reactions of the tentacle ligand and the initial, unstable disproportionation products is a genuine example of supramolecular reactivity; i.e., it is an example of two components of a molecule inducing or effecting reactivity not observed with either alone or if the components are not bonded together.[42] (The free amine will also react with a CO to form carbamoyl **13**.) The supramolecular reactivity may or may not be desirable, depending on the desired reactions.[42] For those cases where a noninterfering, water-solubilizing tentacle ligand is required, the chemistry of $CpCH_2CH_2NMe_3^+$ complexes is being developed.

## Experimental Section

All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere by using standard Schlenk techniques or by handling the materials and solutions in a Vacuum Atmospheres Co. glovebox.

**Materials.** Dimer **1** and $(MeCp)_2Mo_2(CO)_6$ were synthesized using literature methods.[45] $PPh_3$ (Aldrich) was recrystallized from hexanes. THF (Baker) was freshly distilled as needed from sodium benzophenone ketyl under nitrogen. Carbon tetrachloride (Baker) was distilled from $P_2O_5$ under nitrogen. Triethylamine was dried over calcium sulfate. Proton

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[43] The proton-transfer step shown in eq 16 of Scheme II is intended to show a net proton-transfer reaction and not necessarily an elementary step. Thus, the actual sequence of steps may involve rapid intramolecular proton transfer to form the hydride, followed by intermolecular proton transfer from the ammonium group on the metal cation complex to that on the hydride complex.

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[45] Birdwhistell R.; Hackett P.; Manning A. R. *J. Organomet. Chem.* **1978**, *157*, 239–241.

Sponge, phenethylamine, and $HPF_6$ (60% in $H_2O$) (Aldrich) were used without further purification.

**Instrumentation.** Photochemical reactions were carried out with an Oriel Co. 200W high-pressure mercury arc lamp. A Corning CS 3–68 cutoff filter ($\lambda > 525$ nm) was used for all of the irradiations except the quantum yield determinations. For the quantum yields, a Beckman DU monochrometer was used to select 550-nm light from an Oriel 200W high-pressure mercury arc lamp. Infrared spectra were obtained with a Nicolet 5DXB FT-IR and 0.10-mm path length calcium fluoride sealed cells. Electronic spectra were obtained with a Perkin-Elmer lambda 6 UV–vis spectrophotometer. Proton NMR data were collected on a General Electric QE-300 spectrometer.

Quantum yields were calculated from data obtained with a Beckman DU spectrophotometer using 1.00-cm Pyrex cells with freeze–pump–thaw side arms and magnetic stir bars. All solutions were magnetically stirred during irradiation, and the disappearance of dimer **1** was monitored at 503 nm. Lamp intensities were measured with Aberchrome 540 according to the method of Heller and Langan.[46] Lamp intensities at 550 nm were typically $1 \times 10^{-9}$ einsteins/s when equipped with a 0.5 neutral density filter.

**Disproportionation of Dimer 1 in THF.** A solution of dimer **1** (7.1 mM) in THF was prepared and transferred to an IR cell via a gastight syringe. There was no dark reaction detected over a period of 5 min. The solution was irradiated in the IR cell and monitored by IR spectroscopy every 15 s. The reaction was complete after 60 s of irradiation as indicated by the loss of the dimer absorption bands at 2010, 1954, and 1912 $cm^{-1}$. The products were cation **2** and hydride **3** as identified by their IR spectra (see Results and Discussion section and Table II). A similar reaction was carried out in a NMR tube with THF-$d_8$ as the solvent. The red solution was irradiated in the tube for 10 min after which it was a yellow/orange color. The $^1H$ NMR spectrum showed the characteristic resonances for the hydride **3**: (THF-$d_8$) $\delta$ 7.27 (s (br), 3H, $\mathrm{CpCH_2CH_2N}\mathit{H}_3^+$), 5.50 (s, 2H, $\mathit{Cp}\mathrm{CH_2CH_2NH_3^+}$), 5.64 (s, 2H, $\mathit{Cp}\mathrm{CH_2CH_2NH_3^+}$), 3.04 (t, $J_{H-H} = 6.3$ Hz, 2H, $\mathrm{CpCH_2C}\mathit{H}_2\mathrm{NH_3^+}$), 2.65 (t, $J_{H-H} = 6.3$ Hz, 2H, $\mathrm{CpC}\mathit{H}_2\mathrm{CH_2NH_3^+}$), −5.48 (d, 1H, M–$\mathit{H}$). The spectrum also showed resonances assigned to compound **2**: (THF-$d_8$) $\delta$ 6.41 (d, $J_{H-H} = 1.8$ Hz, 2H, $\mathit{Cp}\mathrm{CH_2CH_2NH_2}$), 5.41 (d, $J_{H-H} = 1.8$ Hz, 2H, $\mathit{Cp}\mathrm{CH_2CH_2NH_2}$), 4.65 (s (br), 2H, $\mathrm{CpCH_2CH_2N}\mathit{H}_2$), 3.59 (m, 2H, $\mathrm{CpCH_2C}\mathit{H}_2\mathrm{NH_2}$), 2.49 (t, $J_{H-H} = 6.4$ Hz, 2H, $\mathrm{CpC}\mathit{H}_2\mathrm{CH_2NH_2}$). Spectrum assignments were confirmed by COSY and decoupling NMR experiments. The disappearance quantum yield at 550 nm for the disproportionation of $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6(PF_6^-)_2$ (**1**) in THF was $0.36 \pm 0.05$.

Crystals of the complex **2** were obtained by irradiating a 5-mL solution of dimer **1** (46 mM) in an 8-in. test tube (with magnetic stirring in the glovebox) until the IR spectrum showed that the reaction was complete ($\approx$10 min). Hexane was then layered on top of the solution, and the test tube was placed in the freezer overnight. Orange crystals of compound **2** formed. The IR spectrum of **2** showed the following absorptions: 3310 (w), 3135 (w), 2917 (m), 2059 (s), 1996 (s), 1960 (vs), 1461 (w), 1433 (w), 842 (s, br).

**Reaction of the Disproportionation Products 2 and 3 with $PPh_3$.** A 10-fold excess (71 mM) of $PPh_3$ was added to the disproportionation products (**2** and **3**) formed as described above and stirred for 10 min. The reaction was monitored by IR spectroscopy. The spectrum of **3** disappeared, and the bands attributed to the substituted hydrides **6** and **7** formed. Over several hours, the intensity of the complex **2** spectrum slowly decreased in intensity while the intensity of the spectrum due to the chelated disubstituted cations **4** and **5** increased. A similar experiment was carried out in THF-$d_8$ in an NMR tube. After 10 min the solution contained cation **2**, substituted hydrides **6** and **7**, hydride **3**, and deprotonated cation **9** (trace). After the solution was allowed to stand for several hours, formation of the cis- and trans-substituted cations **4** and **5** (in an approximately 2:1 ratio, respectively) and the cis- and trans-substituted hydrides **6** and **7** (in an approximately 2:3 ratio) was evident, along with those ascribed to unreacted **2**. The overall ratio of cations to hydrides was 1:1 as determined from the $^1H$ NMR integration of each species.

Crystals of the cations **4** and **5** were obtained by irradiating a 5-mL solution of dimer **1** (46 mM) in an 8-in. test tube with magnetic stirring in the glovebox until the reaction was complete as shown by IR spectroscopy ($\approx$10 min). $PPh_3$ was added (460 mM), and the solution was stirred for 5 min. Hexane was then layered on top of the solution, and the test tube was capped with a rubber septum and allowed to remain in the drybox for several weeks. Orange crystals of the cis compound **5** formed along with yellow crystals of the trans compound **4**. The cis and trans cations **5** and **4** were separated by hand under a microscope on the basis of color. The substituted hydrides **6** and **7** did not produce crystalline products. The trans-substituted cation **4** had the following IR and $^1H$ NMR spectra: IR (KBr) 3310 (w), 3240 (vw), 3135 (w, br), 2924 (w, br), 2882 (w, br), 1982 (s), 1897 (vs), 1482 (w), 1433 (w), 1096 (w, br), 1089 (w), 842 (s, br); $^1H$ NMR (THF-$d_8$) $\delta$ 7.45 (s (br), 15H, $\mathit{PPh_3}$), 6.24 (m, 2H, $\mathit{Cp}\mathrm{CH_2CH_2NH_2}$), 4.64 (s (br), 2H, $\mathrm{CpCH_2CH_2N}\mathit{H}_2$), 4.17 (m (br), 2H, $\mathit{Cp}\mathrm{CH_2CH_2NH_2}$), 3.56 (m, 2H, $\mathrm{CpCH_2C}\mathit{H}_2\mathrm{NH_2}$), 2.36 (t, $J_{H-H} = 6.3$ Hz, 2H, $\mathrm{CpC}\mathit{H}_2\mathrm{CH_2NH_2}$). The cis-substituted cation **5** had the following IR and $^1H$ NMR spectra: IR (KBr) 3332 (m), 3275 (m), 1982 (vs), 1898 (vs), 1595 (w), 1475 (w), 1433 (m), 1152 (w), 1089 (w), 843 (s), 751 (m), 695 (m); $^1H$ NMR (THF-$d_8$) $\delta$ 7.45 (m, 15H, $\mathit{PPh_3}$), 6.30 (s, 1H, $\mathit{Cp}\mathrm{CH_2CH_2NH_2}$), 6.25 (s, 1H, $\mathit{Cp}\mathrm{CH_2CH_2NH_2}$), 5.05 (s, 1H, $\mathit{Cp}\mathrm{CH_2CH_2NH_2}$), 4.97 (s, 2H, $\mathit{Cp}\mathrm{CH_2CH_2NH_2}$), 4.66 (d (br), 2H, $\mathrm{CpCH_2CH_2N}\mathit{H}_2$), 3.22 (m, 2H, $\mathrm{CpCH_2C}\mathit{H}_2\mathrm{NH_2}$), 2.36 (t, $J_{H-H} = 6.3$ Hz, 2H, $\mathrm{CpC}\mathit{H}_2\mathrm{CH_2NH_2}$).

**Reaction of Disproportionation Products 2 and 3 with $PPh_3$ and Base.** A 5-mL volume of a magnetically stirred solution of dimer **1** (46 mM) was irradiated in a 10-mL round-bottom flask in the glovebox. After 10 min of irradiation, the reaction solution contained compounds **2** and **3** as shown by IR spectroscopy. Triphenylphosphine was then added to the flask and stirred for 1 min. An IR spectrum showed the formation of the cation **2** and complexes **4** and **5**. Proton Sponge was added to the solution and stirred for several minutes. An IR spectrum of the solution showed the formation of carbamoyl **13**, anion **12**, disubstituted cations **4** and **5**, and substituted hydrides **6** and **7**. Anion **12** formed quantitatively as determined from the IR spectra intensities (see Discussion section). An identical experiment, carried out in an NMR tube, showed the formation of cations **4** and **5**, the anion **12**, and the intramolecular carbamoyl **13**. Carbamoyl **13** showed the following absorbances in the $^1H$ NMR (THF-$d_8$): $\delta$ 5.65 (AA′BB′, 2H, $\mathit{Cp}\mathrm{CH_2CH_2NHCO}$), 4.39 (m, 2H, $\mathit{Cp}\mathrm{CH_2CH_2NHCO}$), 3.84 (m, 2H, $\mathrm{CpCH_2C}\mathit{H}_2\mathrm{NHCO}$), 2.39 ( m, 2H, $\mathrm{CpC}\mathit{H}_2\mathrm{CH_2NHCO}$), ($\mathrm{CpCH_2CH_2N}\mathit{H}\mathrm{CO}$, obscured by other resonances).

**Conversion of 5 to 4.** A sample of **5** (20 mg) was placed in an NMR tube and dissolved in THF-$d_8$. An initial spectrum showed the existence of only the cis isomer. However after 4 days under room light in the drybox, the spectrum showed both compounds **5** and **4** in a ratio of 1:1.85, as calculated from the integration of the 5.05, 4.97, and 4.18 ppm resonances. The sample was wrapped in aluminum foil and stored in the drybox for 4 days, after which time a spectrum was taken. The spectrum consisted of both cis and trans isomers **5** and **4** in a ratio of 1:3, respectively. After 2 weeks the only species detectable by NMR was the trans species **4**.

**Stability of Compound 4.** A sample of **4** (20 mg) was placed in an NMR tube and dissolved in THF-$d_8$. The initial spectrum and the spectrum after 3 days of storage in the drybox under room light were identical. A 77-fold excess of $PPh_3$ was added to the solution, and no change in the spectrum was observed after 1 week of storage in the drybox under room lights. A 10% molar ratio amount of dimer **1** was added to the tube, and the tube was irradiated for 5 min. No change in the spectrum of **4** was observed.

**Disproportionation of Dimer 1 in THF with $PPh_3$.** A solution of dimer **1** (7.1 mM) and $PPh_3$ (115 mM) in THF was prepared and transferred to an IR cell via syringe. There was no dark reaction detected over a period of 5 min. The solution was irradiated in the IR cell and monitored by IR spectroscopy after every 15 s of irradiation. The reaction was complete after 75 s as indicated by the loss of the dimer **1** absorptions at 2010, 1954, and 1912 $cm^{-1}$. Product bands were observed at 2059 (s), 2022 (vw), 1980 (m, sh), 1956 (s), 1939 (s), 1913 (m), 1865 (m), 1813 (m), and 1786 (m). The products, identified by their IR spectra, are cation **9**, anion **11**, hydride **3** (trace), substituted dimer **10**, and disubstituted cation **8** (see Results and Discussion and Table I). Note that upon continued irradiation the substituted dimer **10** absorption bands continued to decrease and the other product absorptions increased. After 12 h in the dark, 30% of dimer **1** had re-formed, and the both cation **9** and anion **11** peaks had decreased by a corresponding amount. An identical experiment was carried out in a NMR tube. The tube was irradiated in the drybox for 20 min during which time the red solution became yellow. The NMR spectrum showed the presence of cation **9**

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(22%), anion **11** (28%), hydride **3** (22%), **5** (4%), **4** (2%), and cation **2** (22%). After 24 h in the drybox the solution contained cation **9** (15%), anion **11** (17%), hydride **3** (10%), **5** (18%), **4** (14%), cation **2** (2%), and cis- and trans-substituted hydrides **6** and **7** (24%). After the solution was allowed to stand for 2 weeks, the only products present were **4**, the cis and trans hydrides **5** and 6, and the disubstituted hydride $[(CpCH_2CH_2NH_3^+)Mo^0(CO)(PPh_3)_2H]^+$. After 4 weeks, the only observed compound in the NMR spectrum was compound **4**. Compound **9** compound showed the following $^1$H NMR absorbances (THF-$d_8$): δ *7.3* ($CpCH_2CH_2N\mathit{H}_3^+$), *7.5* ($PPh_3$), 6.18 (s, 2H, $\mathit{Cp}CH_2CH_2NH_2$), 5.67 (s, 2H, $\mathit{Cp}CH_2CH_2NH_2$), *3.15* ($CpCH_2C\mathit{H}_2NH_2$), 2.83 ($CpC\mathit{H}_2CH_2NH_2$). (Chemical shifts in italics are approximate due to overlapping signals.) IR in THF: 2059 (s), 1987 (m), and 1965 (s).

**Synthesis of $K^+[(CpCH_2CH_2NH_2)Mo(CO)_3]^-$, 12.** A THF solution of dimer **1** (7.6 mM) was stirred with an excess of $NaK_{2.8}$ for 1 h. The yellow solution was filtered through a plug of glass wool to remove the unreacted $NaK_{2.8}$ and then transferred to an IR cell via syringe. The IR spectrum showed the presence of anion **12** exclusively. An identical experiment was carried out in THF-$d_8$. After the reaction was complete, as indicated by the color of the solution changing from red to yellow, the solution was filtered through a plug of glass wool in order to remove the unreacted $NaK_{2.8}$ prior to taking the NMR. Anion **12** showed the following $^1$H NMR absorbances (THF-$d_8$): δ 4.94 (d, 2H, $J$ = 2.1 Hz, $\mathit{Cp}CH_2CH_2NH_2$), 4.85 (d, 2H, $J$ = 2.1 Hz, $\mathit{Cp}CH_2CH_2NH_2$), 2.66 (pent, 2H, $J$ = 7.0 Hz, $CpCH_2C\mathit{H}_2NH_2$), 2.33 (m, 2H, $J$ = 6.9 Hz, $CpC\mathit{H}_2CH_2NH_2$), 1.23 (t, $J$ = 6.9 Hz, 2H, $CpCH_2CH_2N\mathit{H}_2$).

**Synthesis of $[(CpCH_2CH_2NH_3^+)Mo(CO)_3H][CF_3CO_2^-]$, 3.** Several drops of $CF_3CO_2H$ were added to the THF solution of anion **12** prepared as above. Hydride **3** was identified by IR as the only carbonyl-containing compound in solution. In the NMR experiment, several drops of $CF_3CO_2H$ were added directly to the NMR tube. $^1$H NMR (THF-$d_8$): δ 7.79 (s (br), 3H, $CpCH_2CH_2N\mathit{H}_3^+$), 5.62 (s, 2H, $\mathit{Cp}CH_2CH_2NH_3^+$), 5.41 (s, 2H, $\mathit{Cp}CH_2CH_2NH_3^+$), 3.10 (s (br), 2H, $CpCH_2C\mathit{H}_2NH_3^+$), 2.72 (t, 2H, $J$ = 7.5 Hz, $CpC\mathit{H}_2CH_2NH_3^+$), −5.55 (s, 1H, Mo–*H* ).

**Reaction of $[(CpCH_2CH_2NH_3^+)Mo(CO)_3H][CF_3CO_2^-]$, 3, with $PPh_3$.** $PPh_3$ (50 mg) was added to 2 mL of a 7.6 mM solution of hydride **3** prepared as described above. The solution was stirred for 15 min and then transferred to an IR cell. The IR showed a clean spectrum of the cis- and trans-substituted hydrides **6** and **7**. In the NMR experiment, the $PPh_3$ was added directly to the NMR tube. The tube was shaken vigorously to mix and aid in the dissolution of the phosphine. The spectrum of the solution showed mostly starting material **3** and only a small amount of the substituted hydrides **6** and **7**. After the sample was allowed to stand for 5 h, the concentration of **6** and **7** had continued increasing and only a small amount of the unsubstituted starting material **3** was present. After 24 h, only the substituted hydrides were present. $^1$H NMR (THF-$d_8$): δ 7.82 (s (br), 3H, $CpCH_2CH_2N\mathit{H}_3^+$), 7.6 $PPh_3$ (approximate; obscured by excess $PPh_3$), 5.21 (s, 2H, $\mathit{Cp}CH_2CH_2NH_3^+$), 4.85 (s, 2H, $\mathit{Cp}CH_2CH_2NH_3^+$), 3.18 (s (br), 2H, $CpCH_2C\mathit{H}_2NH_3^+$), 2.64 (m, 2H, $CpC\mathit{H}_2CH_2NH_3^+$), −5.36 cis **7**, −5.50 trans **6** (s, 1H, Mo–*H* ).

**Disproportionation of Dimer 1 in $CH_3CN$.** A solution of dimer **1** (7.1 mM) in $CH_3CN$ was prepared and transferred to an IR cell via syringe. No dark reaction was detected over a period of 5 min. The solution was irradiated in the IR cell and monitored by IR spectroscopy after every 15 s of irradiation. The reaction was complete after 60 s as indicated by the loss of the dimer **1** absorptions at 2010, 1954, and 1912 cm$^{-1}$. The products were $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3CH_3CN]^{2+}$, hydride **3**, cation **2**, and anion **11** as identified by their IR spectra (see Results and Discussion and Table I). Irradiation was stopped, and the reaction was monitored every 5 min for a total of 20 min. The $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3CH_3CN]^{2+}$ absorbances disappeared after 10 min, at which time the absorbances for $[(CpCH_2CH_2NH_2)Mo^{II}(CO)_3]^+$, **2**, and hydride **3** had reached a maximum. The hydride **3** absorbances began to decrease and were completely gone in 10 min.[35]

**Reaction of Dimer 1 with TCNQ in THF.** A solution of dimer **1** (11 mM) and TCNQ (230 mM) was prepared in the drybox. An initial IR spectrum of the solution and one after 5 min in the dark were identical. After 1 min of irradiation of the solution in the IR cell, the spectrum showed the disappearance of dimer **1** and the formation of $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3(THF)]^{2+}$ and reduced TCNQ.

**Reaction of Dimer 1 in THF with $CCl_4$.** A solution of dimer **1** (7.1 mM) and $CCl_4$ (1 M) in THF was prepared and transferred to an IR cell via syringe. No dark reaction was detected over a period of 5 min. The solution was irradiated in the IR cell and monitored after every 15 s of irradiation. The reaction was complete after 60 s of irradiation. The product of the reaction was $[(CpCH_2CH_2NH_3^+)Mo(CO)_3Cl]$, **14**, as identified by the IR spectrum (see Results and Discussion and Table I). A similar reaction was carried out in a NMR tube with THF-$d_8$ as the solvent. The solution was irradiated in the tube for 5 min, after which time it was an orange color. The NMR spectrum showed the characteristic resonances for the **14** $^1$H NMR (THF-$d_8$): δ 7.90 (s (br), 3H, $CpCH_2CH_2N\mathit{H}_3^+$), 5.99 (s, 2H, $\mathit{Cp}CH_2CH_2NH_3^+$), 5.40 (s, 2H, $\mathit{Cp}CH_2CH_2NH_3^+$), 3.07 (s (br), 2H, $CpCH_2C\mathit{H}_2NH_3^+$), 2.61 (t, $J_{H\text{-}H}$ = 7.2 Hz, 2H, $CpC\mathit{H}_2CH_2NH_3^+$). The disappearance quantum yield at 550 nm for the reaction of $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6(PF_6^-)_2$ with $CCl_4$ in THF was 0.36 ± 0.05.

**Reaction of Dimer 1 in THF with $CHCl_3$.** A solution of dimer **1** (7 mM) and $CHCl_3$ (1 M) in THF-$d_8$ was prepared in a NMR tube. There was no dark reaction after a period of 15 min. Irradiation of the sample for 10 min resulted in formation of the disproportionation products **2** and **3** along with the metal chloride species **14** in a 1.9 to 1 molar ratio.

**Synthesis of $(C_6H_5CH_2CH_2NH_3^+)(PF_6^-)$.** $C_6H_5CH_2CH_2NH_2$ (1 g) was added to 10 mL of $H_2O$. An aqueous solution of $HPF_6$ was added dropwise until the pH was 7 as indicated by pH paper. The solution was dried in vacuo. The complex was used without further purification.

**Reaction of $(MeCp)_2Mo_2(CO)_6$ in THF with $(C_6H_5CH_2CH_2NH_3^+)(PF_6^-)$.** A solution of $(MeCp)_2Mo_2(CO)_6$ (7.1 mM) and $(C_6H_5CH_2CH_2NH_3^+)(PF_6^-)$ (0.1 M) in THF was prepared and transferred to an IR cell via syringe. There was no dark reaction detected over a period of 5 min. The solution was irradiated in the IR cell. No reaction was detected even after 20 min of irradiation.

**Photochemical Reaction of $(CpCH_2CH_2NH_2)_2Mo_2(CO)_6$ (15) in THF.** A THF solution of dimer **1** (7.0 mM) and triethylamine (70 mM) was prepared and transferred to an IR cell via syringe. There was no dark reaction over a period of 5 min. The solution was irradiated in the IR cell for 30 s, after which time the reaction was complete. The products were anion **12** and cation **2** as shown by the IR spectrum. After 2 h in the dark, 75% of the original amount of the dimer had re-formed. The only other species evident in the IR spectrum was a small amount (<10%) of the anion.

**Synthesis of $[(CpCH_2CH_2NH_2)Mo^0(CO)_3]^+[PF_6^-]$, 2.** A solution of dimer **1** (7.4 mM) in a 1 M solution of $CCl_4$ in THF was irradiated in the drybox with stirring until the IR spectrum showed only the presence of complex **14**. Proton Sponge (70 mM) was added to the solution and stirred for 10 min. The light yellow solution was filtered through a plug of glass wool, and an IR spectrum was taken. The only carbonyl-containing product evident in the spectrum was compound **2**. An identical reaction in an NMR tube produced **2**. All attempts to obtain crystalline products failed.

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**Supplementary Material Available**: Text providing a description of the crystal structure analysis and tables of crystallographic information, atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, nonbonded contacts, coordinates of hydrogen atoms, anisotropic thermal parameters, least-squares planes, and torsion angles (42 pages); tables of structure factors (61 pages). Ordering information is given on any current masthead page.