Mercuration of 28a. To a solution of **28a** (1.00 g, 2.6 mmol) in methanol was added 0.80 g of mercuric acetate (2.5 mmol); the mixture was refluxed for 4 h and allowed to cool to room temperature. The resulting white crystals were filtered off, washed with methanol, and dried in vacuo to give **28b**.

Compounds **29b–31b** were prepared by using the above method.

4-(Chloromercurio)-*N*-benzylidene-2-toluidine (32b). Crystallization of the filtered solid from methanol yielded white crystals of **32b**.

4-(Chloromercurio)-*N*-(nitrobenzylidene)-2-toluidine (33b). Crystallization of the filtered solid from 1,4-dioxane gave **33b** as yellow needles.

2,4-Bis(acetomercurio)-6-methoxy-*N*-(4-nitrobenzylidene)aniline (34b). Crystallization from methanol yielded orange crystals of **34b**.

2,4-Bis(chloromercurio)-*N*-(2-nitrobenzylidene)aniline (35b). Crystallization of the filtered solid from 1,4-dioxane gave yellow crystals of **35b**$\cdot{}^1/_2C_4H_8O_2$.

2,4-Bis(chloromercurio)-6-methyl-*N*-(2-nitrobenzylidene)aniline (36b). The filtered solid was recrystallized from 1,4-dioxane to give yellow needles of **36b**.

4-(Chloromercurio)-*N*-(4-nitrobenzylidene)aniline (37b). To a solution of **1a** (1.13 g, 5 mmol) and BTMAC (benzyltrimethylammonium chloride) (0.95 g, 5 mmol) in dry methanol (50 mL) was added 1.60 g (5 mmol) of mercuric acetate. The mixture was stirred and refluxed for 6 h, during which a yellow solid deposited. This solid was filtered off and dried in vacuo and then extracted with hot chloroform until the extracts were nearly colorless. Concentration of the extracts and subsequent crystallization gave yellow needles of **37b** as the main product. The remaining insoluble solid was recrystallized from DMSO to give yellow needles of **3b**.

X-ray Structure Determination of 7b. Single crystals of **7b** suitable for X-ray diffraction study were obtained by slow evaporation of the solution of **7b** in 1,4-dioxane at room temperature. A single crystal of approximate dimensions 0.2 × 0.2 × 0.25 mm was mounted on the end of a glass fiber. The X-ray diffraction intensity data of 3196 independent reflections, of which 2666 with $I > 3\sigma(I)$ were observable, were collected with an Enraf-Nonius CAD-4 diffractometer by using graphite monochromated Cu Kα radiation with the ω-2θ scan mode within the range of $2 \leqslant 2\theta \leqslant 120°$. The structure was solved by direct methods using the MULTAN82 program. The non-hydrogen atoms were found by difference Fourier (ΔF) synthesis and blocked diagonal matrix least-squares procedures. Hydrogen atoms were fixed by the theoretical method. After three cycles of refinement by full-matrix least-squares procedure with anisotropic thermal parameters for all non-hydrogen atoms, the final values of R $[=\sum\|F_o| - |F_c\|/|F_o|] = 0.073$ and R_w $\{=[\sum w(|F_o| - |F_c|)^2/\sum_w F_o{}^2]^{1/2}\} = 0.075$ were obtained.[19] An ORTEP drawing of **7b** is shown in Figure 1.

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Supplementary Material Available: A listing of spectral data for compounds **2b–37b**, figures showing the thermal analysis curve and molecular packing in the unit cell for **7b**, and tables of positional parameters and their estimated deviations for all non-hydrogen atoms, bond distances, bond angles, deviations of atoms from the mean plane, and crystal data and experimental details for the structure determination of **7b** (14 pages). Ordering information is given on any current masthead page.

OM920366N

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(18) Hyde, E. M.; Shaw, B. L.; Shepherd, I. *J. Chem. Soc., Dalton Trans.* 1978, 1696–1705.

(19) All crystallographic calculations were carried out on a PDP 11/44 computer with the CAD4-SDP program package (Enraf-Nonius, Delft, The Netherlands).

Synthesis and Photochemistry of the Aqueous-Soluble (η^5-$C_5H_4CH_2CH_2NH_3{}^+)_2Mo_2(CO)_6$ Complex. Generation of 19-Electron Complexes in Aqueous Solution

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The synthesis and photochemistry of the (η^5-$C_5H_4CH_2CH_2NH_3{}^+)_2Mo_2(CO)_6$ complex are described. The $NO_3{}^-$ salt is soluble in aqueous solutions at pH 8 or lower; the $PF_6{}^-$ salt was used in organic solvents. The photochemistry of the molecule is similar to the photochemistry of the $Cp_2Mo_2(CO)_6$ (Cp = η^5-C_5H_5) complex: irradiation into the low-energy tail of the lowest energy absorption band ($\lambda_{max} \approx 503$ nm; $d\pi \rightarrow \sigma^*$) results in homolytic cleavage of the Mo–Mo bond to form (η^5-$C_5H_4CH_2CH_2NH_3{}^+$)$Mo(CO)_3$ radicals. These 17-electron radicals can be trapped with chlorine atom donors (e.g., CCl_4 in nonaqueous solution or CCl_3CH_2OH in aqueous solution) to form (η^5-$C_5H_4CH_2CH_2NH_3{}^+$)$Mo(CO)_3Cl$. Irradiation of (η^5-$C_5H_4CH_2CH_2NH_3{}^+)_2Mo_2(CO)_6$ in the presence of ligands [e.g., phosphines in nonaqueous solution or water-soluble phosphines such as PTA (phosphatriazaadamantane) in aqueous solution] resulted in disproportionation of the dimer complex. The disproportionation reactivity is consistent with the intermediate formation of 19-electron adducts. Like their counterparts in nonaqueous solvents, the putative 19-electron adducts generated in aqueous solution are good reductants. They were used to reduce methylviologen and cytochrome *c* in aqueous solution. Reduction of protons to H_2 did not occur, and this led us to reexamine our earlier results in which we suggested that 19-electron complexes formed by irradiation of $(CpCOOH)_2W_2(CO)_6$ in basic aqueous solution reduced water to H_2. CO_2 is formed in a 1:1 ratio with H_2 in this reaction, and we propose the water-gas shift reaction is the source of the H_2.

We recently began a research program to explore the reactivity of 19-electron organometallic complexes in aqueous solution.[1-4] Nineteen-electron complexes have several features that make them ideal reducing agents,[8]

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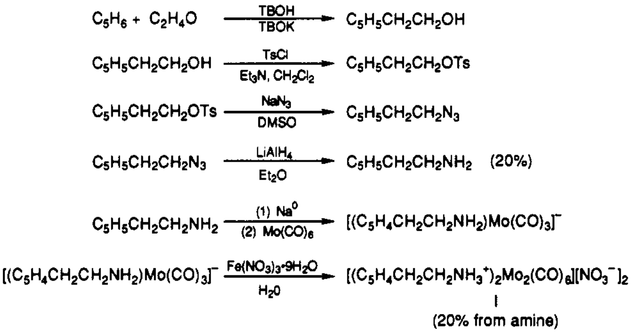
Scheme I. Synthesis of the $[(C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ Complex



$$C_5H_6 + C_2H_4O \xrightarrow[TBOK]{TBOH} C_5H_5CH_2CH_2OH$$

$$C_5H_5CH_2CH_2OH \xrightarrow[Et_3N,\ CH_2Cl_2]{TsCl} C_5H_5CH_2CH_2OTs$$

$$C_5H_5CH_2CH_2OTs \xrightarrow[DMSO]{NaN_3} C_5H_5CH_2CH_2N_3$$

$$C_5H_5CH_2CH_2N_3 \xrightarrow[Et_2O]{LiAlH_4} C_5H_5CH_2CH_2NH_2 \quad (20\%)$$

$$C_5H_5CH_2CH_2NH_2 \xrightarrow[(2)\ Mo(CO)_6]{(1)\ Na^0} [(C_5H_4CH_2CH_2NH_2)Mo(CO)_3]^-$$

$$[(C_5H_4CH_2CH_2NH_2)Mo(CO)_3]^- \xrightarrow[H_2O]{Fe(NO_3)_3\cdot 9H_2O} \underset{\text{(20\% from amine)}}{\underset{I}{[(C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2}}$$

Table I. Electronic Spectroscopic Data

complex[a]	λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)	ref
$[(CpCH_2CH_2NH_3^+)_2\text{-}Mo_2(CO)_6][NO_3^-]_2$[b,e]	503 (2100), 388 (18000)	this work
$[(CpCH_2CH_2NH_3^+)_2\text{-}Mo_2(CO)_6][NO_3^-]_2$[d]	505 (2080), 389 (20100)	this work
$(MeCp)_2Mo_2(CO)_6$[c]	506 (2400), 390 (20000)	16
$Cp_2Mo_2(CO)_6$[d]	505 (1610), 385 (17400)	17
cytochrome c^{II}[e]	550, 521, 415	18
cytochrome c^{III}[e]	530, 408	18
$MV^{\cdot+}$[e]	396 (42100), 606 (13700)	19
MV^{2+}[e]	257 (20700)	19

[a] Cp = $(\eta^5\text{-}C_5H_5)$; MeCp = $(\eta^5\text{-}C_5H_4CH_3)$; $CpCH_2CH_2NH_3^+$ = $(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)$; MV = methylviologen. [b] H_2O pH 2 buffer. [c] CCl_4. [d] MeOH. [e] H_2O pH 7 buffer.

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).

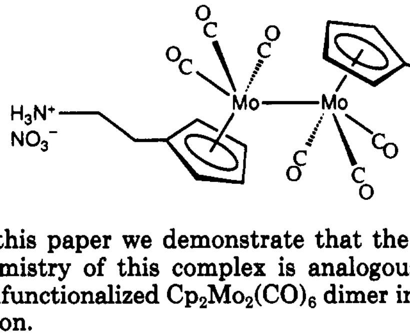
A scheme showing how 19-electron complexes are generated from 17-electron radicals is shown as follows:[6]

$$Cp_2Mo_2(CO)_6 \xrightarrow{h\nu} \underset{17e^-}{2\ CpMo(CO)_3} \overset{L}{\rightleftharpoons} \underset{19e^-}{CpMo(CO)_3L} \qquad (1)$$

L = a ligand

Generating the 19-electron complexes in aqueous solution by a similar route is problematic because the metal–metal-bonded dimer precursors are insoluble in aqueous solution. Most organometallic complexes are water-solubilized by using appropriately functionalized phosphines as the water-solubilizing moiety; e.g., $HRh(CO)(PPh_3)_3$ is not soluble in water but $HRh(CO)(P(C_6H_4SO_3^-)_3)_3$ is soluble.[3] However, this approach has its obvious limitations in the case of the metal–metal-bonded dimers because there are no phosphines coordinated to the metals. It was necessary therefore to develop another method to render the dimer complexes water soluble. The method we are pursuing in our laboratory is to functionalize the Cp rings with an ionizable substituent.[1,13]

We demonstrated in an earlier paper[1] 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. In order to explore the reactivity of 19-electron organometallic species in aqueous solution in the low-pH range, we synthesized the acid-soluble $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ complex.



In this paper we demonstrate that the aqueous photochemistry of this complex is analogous to that of the nonfunctionalized $Cp_2Mo_2(CO)_6$ dimer in nonaqueous solution.

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(1) For the preceding paper in this series, see: Avey, A.; Tenhaeff, S. C.; Weakley, T. J. R.; Tyler, D. R. *Organometallics* **1991**, *10*, 3607–3613.

(2) The synthesis of water-soluble organometallic complexes for use as homogeneous catalysts in aqueous solution is a rapidly growing area of chemistry. For early references dealing with aqueous-soluble organometallic complexes with sulfonated triphenylphosphine ligands, see: (a) Ahrland, S.; Chatt, J.; Davies, N. R.; Williams, A. A. *J. Chem. Soc.* **1958**, 276. (b) Ahrland, S.; Chatt, J.; Davies, N. R.; Williams, A. A. *J. Chem. Soc.* **1958**, 1403. (c) Pettit, L. D.; Irving, H. *J. Chem. Soc.* **1964**, 5336. The following lead references and the references therein should be consulted for the application of water-soluble complexes to catalysis: (d) Dror, Y.; Manassen, J. *J. Mol. Catal.* **1977**, *2*, 219. (e) Borowski, A. F.; Cole-Hamilton, D. J.; Wilkinson, G. *Noov. J. Chem.* **1978**, *2*, 145. (f) Smith, R. T.; Ungar, R. K.; Sanderson, L. J.; Baird, M. C. *Organometallics* **1983**, *2*, 1138. (g) Smith, R. T.; Baird, M. C. *Inorg. Chim. Acta* **1982**, *62*, 135. (h) Sinou, D.; Amrani, Y. *J. Mol. Catal.* **1986**, *36*, 319 (and references therein). (i) Horvath, I. T.; Kastrup, R. V.; Oswald, A. A.; Mozeleski, E. J. *Catal. Lett.* **1989**, *2*, 85. (j) Escaffre, P.; Thorex, A.; Kalck, P. *J. Chem. Soc., Chem. Commun.* **1987**, 146. (k) Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 3683 (and references therein). (l) Amrani, Y.; Lecomte, L.; Sinou, D.; Bakos, J.; Toth, I.; Heil, B. *Organometallics* **1989**, *8*, 542–547. (m) Fache, E.; Senocq, F.; Santini, C.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1990**, 1776–1778. (n) Herrmann, W.; Thiel, W. R.; Huchler, J. G.; Behm, J.; Herdtweck, E. *Chem. Ber.* **1990**, *123*, 1963–1970. (o) Benyei, A.; Joo, F. *J. Mol. Catal.* **1990**, *58*, 151–163. (p) Kullberg, M. L.; Kubiak, C. P. *Organometallics* **1984**, *3*, 632–634. (q) Bruce, M. I.; Skelton, B. W.; Wallic, R. C.; Walton, J. K.; White, A. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1981**, 428–430.

(3) For a recent review, see: Barton, M.; Atwood, J. M. *J. Coord. Chem.* **1991**, *24*, 43–67.

(4) 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 2 electrons from the ligand is 19. Note, however, that no implication about the electronic or geometric structures of these complexes is necessarily implied by this name. See refs 5–7 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.

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

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

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

(8) The 19-electron adducts have three notable properties which make them outstanding choices as photogenerated reducing agents: (1) They are powerful reductants, their potentials are estimated as ≈−1.5 V vs SCE.[5,9–12] Although back-electron-transfer is a problem with many photogenerated reducing agents and sensitizers, this very negative potential effectively inhibits back-electron-transfer from the reduced substrate to the 18-electron complex. (2) The 19-electron complexes are easy to generate. As the scheme in the Introduction shows, visible light irradiation of a metal–metal-bonded dimer in the presence of a suitable ligand is all that is required to generate these species. (The dimers and ligands are commercially available.) Because the dimers absorb light throughout the visible region, irradiation at wavelengths even longer than 500 nm is possible. Most substrates for reduction do not absorb at such long wavelengths, so concurrent irradiation of the substrate is not a problem. (3) The 19-electron complexes are versatile reductants. Our work has demonstrated that a wide variety of organic, inorganic, and organometallic complexes can be reduced with the 19-electron complexes in nonaqueous solvents.[9–12] Their versatility is attributed to their outer-sphere electron-transfer mechanism.

(9) MacKenzie, V.; Tyler, D. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1783–1784.

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

(11) Stiegman, A. E.; Goldman, A. S.; Leslie, D. B.; Tyler, D. R. *J. Chem. Soc., Chem. Commun.* **1984**, 632–633.

(12) Silavwe, N. D.; Goldman, A. S.; Ritter, R.; Tyler, D. R. Inorg. *Chem.* **1989**, *28*, 1231–1236.

(13) We have also been able to generate 19-electron species in micellar solutions.[9]

Table II. Selected Infrared Data

complex[a]	ν(CO), cm^{-1}	ref
$(MeCp)_2Mo_2(CO)_6$[b]	2012 (m), 1956 (s), 1912 (s)	16
$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]$[c]	2009 (m), 1958 (s), 1908 (s)	this work
$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]$[d]	2010 (m), 1958 (s), 1913 (s)	this work
$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$[e]	2010 (m), 1953 (8000),[k] 1913 (s)	this work
$(MeCp)Mo(CO)_3Cl$[f]	2051, 1981 (3300),[k] 1957	16, this work
$[(CpCH_2CH_2NH_3^+)Mo(CO)_3Cl]^+$[e,g]	2050 (m), 1971 (s), 1956 (sh)	this work
$[(CpCH_2CH_2NH_3^+)Mo(CO)_3Cl]^+$[c,f]	2060 (m), 1968 (s), 1955 (sh)	this work
$[(CpCH_2CH_2NH_3^+)Mo(CO)_3Cl]^+$[d,f]	2067 (m), 2060 (sh), 1981 (s)	this work
$[CpMo^{II}(CO)_3PPh_3^+][BF_4^-]$[h]	2062, 2001, 1975	22
$[CpMo^{II}(CO)_3(PEt_3)^+][BF_4^-]$[h]	2056 (s), 1993 (m), 1966 (vs)	22
$[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3(PTA)]^{2+}$[c,f]	2066 (s), 1993 (m), 1966 (s)	this work
$[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3(PPh_3)]^{2+}$[e,g]	2059 (s), 1987 (m), 1965 (s)	this work
$[CpMo^{II}(CO)_2(PPh_3)_2^+][BF_4^-]$[h]	1978 (s), 1901 (vs)	22
$[CpMo^{II}(CO)_2(PEt_3)_2^+][BF_4^-]$[h]	1963 (s), 1884 (vs)	22
$[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(PTA)_2]^{2+}$[c,f]	1957 (s), 1910 (s)	this work
$[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(PPh_3)_2]^{2+}$[e,g]	1965 (s), 1900 (s)	this work
$[CpMo^{II}(CO)_3H_2O^+][BF_4^-]$[i]	2067, 1998, 1973	23
$[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3(H_2O)]^{2+}$[c,f]	2062 (s), 1996 (m), 1967 (s)	this work
$[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3(H_2O)]^{2+}$[d,f]	2067 (s), 1993 (m), 1981 (s)	this work
$CpMo^{II}(CO)_3H$[j]	2030 (vs), 1949 (vs), 1913 (w)	24
$[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3H]^+$[d,f]	2024, 1943, 1929	this work
$K^+[CpMo(CO)_3^-]$[e]	1898 (s), 1790 (s), 1750 (s)	25
$[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3]$[c]	1905 (s), 1783 (s), 1729 (s)	this work
$[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3]$[e]	1908 (s), 1813 (s), 1786 (s)	this work
$Cp_2Mo_2(CO)_5PPh_3$[b]	1968 (s), 1900 (s), 1827 (m)	26
$[(CpCH_2CH_2NH_3^+)_2Mo^I_2(CO)_5(PPh_3)]^{2+}$[e,g]	1939 (s), 1913 (s), 1863 (s)	this work

[a] Cp = (η^5-C_5H_5); MeCp = (η^5-$C_5H_4CH_3$); $CpCH_2CH_2NH_3^+$ = (η^5-$C_5H_4CH_2CH_2NH_3^+$). [b] CCl_4. [c] H_2O pH 7 buffer. [d] H_2O pH 2 buffer. [e] THF. [f] NO_3^- counterion. [g] PF_6^- counterion. [h] CH_2Cl_2. [i] Nujol. [j] CS_2. [k] ϵ in M^{-1} cm^{-1}.

Results and Discussion

Synthesis and Solubility of the $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ Complex. The $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ complex was synthesized by the route in Scheme I.[14,15] The product is soluble in aqueous solutions at pH 8 or lower. Quantitative measurements showed that the dimer is soluble up to 2.0 g/L (2.8 mM) in pH 7 buffer at 25 °C. Note that the amine functionality will be protonated in all of the reactions described in this paper. The dimer with the nitrate counterion was insoluble in almost all common organic solvents except methanol. For that reason, the NO_3^- counterion was exchanged by PF_6^-, rendering the dimer soluble in THF.

Electronic Spectrum of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$. In both aqueous and nonaqueous solvents, the electronic absorption spectrum of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ exhibits two bands in the visible/near-UV region (Table I). In aqueous solution at pH 7 or pH 2, there is a weak band at 503 nm (2100 M^{-1} cm^{-1}) and an intense band at 388 nm (18 000 M^{-1} cm^{-1}). This spectrum is essentially identical to the spectra of $Cp_2Mo_2(CO)_6$ and $(CpMe)_2Mo_2(CO)_6$ in nonaqueous solvents (Table I), and similar band assignments are therefore proposed:[16,18-21] The band at 388 nm is assigned to the $\sigma \rightarrow \sigma^*$ transition and the band at 503 nm to a $d\pi \rightarrow \sigma^*$ transition. All of the photochemical reactions in this paper were carried out by irradiation 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).

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 text	Φ
1 M CCl_4 in THF	2	0.39 ± 0.04
0.050 M CCl_3CH_2OH in H_2O[b]	3	0.78 ± 0.15
PTA in H_2O[b]	5	0.32 ± 0.05
H_2O[b]	6	0.16 ± 0.01
1 M CCl_4 in THF[c]	na	0.55 ± 0.05

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

Photolysis of the Mo–Mo Bond. In order to use $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6$ as a source of 17-electron radicals for the generation of 19-electron complexes, it was first necessary to establish that irradiation of the complex resulted in cleavage of the Mo–Mo bond.[5] This was accomplished by doing standard metal radical trapping experiments[19] in both aqueous and nonaqueous solutions. Thus, irradiation of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ in 1 M CCl_4 in THF led to the quantitative formation of $[(CpCH_2CH_2NH_3^+)_2Mo(CO)_3Cl][PF_6^-]$ (eq 2). Metal chloride products such as this are taken as evidence of metal–metal bond homolysis in analogous systems.[19] Similarly, irradiation of aqueous solutions of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ and CCl_3CH_2OH (a water-soluble chlorine atom donor) at pH 7 or pH 2 led to the quantitative formation of $[(CpCH_2CH_2NH_3^+)Mo(CO)_3Cl]^+$ as detected by infrared spectroscopy (eq 3; Table II).

$$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2 \xrightarrow[\text{THF/CCl}_4]{h\nu} 2\,[(CpCH_2CH_2NH_3^+)Mo(CO)_3Cl][PF_6^-] \qquad (2)$$

$$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2 \xrightarrow[\substack{\text{H}_2\text{O (pH 2 and 7)} \\ \text{CCl}_3\text{CH}_2\text{OH}}]{h\nu} 2\,[(CpCH_2CH_2NH_3^+)Mo(CO)_3Cl][NO_3^-] \qquad (3)$$

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(14) Macomber, D. W.; Rausch, W. D. *J. Organomet. Chem.* **1983**, *258*, 331–341.

(15) Birdwhistel, I. R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239–241.

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

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

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

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

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

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

The quantum yield for disappearance of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ in 1.0 M CCl_4 in THF (0.39 ± 0.04) is considerably smaller than for the analogous reaction in aqueous solution (0.78 ± 0.15 at pH 7; Table III). We explain these results as follows. In THF, the cationic dimer and its counterions probably exist as a closely associated ion pair. This may slow the rate of diffusion of the photogenerated geminate radical pair out of the cage, due to the increased mass and bulk of the diffusing species. Slower diffusion out of the cage will favor geminate recombination, resulting in lower quantum yields for nonaqueous systems. On the other hand, in aqueous systems, the dimer and its counterions probably exist as highly solvated ions, reducing the apparent mass and bulk and, thus, favoring diffusion of the caged radical pair out of the solvent cage (relative to cage recombination). The effect of mass and sterics on the quantum yields is also apparent in the comparison of $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6$ to $(MeCp)_2Mo_2(CO)_6$: the quantum yield for disappearance of $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6$ in 1.0 M CCl_4 in THF (0.39 ± 0.04) is smaller than that for disappearance of $(MeCp)_2Mo_2(CO)_6$ under identical conditions (0.55 ± 0.05). The effects of mass, steric bulk, ion pairing and Coulombic effects on quantum yields are currently being studied in detail in our laboratory.[27]

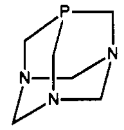
M–CO Dissociation. The section above is not meant to imply that Mo–Mo photolysis is the only primary photoprocess. Abrahamson showed that W–W homolysis and W–CO bond dissociation both occurred as primary photoprocesses when the $Cp_2W_2(CO)_6$ complex (Cp = $\eta^5\text{-}C_5H_5$) is irradiated with visible light;[28] it is logical to assume that Mo–CO bond dissociation also occurs when the $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6$ complex is irradiated. One ostensible outcome of Mo–CO dissociation would be the formation of substitution products, e.g., $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_5(L)$ would form when $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6$ is irradiated in the presence of a ligand. However, this product would photochemically disproportionate[29,30] (see Experimental Section). As Mo–CO dissociation is not relevant to 19-electron complex formation, our investigation did not pursue this photoprocess further.

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.[10,29,30] Therefore, if disproportionation of the $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ complex occurred, it would strongly suggest the intermediate formation of 19-electron complexes. In fact, disproportionation did occur in both nonaqueous and aqueous solution. Irradiation of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ in the presence of PPh_3 in THF gave the disproportionation products shown in eq 4. Note that both $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3(PPh_3)]^{2+}$ and $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(PPh_3)_2]^{2+}$ form. Analogous mono- and disubstituted cationic products also form in the disproportionation reactions of the $Cp_2M_2(CO)_6$ complexes in nonaqueous solvents, so the formation of both products in eq 4 should not be construed as unusual. The disproportionation chain mechanism accounts for both products. See ref 10 for further discussion. It is also important to note that the ammonium ion does not play a role in the overall disproportionation reaction when a good ligand such as a phosphine is present. However, in the absence of a better ligand, the ammonium functionality does play a role during photolysis of the dimer in nonaqueous solvent; this reactivity is complex, and consequently it will be described in a separate paper.[31]

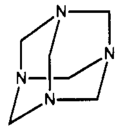
$$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2 \xrightarrow[PPh_3/THF]{h\nu} \begin{array}{l} [(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3PPh_3]^{2+} \\ [(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(PPh_3)_2]^{2+} \\ [(CpCH_2CH_2NH_3^+)Mo^{0}(CO)_3]^{0} \end{array} \tag{4}$$

The reaction of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ in *aqueous* solution in the presence of the water-soluble phosphine PTA gave the disproportionation products shown in eq 5. Note again that both mono- and disubstituted cationic products $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3(PTA)]^{2+}$ and $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(PTA)_2]^{2+}$ are formed, just as in nonaqueous solvents. Although the PTA ligand has nitrogen atoms that could conceivably coordinate to the molybdenum, it is more likely that coordination is through the phosphorus atom. Two points support this claim. First, previous work showed that the phosphorus atom in the PTA ligand preferentially binds to low-valent group VI metals.[32] Second, in control experiments using tetraazaadamantane in place of PTA, no cationic products containing the $N_4(CH_2)_6$ ligand formed.

$$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2 \xrightarrow[PTA/H_2O\ pH\ 7]{h\nu} \begin{array}{l} [(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3PTA]^{2+} \\ [(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(PTA)_2]^{2+} \\ [(CpCH_2CH_2NH_3^+)Mo^{0}(CO)_3]^{0} \end{array} \tag{5}$$



phosphatriazaadamantane (PTA)



tetraazaadamantane $[N_4(CH_2)_6]$

When no suitable ligands are present, H_2O will act as the disproportionating ligand, giving the products shown in eqs 6 and 7. These disproportionation reactions are analogous to the reactions in coordinating organic solvents in the absence of a ligand.[29,30]

$$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2 \xrightarrow[pH\ 7\ H_2O]{h\nu} \begin{array}{l} [(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3H_2O]^{2+} \\ [(CpCH_2CH_2NH_3^+)Mo^{0}(CO)_3]^{0} \end{array} \tag{6}$$

$$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2 \xrightarrow[pH\ 2\ H_2O]{h\nu} \begin{array}{l} [(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3H_2O]^{2+} \\ [(CpCH_2CH_2NH_3^+)Mo^{0}(CO)_3H]^{+} \end{array} \tag{7}$$

In summary of this section, because 19-electron species are generally accepted as intermediates in the dispropor-

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[22] Sunkel, K.; Ernst, H.; Beck, W. *Z. Naturforsch.* **1981**, *36B*, 474–481.

[23] Beck, W.; Schloter, K. *Z. Naturforsch.* **1978**, *33B*, 1214–1222.

[24] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *4*, 104–124.

[25] Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263–268.

[26] Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 43–46.

[27] Covert, K.; Tyler, D. R. *J. Am. Chem. Soc.*, in press.

[28] Van Vlierberge, B. A.; Abrahamson, H. B. *J. Photochem. Photobiol. A* **1990**, *52*, 69–81.

[29] Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032–6037.

[30] Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217–140.

[31] Avey, A. A.; Tyler, D. R. Manuscript in preparation.

[32] Darensbourg, M. Y.; Daigle, D. *Inorg. Chem.* **1975**, *14*, 1217–1218.

tionation reactions, the disproportionation reactivity in eqs 5–7 suggests (but does not definitively establish, of course) that irradiation of the $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6$ complex in the presence of PTA or H_2O results in the formation of 19-electron species:

$$(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6 + 2\,L \xrightarrow[\text{aqueous solution}]{h\nu} 2\,\underset{19e^-}{(CpCH_2CH_2NH_3^+)Mo(CO)_3L} \qquad (8)$$

$$L = PTA,\ H_2O$$

The quantum yields for the disproportionation reactions in water with H_2O or PTA were 0.16 ± 0.01 and 0.32 ± 0.05, respectively (Table III). The difference in the quantum yields is probably due to the ability of the phosphine to form a more stable 19-electron intermediate.[5]

Reduction of Water-Soluble Substrates. Our previous work[1,6,10–12] established that disproportionation did not occur in nonaqueous solvents when metal–metal-bonded dimers and ligands were irradiated in the presence of a reducible substrate. This reactivity was ascribed to preferential reduction of the substrate by the 19-electron complex and the consequent inhibition of the disproportionation chain mechanism. Similar behavior was observed in aqueous solution; in effect, the 19-electron complexes generated in aqueous solution can be used as photogenerated reducing agents (eq 9). The substrates reduced in this study were methylviologen (MV^{2+}) and cytochrome *c*. For each of these substrates, one-electron reduction occurred. The mass balance for the reaction was studied for the case of the MV^{2+} reduction: in the presence of excess MV^{2+}, the reduction of MV^{2+} to $MV^{\bullet+}$ was quantitative, based on the amount of dimer present (complete details are given in the Experimental Section).

$$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6]^{2+} + 2\,PTA + 2\,S^- \xrightarrow[\text{pH 7 } H_2O]{h\nu} 2\,S^- + [(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3PTA]^{2+} \qquad (9)$$

$$S = MV^{2+}\ \text{(methyl viologen), cytochrome } c^{III}$$

The electrochemical potential of the $[(CpCH_2CH_2NH_3^+)Mo(CO)_3(PTA)]^{+/0}$ couple can be estimated by its ability to reduce the substrates in reaction 9. The potential of the $MV^{2+}/MV^{\bullet+}$ couple (the most difficult to reduce substrate in eq 9) is −0.46 V vs SCE;[33] thus, the potential of the 18-/19-electron complex couple is more negative than this value. In fact, the potential is probably much more negative than −0.46 V vs SCE because one of the key steps in the disproportionation reaction chain mechanism is the reduction of the dimer reactant by a 19-electron complex (i.e., the reduction of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6]^{2+}$ by $[(CpCH_2CH_2NH_3^+)Mo(CO)_3L)]^+$ (L = PPh_3, PTA, H_2O) is a key step in the disproportionation).[5,10,27,28] The electrochemical potential of the 18-/19-electron complex couple must, therefore, be more negative than the reduction potential of the dimer complexes. The potentials of the metal carbonyl dimers are less than −1 V vs SCE,[34] and thus, the potential of the 18-/19-electron complex couple can be estimated as less than −1 V vs SCE.

Attempted Photoproduction of H_2. In an earlier paper[1] we described the photoproduction of H_2 when a solution of $(CpCOOH)_2W_2(CO)_6$ was irradiated in pH 7 buffer in the presence of $P(C_6H_5)_2(C_6H_4SO_3^-)$. We suggested that H_2 might be formed by 19-electron complex reduction of H^+. However, irradiation of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ in pH 2 buffered aqueous solution in the presence of PTA and 1,1′-dicarboxycobaltocenium (a known catalyst for the reduction of H^+) did not produce a detectable amount of H_2 (see Experimental Section). Because we were unable to produce H_2 at pH 2, where H^+ reduction is thermodynamically more favorable, we examined more closely the H_2-producing reaction in our previous paper.[1] An analysis of all the gaseous products showed that CO_2 is formed in amounts equal to H_2. The $[(CpCO_2^-)_2W^{II}(CO)_3P(C_6H_4SO_3^-)_3]^{2-}$ species is apparently reacting with water to undergo the water-gas shift reaction (eq 10). (Complexes of the type $CpM^{II}(CO)_3L^+$ should be especially susceptible to nucleophilic attack by water.[35]) We conclude that 19-electron complex reduction of H^+ does not occur.

$$[(CpCO_2^-)W^{II}(CO)_3(P(C_6H_4SO_3^-)_3]^{3-} + H_2O + P(C_6H_4SO_3^-)_3 \xrightarrow{\text{pH 7}} [(CpCO_2^-)W^{II}(CO)_2(P(C_6H_4SO_3^-)_3)_2]^{6-} + H_2 + CO_2 \qquad (10)$$

Conclusions

$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ is soluble in aqueous solution at pH 8 or lower. The photochemistry in both aqueous and nonaqueous solutions is essentially identical with the photochemistry of the $Cp_2Mo_2(CO)_6$ complex in nonaqueous solvents: Irradiation at wavelengths longer than 500 nm results in homolytic cleavage of the Mo–Mo bond. (Mo–CO bond dissociation probably also occurs, but no evidence for this process was observed.) Evidence for homolysis comes from $(CpCH_2CH_2NH_3^+)Mo(CO)_3$ trapping reactions with, for example, CCl_3CH_2OH to give $(CpCH_2CH_2NH_3^+)Mo(CO)_3Cl$. In the presence of a suitable water-soluble ligand, such as PTA, photochemical disproportionation of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ occurs. No disproportionation occurs, however, if a reducible substrate is present. Rather, the substrate is reduced and $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3PTA]^{2+}$ is formed. The disproportionation reaction and the substrate-reduction reaction are consistent with the intermediate formation of 19-electron adducts, formed by reaction of the photogenerated 17-electron radical with a ligand.

Experimental Section

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

Materials. Methylviologen dichloride hydrate ($[MV^{2+}]Cl_2\cdot H_2O$) (Aldrich), cytochrome *c* (Sigma), NaN_3 (Aldrich), $LiAlH_4$ (Aldrich), $Mo(CO)_6$ (Pressure Chemical), NH_4PF_6 (Aldrich), and pH 7 and pH 2 buffers (Baker and Micro Essential Laboratory, respectively) were used as received. Diethyl ether and THF (Baker) were freshly distilled as needed from sodium benzophenone ketyl under N_2. Methylene chloride (Baker) was freshly distilled under N_2 from CaH_2. 2,2′,2″-Trichloroethanol (Aldrich) was freshly distilled under N_2. DMSO (Baker) was freshly distilled from BaO under N_2. Carbon tetrachloride (Baker) was distilled from P_2O_5 under N_2. Triethylamine was dried over calcium sulfate. Cyclopentadienylethanol was synthesized using literature procedures.[36] The PTA ligand (phosphatriazaadamantane) was a gift from Prof. D. J. Darensbourg (Texas A&M). $N_4(CH_2)_6$ (tetraazaadamantane) (Fisher) was used as received.

Instrumentation. Photochemical reactions were carried out with an Oriel 200-W high-pressure mercury arc lamp. A Corning CS 3-68 cutoff filter (λ > 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

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(33) Tsukahara, K.; Wilkins, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2632–2635.

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

(35) Darensbourg, D. J.; Baldwin, D. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 4688–4694.

(36) Tenhaeff, S. T.; Tyler, D. R. *Organometallics* **1991**, *10*, 473–482.

550-nm light from an Oriel 200-W high-pressure mercury arc lamp. Infrared spectra were obtained with a Nicolet 5DXB FT-IR and a 0.025-mm path length calcium fluoride sealed cell. 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 the $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6$ complex was monitored at 503 nm. The lamp intensities were measured with Aberchrome 540 according to the method of Heller and Langan.[37] Lamp intensities at 550 nm were typically 1×10^{-9} einsteins/s when equipped with a 0.5 neutral density filter.

Gas analyses were carried out on a Hewlett-Packard 5790A series gas chromatograph with a 3390A integrator and an 18 ft/$^1/_8$ in. i.d. stainless steel column packed with 60/80 mesh silica gel from Alltech Co. The injector and detector were maintained at room temperature, and the column was cooled to −78 °C. Argon was used as the carrier gas with a flow rate of 25 mL/min.

Synthesis of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$. $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ was synthesized previously in our lab.[38] Outlined below is a simpler procedure leading to an improved yield of the (cyclopentadienylethyl)amine ligand. Cyclopentadienylethanol (16 g, 0.146 mol) and *p*-toluenesulfonyl chloride (34 g, 0.178 mol) were dissolved in 400 mL of dichloromethane. Triethylamine (40.0 mL) was added to the solution and mixed well with magnetic stirring. The reaction was then cooled to 5 °C for 12 h. A TLC (silica gel, 1:1 ethyl acetate/hexanes v/v) showed that no alcohol was present. (The reaction must go to completion because the alcohol is difficult to remove subsequently.) The reaction mixture was washed with 1:1 H_2O/saturated NaCl solution (1 × 300 mL), saturated sodium bicarbonate solution (4 × 300 mL), H_2O (2 × 300 mL), and saturated NaCl solution (2 × 300 mL) and then dried over sodium sulfate. The dichloromethane was then removed on a rotary evaporator at room temperature yielding the tosylate complex as a thermally sensitive brownish viscous liquid. ^1H NMR ($CDCl_3$): δ 7.78 (d, *J* = 8.6 Hz, 2 H, Ts), 7.34 (d, *J* = 8.3 Hz, 2 H, Ts), 6.3 (m, 3 H, Cp vinylic), 4.17 (m, 2 H, RCH_2OTs), 2.74 (m, 2 H, RCH_2CH_2OTs), 2.94 (m, 2 H, Cp allylic), 2.46 (s, 3 H, Ts). A small amount of *p*-toluenesulfonic acid was evident in the spectrum. The tosylate was dissolved in 250 mL of freshly distilled DMSO and cooled in an ice bath. Sodium azide (16 g, 0.25 mol) was added slowly to the rapidly stirred solution. The solution was warmed to room temperature and stirred for 18 h. The dark brown solution was cooled in an ice bath, and 300 mL of H_2O was added. The aqueous DMSO solution was then extracted with ether (4 × 200 mL). The ether layers were combined and washed with H_2O (4 × 500 mL) and saturated NaCl solution (2 × 500 mL). The straw-colored ether layer was dried with magnesium sulfate and filtered. The ether solution was concentrated on a rotary evaporator at room temperature yielding a brownish yellow oil. The azide complex was dissolved in 100 mL of ether, and the solution was put into an addition funnel. The addition funnel was fitted to a 500-mL three-neck flask to which a N_2 inlet and a rubber septum had been affixed. Anhydrous ether (200 mL), lithium aluminum hydride (16.0 g, 0.42 mol), and a magnetic stir bar were then added to the flask. The azide complex was added dropwise to the rapidly stirred solution over a period of several hours. The reaction was stirred overnight. The excess $LiAlH_4$ was then quenched by *carefully* adding 4 mL each of 5% aqueous KOH solution and H_2O. Magnesium sulfate was added to the yellow suspension to dry the solution. The mixture was filtered, and the solid was washed with ether. The ether layer was dried with magnesium sulfate again and filtered. The ether was removed by rotary evaporation at room temperature leaving the straw-colored (cyclopentadienylethyl)amine in 7.8-g yield (0.072 mol, 49% overall). The amine was then vacuum distilled (0.5 Torr, 50–70 °C) to yield 3.24 g (0.030 mol, 20% overall). ^1H NMR ($CDCl_3$): δ 6.2 (m, 3 H, Cp vinylic), 2.84 (m, 2 H, $CpCH_2CH_2NH_2$), 2.49 (m, 2 H, $CpCH_2CH_2NH_2$), 2.13 (d, 2 H, Cp allylic), (s (br), 2 H, $CpCH_2CH_2NH_2$). The (cyclopentadienylethyl)amine slowly oxidizes during prolonged exposure to air.

Sodium sand (0.667 g, 29 mmol) was prepared in xylene and then washed with three 30-mL portions of THF. THF (200 mL) was added via cannula to the sodium sand. The degassed (cyclopentadienylethyl)amine (3.24 g, 30 mmol) was then added via cannula to the reaction flask. The solution was magnetically stirred for 20 h. The solution turned grayish with a small amount of white precipitate. $Mo(CO)_6$ (7.656 g, 30 mmol) was degassed by four pump-refill cycles and then added through the top of the reflux condenser with a counterflow of nitrogen. The solution was refluxed for 13 h. The yellow solution was then cooled to room temperature. The reaction volume was reduced to approximately 50 mL in vacuo. A deoxygenated solution of $Fe(NO_3)_3{\cdot}9H_2O$ (12 g, 30 mmol) in 200 mL of H_2O was added dropwise via cannula. The solution turned a deep red with a red precipitate. The solution was then reduced in vacuo to approximately 125 mL. The red precipitate was filtered out in air, washed with distilled water, and dried in vacuo for 12 h. The crude product was recrystallized from methanol/diethyl ether (1.7 g, 20%). NMR (DMSO-d_6): δ 7.9 (s (br), 6 H, $CpCH_2CH_2NH_3^+$), 5.45 (m, 8 H, $CpCH_2CH_2NH_3^+$), 2.96 (m, 2 H, $CpCH_2CH_2NH_3^+$), 2.67 (m, 2 H, $CpCH_2CH_2NH_3^+$). NMR (D_2O): δ 5.49–5.38 (m, 8 H, $CpCH_2CH_2NH_3^+$), 3.14 (t, *J* = 5.4 Hz, 2 H, $CpCH_2CH_2NH_3^+$), 2.78 (t, *J* = 5.3 Hz, 2 H, $CpCH_2CH_2NH_3^+$). IR (KBr, cm^{-1}): 3100 (m, br), 2986 (w), 2012 (w), 1950 (s), 1912 (s), 1887 (s), 1387 (s).

Anion Exchange. The nitrate counterion in $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ was exchanged with PF_6^- by dissolving the dimer (0.1 g, 0.14 mmol) in 100 mL of H_2O and then adding a solution of NH_4PF_6 (0.5 g, 3.0 mmol) in 5 mL of H_2O via cannula. The red solution slowly turned a red opalescent color. The flask was placed in a freezer for several hours and then vacuum filtered in air. The opalescent red flakes were taken into the glovebox and recrystallized by dissolving them in THF and vacuum filtering through a fine-porosity glass frit. Diethyl ether was then added to the solution until a precipitate began to form. The flask was fitted with a rubber septum and placed in the freezer (−18 °C) overnight. The red crystals were then filtered out and dried (0.12 g, 0.14 mmol).

Thermal Stability of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ in Buffered Aqueous Solutions. A pH 2 buffer solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ (0.34 mM) was prepared. A 4-mL aliquot of the solution was transferred to a freeze–pump–thaw UV/vis cell via syringe. The solution was then degassed by three freeze–pump–thaw cycles. The 503-nm absorbance of the solution remained unchanged over 3 days in the dark. An identical experiment in pH 7 buffer also showed no change after 3 days in the dark. Upon exposure of the solutions to room light, the pH 7 sample turned clear and the pH 2 sample turned blue.

Reaction of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ with CCl_4 in THF. A THF solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ (6 mM) and CCl_4 (60 mM) was prepared and transferred to a sealed IR cell. An initial spectrum and a spectrum taken after 5 min in the dark were compared, and no change was observed. The cell was irradiated for 1 min after which no starting material peaks were observed and the 2050- and 1971-cm^{-1} bands (see Table II) corresponding to $(CpCH_2CH_2NH_3^+)Mo(CO)_3Cl$ had grown in. The product formed in quantitative yield (100 ± 10%) using the known extinction coefficients for $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ and $MeCpMo(CO)_3Cl$ (see Table I). The disappearance quantum yield at 550 nm for the reaction of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ in THF with 1 M CCl_4 was 0.39 ± 0.04.

Reaction of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ with CCl_3CH_2OH in pH 7 Buffered Aqueous Solution. A pH 7 solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ (2.8 mM) and CCl_3CH_2OH (28 mM) was prepared. The solution was then transferred via syringe to a sealed IR cell. The initial spectrum and one taken after 5 min in the dark were identical. The reaction was monitored every 30 s of irradiation; after 2 min of irradiation the reaction was complete. The product $(CpCH_2CH_2NH_3^+)Mo(CO)_3Cl$ was identified by the 2060- and 1967-cm^{-1} bands in the IR spectrum. The product was formed in quantitative yield using the known extinction coefficients for $[(CpCH_2CH_2NH_3^+)_2Mo_2$-

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[37] Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* 1981, 341–343.

[38] Tenhaeff, S. C.; Tyler, D. R. *Organometallics* 1992, *11*, 1466–1473.

$(CO)_6][PF_6^-]_2$ and $MeCpMo(CO)_3Cl$ (see Table II). The spectrum did not change after 1 h in the dark. The disappearance quantum yield at 550 nm for the reaction of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ in pH 7 buffered aqueous solution with 50 mM solution of CCl_3CH_2OH was 0.78 ± 0.15.

Reaction of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ with CCl_3CH_2OH in pH 2 Buffered Aqueous Solution. A pH 2 solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ (2.8 mM) and CCl_3CH_2OH (28 mM) was prepared, and the solution was transferred via syringe to a sealed IR cell. The initial spectrum and one taken after 5 min in the dark were identical. The reaction was complete after 1 min of irradiation. The product $(CpCH_2CH_2NH_3^+)Mo(CO)_3Cl$ was identified by the 2067-, 2060- (shoulder), and 1981-cm^{-1} bands in the IR spectrum. The product was formed in quantitative yield using the known extinction coefficients for $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ and $MeCpMo(CO)_3Cl$ (see Table II). The spectrum of the product did not change after 1 h in the dark.

Disproportionation of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ in THF. A solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][PF_6^-]_2$ (7.1 mM) and triphenylphosphine (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 after every 15 s. The reaction was complete after 75 s of irradiation as indicated by the loss of the dimer absorption bands at 2010, 1954, and 1912 cm^{-1}. The products were $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3(PPh_3)]^{2+}$, $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(PPh_3)_2]^{2+}$, $[(CpCH_2CH_2NH_3^+)_2Mo^{I}_2(CO)_5(PPh_3)]^{2+}$, and $[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3]$ identified by the IR spectra (see Results and Discussion and Table II). Note that upon continued irradiation the $[(CpCH_2CH_2NH_3^+)_2Mo^{I}_2(CO)_5(PPh_3)]^{2+}$ absorptions continued to decrease and the other products absorption bands increased. After 12 h in the dark, 30% of the dimer had re-formed and both $[(CpCH_2CH_2NH_3^+)Mo(CO)_3(PPh_3)]^{2+}$ and $[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3]$ had decreased by a corresponding amount.[39]

Disproportionation of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ Aqueous Solution with PTA. A solution of PTA (2.8 mM) and $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ (115 mM) in pH 7 buffer was prepared and transferred to an IR cell using a syringe. An initial spectrum and a spectrum taken after 5 min in the dark were identical. The solution was then irradiated for 1 min after which time the reaction had gone to completion. The products were $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3(PTA)]^{2+}$, $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(PTA)_2]^{2+}$, and $[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3]$ as identified by their IR spectra (Table II). The $[(CpCH_2CH_2NH_3^+)Mo(CO)_3(PTA)]^{2+}$ product was unstable, and complete loss of its characteristic carbonyl stretches occurred in less than 1 min in the dark. An analogous control experiment using $N_4(CH_2)_6$ in place of PTA only produced disproportionation products in which H_2O was acting as the ligand (see below). The disappearance quantum yield at 550 nm for the disproportionation in pH 7 aqueous solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ with PTA was 0.32 ± 0.05.

Disproportionation of $[(CpCH_2CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ Aqueous Solution at pH 7. A solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ (2.8 mM) in pH 7 buffer was irradiated in the IR cell for 2 min. The products of the reaction were identified as $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3(H_2O)]^{2+}$ and $[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3]$ by comparison of their IR spectra with known complexes (see Table II). After 3 h in the dark IR absorptions corresponding to approximately 80% of the original dimer had grown in and the product bands had decreased by the same amount. The same reactivity was observed in an analogous experiment using distilled water instead of pH 7 buffer. The disappearance quantum yield at 550 nm for the disproportionation of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ in aqueous pH 7 buffer was 0.16 ± 0.01.

Disproportionation of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ Aqueous Solution at pH 2. A solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ (2.8 mM) in pH 2 buffer was irradiated in an IR cell for 2 min. The products of the reaction were identified as $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3(H_2O)]^{2+}$ and $[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3H]^+$ by comparison of their IR spectra with known complexes (see Table II). After 1 h in the dark, IR absorptions corresponding to the hydride complex were no longer evident, and approximately $^1/_3$ of the original dimer absorbance had reappeared and the absorbance of the cation had decreased by a corresponding amount. After 2 h in the dark, the dimer absorptions stopped increasing at approximately 50% of the original absorbance and the cation absorbance stopped decreasing at approximately 50% of its original absorbance.

Reduction of Methylviologen. A solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6[NO_3^-]_2$ (3.5×10^{-2} mM), methylviologen (3.5 mM), and PTA (6.4 mM) in pH 7 buffer was degassed by four freeze–pump–thaw cycles. The solution was kept in the dark for 20 min, and no reduced methylviologen was observed by UV/vis spectroscopy. The solution was irradiated for 1 min with stirring. The characteristic 606-nm absorbance band of reduced methylviologen[20] appeared, and the dimer absorption at 503 nm disappeared. Further irradiation produced no more reduced methylviologen. Reduced methylviologen was produced in quantitative yield based on dimer as calculated from the electronic spectrum: 4.2×10^{-5} mmol of dimer yielded 8.7×10^{-5} mmol of $MV^{\bullet+}$.

Reduction of Cytochrome *c*. A solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6[NO_3]_2$ (3.5×10^{-2} mM), PTA (16 mM), and cytochrome c^{III} (3.5×10^{-2} mM) in pH 7 buffer was prepared in a freeze–pump–thaw cuvette and degassed in four freeze–pump–thaw cycles. The UV–vis spectrum remained unchanged in the dark. After 1 min of irradiation, however, growth of the cytochrome c^{II} absorbance at 550 nm was evident.[18,40,41] Upon further irradiation no additional increase in intensity of the cytochrome c^{II} absorption was observed.

Preparation of Crystalline $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$. Crystals of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ were grown by dissolving the complex in THF, methanol, or dioxane and then layering on a 3- to 4-fold volume excess of hexane, ether, or toluene and storing at −20 °C in a freezer. Crystals of the dimer with the counterions BF_4^-, PF_6^-, $B(C_6H_5)_4^-$, *p*-toluenesulfonate, and NO_2^- were grown and mounted for X-ray diffraction studies, but none proved suitable for X-ray diffraction studies.

The $(CpCH_2CH_2NH_2)_2Mo_2(CO)_6$ complex was made by dissolving 50 mg of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ in 50 mL of deoxygenated H_2O and then layering on 20 mL of deoxygenated ether. Deoxygenated saturated sodium bicarbonate (5 mL) was then added via syringe. The solution was magnetically stirred for several minutes, after which the ether layer was deep red. The ether layer was cannulated off and dried in vacuo yielding 10 mg of the amine dimer. No suitable crystals were obtained from THF/hexanes recrystallization as described above.

The amide derivatives $(CpCH_2CH_2NHCOC_6H_5)_2Mo_2(CO)_6$ and $(CpCH_2CH_2NHCOCH_3)_2Mo_2(CO)_6$ were prepared by adding 0.162 mmol of the $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ complex to a solution of 1.6 mmol of triethylamine and 0.352 mmol of benzoic anhydride or acetic anhydride, respectively, in 10 mL of THF. The solution was stirred in the dark for 12 h and then quenched with 50 mL of deoxygenated H_2O. The red precipitate was filtered out in air and recrystalized in the drybox from THF/hexanes. $(CpCH_2CH_2NHCOC_6H_5)_2Mo_2(CO)_6$: IR (KBr; cm^{-1}) 2926 (m), 2855 (w), 2006 (vw) (ν(CO)), 1953 (s) (ν(CO)), 1941 (s) (ν(CO)), 1912 (s) (ν(CO)), 1889 (s) (ν(CO)), 1631 (m) (amide I), 1549 (w) (amide II), 1443 (w), 1309 (w), 1232 (w); NMR (DMSO-d_6) δ 8.54 (s (br), 1 H, $CpCH_2CH_2NHCOC_6H_5$), 7.59 (m (br), 5 H, $CpCH_2CH_2NHCOC_6H_5$), 5.4 (m (br), 4 H, $CpCH_2CH_2NHCOC_6H_5$), 3.36 (m (br), 2 H, $CpCH_2CH_2NHCOC_6H_5$), 2.59 (m (br), 2 H, $CpCH_2CH_2NHCOC_6H_5$). $(CpCH_2CH_2NHCOCH_3)_2Mo_2(CO)_6$: IR (KBr; cm^{-1}) 3254 (w), 3071 (w), 2931 (w), 2853 (w), 2003 (w), 1953 (s), 1904 (vs), 1890 (vs), 1630 (m) (amide I), 1567 (w) (amide II), 1433 (w), 1370 (w), 1300 (w); NMR (DMSO-d_6) δ 7.13 (s (br), 1 H, $CpCH_2CH_2NHCOCH_3$), 4.83 (m (br), 4 H, $CpCH_2CH_2NHCOCH_3$), 2.88 (m (br), 2 H, $CpCH_2CH_2NHCOCH_3$),

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[39] 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.

[40] Butler, J.; Davies, D. M.; Sykes, A. G. *J. Inorg. Biochem.* **1981**, *15*, 41–53.

[41] Adar, F. *The Porphyrins*; Academic: New York, 1978.

2.18 (m (br), 2 H, $CpCH_2CH_2NHCOCH_3$), 1.52 (s (br), 3 H, $CpCH_2CH_2NHCOCH_3$). Crystals of neither derivative were suitable for X-ray diffraction studies.

Attempted Photoproduction of H_2. A solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ (1.4 mM), PTA (10 mM), and 1,1′-dicarboxycobaltocenium hexafluorophosphate (12 mM) in 100 mL of pH 2 buffer was prepared in a 100-mL Schlenk flask. The headspace on the flask was approximately 1 mL. The solution was irradiated for 30 min with magnetic stirring. A 50-μL aliquot of the cover gas was analyzed by GC every 5 min. Only a small amount of CO was detected, and no H_2 was detected. Similar results were obtained in analogous experiments in pH 7 and pH 2 solutions with and without PTA or the 1,1′-dicarboxycobaltocenium.

Detection of CO_2. A CO_2- and O_2-free pH 12 aqueous NaOH solution (10 mL) of the $(CpCOOH)_2W_2(CO)_6$ dimer (20 mM) and $Na_3[P(C_6H_5SO_3^-)_3]$ (200 mM) was prepared in a septum-capped test tube. The tube was irradiated for 30 min while the solution was magnetically stirred. A cannula was used to connect the test tube (A) to another test tube (B) containing 4 mL of a clear saturated aqueous solution of $Ba(OH)_2$. The solution containing the photolysis products was acidified with 2 mL of 6 M H_2SO_4. Effervescent was immediate, and bubbles could be seen going through the $Ba(OH)_2$; the solution in B gradually became cloudy. The precipitate in test tube B was vacuum filtered, dried in an oven, and analyzed by IR spectroscopy (KBr pellet). The product was identified as $BaCO_3$ by comparison with an authentic sample. In a quantitative experiment, 7.9×10^{-5} mol of dimer produced 1.4 mg (7.1×10^{-6} mol) of $BaCO_3$ (10%). H_2 was also formed in 10% yield.[1] A control experiment without $(CpCOOH)_2W_2(CO)_6$ did not produce a precipitate.

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Intramolecular Redox Chemistry of Molecules with Alkyne and CCo_3 Cluster Functionalities: Electronic Interaction and Structural Isomerism in Reduced Clusters with Multiple Redox Centers

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The redox chemistry of the tricobaltcarbon clusters $[CCo_3(CO)_9]_2$, $OC[CCo_3(CO)_9]_2$, and $C_n[CCo_3(CO)_9]_2$ ($n = 2, 4$), linked by formal single and/or triple carbon–carbon bonds, is contrasted with that of molecules with only a single cluster redox center, $RC_nCCo_3(CO)_9$. The latter clusters undergo a reversible reduction process, whereas molecules with linked clusters display electrochemical responses indicative of interacting redox centers. After the formation of a radical anion, in which the electron is delocalized via the Co_3C–C_n–CCo_3 link, a CE mechanism gives a new species with a reversible redox couple. Spectroscopic evidence suggests that this new species is a bridged-carbonyl isomer of the initial radical anion. Formation of the isomers is attributed to electron delocalization through the carbyne link and steric influence of the equatorial CO groups. An improved synthesis of $[CCo_3(CO)_9]_2$ and the X-ray structure analysis of the compound $(MeO)_3P(CO)_8Co_3CC{\equiv}CCCo_3(CO)_7[P(OMe)_3]_2$, (*Pbca*; $a = 18.074\ (4)$ Å, $b = 37.534\ (7)$ Å, $c = 12.918\ (4)$ Å, $Z = 8$) are also reported.

Electronic interaction between adjacent organometallic moieties which are readily oxidized or reduced can lead to a range of electron-transfer responses.[1] These responses are normally classified according to the degree to which the interaction brings about a change in physical properties.[2] Redox studies on many transition-metal carbonyl clusters have shown[1,3] that they are structurally flexible electron reservoirs with "tunable" redox properties dependent on the coordination sphere of the metal framework. Extension of this work to systems where the clusters are linked to other redox centers, such as ferrocene, demonstrated that the clusters can participate in electronic interactions which lead to classical mixed-valence molecules.[4] However, interpolation of an electronically saturated system such as CH_2 or SiR_2 between the ferrocene and cluster removes the possibility of electronic communication between the two redox centers.[5] This raised the question of whether intracluster communication could be established if two cluster reactions were directly linked by an unsaturated carbon–carbon bridge, a communication which is well-established in ferrocene chemistry.[6] Controlled thermal decomposition of this type of molecule

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[1] Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985**, *24*, 87.

[2] Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1980**, *58*, 451. Hush, N. S. *Chem. Phys.* **1975**, *10*, 361.

[3] Robinson, B. H.; Simpson, J. In *Paramagnetic Organometallic Species in Activation/Selectivity, Catalysis*; Chanon, M., Juillard, M., Poite, J. C., Eds.; NATO ASI Series 257; Kluwer: Dordrecht, The Netherlands, 1989; p 357. Lemoine, P. *Ibid.*, p 397.

[4] Colbran, S. B.; Robinson, B. H.; Simpson, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1362.

[5] Borgdorff, J.; Ditzel, E. J.; Duffy, N. W.; Robinson, B. H.; Simpson, J. *J. Organomet. Chem.*, in press.

[6] Cowan, D. D.; Le Vanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1. Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 4393.

0276-7333/92/2311-3863$03.00/0