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Generation of 19-Electron Adducts in Aqueous Solution Using the Water-Soluble $(HOCH_2)_2PCH_2CH_2P(CH_2OH)_2$ Ligand

Gregory F. Nieckarz,[†] T. J. R. Weakley,[†]
Warren K. Miller,[‡] Brian E. Miller,[§]
David K. Lyon,[‡] and David R. Tyler*,[†]

Department of Chemistry, University of Oregon,
Eugene, Oregon 97403-1253, Bend Research,
64550 Research Road, Bend, Oregon 97701-8599, and
Department of Chemistry, Wheaton College,
Wheaton, Illinois 60187

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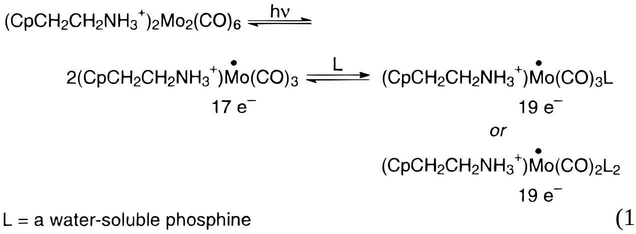
Nineteen-electron adducts have several features that make them ideal reducing agents.[1−12] One of the long-range goals of the group at the University of Oregon is to exploit the reducing ability of 19-electron complexes and to use them as electron-transfer initiators and relays in aqueous catalytic cycles (e.g., in photochemical water-splitting schemes for solar energy conversion). In several recent papers,[6−8] we demonstrated that *water-soluble* 19-electron adducts can be generated from water-soluble metal−metal bonded dimers and water-soluble phosphines, e.g.:



$$\begin{array}{l} (CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6 \xrightleftharpoons{h\nu} \\ \underset{17\ e^-}{2(CpCH_2CH_2NH_3^+)\dot{Mo}(CO)_3} \xrightleftharpoons{L} \underset{19\ e^-}{(CpCH_2CH_2NH_3^+)\dot{Mo}(CO)_3L} \\ \qquad\qquad\qquad\qquad\qquad\qquad or \\ \qquad\qquad\qquad\qquad \underset{19\ e^-}{(CpCH_2CH_2NH_3^+)\dot{Mo}(CO)_2L_2} \end{array}$$

L = a water-soluble phosphine (1)

A potential drawback to the reactions reported in our previous papers is that most water-soluble ligands are monodentate; generally, bidentate ligands form 19-electron species more efficiently.[11] In this note, we report the generation of 19-electron complexes using the previously reported[13] ligand 1,2-bis(dihydroxymethylphosphino)ethane) (dhmpe), the crystal structure of dhmpe, and the crystal structure of the $[Ni(dhmpe)_2]Cl_2$ complex.

$$\begin{array}{c} (HOCH_2)_2P-CH_2CH_2-P(CH_2OH)_2 \\ \text{dhmpe} \end{array}$$

Results and Discussion

Formation of 19-Electron Complexes. As previously described,[6,7] two key tests for the formation of 19-electron species are (1) the occurrence of disproportionation, when metal−metal bonded dimers are irradiated in the presence of a ligand,[9−11] and (2) the reduction of substrates, when dimers are irradiated in the presence of a ligand and a reducible substrate.[7] (The first point follows because 19-electron complexes are key intermediates in the photochemical disproportionation reactions of metal−metal bonded carbonyl dimers.[9−11]) Both tests were positive when dhmpe was used as the ligand in aqueous solution. Thus, irradiation ($\lambda > 500$ nm) of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ in the presence of dhmpe in aqueous solution gave the disproportionation products shown in eq 2.

$$(CpCH_2CH_2NH_3^+)_2Mo^I_2(CO)_6 + dhmpe \xrightarrow[H_2O,\ pH\ 2]{\lambda > 500\ nm} [(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(dhmpe)]^{2+} + [(CpCH_2CH_2NH_3^+)Mo^0(CO)_3H]^+ \quad (2)$$

(Although the dimer is soluble at pH 7, the reaction was run at pH 2 because of enhanced solubility at low pH.[7]) Infrared spectroscopic monitoring of the reaction showed the complete disappearance of the $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ bands[7] at 2010, 1957, and 1910 cm^{-1} and the appearance of a relatively intense new band at 1986(s) along with a broad peak centered at 1921(s) cm^{-1}. In addition, a set of weak bands appeared at 2024 and 1943 cm^{-1}. The bands at 1986 and 1921 are assigned to $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(dhmpe)]^{2+}$ by comparison to the spectra of similar $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(PR_3)_2]^{2+}$complexes (Table 1).[7,8,14] The weak bands are consistent with two of the three bands previously assigned to $[(CpCH_2CH_2NH_3^+)Mo^0(CO)_3H]^+$ (Table 1), but their weak intensity and the absence of the 1929 cm^{-1} band preclude a definitive assignment. As discussed previously, the hydride product is formed by protonation of the $(CpCH_2CH_2NH_3^+)Mo^0(CO)_3$ disproportionation product.[7]

The second test for 19-electron adducts further established that these species formed in aqueous solution. Thus, irradiation ($\lambda > 500$ nm) of a pH 2 aqueous solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ in the presence of dhmpe and MV^{2+} (methyl viologenlogen dication) led to the formation of the dark blue MV^+ species[15] and the $[(CpCH_2CH_2NH_3^+)Mo(CO)_2(dhmpe)]^{2+}$ cation (eq 3). The reaction was monitored by electronic absorption spectroscopy, which showed the disappearance of the dimer bands at 503 and 388 nm and the appearance of bands at 605 nm and 395 nm, attributed to MV^+.[15] Infrared spectroscopic monitoring of the reaction showed a decrease in intensity of the dimer bands at 2010, 1957, and 1910 cm^{-1} and the appearance of bands at 1975 and 1932 cm^{-1} attributed to $[(CpCH_2CH_2NH_3^+)Mo(CO)_2(dhmpe)]^{2+}$ (Table 1). (In previous studies using other water-soluble ligands,[6−8] the

$$(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6 + 2dhmpe + 2\ MV^{2+} \xrightarrow[H_2O,\ pH\ 2]{h\nu} 2[(CpCH_2CH_2NH_3^+)Mo(CO)_2(dhmpe)]^{2+} + 2MV^{\bullet +} \quad (3)$$

[†] University of Oregon.

[‡] Bend Research.

[§] Wheaton College.

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Table 1. Selected Infrared Data

complex[a]	ν(CO), cm^{-1}	ref
$(MeCp)_2Mo_2(CO)_6$[b]	2012 (m), 1956 (s), 1912 (s)	21
$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$[c]	2009 (m), 1958 (s), 1908 (s)	7
$[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$[d]	2010 (m), 1957 (s), 1910 (s)	7
$[CpMo^{II}(CO)_2(PPh_3)_2^+][BF_4^-]$[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,l]	1957 (s), 1910 (s)	7
$[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(PPh_3)_2]^{2+}$ [e,g]	1965 (s), 1900 (s)	7
$[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(dhmpe)]^{2+}$ [d]	1986 (s), 1921 (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)	7
$[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3(H_2O)]^{2+}$ [d,f]	2067 (s), 1993 (m), 1981 (s)	7
$CpMo^{II}(CO)_3H$[j]	2030 (vs), 1949 (vs), 1913 (w)	24
$[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3H]^+$ [d,f]	2024, 1943, 1929	7

[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, M^{-1} cm^{-1}. [l] PTA = phosphatriazaadamantane, $[PN_3(CH_2)_6]$.

reduction of MV^{2+} to $MV^{\bullet+}$ was quantitative when excess MV^{2+} was used. In the case of reaction 3, measurements showed that only about half of the theoretical yield of $MV^{\bullet+}$ was formed. We have no explanation for this anomaly when dhmpe is used as the ligand.)

Note that disproportionation does not occur in either aqueous or nonaqueous solvents when metal–metal-bonded dimers and ligands are irradiated in the presence of a reducible substrate. This result is ascribed to preferential reduction of the substrate by the 19-electron complex and the consequent inhibition of the disproportionation chain mechanism. In effect, the 19-electron complexes can be used as photogenerated reducing agents, eq 3.

As discussed previously,[6] the electrochemical potential of the $[(CpCH_2CH_2NH_3^+)Mo(CO)_3(dhmpe)]^{+/0}$ couple can be estimated by its ability to reduce substrates of various reduction potentials. The potential of the $MV^{2+}/MV^{\bullet+}$ couple is −0.46 V vs SCE;[16] 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 $[(CpCH_2CH_2NH_3^+)Mo(CO)_2(dhmpe)]^+$ is a key step in the disproportionation). 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,[17] and thus the potential of the 18-/19-electron complex couple can be estimated as less than −1 V vs SCE.

In summary, both the disproportionation reaction and the reduction of MV^{2+} indicate that the dhmpe ligand reacts with 17-electron $(CpCH_2CH_2NH_3^+)Mo(CO)_3$ radicals in aqueous solution to form 19-electron complexes. These studies also demonstrate that dhmpe is a useful ligand in aqueous organometallic chemistry.

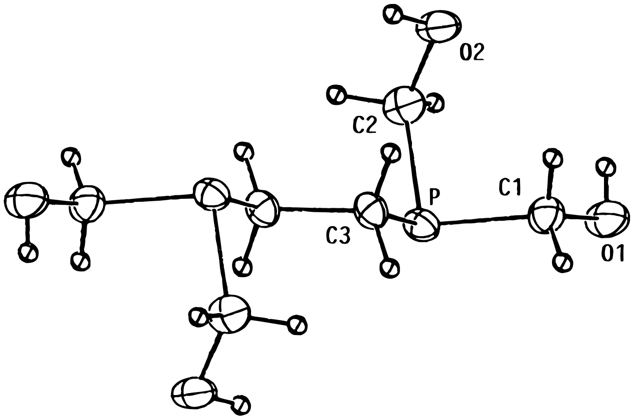

Figure 1. Molecular structure of the dhmpe ligand.

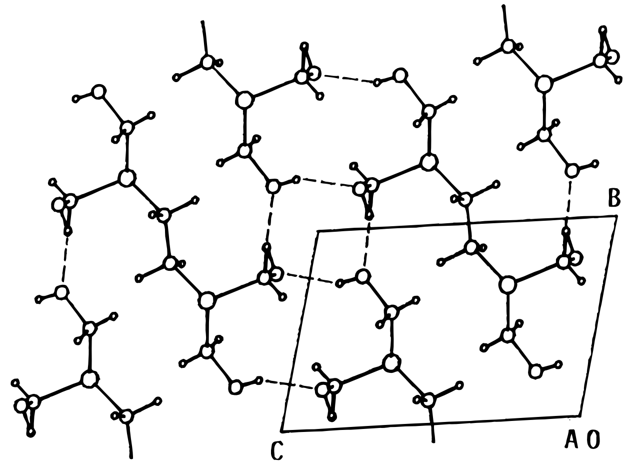

Figure 2. Packing of the dhmpe ligand showing the hydrogen bonding.

X-ray Crystal Structures of dhmpe and $Ni(dhmpe)_2Cl_2$. The structure of the dhmpe ligand was confirmed by X-ray crystallography (Figures 1 and 2; Tables 2 and 3). As indicated in the tables, there are no unusual bond lengths or angles in the structure. Note that each hydroxyl group acts as a donor in one hydrogen bond and as an acceptor in a second hydrogen bond. Although X-ray quality crystals of the ligand were eventually obtained, the initial attempts at crystallization were unsuccessful. For that reason, a Ni complex of the ligand was synthesized and crystallized as an alternative means of verifying the structure of the ligand. Mixing equimolar solutions of $NiCl_2{\cdot}6H_2O$ and dhmpe resulted in the formation of $[Ni(dhmpe)_2]^{2+}$:[14]

$$NiCl_2{\cdot}6H_2O + 2dhmpe \rightarrow Ni(dhmpe)_2^{\ 2+} + 2Cl^- + 6H_2O \tag{4}$$

The $Ni(dhmpe)_2^{2+}$ product was obtained despite the 1:1 ratio of the reactants. Similar results were obtained by Pringle with the dhmpe ligand and $PdCl_2$ and were attributed to hydrogen-bonding effects.[18] The results of the X-ray structure determination are summarized in Tables 2 and 3 and Figure 3. The molecule is square planar, and the chloride counterions are not

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Table 2. Crystallographic Data

	$C_6H_{16}O_4P_2$	$C_{12}H_{32}Cl_2NiO_8P_4$
fw	214.1	557.9
space group	$P\bar{1}$	Pbca
a, Å	5.1088(7)	9.216(3)
b, Å	6.2415(8)	14.634(1)
c, Å	8.880(2)	15.870(1)
α, deg	99.71(1)	90
β, deg	98.31(1)	90
γ, deg	108.96(1)	90
V, $Å^3$	257.8(2)	2140(1)
Z	1	4
d_{calc}, g cm^{-3}	1.379	1.731
T, ° C	21	21
λ, Å	0.710 73	0.710 73
μ, cm^{-1}	3.90	14.9
rel transm coeff (ψ-scans)	0.95−1.00	0.94−1.00
no. obsd rflns [$I \geq 1.5\sigma(I)$]	785	1272
$R(F)^a$	0.050	0.042
w$R_w(F)^b$	0.063	0.035

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

within bonding distance of the Ni atom (3.249(2) Å). There are no unusual bond lengths or angles. As was the case in the structure of the free ligand, all hydroxyl groups participate in hydrogen bonds, either to other OH groups or to a chloride.

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 and Reagents. 1,2-bis(diphosphino)ethane was purchased from Strem Chemical Co. and used as received. All solvents were reagent grade and deoxygenated by a nitrogen or argon purge. Toluene was dried over CaH_2 and distilled under nitrogen. Deuterium oxide (D_2O) and methyl viologen dichloride hydrate ($[MV^{2+}]Cl_2 \cdot H_2O$) were purchased from Aldrich. $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ was synthesized according to a literature procedure.[7] The pH 2 aqueous buffer solution was made with a Metrepak pHydrion buffer tablet (Micro Essential Laboratory).

Instrumentation and Procedures. ^1H NMR were obtained on a GE QE-300 spectrometer at 300.15 MHz. Electronic absorption spectra were obtained on a Perkin-Elmer Lambda 6 UV−vis spectrophotometer. Infrared spectra were run on a Nicolet Magna 550 FT-IR spectrometer run by OMNIC software loaded on a Gateway 2000 4DX-33V computer. Solution infrared spectra were obtained using a sealable 0.03 mm path length calcium fluoride cell. The infrared spectra were obtained by taking approximately 130 scans and by using a pH 2 buffer solution as the background. ^{31}P NMR were obtained on a modified Nicolet NTC-360 spectrometer operating at 145.3 MHz and referenced to 1% H_3PO_4. Data was acquired with a modified Hare Research FELIX acquisition program. Resolution for ^1H NMR was 8K for a sweep width of 1064 Hz, and for ^{31}P NMR, it was 8K for a sweep width of 10 000 Hz. Photochemical irradiations were done with an Oriel Co. 200W high-pressure mercury arc lamp. A Corning CS 3−68 cutoff filter (λ > 525 nm) was used for all irradiations. All irradiations were done by placing the sample cell 4−6 in. away from the lamp to avoid thermal reactivity. Elemental analyses were performed by E&R Microanalytical Laboratory, Inc., Corona, NY.

X-ray Crystallography. Data were collected at 21 °C with an Enraf-Nonius CAD-4 diffractometer. The data crystal of the dhmpe ligand ($C_6H_{16}O_4P_2$) was sealed in a special glass capillary. Its structure was determined from a MITHRIL *E*-map.[19] The crystal of the nickel complex, $[Ni(dhmpe)_2]Cl_2$ ($Cl_2C_{12}H_{32}Cl_2NiO_8P_4$), was coated with epoxy and mounted on a glass fiber. The structure was determined by use of the PHASE routine of DIRDIF.[20] Table 2 summarizes the crystal data and gives the residuals. Full accounts of data collection and structure solution and tables of atomic coordinates, thermal parameters, and derived dimensions are given in the Supporting Information.

Table 3

(a) Principal Bond Lengths (Å) and Angles (deg) for the Ligand $C_6H_{16}O_4P_2$[a]

P−C(1)	1.835(5)	O(1)−C(1)	1.416(6)
P−C(2)	1.833(5)	O(2)−C(2)	1.421(6)
P−C(3)	1.842(5)	C(3)−C(3^i)	1.528(8)
C(1)−P−C(2)	99.5(2)	P−C(1)−O(1)	112.0(4)
C(1)−P−C(3)	97.6(2)	P−C(2)−O(2)	116.3(3)
C(2)−P−C(3)	102.1(2)	P−C(3)−C(3i)	113.0(4)
O(1)··O(2^{ii})	2.683(5)	O(1)··O(2^{iii})	2.690(5)

(b) Principal Bond Lengths (Å) and Angles (deg) for the Ni Complex $C_{12}H_{32}Cl_2NiO_8P_4$[b]

N−P(1)	2.209(1)	P(2)−C(6)	1.850(6)
Ni−P(2)	2.224(1)	O(1)−C(3)	1.399(6)
P(1)−C(1)	1.825(5)	O(2)−C(4)	1.400(7)
P(1)−C(3)	1.852(5)	O(3)−C(5)	1.411(7)
P(1)−C(4)	1.836(5)	O(4)−C(6)	1.415(7)
P(2)−C(2)	1.832(5)	C(1)−C(2)	1.511(7)
P(2)−C(5)	1.836(6)		
P(1)−Ni−P(2)	84.90(5)	C(2)−P(2)−C(5)	102.4(3)
Ni−P(1)−C(1)	108.5(2)	C(2)−P(2)−C(6)	101.3(2)
NI−P(1)−C(3)	126.7(2)	C(5)−P(2)−C(6)	106.1(3)
Ni−P(1)−C(4)	110.2(2)	P(1)−C(1)−C(2)	107.7(4)
C(1)−P(1)−C(3)	102.2(2)	P(2)−C(2)−C(1)	110.4(4)
C(1)−P(1)−C(4)	103.1(3)	P(1)−C(3)−O(1)	112.3(3)
C(3)−P(1)−C(4)	103.6(3)	P(1)−C(4)−O(2)	114.9(4)
Ni−P(2)−C(2)	110.1(2)	P(2)−C(5)−O(3)	113.5(4)
Ni−P(2)−C(5)	115.7(2)	P(2)−C(6)−O(4)	110.8(4)
Ni−P(2)−C(6)	119.1(2)		
Ni··Cl	3.249(2)	O(2)··O(3^{ii})	2.763(7)
Cl··O(1^i)	3.013(4)	O(2)··O(3^{iii})	2.880(7)
Cl··O(4)	3.091(5)		

[a] Symmetry code: (i) $1 - x, 2 - y, 1 - z$; (ii) $x, -1 + y, z$; (iii) $-x, 1 - y, -z$. [b] Symmetry code: (i) $^1/_2 + x, ^1/_2 - y, 1 - z$; (ii) $1^1/_2 - x, -^1/_2 + y, z$; (iii) $1 - x, -^1/_2 + y, ^1/_2 - z$.

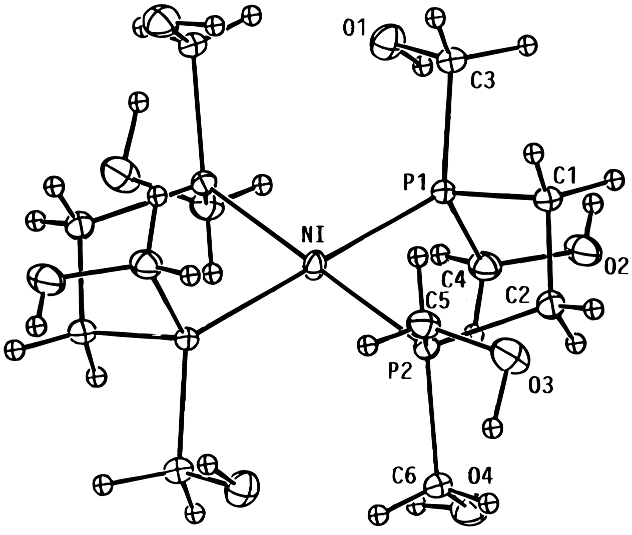

Figure 3. Molecular structure of the $[Ni(dhmpe)_2]^{2+}$ cation.

1,2-Bis[(dihydroxymethyl)phosphino]ethane. This material was prepared by a modification of the literature method.[13] 1,2-Bis-

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diphosphino)ethane (1.00 g, 10.6 mmol) and paraformaldehyde (1.30 g, 43.3 mmol) were mixed in 5 mL of toluene. The mixture was sealed under a nitrogen atmosphere in a 100 mL Schlenk tube with a Teflon valve. The mixture was heated with stirring at 85 °C in an oil bath for 6 h. Cooling to room temperature gave a white solid, which was isolated by filtration on a glass fritted funnel and then rinsed with several milliliters of toluene. Drying in vacuo gave 2.10 g (9.8 mmol), 92% yield. Anal. Calcd for $C_6H_{16}O_4P_2$: C, 33.65; H, 7.53; P, 28.93. Found: C, 33.25; H, 7.63; P, 29.05. ^{1}H NMR (D_2O): δ 1.746 (s, 4H, $-CH_2CH_2-$), 4.068 (m, 8H, CH_2OH), 4.800 (s, $-OH$). ^{31}P NMR (D_2O): -22.122 ppm (s), referenced to 1% H_3PO_4.

[Ni(dhmpe)$_2$]Cl$_2$. $NiCl_2\cdot 6\ H_2O$ (1.22 g, 5.13 mmol) and dhmpe (1.10 g, 5.14 mmol) were each dissolved in 20 mL of methanol. The two solutions were combined rapidly with stirring, giving a dark yellow-brown solution. Within 1−2 min, the product crystallized from the solution. The product was collected by filtration, rinsed with methanol (5 mL), and dried in vacuo. Yield: 1.21 g (4.32 mmol), 84%. The product was prepared for elemental analysis as follows. In the drybox, a slurry of Ni(dhmpe)$_2$Cl$_2$ in methanol was poured into a fine porosity glass frit and then vacuum filtered. The orange microcrystals were rinsed with ethanol (4 × 1 mL) and then dried in vacuo for 72 h. Anal. Calcd for $C_{12}H_{32}Cl_2NiO_8P_4$: C, 25.84; H, 5.78; P, 22.21; Ni, 10.52. Found: C, 25.52; H, 5.30; P, 22.26; Ni, 10.54. ^{31}P NMR (D_2O): 65.075 ppm (m).

Disproportionation of $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6$ in the Presence of dhmpe in a pH 2 Buffered Aqueous Solution. A 2 mL aliquot of a pH 2 solution containing $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6[NO_3^-]_2$ (1.8 mg; 2.6 × 10^{-3} mmol) and dhmpe (48.9 mg; 0.228 mmol) were prepared. In the dark, the solution was syringed into a CaF_2 infrared cell. The spectrum showed bands at 2010 (w), 1957 (s), and 1910 cm^{-1} (s), all attributable to the dimer. The spectrum was unchanged after 5 min in the dark, indicating there was no dark reaction. The sample was then irradiated for 1 min. The bands at 2010, 1957, and 1910 cm^{-1} disappeared and new bands appeared at 2024 (w), 1986 (s), 1943 (w), and 1921 cm^{-1} (s). These bands are assigned to $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(dhmpe)]^{2+}$ by comparison to $[(CpCH_2CH_2NH_3^+)Mo(CO)_2(PTA)_2]^{2+}$ (Table 1; PTA = phosphatriazaadamantane, $[PN_3(CH_2)_6]$).[5,6]

Reduction of Methyl Viologen by Irradiation of $(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6$ in the Presence of dhmpe in a pH 2 Buffered Aqueous Solution. A pH 2 aqueous solution of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-\ ]$ (2.0 mg; 2.85 × 10^{-3} mmol), dhmpe (40.7 mg; 0.19 mmol), and methyl viologen (23.1 mg; 8.98 × 10^{-2} mmol) was prepared. Under nitrogen, the solution was syringed into a glass cuvette that was sealable with a teflon stopcock. The cuvette was wrapped in aluminum foil to exclude light[11−13] and then degassed by three freeze−pump−thaw cycles. An electronic absorption spectrum of the degassed solution showed only the dimer absorption bands at 388 and 503 nm.[7] The sample solution was then irradiated for 1 min, after which time the dimer bands had decreased in intensity and new bands had appeared at 395 nm and 605 nm. These latter bands are characteristic of reduced methyl viologen, MV^{1+}.[4,5] The reaction was also monitored by infrared spectroscopy as described next. (All of the following procedures were done in the dark.) Stock solutions of $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-\ ]_2$ (0.28 mM) and dhmpe (2.69 x 10^{-4} mM)/MV^{2+} (1.57 × 10^{-4} mM) were prepared as follows: In the drybox, $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ (1.0 mg, 1.4 × 10^{-3} mmol) was placed into a 1 dr vial, and dhmpe (65.5 mg, 0.31mmol) and methyl viologen (20.2 mg, 7.85 × 10^{-2} mmol) were loaded into a second 5 dr vial. Then 1 and 4 mL aliquots of deoxygenated pH 2 aqueous buffer were syringed into the 1 and 5 dr vials, respectively. The solutions were then mixed well. The $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-\ ]_2$ solution was syringed into the vial containing the methyl viologen and phosphine solution and mixed well. The reaction solution was then syringed into the CaF_2 cell and sealed in the dark. An initial spectrum and one run after 5 min after revealed no dark reaction. (Only the characteristic $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-\ ]_2$ $\nu(C{\equiv}O)$ bands at 2010 (w), 1957 (s), and 1910 cm^{-1} (s) were observed.) The sample was then irradiated for 2 min. The spectrum of the solution showed the reaction had gone to completion, as evidenced by complete loss of the $[(CpCH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-\ ]_2$ $\nu(C{\equiv}O)$ bands. The major product was identified as $[(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_2(dhmpe)]^{2+}$, as determined by infrared absorbances at 1975 (s) and 1932 cm^{-1} (m). A minor product was the aquo complex $\{(CpCH_2CH_2NH_3^+)Mo^{II}(CO)_3(H_2O)\}^{2+}$, which had IR absorbances at 2060 (w), 1992 (w), and 1973 cm^{-1} (w).

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Supporting Information Available: Text discussing the structure determination and tables of crystallographic information, bond length and bond angles, nonbonded contact distances, calculated coordinates and thermal parameters for hydrogen atoms, anisotropic thermal parameters, torsion angles, and least-squares planes for dhmpe and [Ni(dhmpe)$_2$]Cl$_2$ (20 pages). Ordering information is given on any current masthead page.

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