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Synthesis and Photochemical Redox Reactivity of an Unsymmetrically Substituted Mn–Mn Bond: *mer, fac*-$Mn_2(CO)_6(PMe_2CH_2PMe_2)_2$

FREDERICK R. LEMKE and CLIFFORD P. KUBIAK*

Department of Chemistry, Purdue University, West Lafayette, Ind. 47907, U.S.A.

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Abstract

The reaction of $Mn_2(CO)_{10}$ with the diphosphine bis(dimethylphosphino)methane, dmpm, gives a mixture of two isomers: *mer, fac*-$Mn_2(CO)_6(dmpm)_2$, **1**, and *mer,mer*-$Mn_2(CO)_6(dmpm)_2$, **2**. Complex **1** is the first example of a bis(dmpm) complex with a *cis,trans* arrangement of the dmpm ligands. Both **1** and **2** can be thermally oxidized by one-electron to give the relatively stable binuclear radial cations [*mer,fac*-$Mn_2(CO)_6(dmpm)_2]^+$, **3**, and [*mer,mer*-$Mn_2(CO)_6(dmpm)_2]^+$, **4**, respectively. The EPR spectra of **3** and **4** in THF indicate localization of unpaired spin density on one of the two Mn metal centers. The EPR of **4** in CH_2Cl_2 indicates delocalization of unpaired spin density over both Mn metal centers. The unsymmetrical isomer, **1**, is a strong one-electron photoreductant. The excited state redox potential of **1**, E° (**3**/**1***), has been approximated to be $-1.35 \leqslant E^\circ$ (**3**/**1***)$\leqslant -1.87$ V *vs.* SCE. Under the same experimental conditions the symmetrical isomer **2** exhibits no photochemical redox behavior.

Introduction

The chemistry of diphosphine bridged di-manganese complexes has been actively studied by a number of groups over the past ten years. Synthetic and reactivity studies of di-manganese complexes bridged by bis(dimethylphosphino)methane (dmpm) [1], bis(diphenylphosphino)methane (dppm) [2], as well as a variety of other bis(dialkylphosphino)-methanes [1b, 2a, 3] have been described. There are however surprisingly few reports of photochemical studies of diphosphine bridged di-manganese complexes. This contrasts with the rich photochemistry of the unbridged Mn–Mn bonds of $Mn_2(CO)_nL_m$ (L = tertiary phosphine) complexes [4]. We report herein our initial studies of the synthesis and photochemistry of dmpm bridged complexes, $Mn_2(CO)_6(dmpm)_2$. The synthesis of a novel, unsymmetrically substituted isomer, *mer, fac*-$Mn_2(CO)_6(dmpm)_2$, **1**, is described as well as its photo-redox chemistry. The unsymmetrical, binuclear radical cation, [*mer, fac*-$Mn_2(CO)_6(dmpm)_2]^{+\bullet}$ is found to be the principal product of photo-redox reactions involving **1**.

Experimental

General

All reactions were carried out under an atmosphere of dry N_2 using standard Schlenk or dry-box techniques. Solvents and air-sensitive solutions were transferred via syringe or stainless steel cannula.

Materials

All solvents were deoxygenated prior to use. Tetrahydrofuran and toluene (Fischer Scientific Co.) were distilled from sodium and benzophenone. Methylene chloride (J. T. Baker Chemical Co.) was distilled from calcium hydride. Acetonitrile (J. T. Baker Chemical Co.) was dried and distilled from activated Linde 3 Å molecular sieves. Anhydrous diethyl ether (Mallinckrodt) and hexanes (Fischer Scientific Co.) were used as received. $Mn_2(CO)_{10}$ (Strem Chemical Co.) was used as received. Dmpm was either prepared by a modification [5] of literature procedures or obtained from Strem Chemical Co. Tropylium hexafluorophosphate (Aldrich), methyl viologen (Sigma), 1,4-dinitrobenzene (Aldrich), maleic anhydride (Fischer Scientific Co.), nitrobenzene (Mallinckrodt) and benzophenone (Fischer Scientific Co.) were used as received. $Ru(bipy)_3Cl_2$ [6] and $[Fe(C_5H_5)_2]X$ [7] (X = BF_4, PF_6) were prepared according to literature procedures.

Physical Measurements

Elemental analyses were performed by Dr. H. D. Lee of the Microanalytical Laboratory, Department of Chemistry, Purdue University. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 200 and 81 MHz respectively on a Varian XL-200 NMR spectrophotometer. ^1H NMR spectra were measured *vs.*

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*Author to whom correspondence should be addressed.

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internal TMS while $^{31}P\{^1H\}$ NMR spectra were measured *vs.* external 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer Model 700 spectrophotometer or a Perkin-Elmer Model 1710 FTIR. Electronic spectra were recorded on a Hewlett Packard 8450A diode array spectrophotometer. Gas samples were analyzed with a Carle Series S Analytical Gas Chromatograph. Lamps used for photolyses included a Xenon Corp. 150 W Xe arc lamp or an Ace/Hanovia 550 W medium pressure Hg lamp. X-band EPR spectra were recorded using a Varian E-109 spectrophotometer.

Preparation of mer, fac-$Mn_2(CO)_6(dmpm)_2$, (1), and mer, mer-$Mn_2(CO)_6(dmpm)_2$, (2)

$Mn_2(CO)_{10}$ (0.50 g, 1.28 mmol) and dmpm (0.50 ml, 3.23 mmol) in 20 ml toluene were refluxed for 4–6 h. The solvent was removed under vacuum and the residue dissolved in 5 ml THF. Diethyl ether was added to initiate precipitation and the mixture was cooled to –20 °C. The yellow–orange solid was filtered, washed with diethyl ether, and dried *in vacuo*. Yield 0.45 g (0.82 mmol, 63% based on $Mn_2(CO)_{10}$) of a mixture containing complexes **1** and **2**.

Complexes **1** and **2** can be separated by Soxhlet extraction. The solid obtained was extracted with diethyl ether until the extracts were colorless. The diethyl ether solution was transferred to another vessel via cannula. The diethyl ether was removed under vacuum. The residue was dissolved in a minimum of THF. Diethyl ether was added to initiate precipitation and the mixture was cooled to –20 °C to give **2** as an orange solid. The residue remaining was then extracted with THF until the extracts were colorless. The extract solution was then concentrated under vacuum, diethyl ether was added to initiate precipitation, and the mixture was cooled to –20 °C to give **1** as a yellow solid.

mer, fac-$Mn_2(CO)_6(dmpm)_2$, (**1**): *Anal.* Calc. for $C_{16}H_{28}Mn_2O_6P_4$: C, 34.93; H, 5.14. Found: C, 34.74; H, 5.15%. ^1H NMR (CD_2Cl_2): δ 3.25 (m, 2H, CH_2), 1.73 (d, J_{PH} 4 Hz, 6 H, CH_3), 1.58 (d, J_{PH} 8 Hz, 3 H, CH_3), 1.47 (d, J_{PH} 8 Hz, 3 H, CH_3). $^{31}P\{^1H\}$ NMR (CD_3CN/CH_3CN): [AA′BB′] centered at δ ~6.5. IR (THF): ν(CO) 2020(vw), 1940(m), 1890(s), 1860(s) cm^{-1}.

mer,mer-$Mn_2(CO)_6(dmpm)_2$, (**2**): *Anal.* Calc. for $C_{16}H_{28}Mn_2O_6P_4$: C, 34.93; H, 5.14. Found: C, 34.60; H, 5.33%. ^1H NMR (CD_2Cl_2): δ 2.15 (s, 1H, CH_2), 1.45 (s, 6H, CH_3). $^{31}P\{^1H\}$ NMR (CD_3CN/CH_3CN): δ 38.0(s). IR (THF): ν(CO) 1910(s), 1899(s), 1856(m) cm^{-1}.

Thermal Conversion of 1 to 2

Refluxing a sample of **1** in toluene for 12 h followed by the appropriate work-up (*vide supra*) yields **2** as the only isolated product.

Photochemical Conversion of 1 to 2

Broad band photolysis of a sample of **1** in THF under N_2 or CO atmosphere yields **2** as monitored by IR or $^{31}P\{^1H\}$ NMR spectrophotometry.

Oxidation of 1 and EPR Spectra

A THF solution (4 ml) of **1** (0.01 g, 0.018 mmol) was added to solid $[Fe(Cp)_2]X$ (X = BF_4, PF_6) (0.018 mmol). The slurry was stirred until all the ferricinium salt reacted. The solution was filtered, concentrated under vacuum, and placed in a quartz EPR tube. The EPR spectra were run in the temperature range of 0–60 °C; generally at room temperature. Reduction of the EPR sample in THF with cobaltacene (0.0034 g, 0.018 mmol) gave back **1** as determined by IR spectrophotometry. **3**: IR (THF): ν(CO) 2055(m), 2020(s), 1980(m), 1940(s), 1885(s) cm^{-1}.

Oxidation of 2 and EPR Spectra

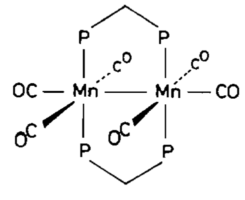
Oxidation of **2** and subsequent recording of EPR spectra were carried out in methylene chloride or THF in the same manner as for **1**. Reduction of the sample with cobaltacene gave back **2** as determined by IR spectrophotometry. **4**: IR (THF): ν(CO) 2060(w), 1960(s), 1915(s).

Photoredox Reactions of **1** *and* **2**

Acetonitrile and THF solutions which were approximately 2×10^{-5} M in metal complex and approximately 1×10^{-4} M in redox substrate (redox substrate = methyl viologen, 1,4-dinitrobenzene, maleic anhydride, nitrobenzene, $Ru(bipy)_3Cl_2$, or benzophenone) were prepared in evacuable 1 cm UV–Vis quartz cells. The samples were freeze-pump-thaw degassed three times on a high vacuum line. Samples were photolyzed using broad band irradiation from an Ace/Hanovia 550 W medium pressure Hg lamp. The irradiated samples were monitored periodically (5 to 15 minute intervals) by UV–Vis spectrophotometry. The electronic spectra obtained were compared to reported or experimentally determined electronic spectra of the reduced forms of the substrates to determine the extent of photoreduction.

Results and Discussion

The preparations of several diphosphine bridged dimanganese complexes, having the general structure **I**,

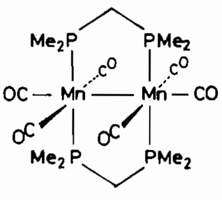


I

have been described previously by King and Raghuveer [1], Colton [2b–d] and Klemann [3]. In our studies of binuclear complexes bridged by dmpm, we sought to examine the chemistry and photochemistry of $Mn_2(CO)_6(dmpm)_2$. In our hands, the reaction of $Mn_2(CO)_{10}$ with 2 equivalents of dmpm, eqn. (1), gives a mixture composed of two isomers of

$$Mn_2(CO)_{10} + 2\ \mathrm{dmpm} \xrightarrow[\substack{110\,^\circ\mathrm{C} \\ 4\text{–}6\,\mathrm{h}}]{\mathrm{toluene}} Mn_2(CO)_6(dmpm)_2 + 4CO \qquad (1)$$

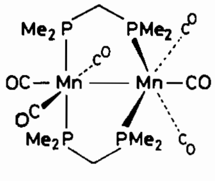
the general formula $Mn_2(CO)_6(dmpm)_2$. The isomers are separated by Sohxlet extraction with diethyl ether, followed by extraction with THF. Work up of the diethyl ether extract gives an orange crystalline solid, 2. Complex 2 exhibits only terminal carbonyl stretches in the range 2000–1800 cm^{-1}. The $^{31}P\{^1H\}$ NMR consists of a singlet at δ 38.0. The ^1H NMR consists of two broad singlets at δ 2.15 (CH_2) and δ 1.45 (CH_3) arising from the dmpm ligand. The spectroscopic data for 2 correspond well with the $Mn_2(CO)_6(dmpm)_2$ complex reported by King [1]. This complex is assigned a structure with a pair of transoid dmpm ligands and will be subsequently referred to as *mer,mer*-$Mn_2(CO)_6(dmpm)_2$, 2.



2

The THF extract, upon work-up, gives a yellow solid, 1. Complex 1 also possesses only terminal carbonyl stretches in the range 2000–1800 cm^{-1}. However, these appear at a different set of frequencies compared to 2. The $^{31}P\{^1H\}$ NMR of 1 is an AA′BB′ coupling system, characteristic of a asymmetric diphosphine bridged structure [9–11]. The ^1H NMR shows one broad multiplet at δ 3.25 for the methylene protons of the dmpm ligand; and three methyl resonances at δ 1.73, 1.58, and 1.47 all doublets, with relative intensities of 2:1:1 respectively. On the basis of these spectroscopic data, and our studies described below, we propose a *mer,fac*-$Mn_2(CO)_6(dmpm)_2$, structure for 1.

In the proposed structure of 1, we expect that the phosphorus nuclei are *trans* on one Mn center and *cis* on the other. The *cis,trans* dmpm coordination gives rise to a meridional arrangement of the three carbon monoxide ligands on one Mn and a facial arrangement on the other. The *cis,trans* diphosphine configuration, although unusual, does have several precedents. The compounds $[Rh_2(CO)Cl_2(P(OPh)_2N(Et)P(OPh)_2)_2]$ [8], $[Pt_2Me_3(dppm)_2]^+$ [9], $[Rh_2(CO)_3(dppm)_2]$ [10], and $[Ni_2(CNMe)_4(dppm)_2]^{+2}$ [11] all have bridging diphosphine ligands that are in a *trans* arrangement on one metal center and *cis* on the other. However, 1 represents the first example of a *cis,trans* configuration for a bis(dmpm) complex.



1

Complex 1 is readily converted to 2 thermally or photochemically. Increasing the reflux time of the original reaction (eqn. (1)) results in an increased yields of 2 and decreased yields of 1. After approximately 12 h, only 2 can be isolated. Likewise, refluxing 1 in THF or toluene results in its complete conversion to 2. The photochemical conversion of 1 in THF is readily monitored by IR and $^{31}P\{^1H\}$ NMR spectroscopies. In the IR, the carbonyl stretches of 1 at 1940 and 1860 cm^{-1} decrease in intensity while the carbonyl stretch at 1912 cm^{-1} for 2 increases as a function of photolysis time. The $^{31}P\{^1H\}$ NMR demonstrates this conversion more dramatically. The AA′BB′ coupling system centered at δ 6.5 for 1 decreases in intensity with increasing photolysis time. This is accompanied by the appearance and the continued increase in intensity of the singlet at δ 38.0 which corresponds to 2.

Complex 1 is easily oxidized by one electron to form an unusual binuclear radical cation, 3. Complex 1 is oxidizable by methyl viologen, tropylium, Ag(I), and ferricinium. This oxidation has been demonstrated to involve one electron by constant potential coulometry and by redox titrations with methyl viologen. The EPR spectrum of 3, Fig. 1, generated from 1 and $[Fe(Cp)_2]PF_6$, exhibits a six line pattern in THF with g $\sim$2.005 and a_{Mn} = 91 G at 60 °C. When the solvent is changed from THF to acetonitrile or methylene chloride only a broad featureless EPR resonance is observed. Complex 1 can be regenerated from the EPR sample in THF by reduction of 3 with $Co(Cp)_2$, as monitored by IR spectroscopy. The six line EPR spectrum in THF suggests localization of the unpaired electron on one of the two Mn (I = 5/2) centers. Localization of the unpaired spin could arise from coordination of solvent to a $16e^-$ Mn^I center. This would give one $18e^-$ $Mn^IP_2(CO)_3(THF)$ center and one 17e $Mn^0P_2(CO)_3$ radical center. Whether the unpaired electron is localized on the meridionally

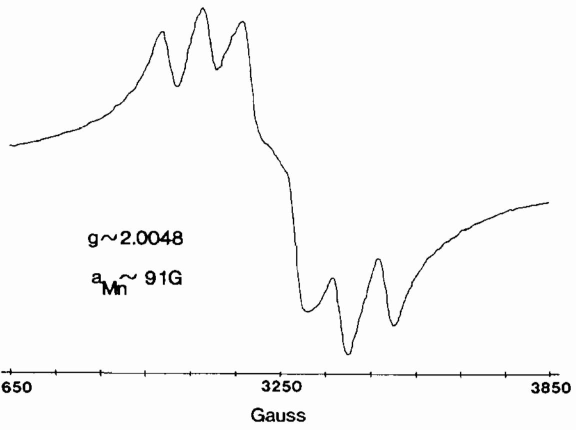
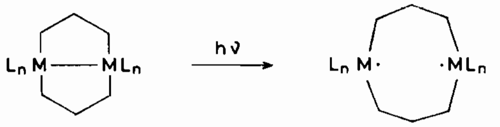


Fig. 1. X-band EPR spectrum of [*mer, fac*-$Mn_2(CO)_6(dmpm)_2]^{+\bullet}$, 3, in THF solution at 60 °C.

or facially coordinated Mn, however, is not clear at the present time.

Complex 2 can also be oxidized by one electron with Ag(I) or ferricinium to give a binuclear radical cation 4. The EPR spectrum of 4 in THF also exhibits a six line pattern with g ~2.009 and a_{Mn} ~96 G at 25 °C. However, upon changing the solvent to methylene chloride, an approximate eleven line pattern with g ~2.009 and a_{Mn} ~24 G becomes evident. As with 1 and 3, 2 analogously can be regenerated by reduction of 4 with $Co(Cp)_2$. The eleven line EPR spectrum in methylene chloride suggests that in 4 the unpaired electron is delocalized over both Mn centers. This is consistent with the expected symmetrical *mer,mer* structure of 4.

The photochemistry of $Mn_2(CO)_{10}$ and related unsupported Mn_2L_{10} systems has been studied extensively by Wrighton, Brown *et al.* [4]. Our bridged dimanganese complexes, 1 and 2, offer unique opportunities for the study of the photochemistry of Mn–Mn single bonds. Photolysis of a bridged Mn–Mn single bond may lead to a diradical excited state, in which the radical centers are in sufficiently close proximity, eqn. (2), to lead to cooperative radical chemistry.



(2)

The electronic spectrum of 2 in THF shows an absorbance at λ_{max} = 388 nm with ϵ = 10 000 M^{-1} cm^{-1}. This band is similar to the $\sigma \rightarrow \sigma^*$ absorption bands of related dimanganese complexes. The electronic spectrum of 1 exhibits an absorbance at significantly higher energy, λ = 328 nm (ϵ ~5000 M^{-1} cm^{-1}).

Photochemical experiments have demonstrated that 1 is a strong photoreductant in THF or acetonitrile. The generalized photochemical electron transfer is shown in eqn. (3). In our experiments the electron acceptor substrate, S, can be 1,4-dinitrobenzene, maleic anhydride, nitrobenzene, or $Ru(bipy)_3Cl_2$. Photolysis of a solution containing 1 and any of these substrates, S, results in formation of the corresponding reduced radical, $S^{-\bullet}$, and may be readily monitored by UV–Vis spectroscopy. These results are qualitatively similar to work reported by Tyler *et al.* [12] in which $Cp_2Co_2(CO)_6$, $Cp_2Fe_2(CO)_4$ and $Mn_2(CO)_{10}$, in the presence of phosphorus and nitrogen donors, were used as two-electron photoreducing agents for various organometallic and coordination complexes. The important difference to be noted is that 1, which must retain a rigorously binuclear structure, is observed to behave solely as a one-electron photoreductant to give the binuclear radical cation, 3. We note that under identical experimental conditions, 2 demonstrates no photoreducing capability.

$$1 + S \xrightarrow[CH_3CN]{h\nu} S^- + 3 \qquad (3)$$

A series of experiments with known one-electron acceptors has been employed to approximate the redox potentials, Fig. 2, of the ground and excited

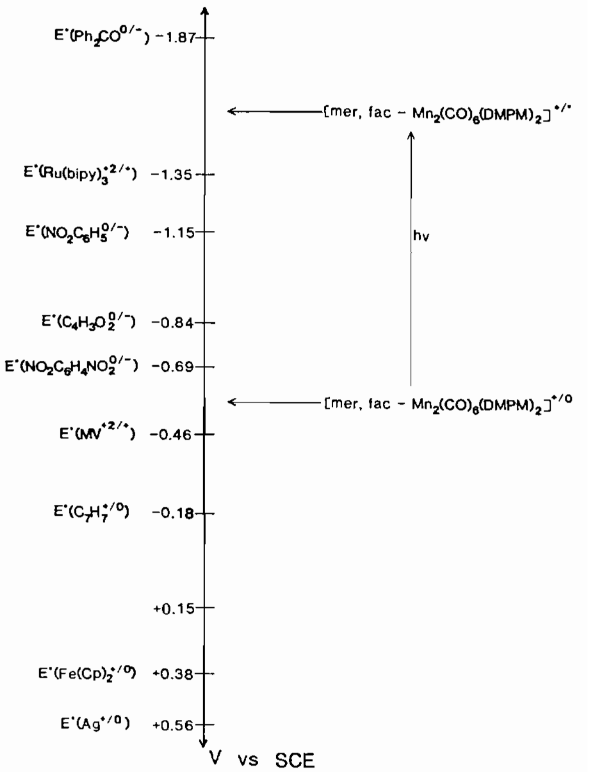


Fig. 2. Approximate excited state redox energy diagram for [*mer,fac*-$Mn_2(CO)_6(dmpm)_2]^{+/*}$ under steady state conditions.

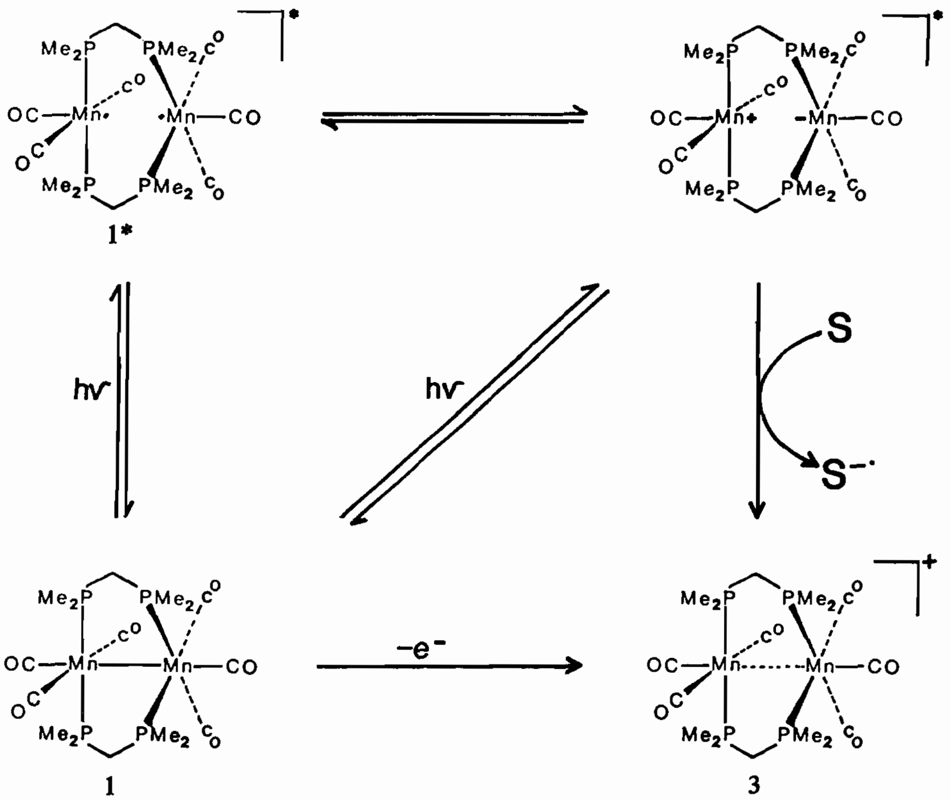


Fig. 3. Generalized scheme for thermal and photochemical electron transfers from [*mer,fac*-$Mn_2(CO)_6(dmpm)_2$].

states of **1**. The ground state of **1** is oxidizable between –0.46 and –0.69 V *vs.* SCE. Complex **1** will thermally reduce methyl viologen, $E_{1/2}$ = 0.46 V, but will only photochemically reduce 1,4-dinitrobenzene, $E_{1/2}$ = –0.69 V. The value of $E°(3/1)$ of –0.5 to –0.6 V determined by chemical methods corresponds well with that estimated from cyclic voltammetry studies of **1** in acetonitrile. The redox potential of the excited state of **1** has been bracketed between –1.35 and –1.87 V *vs.* SCE. For example, complex **1** will photochemically reduce $Ru(bipy)_3^{+2}$ to $Ru(bipy)_3^{+}$ but will not photochemically reduce benzophenone. This clearly shows that **1** is a powerful photoreductant. We note, $E°(3/1^*)$ is estimated to be ~0.5 V more cathodic than $E°(Ru(bpy)^{3+/2+*})$. In contrast to the photoredox behavior of $Ru(bipy)_3^{2+}$ and related systems, however, we do not observe the back electron transfer reaction, eqn. (4).

$$3 + S^{-\cdot} \longrightarrow 1 + S \qquad (4)$$

We believe this irreversibility of the electron transfer is due to rapid incorporation of solvent into the radical cation **3**. The structural change which accompanies solvent incorporation apparently retards the reduction of **3** by $S^{-\cdot}$.

A summary of the photochemical and thermal redox properties of **1** is shown in Fig. 3. Photolysis of the Mn–Mn single bond could proceed via a homolytic $\sigma \rightarrow \sigma^*$ transition resulting in a diradical excited state. However, since the assymetric structure of **1** is expected to significantly differentiate the orbital energies on each of the Mn centers, photolysis of the Mn–Mn single bond may proceed via a heterolytic metal-to-metal charge transfer to give a Zwitterionic excited state. The detailed nature of the excited state is presently under investigation. However, regardless of its nature, the excited state is sufficiently long lived for observable chemistry. The excited state reacts with a variety of redox substrates, S, to give the dinuclear radical cation **3** and radical anions $S^{-\cdot}$.

The photochemical redox behavior of **1** raises the possibility of an alternate pathway in the photochemistry of $Mn_2(CO)_{10-x}L_x$ (L = CO, PR_3) systems. A widely held view [4b,n,p,q] is that manganese carbonyl radicals, $Mn(CO)_{5-y}L_y^{\cdot}$, abstract $X^{\cdot}$ from organic halide substrates, RX, eqn. (5). In view

$$Mn(CO)_{5-y}L_y^{\cdot} + RX \longrightarrow Mn(CO)_{5-y}L_yX + R^{\bullet} \qquad (5)$$

of the potential photoredox ability of Mn_2 systems demonstrated by the present study, an alternate primary electron transfer photoprocess can be considered in which $Mn(CO)_{5-y}L_y^{\bullet}$ reduces RX, eqn. (6).

$$Mn(CO)_{5-y}L_y^{\bullet} + RX \longrightarrow Mn(CO)_{5-y}L_y^{+} + RX^{-\bullet} \quad (6)$$

The $RX^{-\bullet}$ radical may then lose halide, eqn. 7, to give the observed photoproduct, eqn. (8).

$$RX^{-\bullet} \longrightarrow R^{\bullet} + X^{-} \quad (7)$$

$$Mn(CO)_{5-y}L_y^{+} + X^{-} \longrightarrow Mn(CO)_{5-y}L_yX \quad (8)$$

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References

1 (a) R. B. King and K. S. Raghuveer, *Inorg. Chem., 23,* 2482 (1984); (b) K. S. Raghuveer, *Ph.D. Thesis,* University of Georgia, Athens, Ga., 1983.

2 (a) R. H. Reimann and E. Singleton, *J. Organomet. Chem. 38,* 113 (1972); (b) R. Colton, C. J. Commons and B. F. Hoskins, *J. Chem. Soc., Chem. Commun.,* 363 (1975); (c) C. J. Commons and B. F. Hoskins, *Aust. J. Chem., 28,* 1663 (1975); (d) R. Colton and C. J. Commons, *Aust. J. Chem., 28,* 1673 (1975); (e) K. G. Caulton and P. Adair, *J. Organomet. Chem., 114,* C11 (1976); (f) A. L. Balch and L. S. Benner, *J. Organomet. Chem., 135,* 339 (1977); (g) L. S. Benner, M. M. Olmstead and A. L. Balch, *J. Organomet. Chem., 159,* 289 (1978); (h) H. C. Aspinall and A. J. Deeming, *J. Chem. Soc., Chem. Commun.,* 724 (1981); (i) J. A. Marsella and K. G. Caulton, *Organometallics, 1,* 274 (1982); (j) T. W. Turney, *Inorg. Chim. Acta, 64,* L141 (1982); (k) H. C. Aspinall, A. J. Deeming and S. Donovan-Mtunzi, *J. Chem. Soc., Dalton Trans.,* 2669 (1983); (l) H. C. Aspinall and A. J. Deeming, *J. Chem. Soc., Chem. Commun.,* 838 (1983); (m) G. Ferguson, W. J. Laws, M. Parvez and R. J. Puddephatt, *Organometallics, 2,* 276 (1983); (n) H. C. Aspinall and A. J. Deeming, *J. Chem. Soc., Dalton Trans.,* 743 (1985).

3 T. E. Wolff and L. P. Klemann, *Organometallics, 1,* 1667 (1982).

4 (a) S. A. Haallock and A. Wojcicki, *J. Organomet. Chem., 54,* C27 (1973); (b) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc., 97,* 2065 (1975); (c) J. L. Hughey, IV, C. P. Anderson and T. J. Meyer, *J. Organomet. Chem., 125,* C49 (1977); (d) D. R. Kidd and T. L. Brown, *J. Am. Chem. Soc., 100,* 4095 (1978); (e) S. B. McCullen and T. L. Brown, *Inorg. Chem., 20,* 3528 (1981); (f) P. L. Boydan, A. Wong and J. D. Atwood, *J. Organomet. Chem., 229,* 185 (1982); (g) L. J. Rothberg, N. J. Cooper, K. S. Peters and V. Vaida, *J. Am. Chem. Soc., 104,* 3536 (1982); (h) S. B. McCullen, H. W. Walker and T. L. Brown, *J. Am. Chem. Soc., 104,* 4007 (1982); (i) A. F. Hepp and M. S. Wrighton, *J. Am. Chem. Soc., 105,* 5934 (1983); (j) A. F. Hepp, *Ph.D. Thesis,* Massachusetts Institute of Technology, Cambridge, Ma., 1983; (k) A. E. Stiegman and D. R. Tyler, *Inorg. Chem., 23,* 527 (1984); (l) H. W. Walker, R. S. Herrick, R. J. Olsen and T. L. Brown, *Inorg. Chem., 23,* 3748 (1984); (m) I. R. Dunkin, P. Harter and C. J. Shields, *J. Am. Chem. Soc., 106,* 7248 (1984); (n) R. S. Herrick, T. R. Herrinton, H. W. Walker and T. L. Brown, *Organometallics, 4,* 42 (1985); (o) M. S. Wrighton, J. L. Graff, J. C. Luong, C. L. Reichel and J. L. Robbins, 'Reactivity of Metal–Metal Bonds'; ACS Symposium Series No. 155, American Chemical Society, Washington, D.C., 1981, p. 85; (p) A. F. Hepp and M. S. Wrighton, *J. Am. Chem. Soc., 103,* 1258 (1981); (q) S. B. McCullen and T. L. Brown, *J. Am. Chem. Soc., 104,* 7496 (1982).

5 M. L. Kullberg, F. R. Lemke and C. P. Kubiak, *Inorg. Chem., 24,* 3589 (1985).

6 M. Hunziker and A. Ludi, *J. Am. Chem. Soc., 99,* 7370 (1977).

7 D. N. Hendrickson, Y. S. Sohn and H. B. Gray, *Inorg. Chem., 10,* 1559 (1971).

8 R. J. Haines, F. Meintjies and M. Laing, *Inorg. Chim. Acta, 36,* L403 (1979).

9 M. P. Brown, S. J. Cooper, A. A. Frew, L. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt, K. R. Seddon and M. A. Thomson, *Inorg. Chem., 20,* 1500 (1981).

10 C. Woodcock and R. Eisenberg, *Inorg. Chem., 24,* 1287 (1985).

11 D. L. DeLaet, D. R. Powell and C. P. Kubiak, *Organometallics, 4,* 954 (1985).

12 A. E. Stiegman, A. J. Goldman, D. B. Leslie and D. R. Tyler, *J. Chem. Soc., Chem. Commun.,* 632 (1984).