symmetry polytopal rearrangment is required, for example, digonal twisting of one ligand about its quasi-twofold axis. A bond rupture mechanism will also effect methyl group exchange within the C_s isomer, but we regard this mechanism as less likely for the reasons mentioned earlier.[31]

Registry No. [Nb(Me$_2$dtc)$_4$]Cl, 102921-79-9; [Ta(Me$_2$dtc)$_4$]Cl, 57483-73-5; [Ta(Me$_2$dtc)$_4$][TaCl$_6$], 57526-18-8; [Ta(i-Bu$_2$dtc)$_4$][TaCl$_6$], 102940-05-6; [Ta(Me,i-Prdtc)$_4$][TaCl$_6$], 102921-81-3; [Ta(Me,-Chdtc)$_4$][TaCl$_6$], 102921-83-5; [Ta(Me,Phdtc)$_4$][TaCl$_6$], 102921-85-7; [Ta(Me,Bzdtc)$_4$][TaBr$_6$], 102921-87-9; [Nb(Me$_2$mtc)$_4$][NbCl$_6$], 102921-89-1; [Ta(Me$_2$mtc)$_4$][TaCl$_6$], 102921-91-5.

Supplementary Material Available: Figures S1–S3 showing the methyl proton resonances of [Ta(Me,Chdtc)$_4$][TaCl$_6$], [Ta(Me,i-Prdtc)$_4$]-[TaCl$_6$], and [Ta(Me,Bzdtc)$_4$][TaBr$_6$] in CD$_2$Cl$_2$ solution (3 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Oregon, Eugene, Oregon 97403, and Columbia University, New York, New York 10027

Photochemical Disproportionation of Mn$_2$(CO)$_{10}$. Nineteen-Electron Intermediates and Ligand and Intensity Dependence
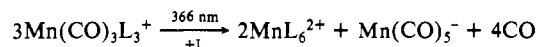
Albert E. Stiegman, Alan S. Goldman, Cecelia E. Philbin, and David R. Tyler*

The photochemical disproportionation of Mn$_2$(CO)$_{10}$ proceeds as

$$Mn_2(CO)_{10} \xrightarrow[+L,\ -2CO]{366\ nm} Mn(CO)_5^- + Mn(CO)_3L_3^+$$
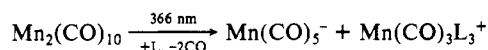
where L is a nitrogen or oxygen donor ligand. With many ligands, but not CH$_3$CN, a secondary disproportionation of Mn(CO)$_3$L$_3^+$ occurs:

$$3Mn(CO)_3L_3^+ \xrightarrow[+L]{366\ nm} 2MnL_6^{2+} + Mn(CO)_5^- + 4CO$$

The net reaction is thus

$$3Mn_2(CO)_{10} + 12L \xrightarrow{h\nu} 2MnL_6^{2+} + 4Mn(CO)_5^- + 10CO$$

The stoichiometry of Mn(CO)$_5^-$ formation in CH$_3$CN solution was measured and found to be as described in the initial equation above. Disproportionation of Mn$_2$(CO)$_{10}$ occurs with nitrogen- and oxygen-donor ligands but not with monodentate phosphines and phosphites; disproportionation does result, however, with the multidentate 1,2-bis(dimethylphosphino)ethane (dmpe), bis-(2-(diphenylphosphino)ethyl)phenylphosphine (triphos), and 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (tetraphos) ligands. These results are interpreted in terms of the previously proposed radical-chain pathway for Mn$_2$(CO)$_{10}$ disproportionation involving 19-electron Mn(CO)$_3$L$_3$ intermediates. It is proposed that steric bulk and electron-donating ability are the dominant factors in determining whether or not the dimer will photochemically disproportionate with a particular ligand. Disproportionation occurs with the chelating ligands because these ligands effectively increase the concentration of the key 19-electron intermediate. Two experiments provide additional evidence for the 19-electron intermediate: (1) Reaction of PMe$_3$ with Mn(CO)$_3$depe (depe = 1,2-bis(diethylphosphino)ethane) in the presence of Mn$_2$(CO)$_{10}$ in the dark gives disproportionation products. It is proposed that PMe$_3$ attacks Mn(CO)$_3$depe, giving the 19-electron complex Mn(CO)$_3$(depe)(PMe$_3$), which then reduces Mn$_2$(CO)$_{10}$. (2) The cationic product from the reaction of Mn$_2$(CO)$_{10}$ with tetraphos is Mn(CO)$_3$(tetraphos-P,P',P'')$^+$. The formation of this product and not Mn(CO)$_2$(tetraphos-P,P',P'',P''')$^+$ supports the proposal that the chain reaction involves electron transfer from a 19-electron Mn(CO)$_3$L$_3$ species rather than from a 17-electron Mn(CO)$_2$L$_3$ intermediate; the latter would yield the Mn(CO)$_2$L$_4^+$ cation product. The dependence of the disproportionation quantum yields on the exciting light intensity was investigated. In agreement with the proposed radical-chain mechanism, the quantum yields are linearly proportional to $I^{-1/2}$ (I = the absorbed intensity).

We have been studying the mechanism of the photochemical disproportionation reactions of Mn$_2$(CO)$_{10}$ (eq 1).[1,2] Our research

$$3Mn_2(CO)_{10} + 12L \xrightarrow{h\nu} 2MnL_6^{2+} + 4Mn(CO)_5^- + 10CO$$
$$L = \text{a ligand} \quad (1)$$
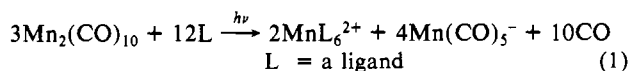
has two specific objectives: (1) we want to know the mechanism of reaction 1 and (2) we want to know why the dimer will photochemically disproportionate with some ligands but not others. In a recent paper, we discussed and answered questions pertaining to the first of these objectives.[3] In this paper we report results relevant to the second objective and we also report results consistent with our earlier proposal[3] that a 19-electron species is a key intermediate in reaction 1. Because the stoichiometry of eq 1 has never been measured, we also report experimental results

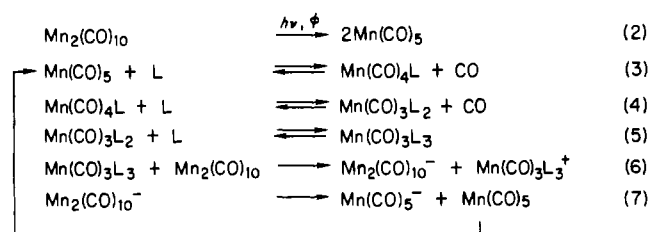concerning the stoichiometry of this reaction.

Experimental Section

Mn$_2$(CO)$_{10}$ was obtained from Strem Chemical Co. and sublimed prior to use. Pyridine (py), triethylamine (NEt$_3$), cyclohexylamine (NH$_2$Cy), and diethylenetriamine (dien) were obtained from Aldrich, stirred over sodium metal, and distilled under argon. Diethylenetriamine was vacuum distilled. Ethylenediamine (en, anhydrous) was obtained from Fisher and used as received. 1,2-Bis(dimethylphosphino)ethane (dmpe), 1,2-bis(diethylphosphino)ethane (depe), 1,2-bis(diphenyl-phosphino)ethane (dppe), bis(2-(diphenylphosphino)ethyl)phenyl-phosphine (triphos), 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphade-cane (tetraphos), di-n-propylphosphine, phenylphosphine, and tri-methylphosphine were obtained from Strem and used as received.

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(1) (a) Hieber, W.; Beck, W.; Zeitler, G. *Angew. Chem.* **1961,** *73,* 364–368. (b) Allen, D. M.; Cox, A.; Kemp, T. J.; Sultana, Q. *J. Chem. Soc., Dalton Trans.* **1976,** 1189–1193.
(2) McCullen, S. B.; Brown, T. L. *Inorg. Chem.* **1981,** *20,* 3528–3533.
(3) Stiegman, A. E.; Tyler, D. R. *Inorg. Chem.* **1984,** *23,* 527–529.

Scheme I

$$Mn_2(CO)_{10} \xrightarrow{h\nu,\ \phi} 2Mn(CO)_5 \qquad (2)$$

$$Mn(CO)_5 + L \rightleftharpoons Mn(CO)_4L + CO \qquad (3)$$

$$Mn(CO)_4L + L \rightleftharpoons Mn(CO)_3L_2 + CO \qquad (4)$$

$$Mn(CO)_3L_2 + L \rightleftharpoons Mn(CO)_3L_3 \qquad (5)$$

$$Mn(CO)_3L_3 + Mn_2(CO)_{10} \longrightarrow Mn_2(CO)_{10}^- + Mn(CO)_3L_3^+ \qquad (6)$$

$$Mn_2(CO)_{10}^- \longrightarrow Mn(CO)_5^- + Mn(CO)_5 \qquad (7)$$

Benzene was dried and distilled under argon.

The [Mn(CO)$_3$depe]$_n$ complex was generated in situ by irradiating (λ > 420 nm) a benzene solution of Mn$_2$(CO)$_{10}$ (10 mM) and depe (20 mM).[4] The appearance of a broad peak at 1886 cm^{-1} in the infrared spectrum was indicative of [Mn(CO)$_3$depe]$_n$ formation.

All photochemical reactions were carried out under anaerobic conditions in benzene, hexane, or cyclohexane solvent as previously described.[3,5] Irradiations were performed with an Oriel 200-W high-pressure mercury arc lamp. The reactions checking for the ligand dependence of the Mn$_2$(CO)$_{10}$ disproportionation were run at both low (0.2 M) and (if necessary) high (50/50; ligand/solvent) ligand concentration and with irradiation wavelengths of 366 nm and >420 nm. In all cases, for a given ligand, the occurrence of disproportionation was independent of ligand concentration and irradiating wavelength. Quantum yields were measured with the assistance of a Beckman DU spectrophotometer. Lamp intensities were determined with use of ferrioxalate actinometry.[6] Typical unattenuated lamp intensities were 2 × 10^{-6} einstein/min. 366 nm light was isolated with a Corning 7-83 narrow-band-pass filter; a Corning CS 3-73 filter was used for irradiations with λ > 420 nm. Lamp intensities were attenuated with neutral density filters obtained from Oriel. The disappearance of Mn$_2$(CO)$_{10}$ was monitored at 343 nm (ϵ = 21 400). Infrared spectroscopy was used to monitor the reactions for the stoichiometry measurements. The following peaks were monitored: Mn$_2$(CO)$_{10}$, 1981 cm^{-1} (ϵ = 2300); Mn(CO)$_5^-$, 1863 cm^{-1} (ϵ = 6300).

Results and Discussion

Measurement of the Stoichiometry. In a recent paper[3] we showed that the disproportionation of Mn$_2$(CO)$_{10}$ by amine ligands followed the pathway in Scheme I. The net reaction according to Scheme I is
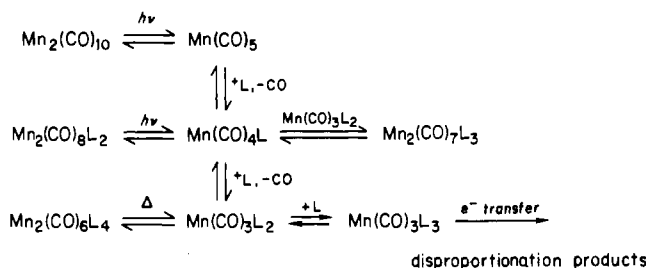
$$Mn_2(CO)_{10} + 3L \xrightarrow{h\nu} Mn(CO)_5^- + Mn(CO)_3L_3^+ + 2CO \qquad (8)$$
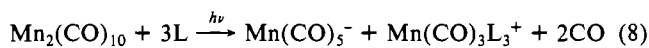
When eq 1 is compared to eq 8, some confusion may result because the cationic product in eq 8 is Mn(CO)$_3$L$_3^+$ whereas MnL$_6^{2+}$ is the cationic product in eq 1. Brown and McCullen[2] clarified this point by showing that Mn(CO)$_3$L$_3^+$ (L = an amine) photochemically disproportionates according to eq 9 to give MnL$_6^{2+}$ and

$$3Mn(CO)_3L_3^+ \xrightarrow[+L]{h\nu} 2MnL_6^{2+} + Mn(CO)_5^- + 4CO \qquad (9)$$

$$L = \text{an amine ligand}$$
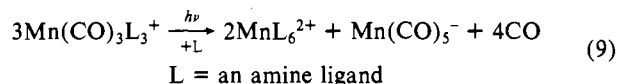
Mn(CO)$_5^-$. This secondary photolysis reaction is thus the origin of the MnL$_6^{2+}$ product in eq 1. Unfortunately, reaction 9 is not a clean stoichiometric reaction and this complicates the measurement of the stoichiometry of the disproportionation reaction.[7] However, we found that Mn(CO)$_3$(CH$_3$CN)$_3^+$ does not disproportionate according to eq 9; irradiation (λ = 366 nm) of Mn(CO)$_3$(CH$_3$CN)$_3^+$ in CH$_3$CN caused the disappearance of Mn(CO)$_3$(CH$_3$CN)$_3^+$, but no Mn(CO)$_5^-$ or other carbonyl-containing metal species formed. The stoichiometry of reaction 8 can, therefore, be measured in part. In a typical experiment, irradiation

Scheme II

$$Mn_2(CO)_{10} \xrightleftharpoons{h\nu} Mn(CO)_5$$

$$\Bigg\updownarrow {}^{+L,\ -CO}$$

$$Mn_2(CO)_8L_2 \xrightleftharpoons{h\nu} Mn(CO)_4L \xrightleftharpoons{Mn(CO)_3L_2} Mn_2(CO)_7L_3$$

$$\Bigg\updownarrow {}^{+L,\ -CO}$$

$$Mn_2(CO)_6L_4 \xrightleftharpoons{\Delta} Mn(CO)_3L_2 \xrightleftharpoons{+L} Mn(CO)_3L_3 \xrightarrow{e^-\ transfer}$$

disproportionation products

(λ = 366 nm) of a 20.4 mM solution of Mn$_2$(CO)$_{10}$ in CH$_3$CN produced 19.3 mM Mn(CO)$_5^-$ as measured by infrared spectroscopy. The 1:1 Mn$_2$(CO)$_{10}$:Mn(CO)$_5^-$ ratio strongly suggests the stoichiometry in eq 8, consistent with the proposed mechanism.

Ligand Dependence. Scheme II, which is a compilation of Scheme I, equilibrium 18 (discussed below), and several previously proposed equilibria,[4] is helpful to discussing the ligand dependence of the Mn$_2$(CO)$_{10}$ disproportionation reactions. As is evident from the scheme, any factor that affects the rate of electron transfer or that affects the concentration of Mn(CO)$_3$L$_3$ will affect the disproportionation process. Thus, if L is very bulky, the formation of Mn(CO)$_3$L$_3$ is slow and disproportionation is inefficient. Or, if L is so bulky that Mn(CO)$_3$L$_3$ cannot form, then disproportionation does not occur at all. Similarly, if L is a poor donor, then the electron-transfer step is slow (if it occurs at all) and disproportionation is again inefficient.[8] The concepts above are general and also apply, for example, to the disproportionation of Cp$_2$Mo$_2$(CO)$_6$. (In a previous paper on Cp$_2$Mo$_2$(CO)$_6$,[10] we presented the concept of electronic and steric "cutoffs". This concept is a more restrictive version of the ideas presented above because it ignores the possibility, for example, that an unfavorable equilibrium for formation of the 19-electron species can be offset by a very fast electron-transfer step.)

Consistent with the interpretation above, we found that, in general, the dimer will photochemically disproportionate with amine and oxygen-donor ligands (good electron donors[10]); monodentate phosphine and phosphite ligands (poorer electron donors compared to the amines[10]) gave only substitution products.[11,12] Specifically, we found that the dimer will photochemically disproportionate with acetone, THF, NEt$_3$, dien, en, pyridine, NH$_2$Ph, dmpe, NH$_2$Cy, and CH$_3$CN but not with P(i-Pr)$_3$, depe, P(n-Bu)$_3$, PPh$_3$, dppe, P(OPh)$_3$, PMe$_3$, PH(n-Pr)$_2$, PH$_2$Ph, and P(OCH$_3$)$_3$. (In the case of PMe$_3$, a product formed with CO stretching bands very similar to those of Mn(CO)$_5^-$, a result which at first suggested that disproportionation was occurring. However, the IR spectrum of the product is unaffected by addition of CF$_3$COOH to the reaction solution. Control experiments showed that Mn(CO)$_5^-$ is converted to HMn(CO)$_5$ under these conditions, and we concluded that the unidentified product is not Mn(CO)$_5^-$.)

Interestingly, Mn$_2$(CO)$_{10}$ will photochemically disproportionate with the tridentate ligand triphos (λ > 420 nm; solvent benzene;

(4) Complete details of the generation and reactivity of [Mn(CO)$_3$depe]$_n$ are found in: Goldman, A. S.; Tyler, D. R., submitted for publication in *J. Organomet. Chem.*

(5) Tyler, D. R. *Inorg. Chem.* **1981**, *20*, 2257–2261.

(6) (a) Calvert, J. G.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966. (b) Bowman, W. D.; Demas, J. N. *J. Phys. Chem.* **1976**, *80*, 2434.

(7) Note in reaction 9 that the Mn complexes that are reduced to Mn(CO)$_5^-$ must acquire two additional CO ligands. This feature of the reaction is probably responsible for the low yields of Mn(CO)$_5^-$ in reaction 8.[2] Qualitatively, we noted that the yield of Mn(CO)$_5^-$ was increased under a CO atmosphere and it decreased with a nitrogen purge of the reaction solution.

(8) The electron-donating ability of a ligand is important in determining whether disproportionation will occur because the 19-electron species Mn(CO)$_3$L$_3$ must have sufficient potential to reduce the Mn$_2$(CO)$_{10}$ complex ($E_{1/2}$ = –1.7 V vs. Ag$^+$/Ag)[9] (see reaction 6 in Scheme I). As the electron-donating ability of L increases, the 19-electron intermediate becomes a better reducing agent.

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

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

(11) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095–4102.

(12) Results from other laboratories are consistent with our conclusion that phosphine ligands will not disproportionate the Mn$_2$(CO)$_{10}$ complex upon irradiation. For example, Brown and co-workers,[4a,11,13] who did much of the original photochemical work with Mn$_2$(CO)$_{10}$ and phosphines, never reported the formation of Mn(CO)$_5^-$ or its substituted derivatives. Instead, they always found Mn(CO)$_3$L$_2$, HMn(CO)$_3$L$_2$, or substituted Mn$_2$(CO)$_{10}$ products, depending on the nature of L and the reaction conditions.

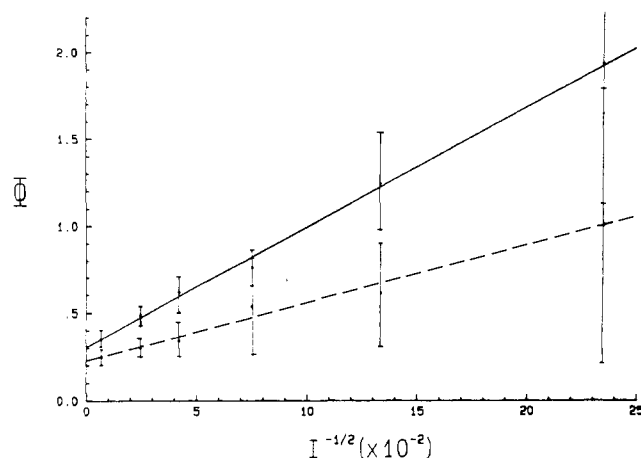(13) McCullen, S. B.; Walker, H. W.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4007–4008.

Figure 1. Plot of the disappearance quantum yield (Φ) for the disproportionation of $Mn_2(CO)_{10}$ at 366 nm in benzene containing 2.0 M pyridine (--) or 0.2 M dien (—) vs. $I^{-1/2}$ ((einstein/min)$^{-1/2}$). [$Mn_2(CO)_{10}$] = 1 × 10^{-2} M.

$Mn(CO)_3triphos^+$, $\nu(C\equiv O)$ = 2026 (s), 1960 (sh), 1945 (s) cm^{-1}; $Mn(CO)_5^-$, $\nu(C\equiv O)$ = 1889 (s), 1865 (vs), 1842 (s) cm^{-1}. When the ionic product was precipitated from the reaction solution by the addition of cyclohexane and then dissolved in CH_2Cl_2, the resulting solution infrared spectrum ($\nu(C\equiv O)$ = 2030 (s), 1959 (s), 1903 (s), 1864 (s) cm^{-1}) was in good agreement with that reported for the thermally generated compound [Mn-(CO)$_3$tripod][Mn(CO)$_5$] (tripod = 1,1,1-tris((diphenylphosphino)methyl)ethane); $\nu(C\equiv O)$ = 2030 (s), 1962 (s), 1902 (ms), 1860 (s) cm^{-1} in CH_2Cl_2.[14] We propose that disproportionation results with the triphos ligand because the chelating nature and the reduced size[15] of coordinated triphos (compared to those of three monodentate phosphines) will favor the formation of the 19-electron $Mn(CO)_3$triphos intermediate. An increased concentration of $Mn(CO)_3$triphos will increase the rate of the electron-transfer step, and therefore disproportionation occurs. A similar argument explains why photochemical disproportionation of $Mn_2(CO)_{10}$ also occurs with tetraphos and dmpe. (Note that dmpe (θ = 107°) is significantly smaller than depe (θ = 115°);[15] the steric bulkiness of the latter chelate apparently prevents it from disproportionating $Mn_2(CO)_{10}$.)

Quantum Yields. The quantum yields for the photochemical disproportionation of $Mn_2(CO)_{10}$ according to the chain mechanism in Scheme I should be intensity-dependent.[16] Specifically, the following relationship between the quantum yields and the absorbed intensity (I) can be derived[16] (at constant ligand and $Mn_2(CO)_{10}$ concentration):

$$\Phi = c_1 + c_2 I^{-1/2} \qquad c_1, c_2 = \text{constants} \qquad (10)$$

Plots of Φ vs. $I^{-1/2}$ for the disproportionation of $Mn_2(CO)_{10}$ by pyridine and dien are shown in Figure 1. Clearly, Φ is linearly proportional to $I^{-1/2}$, a result consistent with the proposed chain mechanism in Scheme I.

One point needs to be clarified. Because Φ is dependent on I, any comparison of the quantum yields for disproportionation for various ligands must be made by using the same radiation intensity. In a previous paper,[3] we compared $Mn_2(CO)_{10}$ disproportionation quantum yields for pyridine, NEt$_3$, ethylenediamine, and diethylenetriamine. The quantum yields increased in the following order: py, NEt$_3$ < en < diene (i.e. monodentate < bidentate < tridentate). We now recognize that the results we reported were unintentionally biased because the quantum yields with dien are measured at lower light intensity, an experimental condition which will increase the dien quantum yields with respect to the others. For that reason, we repeated all of the quantum

Table I. Disappearance Quantum Yields for the Disproportionation^a of $Mn_2(CO)_{10}$ at Constant Exciting Light Intensity (I = 2 × 10^{-6} einstein/min)

ligand	concn,^{c} M	Φ^d
pyridine	2^b	0.34 (0.02)
NEt$_3$	2^b	0.33 (0.02)
NH$_2$Cy	2^b	0.39 (0.04)
NH$_2$CH$_2$CH$_2$NH$_2$	0.2	0.43 (0.05)
NH(CH$_2$CH$_2$NH$_2$)$_2$	0.2	0.52 (0.01)

$^a \lambda$ = 366 nm. ^{b} Substitution products form at lower concentrations. ^{c} In benzene. ^{d} The number in parentheses is the standard deviation.

Scheme III
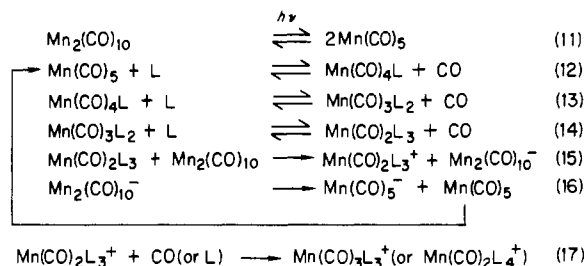
yields with the various amines using a constant lamp intensity. The quantum yields are shown in Table I. Note that the ordering still follows the pattern monodentate < bidentate < tridentate. The difference is that the quantum yields for disproportionation with diene are smaller than our previously measured values because in this case the absorbed intensity was considerably higher. (The dependence on the denticity of the amine ligand is also seen in the plots in Figure 1. Also note that the y intercepts in Figure 1 are less than or equal to ϕ, the quantum yield for homolysis in reaction 2.)

Evidence for a 19-Electron $Mn(CO)_3L_3$ Intermediate. An alternative chain mechanism for the disproportionation of $Mn_2(CO)_{10}$ is shown in Scheme III.[17] The key difference between Schemes I and III is that no 19-electron complex is formed in Scheme III; rather it is the highly substituted 17-electron $Mn(CO)_2L_3$ complex that transfers the electron to $Mn_2(CO)_{10}$ (eq 15). To differentiate between Schemes I and III, we irradiated (λ > 420 nm) $Mn_2(CO)_{10}$ (10 mM) in benzene with the tetradentate ligand tetraphos (15 mM). Disproportionation occurred, and the cationic product was identified as $Mn(CO)_3$(tetraphos-P,P',P'')$^+$ ($\nu C\equiv O$) = 2027 (s), 1946 (s) cm^{-1}; for comparison $\nu(C\equiv O)$ bands for [$Mn(CO)_3(PEt_3)_3^+$][ClO$_4^-$] are 2021 (s) and 1943 (s) cm^{-1} in CH_2Cl_2);[18,19] i.e., one phosphorous atom of the tetraphos ligand is not coordinated. If $Mn(CO)_2L_3$ formed as an intermediate as in Scheme III, then after electron transfer the 16-electron $Mn(CO)_2L_3^+$ complex would result. With a tetradentate ligand and with the assumption that ring-closure steps are fast, $Mn(CO)_2L_4^+$ would be the expected cationic product.[17] Note that numerous products of the type $Mn(CO)_2L_4^+$ are known,[18,20] e.g. $Mn(CO)_2(QP)^+$ (QP = tris(o-(diphenylphosphino)phenyl)phosphine). The formation of $Mn(CO)_3$(tetraphos-P,P',P'')$^+$ is thus consistent with Scheme I and a 19-electron intermediate.

Another key experiment supporting the intermediacy of a 19-electron reductant in the disproportionation pathway utilizes the $Mn(CO)_3$depe complex. As we demonstrate elsewhere, the monomer radical $Mn(CO)_3$depe is in equilibrium (in solution) with the metal–metal-bonded dimer [$Mn(CO)_3$depe]$_2$:[21]

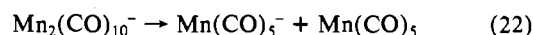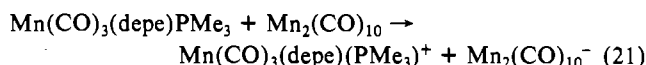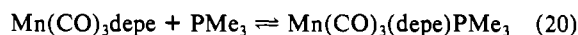$$Mn_2(CO)_6(depe)_2 \rightleftharpoons 2Mn(CO)_3depe \qquad (18)$$
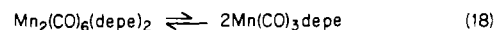
(14) Ellermann, J.; Lindner, H. A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1967**, *31B*, 1350–1355.
(15) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.
(16) Stiegman, A. E.; Tyler, D. R. *J. Am. Chem. Soc.* **1985**, *107*, 967–971.

(17) Goldman, A. S.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 4066–4067.
(18) Uson, R.; Riera, V.; Gimeno, J.; Laguna, M.; Gamasa, M. P. *J. Chem. Soc., Dalton Trans.* **1979**, 996–1002.
(19) The tetraphos-P,P',P'' nomenclature indicates that three phosphorus atoms of the triphos ligand are coordinated to the Mn atom.
(20) Chiswell, B.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 417–419.

Addition *in the dark* of PMe$_3$ to a benzene solution of [Mn-(CO)$_3$depe]$_n$ and Mn$_2$(CO)$_{10}$ (1:2) results in the gradual disappearance of the Mn$_2$(CO)$_{10}$ and [Mn(CO)$_3$depe]$_2$ and the appearance of Mn(CO)$_5$⁻ and Mn(CO)$_3$L$_3$⁺. The anionic product was identified by infrared spectroscopy[3] (ν(C≡O) = 1906 (sh), 1889 (s), 1865 (s), 1842 (sh) cm⁻¹ (in C$_6$H$_6$); ν(C≡O) = 1900 (s), 1861 (s) cm⁻¹ (in CH$_2$Cl$_2$)). By comparison to literature infrared spectra, the cationic product (ν(C≡O) = 2016 (m), 1935 (s) cm⁻¹ (in C$_6$H$_6$); ν(C≡O) = 2021 (m), 1946 (s) cm⁻¹ (in CH$_2$Cl$_2$)) could only be identified as *fac*-Mn(CO)$_3$L$_3$⁺ (L = phosphine). (For example, ν(C≡O) bands for [Mn(CO)$_3$-(PEt$_3$)$_3$][ClO$_4$] are 2021 (s) and 1943 (s) cm⁻¹, in CH$_2$Cl$_2$.[9]) Presumably, the cation can be formulated as *fac*-Mn(CO)$_3$-(depe)(PMe$_3$)⁺. Scheme IV accounts for these results. Essentially we are proposing that the 17-electron Mn(CO)$_3$depe complex

reacts with PMe$_3$ to form the 19-electron Mn(CO)$_3$(depe)PMe$_3$ complex, which then reduces Mn$_2$(CO)$_{10}$ as in the disproportionation mechanism (Scheme I). Note that the three phosphorus ligands of the 19-electron Mn(CO)$_3$(depe)PMe$_3$ species have a smaller cone angle sum (θ_{total} = 348° = 230° (bidentate depe) + 118° (PMe$_3$)) than do those of either Mn(CO)$_3$(PMe$_3$)$_3$ (θ_{total} = 354°) or Mn(CO)$_3$(depe-*P*,*P*′)(depe-*P*) (θ_{total} ≈ 362° = 230° (bidentate depe) + ~132° (monodentate depe, assumed to be approximately equal to θ(PEt$_3$)).[15] Evidently, the smaller total size of the depe and PMe$_3$ ligands permits the formation of the mixed-phosphine 19-electron species and disproportionation occurs.

Scheme IV

$$[\text{Mn(CO)}_3\text{depe}]_2 \rightleftharpoons 2\text{Mn(CO)}_3\text{depe} \qquad (19)$$

$$\text{Mn(CO)}_3\text{depe} + \text{PMe}_3 \rightleftharpoons \text{Mn(CO)}_3(\text{depe})\text{PMe}_3 \qquad (20)$$

$$\text{Mn(CO)}_3(\text{depe})\text{PMe}_3 + \text{Mn}_2(\text{CO})_{10} \rightarrow$$
$$\text{Mn(CO)}_3(\text{depe})(\text{PMe}_3)^+ + \text{Mn}_2(\text{CO})_{10}^- \qquad (21)$$

$$\text{Mn}_2(\text{CO})_{10}^- \rightarrow \text{Mn(CO)}_5^- + \text{Mn(CO)}_5 \qquad (22)$$

(21) Brown and co-workers have found that long-lived radicals of the type M(CO)$_3$L$_2$ (M = Mn, Re; L = tertiary phosphine or phosphite) can be generated by irradiation of the corresponding M$_2$(CO)$_{10}$ dimers in the presence of excess L.[22] The tendency of these species not to undergo dimerization is primarily a result of their great steric bulk. The generation of Mn(CO)$_3$L$_2$ requires prolonged irradiation and frequent removal of the CO generated in order to drive the reaction to completion. As we report elsewhere,[4] complexes of the type Mn(CO)$_3$L$_3$ can be conveniently and quantum efficiently generated by irradiation of 1:2 solutions of Mn$_2$(CO)$_{10}$ and bidentate phosphines such as depe. Because depe is less sterically bulky than the phosphines used by Brown, a greater tendency to dimerization is observed.
(22) (a) Kidd, D. R.; Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4103–4107. (b) McCullen, S. B.; Brown, T. D. *J. Am. Chem. Soc.* **1982**, *104*, 7496–7500. (c) Walker, H. W.; Rattinger, G. B.; Belford, R. L.; Brown, T. L. *Organometallics* **1983**, *2*, 775–776.

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Solution Chemistry of Ethane-1,2-dithiolate Complexes: Equilibria and Electron-Transfer Reactions

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The first-transition-series complexes of ethane-1,2-dithiolate (edt) constitute the structurally most diverse set of homoleptic complexes yet characterized. Following prior reports of synthesis and solid-state structures, the present investigation provides definition of the structures and redox reactions of [Ti(edt)$_3$]²⁻, [V$_2$(edt)$_4$]²⁻, [Cr(edt)$_2$]²⁻, [Co(edt)$_2$]²⁻, [Co(edt)$_2$]⁻, [Fe$_2$(edt)$_4$]²⁻, and [Mn$_2$(edt)$_4$]²⁻ in aprotic solvents. All species possess characteristic absorption spectra dominated by LMCT features, and all are redox-active. The results of coulometric and cyclic voltammetry are presented. [Ti(edt)$_3$]²⁻ ($E_{p,c}$ = -2.09 V vs. SCE (MeCN)) and [Cr(edt)$_2$]²⁻ ($E_{p,c}$ = -1.00 V (DMF)) are irreversibly reduced and oxidized, respectively; all other species exhibit chemically reversible electron-transfer reactions ($i_{p,c}/i_{p,a}$ ≅ 1). [Cr(edt)$_2$]²⁻ (4.95 μ_B) retains its planar structure in solution. Planar [Co(edt)$_2$]⁻ and tetrahedral [Co(edt)$_2$]²⁻ are reversibly interconverted at $E_{1/2}$ = -1.16 V (MeCN). These species were generated separately by controlled-potential electrolysis of acetonitrile solutions prepared from (Me$_4$N)$_3$[Co$_2$(edt)$_4$], which contains a 1:1 ratio of these species. The weak paramagnetism of [V$_2$(edt)$_4$]²⁻ (0.9 μ_B, MeCN) indicates retention of its unusual tetrabridged structure in solution. Oxidation at $E_{1/2}$ = -0.61 V (MeCN) gives the somewhat unstable complex [V$_2$(edt)$_4$]⁻, which was not isolated. The other two [M$_2$(edt)$_4$]²⁻ complexes (M = Fe(III), Mn(III)) have lateral doubly bridged dimeric structures in the solid state. In solution they exhibit solvent- and concentration-dependent magnetic behavior consistent with the equilibrium [M$_2$(edt)$_4$]²⁻ ⇌ 2[M(edt)$_2$(solv)$_2$]⁻. The mole fraction of monomer is higher in Me$_2$SO than in MeCN. [Fe$_2$(edt)$_4$]²⁻ is not detectably dissociated in acetonitrile. These species are reversibly reduced to tetrahedral [M(edt)$_2$]²⁻ at $E_{1/2}$ = -1.13 V (Fe) and -0.94 V (Mn) in acetonitrile. An ECE-type mechanism is established by cyclic voltammetry and chronoamperometry for the reduction of [Fe$_2$(edt)$_4$]²⁻ in acetonitrile. Apparent lability to dissociation prevented a similar determination for the [Mn$_2$(edt)$_4$]²⁻ system. The electrochemistry of acetonitrile and Me$_2$SO solutions prepared from [Mn$_2$(edt)$_4$]²⁻ showed a significant dependence on electrode surface. As manifested in large peak-to-peak separations (ΔE_p) in cyclic voltammetry, the heterogeneous electron-transfer rate constant at a Pt electrode is ~10³ smaller than those at a glassy-carbon or basal pyrolytic graphite electrode. Solutions of the Fe(III) and Mn(III) dimers in acetonitrile solutions exhibited adsorption phenomena at a glassy-carbon electrode that had been initialized near 0 V before potential sweep. This treatment caused oxidation of the complexes and filming of the electrode, and a cathodic shift of the reduction potential of the adsorbed Mn(III) species compared to that of the diffusion-controlled process. These observations provide a rationalization of extremely large ΔE_p values (0.5–1.1 V) previously reported. Any contributions from structural changes to these values is overwhelmed by other effects. Indeed, the reaction [Co(edt)$_2$]⁻ + e⁻ ⇌ [Co(edt)$_2$]²⁻ is a reversible charge transfer under conditions where the Mn systems exhibit ΔE_p ≥ 120 mV.

Introduction

A substantial portion of our recent work aimed at a development of the chemistry of metal thiolates, a subject pertinent to metal coordination units in a variety of proteins and enzymes containing native and nonnative metal ions, has involved complexes of eth-

ane-1,2-dithiolate (edt).[1–4] Some 19 structural determinations of edt complexes of the first transition series,[1–9] including con-

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