formation of $^{*}\mathrm{py}^{\bullet}$, though energetically less favorable, is faster than formation of $\mathrm{py}^{\bullet}$. In the case of back reactions, the lowest electronic excited states of Ir_2 and py^{+} are too energetic to be formed in recombination reactions, and inverted behavior is observed.

Regardless of the disparity between the *ET and ^{b}ET reactions, our data demonstrate that inverted driving-force effects can be observed in *bimolecular* ET reactions. The appearance of inverted effects only for ^{b}ET reactions may be a feature common to many of the other bimolecular ET systems that have been studied. If formation of electronically excited products is indeed the reason for this disparity, then it should be possible to select donors and acceptors that exhibit inverted driving-force effects in bimolecular photoinduced ET reactions as well.

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Supplementary Material Available: Table of rates and driving forces for photoinduced ET and thermal recombinations (1 page). Ordering information is given on any current masthead page.

Haloalkanes as Ligands. Spectroscopic and Energetic Studies of $\mathrm{CpMn(CO)_2XR}$

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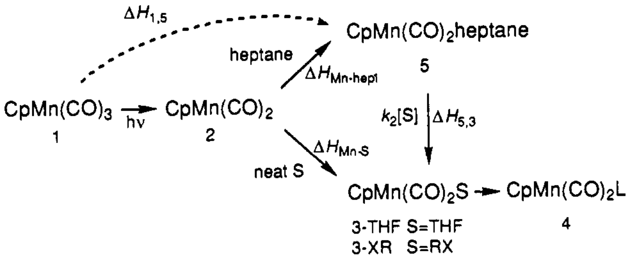
A number of metal complexes containing chloro-, bromo- or iodocarbons ligated through the halide atom have been prepared and, in several instances, characterized by X-ray diffraction.[1,2] While many of these complexes involve chelation of a bound ligand, it is evident that coordination of a haloalkane in an intermolecular fashion is possible. O'Driscoll and Simon have shown that coordination of an alkyl halide to a transition metal complex is a rapid process, complete within 5 ns of light absorption.[3] Recent gas-phase studies by Bogdan, Wells, and Weitz have found that the Cl–W bond strength in $\mathrm{ClF_2CCl{-}W(CO)_5}$ is 19.7 ± 0.6 kcal/mol.[4]

We have found that coordination of a number of haloalkanes (RX) to the formally $16e^-$ $\mathrm{CpMn(CO)_2}$ moiety occurs readily.[5] These complexes have been characterized at low temperature by FTIR and UV/visible spectroscopies, and the Mn–XR bond strengths have been probed by time-resolved photoacoustic calorimetry.

Photolysis ($\lambda < 400$ nm) of $\mathrm{CpMn(CO)_3}$ (**1**) in donor solvents such as THF leads to formation of the solvate $\mathrm{CpMn(CO)_2(THF)}$ (**3-THF**).[6] The coordinatively unsaturated intermediate **2** is presumably involved. Donor molecules present in solution rapidly displace THF from **3-THF** to yield **4** (Scheme I).[6] At low temperature in the absence of L, the solvated species **3** have sufficient lifetimes to be characterized spectroscopically. Thus, photolysis of $\mathrm{CpMn(CO)_3}$ in the presence of a wide variety of haloalkanes at 195 K allows spectroscopic characterization of $\mathrm{CpMn(CO)_2S}$ (**3-XR**). These results are summarized in Table I.

Scheme I



The difference FTIR and UV/visible spectra are very similar for photolyses of $\mathrm{CpMn(CO)_3}$ in different neat haloalkane solutions. In the infrared spectrum at 195 K, bleaching of the starting material absorbances at 1932 and 2021 $\mathrm{cm^{-1}}$ is observed together with the appearance of a single new absorption at ~1870 $\mathrm{cm^{-1}}$. Except for the photolyses in $\mathrm{CH_2Cl_2}$, a second band is obscured by the intense starting material band at 1932 $\mathrm{cm^{-1}}$. In neat $\mathrm{CH_2Cl_2}$ solution the higher energy band is shifted away from the starting material absorption and appears at 1946 $\mathrm{cm^{-1}}$. The difference UV/visible spectra display new absorptions with $\lambda_{\max} = {\sim}395$ and ~500 nm. These absorption maxima are consistent with the appearance of a bright red color during preparative scale photolyses. Complex **3-THF** shows a new CO absorption at 1845 $\mathrm{cm^{-1}}$, with a second band at ~1932 $\mathrm{cm^{-1}}$ hidden by the starting material absorption. Two new intense visible absorptions appear at $\lambda_{\max}(\epsilon_{\mathrm{rel}}) = 390(1.1)$ and 507(1.0) nm. These spectral data agree well with those reported in the literature.[7,8] Photolyses of $\mathrm{CpMn(CO)_3}$ in hexane solutions of the haloalkanes (1.0–2.5 M) at 195 K led to results similar to those obtained in neat haloalkane solutions with only slight shifts of the ν_{CO} bands to higher frequency. These bands are significantly different from ν_{CO} observed in neat hydrocarbon matrix at 12 K,[9] in hydrocarbon glass at 77 K,[8,10,11] and in heptane solution at 293 K.[12] The ν_{CO} and $\lambda_{\max}$ values are also different from those of the absorptions assigned to $\mathrm{Cp_2Mn_2(CO)_5}$ resulting from the reaction of **2** with **1**.[13] Low-temperature studies in $\mathrm{CH_2Br_2}$ solution were not possible because of its high freezing point and low solubility in hexanes at 195 K.

While the IR and UV/visible spectra were consistent with assignment of **3-XR** as complexes of the type $\mathrm{CpMn(CO)_2XR}$, chemical confirmation was needed to support this spectroscopic result. To justify the formulation of **3-XR** as $\mathrm{CpMn(CO)_2XR}$ and to demonstrate the weak nature of the M–XR interaction, $\mathrm{PMe_3}$ was added to neat haloalkane solutions of **3-XR** at 195 K. Over several hours the bright red color of the haloalkane complexes was replaced by a bright yellow color, and $\mathrm{CpMn(CO)_2PMe_3}$ was isolated as the unique product in high yield.[14] This reaction

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[1] For an excellent recent review, see: Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89–115.

[2] See also: (a) Fernández, J. M.; Gladysz, J. A. *Inorg. Chem.* **1986**, *25*, 2672–2674. (b) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207–219 and references cited therein. (c) Winter, C. H.; Veal, W. R.; Garner, C. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 4766–4776. (d) Kulawiec, R. J.; Faller, J. W.; Crabtree, R. H. *Organometallics* **1990**, *9*, 745–755. (e) Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfsberg, G. P.; Frye, J. S.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 2349–2362. (f) Bown, M.; Waters, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2442–2443. (g) Gomes-Carneiro, T. M.; Jackson, R. D.; Downing, J. H.; Orpen, A. G.; Pringle, P. G. *J. Chem. Soc., Chem. Commun.* **1991**, 317–319.

[3] O'Driscoll, E.; Simon, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 6580–6584.

[4] Bogdan, P. L.; Wells, J. R.; Weitz, E. *J. Am. Chem. Soc.* **1991**, *113*, 1294–1299.

[5] Casey and Fraley have prepared $(\overline{\mathrm{BrCH_2CH_2Cp)Mn}}\mathrm{(CO)_2}$, which contains an intramolecularly bound bromine atom. Fraley, M. E.; Casey, C. P. Personal communication of unpublished results.

[6] (a) Strohmeier, W. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 730–737. (b) Caulton, K. G. *Coord. Chem. Rev.* **1981**, *38*, 1–43.

[7] Giordano, P. J.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 160–166.

[8] Black, J. D.; Boylan, M. J.; Braterman, P. S. *J. Chem. Soc., Dalton Trans.* **1981**, 673–677.

[9] Rest, A. J.; Sodeau, J. R.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1978**, 651–656.

[10] Hill, R. H.; Wrighton, M. S. *Organometallics* **1987**, *6*, 632–638.

[11] Bitterwolf, T. E.; Lott, K. A.; Rest, A. J.; Mascetti, J. *J. Organomet. Chem.* **1991**, *419*, 113–126.

[12] Creaven, B. S.; Dixon, A. J.; Kelly, J. M.; Long, C.; Poliakoff, M. *Organometallics* **1987**, *6*, 2600–2605.

[13] Data for $\mathrm{Cp_2Mn_2(CO)_5}$: $\lambda_{\max}(\epsilon_{\mathrm{rel}}) = 360(1.7)$, 530(1.0) nm; ν_{CO} (heptane, 293 K), terminal CO, 1993, 1955, 1934, 1907 $\mathrm{cm^{-1}}$; bridging CO, 1777 $\mathrm{cm^{-1}}$; ^{13}CO satellite, 1740 $\mathrm{cm^{-1}}$. Data from ref 12.

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Table I. IR and UV/Vis Data for Photolysis of $CpMn(CO)_3$ in the Presence of Either Haloalkane or THF at 195 K. Photoacoustic Data, Recorded at 298 K, for the Substitution of CO by Haloalkane or THF According to Scheme I[a]

	ν_{CO} (cm^{-1})						
	neat[b]	hexanes[b]	λ_{max} (rel ϵ) ±5 (nm) (neat)	$\Delta H_{1,5}$ (kcal/mol)	$\Delta H_{5,3}$ (kcal/mol)	$k_2 \times 10^6$ (L/mol·s)	ΔH_{Mn-S} ±2 (kcal/mol)
CH_2Cl_2	1867	1877	393(1.2)	46.7 ± 1.1	−9.0 ± 1.0	4.9 ± 2.6	−17
	1946	1953	501(1.0)				
CH_2Br_2				47.1 ± 0.9	−12.2 ± 1.2	8.1 ± 2.5	−20
n-BuCl	1867	1874	393(1.2)	46.9 ± 1.0	−10.5 ± 1.8	3.4 ± 0.8	−19
	(1932)	(1939)	493(1.0)				
n-BuBr	1870	1876	394(1.9)	46.7 ± 1.0	−13.3 ± 1.3	5.3 ± 1.2	−21
	(1932)	(1939)	508(1.0)				
n-$C_5H_{11}Br$	1869	1877	392(2.3)	46.6 ± 0.6	−13.4 ± 3.2	5.4 ± 2.6	−21
	(1932)	(1939)	494(1.0)				
THF	1845	1858	396(1.1)	46.2 ± 1.2[c]	−16.1 ± 1.4[c]	4.4 ± 0.4[c]	−24
	(1932)	(1939)	507(1.0)				
$CpMn(CO)_3$	2021	2026					
	1932	1939					

[a] Errors are 1σ. [b] Values of ν_{CO} in parentheses are estimated on the basis of overlap with the lower energy ν_{CO} band of $CpMn(CO)_3$. [c] Reference 17.

confirms that **3-XR** contains two CO ligands and that the haloalkane ligand is easily substituted. Since oxidative addition of a haloalkane to the metal center is likely to be difficult to reverse, the haloalkane appears to remain intact and is probably coordinated to the metal center through the halogen lone pairs.[15]

The energetics of coordination of the haloalkanes to the metal center were examined with photoacoustic calorimetry.[16-18] Photolyses of $CpMn(CO)_3$ in heptane solutions of RX (0.2–1.3 M) initially yield the heptane-solvated intermediate **5** with an enthalpy of reaction $\Delta H_{1,5}$ (Scheme I). These values are identical within experimental error and agree well with previously reported values.[17,18] Subsequent substitution of the heptane by haloalkane occurs with the bimolecular rate constant k_2 and enthalpy of reaction $\Delta H_{5,3}$ to give the corresponding **3-XR** (Table I).

In the $CpMn(CO)_2$ system all the haloalkanes studied are weaker ligands than is THF. The bromoalkanes are more strongly bound to the Mn center than are the corresponding chloroalkanes, and although the kinetic data is less definitive, it appears that k_2 values for the bromoalkanes are greater than k_2 values for the corresponding chloroalkanes. The dihalomethanes are less strongly bound to the metal than the corresponding monohaloalkanes, yet k_2 is greater for the dihalomethanes. The weaker bond is a result of the electron-withdrawing character of the second halogen reducing the donating ability of the coordinated halogen. However, the second halogen atom increases the number of possible binding sites for coordination to the metal center; hence k_2 is greater.

If the strength of the Mn–heptane bond ($-\Delta H_{Mn-hept}$, Scheme I) in **5** is known, the enthalpy of the haloalkane–metal bond in **3-XR** (ΔH_{Mn-S}) can be calculated using eq 1.

$$\Delta H_{Mn-S} = \Delta H_{5,3} + \Delta H_{Mn-hept} \qquad (1)$$

From previous studies, $\Delta H_{Mn-hept}$ is −8 ± 1 kcal/mol.[17,18] The calculated values of ΔH_{Mn-S} range from −17 kcal/mol for CH_2Cl_2 to −21 kcal/mol for 1-bromobutane and 1-bromopentane. Thus the bromoalkanes have overall metal–ligand bond strengths that are nearly sufficient to allow isolation of stable intermolecular bromoalkane complexes.

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[14] (a) Strohmeier, W.; Müller, F.-J. *Chem. Ber.* **1967**, *100*, 2812. (b) Herberhold, V. M.; Süss-Fink, M. *Angew. Chem.* **1977**, *89*, 192. (c) Höfler, M.; Hausmann, H.; Schneider, A. *Z. Naturforsch., B* **1978**, *33B*, 1559.

[15] The referees correctly point out that oxidative addition would be expected to be accompanied by a large increase in the observed CO stretching frequencies. Thus, the similarities between ν_{CO} for **3-THF** and **3-XR** suggest that oxidative addition does not occur. While the best models for ν_{CO} values are not available to support this argument, i.e., $CpMn(CO)_2(X)(alkyl)$ (X = Cl or Br), substantially higher CO stretching frequencies are observed for $CpMn(CO)_2(H)(SiCl_3)$ with ν_{CO} = 1977 and 2028 cm^{-1}. See: Jetz, W.; Graham, W. A. G. *J. Am. Chem. Soc.* **1969**, *91*, 3375–3376.

[16] See the following and references cited therein: (a) Marr, K.; Peters, K. S. *Biochemistry* **1991**, *30*, 1254–1258. Peters, K. S.; Snyder, G. J. *Science* **1988**, *241*, 1053–1057. (b) Griller, D.; Wayner, D. D. M. *Pure Appl. Chem.* **1989**, *61*, 717–724. (c) Nitsch, C.; Schatz, G. H.; Braslavsky, S. E. *Biochim. Biophys. Acta* **1989**, *975*, 88–95. (d) Song, X.; Endicott, J. F. *Inorg. Chem.* **1991**, *30*, 2214–2221. (e) Herman, M. S.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 9105–9107. (f) Sorensen. A. A.; Yang, G. K. *J. Am. Chem. Soc.* **1991**, *113*, 7061–7063. (g) Hung, R. R.; Grabowski, J. J. *J. Phys. Chem.* **1991**, *95*, 6073–6075. Hung, R. R.; Grabowski, J. J. *J. Am. Chem. Soc.* **1992**, *114*, 351–353. (h) Caldwell, R. A.; Tang, W.; Schuster, D. I.; Heibel, G. E. *Photochem. Photobiol.* **1991**, *53*, 159–164. (i) Small, J. R.; Libertini, L. J.; Small, E. W. *Biophys. Chem.* **1992**, *42*, 29–48. Small, J. R.; Hutchings, J. J.; Small, E. W. *Proc. SPIE—Int. Soc. Opt. Eng.* **1989**, *1054*, 26–35. (j) Burkey, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8329–8333. (k) Leung, W. P.; Cho, K. C.; Chau, S. K.; Choy, C. L. *Chem. Phys. Lett.* **1987**, *141*, 220–224. (l) Renard, M.; Delmelle, M. *J. Phys., Colloq.* **1983**, *C6*, 383–388. (m) Legrange, J.; Cahen, D.; Caplan, S. R. *Biophys. J.* **1982**, *37*, 4–6.

[17] Klassen, J. K.; Yang, G. K. *Organometallics* **1990**, *9*, 874–876. Klassen, J. K.; Selke, M.; Sorensen, A. A.; Yang, G. K. *ACS Symp. Ser.* **1990**, *428*, 195–204.

[18] Hester, D. M.; Sun, J.; Harper, A. W.; Yang, G. K. *J. Am. Chem. Soc.* **1992**, *114*, 5234–5240.

Electrochemical Probes of Protein Folding

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Intense fundamental and practical interest is focused on the factors that control the thermodynamics and kinetics of protein folding. Yet, most details, particularly regarding the pathways for folding, remain obscure.[1] In part, this situation reflects the difficulties of initiating folding via rapid (submillisecond) processes. To approach this and related problems, we have studied protein folding induced by rapid oxidation/reduction techniques. As a first step in such studies, we have found that, under limiting conditions, unfolding thermodynamics can be estimated using electrochemical techniques. As these conditions are modified, simple electrochemical methods (e.g., cyclic voltammetry) can also provide kinetic information on folding rates and (perhaps) intermediates. Cytochrome *c* is an ideal protein for such investigations. The thermodynamics[2,3] and kinetics[2,4-6] of cytochrome

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[‡] On sabbatical leave from the Department of Chemistry, Earlham College, Richmond, IN 47374.

[1] Kim, P. S.; Baldwin, R. L. *Ann. Rev. Biochem.* **1990**, *59*, 631–660.

[2] (a) McLendon, G.; Smith, M. *J. Biol. Chem.* **1978**, *253*, 4004–4008. In this manuscript, an estimate of ΔG_u for Fe(II) cytochrome *c* is also made. Subsequent experiments have shown this estimate in error due to an autooxidation artifact for the Fe(II) cytochrome *c* during unfolding. (b) Hickey, D. R.; Berghuis, A. M.; Lafond, G.; Jaeger, J. A.; Cardillo, T. S.; McLendon, D.; Das, G.; Sherman, F.; Brayer, G. D.; McLendon, G. *J. Biol. Chem.* **1991**, *266*, 11 686–11 694.

0002-7863/92/1514-6938$03.00/0