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Reactivity of the $CpMn(CO)_2-XR$ Bond [X = Cl, Br]: A Kinetic Study Using Rapid-Scan FTIR Spectroscopy

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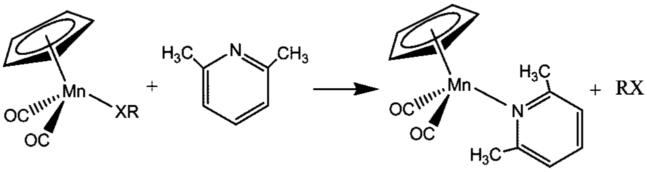
The mechanism and energetics of the displacement of dihaloalkanes from the photolytically generated $CpMn(CO)_2-XR$ (X = Cl, Br) complexes by 2,6-lutidine have been studied using rapid-scan FTIR. The substitution reactions proceed through an I_d mechanism, and theoretical calculations indicate that the Mn−XR bond is mostly broken in the transition state. Activation enthalpies of 16−17 kcal/mol for the Mn−ClR and 18−19 kcal/mol for the Mn−BrR complexes are only slightly lower than previous thermodynamic measurements of the Mn−haloalkane bond dissociation enthalpies. The rate of displacement of bromoalkanes was found to be ∼10 times slower than for the analogous chloroalkanes. *Ab initio* calculations suggest that this difference in reactivity is primarily due to a more stable interaction between the Mn center and bromoalkanes.

Introduction

Transition metal organometallic complexes are used as catalysts to carry out a variety of organic transformations.[1] In many instances, the catalytically active species in condensed phase is a coordinatively unsaturated metal complex in which the solvent weakly binds to the vacant site on the metal. Fast kinetic techniques have clearly demonstrated that photolytically generated unsaturated metal complexes are extremely reactive and rapidly bind to most solvents.[2] Indeed, molecules not usually thought of as donor ligands, such as noble gases and haloalkanes, can also bind to the coordinatively unsaturated metal center. For example, photolysis of $Cr(CO)_6$ in the presence of *n*-bromobutane results in the formation of the $Cr(CO)_5-BrBu$ complex within 3 ns of CO loss.[3]

Although alkyl halides commonly undergo oxidative addition to an acidic metal center,[4] several examples are now known in which the haloalkane weakly coordinates to a metal center through the halogen lone pairs, an η^1-XR interaction.[5] In these complexes, the halogen atom is thought to behave as a weak two-electron σ donor. For example, Yang and co-workers detected the **1**−XR [**1** = $CpMn(CO)_2$, RX = CH_2Cl_2, *n*-BuCl, *n*-BuBr, *n*-$C_5H_{11}Br$) complexes at low temperatures formed upon photolysis of $CpMn(CO)_3$ in RX solvent.[6] The technique of photoacoustic calorimetery (PAC) was used to estimate values of 16−21 kcal/mol for the strength of the **1**−XR interaction. Recently, Zhang et al. isolated the $[(PCP)Ru(CO)(\eta^1\text{-}ClCH_2Cl)][BAr'_4]$ (PCP = 2,6-$(CH_2P^tBu_2)_2C_6H_3$) complex and calculated a value of 12 kcal/mol for the $Ru-ClCH_2Cl$ binding energy.[5f] Intramolecular coordination of a halide atom to the Mn center has also been shown to occur upon photolysis of $(\eta^5\text{-}C_5H_4CH_2CH_2X)Mn(CO)_3$ complexes [X = Br, I].[7] Weakly bound alkyl halide complexes have been proposed as intermediates in the oxidative addition of the C−X bond to metal centers.[8] It is therefore of interest to study the reactivity of metal−haloalkane adducts to explore the factors that influence this type of binding.

Scheme 1



In the present work, we report the results of an investigation in which the displacement of a variety of haloalkanes from the **1**−XR [RX = $Cl(CH_2)_2Cl$, $Cl(CH_2)_3Cl$, $Cl(CH_2)_6Cl$, $Br(CH_2)_3Br$, $Br(CH_2)_6Br$, $Br(CH_2)_2CH_3$, and $Br(CH_2)_5CH_3$] complexes by 2,6-lutidine was studied (Scheme 1). The Mn−haloalkane adducts were formed upon photolysis of $CpMn(CO)_3$ in the presence of the appropriate alkyl halide solvent. In addition to understanding the factors that influence the reactivity of the **1**−XR bond, this study was also undertaken to determine whether activation parameters from kinetic studies can be used to provide reliable estimates for the strength of metal−solvent interactions.

The **1**−XR complexes span a wide range of stabilities, and so a combination of step-scan and rapid-scan FTIR was used

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to investigate their substitution chemistry. The reactivity of the **1**−XR bond was studied as a function of the identity of both the coordinated halogen atom and the length of the alkane chain. *Ab initio* calculations were also performed on the **1**−ClCH$_3$, **1**−BrCH$_3$, **1**−ClCH$_2$Cl, and **1**−ClCH$_2$CH$_2$Cl complexes to better understand the Mn−XR interaction.

Experimental Section

All kinetic experiments were performed using a Bruker Vertex 80 FTIR with both rapid-scan and step-scan capabilities. Sample photolysis was performed using the third harmonic (355 nm) of a Continuum Surelite I-10 Nd:YAG laser operating at 1 Hz. For the step-scan experiments, a syringe pump was used to flow solution through a temperature-controlled 0.5 mm path length IR cell with CaF$_2$ windows (Harrick Scientific). The temperature was monitored by a thermocouple located close to the photolysis solution and maintained by a water circulator to within ±0.5 °C.

The photolysis solution contained 4−6 mM CpMn(CO)$_3$ in the appropriate haloalkane solvent to which varying amounts of 2,6-dimethylpyridine (2,6-lutidine) was added as the displacing ligand. All kinetic runs were conducted under pseudo-first-order conditions in which the concentration of the incoming ligand was at least 10 times greater than that of the reactant **1**−XR complexes. The 2,6-lutidine ligand was used since it is a weak, sterically encumbered nucleophile, which does not displace the halogen from the halogenated solvents. In contrast, addition of piperdine to brominated solvents resulted in the solution clouding up, suggestive of alkylation at the nitrogen atom. The reactions were studied over a greater than 10-fold range of lutidine concentration and a 20−35 K temperature range. The errors in the reported parameters were obtained from linear least-squares fits to the available data. All chemicals used in the experiments were of >97% purity (Aldrich and Alfa Aesar).

Computation

The geometries and binding enthalpies of the reactants, products, intermediates, and transition states involved in the reaction were calculated using the Gaussian 03 suite of programs.[9] The main objective of the computational study was to determine if any trends emerged in the stability of the molecular complexes upon varying the ligand set rather than trying to produce accurate absolute stabilization energies. The method applied consisted of a Hartree−Fock calculation, followed by second-order Møller−Plesset correlation energy correction (MP2) with the LANL2DZ basis set.[9,10] All structures were simulated with zero-point-corrected energies and harmonic frequencies calculated at the optimized geometries to characterize the stationary points as equilibrium structures, and transition states included one imaginary frequency. To minimize computational time, 2,6-lutidine was replaced with pyridine as the displacing ligand, and only the properties of a selected number of complexes with halogenated ligands were calculated in order to predict trends in the **1**−XR binding strengths. Solvent effects were introduced using the basic PCM model (polarizable continuum model, ε(dichloromethane) = 8.93). However the inclusion of the solvent effect caused only small changes to the energies of the molecular complexes presumably due to the small value of the dielectric constant. Thus, energies for only the gas-phase structures have been reported instead.

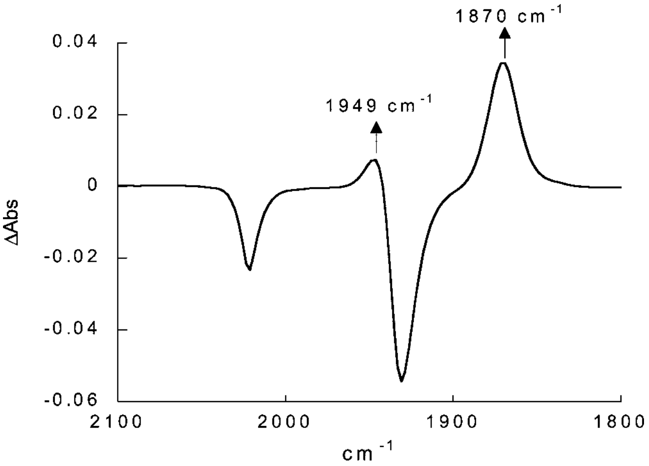

Figure 1. Difference spectra obtained upon photolysis of CpMn(CO)$_3$ in CH$_2$Cl$_2$ solvent at 283 K. The positive peaks are due to the formation of **1**−ClCH$_2$Cl, while the negative absorptions indicate destruction of the tricarbonyl complex.

Results and Discussion

(a) Chloroalkanes: CH$_2$Cl$_2$, Cl(CH$_2$)$_2$Cl, Cl(CH$_2$)$_3$Cl, Cl(CH$_2$)$_6$Cl. As shown in Figure 1, photolysis of CpMn(CO)$_3$ in CH$_2$Cl$_2$ solvent results in the formation of a complex with CO stretching peaks at 1870 and 1949 cm^{-1}, assigned to the previously observed **1**−ClCH$_2$Cl molecule.[6]

The position of the CO bands suggest that oxidative addition of the R−Cl bond to the Mn center does not occur since a large increase in the CO stretching frequency would then be expected. Thus, as discussed previously, the haloalkane is most likely coordinated to the metal center via a lone pair on the Cl atom.[6] At 283 K the background decay rate constant for **1**−ClCH$_2$Cl in the absence of 2,6-lutidine is 2.79 s^{-1}, while with [2,6-lutidine] = 0.48 M, a value of 3.94 s^{-1} is observed. These values indicate that the decay of **1**−ClCH$_2$Cl is primarily due to an unknown decomposition channel that competes with the displacement of CH$_2$Cl$_2$ from the Mn center. Consistent with this conclusion, judging by the weak intensities of the product CO stretching bands relative to the reactant, reaction of 2,6-lutidine with **1**−ClCH$_2$Cl resulted only in partial conversion to the **1**−lutidine complex with CO stretching absorbances at 1839 and 1913 cm^{-1}. As discussed below, this behavior is unlike that of the other chloroalkanes studied, where the background decay rate is more than 50 times less than the displacement rate constant and quantitative conversion is observed to the **1**-lutidine product.

Unfortunately, the rate of displacement of the CH$_2$Cl$_2$ solvent from the Mn center could not easily be probed since the reaction was too fast for the rapid-scan technique but too slow for step-scan FTIR due to the need to flow solution through the IR cell.

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[10] The more widely used DFT model at the B3LYP/LANL2DZ or B3LYP/6-31G* level did not yield acceptable agreement with the experimental values, especially for the chloroalkanes. At this level of theory, the **1**−ClCH$_3$ bond enthalpy was calculated to be ~12 kcal/mol, considerably lower than the experimental value of ~20 kcal/mol for the strength of the related **1**−ClBu interaction.

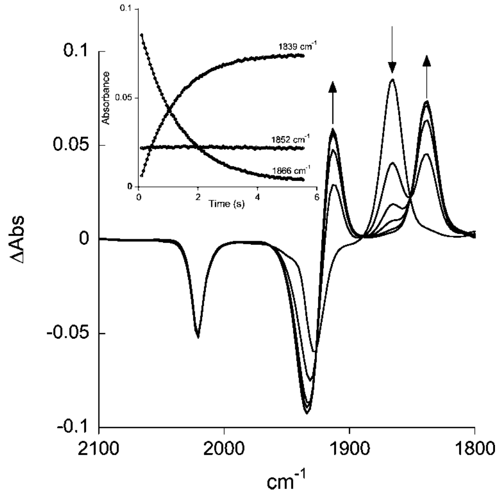


Figure 2. IR spectral changes observed upon reaction between photolytically generated **1**−Cl(CH$_2$)$_3$Cl at T = 288 K and [2,6-lutidine] = 0.33 M. The inset shows the absorbance of the reactant and product complexes as a function of time. An isosbestic point is observed at 1852 cm^{-1}.

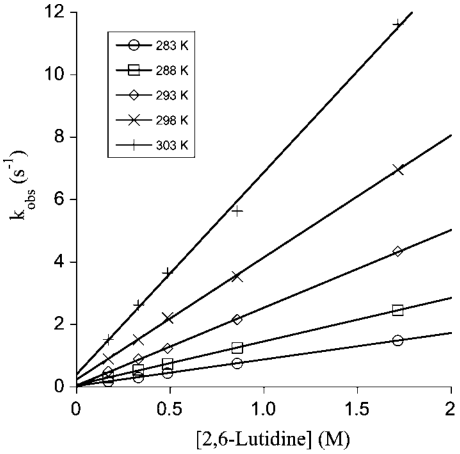


Figure 3. Plot of k_{obs} vs [2,6-lutidine] for the reaction of **1**−Cl(CH$_2$)$_6$Cl with 2.6-lutidine at several temperatures.

Table 1. Second-Order Rate Constants (k_{2nd}) Obtained from a Linear Fit to the k_{obs} vs [2,6-Lutidine] Data for the Displacement of RX from 1−XR by 2,6-Lutidine[a]

RX	k_{second} (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)
Cl(CH$_2$)$_3$Cl	3.86 ± 0.15	16.0 ± 0.6	−1.0 ± 2.0
Cl(CH$_2$)$_6$Cl	2.49 ± 0.03	16.8 ± 0.3	1.0 ± 1.0
Br(CH$_2$)$_3$Br	0.33 ± 0.02	17.7 ± 0.2	−0.5 ± 0.7
Br(CH$_2$)$_6$Br	0.25 ± 0.01	19.0 ± 0.3	+3.9 ± 0.9
Br(CH$_2$)$_2$CH$_3$	0.36 ± 0.01	18.3 ± 0.2	+2.2 ± 0.6
Br(CH$_2$)$_5$CH$_3$	0.42 ± 0.01	19.3 ± 0.4	+5.8 ± 1.3

[a] Bimolecular rate constants are reported at 293 K. Activation parameters were obtained from the temperature dependence of k_{2nd}.

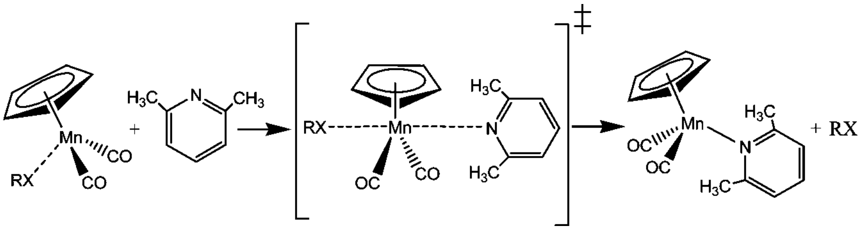
For the step-scan technique to yield acceptable results, the solution flow rate must be fast enough to replace the sample between each laser shot (1 Hz) but slower than the rate at which the transients react. In view of these constraints, ideal flow conditions could not be achieved to study the reactivity of **1**−ClCH$_2$Cl over a wide enough range of temperature and lutidine concentrations for meaningful interpretation of the experimental data. Furthermore, the low boiling point of CH$_2$Cl$_2$ and moisture condensation on the cell windows at low temperatures did not allow for significant temperature-controlled variation of the reaction rate in order to bring it into the range where either the rapid-scan or step-scan technique would become feasible to probe the reaction. Given the experimental difficulties in monitoring the reaction of **1**−ClCH$_2$Cl, only a few rate constant determinations for the displacement reaction were obtained for comparison with other chloroalkanes. These determinations were made by subtracting the background decay rate constant from that measured in the presence of the incoming ligand.

Photolysis of the CpMn(CO)$_3$ complex in neat 1,2-dichloroethane, 1,3-dichloropropane, and 1,6-dichlorohexane results in the formation of the respective solvate complexes. As shown in Figure 2, in the presence of 2,6-lutidine, the **1**−ClRCl [R = −(CH$_2$)$_2$, −(CH$_2$)$_3$, −(CH$_2$)$_6$] complexes undergo a first-order exponential decay and the **1**−lutidine complex grows at a similar rate. Assuming that the absorption coefficients for the reactant and product complexes are similar, the almost equal intensities of the CO bands suggest quantitative conversion of reactant to product. The presence of an isosbestic point in all the reactions indicates that the reactant complexes are converted to a single product.

As shown in Figure 3, the observed rate constants (k_{obs}) obtained from a single-exponential fit to the decay of the reactant **1**−XR complexes vary linearly with the lutidine concentration. Second-order rate constants obtained from a fit to this data are presented in Table 1.

Unfortunately, under the experimental conditions and as previously noted,[11] a linear dependence of k_{obs} on ligand concentration does not assist in distinguishing between associative, dissociative, or interchange mechanisms of solvent displacement from the metal center. Some insight into the mechanism of the substitution reaction was obtained by determining the relevant activation parameters. As shown in Table 1, activation enthalpies of 16.0 ± 0.6 and 16.8 ± 0.3 kcal/mol were determined for the displacement of the Cl(CH$_2$)$_3$Cl and Cl(CH$_2$)$_6$Cl molecules from the Mn center. In both cases, activation entropies of ~0 eu were obtained. The $\Delta H^{\ddagger}$ values are slightly lower than estimates of 17−19 kcal/mol for the **1**−XR (RX = CH$_2$Cl$_2$, *n*-BuCl) bond strengths obtained from thermodynamic measurements using PAC.[6] It should be noted that the PAC values required an estimate for the **1**−heptane bond dissociation energy, which was estimated to be 8 kcal/mol. However, recent studies have suggested that the 8 kcal/mol value may be a lower limit to the Mn−heptane bond enthalpy.[12] Consequently, the 17−19 kcal/mol estimate of the **1**−ClR bond enthalpy may also be a lower limit. Nonetheless, the similarity between the thermodynamic and kinetic values suggests that in the present case the Mn−ClRCl

Scheme 2



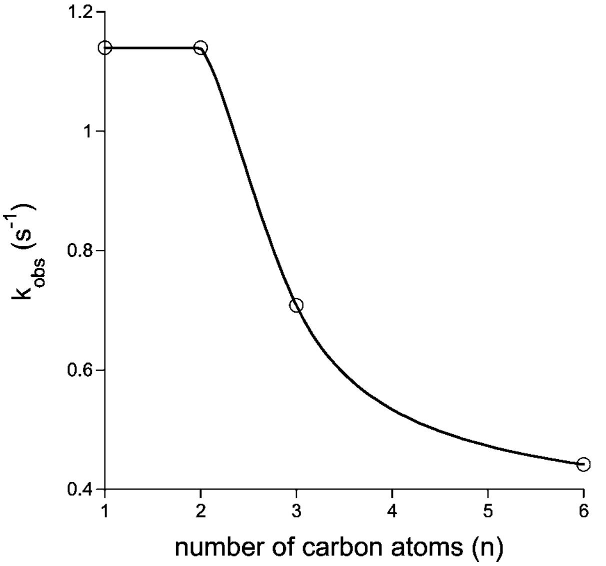


Figure 4. Plot showing the variation in the observed rate constant for the decay of the **1**$-Cl(CH_2)_nCl$ complex. Decay rates were measured at 283 K with [2.6-lutidine] = 0.49 M.

bond is mostly dissociated in the transition state. In the absence of spectroscopic evidence for an intermediate with reduced coordination number, it is likely that the displacement of the haloalkane proceeds through an I_d mechanism with a single transition state in which the Mn−XR bond is mostly broken with the incoming lutidine ligand either present in the first solvation shell or loosely associated with the activated complex (Scheme 2). This description of the transition state is also consistent with the ~0 eu value for the activation entropies. Furthermore, given the nature of the bulky 2,6-lutidine ligand, it is plausible that significant cleavage of the Mn−XR bond has to occur before the incoming ligand can bind to the Mn center. There are other instances of an I_d mechanism for the displacement of weakly coordinated solvents from the $CpMn(CO)_2$ fragment. For example, the substitution of cyclohexane (CyH) from the $CpMn(CO)_2(CyH)$ complex by a variety of ligands is thought to occur via an I_d pathway.[13]

While the overall differences in the rate constants for the displacement of the dichloroalkanes from **1**−ClRCl are small, as shown in Figure 4, they do exhibit an interesting trend. Under identical conditions of temperature and 2,6-lutidine concentration, the observed rate constant is the same for $ClCH_2Cl$ and $Cl(CH_2)_2Cl$ but then decreases as the separation between the coordinated and uncoordinated halogen increases. A possible explanation for this trend may be that the electron-withdrawing effect of the second Cl atom reduces the ability of the bound Cl to act as a σ donor. This influence is expected to decrease as the separation between the two halogens increases, resulting in a stronger bond and a lower displacement rate constant in the case of **1**$-Cl(CH_2)_6Cl$ relative to the other chloroalkanes. However, the trend in the reactivities may also be explained by steric considerations if the transition state in the case of the larger $Cl(CH_2)_6Cl$ molecule is more dissociative than for the smaller haloalkanes. In addition to these enthalpic considerations, small differences in the activation entropies could also be responsible. Theoretical calculations discussed below suggest that there is relatively little change in the binding enthalpy of the haloalkane as the separation between the Cl atoms increases. Consequently, it is likely that the trend in the reaction rate constants is due to slight differences in the structure of the transition state as the size of the alkane chain separating the Cl atoms increases.

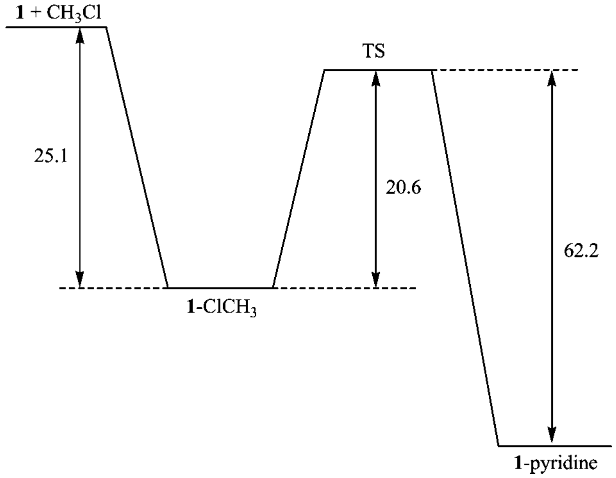


Figure 5. Reaction enthalpy diagram for the displacement reaction of **1**$-ClCH_3$ by pyridine calculated using the MP2/LANL2DZ level of theory in Gaussian 03. All values are in kcal/mol.

Table 2. Binding Enthalpies of Various 1−XR Complexes Determined Using the MP2 LANL2DZ Level of Theory in Gaussian 03

complex	1−XR bond enthalpy (kcal/mol)
1 (singlet) + RX	0
1$-ClCH_3$	−25.1
1$-ClCH_2Cl$	−25.7
1$-ClCH_2CH_2Cl$	−25.5
1$-BrCH_3$	−28.9

***Ab Initio* Calculations.** To better understand the reactivity of the metal−haloalkane adducts, the thermochemical properties of some **1**−XR complexes were determined at the MP2/LANL2DZ level of theory. The enthalpy diagram for the reaction of the model **1**$-ClCH_3$ complex with pyridine is shown in Figure 5. The calculated binding enthalpies of several **1**−XR complexes are shown in Table 2.

It was found that for complexes with RCl ligands, such as CH_3Cl, CH_2Cl_2, and $ClCH_2CH_2Cl$, the differences in the Mn−XR bond enthalpies are insignificant (within ±0.5 kcal/mol). The calculated values of ~25 kcal/mol are larger than the activation enthalpies determined in the present study, but closer to the binding strengths obtained from previous PAC studies.[6] It should be noted, however, that the computational studies were carried out using a relatively small basis set, as the focus was primarily on predicting trends in the Mn−XR energies rather than obtaining accurate absolute values. In addition, MP2 calculations are known to overestimate bond energies and a correction of ~20% would result in much better agreement with the PAC values.[14]

To lend support for the experimental determination of an I_d mechanism of haloalkane displacement from the Mn center, the structure and energy of the expected transition state for the substitution reaction were also determined at the same level of theory. As shown in Figure 6 and consistent with the experimental findings, the calculated transition state structure indicates

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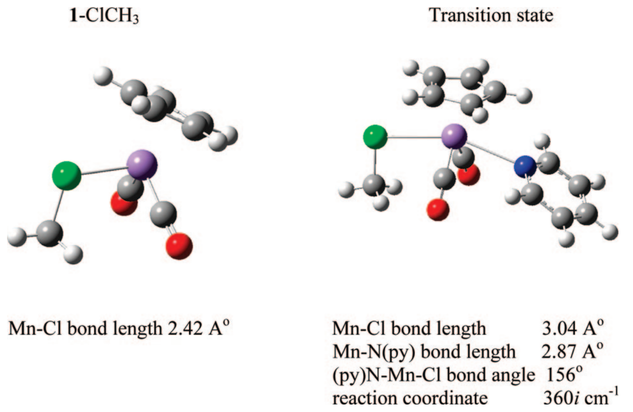

Figure 6. Structures of the reactant and activated complexes calculated at the MP2/LANL2DZ level using Gaussian 03.

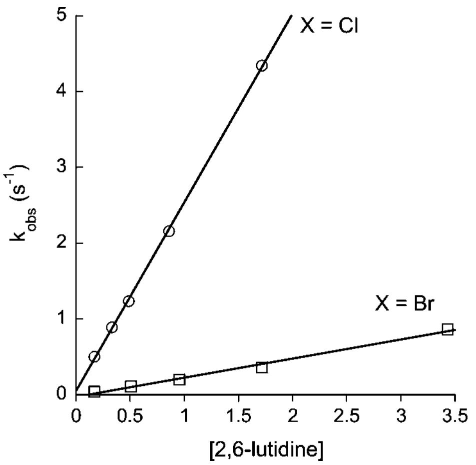

Figure 7. Plot of k_{obs} vs [2,6-lutidine] at 293 K for the displacement of $X(CH_2)_6X$ from **1**$-X(CH_2)_6X$. The substitution reaction is almost 10 times slower when X = Br.

that the **1**−XR bond is considerably longer in the activated complex (3.04 vs 2.42 Å in **1**$-ClCH_3$). The reaction coordinate shows motion associated with the formation of the **1**−pyridine bond and breaking of the **1**−XR interaction. The RX solvent is still weakly attached to Mn, while the **1**−pyridine bond is not fully formed in the transition state. The structure of this transition state indicates that an activation barrier with a slightly lower enthalpy compared to the **1**−XR bond strength is to be expected since this bond has not fully dissociated. Indeed, calculations predict the transition state to lie about 20 kcal/mol above the reactant **1**$-ClCH_3$ complex, 5 kcal/mol less than the calculated value of 25 kcal/mol for the **1**$-ClCH_3$ bond enthalpy. The experimentally determined activation enthalpy of 16−17 kcal/mol is in good agreement with the calculated energy and structure of the transition state.

The lack of variation in the calculated bond enthalpies as a function of alkane length in the case of the dicholoralkanes also suggests that the trend in the displacement rate constants shown in Figure 4 is not due to electronic effects. Rather, it is likely that steric factors play a primary role in determining the reactivity trend. It may be suggested that a more dissociative transition state is accessed in the case of the larger chloroalkanes, resulting in a slightly higher activation enthalpy and hence a lower rate constant for the displacement reaction. The slightly higher activation entropies for the sterically larger chloro- and bromoalkanes (Table 1) is also consistent with this conclusion.

(b) Bromoalkanes: CH_2Br_2, *n*-C_3H_7Br, *n*-$C_6H_{13}Br$, $Br(CH_2)_3Br$, $Br(CH_2)_6Br$. As in the case of CH_2Cl_2, photolysis of $CpMn(CO)_3$ in dibromomethane solvent generates the **1**$-BrCH_2Br$ complex with a CO stretching absorbance at 1869 cm^{-1}. The second CO band is obscured by the parent tricarbonyl absorption at 1929 cm^{-1}. These peak locations are consistent with those of the previously observed **1**$-BrC_4H_9$ and **1**$-BrC_5H_{11}$ complexes.[6] Although **1**$-ClCH_2Cl$ and **1**$-BrCH_2Br$ exhibit similar kinetic behavior, their reactivity is different in one important respect. As discussed below and shown in Table 1, the bromoalkane complexes **1**$-Br(CH_2)_3Br$ and **1**$-Br(CH_2)_6Br$ react almost 10 times slower than the Cl analogues. However, at the same temperature (in the absence of lutidine) the **1**$-BrCH_2Br$ complex has a significantly shorter lifetime than the **1**$-ClCH_2Cl$ complex. At 295 K, the 8 ms half-life of **1**$-BrCH_2Br$ is almost 10 times less than that of **1**$-ClCH_2Cl$. Similar to **1**$-ClCH_2Cl$, the products of the decomposition of **1**$-BrCH_2Br$ do not have terminal CO's attached to the Mn center since no new peaks appear in the 1800−2200 cm^{-1} region of the IR spectrum. However, in contrast to **1**-CH_2Cl_2, under identical conditions of temperature and 2,6-lutidine concentration, the **1**$-BrCH_2Br$ complex does not react with lutidine to form the Mn−lutidine complex (CO stretching absorbances of the Mn−lutidine complex are not observed). These observations suggest that while **1**$-BrCH_2Br$ forms, it dissociates to an unknown product before reaction with 2,6-lutidine can occur. In the case of **1**$-ClCH_2Cl$, the decomposition channel is competitive with the displacement reaction. However, decomposition of **1**$-BrCH_2Br$ appears to have a lower energetic barrier than substitution such that reaction with 2,6-lutidine does not occur (even when [2,6-lutidine] = 1.3 M). It may be speculated that complexation of CH_2Cl_2 or CH_2Br_2 oxidizes the Mn center, resulting in the loss of the CO ligands with the latter solvent being more efficient in this respect. Interestingly, in the PAC study, **1**$-BrCH_2Br$ was not directly observed since low-temperature photolysis could not be attempted because of its high freezing point and low solubility in hexanes at 195 K.

Unlike dibromomethane, the reaction of other **1**−bromoalkane complexes with 2,6-lutidine results in the formation of the product **1**−lutidine complex. As in the case of the chloroalkanes, the observed rate constants exhibit a linear dependence on the concentration of the lutidine ligand. The second-order rate constants are presented in Table 1. The $\Delta H^{\ddagger}$ values of 17−19 kcal/mol are similar to PAC values of 20−21 kcal/mol for the binding enthalpy in **1**$-BrC_4H_9$ and **1**$-BrC_5H_{11}$. Once again, the similarity between the kinetic and thermodynamic parameters suggests that the Mn−Br bond is mostly dissociated in the transition state. The activation enthalpy for the displacement reaction is slightly lower in the case of 1,3-dibromopropane compared to 1,6-dibromohexane. This difference may suggest a more stable interaction between the Mn center and $Br(CH_2)_6Br$ relative to $Br(CH_2)_3Br$. However, a similar difference in activation enthalpies is also observed for the substitution of the bromoalkane from **1**$-Br(CH_2)_2CH_3$ and **1**$-Br(CH_2)_5CH_3$. Furthermore, the activation enthalpies for the 1-bromopropane and 1,3-dibromopropane and 1-bromohexane and 1,6-dibromohexane complexes are similar. This observation implies that the presence of the second halogen does not measurably impact the stability of the Mn−dibromoalkane interaction. Consequently, as in the case of the chloroalkanes, and consistent with the theoretical study, differences in $\Delta H^{\ddagger}$ between the **1**$-Br(CH_2)_3Br$ and **1**$-Br(CH_2)_6Br$ complexes are likely due to small differences in the structure of the transition state due to steric factors rather than electronic effects.

As shown in Figure 7, the substitution reaction of the bromoalkanes from the Mn center is almost 10 times slower than that of the corresponding chloroalkane complexes. Consistent with earlier thermochemical measurements, which demonstrate that the bromoalkanes are more strongly bound to the Mn center,[6] the activation enthalpies for bromoalkane displacement are 2–3 kcal/mol higher than for the analogous chloroalkane solvates. The calculated value for the strength of the **1**–$BrCH_3$ bond is also ~3 kcal/mol larger than the corresponding chloro complex. Thus, differences in the activation enthalpies for the chloro- and bromoalkanes accurately reflect the relative stabilities of the **1**–ClR and **1**–BrR bonds. Previously, equilibrium studies also found that bromoarenes were more strongly bound to a Ru center than chloroarenes.[15] The origin of this difference is most likely due to the presence of more diffuse orbitals on the Br atom, resulting in better overlap with the metal-centered orbitals.

Conclusions

Photolysis of $CpMn(CO)_3$ in a variety of dichloro- and dibromoalkanes results in the formation of the corresponding **1**–XR [**1** = $CpMn(CO)_2$] adducts in which the haloalkane is coordinated to the metal center through the lone pairs on the halogen atom. In general, the displacement of bromoalkanes from the Mn metal center proceeds at a slower rate than the corresponding chloroalkanes. Consistent with *ab initio* calculations and previous thermodynamic measurements, this difference in reactivity is primarily due to a weaker interaction between the metal center and RCl relative to RBr. However, in the case of dibromomethane, the **1**–$BrCH_2Br$ complex has a significantly shorter lifetime than **1**–$ClCH_2Cl$.

For the dichloroalkanes, the rate of substitution decreases as the separation between the coordinated and uncoordinated Cl atoms increases. Steric influences rather than electronic effects are thought to be responsible for this trend in reactivities. Thus, the difference in activation enthalpies for the displacement of $Br(CH_2)_3Br$ and $Br(CH_2)_6Br$ is similar to that between C_3H_5Br and $C_6H_{11}Br$, suggesting that the second Br atom does not significantly impact the reactivity of the Mn–BrRBr bond.

Computational studies at the MP2/LANL2DZ level of theory are consistent with the experimental data and previous thermochemical measurements in calculating the strength of the **1**–XR interaction. The calculated transition state structure indicating that the **1**–XR bond is mostly dissociated in the activated complex also supports the experimental conclusion that the displacement reaction proceeds through an I_d mechanism.

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