***trans*-[PtMe(I)(PPh$_3$)$_2$].** Under an inert environment, [Pt(PPh$_3$)$_4$] (20 mg) was dissolved in MeI (1.0 mL) at 25 °C. After 3 h of stirring, the solution was evaporated into a solid, which was extracted with C_6H_6 (0.5 mL) and analyzed by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR data of a C_6H_6 solution of this complex are as follows: $\delta(P) = 26.8$ ppm [$^1J(Pt,P) = 3066$ Hz].

***trans*-[PtMe(Cl)(PPh$_3$)$_2$].** Under an inert environment, *trans*-[PtMe(I)(PPh$_3$)$_2$] (10 mg, dissolved in 1.0 mL of CH_2Cl_2) was treated with a solution of NaCl (14 mg) dissolved in Me_2CO (10 mL). After 4 h of stirring, the solution was evaporated to a solid, which was extracted with C_6H_6 (0.5 mL) and analyzed by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR data of a C_6H_6 solution of this complex are as follows: $\delta(P) = 28.33$ ppm [$^1J(Pt,P) = 3146$ Hz (65%)]. Also present in the spectrum were peaks for residual *trans*-[PtMe(I)(PPh$_3$)$_2$] (31.3%).

Gas Chromatographic Identification of NBu$_3$. The 20-μL samples of 6×10^{-3} M solutions of NBu$_3$ in a 5/2 CH_3CN/C_6H_6 solvent system showed a retention time of 5 min. The solution (6.7 mL) resulting from the electrolysis of a 1.61×10^{-3} M solution of *cis*-[PtCl$_2$(PEt$_3$)$_2$] was concentrated to 1.8 mL (thus, if there was a stoichiometric relationship between the production of NBu$_3$ and *cis*-[PtCl$_2$(PEt$_3$)$_2$], the concentration of NBu$_3$ would be 6×10^{-3} M). This sample (20 μL) showed the same peak at a retention time of 5 min with essentially the same area as the peak for the known sample of known concentration. Experiments were performed by using a Varian 90-P3 chromatograph equipped with a 20% Apiezon L column, with a carrier gas flow rate of 40 mL/min. The column temperature was held at 180 °C.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. The FTIR spectrometer was purchased with a grant from the National Science Foundation (Grant R118304405 to J.A.D.). We thank Mr. Richard J. Staples for technical assistance.

Registry No. *cis*[PtCl$_2$(PPh$_3$)$_2$], 15604-36-1; [Pt(PPh$_3$)$_3$], 13517-35-6; HCl, 7647-01-0; *trans*-[PtH(Cl)(PPh$_3$)$_2$], 16841-99-9; *trans*-[PtCl$_2$(PPh$_3$)$_2$], 14056-88-3; MeI, 74-88-4; *trans*-[PtMe(I)(PPh$_3$)$_2$], 28850-19-3; *trans*-[PtMe(Cl)(PPh$_3$)$_2$], 28850-21-7; C_6H_5COCl, 98-88-4; *trans*-[PtCOC$_6$H$_5$(Cl)(PPh$_3$)$_2$], 18421-48-2; [Pt(Ph(≡CPh)(PPh$_3$)$_2$], 15308-61-9; [Pt(MeOCOC≡CCOOMe)(PPh$_3$)$_2$], 22853-55-0; [PtO$_2$(PPh$_3$)$_2$], 15614-67-2; [PtCO$_3$(PPh$_3$)$_2$], 17030-86-3; OPPh$_3$, 791-28-6; *trans*-[PtPh(Cl)(PPh$_3$)$_2$], 18421-49-3; CO$_2$, 124-38-9; *cis*-[PtCl$_2$(PEt$_3$)$_2$], 15692-07-6; $H_3C(CH_2)_3N^+Bu_3$, 10549-76-5; *trans*-[PtH(Cl)(PEt$_3$)$_2$], 16842-17-4; *trans*-[PtMe(Cl)(PEt$_3$)$_2$], 13964-96-0; [Pt(PhC≡CPh)(PEt$_3$)$_2$], 75983-00-5; PhCl, 108-90-7; PhF, 462-06-6; PhCn, 100-47-0; *trans*-[PtPh(CN)(PEt$_3$)$_2$], 33914-65-7; [Pt(CO)$_3$(PEt$_3$)$_2$], 56953-87-8; *trans*-[PtH(CH$_2$CN)(PEt$_3$)$_2$], 118831-46-2; *trans*-[PtCH$_3$(CN)(PEt$_3$)$_2$], 22289-45-8; *trans*-[PtPh(Cl)(PEt$_3$)$_2$], 13938-93-7; [Pt(PPh$_3$)$_4$], 14221-02-4; MeCN, 75-05-8; *trans*-[PtPh(CO)(PPh$_3$)$_2$]Cl, 101519-44-2; PPh$_3$, 603-35-0.

A Theoretical Study of Ketene Forming Reactions Involving Halogen Abstraction by Metal Carbonyl Anions

A. P. Masters, T. S. Sorensen, and T. Ziegler*

Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4, Canada

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Hartree–Fock–Slater calculations have been carried out on the abstraction of bromine from 2-bromoacetyl chloride by $Mn(CO)_5^-$ in the reaction $Mn(CO)_5^- + ClC(O)CH_2Br \rightarrow BrMn(CO)_5 + H_2CC(O)Cl^-$. It was found that this unusual reaction step is favorable with a neglectable activation barrier and a reaction enthalpy of -79 kJ mol^{-1}. The abstraction reaction is primarily driven by the stabilization of a negative charge by the enolate. It is argued that the abstraction process is a key step in ketene forming reactions [Masters, A. P.; Sorensen, T. S.; Ziegler, T. *J. Org. Chem.* **1986**, *51*, 3558] involving metal carbonyl anions and 2-bromo-substituted acyl halides.

I. Introduction

The reaction between either alkyl halides (eq 1a) or acyl halides (eq 1b) and anionic metal carbonyls has been used[1] extensively to synthesize metal–alkyl and metal–acyl complexes.

$$M(CO)_n^- + RX \rightarrow RM(CO)_n + X^- \tag{1a}$$

$$M(CO)_n^- + R\text{—}C(\text{=}O)\text{—}X \rightarrow R\text{—}C(\text{=}O)\text{—}M(CO)_n + X^- \tag{1b}$$

The metal center in $M(CO)_n^-$ is electron rich[2] and strongly nucleophilic with basicities comparable to NH_3. It is thus not surprising that mechanistic studies carried out on eq 1a have revealed a S_N2 mechanism.[3]

We have recently[4] studied the reaction between $Mn(CO)_5^-$ and ω-bromoacyl halides, and for most cases where the bromine is remote from the acyl group, a simple acylation process occurs.

$$Mn(CO)_5^- + X\text{—}C(\text{=}O)\text{—}(CH_2)_nCH_2Br \rightarrow Mn(CO)_5\text{—}C(\text{=}O)\text{—}(CH_2)_nCH_2Br + X^- \tag{1c}$$

Given the numerous precedents, this reaction is entirely predictable. However, when $Mn(CO)_5^-$ reacted with a 2-bromo-substituted acyl halide, e.g. 2-bromoacetyl chloride, the product was not the expected acyl complex (eq 2a) but rather $Mn(CO)_5Br$ and ketene (eq 2b).

Some additional studies of the reaction in eq 2b have led us to suggest that $Mn(CO)_5^-$, and probably also other

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[1] (a) Yamamoto, A. In *Organotransition Metal Chemistry*; John Wiley & Sons: New York, 1986; p 134. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[2] (a) Walker, H. W.; Kresge, C. T.; Ford, P. C.; Pearson, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 7428 and references therein. (b) Ziegler, T. *Organometallics* **1985**, *4*, 675.

[3] Johnson, R. W.; Pearson, R. G. *J. Chem. Soc. D* **1970**, 986.

[4] (a) Masters, A. P. Ph.D. Thesis, University of Calgary, 1987. (b) Masters, A. P.; Sorensen, T. S.; Ziegler, T. *J. Org. Chem.* **1986**, *51*, 3558.

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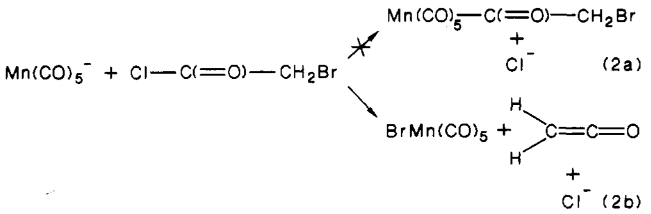


anionic metal carbonyls, reacts with 2-bromo- and 2-iodoacyl halides at the bromine or the iodine atom (the metal–halogen exchange reaction). While there are numerous examples of metal–halogen exchange reactions, the unique feature of the $Mn(CO)_5^-$ reaction is the extreme reactivity of the abstraction process; i.e. it successfully competes with acyl halide reactivity, itself a reaction which occurs with extreme ease in the presence of good nucleophiles like $Mn(CO)_5^-$. There is also considerable selectivity among nucleophiles, since 2-bromoacetyl chloride reacts with alcohols, water, primary amines, etc. to give esters, acids, or amides, leaving the bromine intact.

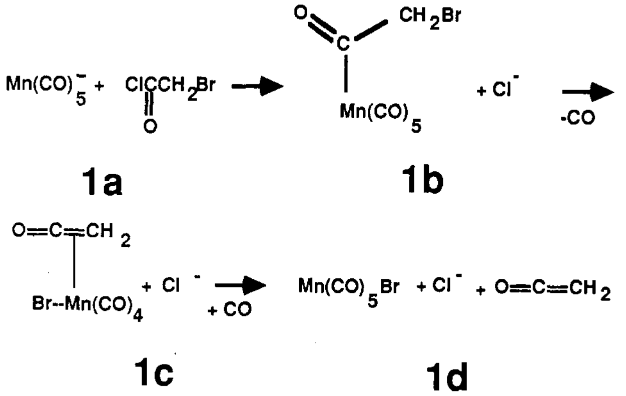
II. Computational Details

All calculations were based on the LCAO-HFS method due to Baerends et al.[5] with a standard exchange factor of $\alpha = 0.7$. Energies were calculated by the generalized transition-state method.[6] A double-ζ STO basis[7] set was employed for 1s on H, 2p and 2s on C and O, 3s and 3p on Cl, and 4s and 4p on Br as well as 5s and 5p on I. The 3s, 3p, 3d, 4s, and 4p shells on Mn were represented by a triple-ζ STO basis.[7] The electrons in lower shells on the different atoms were considered as the core and treated by the frozen-core approximation according to the scheme by Baerends et al.[5] The total molecular electron density was fitted in each SCF cycle by auxiliary s, p, d, f, and g STO fit functions[8] centered on the different atoms, in order to represent the Coulomb and exchange potentials accurately. Standard values were used for the bond distances and bond angles of the organic molecules. The d^8 $Mn(CO)_5$ framework was considered throughout this study as square pyramidal with geometrical parameters taken from ref 9.

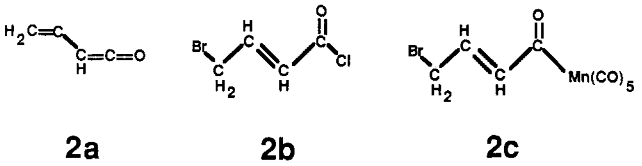
III. Exploratory Theoretical Calculations on the Bromine Abstraction from 2-Bromoacetyl Chloride by $Mn(CO)_5^-$.

The reaction of $Mn(CO)_5^-$ and other metal carbonyls with acyl halides (eq 1c) is, as already mentioned, a relatively facile process used extensively to synthesize acyl complexes.[1] It is thus surprising that a 2-bromo substitution on the acyl halide changes the course of the attack by $Mn(CO)_5^-$ from a simple acylation process (eq 2a) to a reaction in which a ketene (eq 2b) is the only product.

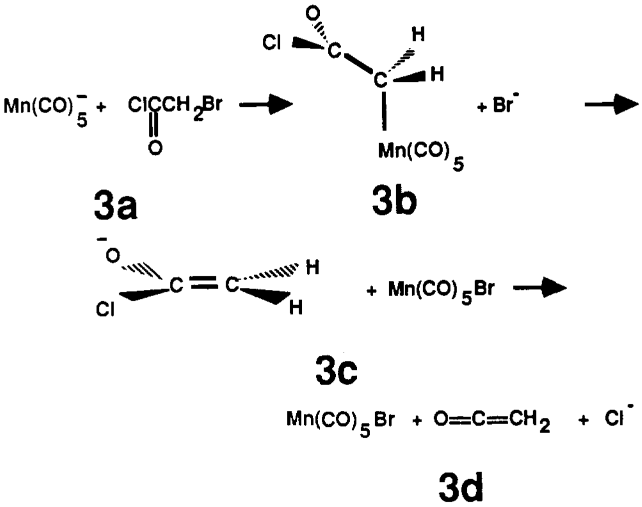
One could, based on proven reaction steps, imagine the process in eq 2b) to proceed via the initial formation of an acyl complex, **1a** → **1b**, followed by the dissociation of CO and migration of bromide to the metal center, **1b** → **1c**, with the subsequent liberation of ketene and complexation of CO to form $BrMn(CO)_5$ (**1c** → **1d**).



The fact[4] that vinylketene **2a** is formed readily from the attack of $Mn(CO)_5^-$ on 4-bromo-2-butenoyl chloride (**2b**), a reaction for which migration of bromine in **2c** to the metal center is less likely, has led us to discard **1a** → **1d** as a possible mechanism for the process in eq 2b. Further, the mechanism by which ketene is formed must clearly involve steps with low activation barriers since the process in eq 2b takes place[4] even at –40 °C, a temperature too low for the CO dissociation in **1b** → **1c** to be a plausible step in the reaction.



Another possible mechanism involves a nucleophilic attack by $Mn(CO)_5^-$ on the 2-carbon, **3a** → **3b**, rather than the 1-carbon as in **1a** → **1b**, to produce the alkyl complex, with subsequent displacement of enolate by bromide, **3b** → **3c**, and decomposition of enolate to ketene and chloride, **3c** → **3d**.



We do not, however, favor this mechanism either since we observe[4] the reaction between $Mn(CO)_5^-$ and 2-bromo-2-methylpropanoyl chloride, where the attack by $Mn(CO)_5^-$ would be on a tertiary carbon, to produce ketene as readily as the reaction between $Mn(CO)_5^-$ and 2-bromoacetyl chloride, a primary carbon center.

Even 2-bromopropenoyl chlorides (a "vinylic" bromine) react very rapidly with $Mn(CO)_5^-$ to produce methylene ketenes, with no indication of attack at the acyl center. Vinylic halides are normally very inert to nucleophilic displacement, and this again indicates attack directly on the bromine atom.

The mechanism which we do favor, since it seems as likely to proceed with 2-bromoacetyl chloride as with the

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[5] Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 71.

[6] Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

[7] (a) Snijders, G. J.; Baerends, E. J.; Vernooijs, P. *At. Nucl. Data Tables* **1982**, *26*, 483. (b) Vernooijs, P.; Snijders, G. J.; Baerends, E. J. *Slater-type Functions of the Whole Periodic System*, International Report; Free University: Amsterdam, The Netherlands, 1981.

[8] Krijn, J.; Baerends, E. J. *Fit Functions in the HFS-method*, Internal Report (in Dutch); Free University: Amsterdam, The Netherlands, 1984.

[9] Ziegler, T.; Versluis, L.; Tschinke, V. *J. Am. Chem. Soc.* **1986**, *108*, 612.

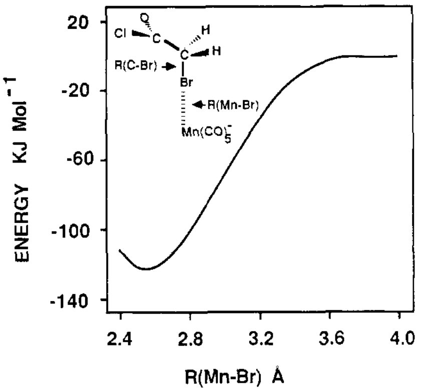
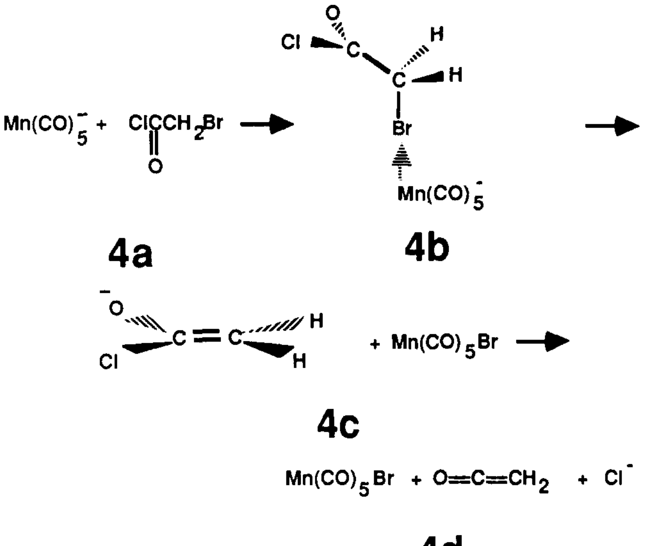


Figure 1. Calculated energy profile for the abstraction reaction **5a** to **5b** as a function of R(Mn–Br). The distance R(C–Br) was optimized as a function of R(Mn–Br) and the remaining geometrical parameters interpolated linearly (linear transit).

vinylogous 4-bromo-2-butenoyl chloride or with the tertiary bromine in 2-bromo-2-methylpropanolyl chloride, involves the initial abstraction of bromine by Mn(CO)$_5^-$ to form the enolate ion (**4b** → **4c**), followed by subsequent decomposition to ketene and chloride, **4c** → **4d**.



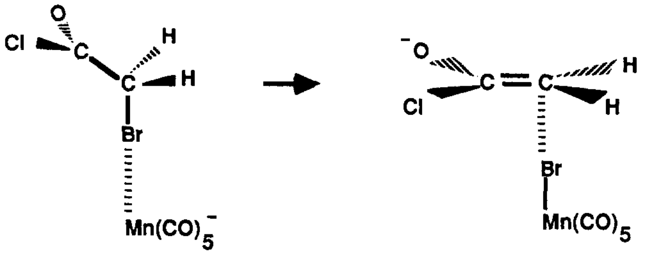
4a **4b** **4c** **4d**

In practice these steps could also be completely concerted. The abstraction of bromine from an organic molecule by an organometallic nucleophile such as Mn(CO)$_5^-$ (halogen–metal exchange) has not been much studied from a mechanistic viewpoint. We have for this reason carried out exploratory calculations on the abstraction step **4b** → **4c** with the aid of the Hartree–Fock–Slater method as implemented by Baerends et al.[5]

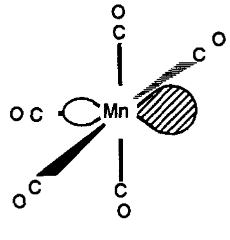
The primary objective of our calculations has been to estimate the reaction enthalpy of the abstraction step **4b** → **4c**, a property which we, on the basis of past experience,[9] feel can be reasonably well reproduced by the HFS method. We have, however, also attempted to trace the energy profile for **4b** → **4c** where 2-bromoacetyl chloride is involved. Comments will also be given on the feasibility of analogous abstraction reactions between Mn(CO)$_5^-$ and either 2-chloroacetyl chloride or 2-iodoacetyl chloride.

It follows from our calculations that the bromine atom in the early stages of the abstraction reaction **4b** → **4c** is approached by Mn(CO)$_5^-$ without relaxation of the 2-bromoacetyl chloride framework **5a**.

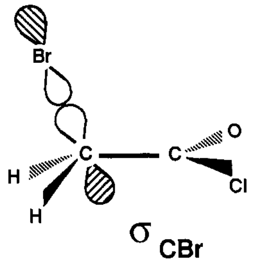
The driving force for the reaction at this point is a donor–acceptor interaction between the HOMO of Mn(CO)$_5^-$, a metal-based (s,p,d)-hybrid orbital, **6a**, and respectively the LUMO **6e** and NLUMO **6f** (next lowest unoccupied molecular orbital) of 2-bromoacetyl chloride. The LUMO of 2-bromoacetyl chloride is an in-phase combination between the π^*_{CO} orbital (65%) of the acetyl group **6c** and the σ^*_{CBr} orbital (35%) **6d**, as indicated in **6e**, whereas the NLUMO **6f** is the corresponding out-of-phase combination. The donor–acceptor adduct **5a** is at the touching distance R (Mn–Br) = 3.06 Å already stabilized by 42 kJ mol^{-1}.



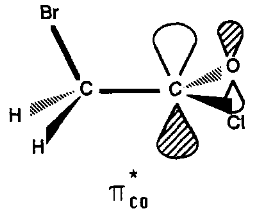
5a **5b**



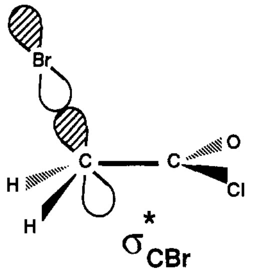
6a



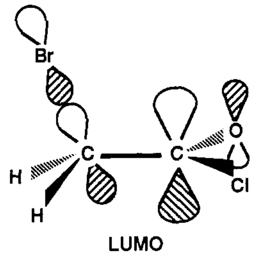
6b



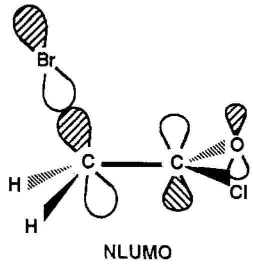
6c



6d



6e



6f

An energy profile of the entire abstraction reaction **5a** → **5b** is given in Figure 1. The profile is based on calculations in which the R(C–Br) distance was optimized as Mn(CO)$_5^-$ approaches the bromine atom with gradual relaxation of the remaining geometrical parameters by a linear interpolation (linear transit) of internal coordinates between the initial (e.g. R(Mn–Br) at infinite separation in **5a**) and final (e.g. R(Br–C) at infinite separation in **5b**) conformations. The reaction **5a** to **5b** is calculated to be exothermic with a reaction enthalpy of −118 kJ mol^{-1} and does not exhibit any activation barrier; see Figure 1. The

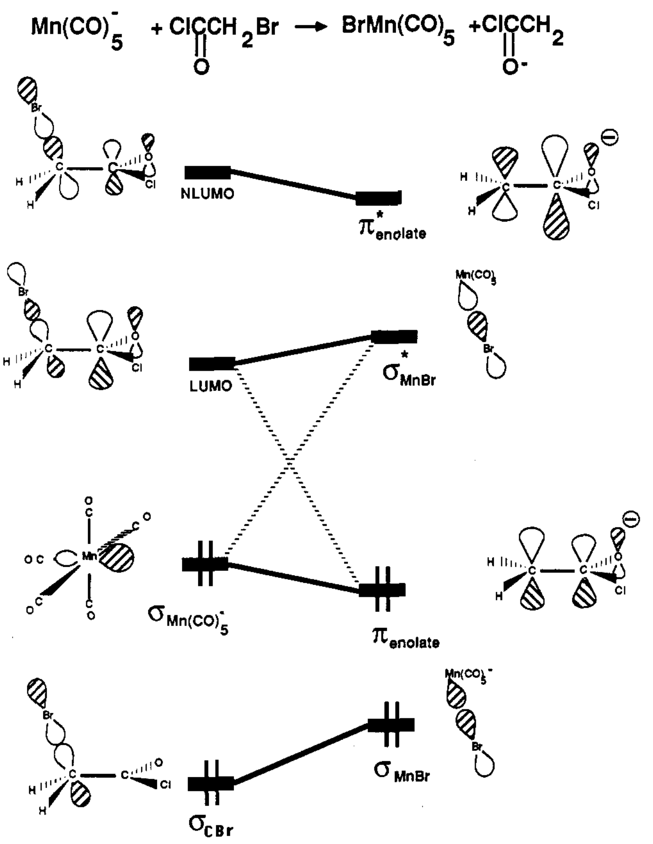


Figure 2. Correlation diagrams between orbitals of reactants (left) and orbitals of products (right) for the abstraction reaction **5a** to **5b**. Solid lines indicate actual correlations and dashed lines intended correlations.

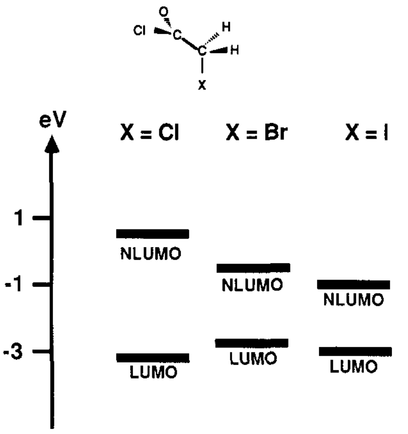


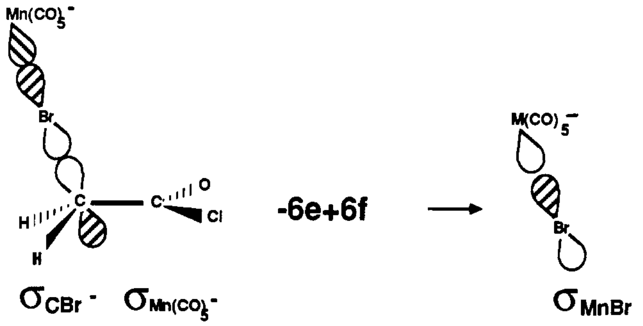
Figure 3. Orbital energies for the LUMO **6e** and NLUMO **6f** of XH_2CCOCl, with X = Cl, Br, and I.

abstraction step **5a** to **5b** should thus be quite feasible, at least in the case of 2-bromoacetyl chloride.

The structure **5b** represents an adduct between $BrMn(CO)_5$ (with R(Mn–Br) = 2.56 Å) and an enolate ion. The R(C–Br) bond distance in **5b** was optimized at 2.65 Å (the R(C–Br) distance in 2-bromoacetyl chloride is 1.94 Å). The stability of the adduct **5b** compared to $BrMn(CO)_5$ (D(Mn–Br) optimized at 2.44 Å) and the enolate ion at infinite separation was calculated to be 39 kJ mol^{-1}. Thus the enthalpy for the reaction **4a** → **4c** is estimated to be −79 kJ mol^{-1}. The stability of **5b** is primarily due to a transfer of charge (0.16 e) from the σ_{MnBr} HOMO of $BrMn(CO)_5$ to the $\pi^*_{enolate}$ LUMO.

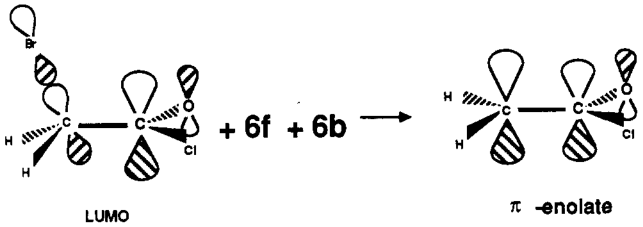
The four key orbitals among the reactants are correlated in Figure 2 with the resulting orbitals among the products. There is essentially two electron pairs involved in the reaction. One of the electron pairs is on the reactant side (Figure 2) in the σ_{CBr} orbital **6b**. This orbital will be stabilized "from above" by the HOMO **6a** under the formation of the in-phase bonding combination 7. The in-phase combination 7 correlates smoothly (Figure 2) with the σ_{MnBr} orbital on the product side by the aid of in-phase admixtures from the LUMO **6e** and the NLUMO **6f** of 2-bromoacetyl chloride.

7



8

The second electron pair resides on the reactant side in the HOMO **6a** of $Mn(CO)_5$. This orbital is destabilized "from below" by the σ_{CBr} orbital **6b** under the formation of the out-of-phase combination 8 between **6a** and **6b**. The orbital 8 evolves during the reaction (Figure 2) into the unoccupied orbital on the product side. There is thus for the orbital **6a**, holding the electron pair of highest energy on the reactant side, an intended correlation with the unoccupied σ^*_{MnBr} on the product side (Figure 2).



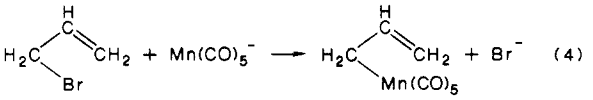
9

Fortunately, however, the linear combination between σ_{CBr} **6b** and the LUMO **6e** and NLUMO **6f** of 2-bromoacetyl chloride, which evolves into the occupied π-orbital 9 of the enolate ion, drops early on in the reaction (Figure 2) below 8, thus avoiding an activation barrier for the abstraction reaction **5a** to **5b**.

The relatively high stability of the enolate ion in comparison to other organic anions seems to be of crucial importance for the viability of bromine abstraction by $Mn(CO)_5^-$ from 2-bromoacetyl chloride. Thus, alkyl bromides normally react with $Mn(CO)_5^-$ by nucleophilic displacement of Br^- to form the alkyl complex rather than $BrMn(CO)_5$ and R^-

$$\mathrm{Mn(CO)_5^- + RBr \rightarrow BrMn(CO)_5 + Br^-} \quad (3)$$

Even the allyl bromide, 3-bromo-1-propene, was observed[10] to form the σ-allylic complex of eq 4 rather than the modestly stable allyl anion and $\mathrm{BrMn(CO)_5}$. The ability

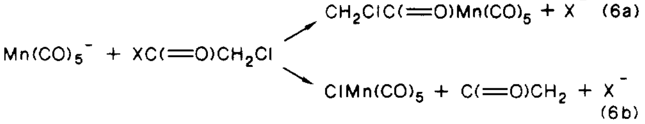


to form ketene in the reaction with $\mathrm{Mn(CO)_5^-}$ is not restricted to 2-bromoacyl chlorides. We observe[4] 2-bromoacyl bromides to react as readily with $\mathrm{Mn(CO)_5^-}$ to form ketenes, as shown in eq 5 for the case of 2-bromoacetyl bromide. The reaction in eq 5 would, in view of our

$$\mathrm{Mn(CO)_5^- + BrC({=}O)CH_2Br \rightarrow BrMn(CO)_5 + CC({=}O)H_2 + Br^-} \quad (5)$$

proposed mechanism, indicate that the abstraction of bromine can compete with the acylation process of eq 2a, even when chlorine is replaced with the better leaving group bromine.

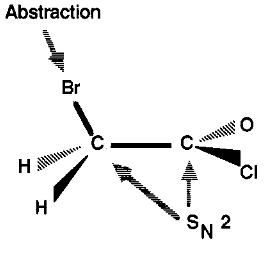
The abstraction of 2-chlorine in 2-chloroacyl chlorides does not appear to be as facile a process as the corresponding bromine abstraction. Thus, both 2-chloroacetyl chloride and 2-chloroacetyl bromide reacted[4] with $\mathrm{Mn(CO)_5^-}$ to form the acetyl complex, presumably by a simple acetylation process.



That chlorine is less prone to abstraction by $\mathrm{Mn(CO)_5^-}$ than bromine can be related to differences in the energies and compositions of the LUMO's **6e** and NLUMO's **6f** of *n*-chloroacetyl halide (**1**) and 2-bromoacetyl halide (**2**), respectively. The LUMO **6e** is, as already mentioned, an in-phase combination between σ^*_{CX} (X = Br, Cl) and π^*_{CO}. For X = Br the σ^*_{CX} orbital is relatively low in energy and σ^*_{CBr} contributes as a consequence substantially (35%) to the LUMO **6e** of **2**. Further σ^*_{CBr} has a large amplitude on Br. Both factors are of importance for ensuring a sizable donor–acceptor interaction in the early stages of the abstraction interaction **5a** to **5b** involving **2**. The σ^*_{CCl} orbital is on the other hand of higher energy than σ^*_{CBr} and contributes as a consequence only modestly (10%) to the LUMO **6e** of **1**. Further σ^*_{CCl} has a smaller amplitude on the halide than σ^*_{CBr}. One would thus expect the initial donor–acceptor interaction between $\mathrm{Mn(CO)_5^-}$ and **1** to be less favorable than the same interaction between $\mathrm{Mn(CO)_5^-}$ and **2** in the early stages of the abstraction reaction **5a** to **5b**. We give in Figure 3 the energies of the LUMO's and NLUMO's for $\mathrm{XCH_2COCl}$ with X = Cl, Br, and I. Note that the LUMO for X = Cl, which is almost exclusively σ^*_{CCl}, is very high in energy.

Our admittedly qualitative consideration would suggest that the reaction between $\mathrm{Mn(CO)_5^-}$ and 2-iodoacetyl chloride with abstraction of iodine and formation of ketene should be at least as favorable as the corresponding reaction between $\mathrm{Mn(CO)_5^-}$ and 2-bromoacetyl chloride. Thus, σ^*_{CI} is of lower energy than σ^*_{CBr} with a larger amplitude on the halide. The LUMO of 2-iodoacetyl chloride with a 39% contribution from σ^*_{CI} should as a consequence be ideally suited for a stabilizing donor–acceptor interaction in the early stages of the abstraction reaction **5a** to **5b**.

We have in this paper discussed the three competing reaction modes shown in **10**. A full theoretical treatment would have required calculations on the reaction enthalpies and activation energies of each reaction mode in **10** for X = Cl, Br, and I. Such a task is unfortunately not feasible at the present time, and we have as a consequence been restrained to calculations on the energetics of the abstraction reaction **5a** to **5b**. These calculations have, however, shown that the abstraction reaction is energetically favorable, and they fully support the proposed mechanism for the ketene formation.



10

A recent study[11] of the reaction of $\mathrm{Mn(CO)_5^-}$ with 2-chloro-, 2-bromo-, or 2-iodoacyl esters has provided additional evidence that our proposed mechanism is correct. In the above reactions, the expected products were the σ-$\mathrm{Mn(CO)_5}$ derivatives, formed by $\mathrm{S_N2}$ displacement. However, where the halogen was Br or I, considerable halogen–metal exchange was commonly observed, sometimes to the complete exclusion of the σ-product. The corresponding chloroesters however, never showed any metal–halogen exchange reactivity.

IV. Concluding Remarks

Reactions between either alkyl halides or acyl halides and anionic metal carbonyls are usually associated with a nucleophilic displacement of the halide $\mathrm{X^-}$ by the metal center via a $\mathrm{S_N2}$ mechanism (**10**). An analysis of recent experimental studies[4] on the reactions between $\mathrm{Mn(CO)_5^-}$ and 2-bromo-substituted acyl halides (**2a**) have led us to suggest a more unusual mechanism, in which bromine is abstracted by the anionic metal carbonyl through a direct attack of the metal center on Br (**10**). We have investigated the feasibility of the postulated abstraction reaction by tracing its energy profile (Figure 1). Our calculations indicate that the abstraction reaction **4a** to **4c** is energetically favorable with a reaction enthalpy of $-79\ \mathrm{kJ\ mol^{-1}}$. The enthalpy ΔH_4 for the abstraction reaction **4a** to **4c** can according to eq 7

$$\mathrm{Mn(CO)_5^- \rightarrow Mn(CO) + e^-} + A[\mathrm{Mn(CO)_5}] \quad (7a)$$

$$\mathrm{Mn(CO)_5 + ClC(O)CH_2Br \rightarrow BrMn(CO)_5 + ClC(O)CH_2Br} + D(\mathrm{ClC(O)CH_2\text{–}Br}) - D(\mathrm{Br\text{–}Mn(CO)_5}) \quad (7b)$$

$$\mathrm{ClC(O)CH_2 + E^- \rightarrow ClC(O)CH_2^-} - A[\mathrm{ClC(O)CH_2}] \quad (7c)$$

be written as

$$\Delta H_4 = D(\mathrm{ClC(O)CH_2\text{–}Br}) - D(\mathrm{Br\text{–}MN(CO)_5}) + A[\mathrm{Mn(CO)_5}] - A[\mathrm{ClC(O)CH_2}] \quad (8)$$

Experimental C–Br and Br–$\mathrm{Mn(CO)_5}$ bond energies are of about the same magnitude with $D(\mathrm{CH_3\text{–}Br})^{1b} = 285$ kJ

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[10] (a) Kaesz, H. D.; King, R. B.; Stone, F. G. A. *Z. Naturforsch., B* **1960**, *15*, 6. (b) McClellan, W. R.; Hoehn, M. H.; Cripps, H. N.; Muetterties, E. I.; Hawk, B. W. *J. Am. Chem. Soc.* **1961**, *83*, 1601.

[11] Masters, A. P.; Sorensen, T. S. *Can. J. Chem.*, submitted for publication.

mol^{-1} and $D(Br–Mn(CO)_5)^{1b}$ = 276 kJ mol^{-1}, and we calculate the difference $D(ClC(O)CH_2–Br) - D(Br–Mn(CO)_5)$ to be 4 kJ mol^{-1}. This difference adds as a consequence little to ΔH_4. The difference between the electron affinities of $Mn(CO)_5$ and $ClC(O)CH_2$ was on the other hand calculated as $A[Mn(CO)_5] - A[ClC(O)CH_2] = -83$ kJ mol^{-1}. It is thus clear that the driving force behind the abstraction reaction is due to the strong stabilization of a negative charge by the enolate.

We have assumed that reaction 2a proceeds in a stepwise fashion (**4a** through **4d**). It is also possible that ketene and Cl^- is liberated directly from the adduct **5b** in a concerted mode. We expect in either case ketene and Cl^- to be produced readily once bromine has been abstracted in the step **5a** to **5b**.

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Registry No. $Mn(CO)_5^-$, 14971-26-7; 2-bromoacetyl chloride, 22118-09-8; 2-chloroacetyl chloride, 79-04-9; 2-iodoacetyl chloride, 38020-81-4.

Reaction of Trialkylboranes with Alkylamines: Synthesis of Dialkylamines

George W. Kabalka* and Zhe Wang

Departments of Chemistry and Radiology, University of Tennessee, Knoxville, Tennessee 37996-1600

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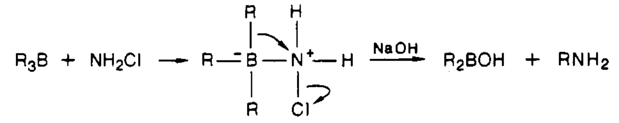
Trialkylboranes react with alkylamines, in the presence of sodium hypochlorite, to form dialkylamines. The reaction proceeds via an anionotropic rearrangement of the organoborate complex formed by the organoborane and the *N*-chloroalkylamine generated in situ.

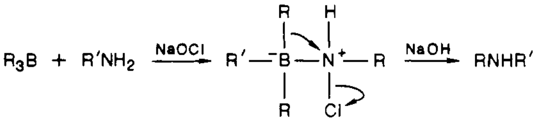
Introduction

Organoboranes have proven to be valuable synthetic intermediates due to their ease of formation and facile reactivity.[1,2] Many of the borane rearrangements involve anionotropic rearrangements of appropriately substituted organoborate complexes; generally, an alkyl group migrates from an electron-rich boron atom to an electron-deficient neighboring atom.[3] The reaction has been used to prepare a wide variety of organic molecules including those in which the migration terminus is a nitrogen atom.[4-6]



$$R_3B + NH_2Cl \longrightarrow R-\underset{R}{\overset{R}{B^-}}-\underset{Cl}{\overset{H}{N^+}}-H \xrightarrow{NaOH} R_2BOH + RNH_2$$

The nature of the leaving group[7-11] and the groups attached to nitrogen have been varied extensively.[7-13] We wish to report a simple reaction sequence involving the in situ preparation of an *N*-chloroalkylamine which leads to dialkylamine products.



$$R_3B + R'NH_2 \xrightarrow{NaOCl} R'-\underset{R}{\overset{R}{B^-}}-\underset{Cl}{\overset{H}{N^+}}-R \xrightarrow{NaOH} RNHR'$$

Results and Discussion

The rapid reaction of sodium hypochlorite with amines is well documented.[14] On the basis of our earlier studies, the reaction of organoboranes with *N*-chloroalkylamines formed in situ appeared likely.[15,16] Our investigations involved two different protocols for preparing the *N*-chloroalkylamines: route A in which the sodium hypochlorite was added dropwise to a mixture of organoborane and alkylamine and route B in which the sodium hypochlorite was first added to the alkylamine and this solution was then added to the organoborane. Both protocols were utilized throughout the study. In general, method B leads to slightly higher yields of the desired product.

The reactions were run at 0 °C utilizing equimolar quantities of organoborane, alkylamine, and sodium hypochlorite. Preliminary experiments using trihexylborane and *n*-hexylamine revealed that excess quantities (50% and 100%) of amine and hypochlorite did not increase the yield of product. Evaluation of reaction temperatures demonstrated that optimum yields were obtained when reactions were carried out at 0 °C and allowed to warm to room temperature.

The reaction does not appear to be sensitive to the steric requirements of the organoborane. As illustrated in Table

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(1) Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1972.

(2) Pelter, A.; Smith, A. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Olcis, W. D., Eds.; Pergamon: New York, 1979.

(3) Negishi, E.; Idecavage, M. K. *Org. React.* (*N.Y.*) **1985**, *33*, 1.

(4) Kovacic, P.; Lowery, M. K.; Field, K. W. *Chem. Rev.* **1970**, *70*, 639.

(5) Steinberg, H.; Brotherton, R. J. *Organoborane Chemistry*; John Wiley & Sons: New York, 1966; Vol. II, p 17.

(6) Kabalka, G. W.; Sastry, K. A.; McCollum, G. W.; Yoshioka, H. *J. Org. Chem.* **1981**, *46*, 4296.

(7) Rathke, M. W.; Inoue, N.; Varma, K. R.; Brown, H. C. *J. Am. Chem. Soc.* **1966**, *88*, 2870.

(8) Tamura, Y.; Minaimikawa, J.; Fuji, S.; Ikeda, M. *Synthesis* **1974**, 196.

(9) Jiganni, V. B.; Pelter, A.; Smith, K. *Tetrahedron Lett.* **1978**, 181.

(10) Kabalka, G. W.; Henderson, D. A.; Varma, R. S. *Organometallics* **1987**, *6*, 1369.

(11) (a) Rotermund, G. W.; Köster, R. *Justus Liebigs Ann. Chem.* **1965**, *686*, 153. (b) Brown, H. C.; Negishi, E.; Mueller, R. M. *J. Org. Chem.* **1985**, *50*, 520.

(12) Brown, H. C.; Kim, K.-W.; Srebnik, M.; Singaram, B. *Tetrahedron* **1987**, *43*, 4071.

(13) suzuki, A.; Sono, S.; Itoh, M.; Brown, M. C.; Midland, M. M. *J. Am. Chem. Soc.* **1971**, *93*, 4329.

(14) Coleman, G. H.; Johnson, H. C. *Inorg. Synth.* **1938**, *1*, 59.

(15) Kabalka, G. W.; McCollum, G. W.; Kunda, S. A. *J. Org. Chem.* **1984**, *49*, 1656.

(16) Sharefkin, J. C.; Banks, H. D. *J. Org. Chem.* **1965**, *30*, 4313.

0276-7333/89/2308-1093$01.50/0