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#### THE GAS PHASE CHEMISTRY OF TRANSITION

## **METAL-CONTAINING ANIONS WITH ORGANIC MOLECULES**

By

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#### ABSTRACT

# THE GAS PHASE CHEMISTRY OF TRANSITION METAL-CONTAINING ANIONS WITH ORGANIC MOLECULES

By

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The gas-phase chemistry of metal-containing anions with 1-chloro-n-alkanes, 1-hydroxy-n-alkanes, 1-bromo-n-chloro-alkanes, 1-chloro-n-alcohols (n=1 to 6), 1-nitro-n-alkanes (n = 1 to 4), and n-butyl nitrite is presented. The metal-containing anions studied ( $Fe(CO)_{3,4}^{-}$ ,  $Cr(CO)_{3-5}^{-}$ ,  $Co(CO)_{2,3}^{-}$ , and  $CoNO(CO)_{1,2}^{-}$ ) are formed by low energy electron impact on the corresponding metal carbonyls,  $M(CO)_{n}$ .

The results suggest a common mechanism in which the metal inserts into the C-functional group bond and the charge is transferred (delocalized) to the electronegative group (e.g., Cl, OH, and  $NO_2$ ). Metal insertion into C-C and C-H bonds which is seen in the corresponding positive metal ion reactions is <u>not</u> observed in the reactions of metal-containing anions. The metal anions also attack bonds within the functional group in reactions with n-alcohols (O-H bond) and n-nitroalkanes (N-O bond).

Following formation of the metal insertion/charge transfer intermediate, rearrangement of the ion may occur. Evidence is presented for a  $\beta$ -H shift process in reactions of metal-containing anions, which is also common in the corresponding positive metal ion reactions. The products from the reaction of nitroalkanes are shown to result from rearrangements of the metal insertion/charge transfer intermediate. The excess energy which remains in these complexes is then lost through a competitive ligand loss process. This ligand loss process is quite different from the analogous process for positive metal ions.

The exothermicity of the charge transfer process appears to determine the products which are observed. The reaction trends of the various metal-containing anions suggests the following order of electron affinities of the metal-containing species: E.A. $(Cr(CO)_3) < E.A.(Co(CO)_2) < E.A.(CoCONO)$  $< E.A.(Co(CO)_3) < E.A.(Fe(CO)_3).$ 

Several ligand effects observed in the reactions of metal-containing anions are discussed. These include the decrease in reactivity as the number of ligands present on the metal increases and the possible participation of carbonyl ligands in the metal insertion and rearrangement processes.

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#### **CHAPTER 1**

#### **INTRODUCTION**

In recent years there has been a growing interest in the study of the gas-phase reactions of atomic metal and metal-containing positive ions with organic molecules. Studies of these reactions using ion cyclotron resonance  $(ICR)^{1-4}$  and ion beam techniques<sup>5-8</sup> yield information on the activation of bonds in organic molecules by metal ions in the absence of complicating solvent effects. Thermodynamic, kinetic, and mechanistic information concerning the organometallic and coordination chemistry of metal ions can be obtained from these studies.

An important area of interest has been the study of the interaction of metal ions with organic molecules containing specific functional groups. Metal ions appear to insert into polar bonds such as the C-Cl bond in isopropyl chloride<sup>9</sup>. The metal ion (Co<sup>+</sup>) inserts into the C-Cl bond as shown in reaction 1.

$$Co^{+} + CI \rightarrow \sum_{H} Co^{+} - CI \xrightarrow{\beta - H} \int \cdots Co^{+} \leftarrow CIH$$
 (1)

In this intermediate structure, one carbon is **a** to the metal and two carbons are  $\beta$  to the metal. A hydrogen which is on a  $\beta$ -carbon (i.e. a  $\beta$ -H) is observed to shift onto the metal as shown in reaction 1. This  $\beta$ -H shift mechanism is common in both solution<sup>10</sup> and gas-phase positive metal ion/molecule reactions<sup>11</sup>. Following the  $\beta$ -H shift, rearrangement may occur producing an HCl ligand on the metal as shown in reaction 1. The metal insertion/ $\beta$ -H shift mechanism produces two molecules (HCl and propene) from one. These two molecules then compete as ligands on the metal ("competitive ligand loss") as shown in reaction 2.

The proton affinities of ligands have been shown to parallel the strength of the metal-ligand interaction<sup>12</sup>. Ligands which have low proton affinities are lost preferentially to ligands with higher proton affinities in the competitive ligand loss process. Ligands which are  $\pi$  -donors (e.g. olefins) also interact strongly with positive metal ions and frequently are preferentially retained in the competitive ligand loss process.

In addition to studies of the reaction of metal ions with alkyl chlorides<sup>2,9,11</sup>, the reactions of transition metal ions with organic species such as alkanes<sup>5,6,13-15</sup>, alkenes<sup>3,6,17</sup>, alcohols<sup>9</sup>, amines<sup>18</sup>, aldehydes<sup>19,20</sup>, ketones<sup>19,20</sup>, carboxylic acids<sup>19</sup>, esters<sup>19</sup>, ethers<sup>20</sup>, sulfides<sup>21</sup>, and nitroalkanes<sup>22</sup> have also been reported. The major reaction pathway for the majority of these compounds involves insertion of the metal ion into the

relatively weak C-functional group bond as the first mechanistic step. This may be followed by the  $\beta$ -H shift and competitive ligand loss process similar to that of the alkyl chlorides. Metal insertion has been observed not only into C-functional group bonds but also C-C bonds, C-H bonds (e.g. alkanes<sup>5,6,13-15</sup>) and even into bonds within functional groups (e.g. nitroalkanes<sup>22</sup>).

The products which are observed in the positive metal ion reactions can usually be explained by the general mechanism: metal insertion/ $\beta$ -H shift/competitive ligand loss<sup>11</sup>. The ability to explain and even predict the products observed in metal ion/molecule reactions with neutral organic molecules containing various functional groups has led to the utilization of these metal and metal-containing ions as chemical ionization (CI) reagents<sup>19,23-26</sup>. Metal and metal-containing ion/molecule reactions have been shown to provide molecular weight, functional group, and structural information about the neutral organic reactant species.

The metal ions used in these studies may be formed in several ways. The two most common sources of metal ions utilized have been laser ionization of metal foils<sup>27</sup> which generates the bare metal ion, M<sup>+</sup>, and 70 eV electron impact on metal carbonyls  $(M(CO)_n)^{28}$ . One advantage of the use of metal carbonyls is that metal ions with various ligands present (e.g.  $M(CO)_x^+(x=1$  to n)) are formed in addition to the bare metal ion M<sup>+</sup>. This allows the study of ligand effects<sup>1,12,18,22,25,29</sup> (i.e. changes in reactivity as the number of ligands on the metal is varied).

The majority of the gas-phase organometallic ion/molecule reactions studied have dealt with metal and metal-containing positive ions. These previous studies have reported changes in reactivity as the type of metal, number of ligands on the metal (ligand effects), and the neutral organic molecule are varied. Relatively few studies have been performed on the corresponding

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metal and metal-containing anions; i.e., none has determined changes in the chemistry of an isolated metal "center" due to a change in the charge on the metal species.

Early mass spectrometric studies have shown that  $M(CO)_{n-1}^{-1}$  is the predominant anion formed by 70 eV electron impact on transition metal carbonyls,  $M(CO)_n$ , with a small percentage of  $M(CO)_{n-2}^{-1}$  also being formed<sup>30-32</sup>. The first metal anion/molecule reactions studied with ICR were performed by Dunbar<sup>33</sup> and Beauchamp<sup>34</sup>. The stable 17-electron species,  $M(CO)_{n-1}^{-1}$ , were found to be generally unreactive in the gas phase, whereas the  $M(CO)_{n-2}^{-1}$  anions (15-electron species) were observed to react with the neutral  $M(CO)_n^{33}$  as shown in reaction 3.

$$Fe(CO)_3^- + Fe(CO)_5 \longrightarrow Fe_2(CO)_6^- + 2CO$$
(3)

Recently Wronka and Ridge<sup>4</sup> have observed sequential anion/molecule reactions in  $Fe(CO)_5$  up to  $Fe_4(CO)_{13}^{-}$ .

Reactions of these metal-containing anions with organic molecules have been studied using ICR and flowing afterglow techniques. Weddle and Ridge<sup>35</sup> reported the chemistry of  $Fe(CO)_3^-$  and  $Fe(CO)_4^-$  with a series of thirteen organic molecules. Ligand substitution of the neutral organic molecule for one or two carbonyl ligands was observed for 9 of the 13 compounds studied. Only one rearrangement-type reaction was reported, ion-induced decarbonylation of maleic anhydride. The predominance of ligand substitution reactions and lack of (apparent) bond-breaking and rearrangement reactions for  $Fe(CO)_3^$ and  $Fe(CO)_4^-$  is not surprising since, in the reactions of <u>positive</u> metal ions, as the number of ligands on the metal increases ligand substitution processes dominate the products observed<sup>1,12,18,22,25,29</sup>. Freiser et. al.<sup>36</sup> were able to study the chemistry of the bare metal anion  $Cr^-$  with a series of Bronsted acids. Only proton abstraction reactions were observed. The bare metal anion  $Cr^-$  was formed during collision induced dissociation on the  $Cr(CO)_5^-$  anion which was produced by electron impact on  $Cr(CO)_6$ .

Squires et. al.<sup>37</sup> have formed metallocarboxylic anions in the gas phase  $(Fe(CO)_4COOH^-)$  by reacting OH<sup>-</sup> with neutral  $Fe(CO)_5$  in a flowing afterglow apparatus, in an attempt to study the water gas shift reaction. McDonald et. al.<sup>38,39</sup> have also used a flowing afterglow apparatus to study the reaction of anions formed by electron impact on  $Fe(CO)_5$ . The anion  $Fe(CO)_4^-$  reacts with a series of halo-methanes to yield halogen atom transfer products and in some cases ligand substitution with loss of one or two carbonyl ligands<sup>38</sup>. The reactions of  $Fe(CO)_3^-$  were also studied<sup>39</sup> in which adduct products with the neutral molecule were observed due to the termolecular collisional stabilization with the  $He/CH_4$  buffer gas, in addition to ligand substitution of the neutral molecule for carbonyl ligands. The reaction of  $Fe(CO)_3^-$  with  $CH_3Br$  yields a ligand substitution product of  $CH_3Br$  for two carbonyl ligands and abstraction of a bromine atom from  $CH_3Br$  (reactions 4 and 5).

$$Fe(CO)_3^- + CH_3Br \longrightarrow Fe(CO)(CH_3Br)^- + 2CO \qquad (4)$$
$$Fe(CO)_3Br^- + CH_3. \qquad (5)$$

The mechanism proposed was the formation of an ion/radical collision complex produced by the bromine atom transfer, although oxidative addition is still possible since  $Fe(CO)_3^-$  has two available coordination sites. It is suggested that the ion/radical complex could dissociate to produce the bromine abstraction product or the methyl radical could form a bond with the metal and displace two carbonyl ligands to yield the substitution product of the neutral CH<sub>3</sub>Br

$$\begin{bmatrix} CO \\ H_3C - Fe \\ Br \end{bmatrix}$$

To date, there has been no attempt to formulate a general mechanism to describe metal-containing anion/organic molecule interactions. The studies described in this dissertation were initiated in an attempt to obtain an understanding of the reactions and mechanisms of these metal-containing anions. Low energy (0 to 5 eV) electron impact was used to produce a greater percentage of the more reactive  $M(CO)_{n-2}^{-}$  and  $M(CO)_{n-3}^{-}$  species from  $Co(CO)_3NO$ ,  $Fe(CO)_5$ , and  $Cr(CO)_6^{30-32}$ . The reactions of these metal-containing anions with a series of n-chloroalkanes, n-alcohols, n-nitroalkanes, and several bifunctional compounds were studied in order to propose a general mechanism for the reaction of metal anions with polar organic molecules.

Based on the current literature, then, what similarities and differences would be expected in the chemistry of organometallic anions and cations? Metal anions may be expected to insert into bonds in a manner similar to that of cations. There is <u>no</u> evidence in the literature which suggests that  $\beta$ -H shifts may occur for anions, however organometallic anions containing M-H bonds have been reported<sup>40</sup>. If a rearrangement such as

$$M^{a} + C_{3}H_{7}Cl \longrightarrow C_{3}H_{7}-M^{a}-Cl \xrightarrow{\beta -H} (C_{3}H_{6})M^{a}(HCl)$$
  
shift

occurs when a is (+), ligand loss correlates with the ligands' proton affinities. When a is (-), ligand loss appears to correlate with Lewis acidity<sup>41</sup>. Thus, we may expect both similarities and differences in anion and cation reactions.

The previous studies mentioned have not addressed the question concerning the location of the negative charge in these anions. In the corresponding positive ion reactions, the positive charge remains predominantly on the metal due to the lower ionization potential of the metal compared to that of the ligands present. In the discussion of the anion reactions, the electron affinities of the metal species and ligands must be considered when determining the location of the negative charge. The electron affinities relevant to this work which are available are listed in Appendix A. The amount of electron affinity data available on metal carbonyl species is small and incomplete but proves invaluable in explaining the anion/molecule reactions observed. For example, the electron affinities of all three bare metals (Fe, Cr, and Co) have been determined, but the various carbonyl-containing species of only one metal (Fe) have been determined. It will be shown that the location of the negative charge and the types of ligands present play an important role in explaining the reactions and mechanisms observed.

#### **CHAPTER 2**

#### EXPERIMENTAL

## A. The Ion Cyclotron Resonance Technique

## 1. The ICR Cell

Several reviews have been published on the ion cyclotron resonance (ICR) technique $^{42-45}$ . The technique is extremely powerful in the study of bimolecular gas-phase ion/molecule reactions. A typical three-region ICR cell is shown in Figure 1.



Figure 1. Three-region ICR  $cell^{43}$ .

The cell is placed between the poles of an electromagnet with the magnetic field B (H) directed as shown. Electron impact is utilized to ionize the sample molecules in the source region of the cell. Electrons are emitted from a hot rhenium filament (collimated by B) located outside the cell, pass through the cell (if not scattered by collisions) and strike the collector.

The motion of a charged particle in a uniform magnetic field (B) is constrained to a circular orbit of angular frequency  $\omega_c$  in a plane normal to B and is unrestricted along the axis parallel to B. The potential applied to the trapping plates (<.5 V) prevents the ions from drifting to the sides of the cell. The polarity of the trapping plate potential is made positive to trap positive ions and negative to trap negative ions. The force on an ion in the plane perpindicular to B is given by

$$F = ma = evB$$

For an ion of mass m, charge e, and velocity v normal to B, an acceleration <u>a</u> will occur. The force, F, is normal to both B and v. Circular motion results for sufficiently large values of B with  $a = v^2/r$  where r is the radius of the ion path, resulting in the equation of force:

$$F = ma = mv^2/r = evB$$

If  $\omega_c$  is the angular frequency of the ion, then the basic cyclotron equation (1) may be derived:

$$mv/r = m\omega_c = eB$$

$$\omega_{\rm C} = eB/m$$
 (radians/second) (1)

or  $v_c = eB/2 \pi m$  (cycles/second)

The cyclotron equation may be rewritten as

$$m/e = B/2 \pi v_c \qquad (2)$$

which shows that at constant frequency, m/e varies linearly with B. Therefore, a linear mass scale for resonant ions may be produced by varying B.

The ions are made to drift from the source region to the resonance (analyzer) region of the cell by applying a potential difference between the plates above and below the electron beam (drift plates). The resulting crossed electric and magnetic fields cause ions to drift in a direction perpendicular to both fields. The drift velocity is given by

$$v_{drift} = \varepsilon_{drift}/B$$
 (3)

where  $\varepsilon_{drift}$  is the electric field intensity. The relationship between the three vectors (B,  $\varepsilon_{drift}$ ,  $v_{drift}$ ) involved is shown in Figure 2.



Figure 2. Vector contributions resulting in the drift motion 42.

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The drift velocity for a typical cell (8.6 cm. in length) under normal conditions is v50 m/sec. Under these conditions the ion spends  $v2 \times 10^{-3}$  seconds in the cell. This relatively long ion residence time (compared to conventional mass spectrometric techniques) results in the formation of ion/molecule reaction products due to collisions of the reactant ions with a neutral species.

#### 2. Detection of Ions

If a radiofrequency (rf) field is applied to the drift plates of the ICR cell, an ion in resonance with this field (i.e., the cyclotron frequency of the ion and the frequency of the applied field are equal) absorbs energy which results in an increase in the velocity of the ion. Equation 1 shows that  $v_c$  is independent of v and r separately but is dependent on their ratio v/r. Thus, an ion remains in resonance by increasing its radius in proportion to the increase in velocity.

The absorption of power from an rf field is the basis for the detection of ions in ICR. The most common form of detector utilized in ICR is the marginal oscillator (MO) shown in Figure 3.



Figure 3. Simplified circuit diagram of the marginal oscillator detector 43.

The oscillator may be considered to be a constant current generator which drives a parallel LC tank circuit at its resonance frequency. The two analyzer drift plates are a capacitive element of the marginal oscillator. Ions are detected when their cyclotron frequency (equation 2) is equal to that of the oscillator. The detector response reflects the change in rf voltage across the tank circuit. When a signal is observed, a current is generated in the circuit due to the power absorbed by the ions. The frequency of the marginal oscillator is usually chosen such that a change of 100 gauss in B corresponds to a change of one atomic mass unit (u). Using equation 2 this frequency corresponds to 153.57 kHz:

$$v_{\rm C} = \frac{1.6021 \times 10^{-19} \,{\rm C} \times 0.01 \,{\rm T}}{6.2832 \times 10. \times 1.6604 \times 10^{-27} \,{\rm kg./u.}} = 153.57 \,{\rm kHz}$$

The force (field intensity times charge) exerted on the ion which is in resonance with the rf field will be

$$F = ma = (\epsilon_{rf}/2)e$$

where  $\varepsilon_{rf}$  is the rf electric field intensity. The velocity of the ion which has been in resonance for time t is given by:

$$v = \int_{0}^{t} a dt = (\epsilon_{rf} et)/2m$$

The product of the force on the ion and its velocity yields the equation for instantaneous power absorption:

$$A(t) = Fv = (\varepsilon_{rf}^2 e^2 t)/4m$$

The average power absorbed by an ion from the rf field while in the analyzer region for a time  $(0 < t < \tau)$  is

$$A(\tau) = A(t) = \frac{1}{\tau} \int_{0}^{\tau} A(t) dt = (\epsilon_{rf}^2 e^2 \tau)/8m$$
 (4)

Note that in equation 4 the power absorbed by an ion depends inversely on its mass. It has been shown<sup>42</sup> that in marginal oscillator detection the signal intensity must be divided by the mass of the ion in order to be proportional to the relative ionic abundance. This is due to the fact that the power absorbed by the ions is proportional to the time spent in the analyzer region and that the drift velocity is inversely proportional to the magnetic field (equation 3) (i.e., higher mass ions move slower and thus absorb power from the marginal oscillator more time than the lower mass ions).

The signal/noise ratio is greatly enhanced by signal modulation and phase-sensitive detection. Common modulation methods include modulation of the magnetic field (by a few gauss), the electron beam voltage or current, or the trapping voltage. Modulation of the trapping voltage (15 to 25 Hz) by applying a square wave  $(+V_t \text{ to } -V_t)$  to one trapping plate is the most common modulation technique.

#### 3. Ion Cyclotron Double Resonance

A distinguishing feature of ICR spectrometry is the correlation that can be made between a product ion and the reactant ion in an ion/molecule reaction. This technique is known as ion cyclotron double resonance (ICDR). This is accomplished by applying an rf signal of variable frequency and amplitude to the drift plates of the cell. Thereby adding energy to possible reactant ions while leaving the product ion in resonance with the detector. If the amplitude of the rf field on the drift plates is large enough, it is possible for the ions to absorb enough energy to cause them to collide with the drift plate (i.e., their radius exceeds the dimensions of the cell).

Suppose  $A^+$  reacts with B to yield  $C^+$  and D as seen in reaction 6.

$$A^+ + B \longrightarrow C^+ + D \tag{6}$$

It can be seen from equation 2 that  $m_C v_C$  is a constant when the product ion  $(C^+)$  is in resonance at the required value of B. Possible reactant ions  $(m_X')$  can be brought into resonance at that value of B by supplying the frequency v' such that  $m_C v_C = m_X' v_X'$ . Since  $A^+$   $(m_A)$  is reacting to form  $C^+$   $(m_C)$ , increasing the velocity (or rate of ejection) of  $A^+$  will cause a change in the amount of  $C^+$  which is observed by the detecting oscillator. If reaction 6 is exothermic, the double resonance ejection of  $A^+$  will result in a decrease in the  $C^+$  signal observed. If reaction 6 is endothermic, the acceleration of the  $A^+$  ions by the rf field may drive the reaction faster and cause an increase in the  $C^+$  intensity prior to the ejection of  $A^+$ .

A block diagram of a basic ICR, capable of performing all of the operations discussed previously, is shown in Figure 4.



Figure 4. Block diagram of the ICR spectrometer<sup>46</sup>.

#### **B.** Experimental Parameters for Negative Ion Studies

The ion cyclotron resonance mass spectrometer used to perform all of the ion/molecule reacton studies in this dissertation was built at Michigan State University from conventional design. The dimensions of the three-section ICR cell are 0.88 in. X 0.88 in. X 6.25 in. The source and analyzer regions are 2.00 in. and 3.75 in. long respectively. In normal operation the electron filament is emission regulated. The filament controller and plate voltage controller for the ICR cell were designed and constructed at M.S.U. The data presented here were obtained under normal drift-mode conditions by using trapping voltage modulation and phase-sensitive detection. The marginal oscillator detector was constructed at M.S.U. based on the design of Warnick, Anders, and Sharp<sup>47</sup>. A Wavetek Model 144 sweep generator was used as the secondary oscillator for double resonance experiments.

The ICR cell is housed in a stainless steel vacuum system and is situated between the polecaps of a Varian 12 in. electromagnet (1.5 in. gap). The electromagnet is controlled by a Varian V-7800, 13 kW power supply and a Fieldial Mark I Magnetic Field Regulator. The instrument is pumped by a 4 in. diffusion pump with a liquid nitrogen cold trap and an Ultek 20 l/s ion pump. Samples are admitted from a dual inlet with Varian 951-5106 precision leak valves. Approximate pressures are measured with a Veeco RG 1000 ionization guage. All chemicals used in this work were high-purity commercial samples which were used as supplied except for multiple freeze-pump-thaw cycles to remove noncondensible gases.

Although ICR is most often used to study positive ion/molecule reactions, it is extremely simple to convert the system to study negative ions. The only experimental condition which must be changed to detect negative ions is the polarity of the trapping plates (negative potential to trap negative ions). All other experimental conditions remain the same with the exception of "re-tuning" the plate voltages for optimum peak height and peak shape.

The early mass spectrometric studies of negative ions formed by electron impact on metal carbonyls  $(M(CO)_n)$  report that the major ion produced by 70 eV electron impact is the  $M(CO)_{n-1}^-$  anion (loss of one CO) with a small amount of  $M(CO)_{n-2}^-$  also being formed<sup>30-32</sup>. Recall that the previous metal anion/molecule reaction studies found the 17- electron  $M(CO)_{n-1}^-$  species to be unreactive. The early mass spectrometric studies of negative metal ions also reported the energy dependence of the negative ions formed by collision of slow electrons (0 to 10 eV) with metal carbonyls. The energy dependence of negative ions formed by dissociative electron capture of slow electrons with Fe(CO)<sub>5</sub> is shown in Figure 5. Note that it is possible to maximize the relative amount of each fragment anion by varying the ionizing electron energy.



Figure 5. Energy dependence of negative ions formed from  $Fe(CO)_5^{32}$ .

Since the  $M(CO)_{n-1}^{-}$  anions were reported to be unreactive, this study utilized low energy electron impact to maximize the relative concentrations of species with fewer ligands present  $(M(CO)_{n-2}^{-}, M(CO)_{n-3}^{-})$ . The ionizing energies utilized for this study of anions from  $Fe(CO)_5$ ,  $Cr(CO)_6$ , and  $Co(CO)_3NO$  are listed in Table 1 along with the anions which are formed. The  $M(CO)_{n-1}^{-}$  anion is still the major ion formed under these conditions, but a sufficient amount of the lower fragment anions are produced to allow the study of their ion/molecule reactions. In Figure 5 a maximum for the formation of  $Fe(CO)_2^{-}$ is observed at  $\sim 4.5$  eV, but note that its intensity is magnified 10X compared to that of  $Fe(CO)_4^{-}$ . Although it would be desirable to form these lower fragments, even at the suggested energy for maximum production of  $Fe(CO)_2^{-}$ a sufficient amount of  $Fe(CO)_2^{-}$  is <u>not</u> formed which prevents the study of their ion/molecule reactions. Typical low energy electron impact negative

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<u>Neutral</u>	Ionizing Energy	Anions Formed
Fe(CO)5	1 eV	Fe(CO)4 <sup>-</sup>
-		Fe(CO)3 <sup>-</sup>
Cr(CO) <sub>6</sub>	4.5 eV	Cr(CO)5 <sup>-</sup>
		$Cr(CO)_4^-$
		Cr(CO) <sub>3</sub> -
Co(CO) <sub>3</sub> NO	1.5 eV	Co(CO) <sub>2</sub> NO <sup>-</sup>
		Co(CO)3-
		CoCONO-
		Co(CO)2 <sup>-</sup>

## Table 1. Metal-Containing Anions Formed by Low Energy Electron Impact

ion mass spectra for the three metals (Fe(CO)<sub>5</sub>, Cr(CO)<sub>6</sub>, and Co(CO)<sub>3</sub>NO) at pressures of approximately 2 X 10  $^{-6}$  torr are shown in Figures 6 through 8.

In a typical experiment, low pressure 70 eV positive ion mass spectra of both the metal carbonyl and organic compound were taken to determine the purity of the samples. The ICR was then configured for negative ion studies (i.e., the trapping voltage and ionizing electron energy were changed). Spectra were then recorded of a 1:1 mixture (by pressure) of the metal carbonyl to organic compound at a total pressure of approximately 1 X  $10^{-5}$  torr. Spectra were always taken to masses greater than the sum of the molecular weight of the metal carbonyl and the organic compound. The anion/molecule reaction products were identified and precursors of each determined using double resonance techniques. The branching ratios listed for the reactant ions are accurate to within  $\pm 10\%$ . Although in some cases empirical formulas other than those listed may also be possible for the products, those listed are believed to be the most reasonable based on observed reaction trends and the reactions of the other metal anions.













#### **CHAPTER 3**

#### **REACTIONS OF N-CHLOROALKANES**

The ion/molecule reaction products and their branching ratios for the reactions of chromium, iron, and cobalt-containing anions with the series of 1-chloro-n-alkanes (n-chloroalkanes) (n = 1 to 6) are listed in Table 2. Three types of reactions are observed for the metal-containing anions with n-chloroalkanes: ligand substitution by the chloroalkane molecule for two or three carbonyl ligands (Parent substitution); abstraction of chlorine from the chloroalkane (Cl abstraction); and abstraction of chlorine and hydrogen from the chloroalkane (HCl abstraction).

#### A. Parent Substitution

The general reaction for substitution of the chloroalkane molecule for carbonyl ligands is shown in reaction 7.

$$M(CO)_{\mathbf{x}}^{-} + C_{\mathbf{n}}H_{2\mathbf{n}+1}CI \longrightarrow M(CO)_{\mathbf{x}-\mathbf{a}}(C_{\mathbf{n}}H_{2\mathbf{n}+1}CI)^{-} + aCO \qquad (7)$$

Parent substitution reactions by the chloroalkanes are observed for the metal-containing anions  $Cr(CO)_3^-$ ,  $Fe(CO)_3^-$ , and  $Co(CO)_2^-$ . The reaction of  $Fe(CO)_3^-$  and  $Co(CO)_2^-$  are accompanied by a loss of two carbonyl ligands

Table 2. Reactions of Chromium, Iron, and Cobalt-Containing Anions with n-Chloroalkanes

			Bra	nching Rat	.8	
Reaction	[ <u>=</u> u	n=2	<b>2</b> = <b>0</b>	<b>₩</b> =0	S= E	<u>9=0</u>
Cr(CO)3 <sup>-</sup> + C <sub>n</sub> H <sub>2n+1</sub> Cl CrC <sub>n</sub> H <sub>2n+1</sub> Cl <sup>-</sup> + 3CO	.36	.28	.27	q(6£.)	.27	.20
$cr(c0)_2C1^- + C_nH_{2n+1} + C0$	.22	.23	.15	.13	.10	.08
$cr(co)_3 cl^- + c_n H_{2n+1}$	.42	.36	.43	.48	.47	.52
$cr(co)_2Hc1^- + C_nH_{2n} + Co$		.13	.15	(.39)	.16	.20
Cr(CO)4 <sup>-</sup> + C <sub>n</sub> H <sub>2n+1</sub> Cl						
$cr(co)_5^- + c_nH_{2n+1}cl$ wr						
$Fe(CO)_3^{-} + C_nH_{2n+1}C1 - FeCOC_nH_{2n+1}C1^{-} + 2CO$		(.25)	.19	.12	.10	.08
$Fe(CO)_{3}Cl^{-} + C_{n}H_{2n+1}$	1.00	.75	.70	.78	.71	.70
Fe(CO) <sub>2</sub> HCl <sup>-</sup> + $C_nH_{2n}$ + CO		(.25)	.11	.10	.19	.22
Fe(CO)4 <sup>-</sup> + C <sub>n</sub> H <sub>2n+1</sub> Cl NR						
$c_{0}(c_{0})_{2}^{-} + c_{n}H_{2n+1}c_{1}$	.67	(.65)	.26	(.28)	.10	.08
$c_{0}COC1^{-} + C_{n}H_{2n+1} + CO$	.07	.11				
$co(CO)_2C1^- + C_nH_{2n+1}$	.26	.24	.26	.26	.17	.20
$\sim$ cocoHcl <sup>-</sup> + C <sub>n</sub> H <sub>2n</sub> + CO		(.65)	.43	.46	.61	.60
$c_0(CO)_2HCl^- + C_nH_{2n}$			.05	(.28)	.12	.12
the A continues				•		

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Table 2 continues

Table 2 continued

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			Bra	nching Ra	tios	
Reaction	<u>n=1</u>	<b>n=2</b>	<u>n=3</u>	<b>y</b> =0	2 = U	<b>u=6</b>
$c_{o}cono^{-} + c_{n}H_{2n+1}c_{1}$	1.00	.56	.39	.62	.55	.53
$\sim$ CoNOHCI <sup>-</sup> + C <sub>n</sub> H <sub>2n</sub> + CO		. 44	.61	.38	.45	.47
$Co(CO)_3^- + C_nH_{2n+1}Cl$ NR						
$Co(CO)_2NO^- + C_nH_{2n+1}CI$						

<sup>a</sup> NR indicates the ion did not undergo any reactions

**b** values in parentheses are the sum of branching ratios for isobaric product ions

(a=2 in reaction 7) while  $Cr(CO)_3^-$  loses all three carbonyl ligands (a = 3). Two possible product ion structures are suggested, structures 1 and 2 (where x = 0 for M = Cr, Co; x = 1 for M = Fe).

$$(CO)_{x} \longrightarrow M^{-} \leftarrow CIC_{n}H_{2n+1} \longrightarrow CI \longrightarrow M^{-} \leftarrow C_{n}H_{2n+1}$$

$$(CO)_{x} \longrightarrow M^{-} \leftarrow CIC_{n}H_{2n+1} \longrightarrow C_{n}H_{2n+1}$$

$$(CO)_{x} \longrightarrow C_{n}H_{2n+1} \longrightarrow C_{n}H_{2n+1}$$

Structure 1 results from ligand substitution by the chloroalkane for two or three carbonyl ligands with the chloroalkane molecule remaining intact as a ligand on the metal anion. The negative charge must remain on the metal species in structure 1 due to the large <u>negative</u> electron affinity of the chloroalkane ligand (e.g. E.A.(CH<sub>3</sub>Cl) = -79.6 kcal/mole). While an electron pair on the chlorine may form a dative bond to the metal, there will certainly be a strong ion-dipole repulsive interaction in this intermediate. The magnitude of this repulsion may be estimated using equation 5<sup>49</sup> which describes the interaction between a point charge  $\epsilon$  and dipole  $\mu$  in the gas phase which are separated by a distance r at an angle  $\theta$ .

$$U(\mathbf{r}) = \frac{\varepsilon u}{r^2} \cos \theta \tag{5}$$

Assuming a distance of 2 Å between the ion and dipole and  $\theta = 0^{\circ}$ , the magnitude of this repulsion is estimated to be 35 kcal/mole for 1-chlorobutane and 29 kcal/mole for 1-butanol<sup>50</sup>. Similar calculations for a distance of 5 Å yields
ion-dipole repulsions of approximately 6 kcal/mole and 5 kcal/mole for 1-chlorobutane and 1-butanol respectively. Comparison of the electron affinities for the metal-containing species  $Fe(CO)_3$  (41.5 kcal/mole) and Cl (83.3 kcal/mole) suggests the possibility that, once the metal anion-chloroalkane. complex is formed, it is thermodynamically favorable for the charge to be transferred from the metal anion to a chlorine atom. Structure 2 results from metal insertion into the C-Cl bond (which occurs in positive metal ion reactions) with transfer of the electron to the chlorine atom. Presumably the metal anion insertion/charge transfer process is sufficiently exothermic such that excess energy results in the loss of two or three carbonyl ligands.

If we are actually observing metal insertion into the C-Cl bond, a metal-carbon  $\sigma$ -bond is also formed. Reactions of aliphatic halides with Na<sub>2</sub>Fe(CO)<sub>4</sub> in solution<sup>54</sup> also proceed through intermediates which have a metal-carbon  $\sigma$ -bond from the alkyl group to the metal anion Fe(CO)<sub>4</sub><sup>-</sup>. The electron affinities of these alkyl ligands (15 to 26 kcal/mole) indicate that the presence of the alkyl ligand may help delocalize the negative charge in structure 2. Therefore, structure 2 seems to be the most reasonable structure for the Parent substitution product ion from the electron affinity data and the mechanisms predicted from condensed phase reactions. Note that the Parent substitution product ion, structure  $2_V$  does not consist of an intact parent organic molecule (predicted from positive ion reactions), but instead is a metal insertion structure which contains the organic molecule as two separate ligands on the metal.

The amount of excess energy released in the metal anion insertion/charge transfer process (reaction 8) is dependent upon both the exothermicity of the metal insertion (i.e. the bonds which are broken and formed) and the exothermicity of the charge transfer process (i.e. the difference in the electron affinities of the metal species and the ligand).

$$M(CO)_{x}^{-} + Cl - C_{n}H_{2n+1} \longrightarrow Cl - M - C_{n}H_{2n+1} + aCO \qquad (8)$$

Assuming that the differences in the metal-ligand bond strengths are small for the three metals, the differences in the exothermicity for the metal insertion/charge transfer process for the metal species is an indication of the difference in the electron affinities for the metal species. Since  $Fe(CO)_3^$ reacts by loss of only two carbonyl ligands and  $Cr(CO)_3^-$  reacts by losing all three carbonyl ligands (and assuming that this reflects the fact that the metal insertion/charge transfer process is more exothermic for  $Cr(CO)_3^-$ ), then presumably the electron affinity of  $Cr(CO)_3$  is less than the electron affinity of  $Fe(CO)_3$  (E.A.( $Cr(CO)_3$ ) < E.A.( $Fe(CO)_3$ ) = 41.5 kcal/mole)

# **B.** Cl Abstraction

Once the metal insertion/charge transfer intermediate 2 is formed, the excess energy may not only result in loss of carbonyl ligands (Parent substitution) but may also lead to loss of the alkyl ligand (reaction 9).

$$M(CO)_{x}^{-} + C_{n}H_{2n+1}Cl \longrightarrow M(CO)_{x-b}Cl^{-} + C_{n}H_{2n+1} + bCO$$
 (9)

This reaction is observed for the anions  $Cr(CO)_3^-$ ,  $Fe(CO)_3^-$ ,  $Co(CO)_2^-$ , and  $CoCONO^-$  with the n-chloroalkanes for n = 1 to 6. Competitive ligand loss of the alkyl ligand with concurrent loss of zero or one carbonyl ligands leads to the chlorine abstraction products ( $M(CO)_{x-b}Cl^-$ ) observed in Table 2.

# C. HCl Abstraction

The third reaction type observed for n-chloroalkanes ( $n \ge 2$ ) is abstraction of HCl as shown in reaction 10.

$$M(CO)_{\mathbf{x}}^{-} + C_{\mathbf{n}}H_{2\mathbf{n}+1}CI \longrightarrow M(CO)_{\mathbf{x}-\mathbf{c}}HCI^{-} + C_{\mathbf{n}}H_{2\mathbf{n}} + cCO$$
(10)

This product may also result from metal insertion into the C-Cl bond as a first step. A common mechanism in both solution and gas-phase organometallic reactions involves the shift of a  $\beta$ -hydrogen atom onto the metal center<sup>10,11</sup>. This apparently occurs in the metal-containing anion reactions as well. In the case of chloromethane, the intermediate resulting from metal insertion into the C-Cl bond does not have any  $\beta$ -H's to shift onto the metal. As a result, the HCl abstraction product is <u>not</u> observed for chloromethane (Table 2). For the larger n-chloroalkanes (n = 2 to 6) however,  $\beta$ -H's are available to shift onto the metal. Once the  $\beta$ -H shift occurs, the alkene ligand produced ( $C_nH_{2n}$ ) is lost, yielding the HCl abstraction products (M(CO)<sub>X-C</sub>HCl<sup>-</sup>). The two possible structures for this product ion are shown in structures  $\frac{3}{2}$  and  $\frac{4}{3}$ .



Structure  $\frac{3}{2}$  represents the structure if HCl exists as a single ligand on the metal. The electron affinities of H (17.4 kcal/mole) and Cl (83.3 kcal/mole) suggest that structure 4, where H and Cl are separate ligands on the metal, may be the more stable structure. The addition of the hydrogen atom as a ligand, which has a positive electron affinity, may help delocalize the negative charge. This effect is also seen in the comparison of the electron affinities of Fe (3.8 kcal/mole) and FeH (21.5 kcal/mole).

The alkene ligand which is formed following metal insertion and  $\beta$ -H shift

in the corresponding positive metal ion reactions is retained preferentially over the HCl ligand<sup>9</sup>. In the metal anion reactions however, the alkene ligand is never retained and is always lost in the competitive ligand loss process. This is not unexpected if the electron affinity of the alkene is considered and structure 4 is assumed to be the HCl abstraction product. The electron affinity of ethylene (-35.7 kcal/mole) suggests that the alkene ligand would be lost preferentially relative to ligands which possess a positive electron affinity, i.e., those which help to delocalize the negative charge. The difference in metal-ligand bonding in positive and negative metal ions has been studied by Corderman and Beauchamp<sup>41</sup> suggesting that the competitive ligand loss process for positive and negative metal ions may be quite different. The metal-ligand bond energy in positive ions is determined largely by the -donor ability of the ligand while back-bonding effects are less important. In the negative ions however, the bond energy is predominantly dependent upon the  $\pi$ -acceptor ability of the ligand with the  $\pi$ -donor ability playing a less important role. Thus, the difference in the metal-ligand bonding in positive and negative ions may be a factor in the retention or loss of the alkene in the positive and negative ion reactions.

# D. Reaction Trends and Mechanisms

The general mechanism for the reactions of the metal-containing anions with n-chloroalkanes (n = 1 to 6) is shown in Scheme I. Note that all three types of products observed (Parent substitution, Cl abstraction, and HCl abstraction) proceed through intermediate structure 2.





Two possible mechanisms for forming structure 2 are presented in Scheme II. Note that structure  $_{0}^{6}$  is equivalent to structure 2 for X = Cl.



In the first mechanism, the metal anion initially inserts into the R-X bond (analogous to positive metal ion insertion) to give structure  $\xi$ . If the charge transfer from the metal species to X is exothermic, structure  $\xi$  (the metal anion insertion/charge transfer intermediate) is formed. If the charge transfer is not exothermic then  $\xi$  may reform the metal anion and RX. In the second mechanism (Scheme II), the metal anion interacts with both X and the alkyl R as seen in structure  $\chi$ . This type of initial complexation may reduce the ion-dipole repulsive interaction discussed previously. If the charge transfer is exothermic, an M-X<sup>-</sup> bond is formed along with the cleavage of the R-X bond and formation of the M-R bond yielding structure  $\xi$ . Regardless of the mechanism, it appears that all reactions observed proceed through the metal insertion/charge transfer intermediate  $\xi$  and the driving force for the reactions appears to be the exothermicity of the charge transfer process.

Additional information may be obtained through trends observed in the branching ratios of product ions as the alkyl chain length (n) increases (Table 2). For all three metal-containing anions, Parent substitution and Cl abstraction decrease and HCl abstraction increases as n increases. These trends support a mechanism in which all products observed proceed through a common intermediate (structure 2). One possible explanation for the increase in the amount of HCl abstraction observed may be the thermodynamics of the reaction. Thermodynamic calculations indicate that less energy is required to form an alkene from the corresponding alkyl chloride as the length of the alkyl chain increases. For example, if the reactions of 1-chloroethane and 1-chloropentane are considered (reactions 11 and 12), thermodynamic calculations indicate that  $\Delta H_{12}$  (C<sub>5</sub>H<sub>11</sub>Cl) is 4.3 kcal/mole less than  $\Delta H_{11}$  (C<sub>2</sub>H<sub>5</sub>Cl)<sup>58</sup>

$$C_{2}H_{5}Cl \longrightarrow HCl + C_{2}H_{4}$$
 (11)  
 $C_{5}H_{11}Cl \longrightarrow HCl + C_{5}H_{10}$  (12)

The effects that the number and types of ligands present on the metal have on reactivity and mechanisms in positive metal ion reactions have been described previously<sup>1,12,18,22,25,29</sup>. Several ligand effects are also observed in the reaction of metal-containing anions. The carbonyl ligand is lost preferentially to the nitrosyl ligand as seen in the reaction of CoCONO<sup>-</sup> with n-chloroalkanes (Table 2). This effect is also observed in the positive metal ion reactions and is due in part to the fact that the nitrosyl ligand is a three electron donor and the carbonyl ligand is a two electron donor. Another ligand effect observed for metal anions is that the reactivity of the metal-containing anions decreases as the number of ligands present increase. As expected, the stable 17 electron species,  $M(CO)_{n-1}^{-}$  is unreactive towards the n-chloroalkanes.

In summary, the reactions of the metal-containing anions with chloroalkanes

proceed through a mechanism in which the metal inserts into the C-Cl bond with transfer of the electron to the chlorine, due to the higher electron affinity of Cl. This complex may then undergo rearrangements ( $\beta$ -H shift) and ligand loss processes to yield all products which are observed. In the corresponding positive metal ion reactions with n-chloroalkanes, products resulting from metal insertion into C-C and C-H bonds are also seen in addition to C-Cl insertion products<sup>12</sup>. All reactions for metal-containing anions appear to result from interaction with chlorine which has a relatively high electron affinity, and thus no products resulting from C-C or C-H insertion are observed. This may reflect the importance of the charge transfer step, since, if Fe(CO)<sub>3</sub><sup>-</sup> inserted into a C-C bond, the charge would remain on the metal (E.A.(Fe(CO)<sub>3</sub>) = 41.5 kcal/mole, E.A.(C<sub>n</sub>H<sub>2n+1</sub>) =  $\sim 20$  kcal/mole), and no chemistry from such intermediates is observed.

# **CHAPTER 4**

# **REACTIONS OF N-ALCOHOLS**

# A. Reactions Resulting From Metal Insertion into the C-OH Bond

The ion/molecule reaction products and branching ratios for the reactions of chromium, iron, and cobalt-containing anions with the series of 1-hydroxy-n-alkanes (n-alcohols) (n = 1 to 6) are listed in Table 3. Parent substitution reactions are observed in the reaction of  $Cr(CO)_3^-$  with the series of n-alcohols for n = 1 to 6 and are accompanied by the loss of one or two carbonyl ligands (reaction 13)

$$Cr(CO)_3^- + C_nH_{2n+1}OH \longrightarrow Cr(CO)_{3-x}C_nH_{2n+1}OH^- + xCO$$
 (13)

If metal insertion into the C-OH bond is assumed in the Parent substitution process (analogous to C-Cl insertion in the chloroalkanes), the charge would be transferred to the OH ligand due to it's relatively high electron affinity (42.2 kcal/mole) as shown in structure g (Scheme III). Clearly, the charge will be distributed over a number of atoms, however, we will continue wherever possible, to put the charge on the most electronegative species in a given structure, to parallel what is done for the positive ion analogs. This intermediate Table 3. Reactions of Chromium, Iron, and Cobalt-Containing Anions with n-Alcohols

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	<u>u=6</u>	.37	.19	.24	.07	.03	.05	90	cn.						
	<u>1=5</u>	.38	.22	.22	.09			ġ	<b>6</b> 0.			1-6)			_
latios		.33	. 28	.27	.06			;	.06			CO (n =		(n=1-6)	0 (n=5,6
ranching I	<u>n=3</u>	.33	.47	11.	.04				.05			)- + H <sub>2</sub> +		0 <sup>-</sup> + H <sub>2</sub>	+ H <sub>2</sub> + C
ā)	<u>n=2</u>	.40	.50		.02				.08			))2CnH2nC		)2CnH2n	C <sub>n</sub> H <sub>2n</sub> 0 <sup>-</sup>
	<u>n=1</u>	.43	.53						.04	NR <sup>8</sup>	AR RR	Fe(CC	NR NR		CoNO
	loi		$1_{2n+1}$ OH $-1_{2n+1}$ CO $1_{2n+1}$ CO $-1_{2n+1}$ CO $-1_{2n$	$c_{1}(CO)_{0}C_{-H_{n-0}}^{-1}$	$\alpha = \alpha + $		$CrCOC_{n}H_{2n}O$ + $H_{2}$ + 200	$ CrCOC_{n}H_{2n-2}O^{-} + 2H_{2} + 2CO$	$Cr(CO)_{3}OH^{-} + C_{n}H_{2n+1}$	$c_{r}(c_{0})_{4}^{-} + c_{n}H_{2n+1}OH$	$Cr(CO)_{5}^{-} + C_{n}H_{2n+1}OH$	$Fe(CO)_{3}^{-} + C_{n}H_{2n+1}OH$	$Fe(CO)_{4}^{-} + C_{n}H_{2n+1}OH$	$C_0(CO)_2^- + C_nH_{2n+1}OH$	$C_{o}CONO^{-} + C_{n}H_{2n+1}OH$
	Reactiv	:	$Cr(CO)_3^- + C_nH$												

<sup>a</sup>NR indicates the ion did not undergo any reactions

.

Co(CO)2NO<sup>-</sup> + C<sub>n</sub>H<sub>2n+1</sub>OH ----- NR

¥ NR

 $C_0(CO)_3^{-} + C_n H_{2n+1}OH --$ 



may undergo a competitive ligand loss process to lose the excess energy produced in the metal insertion/charge transfer process. Loss of carbonyl ligands yield Parent substitution products (Cr(CO) $_{3-x}C_nH_{2n+1}OH^-$ ) and loss of the alkyl radical ( $C_nH_{2n+1}$ ) yields the OH abstraction product ( $Cr(CO)_3OH^-$ ) as seen in Scheme III. The formation of the OH abstraction product is analogous to the Cl abstraction product observed in chloroalkanes. Note that the OH abstraction products are observed only for  $Cr(CO)_3^-$  (Table 3) suggesting that the C-OH insertion intermediate § (Scheme III) occurs exclusively for the reaction of  $Cr(CO)_3^-$ . The loss of only one or two carbonyl ligands in the Parent substitution of n-alcohols, in contrast to three carbonyls displaced in the chloroalkane reactions, may be due to a decrease in the energy released in the charge transfer step, which would arise due to the lower electron affinity of OH (42.2 kcal/mole) compared to Cl (83.3 kcal/mole). Parent substitution reactions are not observed for either cobalt or iron-containing anions presumably due to the comparable electron affinity of OH (42.2 kcal/mole) and the metal species (e.g. E.A.( $Fe(CO)_3$ ) = 41.5 kcal/mole). Thus, the charge transfer process is not favorable in this case resulting in the absence of Parent substitution and OH abstraction products.

Since the cobalt anion  $Co(CO)_2^-$  does not react with the alcohols by Parent substitution or OH abstraction, the difference in the electron affinity of  $Co(CO)_2$ and OH must not be large enough to cause these reactions to occur. Therefore, we may infer (making the same assumptions as in the chloroalkane discussion) that the electron affinity of  $Cr(CO)_3$  is less than the electron affinity of  $Co(CO)_2$  (E.A. $(Cr(CO)_3) < E.A.(Co(CO)_2)$ ).

Products indicative of  $H_2O$  abstraction may be expected in the  $Cr(CO)_3^$ reactions (analogous to HCl abstraction in chloroalkanes) since  $\beta$ -H atoms are present after the metal inserts into the C-OH bond of all the n-alcohols ( $n \ge 2$ ). Thermodynamic calculations for the production of 1-butene from the corresponding 1-chlorobutane and 1-butanol (reactions 14 and 15) show that less energy is required to form the alkene from n-alcohols than from the analogous n-chloroalkanes<sup>58</sup>.

$$C_4H_9Cl \longrightarrow C_4H_8 + HCl \quad \Delta H = +13.31 \text{ kcal/mole}$$
 (14)  
 $C_4H_9OH \longrightarrow C_4H_8 + H_2O \quad \Delta H = +8.67 \text{ kcal/mole}$  (15)

The H<sub>2</sub>O abstraction product, however, is <u>not</u> observed for the reaction of  $Cr(CO)_3^-$ . Apparently sufficient energy is released in the electron transfer to the Cl ligand to result in rearrangement ( $\beta$ -H shift) and loss of the alkene ligand in the chloroalkane reactions, but not enough energy is released in the electron transfer to the OH ligand (due to it's lower electron affinity) to result in rearrangement and loss of the alkene in the n-alcohol reactions. Therefore, a barrier to the  $\beta$ -H shift process appears to exist.

### B. Reactions Resulting From Metal Insertion into the O-H Bond

The only reaction observed for the cobalt and iron-containing anions with n-alcohols is the elimination of  $H_2$  (n = 1 to 6) with  $Co(CO)_2^-$ ,  $CoCONO^-$ , and  $Fe(CO)_3^-$  as shown in reaction 16. This hydrogen elimination product is also observed for the chromium anion  $Cr(CO)_3^-$ .

$$M(CO)_{x^{-}} + C_{n}H_{2n+1}OH \longrightarrow M(CO)_{x-a}C_{n}H_{2n}O^{-} + H_{2} + aCO$$
 (16)

The hydrogen elimination product is <u>not</u> expected to proceed through metal insertion into the C-OH bond since products indicative of C-OH insertion (Parent substitution and OH abstraction) are not observed for the cobalt or iron-containing anions. A possible mechanism for the elimination of  $H_2$  following metal insertion into the C-OH bond is shown below.

$$C_{n} H_{2n+1} OH + M(CO)_{x}^{-} \rightarrow C_{n} H_{2n+1} - M - OH^{-}$$

$$\downarrow^{\beta-H}_{shift}$$

$$(CO)_{x-a} \qquad (CO)_{x-a} \qquad (CO)_{x} \qquad (CO)_{x}$$

This mechanism however, does not explain the observance of this product for methanol (n=1) since no  $\beta$ -H atoms are present following insertion into the C-OH bond. Therefore, a more comprehensive mechanism must be proposed.

Scheme IV illustrates the formation of an intermediate in which the metal inserts into the O-H bond. This intermediate is predicted to be stable due to the relatively high electron affinities of the alkoxy group (~40 kcal/mole) and the atomic hydrogen (17.4 kcal/mole) ligands on the metal following O-H insertion. The charge may then be transferred to the alkoxy ligand due to its relatively high electron affinity. Note that a  $\beta$ -H is available to shift onto the metal in this intermediate even for methanol (n = 1). Following metal insertion into the O-H bond and charge transfer, the  $\beta$ -H shift and loss of H<sub>2</sub> may lead to two different structures (9 and 10) in Scheme IV. In structure 9, the alkoxy ligand is converted into an aldehyde ( $\pi$ -donor) ligand following the  $\beta$ -H shift with the negative charge being transferred back to the metal. In positive metal ion reactions, these  $\pi$ -donor ligands are found to form strong



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bonds with the metal. Recall that in the metal anion reactions with chloroalkanes however, the  $\pi$ -donor alkene ligand produced following the  $\beta$ -H shift to yield HCl was lost preferentially to the other ligands on the metal. In contrast to the positive ion studies, these  $\pi$ -donor ligands do <u>not</u> appear to form strong bonds to the metal in these negative ion studies. The alkyl ligand (metal-carbon bond) appears to be a relatively strongly bound ligand in the metal anion reactions, since the alkyl ligand is in some cases retained during the competitive ligand loss process (e.g. Parent substitution) for chloroalkanes and alcohols. Therefore, structure 10 (Scheme IV) is the more probable structure for the product ion resulting from H<sub>2</sub> elimination from alcohols. Following the  $\beta$ -H shift, the metal may form a bond to the carbon which is  $\beta$  to the metal resulting in the metal-alkoxy structure 10. In this structure, the negative charge remains on an alkoxy ligand which has a high electron affinity.

The anion  $Cr(CO)_3^-$  reacts further with the alcohols to eliminate a second molecule of hydrogen. This product is only observed for  $Cr(CO)_3^-$  presumably due to its lower electron affinity than those of other metal species. Elimination of two hydrogen molecules does not occur for methanol and ethanol, but does occur for  $n \ge 3$ . A general mechanism for the elimination of the second molecule of hydrogen is shown in Scheme V. The mechanism begins with structure 1,0(following elimination of one H<sub>2</sub>) which may proceed through a  $\beta$ -H shift to produce structure 1,1 which contains two metal-carbon bonds. Another  $\beta$ -H is now available to shift from the C<sub>3</sub> carbon to yield structure 1,2. Note that, in the proposed mechanism, the charge <u>remains</u> on the alkoxy oxygen (the most electronegative site) and that the mechanism accounts for the formation of this product ion for  $n \ge 3$  only.

In summary, the metal anion attacks exclusively at the functional group







(no evidence for C-C or C-H insertion) due to the relatively high electron affinity of OH. In comparison to the chloroalkane reactions, however, the metal appears to insert into not one but <u>two</u> bonds (C-OH and O-H) in the reactions of n-alcohols. Further evidence is seen in the n-alcohol reactions for the formation of a metal anion insertion/charge transfer intermediate followed by possible rearrangements ( $\beta$ -H shifts) and competitive ligand loss. The enhanced reactivity of the Cr(CO)<sub>3</sub><sup>-</sup> anion with n-alcohols confirms the inference from the n-chloroalkane reactions that Cr(CO)<sub>3</sub> has the lowest electron affinity of the metal species studied. The ligand effects observed in the reactions of chloroalkanes also were observed for alcohols: the nitrosyl ligand is retained in the reaction of CoCONO<sup>-</sup> and the stable 17 electron metal anion species are unreactive.

### **CHAPTER 5**

### **REACTIONS OF BIFUNCTIONAL ORGANIC MOLECULES**

The reaction of positive metal ions with bifunctional organic molecules (e.g. 1-chloro-2-ethanol) have been studied previously 12,25,26 and compared to the reactions of the corresponding monofunctional compounds in an attempt to determine the utility of metal ions as chemical ionization (CI) reagent ions. The reactions observed for the bifunctional molecules include: products indicative of both functional groups; products only typical of one functional group (indicating the metal shows a preference for one functional group over another); and products unique to the particular combination of functional groups. The reaction of metal-containing anions with two series of bifunctional compounds (1,n-bromochloroalkanes and 1,n-chloroalcohols) were studied to determine the similarities and differences from the corresponding monofunctional compounds (n-chloroalkanes and n-alcohols).

### A. Reactions of 1,n-Bromochloroalkanes

The ion/molecule reaction products and branching ratios for the reactions of 1-bromo-n-chloro-alkanes (1,n-bromochloroalkanes) (n = 2 to 6) and 1,1-bromochloroethane with iron and chromium-containing anions, and with cobalt-containing anions are listed in Tables 4 and 5, respectively. Parent

Table 4. Reactions of iron and chromium-containing anions with 1,n-bromochloroalkanes

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		Branchin	g Ratios			
Reaction	<u>n=2;1,18</u>	<u>n=2</u>	<u>n=3</u>	<b>y</b> =U	<u>n=5</u>	<u>u=6</u>
Fe(CO)3 <sup>-</sup> + Br(CH <sub>2</sub> ) <sub>n</sub> Cl FeCOBr(CH <sub>2</sub> ) <sub>n</sub> Cl <sup>-</sup> + 2CO			60.	.28	.23	.26
FeClBr <sup>-</sup> + $C_n H_{2n}$ + 3CO		.15	.11	.04	.11	
Fe(CO) <sub>2</sub> Cl <sup>-</sup> + $(CH_2)_nB_r$ + CO	.04	.04				
$ Pe(CO)_3Cl^- + (CH_2)_nBr$	.44	.28	.38	.28	.23	.22
<b>Fe(CO)</b> <sub>2</sub> Br <sup>-</sup> + (CH <sub>2</sub> ) <sub>n</sub> Cl + CO	.19	.16	.04			
Fe(CO) <sub>3</sub> Br <sup>-</sup> + (CH <sub>2</sub> ) <sub>n</sub> Cl	.33	.37	. 38	.35	.30	.32
Fe(CO) <sub>2</sub> HBr <sup>-</sup> + $C_nH_{2n-1}C1$ + C	0			.05	.13	.20
Fe(CO)4 <sup>-</sup> + Br(CH <sub>2</sub> ) <sub>n</sub> C1 NR <sup>b</sup>						
$cr(co)_3^{-} + Br(cH_2)_n cl_{-} crclBr^{-} + c_nH_{2n} + 3co$	.22	.21	.28	.30	.33	.31
$\sim$ crHclBr <sup>-</sup> + C <sub>n</sub> H <sub>2n-1</sub> + 3co					.06	.05
$cr(co)_2 c1^- + (cH_2)_n Br + co$	.26	.19	.14	.16	60.	.05
	.10	.10	.18	.19	.19	.22
	.34	.36	.26	.18	.13	60.
$\sim$ cr(co) <sub>3</sub> Br <sup>-</sup> + (cH <sub>2</sub> ) <sub>n</sub> c1	.08	.14	.14	60.	.12	.15
$r cr(co)_2Hcl^- + C_nH_{n-1}B_r + C$	0			.04	.04	.05
- cr(co) <sub>2</sub> IIBr <sup>-</sup> + C <sub>n</sub> H <sub>2n-1</sub> Cl + C	0			.04	.04	.08

Table 4 continues

Table 4 continued

			sranching R.	atios		
Reaction	<u>n=2;1,1</u> 8	<u>n=2</u>	<u>u=3</u>	Ţ	S= U	9 <u>-</u> 1
$cr(co)_{4}^{-} + Br(cH_{2})_{n}c1 - cr(co)_{3}c1^{-} + (cH_{2})_{n}Br + co$	.55	.32	.33	.44	.37	.36
$-cr(co)_{3Br^{-}} + (cH_{2})_{n}c1 + co$	.45	.68	.67	.56	.63	.64
$Cr(CO)_5^- + Br(CH_2)_n Cl \longrightarrow NR$						

- 8 1,1-bromochloroethane
- b NR indicates the ion did not undergo any reactions

-bromochloroalitanes
1
nions with l
-containing
f cobalt
Reactions o
Table 5.

			Branching	Ratios		
Reaction	<u>n=2;1,1<sup>8</sup></u>	<u>n=2</u>	<u>n=3</u>	Ĩ	<u>n=5</u>	9=U
Co(CO) <sub>2</sub> <sup>-</sup> + Br(CH <sub>2</sub> ) <sub>n</sub> Cl - CoBr(CH <sub>2</sub> ) <sub>n</sub> Cl <sup>-</sup> + 2CO	.03					
$\sim$ CoClBr <sup>-</sup> + C <sub>n</sub> H <sub>2n</sub> + 2CO	.15	.35	.54	.40	.32	.23
$\sim$ CoCOCI <sup>-</sup> + (CH <sub>2</sub> ) <sub>n</sub> Br + CO	.18	.12	-07			
- Co(CO) <sub>2</sub> Cl <sup>-</sup> + (CH <sub>2</sub> ) <sub>n</sub> Br	.16	.11	.13	.12	.08	.08
$\sim$ CoCOBr <sup>-</sup> + (CH <sub>2</sub> ) <sub>n</sub> C1 + CO	.36	.31	.11	.10	.08	.07
$\sim Co(CO)_{2Br^{-}} + (CH_{2})_{n}CI$	.12	.11	.11	60.	60.	.08
$\sim$ coconcir + c <sub>n</sub> H <sub>2n-1</sub> Br + co				.04	.11	.17
- cocoHBr <sup>-</sup> + C <sub>n</sub> H <sub>2n-1</sub> Cl + CO			.04	.21	.26	.29
$\sum co(co)_2HBr^2 + C_nH_{2n-1}CI$				.04	.06	.08
CoCONO <sup>-</sup> + Br(CH <sub>2</sub> ) <sub>n</sub> Cl - CoNOCl <sup>-</sup> + (CH <sub>2</sub> ) <sub>n</sub> Br + CO	.08	.08				
$\sim$ CoCONOCI <sup>-</sup> + (CH <sub>2</sub> ) <sub>n</sub> Br	.10	.19	.15	.11	60.	.12
$\sim$ CoNOBr <sup>-</sup> + (CH <sub>2</sub> ) <sub>n</sub> Cl + CO	.47	.47	.34	.14	.14	
CoCONOBr <sup>-</sup> + (CH <sub>2</sub> ) <sub>n</sub> Cl	.35	.26	.36	.22	.20	.23
$\sim$ CoNOHCI <sup>-</sup> + C <sub>n</sub> H <sub>2n-1</sub> Br + CO					.05	.14
$\sim$ conorder + c <sub>n</sub> H <sub>2n-1</sub> C1 + co			.15	.53	.52	.51

Table 5 continues

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**Table 5** continued

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			-1	Branching Re	Itios		
Reaction		<u>n=2;1,1</u> 8	<u>n=2</u>	n=3	<b>y</b> =u	<u>;</u>	<u>9=u</u>
Co(CO)3 <sup>-</sup> + Br(CH <sub>2</sub> ) <sub>n</sub> C1 <mark>→</mark>	►Co(CO) <sub>2</sub> Br <sup>-</sup> + (CH <sub>2</sub> ) <sub>n</sub> Cl + CO	1.00	1.00	1.00			
<b>↑</b>	-Co(CO) <sub>2</sub> HBr <sup>-</sup> + C <sub>n</sub> H <sub>2n-1</sub> C1 + CC	0			1.00	1.00	.59
	► CoCOHBr <sup>-</sup> + C <sub>n</sub> H <sub>2n-1</sub> C1 + 2CO						.41
Co(CO)2NO <sup>-</sup> + Br(CH <sub>2</sub> ) <sub>n</sub> Cl∌	-Co(CO)2NOBr <sup>-</sup> + (CH <sub>2</sub> ) <sub>n</sub> Cl	1.00	1.00	NRb	NR	NR	NR

a 1,1-bromochloroethane

b NR indicates the ion did not undergo any reactions

substitution (to form products of the type  $M(CO)_{a-b}ClC_{n}H_{2n}Br^{-}$ ), bromine or chlorine abstraction (to form  $M(CO)_{a-c}Cl^{-}$  and  $M(CO)_{a-c}Br^{-}$ ), and HCl or HBr abstraction products (to form  $M(CO)_{a-d}HCl^{-}$  and  $M(CO)_{a-d}HBr^{-}$ ) are observed in the reactions of 1,n-bromochloroalkanes. These products may also be predicted from the (monofunctional) chloroalkane reactions. A product corresponding to abstraction of bromine <u>and</u> chlorine (to form MClBr<sup>-</sup> with loss of all carbonyl ligands present) is observed and is unique to the reaction of the 1,n-bromochloroalkanes (i.e., is not expected from the chloroalkane reactions).

The same mechanism utilized in the chloroalkane reactions may also be used to explain most of the 1,n-bromochloroalkane reactions as shown in Scheme VI. The metal anion inserts into the C-X bond (X = Cl or Br) with transfer of the electron to the halogen (metal insertion/charge transfer). This intermediate may undergo either loss of carbonyl ligands to yield Parent substitution products or loss of carbonyl and alkyl ( $C_nH_{2n}Y$ ) ligands to yield halogen abstraction products. A  $\beta$ -H shift rearrangement may occur resulting in the formation of HCl or HBr abstraction products.

The presence of two halogen atoms on the neutral molecule is seen to effect the distribution of the observed products when compared to the chloroalkane products. Parent substitution products are <u>not</u> observed in the reactions of  $Cr(CO)_3^-$ . Recall that all three carbonyl ligands were lost in the Parent substitution reactions of  $Cr(CO)_3^-$  with the chloroalkanes. Apparently the metal insertion/charge transfer process for the bromochloroalkanes is more exothermic than for the chloroalkanes resulting in only X and HX abstraction and no Parent substitution.

The reactions of 1,n-bromochloroalkanes allow the study of the preference for the site of attack (Br or Cl) by the metal-containing anions. Table 6 lists

(HX abstraction)

(CO)<sub>a-d</sub> | H--<u>M</u>--

-dCO $-C_nH_{2n-1}Y$ 

(Parent substitution) (X abstraction)

 $(CO)_{a-c} M - X^{-} YC_{n} H_{2n-1} M - X^{-}$ 



Scheme VI

Anion	C1 - containing products	Br - containing products	HCl abstraction	HBr abstraction
Fe(CO)3 <sup>-</sup>	41 %	59 %	8 0	100 %
Cr(CO)3 <sup>-</sup>	47	53	45	55
Cr(CO)4 <sup>-</sup>	40	60		
Co(CO)2 <sup>-</sup>	35	65	25	75
CoCONO-	19	81	19	81
Co(CO)3 <sup>-</sup>	0	100	0	100

the average branching ratios for products in which either the bromine or chlorine is exclusively attacked (e.g. Parent substitution is not included) by various metal-containing anions with the 1,n-bromochloroalkanes. These values are calculated by summing the branching ratios for all the 1,n-bromochloroalkanes (n = 2 to 6) in which bromine or chlorine is exclusively attacked and calculating the average value. Also listed in Table 6 is a comparison of the average amount of HCl and HBr abstraction observed for the 1,n-bromochloroalkanes. The preferential attack at the chlorine on the molecule by the metal anion may be expected since the electron affinity of chlorine is 6 kcal/mole greater than that for bromine. The opposite trend, preference for attack at the bromine, is actually observed as seen in Table 6. This trend may reflect the thermodynamics of the metal insertion into the C-X bond. The C-Br bond energy is 14 kcal/mole less than the C-Cl bond energy<sup>51</sup>. Metal-containing species having relatively high electron affinities such as  $Fe(CO)_3$ ,  $Co(CO)_2$ , and  $Co(CO)_3$  (predicted from previous reaction trends) exhibit a preference for attack at the weaker C-Br bond as seen in Table 6. In contrast,  $Cr(CO)_3^$ which has been shown to have a low electron affinity exhibits virtually no preference for reaction at the Cl or Br end of the molecule due to the large amount of energy available from electron transfer to either Br or Cl. Therefore, it appears that both the strength of the C-X bond which must be broken, and the difference in electron affinity between the metal species and the halogen (i.e., the energy available from the charge transfer process) determine the preference of attack by the metal anion. The difference in the amount of HCl and HBr abstraction observed also reflects the corresponding electron affinity of the reactant metal anions. Virtually no preference is seen for metal species with a relatively low electron affinity  $(Cr(CO)_3)$ , but HBr abstraction occurs exclusively for metal species with high electron affinities (Fe(CO)<sub>3</sub>

and  $Co(CO)_3$ ). The following order of electron affinities of the metal species is suggested by the results in Table 6: E.A. $(Cr(CO)_3) < E.A.(Co(CO)_2) <$ E.A. $(CoCONO) < E.A.(Co(CO)_3) < E.A.(Fe(CO)_3) = 41.5$  kcal/mole. These relationships are consistent with those inferred in the chloroalkane and alcohol reactions.

Unfortunately the electron affinities of only the iron-containing species have been experimentally determined<sup>52</sup>. These values were obtained using photoelectron spectrometry. An attempt was made to experimentally estimate the electron affinities of these metal-containing species using ICR in order to confirm the ordering proposed above. Bracketing techniques<sup>42</sup> have been used to determine upper and lower limits for the proton affinities (P.A.) of species in the gas phase. For example, if the following ion/molecule reactions

 $A + BH^+ \longrightarrow AH^+ + B$ 

 $CH^+ + B \longrightarrow BH^+ + C$ 

are observed, then the following must be true: P.A.(C) < P.A.(B) < P.A.(A). If the proton affinities of A and C are known, upper and lower limits on the unknown P.A.(B) may be deduced. Double resonance experiments may also be performed to verify these reactions. A similar process was applied to the negative ions in which electron transfer reactions were observed. If the following reaction

 $A + B^- \longrightarrow A^- + B$ 

is observed, then the following assumption may be made: E.A.(B) < E.A.(A).

Species A may then be varied to determine upper and lower limits of the E.A.(B) (metal species in this case). In order to test this technique, the metal-containing anions from  $Fe(CO)_5$  (since these electron affinities are known) were reacted with Br<sub>2</sub>. Reaction 17 would be expected to occur since E.A.(Fe(CO)<sub>3</sub>) = 41.5 kcal/mole < E.A.(Fe(CO)<sub>4</sub>) = 55.3 kcal/mole < E.A.(Br<sub>2</sub>) = 57.7 kcal/mole.

$$Fe(CO)_3^-$$
 (or  $Fe(CO)_4^-$ ) +  $Br_2 \longrightarrow Br_2^-$  +  $Fe(CO)_3$  (or  $Fe(CO)_4$ ) (17)

When this experiment was performed however, no  $Br_2^-$  was observed. It was thought that the  $Br_2^-$  formed may have dissociated to  $Br^-$  (already present from electron impact on  $Br_2$ ) and Br. Double resonance on  $Br^-$  however showed no response from  $Fe(CO)_3^-$  or  $Fe(CO)_4^-$ . Many ion/molecule reaction products besides electron transfer were observed between the iron-containing anions and  $Br_2$ . Many other anions were present in the mass spectrum due to electron impact on products from the neutral-neutral reaction of  $Fe(CO)_5$  and  $Br_2$  (no double resonance responses observed). Apparently these processes interfere and prohibit the observance of reaction 17. Even if this technique had been successful, the applicability would have been limited since very few neutral molecules exist which have known high electron affinities.

The product resulting from abstraction of <u>both</u> bromine and chlorine  $(MC1Br^{-})$  from the 1,n-bromochloroalkanes is observed for  $Co(CO)_2^{-}$ ,  $Cr(CO)_3^{-}$ , and  $Fe(CO)_3^{-}$  (for n = 2 to 6) and is accompanied by the loss of all carbonyl ligands on the metal. In the reaction of 1,2-bromochloroethane, the metal may complex with the chlorine and bromine simultaneously (Scheme VII) resulting in abstraction of both Br and Cl and loss of a neutral ethylene molecule. A similar product is observed in the reaction of Co<sup>+</sup> with 1,2-bromochloroethane<sup>25</sup> but is not observed for the larger



1,n-bromochloroalkanes ( $n \ge 3$ ). The two possible mechanisms for the reaction of the larger 1,n-bromochloroalkanes (n = 3 to 6) with metal-containing anions are shown in Scheme VIII. The first mechanism is similar to Scheme VII for 1,2-bromochloroethane except that the neutral lost is the corresponding cycloalkane (as opposed to the loss of a biradical species). The second mechanism involves insertion of the metal <u>and</u> one of the carbonyl ligands into a C-X (X = Cl or Br) bond. The other halogen (Y) is then transferred to the metal through a cyclic intermediate. The carbonyl ligand is now incorporated in the neutral product which is in the form of a cyclic ketone. In gas-phase positive metal ion reactions, evidence for active participation of carbonyl ligands in insertion processes has occasionally been observed<sup>12,22,29</sup>.

To this point, it has not been necessary to invoke active participation of ligands on the metal anion to explain the products observed. Reaction 18 shows the formation of Br, Cl, and the cycloalkane from the 1,n-bromochloroalkane. Reaction 19 shows the incorporation of CO with the 1,n-bromochloroalkane to form Br, Cl, and a cyclic ketone.

 $Cl(C_nH_{2n})Br \longrightarrow Cl + Br + cyclo-C_nH_{2n}$  (18)

$$Cl(C_nH_{2n})Br + CO \longrightarrow Cl + Br + cyclo-C_{n+1}H_{2n}O$$
 (19)

The difference in AH for these two reactions is given by:

$$\Delta H_{diff} = \Delta H_{18} - \Delta H_{19} = \Delta H(cyclo - C_n H_{2n}) - \Delta H(cyclo - C_{n+1} H_{2n}O) + \Delta H(CO)$$

Thermodynamic calculations<sup>58</sup> indicate that the loss of the cyclic ketone is favored over the loss of the cycloalkane in the reactions of





Scheme VIII







 $M(CO)_{a}^{-}$  +  $X(CH_{2})_{n}Y$ 

1,n-bromochloroalkanes by 26.2 kcal/mole for n = 4, 9.23 kcal/mole for n = 5, and 3.27 kcal/mole for n = 6. As the alkyl chain length increases, the thermodynamic advantage of forming the cyclic ketone over the cycloalkane decreases due to the decreased difference in ring strain for the two structures.

The same ligand effects are observed in the 1,n-bromochloroalkane reactions as seen in the chloroalkanes and alcohols: retention of NO in reactions of CoCONO<sup>-</sup>, and unreactivity of the 17 electron metal anions. Also, the same trends in the branching ratios are observed as in the chloroalkane reactions; i.e., an increase in HX abstraction and decrease in X abstraction as the alkyl chain length (n) increases.

#### B. Reactions of 1,n-Chloroalcohols

The products and branching ratios for the reactions of 1-chloro-n-alcohols (1,n-chloroalcohols) (n = 2 to 6) with iron and cobalt-containing anions and chromium-containing anions are listed in Tables 7 and 8, respectively. These studies allow the determination of the preference for attack at Cl vs. OH by the metal-containing anions. Parent substitution ( $MClC_nH_{2n}OH^-$ ) is observed for the three metal anions  $Cr(CO)_3^-$ ,  $Fe(CO)_3^-$ , and  $Co(CO)_2^-$  with the loss of all carbonyl ligands. Since Parent substitution was not observed in the reactions of  $Co(CO)_2^-$  and  $Fe(CO)_3^-$  with alcohols, but was seen for all three metal anions with chloroalkanes, the mechanism for Parent substitution in reactions of 1,n-chloroalcohols presumably involves metal insertion/charge transfer into the C-Cl bond (and not the C-OH bond) with competitive ligand loss of the carbonyl ligands similar to Scheme I for the chloroalkanes. If the metal inserts into the C-Cl bond in the 1,n-chloroalcohols, other products typical of chloroalkane reactions would be expected. The abstraction of Cl and HCl from the chloroalcohols by all three metal anions are observed as seen in Tables 7 and 8. These products also result from metal insertion/charge

1,n-Chloroalcohols
nions with
ntaining ar
cobalt-co
iron and
Reactions of
Table 7.

				£	nching Rat	.8	
Reaction			<u>n=2</u>	<u>n=3</u>	<u>1=4</u>	<u>u=5</u>	<u>n=6</u>
Fe(CO) <sub>3</sub> <sup>-</sup> + Cl(CH <sub>2</sub> ) <sub>n</sub> он —	Fecl(CH <sub>2</sub> ) <sub>n</sub> OH <sup>-</sup>	+ 3CO	.04	.14	.10	.17	.12
	$Fe(CO)_{3}C1^{-} + ($	(сн <sub>2</sub> ) <sub>п</sub> он	.84	.73	.72	.76	.75
	Fe(CO)2HC1- +	c <sub>n</sub> H <sub>2n</sub> O + CO	.05	.14	.18	.07	.13
	Fe(CO) <sub>2</sub> C <sub>n</sub> H <sub>2n</sub> O	- + HCl + CO	.07				
Fe(CO)4 <sup>-</sup> + CI(CH <sub>2</sub> ) <sub>n</sub> OH -	NR <sup>a</sup>						
$Co(CO)_{2}^{-} + CI(CH_{2})_{n}OH -$	сост(сн <sub>2</sub> ) <sub>п</sub> он-	. + 2CO	.04	.33	.19	.19	.11
	Cococi- + (CH	(2) <sub>n</sub> oh + Co	.14				
	$c_{0}(c_{0})_{2}c_{1} + (c_{0})_{2}c_{1}$	(СН <sub>2</sub> ) <sub>п</sub> ОН	.36	.38	.23	.27	.24
	CoHCI- + C <sub>n</sub> H <sub>2</sub>	no + 200			.04	.04	.01
	Cocohci + C	$^{\rm H}2nO + CO$	.17	. 29	.35	.32	.49
	Co(CO)2HC1- +	C <sub>n</sub> H <sub>2n</sub> O			60.	.18	.15
	CoCIOH- + CnH	I <sub>2n</sub> + 2CO	. 29				
	$\sim$ $coc_nH_{2n}O^- + H$	CI + 2CO			.03		
		$HC1 + H_2 + 2C0$			.07		

Table 7 continues

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**Table 7 continued** 

Branching Ratios

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Reaction	<u>n-2</u>	0=0		<u>u=5</u>	9-U
$c_{0}c_{0}ono^{-} + c_{1}(cH_{2})_{n}OH$ - $c_{0}c_{0}onoc_{1} - (cH_{2})_{n}OH$	1.00	.67	.57	.67	.68
$\sim$ CoNOHCI - + C <sub>n</sub> H <sub>2n</sub> O + CO		.33	.43	.33	.32
$C_0(CO)_3^- + CI(CH_2)_nOH$ - NR					
$C_0(CO)_2NO^- + CI(CH_2)_nOH$					

<sup>a</sup> NR indicates the ion did not undergo any reactions

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Table 8. Reactions of chromium-containing anions with 1,n-chloroalcohols

		Bra	nching Rat	ios	
Reaction	<u>n=2</u>	0=E	<u>n=4</u>	<u>n=5</u>	<u>n=6</u>
$cr(co)_{3}^{-} + cl(cH_{2})_{n}OH - crcl(cH_{2})_{n}OH^{-} + 3cO$	.16	. 29	.22	.18	.24
	.08	(.17) <sup>8</sup>	.17	.21	.12
			.06	.14	.03
$c_{c}(c_{0})_{2}C_{1}(c_{H_{2}})_{n}OH^{-} + CO$				.07	90.
$r(co)_2 CIC_n H_{2n-1}O^- + H_2 + CO$				.05	.03
$-cr(CO)_2CIC_nH_{2n-3}O^- + 2H_2 + CO$					.02
$r(co)_{2}C_{n}H_{2n}O^{-} + HC1 + CO$	.06				
$cr(co)_{2}Cl^{-} + (CH_{2})_{n}OH + CO$	.16	11.	60.	.04	.06
Cr(CO) <sub>3</sub> Cl <sup>-</sup> + (CH <sub>2</sub> ) <sub>n</sub> OH	. 28	.23	.25	.21	.27
$\sim$ CrHCl <sup>-</sup> + CnH <sub>2</sub> n <sup>0</sup> + 3C0		.16	.04	.03	.04
$r(co)_2HCl^- + C_nH_2nO + CO$	.07	(.17)	.11	.04	60.
$r(co)_3OH^- + (CH_2)_nCl$	.05	.04	.06	.03	.04
$CrcloH^{-} + C_nH_{2n} + 3CO$	.14				
Cr(CO)4 <sup>-</sup> + Cl(CH <sub>2</sub> ) <sub>n</sub> OH - Cr(CO) <sub>3</sub> Cl <sup>-</sup> + (CH <sub>2</sub> ) <sub>n</sub> OH + CO	1.00	.79	1.00	.60	.77
$c_{r}(c_{0})_{4}c_{1}^{-} + (c_{H_{2}})_{n}^{-}OH$		.21		.40	.23
$Cr(CO)_5^- + CI(CH_2)_nOH \longrightarrow NR^b$					
<sup>a</sup> Values in parentheses are the sum of branching ratios for isobaric prod	ict ions				
b NR indicates the ion did not under go any reactions					

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transfer into the C-Cl bond followed by a  $\beta$ -H shift and competitive ligand loss similar to Scheme I.

The chromium anion  $Cr(CO)_3^-$  reacts with the 1,n-chloroalcohols to yield products expected from the n-alcohol reactions. These include OH abstraction and elimination of one or two hydrogen molecules. The mechanisms for these reactions are similar to those for the reactions of n-alcohols in Schemes III, IV, and V. Since both OH abstraction and Parent substitution products proceed through the same intermediate (C-OH insertion) in the n-alcohol reactions (Scheme III), the Parent substitution ion for 1,n-chloroalcohols (with  $Cr(CO)_3^-$ ) probably consists of both insertion into the C-Cl and C-OH bonds. Products predicted from the reactions of n-alcohols (loss of H<sub>2</sub>) are not observed for iron and cobalt-containing anions with 1,n-chloroalcohols.

Products which are unique in the reactions of 1,n-chloroalcohols include the abstraction of both Cl and OH (MClOH<sup>-</sup>) and the elimination of HCl  $(M(CO)_{X-B}C_2H_4O^-)$ . The abstraction of both Cl and OH is observed for the anions  $Co(CO)_2^-$  and  $Cr(CO)_3^-$  with 1,2-chloroethanol and is accompanied by the loss of all carbonyl ligands on the metal. This product is not observed for the larger 1,n-chloroalcohols (n  $\geq$  3). The mechanism for abstraction of Cl and OH is shown in Scheme IX. The metal does not insert into the C-Cl or C-OH bonds but complexes with both Cl and OH simultaneously. Abstraction of Cl and OH with electron transfer to the ligands with higher electron affinity is accompanied by the loss of a neutral ethylene molecule similar to Br and Cl abstraction in the 1,n-bromochloroalkanes. The elimination of HCl from 1,2-chloroethanol is observed for the anions  $Fe(CO)_3^-$  and  $Cr(CO)_3^-$ . This product is also not observed for the larger 1,n-chloroalcohols (n  $\geq$  3). Following metal insertion into the C-Cl bond and electron transfer to the chlorine (Scheme X), a six-member ring intermediate may form (only for n = 2). Cleavage of



Scheme IX



the C-Cl bond and electron pair transfer results in loss of HCl and structure 13 in which the charge has migrated to the alkoxy ligand.

The reactions of 1,n-chloroalcohols indicate that the preference for attack (Cl or OH) by the metal anions is at the chlorine end of the molecule. The preference for chlorine is due to the higher electron affinity of Cl (83.3 kcal/mole) compared to OH (42.2 kcal/mole). The thermodynamics of the metal insertion may also play a role since the C-Cl bond strength is 10 kcal/mole less than the C-OH bond strength<sup>51</sup>. The same ligand effects are observed in the reactions of 1,n-chloroalcohols that were seen in the previous reactions.

The reactions of the bifunctional molecules have shown that the reactions observed and the general mechanism proposed for the corresponding monofunctional compounds may be used in explaining products indicative of one functional group. The preference for attack at a particular functional group may be explained in terms of the difference in electron affinities of the metal-containing anion and the functional group and also the C-functional group bond energy. The trends observed for the preference of attack were used to propose an ordering of the electron affinities of the metal-containing species. Several unique reactions (not predicted from the monofunctional reactions) involving both functional groups were also observed.

#### **CHAPTER 6**

# **REACTIONS OF NITROALKANES**

The ion/molecule reactions of metal-containing anions formed by low energy electron impact on  $Fe(CO)_5$ ,  $Co(CO)_3NO$ , and  $Cr(CO)_6$  with a series of nitroalkanes and n-butyl nitrite were studied as a continuation of the previous work with alkyl halides and alcohols. The general mechanism proposed previously invoked the initial formation of a metal anion insertion/charge transfer intermediate with insertion occurring at the C-functional group bond only. The exothermicity of the charge transfer process appears to determine the products which are observed. Also, the electron affinity data available enables one to predict the types of ligands which may be formed or lost (e.g., Cl has a high electron affinity and always remains on the metal in the alkyl halide reactions). This general mechanism may now be applied to the reactions of metal-containing anions with nitroalkanes.

The corresponding positive ion reactions of  $Co^+$  and  $Co(ligand)_n^+$  with nitroalkanes and alkyl nitrites was studied previously<sup>22</sup> and is included in Appendix B. The nitroalkanes were extremely reactive compared to the reactivity of other monofunctional organic molecules. The products observed for Co<sup>+</sup> with nitroalkanes resulted from metal insertion into C-H, C-C, C-N,

and N-O bonds. Many nitroalkane products were best explained via a "nitrite-like" intermediate – possibly indicating a metal-induced nitro-to-nitrite (RNO<sub>2</sub> to RONO) isomerization. Although metal anion insertion into the C-H and C-C bonds is not expected (from the results of the previous study of metal anion reactions), metal anion insertion into the C-N and N-O bonds in the nitroalkanes is possible. The relatively high electron affinities of NO<sub>2</sub> (53 kcal/mole) and O (33.7 kcal/mole) suggest that the nitroalkanes may be reactive with the metal-containing anions by insertion into the R-NO<sub>2</sub> and N-O bonds.

#### A. Reactions of n-Nitroalkanes

The ion/molecule reaction products and their branching ratios for the reactions of iron, cobalt, and chromium-containing anions with the series of 1-nitro-n-alkanes (n-nitroalkanes) (n = 1 to 4) are listed in Tables 9 to 11, respectively. The number of products observed for  $Fe(CO)_3^-$ ,  $Co(CO)_2^-$ , and  $Cr(CO)_3^-$  (8, 9, and 17 products, respectively) correlates with the electron affinities predicted for these metal-containing species from the alkyl halide and alcohol reactions (E.A.( $Cr(CO)_3$ ) < E.A.( $Co(CO)_2$ ) < E.A.( $Fe(CO)_3$ )). A greater amount of energy is released in the charge transfer process for the metal species with lower electron affinities and thus a larger variety of products is observed.

Substitution of the neutral nitroalkane for 1 to 3 CO ligands (Parent substitution) is observed for the reactive (i.e. non-17 electron) metal-containing anions for all three metals studied (reaction 20).

$$M(CO)_{\mathbf{x}} + C_{\mathbf{n}}H_{2\mathbf{n}+1}NO_2 \longrightarrow M(CO)_{\mathbf{x}-\mathbf{a}}C_{\mathbf{n}}H_{2\mathbf{n}+1}NO_2 + \mathbf{a}CO \qquad (20)$$

The nitroalkanes displace 1 or 2 CO ligands in the reaction of  $Fe(CO)_3^-$  and  $Co(CO)_2^-$ , but all three CO ligands are lost in the Parent substitution products

Table 9. Reactions of Iron-Containing Anions with n-Nitroalkanes and 2-Methyl-2-Nitropropase

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	Intermediate			Branching Ratio	w 1	
Reaction	Structure	Ë	n=1	€=U	Ĩ	n=4 ((CH <sub>3</sub> ) <sub>3</sub> CNO <sub>2</sub> )
$Fe(CO)_{3}^{-} + C_{n}H_{2n+1}NO_{2} + Fe(CO)C_{n}H_{2n+1}NO_{2}^{-} + 2CO$		5	23	13	7	35
Fe(CO)2CnH2n+1NO2 <sup>-</sup> + CO		15	10	7	3	
$FeC_{nH_{2n+1}NO^{-}} + CO_{2} + 2CO$	r, 111	42	8)8	21	20	65
$Fe(CO)C_{n}H_{2n+1}NO^{-} + CO_{2} + CO$	r, 111	61	16	80	4	
FeH20 <sup>-</sup> + C <sub>n</sub> H <sub>2</sub> n-1NO + 3CO	111		19	7	18	
Fe(CO)H2O <sup>-</sup> + C <sub>n</sub> H2n-1NO + 2CO	111		9	9	14	
or FeNO2 <sup>-</sup> + C <sub>n</sub> H <sub>2n+1</sub> + 3CO	Ш					
$\rightarrow$ Fe(CO)NO <sup>-</sup> + C <sub>n</sub> H <sub>2n+1</sub> + CO <sub>2</sub> + CO	111	4				
$\rightarrow Fe(CO)HNO^{-} + C_nH_{2n} + CO_2 + CO$	III		(8)	25	32	
FeCn <sup>11</sup> 2n-1NO <sup>-</sup> + H <sub>2</sub> O + 3CO	-	7				
or $Fe(CO)C_nH_{2n+1} + NO + CO_2 + CO$	III					
. ► Fe(CO)C <sub>n</sub> H <sub>2n-1</sub> NO <sup>-</sup> + H <sub>2</sub> O + 2CO	и, ш		18	13	2	
or Fe(CO)2CnH2n+1 + NO + CO2	111					
	I	4				
or $Fe(CO)_2C_nH_2nNO^- + OH + CO$	1					

Fe(CO)4<sup>-</sup> + C<sub>n</sub>H<sub>2n+1</sub>NO<sub>2</sub> ----- N.R.<sup>b</sup>

A Values in pararentheses are the sum of branching ratios for isobaric product ions.

b N.R. indicates the ion did not undergo any reactions.

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	Intermediate			Branching R	atios	
Reaction	Structure	Ĩ	2=U	5=1	I	n=4 ((CH <sub>3</sub> ) <sub>3</sub> CNO <sub>2</sub> )
$Co(CO)_2^{-} + C_nH_{2n+1}NO_2 - CoC_nH_{2n+1}NO_2^{-} + 2CO$		Q	8(11)			
		13	14	7	6	
	-	32	37	28	32	50
$\leftarrow$ $coc_nH_{2n+1}NO^+ + CO_2 + CO_2$	r, III <sup>-</sup>	36	7	17	م	
	Ш		5	13	20	
$ COHNO^{-} + C_n H_{2n} + CO_2 + CO$	.111		19	7	10	
$\leftarrow$ CoHNO2 <sup>-</sup> + C <sub>n</sub> H <sub>2n</sub> + 2CO	н		ñ	5	6	
$\sim$ Co(CO)HNO <sub>2</sub> + C <sub>n</sub> H <sub>2n</sub> + CO	п		(11)	12	20	50
CoCnH2n-1NO <sup>-</sup> + H2O + 2CO	_	13	۵	11	۵	۵
or Co(CO)CnH2n+1 + NO + CO2	II					
$C_{0}CONO^{-} + C_{n}H_{2n+1}NO_{2} - C_{0}NO_{n}H_{2n+1}NO_{2}^{-} + CO$		13	2	9	10	
$\sim$ cocono(o) + c <sub>n</sub> H <sub>2n+1</sub> NO	_	12	12	10	6	
$\sim$ cono(o) + c <sub>n</sub> H <sub>2n+1</sub> NO + co	-	53	46	54	52	
or $Co(CO)H_2O^- + C_nH_{2n-1}NO + NO$	Η					
$ CoH_2O_2^- + C_nH_{2n-1}N + CO + NO$	N	80	7	11	51	
$co(co)NO_2^- + C_nH_{2n+1}$	11	14	28	19	20	100
Co(CO)3 <sup>-</sup> + C <sub>n</sub> H <sub>2n+1</sub> NO <sub>2</sub> N.R. <sup>c</sup>						
Co(CO) <sub>2</sub> NO <sup>−</sup> + C <sub>n</sub> H <sub>2n+1</sub> NO <sub>2</sub> N.R. <sup>c</sup>						

<sup>a</sup> Values in parentheses are the sum of branching ratios for isobaric product ions.

<sup>b</sup> These product ions are expected, but no double resonance response is observed due to interference from electron impact fragments of Co(CO)<sub>3</sub>NO.

<sup>c</sup> N.R. indicates the ion did not undergo any reactions.

Table 11. Reactions of Chromium-Containing Anions with n-Nitroalkases and 2-Methyl-2-Nitropropase

				Branchin	g Ratios	
Reaction	Intermediate Structure	II	n=2	2	1	n=4 ((CH <sub>3</sub> ) <sub>3</sub> CNO <sub>2</sub> )
$Cr(CO)_{3}^{-} + C_{n}H_{2n+1}NO_{2} - CrC_{n}H_{2n+1}NO_{2}^{-} + 3CO_{2n+1}NO_{2}^{-}$		13	G	2	4	4
$c_{r}(c_{0})_{2}O^{-} + C_{n}H_{2n+1}NO + CO$	1, 111	18	11	-	•	e
	1	20	25	18	22	22
$rcr(co)_2OH^- + C_nH_2nNO + CO$	-	4	(2)8 <sup>4</sup>	(4)	3	
$c_{r}(co)_{3}OH^{-} + C_{n}H_{2}NO$	I	£	e	2	(1)	4
	r, 111	-	•	(4)	2	7
$c_{r}(c_{0})NO^{-} + C_{n}H_{2n+1} + CO_{2} + CC_{2}$	0 III'	1	•	3	2	
$c_{r}(c_{0})c_{n}H_{2n+1}O^{-} + NO + 2CO$	Ш	5	(3)	1	•	
	N	п	80	10	7	
$c_{r}(c_{0})o_{2}^{-} + c_{n}H_{2n+1}N + 2c_{0}$	2	3	3	ß	£	
$c_{1}(c_{0})_{2}O_{2}^{-} + C_{n}H_{2n+1}N + CO$	N					49
	١٧	S	7	5	•	
	N	10	20	33	30	
$c_{1}(c_{0})NO_{2}^{-} + C_{n}H_{2n+1} + 2CO$	Ш					£
$c_{1}(c_{0})_{2}NO_{2}^{-} + C_{n}H_{2n+1}^{-} + CO$	11	3	4	4	9	89
$\leftarrow$ CrHNO2 <sup>-</sup> + C <sub>n</sub> H <sub>2n</sub> + 3CO	11			4	3	
				4	2	
				6	•	
	-	e				

Table 11 continues

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or  $Cr(CO)C_nH_{2n+1}^-$  + NO + CO<sub>2</sub> + CO

**Table 11 continued** 

					Branching	g Ratios	
Reaction		Intermediate Structure	1 = u	n=2	<b>5</b> =0	T	n=4 ((CH <sub>3</sub> ) <sub>3</sub> CNU <sub>2</sub> )
$cr(co)_{4}^{-} + c_{n}H_{2n+1}NO_{2}$					6		
1			49	80	58	100	
<b>I</b>	$r = Cr(CO)_{3}O^{-} + C_{n}H_{2n+1}NO + CO$	1	38	20	11		
	$r \sim Cr(CO)_3OH^- + C_nH_{2n}NO + CO$	<b>–</b>			22		
	$\sim$ CrC <sub>n</sub> H <sub>2n+1</sub> NO <sup>-</sup> + CO <sub>2</sub> + 3CO	r, 11r	13				100
Cr(CO)s <sup>-</sup> + C <sub>n</sub> H <sub>3n+1</sub> NO <sub>3</sub>	• N.R.b						

Cr(CO)5<sup>-</sup> + C<sub>n</sub>H<sub>2n+1</sub>NO<sub>2</sub> −−−−► N.R.

<sup>a</sup> Values in parentheses are the sum of branching ratios for isobaric product ions.

b N.R. indicates the ion did not undergo any reactions.

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with  $Cr(CO)_3^-$ . This trend correlates well with the electron affinities (and thus exothermicity of the charge transfer processs) of the three metal species mentioned previously. This suggests that a metal insertion/charge transfer mechanism may account for the Parent substitution products. In the chloroalkane and alcohol reactions, the Parent substitution product structure presumably does <u>not</u> consist of an intact organic molecule as a ligand, but was predicted to result from metal insertion/charge transfer into the C-functional group bond. This was proposed due to the negative electron affinity of the neutral molecule and due to the fact that all the products observed could be formed through this common intermediate. The electron affinity of the neutral nitroalkanes, however, is positive (e.g. E.A.(CH<sub>3</sub>NO<sub>2</sub>) = 9.2 kcal/mole) suggesting that the Parent substitution product structure may be either an intact nitroalkane on the metal or a metal insertion type structure.

Two metal insertion structures may be predicted for the reactions of nitroalkanes with metal-containing anions. Intermediate I results from metal insertion into the N-O bond. This structure is predicted to be stable due to the relatively high electron affinity of O (33.7 kcal/mole). The electron affinity of  $C_nH_{2n+1}NO$ , however, is not known. The electron affinities of  $NO_2$  (53 kcal/mole) and  $C_nH_{2n+1}$  (~20 kcal/mole) suggest that intermediate II (C-N insertion) would also be stable.

In the nitroalkane discussion, structures will be depicted with the negative charge on the metal center. However, recall that charge transfer/charge delocalization over the various ligands present still occurs as in the alkyl halide and alcohol reactions. Metal insertion into C-C and C-H bonds are <u>not</u> predicted for the nitroalkane reactions since they were not observed in the alkyl halide and alcohol reactions.

The proposed intermediate structures which lead to the various product ions are also listed in Tables 9 to 11. The mechanisms for the formation of product ions from intermediates I and II are shown in Schemes XI and XII, respectively. A large number of products, however, do not result from intermediates I and II. These products result from intermediates III and IV as shown in Schemes XIII and XIV, respectively.



In intermediate III, the nitroalkane exists as three ligands  $(C_nH_{2n+1})$ , NO, and O) on the metal. Intermediate III may result from rearrangement of intermediate I (N-O insertion) through an alkyl migration as shown in Scheme XIII. An analogous process has been observed in the reactions of Fe<sup>+</sup> and ketones<sup>20</sup> (reaction 21).



Scheme XI





Scheme XIII



Scheme XIV



Intermediate III may also be formed from intermediate II as a result of the oxygen shifting onto the metal center (Scheme XIII). Several products observed in the reactions of nitroalkanes result from an intermediate in which both oxygens are present on the metal as shown in intermediate IV. Intermediate IV may be formed from intermediate I as shown in Scheme XIV. A similar intermediate was observed in the reactions of Co<sup>+</sup> with nitroalkanes<sup>22</sup>.

The reaction products observed from the four intermediates will now be discussed in detail. Once intermediate I is formed (Scheme XI), it may undergo a ligand loss process to form  $M(CO)_{X-a}O^-$ . This product is observed for metal-containing anions from all three metals studied. The retention of the O ligand is expected since it has a relatively high electron affinity (33.7 kcal/mole)(E.A.( $C_nH_{2n+1}NO$ ) is unknown). This product may also be formed through intermediate III (Scheme XIII) with the loss of the NO and alkyl  $(C_nH_{2n+1})$  ligands. Note that the electron affinities of the two ligands which are lost (0.5 kcal/mole and  $\sim 20$  kcal/mole respectively) are less than the electron affinity of O (33.7 kcal/mole) which is retained. In some cases however, the formation of  $M(CO)_{X-a}O^-$  cannot proceed through intermediate III due to the larger number of ligands which would be present on the metal in intermediate III compared to intermediate I, i.e., in intermediate III the nitroalkane is broken into three ligands on the metal but in intermediate I it exists as only two ligands. For example,  $Cr(CO)_2O^-$  may proceed through intermediate III since only five ligands would be present at any one time. The product  $Cr(CO)_3O^-$  cannot result from intermediate III since it requires six ligands to be present on the metal which violates the 18 electron rule.

The corresponding product ion  $M(CO)_{X-a}C_nH_{2n+1}NO^-$  (i.e., <u>loss</u> of O) is observed for  $Fe(CO)_3^-$ ,  $Co(CO)_2^-$ ,  $Cr(CO)_3^-$ , and  $Cr(CO)_4^-$  (n = 1 to 4). This product is <u>not</u> predicted to result from intermediate I since it would require loss of the oxygen ligand which has a relatively high electron affinity. The active participation of carbonyl ligands in the metal insertion process has been suggested in both positive and negative metal ion reactions. If the metal anion <u>and</u> one of the carbonyl ligands inserts into the N-O bond, intermediate I' (Scheme XI) may be formed. In this structure, the oxygen is never a ligand on the metal but instead exists as a  $CO_2$  ligand on the metal. The  $CO_2$  ligand is then lost due to its negative electron affinity (-13.8 kcal/mole). This product ion may also result from an intermediate similar to intermediate III. If the oxygen in intermediate II shifts onto a CO ligand instead of the metal then a  $CO_2$  ligand is formed. The  $CO_2$  ligand is then lost to yield intermediate II' as seen in Scheme XIII.

A  $\beta$ -H may shift onto the metal in intermediate I to yield structure 1,4 (Scheme XI). The O and H ligands on the metal may exist as a single OH ligand (E.A.(O) = 33.7 kcal/mole, E.A.(H) = 17.4 kcal/mole, and E.A.(OH) = 42.2 kcal/mole) as shown in structure 1,4. The electron affinities suggest that O and H may exist as either one or two ligands on the metal. Structure 1,4 may proceed through a ligand loss process to yield  $M(CO)_{x-a}OH^-$  (retention of OH, for  $Cr(CO)_3^-$ ) or  $M(CO)_{x-a}C_nH_{2n}NO^-$  (loss of OH, for  $Fe(CO)_3^-$ ). Since these products (formation of an OH ligand) are observed for nitromethane (n = 1),

they <u>cannot</u> proceed through intermediate III since <u>no</u>  $\beta$ -H's are present when n = 1.

A second hydrogen may shift onto the metal in structure  $\frac{1}{\sqrt{4}}$  to produce an H<sub>2</sub>O ligand (E.A.(H<sub>2</sub>O) = 0.0 kcal/mole) which is lost to yield the product ion M(CO)<sub>x-a</sub>C<sub>n</sub>H<sub>2n-1</sub>NO<sup>-</sup>. This product is observed for metal-containing anions from all three metal carbonyl compounds as seen in Tables 9 to 11. The formation and subsequent loss of H<sub>2</sub>O may suggest that O and H are present as a single OH ligand on the metal. Since this ion is observed for nitromethane (n = 1), then it must proceed through intermediate I and <u>not</u> from intermediate III (similar to the above argument). In one case,  $Fe(CO)C_nH_{2n-1}NO^-$ , this product ion is <u>not</u> observed for n = 1 but only for n = 2 to 4. Therefore, this ion may result from either intermediate I or III (Scheme XIII), but note that the ion  $Fe(CO)_2C_nH_{2n+1}^-$  (loss of NO<sub>2</sub>) is isobaric with this product ion.

The product ions  $M(CO)_{X-B}NO_2^-$  and  $M(CO)_{X-B}HNO_2^-$  are formed through intermediate II (C-N insertion) as seen in Scheme XII. Once intermediate II is formed, the alkyl ligand may be lost to form  $M(CO)_{X-B}NO_2^-$  since the electron affinity of  $C_nH_{2n+1}$  (~20 kcal/mole) is less than the electron affinity of NO<sub>2</sub> (53 kcal/mole). This ion may also be formed through intermediate III but NO<sub>2</sub> then exists as two ligands (O and NO) on the metal. The electron affinities (E.A.(O) = 33.7 kcal/mole and E.A.(NO) = 0.5 kcal/mole) suggest that the product ion resulting from intermediate II delocalizes the negative charge more than in intermediate III, thus  $M(CO)_{X-B}NO_2^-$  presumably is formed through intermediate II. Note that  $FeNO_2^-$  is observed for n = 2 to 4 but <u>not</u> for n = 1 (Table 9). There is no apparent reason for this product ion not to occur for n = 1. Also note that all three carbonyls are lost in the formation of  $FeNO_2^-$  but only one or two carbonyls are lost in the formation of  $Cr(CO)_{X-B}NO_2^-$  (Table 11). The loss of all three carbonyl ligands is unexpected in the formation of  $\text{FeNO}_2^-$  since the reactions of  $\text{Cr}(\text{CO})_3^-$  are always more exothermic than  $\text{Fe}(\text{CO})_3^-$  (the charge transfer/delocalization process is more exothermic since E.A. $(\text{Cr}(\text{CO})_3) < \text{E.A.}(\text{Fe}(\text{CO})_3)$ ). Therefore, the ion  $\text{FeNO}_2^$ is probably not the correct product assignment with the isobaric ion  $\text{FeCO}(\text{H}_2\text{O})^$ being the more probable product ion structure.

The product ion  $M(CO)_{X-B}HNO_2^-$  is observed for  $Co(CO)_2^-$  and  $Cr(CO)_3^$ with the n-nitroalkanes (n  $\geq 2$ ). This suggests a mechanism in which a  $\beta$ -H shifts onto the metal in intermediate II to yield structure 15 (Scheme XII). The alkene formed is then lost due to it's negative electron affinity (e.g. E.A.(C<sub>2</sub>H<sub>4</sub>) = -35.7 kcal/mole). The two remaining ligands (H and NO<sub>2</sub>) both have positive electron affinities (17.4 and 53 kcal/mole respectively) to help delocalize the negative charge.

The product ions  $M(CO)C_nH_{2n+1}O^-$  and  $M(CO)_{x-a}O^-$  may be formed through intermediate III by loss of NO or NO and  $C_nH_{2n+1}$  ligands respectively as seen in Scheme XIII. The ligands which are lost (NO (0.5 kcal/mole) and  $C_nH_{2n+1}$ ( $\sim 20$  kcal/mole)) both have lower electron affinities than the O ligand which remains on the metal (33.7 kcal/mole). Two H-shifts may occur in intermediate III to yield either structure 16 or 17 in Scheme XIII. Structure 16 loses the  $C_nH_{2n-1}$  ligand to yield the product ion  $M(CO)_{x-a}H_2O^-$  which is observed for  $Fe(CO)_3^-$  and  $Co(CO)_2^-$  with the nitroalkanes ( $n \ge 2$ ). The electron affinity data suggests that  $H_2O$  (0.0 kcal/mole) exists as OH (42.2 kcal/mole) and H (17.4 kcal/mole) ligands in order to delocalize the charge as in structure 16. Structure 17 results from the formation of an  $H_2O$  ligand which is then lost to yield  $M(CO)_{x-a}C_nH_{2n-1}NO^-$  which was discussed previously. The  $C_nH_{2n-1}$ ligand has a positive electron affinity (e.g. E.A.( $C_3H_5$ ) = 12.5 kcal/mole) to help delocalize the charge.

Several products result from intermediate III' (i.e. following the loss of

O as  $CO_2$ ) as seen in Scheme XIII. The loss of the NO ligand from intermediate III' yields  $M(CO)_{x-a}C_nH_{2n+1}^-$  which is observed for metal-containing anions from all three metals studied. This corresponds to a net loss of NO<sub>2</sub> from the nitroalkane. Although it is more straightforward to lose NO<sub>2</sub> from intermediate II (C-N insertion), this process is <u>not</u> predicted since E.A.(NO<sub>2</sub>) > E.A.(C<sub>n</sub>H<sub>2n+1</sub>), i.e. the ligand with the higher electron affinity would have to be lost. If this product is formed through III', however, the NO<sub>2</sub> is lost as  $CO_2$  (-13.8 kcal/mole) and NO (0.5 kcal/mole) which have low or negative electron affinities. The loss of  $C_nH_{2n+1}$  from intermediate III' yields the product ion  $M(CO)NO^-$  which is observed for  $Cr(CO)_3^-$  and  $Fe(CO)_3^-$ . When n  $\geq 2$  for the n-nitroalkanes, a  $\beta$ -H may shift onto the metal in intermediate III' to yield  $M(CO)_{x-2}HNO^-$  with loss of the corresponding alkene (E.A.(C<sub>2</sub>H<sub>4</sub>) = -35.7 kcal/mole) which is formed as seen in Scheme XIII. Note that HNO may exist as one ligand on the metal (E.A.(HNO) = 7.8 kcal/mole) or as H (E.A.(H) = 17.4 kcal/mole) and NO (E.A.(NO) = 0.5 kcal/mole).

All of the reaction products observed with  $Fe(CO)_3^-$  and  $Co(CO)_2^-$  may be explained through intermediates I, II, or III. Approximately 45% of the products from  $Cr(CO)_3^-$  result from intermediate IV (Scheme XIV) in which two oxygen ligands are present on the metal. The electron affinities of the ligands present in intermediate IV (E.A.(O) = 33.7 kcal/mole and E.A.(C<sub>2</sub>H<sub>5</sub>N) = 43 kcal/mole) indicate that this structure should be stable. Loss of the  $C_nH_{2n+1}N$  ligand yields the product  $M(CO)_{X-a}O_2^-$ . This is <u>not</u> expected if the electron affinities of the two ligands are considered (i.e. E.A.(C<sub>n</sub>H<sub>2n+1</sub>N) > E.A.(O)). If the electron affinity of the CrO<sub>2</sub> species (55.3 kcal/mole) is considered then the  $C_nH_{2n+1}N$  ligand <u>is</u> expected to be lost since it has a lower electron affinity. The product ions  $MO_2H^-$  and  $MO_2H_2^-$  result from one and two  $\beta$ -H shifts from intermediate IV respectively as seen in Scheme XIV. It is interesting that products resulting from intermediate IV occur almost exclusively for  $Cr(CO)_3^-$ . Since  $Cr(CO)_3^-$  is predicted to have the lowest electron affinity of the metal-containing anions studied, the largest amount of energy released in the charge transfer (delocalization) process occurs for  $Cr(CO)_3^-$ . Therefore, a large amount of energy appears to be required to form intermediate IV from intermediate I since it only occurs for  $Cr(CO)_3^-$ .

## B. Reactions of 2-Methyl-2-Nitropropane

The reactions of the metal-containing anions from  $Fe(CO)_5$ ,  $Co(CO)_3NO$ , and  $Cr(CO)_6$  with 2-methyl-2-nitropropane are also included in Tables 9 to 11 respectively. The 2-methyl-2-nitropropane appears to be less reactive than the corresponding 1-nitrobutane with only two reactions observed with  $Fe(CO)_3^-$  and  $Co(CO)_2^-$  and eight reactions with  $Cr(CO)_3^-$ .

The only product ion observed for  $Fe(CO)_3^-$  besides the Parent substitution product is  $FeC_nH_{2n+1}NO^-$  (loss of O) resulting from either intermediate I' or III'. If this product is formed through intermediate III', the formation of  $Fe(CO)HNO^-$  would be expected since  $\beta$ -H's are present and it is the largest product observed for 1-nitrobutane. This product is <u>not</u> formed suggesting that  $FeC_nH_{2n+1}NO^-$  is formed through intermediate I'. The other products expected from intermediates I and I' are only minor products for 1-nitrobutane and are not observed for 2-methyl-2-nitropropane.

The two products formed from the reaction of  $Co(CO)_2^-$  with 2-methyl-2-nitropropane are  $Co(CO)_2O^-$  from intermediate I and  $Co(CO)HNO_2^-$  from intermediate II. This is reasonable since these are the only two products observed from these two intermediates for the n-nitroalkanes. Also, there are  $\beta$ -H's available to shift in intermediate II for 2-methyl-2-nitropropane to produce  $Co(CO)HNO_2^-$ .

The reaction of  $Cr(CO)_3^-$  with 2-methyl-2-nitropropane yields the product

ions  $Cr(CO)_2O^-$  and  $Cr(CO)_3O^-$  from intermediate I and  $CrC_nH_{2n+1}NO^-$  from intermediate I'. The product ion  $Cr(CO)_{x-a}OH^-$  seen in the reaction of 1-nitrobutane is <u>not</u> expected in the 2-methyl-2-nitropropane reactions since there are <u>no</u>  $\beta$ -H's present in intermediate I with 2-methyl-2-nitropropane. A small amount of  $Cr(CO)_3OH^-$  is observed, however, which may proceed by a H-shift through a six-member ring intermediate as shown in structure 18.



The largest product formed through intermediate IV in the 1-nitrobutane reactions is  $CrO_2H_2^-$ . In the 2-methyl-2-nitropropane reactions, however, there are <u>no</u>  $\beta$ -H's present in intermediate IV and thus, the only product resulting from intermediate IV is  $Cr(CO)_2O_2^-$ . The product ion  $Cr(CO)_{x-a}NO_2^-$  is formed through intermediate II in the reactions of 2-methyl-2-nitropropane. Although  $\beta$ -H's are available to shift to produce  $Cr(CO)_{x-a}HNO_2^-$ , these  $\beta$ -H's are terminal hydrogens for 2-methyl-2-nitropropane. The lack of terminal  $\beta$ -H shift is not unexpected since the terminal  $\beta$ -H's in the reaction of nitroethane also do <u>not</u> shift to yield  $Cr(CO)_{x-a}HNO_2^-$  (Table 11).

#### C. Reactions of n-Butyl Nitrite

The ion/molecule reaction products and branching ratios for the reactions of n-butyl nitrite ( $C_4H_9ONO$ ) with iron, cobalt, and chromium-containing anions are listed in Table 12. In the corresponding positive ion reactions of n-butyl

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			E	<b>unching Ratios</b>			
Reactions 6	termediate Structure	Pe(CO)3 <sup>-</sup>	Co(CO)2 <sup>-</sup>	CoCONO	Co(CO)3	Cr(CO)3 <sup>-</sup>	cr(c0)4
$M(CO)_{x}(NO)_{y}^{-} + C_{4}H_{9}ONO \longrightarrow M(CO)C_{4}H_{9}ONO^{-} + (x-1)CO$							100
$\longrightarrow$ MC4H9ONO <sup>-</sup> + xCO + yNO		59	20	62	100	9	
or $M(CO)_2 HNO_2^- + C_4 H_8 + (x^{-2})CO$	8						
$m(co)HNO_2^2 + C_4H_8 + Co$	8		8				
M(CO)3NO <sup>-</sup> + C4H <sub>9</sub> O	۲	6					
$m(co)C_4H_9O^- + NO + (x-1)CO$	~		21			•	
$M(CO)_2C_4H_9O^- + NO + (x-2)CO$	v	19				12	
$M(CO)_{2}C_{4}H_{8}O^{-} + HNO + CO$	v	13				S	
MNOC4H8O <sup>-</sup> + HNO + CO	v			38			
M(CO)HNO- + C4H80 + CO	۲		51				
$\longrightarrow$ $M(CO)_{2}C_{4}H_{7}O^{-} + H_{2} + NO + CO$	~					34	
$\longrightarrow$ M(CO) <sub>2</sub> C <sub>4</sub> H <sub>6</sub> O <sup>-</sup> + H <sub>2</sub> + HNO + CO	۲					13	
$M(CO)_2C_4H_5O^- + 2H_2 + NO + CO$	~					16	
- M(CO)3NO2 <sup>-</sup> + C4H9	8					10	

nitrite<sup>22</sup>, the majority of products resulted from metal insertion into the relatively weak O-NO bond (42 kcal/mole)<sup>73</sup> along with metal insertion into the C-O bond. All of the products observed for n-butyl nitrite with the metal-containing anions appear to proceed through two intermediates. Intermediates A and B (nitrite intermediates) result from metal insertion into the weak O-NO bond and the C-O bond, respectively.



Intermediate A may lose the  $C_4H_9O$  ligand to yield  $M(CO)_XNO^-$  or lose the NO ligand to yield  $M(CO)_{X-B}C_4H_9O^-$  as shown in Scheme XV. The electron affinity data (E.A.( $C_4H_9O$ ) = 43.8 kcal/mole and E.A.(NO) = 0.5 kcal/mole) suggest that the loss of  $C_4H_9O$  should not occur. The loss of  $C_4H_9O$  is a minor process, however, and is only observed for  $Fe(CO)_3^-$ , whereas the loss of NO is large (20%) and is observed from all three metals.

The reaction of  $Cr(CO)_3^-$  is unique in that it continues to react following the loss of NO (structure 19, Scheme XV) to eliminate molecules of H<sub>2</sub>. Recall that this reaction was also observed only for  $Cr(CO)_3^-$  with n-alcohols. A  $\beta$ -H may shift onto the metal in 19 to yield structure 20 in which the metal is bonded to the carbon and the charge is moved onto the oxygen. This mechanism is identical to that proposed in the reactions of n-alcohols. Another  $\beta$ -H may shift in 20 with loss of H<sub>2</sub> to yield structure 21 (loss of NO and H<sub>2</sub>). The metal may continue to move down the alkyl chain in a similar manner to eliminate a second  $H_2$  molecule as seen in Scheme XV.

A  $\beta$ -H may shift onto the metal in intermediate A to yield structures 22 and 23. In 22, the charge remains on the metal with the formation of a  $\pi$ -bonded aldehyde which is lost to yield  $M(CO)_{X-1}HNO^-$ . Note that two structures are possible (HNO, or NO and H as ligands) for this product ion as shown in Scheme XV. In structure 23, the metal is bonded to the carbon with the negative charge being transferred to the oxygen, analogous to 19. The HNO ligand which is formed may be lost due to it's low electron affinity (7.8 kcal/mole). This product ion reacts further to lose a molecule of H<sub>2</sub> to yield Cr(CO)<sub>2</sub>C<sub>4</sub>H<sub>6</sub>O<sup>-</sup> (loss of HNO and H<sub>2</sub>) as shown in Scheme XV.

The remaining two products may be explained through intermediate B (C-O insertion) (Scheme XVI). The alkyl radical,  $C_4H_9$ , in intermediate B may be lost to yield  $M(CO)_XONO^-$ . The product ion  $M(CO)_{X-a}HONO^-$  is formed as a result of a  $\beta$ -H shift in intermediate B followed by loss of the 1-butene ligand which is formed.

In summary, the general mechanism proposed in the reactions of metal-containing anions with alkyl halides and alcohols has been successfully applied to the reactions of nitroalkanes. The metal insertion/charge transfer (delocalization)/g-H shift process still occurs exclusively at the functional group (i.e., no C-C or C-H insertion). The nitroalkane reactions parallel the alcohol reactions in complexity relative to the chloroalkane reactions, since the NO<sub>2</sub> and OH groups both <u>contain</u> bonds which are also attacked. The nitroalkane reactions are unique in that several products appear to result from intermediates which are formed by rearrangement of the initial metal insertion intermediate. The electron affinity data available allows one to predict the ligands which are formed and lost in the reactions. The same ligand effects are observed in the reactions of nitroalkanes as in alkyl halides and alcohols





Scheme XVI

(e.g., 17 electron species are unreactive) including further evidence for the active participation of the carbonyl ligands in the reaction mechanisms. The metal-induced nitro-to-nitrite isomerization which was observed in the positive metal ion reactions of  $Co^+$  with nitroalkanes is <u>not</u> observed in the reactions of metal-containing anions.

## D. Further Insights into the Metal Insertion/Charge Transfer Mechanism

There are two possible explanations for the lack of C-C and C-H insertion in the reaction of metal-containing anions with organic molecules. The first involves the stability of the three metal insertion intermediates following insertion into C-C, C-H, and C-X bonds as shown in structures 24 to 26respectively.



Structure 26 (C-X insertion) is predicted to be more stable than structures 24 and 25 due to the relatively high electron affinity of the functional group and thus greater charge delocalization. (This analysis contains a number of assumptions, e.g., without charge delocalization, all of the metal-ligand  $\sigma$  bonds in 24 to 26 are of approximately the same energy.) The other explanation may be that metal insertion occurs via complexation/charge transfer/fragmentation as shown below (i.e., charge transfer occurs prior to metal insertion).

$$M^{-} + \begin{array}{c} X \\ R \end{array} \longrightarrow M^{-} \begin{bmatrix} X \\ I \\ R \end{bmatrix}^{-} \longrightarrow M^{-} \begin{bmatrix} X \\ R \end{bmatrix}^{-}$$

In order to differentiate between these two processes, one must determine when in the mechanistic sequence the charge transfer process occurs. The latter process can be considered analogous to the dissociative electron capture process which occurs during low energy electron impact.

The electron impact negative ion mass spectra of the organic molecules studied here are consistent with a mechanism in which the charge transfer process occurs prior to the metal insertion process. For example, the negative ion mass spectra of alkyl chlorides<sup>77</sup> at high electron energies (> 50 eV) include Cl<sup>-</sup> and several alkyl fragment ions (e.g.  $C_2H^-$ ,  $C_2^-$ , and CH<sup>-</sup>). At lower electron energies, however, the only ion present in the mass spectrum is Cl<sup>-</sup>, i.e., electron attachment leads to the formation of  $Cl^-$  and R. This parallels the metal insertion/charge transfer process in which the R-Cl bond is broken and M-Cl<sup>-</sup> and M-R bonds are formed. The major negative ions present in the 90 eV electron impact mass spectra of alkyl alcohols<sup>78</sup> are (M-H)<sup>-</sup>, OH<sup>-</sup>, and O<sup>-</sup>. The formation of the ion/radical pairs ( $(M-H)^-$  and  $H\cdot$ ) and  $(OH^-$  and  $R\cdot$ ) parallel metal insertion/charge transfer into the O-H and C-OH bonds of n-alcohols, respectively. The predominant negative ions in the low energy (4.5 eV) electron impact mass spectra of nitroalkanes<sup>79</sup> are  $NO_2^-$ ,  $O^-$ , and  $CN^-$ . At higher electron energies more alkyl and rearrangement type ions are present. The formation of the ion/radical pairs (NO $2^{-}$  and R·) and (O<sup>-</sup> and RNO·) in the electron impact process again suggests that the charge transfer process may occur prior to the metal insertion into the  $R-NO_2$  and N-O bonds of nitroalkanes.

Thermodynamic calculations<sup>58</sup> for the dissociative electron capture process (reaction 22) yield values for  $\Delta$  H<sub>22</sub> of  $\sim$ -6 kcal/mole for X = Cl,  $\sim$ -15 kcal/mole for X = Br, and  $\sim$ +48 kcal/mole for X = OH.

$$\mathbf{RX} + \mathbf{e}^{-} \longrightarrow \mathbf{R} \cdot + \mathbf{X}^{-} \tag{22}$$

These results correlate well with the preference for site of attack which was observed in the chemistry of the bifunctional organic molecules. For example, metal insertion/charge transfer into the R-Br bond was preferred over the C-Cl bond in 1,n-bromochloroalkanes, and C-Cl insertion occurs preferentially over C-OH insertion in 1,n-chloroalcohols. These trends may be predicted by the exothermicity of the dissociative electron capture process in reaction 22.

A similar analysis of the formation of RO<sup>-</sup> and H· from n-alcohols, i.e., a process similar to metal insertion/charge transfer into the O-H bond, yields a value of  $\Delta H = v +60$  kcal/mole which is approximately 12 kcal/mole more endothermic than for the formation of OH<sup>-</sup> and R·. This would suggest preference for metal insertion/charge transfer into the R-OH bond over the O-H bond of n-alcohols. The opposite trend, however, was observed in the chemistry of n-alcohols with metal-containing anions. This may reflect the effect which the formation of different bonds (e.g., R-M-OH and RO-M-H) has on the preference of attack by the metal anions in the metal insertion/charge transfer process.

## **CHAPTER 7**

## CONCLUSIONS

A general mechanism has been proposed for the reaction of metal-containing anions with polar organic molecules. Low energy electron impact on  $Fe(CO)_5$ ,  $Cr(CO)_6$ , and  $Co(CO)_3NO$  was utilized as the source of the metal-containing anions in order to obtain a significant amount of the more reactive (non-17-electron) species. The reactions of alkyl halides and alcohols with these metal-containing anions suggest that the initial step is the formation of a metal insertion/charge transfer(delocalization) intermediate into the C-functional group bond. The negative charge may be transferred to a ligand (e.g., Cl) which has a relatively high electron affinity. This is followed by possible rearrangement (e.g.,  $\beta$ -H shift for  $C_nH_{2n+1}X$  when  $n \ge 2$ ) and competitive ligand loss similar to that observed for positive metal ions. Evidence for the occurrence of  $\beta$ -H shifts in the reactions of metal-containing anions has been reported here for the first time. The ligand loss process observed for metal anions is quite different from that for the corresponding positive ions. For example, ligands which are  $\pi$ -donors (e.g., olefins) are strongly bound to the metal in the reactions of positive ions but are always lost in the reactions of metal-containing anions.

The exothermicity of the charge transfer/delocalization process appears to determine the products which are formed. The trends in reactivity of the various metal-containing anions results in a possible ordering of the electron affinities of the metal-containing species: E.A. $(Cr(CO)_3) < E.A.(Co(CO)_2)$  $< E.A.(CoCONO) < E.A.(Co(CO)_3) < E.A.(Fe(CO)_3) = 41.5$  kcal/mole. This ordering of electron affinities is consistent with all of the reactions observed in this dissertation. For example,  $Cr(CO)_3^-$  is always the most reactive species since it is predicted to have the lowest electron affinity and thus the greatest amount of energy is released in the charge transfer process.

The general mechanism which was proposed can be successfully applied in explaining the reactions of several bifunctional organic molecules and nitroalkanes. The products observed in the chemistry of bifunctional organic molecules (e.g., 1,n-bromochloroalkanes) indicates the preference of attack at one functional group over another. The preference for attack appears to depend on both the electron affinity of the functional group (and thus the energy available in the charge transfer process) and the bond energy of the C-functional group bond which must be broken on insertion. Products are also observed which are indicative of metal insertion with both functional groups.

The reactions of n-alcohols and nitroalkanes are unique in that bonds within the functional group are also attacked by the metal anions. Products are observed in the reaction of nitroalkanes which result from rearrangement following formation of the metal insertion/charge transfer intermediate. In contrast to the corresponding positive metal ion reactions, there is no evidence in the chemistry of metal-containing anions for metal insertion into C-C or C-H bonds. The lack of C-C and C-H insertion may be expected if the metal insertion/charge transfer process is compared to the processes which occur in the dissociative electron capture negative ion mass spectra of the organic

molecules. The similarities in the metal insertion/charge transfer process and the dissociative electron capture process suggest that the charge transfer may occur prior to the metal insertion.

Several ligand effects are observed in the reactions of metal-containing anions. The reactivity of the metal decreases as the number of ligands increase. The 17-electron species  $(M(CO)_{n-1})$  from electron impact on a metal carbonyl containing n CO ligands are generally unreactive as reported in earlier studies. Metal species with fewer ligands however are very reactive. Products are observed which indicate the possibility that the carbonyl ligands which are present may actively participate in the metal insertion and rearrangement processes. This has also been suggested in the reactions of positive metal-containing ions.

The original premise for the application of these metal-containing anions as chemical ionization (CI) reagent ions appears to be somewhat limited. The Parent substitution products observed may provide information on the molecular weight of the sample molecule. Functional group information can be obtained through the products observed from metal insertion into the C-functional group bond (e.g.,  $M(CO)_X CI^-$ ). The only structural information which is available from the reactions of metal-containing anions is the presence or absence of products resulting from a  $\beta$ -H shift rearrangement depending on the length of the alkyl chain. The reaction of the corresponding positive metal ions results in a larger variety of product ions and thus more information on the analyte molecule. One example is the presence of products resulting from metal insertion into C-C and C-H bonds which are <u>not</u> observed in the anion reactions. Based on this work, the anion which would provide the most information in a CI experiment would be  $Cr(CO)_3^-$  since the largest variety of products are usually formed with this metal-containing anion.

The results presented in this dissertation suggest several possible future projects on the reactivity of gas-phase metal anions. If the electron affinity of the metal-containing species could be experimentally determined, they could be compared to the ordering which is suggested in this study. The experimentally determined electron affinities would also be beneficial in predicting the products observed in the reactions of metal-containing anions with other organic molecules. The determination of the reactivity of the bare metal anions would also be very interesting. The use of collision induced dissociation and ion ejection techniques with Fourier transform mass spectrometry (FTMS) allows one to form the bare metal anion, M<sup>-</sup>, from the corresponding metal carbonyl,  $M(CO)_n$ . The reactivity of the bare metal anions with the organic molecules studied in this dissertation could be compared to the reactivity of the metal-containing anions,  $M(CO)_x$ . The effect that the presence of the ligands have on the reactivity could then be determined. Squires<sup>80</sup> has reported that the bare metal anion  $Cr^-$  is unreactive towards propene, but  $Cr(CO)_3H^-$  reacts to eliminate  $H_2$ . The presence of the ligands in the reactions of metal-containing anions may be necessary either to remove the excess energy from the charge transfer process (since carbonyl ligands are frequently lost) or to actively participate in the metal insertion or rearrangement process as illustrated in this study.

# APPENDICES

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APPENDIX A

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# Appendix A

Table 13.	Pertinent	Electron	Affinities	(E.A.)	(kcal/mole) <sup>a</sup>
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Anion $(M^-)$	E.A. (M), kcal/mole	Reference
Н-	17.4	56
C1-	83.3	53
Br <sup>-</sup>	77.6	53
Br <sub>2</sub> -	57.7	53
Cr <sup>-</sup>	15.4	74
CrO <sub>2</sub> -	55.3	72
Co-	15.3	75
Fe <sup>-</sup>	3.8	52
Fe(CO) <sup>-</sup>	29.1	52
Fe(CO)2 <sup>-</sup>	28.1	52
Fe(CO)3 <sup>-</sup>	41.5	52
Fe(CO) <sub>4</sub> <sup>-</sup>	55.3	52
FeH <sup>-</sup>	21.5	40
C0-	31.6	76
CO2 <sup>-</sup>	-13.8	66
0-	33.7	64
но-	42.2	53
H <sub>2</sub> O⁻	0.00	67
СH <sub>3</sub> 0-	36.7	60
C <sub>2</sub> H <sub>5</sub> O <sup>-</sup>	39.8	61
n-C3H7O <sup>-</sup>	41.2	61
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Table 13 continues

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Table 13 continued		
n-C <sub>4</sub> H <sub>9</sub> O <sup>-</sup>	43.8	62
CH <sub>3</sub> C1 <sup>-</sup>	-79.6	48
СН3-	26	55
$C_2H_5^-$	23	55
C <sub>3</sub> H <sub>7</sub> -	16	55
C <sub>4</sub> H <sub>9</sub> <sup>-</sup>	15	55
C <sub>2</sub> H <sub>4</sub> <sup>-</sup>	-35.7	57
С <sub>3</sub> н <sub>5</sub> -	12.5	69
CH <sub>3</sub> NO <sub>2</sub> -	9.2	65
NO-	0.5	68
HNO-	7.8	70
NO2 <sup>-</sup>	53	63
C <sub>2</sub> H <sub>5</sub> N <sup>-</sup>	43	71

<sup>a</sup>Electron affinity is defined as  $\Delta H$  for the reaction M<sup>-</sup>  $\longrightarrow$  M + e<sup>-</sup>

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**APPENDIX B** 

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## Gas-Phase Reactions of Co<sup>+</sup> and Co(ligand),<sup>+</sup> with Nitroalkanes

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Abstract: The gas-phase chemistry of Co<sup>+</sup> and ions of the type Co(ligand),<sup>+</sup> with a series of nitroalkanes is presented. Also, for comparison, reactions of methyl nitrite and 1-butyl nitrite are included. The Co<sup>+</sup> ion reacts with nitroalkanes by inserting into C-H, C-C, C-N, and N-O bonds. Many nitroalkane products can be best explained via a "nitrite-like" intermediate—possibly indicating a metal-induced nitro-to-nitrite isomerization. Collision-induced dissociation analysis of (i) primary reaction products and (ii) products of subsequent reactions is used to suggest product ion structures. With ligands present on the metal, dramatic changes of reactivity are observed. While nitroalkanes react by simple ligand displacement with Co(ligand),\* typical of monofunctional alkanes, alkyl aitrites exhibit a much richer chemistry, more typical of multifunctional organic molecules.

In recent years there has been a growing interest in the study of the gas-phase reactions of atomic metal and metal-containing ions with organic molecules. Studies of these reactions using ion cyclotron resonance (ICR) spectrometry<sup>1</sup> and ion beam techniques<sup>2</sup> yield information on the activation of bonds in organic molecules by metal ions in the absence of complicating solvent effects. Thermodynamic, kinetic, and mechanistic information concerning the intrinsic organometallic and coordination chemistry of metal ions can be obtained from these studies. Also, the specific chemistry of metal ions with organic molecules is the basis for a new approach to chemical ionization mass spectrometry.<sup>3,4</sup>

An important area of interest has been the study of the interaction of metal ions with organic molecules containing specific functional groups. In addition to studies of the reactions of a runctional groups. In addition to studies of the reactions of a variety of metal ions with alkanes,<sup>2,3</sup> the reactions of transition-metal ions with organic species such as alkyl halides,<sup>16,4</sup> alkenes,<sup>16,4</sup> alkenes,<sup>16,4</sup> alkenes,<sup>10,4</sup> alkenes,<sup>10,10</sup> ketones,<sup>13,10</sup> carboxylic acids,<sup>11,10</sup> esters,<sup>11,10</sup> ethers,<sup>9,10</sup> sulfides,<sup>11,12</sup> and mercaptans<sup>12</sup> have also been studied. As an example of the types of reactions that have been observed, the reactions of  $Co^+$  with several  $C_2H_3X$  species are given in Table I. With the exception of ethylamine, the major reaction pathway for all of these compounds involves insertion of the metal ion into the relatively weak C-X bond as the first mechanistic step. A  $\beta$ -H shift from the alkyl ligand may then occur, forming  $Co(C_2H_4)(HX)^+$  which then dissociates by competitive ligand loss as seen in reaction 1. For the reactions of

Co\* with complex functional groups, such as carboxylic acids,

Table L. Listing of the Neutrals and Ione Resulting from the Reactions of Co\* with Various Monosubstituted Ethanes

	Co+ + C <sub>2</sub> H,	X - A+ + m	outral		
X	۸*	neutral	rel %	ref	
н	no reaction			5d	
CH,	CoC2H4+	CH4	31	54	
	CoC,H.*	H,	69		
I	CoC <sub>2</sub> H <sub>4</sub> *	HÌ	78	6	
	Col*	C,H,	11		
	CoHI*	C,H	11		
ОН	CoH <sub>2</sub> O*	C,H	13	6	
	CoC <sub>2</sub> H <sub>4</sub> *	H <sub>2</sub> O	87		
SH	CoC <sub>2</sub> H <sub>4</sub> +	H,S	70	12	
	CoSH+	C,H,	7		
	CoH,S*	CH	23		
NH,	CoC <sub>2</sub> H <sub>3</sub> N*	Н,	15	8	
	CoCH <sub>3</sub> N*	CH,	26		
	C <sub>2</sub> H <sub>4</sub> N*	CoĤ	59		
o	CoCO*	C,H	8	10	
сся,	CoC,H.*	C,HO	24		
	CoC,HO*	CH	52		
	CoC,H,O*	CH	11		
	CoC4H4O*	н,	5		
የ	CoH <sub>2</sub> O*	C,H <sub>4</sub> O	36	10	
COH	CoC,H.*	CH-O-	37		
	CoCH,O,*	C.H.	5		
	CoC H.O*	H-O	21		
	CoC,H,O1+	Н,	1		
Q	CoC.H.*	CH.O.	16	10	
осн	Coch.o.+				
		C jrla			

sertion into the C-X bond is still a major reaction pathway, but some cleavage of bonds within the functional group also occurs.<sup>3</sup>

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#### Table II. Listing of Neutrals and Ions Resulting from the Primary Reactions of Co\* with Nitromethane and Methyl Nitrite

		Co <sup>+</sup> + reactant -	+ CoR <sup>+</sup> + neutral(s)		
			CH,NO2		CH,ONO
CoR*	neutral(s)	rel %	intermediate structure	rel %	intermediate structure
CoHNO <sub>2</sub> *	CH,	2	1	0	
CoH*	CH,ONO	2	111, E	15	C. E
CoO*	HCN, H-O	17	IV. V	0	
CoOH*	CH,NO	21	1V, V	0	
Co(OH),*	HCN	6	IV. V	0	
CoCH-NO*	OH	3	IV, V	Ó	
CoCHNO*	H,O	3	IV, V	0	
CoNO*	CH.O	2	E	Ś	E
CoOCH,*	NO	40	E	70	Ē

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Table III. Listing of loss and Neutrals Resulting from the Primary Reactions of Co<sup>+</sup> with Nitroethane

HNO

H2. NO

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C C	$0^{\circ} + C_2 H_3 N O_2 \rightarrow 0$	Cok + neutral(s)	
CoR*	neutral(s)	intermediate structure	rel %
CoHNO2*	C2H4	I	12
Coc H +	HNO.	1	1

CoOCH

CoC2H4*	HNO <sub>2</sub>	1	3
CoC,H,*	H <sub>2</sub> NO <sub>2</sub>	I, III	14
CoCH <sub>1</sub> *	CH,NO,	11	5
CoCH <sub>2</sub> NO <sub>2</sub> *	СН	II	7
CoCH_NO <sub>2</sub> *	CH <sub>2</sub>	11	2
CoO*	CH,CN, H,O	IV, V	2
CoOH*	C <sub>2</sub> H <sub>4</sub> NO	IV, V	20
Co(OH),*	CHICN	IV, V	4
CoC, H, NO*	OH	IV, V	5
CoC, H, NO*	H,O	IV. V	4
CoNO <sup>+</sup>	C,HO	E	3
CoC,H,O*	NO	E	4
CoC,H,O*	HNO	E	10
CoC,H,O*	H <sub>3</sub> , NO	E	5

A logical extension of this area, which has been receiving re interest, is the study of the effect of various ligands on metal ion reactivity. Although this work is still in its infancy, preliminary studies have shown that the presence of a ligand may lead to new reaction mechanisms as well as enhance or deactivate the bare metal ion.1a.4.8.13

As a continuation of our work in this area, the results of a study of the reactions of Co\* with some aliphatic nitro compounds are presented here. In addition, reactions involving CoL+ generated

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Table IV. Listing of Neutrals and lons Resulting from the Primary Reactions of Co $^{\ast}$  with Nitropropane

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 $Co^+ + C_1H_1NO_2 \rightarrow CoR^+ + neutral(s)$ 

Co* +	C,H,NO2	-+ R*	+	neutral(s)
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			re	70
CoR* or R**	neutral(s)	intermediate structure	1- C,H,NO2	2- C <sub>1</sub> H <sub>2</sub> NO <sub>2</sub>
C,H,*	CoNO <sub>2</sub>	I	12	17
CoHNO <sub>2</sub> *	C,H	I	21	16
CoC,H.*	HNŎ,	I	4	3
CoC <sub>1</sub> H <sub>1</sub> *	H <sub>2</sub> , NO <sub>2</sub>	L III	10	6
CoCH <sub>1</sub> *	C <sub>2</sub> H <sub>4</sub> NO <sub>2</sub>	11	2	2
CoC <sub>2</sub> H <sub>4</sub> NO <sub>2</sub> *	CH,	11	8	1
CoC, H, NO,*	CH,	n	2	3
CoCH <sub>2</sub> NO <sub>2</sub> *	C,H,	11	2	2
CoCH,NO,*	C,H	п	1	2
CoOH <sup>+</sup>	C,HANO	IV, V	15	18
CoNO*	C'H'O	E	2	2
CoC,H,O*	NO	E	1	3
CoC HO*	HNO	E	6	7
CoC,H,O*	H <sub>2</sub> NO	E	14	11

as primary products from the interaction of Co<sup>+</sup> with nitroalkan as well as  $Co(CO)_{x}^{+}$  (x = 0-2) and  $Co(CO)_{x}NO^{+}$  (x = 0-3) generated by electron impact on Co(CO), NO are presented.

### **Experimental Section**

The experiments involving the bare metal ion, Co\*, were carried out by using a prototype Nicolet FTMS-1000 which has been previously described in detail.<sup>14</sup> The mass spectrometer is equipped with a 5.2-cm cubic trapping cell situated betwee en the poles of a Varian 15-in. elsetromagnet maintained at 0.9 T. The cell has a 0.25-in -diameter hole in tromagnet maintained at 0.5 1. The cen has a 0.25 in-standard roles in one of the transmitter plates to allow various light sources access to the inside of the cell. Co was generated by focusing the frequency-doubled beam (530 nm) of a Quanta Ray Nd:YAG laser onto a high-parity cobalt foil which was supported by the opposite transmitter plate. Details of the laser ionization experiment have been described elsewhere.<sup>36,9</sup> Laser ionization can produce ions in excited states, and while steps are taken to minimize their presence.<sup>13</sup> the formation of minor products from excited Co<sup>\*</sup> cannot be completely ruled out.

The distributions of primary product ions listed in Tables II-V are reproducible to within  $\pm 10\%$  absolute for the major products and  $\pm 5\%$ absolute for the minor products. Product distributions of subseque reactions of the Co\* primary reaction products were determined by using swept double resonance techniques<sup>16</sup> to isolate the ions of interest.

The CID experiments were performed by using the FTMS. Sample pressures were on the order of  $1 \times 10^{-1}$  torr, and the argon target gas was on the order of  $1 \times 10^{-3}$  for. Pressures were monitored with a Bayard-Alpert ionization gauge. Details of the CID experiments have been described previously.<sup>54,10</sup> The collision energy can be varied

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Table V. Listing of the Neutrals and Ions Resulting from the Primary Reactions of Co\* with Nitrobutane and Butyl Nitrite

### $Co^+C_4H_9NO_2 \rightarrow CoR^+ + neutral(s)$

 $Co^+ + C_4H_9NO_2 \rightarrow R'^+ + neutral(s)$ 

					rei %		
CoR+ or R++	neutral(s)	intermediats (nitro)	I-C <sub>4</sub> H <sub>4</sub> NO <sub>2</sub>	2-C4H4NO2	(CH <sub>1</sub> ),CNO <sub>2</sub>	intermediate (nitrite)	I-C.H.ONO
C'H'+	CoNO <sub>2</sub>	I	38	30	79		3
CoHNO <sub>2</sub> +	C <sub>4</sub> H <sub>8</sub>	1	9	13	.,	~	<b>.</b>
CoC4H4*	HNÔ,	1	i	1	1	•	, v
CoC.H.*	H. NO.	L III	Å	11	i e	^	1
CoC.H.*	H. HNO.	1	ĩ		5		Ů,
CoCH.*	C.H.NO.	'n	ő	2		•	4
CoC.H.NO.*	CH.	ii ii	ů,	, in the second s	4		0
CoC.H.NO.*	С.н.	ii ii	1	-	2		0
CoC.H.NO.*	С.н.	11	14	2	1		0
CoC.H.*	CHNO			1	1		0
Coch NO +	China	11	2	0	0		0
Coc.H.+		11	2	1	0	B	23
Coc H +		11	2	2	0		0
Coolit		11	2	1	0	B	6
Cic II Ot	C <sub>4</sub> H <sub>6</sub> NO	IV, V	7	7	3		0
	NO	E	1	3	1	E	2
CoCtHio	HNO	E	2	4	1	E	7
CoC4H70*	H <sub>2</sub> , NO	E	3	5	0	E	21
CoC+H_O*	H <sub>2</sub> , HNO	E	1	2	0	Ē	
CoC <sub>4</sub> H <sub>5</sub> O*	2H <sub>2</sub> NO	E	2	3	Ō	Ē	27
CoC,H <sub>4</sub> O*	CH,NO	E	1	ī	2	Ē	

Scheme I



typically between 0 and 100 eV. The spread in ion kinetic energies is dependent on the total average kinetic energy and is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.<sup>17</sup>

The studies of the reactions of cobalt-containing ions formed by electron impact on tracarbonylikirosylooball(0) were performed on an ion cyclotron resonance spectromeser of conventional design which has previously been described in detail.<sup>4</sup> Ion/molecule reactions and precuriors were identified by using double resonance techniques. Reported data are results of product ions formed in a 1:1 mixtare (by pressure) of Co(CO),NO to nitroalkane, at total pressures between  $5 \times 10^{-6}$  and  $1 \times 10^{-6}$  form. Spectra were always takes to masses greater than 276 arms, since the sum of the mass of Co(CO),NO (173 amu) and the largest nitroalkane (C<sub>6</sub>H<sub>9</sub>NO, 103 amu) equals 276.

Methyl nitrite and methyl-d<sub>1</sub> nitrite were prepared according to the literature.<sup>10</sup> All other chemicals were high-purity commercial samples which were used as supplied except for multiple freeze-pump-thaw cycles to remove noncondensible gases.

#### **Results and Discussion**

Primary Reactions. The primary products for the reactions of  $Co^+$  with nitroalkanes are listed in Tables II-V. As an aid in elucidating reaction mechanisms, the reactions of  $Co^+$  with methyl nitrite were also studied, with their reaction products being given in Tables II and V, respectively. In the experiments with nitromethane and methyl nitrite, the empirical formulas of all the products were confirmed by using both deuterated and undeuterated reagents. For several products from the larger nitroalkanes, empirical formulas other than those listed

may also be possible for the products. On the basis of a consideration of all of the data, however, including (i) subsequent ion/molecule reactions of the primary products with the nitroalkanes, (ii) collision-induced dissociation results, (iii) the reactions of Co<sup>+</sup> with other nitroalkanes, and (iv) the reactions of other metal ions with nitroalkanes,<sup>15</sup> we believe the formulas listed are the most reasonable. Also listed in the tables is the probable structure of the reaction intermediate that leads to the formation of each product. Structure I results from Co<sup>+</sup> insertion into the C-NO<sub>2</sub> bond. Structure II and III (which are possible inter-



mediates suggested by the observed reactions of Co<sup>+</sup> with amines<sup>4</sup>) are products of metal insertion into the C-C and C-H bonds, respectively. Insertion of Co<sup>+</sup> into the N-O bond, which has a bond strength<sup>19</sup> of 75 kcal/mol, leads to intermediate IV. An analogous set of insertion isomers for Co<sup>+</sup> with alkyl nitrites are also given (structures A-E). Throughout this paper, intermediates which follow from nitroalkanes will be labeled by I-V, and intermediates from alkyl nitrites will be labeled A-E.

As will be discussed below, some products from the reaction of nitroalkanes with  $Co^+$  can be most easily explained via intermediates A-E, suggesting that either a nitro-to-nitrite isomeri-

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zation occurs or, in some other mechanistic step, a "nitro intermediate" is converted to a "nitrite intermediate"

Nitromethane and Methyl Nitrite. From the data in Table II, two interesting points are evident about the reactions of Co<sup>+</sup> with nitromethane. First, in comparison with the reactions of Co\* with other monosubstituted methanes, nitromethane chemistry is considerably richer, having a large number of products. Methane<sup>2</sup>, methyl alcohol,<sup>4</sup> and methylamine<sup>8</sup> have been found to be unreactive with Co\*, while methyl bromide,<sup>4</sup> methyl chloride,<sup>6</sup> and methyl mercaptan<sup>12</sup> each give only one to two products, in contrast to the reaction with nitromethane which yields three major products and seven minor products. Second, the products are not those that might be expected on the basis of C-N bond insertion, but appear to result primarily from insertion into the N-O bond.

In order to explain the reaction products, it is useful to compare the results for nitromethane with those for methyl nitrite. Both compounds are observed to yield the same major primary product, CoOCH<sub>3</sub><sup>+</sup>, as well as having four minor products in common.

There is one distinguishing feature of methyl nitrite chemistry that affects both its solution and gas-phase chemistry. This is a very weak CH<sub>3</sub>O-NO bond. With a bond-dissociation energy of 42 kcal/mol.<sup>20</sup> this bond is considerably weaker than the typical C-C bond (ca. 88 kcal/mol<sup>21</sup>), the C-H bond (ca. 97 kcal/mol<sup>21</sup>), the nitromethane C-N bond (61 kcal/mol<sup>22</sup>), or the N-O bond (75 kcal/mol<sup>19</sup>). Thus, one would expect that the reactions of Co\* with methyl nitrite would involve oxidative addition into the weak O-N bond, giving the insertion intermediate E. As shown in Scheme 1, the formation of E followed by a  $\beta$ -H shift onto the etal can explain all of the products of the methyl nitrite reaction. Products resulting from the possible intermediates A and D are not observed, possibly due to the relatively strong bonds which would have to be broken. It is interesting that the NO group, which is a three-electron donor<sup>23</sup> and has been found to bond strongly to Co<sup>+</sup> in the gas phase,<sup>24</sup> is lost preferentially to the OCH1 group. Since the initial insertion into the O-N bond leads to an NO group which donates only one electron, the lifetime of the intermediate may not be sufficient to allow rearrangement to the linear three-electron donor complex geometry. Of relevance is a study of Walton et al.<sup>25</sup> using secondary ion mass spectrometry (SIMS) on [Cr(NO)(CNCMe<sub>3</sub>)<sub>5</sub>]PF<sub>6</sub> and several other similar complexes. It was found that while initial fragmentation occurs via loss of isocyanide ligands, after the third isocyanide ligand is lost, the fourth ligand lost is exclusively NO. No ions corresponding to Cr(NO)(CNCMe<sub>1</sub>)<sup>+</sup> or Cr(NO)<sup>+</sup> were observed Their rationale for this observation was that while initial ligand loss from large ions is determined by relative bond strengths, in smaller ions the ability of a ligand to delocalize charge becomes an important factor in ligand loss. Other factors such as synergistic ligand effects and the ability of a ligand to carry away excess energy may also play a role in ligand loss.

In the reactions of Co<sup>+</sup> with nitromethane, products are observed due to intermediates predicted from both the nitro and nitrite functional groups. An intramolecular RNO2 to RONO isomerization is observed in the electron impact (EI) mass spectra of many aromatic nitro compounds<sup>26</sup> and in a few aliphatic nitro compounds.27 Such an isomerization can also occur thermally28

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or photochemically.29 However, EI-induced isomerizations arise due to charge/radical sites in the molecule, and thermal and photochemical isomerizations are believed to occur by an NO2 dissociation from the alkyl group followed by a recombination It seems likely in the case of Co<sup>+</sup> reacting with nitromethane that the metal assists in such a nitro-to-nitrite isomerization. Possible mechanisms for the nitro-to-nitrite conversion are presented in Scheme II. There are two general pathways in which this conversion may occur. The first involves the coordination of Co+ to an oxygen while the molecule isomerizes (reaction 1 in Scheme II). Once the nitrite isomer is formed, Co<sup>+</sup> inserts into the O-N bond to give intermediate E. The other possibilities involve participation of the metal (reactions 2 and 3 in Scheme II) by initial N-O or C-N insertion. Note that the actual nitrite isomer is not formed in these mechanisms, but only the metal-insertion intermediate (E) typical of nitrites is formed.

Two major products, CoO+ and CoOH+, and several minor products are seen in the nitromethane reactions which are not present in the methyl nitrite reactions. The most probable mechanism for the formation of these products, Scheme III, involves an intermediate with two oxygen atoms bound to the metal, intermediate V. One fact suggesting the formation of this

intermediate as opposed to a species with only one oxygen bound to the metal, intermediate IV, is that CoO<sup>+</sup> formation from IV would involve loss of CH<sub>3</sub>NO. This process would be approxi-mately 30 kcal/mol endothermic.<sup>30</sup> The formation of CoO<sup>+</sup> from V with loss of HCN and H2O is 13 kcal/mol exothermic. Also, the formation of the minor product Co(OH)2+ (or Co(O)(H2O)+) indicates that, at some point, two oxygen atoms must be bound to the metal.

Collision-induced dissociation experiments were performed on the major primary reaction products of Co<sup>+</sup> with nitromethane. As expected, the products CoO<sup>+</sup> and CoOH<sup>+</sup> lost O and OH,

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Co<sup>+</sup> and Co(ligand),<sup>+</sup> Reactions with Nitroalkanes

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Table VL. Ions and Neutrals Formed in Subsequent Reactions of the Primary Products of the  $[Co^+ + CH_1NO_1]$  Reaction (P =  $CH_1NO_2$ )

$CoR^+ + C$	$H_3NO_2 \rightarrow CoR^{\prime +} ne$	utral	
CoR*	CoR*	neutral	rei %
CaO+	Co(OH),*	HCNO	40
	Co(CH,NO)*	он	30
	CoP*	0	15
	CoOP*		15
CoOH*	Co(OH)(H <sub>2</sub> O)*	HCNO	10
	Co(CH,NO)+	H <sub>2</sub> O	40
	CoP*	он	20
	CoHP*	0	10
	Co(OH)P*		20
CoOCH*	4		
CoH*	•		
CoNO*	NR <sup>4</sup>		
CoOCH,*	CoP*	CH <sub>2</sub> O	100
CoOCH,*	CoHP*	CH <sup>3</sup> O	100
Co(OH),*	CoOP*	H <sub>7</sub> O	75
	Co(OH)P*	он	25
CoCHNO*	CoOP*	HCN	100
CoCH,NO*	Co(OH)P*	HCN	100
CoHNO,*	Co(OH)P*	NO	100
	Description of Pa	admete I ist	-4
3rd Generation (Se	A home)		
a (011)/11 01		H-O	100
Co(OH)(H <sub>2</sub> O)*	Co(UH)P	CH.O	100
CoCH1NO2	C-OPT	CH.NO	10
Col		CH.NO	70
		CH.NO.	20
0.1794		CH.NO	100
Colle		CH.NO.	70
CoOP		HNO	10
		OH	5
		ŏ	15
0.000		HNO.	10
Co(OH)P		H-O	80
			10
	CO(OH)F2		
4th Generation (Su	bequent Reactions of 31	d Generati	06
	Reactions)		
Co(OCH <sub>2</sub> )P <sup>+</sup>	a		
Co(OCH <sub>3</sub> )P <sup>+</sup>	Co(OCH <sub>1</sub> )(CH <sub>2</sub> )	HNO <sub>2</sub>	100
Co(NO)P*	Co(CH <sub>2</sub> NO <sub>2</sub> )P	HNO	30
	CoP <sub>2</sub>	NO	30
	Co(NO)P	1010	40
Co(CH <sub>2</sub> NO <sub>2</sub> )P*	Co(CH <sub>2</sub> )(CH <sub>2</sub> NO <sub>2</sub> )P	HNU	30
	Co(CH <sub>1</sub> NO <sub>2</sub> )P <sub>2</sub>	1010	50
CoP <sub>2</sub> *	Co(CH <sub>2</sub> )P <sub>2</sub> *	HNU	20
	CoP,		
Co(OH)P <sub>2</sub> *	Co(CH <sub>2</sub> NO <sub>2</sub> )P <sub>2</sub> *	H <sup>1</sup> O	100
teh Conserving (C.	heavent Reactions of A	th Generati	08
	Reactions)		•
CAOCH J(CH.)P			
Co(NO)P.*	4		
CACH.)(CH.NO.)P*			
	-		

Co(CH<sub>2</sub>)P<sub>2</sub>\* Co(CH<sub>2</sub>NO<sub>2</sub>)P\* NR CoP<sub>3</sub>\* NR \*Further reactions of this ion could not be determine

\*Further reactions of this ion could not be determined. \*NR indicates that this ion did not undergo any further reactions within the time scale (10 s) of this experiment.

respectively, to form Co<sup>+</sup> as the only CID product. CoOCH<sub>3</sub><sup>+</sup> lost CH<sub>2</sub>O to form CoH<sup>+</sup> exclusively with high-CID efficiency. Deuterium exchange experiments to probe for metal hydride character, i.e., a structure such as

proved inconclusive. No deuterium exchange was observed. Lack of deuterium exchange yields no information since FeH<sup>+</sup>, an ion of obvious metal hydride character, does not undergo deuterium exchange. CoH<sup>+</sup>, however, undergoes deuterium exchange slowly, and NiH<sup>+</sup> exchanges with deuterium readily.<sup>31</sup> Although J. Am. Chem. Soc., Vol. 106, No. 21, 1984 6129



Scheme V



Scheme VI





CoOCH<sub>3</sub><sup>+</sup> does not react with D<sub>2</sub>, NiOCH<sub>3</sub><sup>+</sup>, formed in the reaction of Ni<sup>+</sup> with methyl nitrite, was found to undergo one deuterium exchange.<sup>15</sup> This indicates that NiOCH<sub>3</sub><sup>+</sup> has a hydride structure and most probably CoOCH<sub>3</sub><sup>+</sup> has a similar structure based on the facile loss of CH<sub>2</sub>O when activated, as well as the displacement of CH<sub>2</sub>O when CoOCH<sub>3</sub><sup>+</sup> reacts with CH<sub>3</sub>NO<sub>2</sub> (Table VI) and other Lewis bases. Nitroethams. For the reaction of Co<sup>+</sup> with nitroethame (Table

Nitroethase. For the reaction of Co<sup>+</sup> with nitroethane (Table III), the majority (57%) of the primary products are analogous to those present in nitromethane (note that, as in the case of nitromethane, some products are best explained via the "nitrie like" intermediate. E). Scheme IV suggests a mechanism for forming these products starting with intermediate IV.

Carbon-nitrogen bond insertion (intermediate 1) is also an important process in the nitroethane reaction. In Scheme V. a mechanism is proposed that includes insertion of  $Co^+$  into the C-N bond followed by a *d*-H shift onto the metal. This mechanism could account for the formation of  $CoC_2H_4^+$  and  $CoHNO_2^+$ , which are 15% of the total primary product intensity.

Carbon-carbon bond insertion (intermediate II) also appears to occur and results in 14% of the products, including CoCH<sub>3</sub>\*, CoCH<sub>2</sub>NO<sub>2</sub>\*, and CoCH<sub>3</sub>NO<sub>2</sub>\*. The proposed C-C bond in-

<sup>(31)</sup> Cartin, T. J.; Sallans, L.; Cassady, C. J.; Jacobson, D. B.; Freiser, B. S. J. Am. Chem. Soc. 1983, 105, 6320.

		۵.	(parent)	
reactant	CH,NO,	C,H, NO,	ST C	ton-√
coco.	00 <b>+ 4</b> 00	Coir + CO	CoCOHNO,* + C,H, (0.10) CoCOC,H,* H, + CH,NO, (0.12) CoCC,H,07 + NO + CO (0.09) CoP* + CO (0.69)	Cocolino; + C,II, (0.25) Colino; + Co + C,II, (0.10) Colino; + Co + C,II, (0.10) CoC,II,00; + CII, + CO (0.15) CoC,II,N0; + CII, + CO (0.15)
Co(CO);	CoCOP + CO	CoCOP+ + CO (0.75) CoP+ 2CO (0.25)	NR	NR
CoNO*	NR	NR	NR	NR
CONO	CoNOP + CO	CoNOP + CO	CoNOP + CO	CoNOP + CO
Co(CO),NO	CoNOP + 2CO (0.66) CoCONOP + CO (0.34)	CoNOP* + 2CD (0.74) CoCONOP* + CO (0.26)	CoNOP" + 2CO	CoNOP" + 2CO
Co(CO),NO	CoCONOP + 2CO	CoconoP + 200	Coconop + 200	Coconop + 2CO
reactant	\$	- *-	P (jarent) 	980
0000	Coc, H, MO; + C, H, + CO (0.18) Coc, H, MO; + C, H, + CO (0.35) Coc, H, Or + CO + NO (0.03) Coc, H, Or + CO + NO + H, (0.01) Coc, H, Or + NO + 2H, + CO and/or Coc, H, Or + NO + 2H, + CO and/or Coc, H, Or + CO (0.35) Cor + CO (0.35)	$\begin{array}{c} Coccc, \mu_{1}^{*} + \mu_{10}, \ (0.04)\\ Collino; + C, \mu_{1}, + CO + 0.01,\\ Collino; + C, \mu_{1}, + CO + 0.01,\\ Coc, \mu_{1}, NO; + C, \mu_{1}, + CO + 0.01,\\ Coc, \mu_{1}, NO; + C, \mu_{1}, + CO + 0.01,\\ Coc, \mu_{1}, NO; + CO + NO + 0.01,\\ Coc, \mu_{1}, NO; + CO + HNO + 0.03,\\\\ Coc, \mu_{1}, NO; + CO + HNO + 0.03,\\\\ Coc, \mu_{1}, NO; + CO $	CaHNO' + C,H, + CO (0.12) CaC,H,O' + CO + NO (0.22) CaC,H,NO' + CO + H (0.47) CaC,H,NO' + CO + H and/a CaCOC,H,NO' + C,H, (0.19)	Coc, H, NO, + C, H, + (CO (0.07) Coc, H, CP + CO + NO (0.07) Coc, H, OF + CO + NO (0.07) Coc, H, OF + CO + CH (0.12) Coc, H, NO, + CO + CH (0.11) Coc, H, NO, + CO + HNO (0.11) Coc, H, NO, + CO + H and/or Coc, C, H, NO, + H (0.06) Coc, CH, NO, + H (0.06) Coc, CH, NO, + H (0.06)
ce(C0);	C.4COP + CO	CoCCC H; + (1) + HNO; (0.13) CoC, H, 0 + XCO (0.25) CoC, H, NO; + XCO + C, H, (0.06) CoCOP + CO (0.26)	coc,II,NO; + CII, + X'O (0.75) Coc,H,NO; + X'O + II and/or Cococ,II,NO; + C,H, + CO (0.25)	Cocc.II.NO; + 2CO + II and/or CocCC.II.NO; + 2CO + II and/or CocCC.II.0; + FCO + NO + II, (0.11) CocCC.II.0; + FCO + NO + II, (0.11) CocCC.II.NO; + FCO + H and/or CocCO, JC, H, NO; + FC, II, (0.18)

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NR Concret, No; + C,H, + C,H, (0.41) Concret,No; + C0 + C1, Concret,No; + C,H, + C0	0. COCOMMAY-FOT C24, 013) CARCUPT-FOT HID 0. 0000001 (0.1000000000000000000000000	CoCONOPF + 200 CoCONOC_20 + 2:0400 (and COCONOC_2010 + 2:02 + 10400 (and COCONOC_2010 + 2:02 + 2:02 (and COCONOC_2010 + 2:02 + 2:02 (and COCONOFF + 2:02 (and 2:03)
NR CoNOP + CO (0.5 CoNOC JI, NO5 + C	CoNUP + 2CO (0. CoCONUP + CO (1	CoCONOP + 2CO
NR CoNOP + CO	CONOP + CO (0.13) COCONOP + CO (0.17)	CoCONOP + 2CO
Coronor	Co(CO),NG	Co(CO),NO

Co\* and Co(ligand),\* Reactions with Nitroalkanes

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sertion mechanism is given in Scheme VI. The minor product, CoCH,NO<sub>2</sub><sup>+</sup>, is interesting since it results from the loss of CH<sub>2</sub>. Methylene is also formed in the reaction leading to CoHNO<sub>2</sub><sup>+</sup> from nitromethane. This process is unusual since CH<sub>1</sub> is a high-energy radical and would require either an a-H shift onto Co<sup>+</sup> or alternatively onto an acygen via a cyclic intermediate:



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Collision-induced dissociation experiments were performed on the three major nitroethane products. Again, not surprisingly, CID on CoOH\* formed only Co\* and no CoH\*. For CoHNO<sub>2</sub>\*, reactions 2 and 3 occurred, with the formation of Co\* resulting a higher CID energies. No CoNO\* was formed, placing au upper

 $\label{eq:constraint} \begin{array}{c} (3) \\ \mbox{int} of D(Ca^{-}NO) < C_0(Ca^{-}O) + 1 > 1 < 5 \ {\rm kol} /{\rm kol}^{-1} \mbox{int} \\ \mbox{int} of D(Ca^{-}NO) < C_0(Ca^{-}O) + 1 < 5 \ {\rm kol} /{\rm kol}^{-1} \mbox{int} \\ \mbox{int} of D(Ca^{-}NO) < C_0(Ca^{-}O) + 1 < 1 < 5 \ {\rm kol} < 1 < 5 \ {\rm kol} \\ \mbox{int} of D(Ca^{-}O) + 1 < 5 \ {\rm kol} \mbox{int} \\ \mbox{int} of D(Ca^{-}O) < 0 \ {\rm kol} \mbox{int} \mbox{i$ 

Numeropasses. Table IV shows that, which the limits of experiments errors, the we superspectance were the disk of the state of the sthe state of the state of th

CID on CoOH\* and COHNO<sub>2</sub><sup>+</sup> formed from 1-nitropropane yields the same spectra as those formed from intromethane. The ion believed to be formed by either C-H or C-N insertion, CoC<sub>3</sub>H<sub>2</sub><sup>+</sup>, undervent CID to give three product, as shown in reactions 4–6. The major product at low collision energies was CoC<sub>3</sub>H<sub>2</sub><sup>+</sup>, while the major product at low collision energies was CoC<sub>3</sub>H<sub>2</sub><sup>+</sup>, while the major product at low collision energies was CoC<sub>3</sub>H<sub>2</sub><sup>+</sup>.

 $CaC_{3}H_{0}^{*} \xrightarrow{Ar} CaC_{3}H_{3}^{*} + H_{2}$  (4)  $CaC_{4}H_{3}^{*} + C_{2}H_{2}$  (5)  $Ca^{*} + C_{3}H_{5}$  (6)

(32) Cassady, C. J.; Freiser, B. S. J. Am. Chem. Soc., in press.

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Collision-induced dissociation was also performed on  $CoC_1H_1O^4$ , as ion most probably resulting from the loss of  $H_2$  and NO from intermediate E. This ion dissociates to form five products, reactions 7-11, with  $CoCH_3^+$  being the major product

CoCgHs0* CoCHs* + C2Hz0	(7)
CoCH20+ + C2H3	(8)
CoC2H6* + CO	(9)
CeC2H3 + CH2O	00
Co* + CyHeO	(11

A comparison of these results to the CID data obtained from  $CoC_sH_5O^+$  and  $CoC_sH_7O^+$  formed from 1-butyl nitrite provides some useful information in determining how the loss of  $H_2$  from structure E occurs. The dissociations that occur in the CID of  $CoC_sH_5O^+$  and  $CoC_sH_5O^+$  are given in reactions 12–15 and 16–20, respectively. In both cases the major low-energy product

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$$C_{4}H_{9}O' \xrightarrow{\text{Co}C_{3}H_{9}^{*}} C_{0}C_{3}H_{9}^{*} + CO \qquad (12)$$

$$-C_{0}C_{3}H_{9}^{*} + CH_{2}O \qquad (13)$$

$$-C_{0}CH_{9}^{*} + C_{3}H_{2}O \qquad (14)$$

$$-C_{0}^{*} + C_{4}H_{9}O \qquad (15)$$

$$C_{0}C_{4}H_{7}O' \xrightarrow{\text{Ar}} C_{0}C_{3}H_{9}^{*} + CH_{2}O \qquad (16)$$

$$---- C_0 C_{H_0}^* + C_0 H_0 O \qquad (19)$$

--- Ce<sup>+</sup> + CeH<sub>7</sub>O (20)

is CoC<sub>3</sub>H<sub>3</sub><sup>+</sup> and the two major high-energy products are CoCH<sub>3</sub><sup>+</sup> and Co<sup>+</sup>. The low energy loss of CO from CoC<sub>4</sub>H<sub>3</sub>O<sup>+</sup> and CH<sub>2</sub>O from CoC<sub>4</sub>H<sub>2</sub>O<sup>+</sup> suggests that both hydrogens involved in the  $\beta$ -H shifts to form H<sub>2</sub> come from the carbon  $\alpha$  to the oxygen (see Scheme IV).

Nitresumes. The reactions of Co<sup>+</sup> with three nitrobutane isomers are given in Table V. Products resulting from the proposed nitro-to-nitrite rearrangement are still present in these reactions; however, as the length of the carbon chain increases, C-C bond insertion products (structure II) become more prominent. Carbon-carbon insertion can account for 26% of the 1-nitrobutane products, 12% of the 2-nitrobutane products, and 6% of the 2nitropropane, all of the C-C bonds are terminal. Co<sup>+</sup> has been found to be selective against insertion into terminal C-C bonds.<sup>204</sup> The only major difference in the C-C bond cleavage reactions Cassady et al.

of the three nitrobutanes with Co<sup>+</sup> is that CoC<sub>2</sub>H<sub>3</sub>NO<sub>2</sub><sup>+</sup> is a major product with 1-nitrobutane but only a minor product with 2nitrobutane and 2-methyl-2-nitropropane. This product probably results from insertion of Co<sup>+</sup> into the middle C-C bond of the 1-butyl group followed by a  $\beta$ -H shift onto the Co<sup>+</sup> and the loss of C<sub>2</sub>H<sub>4</sub>. This cannot occur with a 2-methyl-2-propyl group without prior rearrangement of the alkyl chain.

Insertion into the C-N bond (intermediate 1) also appears to be a major process in the reactions of Co<sup>+</sup> with the nitrobutanes. In addition to the products CoHNO<sub>2</sub><sup>+</sup>, CoC<sub>1</sub>H<sub>3</sub><sup>+</sup>, and CoC<sub>4</sub>H<sub>4</sub><sup>+</sup> which can result from a C-N insertion similar to that shown in Scheme V, the major product in the reactions of each of the nitrobutanes with Co<sup>+</sup> is C<sub>4</sub>H<sub>4</sub><sup>+</sup>. This charge migration product is also seen to a limited extent in the reactions of Co<sup>+</sup> with the nitropropanes. The reaction leading to C<sub>4</sub>H<sub>9</sub><sup>+</sup> is apparently not dissociative charge transfer, since this would be exceedingly esdothermic (~60 kcal/mol for 1-nitrobutane). Thus, the neutral products are not Co and NO<sub>2</sub>. The combination of CoO + NO as neutral product is also highly endothermic. If the product is CoNO<sub>2</sub>, the results for 1-nitrobutane suggest  $D(Co-NO_2) \ge$ 60 kcal/mol and  $\Delta H_{1}(CoNO_{1}) \le 48 \text{ kcal/mol}^{4*}$  The prominence of C-N insertion seen for 2-methyl-2-nitropropane may result from the fact that all C-C bonds are terminal, which hinders C-C bond insertion,<sup>2,54</sup> and the fact that steric factors may hinder a nitro-to-nitrite isomerization.

An interesting aspect of the reactions of Co<sup>+</sup> with nitropropane and nitrobutane is the loss of neutral radicals as opposed to stable neutral molecules. For example, in the reaction of 1-nitropropane with Co<sup>+</sup>, following insertion into the terminal C-C bond, a  $\beta$ -shift and loss of CH<sub>4</sub> (reaction 22) would be expected. However,

reaction 21 is actually observed. One possible explanation for the lack of this  $\beta$ -H shift is that, upon insertion of Co<sup>+</sup> into the C-C bond, coordination may also occur to an axygen of the nitro group, producing a stable complex in which the  $\beta$ -H's are geometrically inaccessible to the metal.



Subsequent Reactions of the Primary Products. The primary products for the reactions of Co<sup>+</sup> and nitroalkanes react further with the neutral nitroalkanes. Up to five subsequent reactions may occur after the formation of the primary products. To illustrate the complexity of these reaction sequences. Table VI lists all of the reactions of the primary products for the simplest case, nitromethane.

Some interesting observations can be made from the data in Table VI. For example, with the  $CoOCH_3^+$  ion the only secondary reaction observed is (23), which involves displacement of CH\_O. This supports the conclusion drawn from the CID results that this species has a Co(H)(CH\_2O)<sup>+</sup> structure.

 $CoOCH_3^+ + CH_3NO_2 \rightarrow Co(H)(CH_3NO_2)^+ + CH_2O$  (23)

<sup>(33)</sup> Jacobson, D. B.; Preiser, B. S. J. Am. Chem. Soc. 1984, 106, 1159-1166.

 <sup>(34)</sup> All values calculated from data obtained in ref 30 except D(Co-O)
 87 & 4 kcal/mol which was obtained from Grimley et al. and Smoss et al.:
 (a) Grimley, R. T.; Burns, R. P.; laghram, M. G. J. Chem. Phys. 1966, 45, 4158.
 (b) Smoss, S.; Mandy, F.; Vander Avwara-Mahim, A.; Drowart, J. Bull. Soc. Chim. Belg. 1972, 81, 45.

### Co<sup>+</sup> and Co(ligand),<sup>+</sup> Reactions with Nitroalkanes

It is also interesting that the other major nitromethane products  $(CoO^{+} \text{ and } CoOH^{+})$  do not react with nitromethane to form "nitrite-like" rearrangement products. Other than reactions to form  $CoOP^{+}$  and  $CoOHP^{+}$  ( $P = CH_3NO_3$ ), the only reactions of these ions involve either the gain of H<sub>3</sub>O (loss of HCNO) or the loss of H<sub>2</sub>O, OH, or O. These products could result from an initial insertion of CoOH<sup>+</sup> and CoO<sup>+</sup> into the N-O bond of nitromethane. Again, the loss of radicals, as opposed to stable neutral molecules, is observed in many of the subsequent reactions of the primary products.

Many of the subsequent reactions involve formal extraction of O, OH, or H<sub>2</sub>O from nitromethane. Even the CoHP<sup>+</sup> ion (P = CH<sub>3</sub>NO<sub>2</sub>) formed from reaction 23 rapidly reacts with nitromethane to form Co(OH)P<sup>+</sup>. The ion Co(OH)P<sup>+</sup> also comes from several other sources and dominates the mass spectrum after trapping times of about 1 s. This ion then reacts away slowly with the dominant process being the loas of H<sub>2</sub>O. The loas of OH from all of the ions is less favorable than the loss of H<sub>2</sub>O, while the loss of OH.

Collision-induced dissociation experiments were performed on the two major secondary reaction products of the nitromethane reactions, CoHP<sup>+</sup> and Co(OH)P<sup>+</sup>. For CoHP<sup>+</sup>, reactions 24-29 were observed, with reaction 26 dominating at low energy and reaction 24 dominating at higher energies. Reactions 27-29 are



only minor pathways at all energies. Although these CID data do not confirm a structure for the ion, they do leave open the possibility that  $CoHP^+$  has a structure such as



This structure is also consistent with the further reactions of the CoHP<sup>+</sup> ion (Table VI), which imply the presence of an OH group in the ion.

For the dissociation of the major secondary product, Co(OH)P<sup>+</sup>, three products were observed, as shown in reactions 30-32. By



far the dominant product at all energies was  $CoOH^+$ , and this is an indication of the strength of the  $Co^+-OH$  bond.

The subsequent reactions observed with nitroethane parallel those discussed above for nitromethane (with the exception of CoOH\*, discussed below). The ion  $Co(OH)P^*$  (P = CH<sub>3</sub>CH<sub>3</sub>NO<sub>3</sub>) is still dominant at trapping times around 1 a. Other major ions are CoP\*, Co(NO)P\*, Co(C<sub>2</sub>H<sub>4</sub>NO<sub>2</sub>)P\*, CoP<sub>2</sub>\*, Co(OH)P<sup>\*</sup>, and Co(NO)P\*. At trapping times of 5 s and longer Co(C<sub>2</sub>H<sub>4</sub>NO<sub>3</sub>)P<sup>\*</sup> and Co(P<sub>3</sub>\* are essentially the only ions present. The reactions of the ions CoC<sub>2</sub>H<sub>3</sub>\* and CoCH<sub>3</sub>N\* which do not have analogues in the nitromethane reactions, are given in (33) and (34). Reaction 35 gives the subsequent reactions.

For the CoOH<sup>+</sup> ions formed from nitroethane and the large nitroalkanes, only approximately 20% of the secondary reaction products can be obtained from N-O insertion similar to that observed for the reaction of CoOH<sup>+</sup> with nitromethans. Instead, the major reaction pathway for the reaction of CoOH<sup>+</sup> with larger





nitroalkanes is the formation of alkyl ions, apparently the result of insertion into the C-N bond. These ions then react rapidly with the nitroalkane to form protonated nitroalkane ions, as shown in reactions 36 and 37. In reaction 36, the neutrals formed are

 $C_0OH^+ + CH_3CH_2NO_2 \rightarrow C_2H_3^+ + C_0HNO_1$  (36)

$$C_2H_3^+ + CH_3CH_2NO_2 \rightarrow CH_3CH_2NO_2H^+ + C_3H_4$$
 (37)

not Co and HNO<sub>3</sub> since this reaction would be 93 kcal/mol endothermic.<sup>33</sup> Due to the lack of heat of formation values, no other thermodynamic calculations could be made regarding other possible neutral loss products. The ion CoCH<sub>3</sub><sup>+</sup> is also observed to react with larger nitroalkanes to form primarily alkyl ions, while several other ions do so to a limited extent.

Collision-induced dissociation experiments were carried out on CoP<sup>+</sup> and Co(OH)P<sup>+</sup> (P = nitroethane). For the CID of CoP<sup>+</sup>, the two major products were CoOH<sup>+</sup> and Co<sup>+</sup>, while CoC<sub>2</sub>H<sub>2</sub><sup>+</sup>, CoNO<sup>+</sup>, CoHNO<sub>2</sub><sup>+</sup>, and CoC<sub>2</sub>H<sub>4</sub>O<sup>+</sup> were minor products. This formation of CoOH<sup>+</sup> again indicates the strength of the Co<sup>+</sup>-OH bond. While the CID spectrum provides little definitive structural information, the fragments do resemble the primary reactions products of Co<sup>+</sup> with introethane. CID spectra of Co(OH)P<sup>+</sup> from nitroethane yield the major products Co(OH)P<sup>+</sup> from nitroethane yield the major products Co<sup>+</sup>, CoNO<sup>+</sup>, Co(C<sub>1</sub>H<sub>3</sub>NO<sub>2</sub><sup>+</sup>, and CoP<sup>+</sup>. The function of CoP<sup>+</sup>.

The further reactions of the primary products of the nitropropane and nitrobutane reactions with the neutral are again similar to those observed for nitromethane. The same major reaction channels occur. CID experiments on secondary ions from nitropropane gave an assortment of products similar to those in the nitroethane CID experiments.

Ligand Effects. Table VII lists the products observed for the reactions of the electron-impact fragments of  $Co(CO)_3NO$  with the series of nitroalkanes and 1-butyl nitrite. The results in Table VII can be evaluated in a number of ways to supply information concerning "ligand effects". These include (1) identification of changes in the chemistry of a metal center when one ligand is added (i.e., compare the chemistry of  $Co^*$  with  $CoL^*$ ), (2) identification of "vertical trends" in the table (i.e., mechanistic changes due to the number of ligands on the metal), and (3) identification of "horizontal trends" (i.e., changes in the chemistry related to increases in the alkyl chain length of the organic reactant).

#### General Treads

Small Nitroalkases. The reactions observed for the  $C_1-C_3$ nitroalkanes are typical for metal-containing ions,  $ML_a^+$ , in their chemistry with monofunctional organic compounds in the following ways: (1) The bare metal ion reacts to form the largest variety of products.<sup>4</sup> (2) The organic rearrangement processes observed for CoCO<sup>+</sup> are similar to those observed for Co<sup>+</sup>.<sup>16,4A,13</sup> (3) In direct contrast with the carbonyl ligand, an NO ligand *deactioates* the metal center<sup>16,4A,13</sup> (note that no products are observed for

<sup>(35)</sup> Calculated from thermochemical information obtained in ref 30 and 32.

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CoNO<sup>+</sup> except with 1-butyl nitrits). (4) As the number of ligands present on the metal ion increases, ligand-substitution reactions predominate.<sup>8</sup> In substitution processes, nitroalkanes displace two carbonyls from Co(CO),NO<sup>+</sup>, while 1-butyl nitrite displaces up to three carbonyls. The implications is that  $D(Co^+-RONO) > D(Co^+-RNO_1)$ .

to three catoonya. The implications is that  $D(CO^{+}RO(NO)) \ge D(CO^{+}RO(NO))$ . Larger Nitrealkanes. In contrast to the smaller nitroalkanes, the larger nitroalkanes react with  $CoL_{a}^{+}$  not only by substitution but by bond cleavage processes. In this trend, butyl nitrite bond cleavages/rearrangements occur for all  $CoL_{a}^{+}$  ions, even Co- $(CO)_{2,3}NO^{+}$ . Such reactivity is typically observed for multi-functional organic molecules.<sup>1a,13,14</sup>

Also, a "horizontal trend" can be seen. As the length of the alkyl chain increases  $(C_1 \rightarrow C_4)$ , more reactions involving C-C insertions (intermediate II) are observed. Previous work suggests that the probability of reactions involving intermediate I should be greater for secondary and tertiary nitroalkanes than for primary nitroalkanes.<sup>26</sup> This is apparently the case as shown in Tables V and VII.

The reactions discussed in this work tend to involve intermediates in which two orbitals are required on the metal (e.g., reaction 21) or reactions which require three orbitals on the metal (e.g., reactions 1 and 22). It is no surpise that such reaction products disappear when ligands are added to the metal. Reactions requiring three metal orbitals occur for Co<sup>+</sup>, in some cases for CoCO<sup>+</sup>, and rarely for the other metal-containing species in Table VII. Reactions requiring two orbitals on the metal (as opposed to three orbitals) seem to dominate (in addition to substitution reactions) when the reactant metal center has two or more ligands present, as would be expected.

Nitrogropass. There are many similarities in the reactions observed for Co<sup>+</sup> and CoCO<sup>+</sup> with nitropropane, and some major differences as well. The products CoHNO<sub>2</sub><sup>+</sup> (loss of C<sub>2</sub>H<sub>4</sub> through intermediate I) and CoCO<sup>+</sup> insert into C-C bonds: however, CoCO<sup>+</sup>. Both Co<sup>+</sup> and CoCO<sup>+</sup> insert into C-C bonds: however, CoCO<sup>+</sup> preferentially attacks the C<sub>2</sub>H<sub>3</sub>-CH<sub>2</sub>NO<sub>2</sub> bond. Following this insertion, Co<sup>+</sup> loser the C<sub>2</sub> fragment while CoCO<sup>+</sup> retains the C<sub>2</sub> fragment. This may imply active participation in the reaction by the carbonyl group leading not to a type II intermediate but to the CoCO<sup>+</sup> insertion intermediate shown in (38).<sup>6</sup> There



are a number of possible asutral losses,  $(CH_3NO_2 + H)$  or  $(CH_3NO_2 + H_2)$ , which would generate the butadiseso-like metal complex. Thus, one effect of the CO ligand appears to be an active involvement of the ligand in the reaction.<sup>6</sup>

In most cases, CO is not involved in the reaction directly but appears to be a "spectator" on the metal.<sup>136</sup> Even spectator ligands can influence product distributions, in cases where cleavage of the M<sup>+</sup>-CO bond competes with processes involving eliminations from the organic species. An example of this is seen in the case of 2-nitropropane. The Co<sup>+</sup> ion reacts to form CoC<sub>3</sub>H<sub>3</sub>O<sup>+</sup> by elimination of NO and H<sub>2</sub>. This reaction also occurs for CoCO<sup>+</sup>; however, there appears to be two possible processes following NO elimination: loss of H<sub>2</sub> from C<sub>3</sub>H<sub>3</sub>O or loss of CO from the metal. In the case of CoCO<sup>+</sup> with 2-nitropropane, the loss of NO followed by the loss of CO (to form CoC<sub>3</sub>H<sub>7</sub>O<sup>+</sup>) predominates; however, H<sub>2</sub> vs. CO eliminations frequently appear to be competitive processes.

Nitrobutanes. The outstanding feature in Table VII regarding the nitrobutanes is the "vertical trends"—i.e., changes in the chemistry of the motal center as the *number* of ligands on the metal increases, in particular for 2-nitrobutane and 2-methyl-2sitropropase. For 2-nitrobutane, the predominant reaction intermediate changes as the number of ligands increases. Co<sup>+</sup> reacts through intermediates I, II, IV, and E. With one or two carbonyls present on the metal, reactions are observed via intermediates analogous to I, II, and E; CoCONO<sup>+</sup> only induces organic bond cleavage through an intermediate analogous to II. Note that only one C-C bond is attacked by CoCONO<sup>+</sup>. This may correspond to attack of the weakest bond (since in the corresponding alkane, isopentane, the weakest C-C bond<sup>46</sup> is the C<sub>2</sub>H<sub>2</sub>-C<sub>2</sub>H<sub>1</sub> bond). Presumably, there are not a sufficient number of orbitals available on the metal following C-C insertion of CoCONO<sup>+</sup> to assist in a  $\beta$ -H shift; thus, C<sub>2</sub>H<sub>2</sub>-F is lost. Similar studies with amines show analogous

The 2-methyl-2-nitropropane reactions also show a variety of interesting changes as the number of ligands increases. Inter-mediate structures I, II, III, and E lead to the products observed for 2-methyl-2-nitropropane. Structures II and III predominate when more ligands are present on the metal (e.g.,  $Co(CO)_2^+$ ). sertion into the C-NO2 bond (structure 1) appears to be inhibited due to steric effects of the ligands present on the metal and the bulky 2-methyl-2-propyl group. Thus, the remaining options for the metal are insertion only into bonds such as C-C and C-H. The loss of H (from C-H insertion) is more prominent when the number of ligands present on the metal ion increases. The reaction of  $Co(CO)_2NO^+$  produces  $CoCONO(NO_2)^+$  with a loss of CO and  $C_4H_9$ . At first, one may predict a Co<sup>+</sup> insertion into the C-N bond (structure I) as the intermediate. This intermediate is not possible for several reasons. The cobalt ion already has three ligands present, which does not leave enough empty metal orbitals for metal insertion to occur. If the insertion did occur, there are many  $\beta$ -H's available to shift and produce a strong HNO<sub>2</sub> ligand. No products, however, are observed resulting from a  $\beta$ -H shift. A possible intermediate structure leading to the product ion CoCONO(NO<sub>2</sub>)<sup>+</sup> is shown in the structure below.

Co(CO)(NO)(NO2) + CsHgO+ (39)

The suggested intermediate corresponds to insertion of the CoCO<sup>+</sup> group into the C-NO<sub>2</sub> bond of the nitroalkane. In this intermediate there are no H atoms which are on a carbon which is  $\beta$ to the metal that could shift to produce the HNO<sub>2</sub> ligand. Also, there are no empty orbitals on the metal to assist in any rearrangement of the molecule. Thus, the only product ion observed is CoCONO(NO<sub>2</sub>)<sup>+</sup> with the loss of C<sub>4</sub>H<sub>2</sub>CO as one ligand.

In summary, several typical ligand effects have been observed in reactions of nitroalkanes. Products which require three or more empty orbitals on the metal are seen to be repressed or disappear as the number of ligands on the metal increases. Reactions occurring at branched sites are favored over unbranched sites. Steric effects were observed with 2-methyl-2-nitropropane when ligands were added to the metal ion. Intermediates in which the ligands must be actively involved in the insertion are seen. Also, when a ligand is present on the metal, several options for reaction mechanisms (such as competition between loss of CO and H<sub>2</sub>) are available.

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<sup>(36)</sup> Bood strengths in isopentane may be calculated from data obtained in Cox and Pilcher and McMillen and Golden: (a) Cox, J. D.; Pilcher, G. "Thermschemsitry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. (b) McMillen, D. F.; Golden, D. M. Annu. Rev. Phys. Chem. 1982, 33, 493.

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Registry No. CH3NO2, 75-52-5; CH3ONO, 624-91-9; C2H3NO2, 79-

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APPENDIX C

## Appendix C

### ICR Studies of Trimethylaluminum

manuscript is a study of the The following mass spectra of trimethylaluminum. This study resulted from an attempt to examine the polymerization<sup>81</sup> olefin in Ziegler-Natta catalysts for which both trimethylaluminum  $(Al(CH_3)_3)$  and titanium chloride  $(TiCl_4)$  were admitted into the ICR. The active bimetallic species formed by ion/molecule reactions could then be studied by admitting a series of olefins into the ICR.

The Al(CH<sub>3</sub>)<sub>3</sub>/TiCl<sub>4</sub> mixture did result in a large variety of bimetallic ions. No double resonance responses, however, were observed for these ions, suggesting that they must result from neutral-neutral reactions of trimethylaluminum with titanium chloride. A new inlet system was designed and constructed for the ICR in an attempt to keep the two gases separated until they were near the ICR cell. Double resonance responses were still not observed with the new inlet system. These same results for the Al(CH<sub>3</sub>)<sub>3</sub>/TiCl<sub>4</sub> mixture were reported later by Staley et. al.<sup>82</sup> The use of Fourier transform mass spectrometry and ion ejection techniques may facilitate the study of the Ziegler-Natta catalysts.

The previous mass spectral studies of trimethylaluminum have suggested the presence of associated species in the gas phase (dimer, trimer, etc.). The ICR mass spectra and the ion/molecule reactions observed suggest that trimethylaluminum exists as a monomer only at low pressures as described in the following manuscript. Metal ion chemical ionization was also utilized in an attempt to determine the molecular weight of the species present. Triple quadrupole mass spectrometry (TQMS) was employed to obtain collision induced

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dissociation (CID) spectra of several ions present in the mass spectrum of trimethylaluminum.

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### ABSTRACT

The mass spectra of trimethylaluminum at various pressures are reported using ion cyclotron resonance (ICR) mass spectrometry. Ions indicative of the presence of the dimer are observed at higher pressures. Double resonance results, however, indicate that these ions are formed from ion/molecule reactions of fragment ions of the monomer with the neutral trimethylaluminum monomer. Evidence is also presented for the possible presence of the neutral dimer at higher pressures. The use of metal-containing ions as chemical ionization reagent ions is utilized in an attempt to determine the molecular weight of the species present in gas phase trimethylaluminum. Comparison of the results presented here with previous studies suggests a process in which trimethylaluminum is present as a dimer in solution, but vaporizes as a monomer with the possibility of dimerization occurring in the gas phase.

## INTRODUCTION

Alkyl aluminum compounds have been the subject of a variety of studies because of the possibility of the existence of the molecule as a dimer due to the electron deficient nature of aluminum, and also because of their importance in the industrial Ziegler-Natta polymerization catalysts<sup>1</sup>. Early studies to determine the molecular weight of trimethylaluminum (Al(CH<sub>3</sub>)<sub>3</sub>) cryoscopically in benzene showed that the molecular weight corresponds to that of the dimer,  $Al_2(CH_3)6^{2,3}$ . The molecular weight of gaseous trimethylaluminum has been studied by Laubengayer et. al.<sup>4</sup> using vapor pressure and density measurements. These results suggest that trimethylaluminum is a dimer in the gas phase at 70°C and a pressure of 135 mm. The apparent molecular weight appeared to decrease, however, as the temperature was increased. This same effect has been observed more recently by Henrickson et. al.<sup>5</sup> at a pressure of 30 mm. Several temperature studies have been performed to determine the extent of association of trimethylaluminum. Almenningen et. al.<sup>6</sup> reported that, at 215°C and 30 mm., trimethylaluminum exists as 98% monomer. O'Brien et.al.<sup>7</sup>, using Raman spectroscopy, reported that trimethylaluminum exists primarily as the dimer at 70°C, but at 260°C and 1 atmosphere the dimer species is <u>not</u> detectable. The bonding in the trimethylaluminum dimer has been found to be relatively weak ( $\sim$ 10.2 kcal/mole per Al-CH<sub>3</sub>-Al bridge, or 20.4 kcal/mole for the dimer)<sup>4</sup> which may explain the dissociation to the monomer at high temperature. A more recent study by House<sup>8</sup> estimates that trimethylaluminum is approximately 72% associated in the vapor phase. Thus, there appears to be an equilibrium between the monomer and dimer in the gas phase.

The structure of the trimethylaluminum dimer has been studied by infrared<sup>9</sup> and Raman<sup>7</sup> spectroscopies, electron diffraction<sup>6</sup>, X-ray diffraction<sup>10-12</sup>, and <sup>27</sup>Al nuclear quadrupole resonance<sup>13</sup> in order to determine the structure and type of bridge-bonding in the trimethylaluminum dimer. Results from the early studies suggested the presence of H-bridging from the methyl groups, suggesting two structures with binding of the carbon through two hydrogens to the aluminum (structure 1)<sup>2</sup> or through one hydrogen (structure 2)<sup>14</sup>. More recent results indicate that the three bonds to the hydrogens on the bridging carbon atom are tetrahedral and are symmetrical with respect to a vector directed to the center of the dimer<sup>12</sup>. Therefore, little or <u>no</u> bonding occurs between the bonding methyl hydrogen and the aluminum atom. This leads to the more accepted structure of Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub> (structure 3) which consists of two methyl bridges.

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Mass spectrometry has been utilized to study the ionization and subsequent dissociation of methyl-substituted metal compounds. The first mass spectrometric study of trimethylaluminum was performed by Winters and Kiser<sup>15</sup> in 1967. This study was performed with the inlet at room temperature and the source temperature at 190°C with 70 eV electron impact (source pressure was not reported). The results are summarized in Table 1. The majority of the ions observed appear to result from the dissociation of trimethylaluminum monomer through simple bond cleavage processes (e.g., loss of CH<sub>3</sub>.). Several rearrangement ions are also observed ( $[A1H_2]^+$  and  $[A1HCH_3]^+$ ). The dimer ion,  $[Al_2(CH_3)_6]^+$ , was not observed, however, a small quantity of the ion  $[Al_2(CH_3)_5]^+$  (0.2% of the  $[Al(CH_3)_2]^+$  base peak) was observed suggesting the existence of dimeric species. The effect of electron energy on the mass spectrum of trimethylaluminum was also reported indicating an increase in the monomer molecular ion at low energy but no additional evidence for the existence of the dimer ion.

Chambers et.  $al^{16}$  reported the mass spectrum of trimethylaluminum at source temperatures between 40°C and 200°C. Table 1 lists the reported spectra at 45°C and 195°C. Two ions indicative of the presence of a dimer were reported ([Al<sub>2</sub>(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup> and [Al<sub>2</sub>(CH<sub>3</sub>)<sub>5</sub>]<sup>+</sup>) which were abundant at 40°C but diminished rapidly with an increase in the source temperature. This behavior

ion (m/z)	Possible Composition	Winters and Kiser <sup>15</sup>	Chambers 45–50 <sup>o</sup> C	and Coates <sup>16</sup> 195 <sup>0</sup> C	Tanaka & Smith <sup>17</sup> 60-100°C
1 <b>2</b>	[C] <sup>+</sup>		0.03	0.12	0.1
13	[CH] <sup>+</sup>		0.15	0.17	0.5
14	[CH <sub>2</sub> ] <sup>+</sup>		0.48	0.48	1.3
15	[CH <sub>3</sub> ] <sup>+</sup>	21.3	2.17	3.92	8.0
16	[CH <sub>4</sub> ] <sup>+</sup>		1.74	3.98	9.7
26	[C <sub>2</sub> H <sub>2</sub> ] <sup>+</sup>		0.28	0.19	
27	[A1] <sup>+</sup> ,[C <sub>2</sub> H <sub>3</sub> ] <sup>+</sup>	36.5	12.96	18.99	10.5
28	[A1H] <sup>+</sup> ,[C <sub>2</sub> H <sub>4</sub> ] <sup>+</sup>		1.04	0.91	1.2
29	[A1H <sub>2</sub> ] <sup>+</sup> ,[C <sub>2</sub> H <sub>5</sub> ] <sup>+</sup>	2.3	1.85	1.67	1.5
30	[A1H3] <sup>+</sup> ,[C2H6] <sup>+</sup>				0.2
41	[A1CH <sub>2</sub> ] <sup>+</sup> ,[C <sub>3</sub> H <sub>5</sub> ] <sup>+</sup>	1.0	0.89	1.16	
42	[A1CH3] <sup>+</sup> ,[C3H6] <sup>+</sup>	6.3	5.63	8.04	5.6
43	[A1CH3H] <sup>+</sup> ,[C3H7] <sup>+</sup>	3.4	4.63	5.40	2.7
56	$[A1C_{2}H_{5}]^{+}, [C_{4}H_{8}]^{+}$		2.68	1.76	
57	$[A1(CH_3)_2]^+$	100.0	100.0	100.0	100.0
72	[A1(CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup>	4.9	9.13	7.1	8.0
99	$[A1_2(CH_3)_3]^+$		0.82	0.06	
102	$[A1_2(CH_3)_3H_3]^+$				0.2
115	$[A1_2(CH_3)_4H]^+$				0.2
129	$[A1_2(CH_3)_5]^+$	0.2	4.42	0.22	0.005
145	$[A1_3(CH_3)_4H_4]^+$				0.2
203	[A14(CH3)6H5] <sup>+</sup>				0.2

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# Table 1. Previously reported mass spectra of trimethylaluminum (% rel. int.)

is analogous to that observed in the vapor phase studies described previously and is presumably due to thermal dissociation prior to ionization.

Tanaka and Smith<sup>17</sup> also studied the mass spectra of bridge-bonded aluminum compounds including trimethylaluminum. Their reported mass spectrum of trimethylaluminum at a source temperature of 60 to 100°C is included in Table 1. The ions with m/z > 72 (indicative of dimers) are of low relative intensity (< 0.2% rel. int.) and their sum is < 1% relative intensity. This is in contrast to other dimeric species (AlCl<sub>3</sub>, AlCH<sub>3</sub>Cl<sub>2</sub>, and Al(CH<sub>3</sub>)<sub>2</sub>Cl) whose mass spectra were also reported. In these dimeric species, ions indicative of the presence of the dimer are intense (> 50% of the base peak). In the mass spectrum of trimethylaluminum, however, the  $[Al_2(CH_3)_5]^+$  ion is only 0.005% of the base peak. Ions which could be fragment ions resulting from rearrangement of the dimer,  $[Al_2(CH_3)_3H_3]^+$  and  $[Al_2(CH_3)_4H]^+$ , are also observed in low abundance (0.2% rel. int.). Ions containing three and four aluminum atoms are also observed ( $[A1_3(CH_3)_4H_4]^+$  and  $[A1_4(CH_3)_6H_5]^+$ ) but were believed to be a function of the source pressure suggesting the possibility that ion/molecule reactions account for these higher mass ions. Note that none of the species above m/z 72 could be assigned to simple fragmentation of the dimer, but probably contained Al-H bonds from rearrangement processes.

The results from Tanaka and Smith<sup>17</sup> indicate that the methyl bridge is either extremely weak or susceptible to electron impact, since when more than one aluminum is found it appears to be held together by H-bridges due to the presence of Al-H bonds rather than methyl bridges. This may suggest that while structure  $\frac{3}{2}$  is the probable structure for Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>, structure  $\frac{1}{2}$ or 2 may be more likely for the dimer ion, [Al<sub>2</sub>(CH<sub>3</sub>)<sub>6</sub>]<sup>+</sup>.

Ion cyclotron resonance (ICR) mass spectrometry<sup>18</sup> is a powerful technique for the study of bimolecular gas-phase ion/molecule reactions. Precursors

of ion/molecule reaction products may be determined using ion cyclotron double resonance techniques<sup>18</sup>. ICR seems especially applicable to the study of the mass spectrum of trimethylaluminum since the entire ICR cell is operated at ambient temperature (i.e., the greatest amount of dimer should be present). This study utilizes ICR to study the ion/molecule reactions observed in trimethylaluminum which may lead to an understanding of the presence of the higher mass ions observed in the previous studies. A previous study of trimethylaluminum using ICR by Staley et. al.<sup>19</sup> reports the presence of only one ion/molecule reaction product  $([Al_2(CH_3)_5]^+)$  from the reaction of  $[Al(CH_3)_2]^+$  and  $[Al(CH_3)_3]^+$  with (presumably) the monomer. No ions indicative of the presence of the dimer were reported. This study also utilizes metal-containing ions as chemical ionization (CI) reagent ions in  $ICR^{20-22}$ in an attempt to obtain molecular weight information on the species present in gas phase trimethylaluminum (i.e., monomer or dimer). Collision induced dissociation (CID) was performed on several ions present in the mass spectrum of trimethylaluminum using triple quadrupole mass spectrometry (TQMS) in an attempt to obtain structural information on these ions.

## EXPERIMENTAL

The ion/molecule reactions were studied in an ion cyclotron resonance (ICR) mass spectrometer of conventional design (used in the "drift mode" with a marginal oscillator detector) which was constructed at Michigan State University and is described elsewhere<sup>23</sup>. Pressures were measured with a Veeco RG 1000 ionization guage. Spectra were recorded from m/z 10 to 300.

The trimethylaluminum and tricarbonylnitrosylcobalt(0) were purchased from Alfa Products and were used as supplied except for multiple freeze-pump-thaw cycles to remove noncondensible gases. The trimethylaluminum was sampled from the vapor above a reservoir of liquid trimethylaluminum present on the inlet at room temperature. The vapor was admitted to the ICR through a Varian 951-5106 precision leak valve. The metal ion chemical ionization study was performed with a 3:1 mixture of  $Co(CO)_3NO$  and  $Al(CH_3)_3$  at a total pressure of 4 x 10<sup>-6</sup> torr.

Collison induced dissociation (CID) experiments were performed on an Extranuclear triple quadrupole mass spectrometer (ELQ 400-3). Electron impact fragment ions and possible ion/molecule reaction products were formed in the EI ion source. Pressures were measured with an ionization guage located outside the source in the source housing. Parent ions of interest were mass selected by the first quadrupole and accelerated into the second quadrupole (the CID chamber). The collision gas was argon (typical pressure was  $3 \times 10^{-3}$  torr). Collision energies ranged from 10 to 30 eV (lab). The products of collision induced processes were then mass analyzed by scanning the third mass filter.

## **RESULTS AND DISCUSSION**

### **ICR Studies**

The normalized ICR mass spectra (70 eV) obtained at six different pressures ranging from 5.0 x  $10^{-7}$  torr to 1.2 x  $10^{-5}$  torr are listed in Table 2. The obvious difference between the ICR spectra and the previously reported mass spectra (Table 1) is the lack of alkyl fragments (m/z 12 to 16) in the ICR mass spectra. These alkyl fragments were observed initially in the ICR studies, but following several flushings of the inlet with trimethylaluminum these fragments were no longer observed. This suggests that the alkyl fragments which are observed may be due to water which is present in the inlet, since trimethylaluminum reacts with water to produce CH<sub>4</sub>. Also, the intensities of the alkyl fragments in the previous studies are quite similar to the ion intensities in the electron impact mass spectrum of CH<sub>4</sub><sup>24</sup>. It should be noted, however, that the sensitivity of ICR is lower at small m/z values which may account for the

	Pressure (torr)						
m/z	Probable Ion	5.0x10-7	1.8x10-6	4.0x10-6	6.0x10-6	7.5x10-6	1.2x10-5
27	[A1] <sup>+</sup>	7.0	15.5	15.6	12.3	10.6	9.6
28	[A1H] <sup>+</sup>	2.8	2.3	1.1			
29	[A1H <sub>2</sub> ] <sup>+</sup>	3.1	4.5	2.9	1.0	1.0	0.7
41	[A1CH <sub>2</sub> ] <sup>+</sup>	1.6	1.1	0.8			
42	[A1CH <sub>3</sub> ] <sup>+</sup>	4.5	3.6	3.3	2.0	1.9	1.1
43	[A1CH <sub>3</sub> H] <sup>+</sup>	2.8	2.0	1.7	1.3	0.7	0.7
57	[A1(CH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	100.0	100.0	100.0	100.0	100.0	100.0
72	[A1(CH <sub>3</sub> ) <sub>3</sub> ] <sup>+</sup>	9.7	7.0	3.9	3.2	2.9	1.5
102	[A1 <sub>2</sub> (CH <sub>3</sub> ) <sub>3</sub> H <sub>3</sub> ]	]+				0.6	0.8
113	[A1 <sub>2</sub> (CH <sub>3</sub> ) <sub>3</sub> CH	2] <sup>+</sup>		0.3	0.6	0.9	0.9
115	[A1 <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> H] <sup>+</sup>	•	1.1	1.3	1.0	1.3	0.7
129	$[A1_2(CH_3)_5]^+$	1.6	7.9	12.7	23.1	27.3	37.2
131	[A1 <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub> H <sub>5</sub> ]	+		0.5	0.7	0.9	1.1
145	$[A1_3(CH_3)_4H_4]$	+				0.3	0.4
149	$[A1_4(CH_3)_2H_1]$	1 <sup>]+</sup>			0.4	0.6	1.2
171	[A1 <sub>3</sub> (CH <sub>3</sub> ) <sub>6</sub> ] <sup>+</sup>			0.4	0.5	0.6	0.6
173	[A1 <sub>3</sub> (CH <sub>3</sub> ) <sub>6</sub> H <sub>2</sub> ]	+		0.3	0.4	0.6	0.8
187	[A1 <sub>3</sub> (CH <sub>3</sub> ) <sub>7</sub> H] <sup>+</sup>			0.5	0.5	0.7	0.9
	or $[A1_4(CH_3)_5]$	H <sub>4</sub> ] <sup>+</sup>					
203	$[A1_4(CH_3)_6H_5]$	+		0.4	0.6	0.8	1.3
219	[A1 <sub>4</sub> (CH <sub>3</sub> ) <sub>7</sub> H <sub>6</sub> ]	+			0.2	0.5	0.9

Table 2. ICR mass spectra of trimethylaluminum at various pressures (% rel. int.).

absence of these ions.

At 5.0 x  $10^{-7}$  torr, only one ion is observed above m/z 72 (molecular ion of the monomer). As the pressure is increased, however, up to twelve ions are observed over m/z 72. Several of these ions are identical to those observed in previous studies. Double resonance experiments were performed to determine if these ions resulted from ion/molecule reactions or from electron impact on the associated species. These experiments indicate that all of the ion intensities observed larger than m/z 72 result from ion/molecule reactions, thus suggesting the absence of the associated species at these experimental conditions.

The majority of the probable ion structures listed in Table 2 are suggested by the reaction of the precursor ions (which are determined in the double resonance experiments) with the monomeric species,  $Al(CH_3)_3$ . The majority of these structures follow the trend which was observed by Tanaka and Smith<sup>17</sup> in which the number of constituents on the aluminum atoms is 3n-1, where n is the number of aluminum atoms (e.g.,  $[Al_2(CH_3)_5]^+$  and  $[Al_3(CH_3)_6H_2]^+$ ).

The ion  $[Al(CH_3)_2]^+$  was found to react with (presumably) the monomer to yield the ion/molecule reaction products at m/z 102, 113, 115, and 129 as shown in reactions 1 through 4.

$$[Al(CH_3)_2]^+ + Al(CH_3)_3 \longrightarrow [Al_2(CH_3)_3H_3]^+ (m/z \ 102) + C_2H_3 \quad (1)$$
  
$$= [Al_2(CH_3)_3CH_2]^+ (m/z \ 113) + CH_4 \quad (2)$$
  
$$= [Al_2(CH_3)_4H]^+ (m/z \ 115) + CH_2 \quad (3)$$
  
$$= [Al_2(CH_3)_5]^+ (m/z \ 129) \quad (4)$$

The product ion  $[Al_2(CH_3)_5]^+$  is also formed from the reaction of  $[Al(CH_3)_3]^+$  as reported previously<sup>19</sup> in reaction 5.

$$[Al(CH_3)_3]^+ + Al(CH_3)_3 \longrightarrow [Al_2(CH_3)_5]^+ (m/z \ 129) + CH_3.$$
 (5)

Double resonance experiments indicate that  $[Al(CH_3)_2]^+$  is the only precursor for the formation of the product ions at m/z 131 and 145. The empirical formula for the m/z 131 product ion could be  $[Al_2(CH_3)_5H_2]^+$ , but this structure is improbable since there would be more than three ligands per aluminum atom. A more probable structure for m/z 131 is  $[Al_3(CH_3)_3H_5]^+$ (which follows the "3n-1" rule) which must be formed from the reaction of  $[Al(CH_3)_2]^+$  with the dimer,  $Al_2(CH_3)_6$ , as shown in reaction 6.

$$[Al(CH_3)_2]^+ + Al_2(CH_3)_6 \longrightarrow [Al_3(CH_3)_3H_5]^+ (m/z \ 131) + 5 \ CH_2 \quad (6)$$

Note that a more thermodynamically fovorable process for the loss of 5  $CH_2$  radicals may be the loss of the neutrals ethylene and propene. The structure of the m/z 145 product ion <u>must</u> have three aluminum atoms present. This suggests once again the reaction of  $[Al(CH_3)_2]^+$  with the dimer as shown in reaction 7.

$$[A1(CH_3)_2]^+ + A1_2(CH_3)_6 \longrightarrow [A1_3(CH_3)_4H_4]^+ (m/z \ 145) + 4 \ CH_2$$
 (7)

This product ion could also be formed by a secondary reaction of  $[Al_2(CH_3)_5]^+$  (m/z 129) with the monomer as shown in reaction 8, but <u>no</u> double resonance response was observed at m/z 129 for the m/z 145 product ion.

$$[Al_2(CH_3)_5]^+ + Al(CH_3)_3 \longrightarrow [Al_3(CH_3)_4H_4]^+ (m/z \ 145) + 4 \ CH_2 \quad (8)$$

Several of the primary product ions were observed to react further with

the trimethylaluminum. The product ion  $[Al_2(CH_3)_4H]^+$  (m/z 115) reacts further with the monomer to yield the product ions at m/z 171, 173, and 187 as shown in reactions 9 to 11.

$$[Al_{2}(CH_{3})_{4}H]^{+} + Al(CH_{3})_{3} \longrightarrow [Al_{3}(CH_{3})_{6}]^{+} (m/z \ 171) + CH_{4} \qquad (9)$$
$$= [Al_{3}(CH_{3})_{6}H_{2}]^{+} (m/z \ 173) + CH_{2}(10)$$
$$= [Al_{3}(CH_{3})_{7}H]^{+} (m/z \ 187) \qquad (11)$$

The m/z 131 product ion ( $[Al_3(CH_3)_3H_5]^+$ ) reacts further with the monomer to yield the product ions at m/z 187 and 203 as shown in reactions 12 and 13.

$$[Al_{3}(CH_{3})_{3}H_{5}]^{+} + Al(CH_{3})_{3} - [Al_{4}(CH_{3})_{5}H_{4}]^{+} (m/z \ 187) + CH_{4} (12) - [Al_{4}(CH_{3})_{6}H_{5}]^{+} (m/z \ 203)$$
(13)

Note that the m/z 187 product ion apparently has two different structures,  $[Al_3(CH_3)_7H]^+$  and  $[Al_4(CH_3)_5H_4]^+$ , as seen in reactions 11 and 12, respectively.

The most intense product ion formed,  $[Al_2(CH_3)_5]^+$  (m/z 129), also reacts further to yield product ions at m/z 149 and 219. These apparently are due to the reaction with the dimer as shown in reactions 14 and 15.

Note that all of the product ions which presumably result from reactions of the dimeric species,  $Al_2(CH_3)_6$ , are of relatively small intensity and are observed only at higher pressures. This may suggest a pressure dependence on the amount of dimer present in gas phase trimethylaluminum. The frequent loss of  $CH_2$ 

radicals and formation of Al-H bonds in the observed ion/molecule reactions suggests the presence of H-bridges (structure 1) in these ions.

In summary, the ion/molecule reactions observed in this study indicate that the ions above m/z 72 which were observed in the previous mass spectral studies may have been due to ion/molecule reactions occurring in the source of the mass spectrometer. Several ion/molecule reactions are observed, however, which do indicate the possibility of the presence of the dimeric species,  $Al_2(CH_3)_6$ , at higher pressures. The structures predicted for the ion/molecule reaction products agree with the generalization made by Tanaka and Smith<sup>17</sup> concerning the presence of H-bridges (structures <u>1</u> and <u>2</u>) when more than one aluminum atom is present.

The differences in the mass spectra of trimethylaluminum reported in previous studies and here suggests that sample handling may be an important aspect in acquiring mass spectra of these type of compounds. For example, the amount of alkyl fragment ions varies widely among the reported spectra which may result from water present in the inlet. In this study, an evacuated bulb containing liquid trimethylaluminum was placed on the inlet. The first mass spectra obtained contained large amounts of alkyl ions (possibly due to the presence of water) and (presumably) dimeric ions above m/z 72. The intensity of these higher mass ions, however, quickly disappeared. This suggests a process in which trimethylaluminum exists as a dimer in solution, but vaporizes as a monomer with the possibility of dimerization in the gas phase. If the monomer molecules in the gas phase are present at high enough pressures and for a long enough period of time, it is possible for a monomer/dimer equilibration to occur. This type of process is consistent with both the vapor pressure and mass spectral studies of trimethylaluminum. The mass spectra of the monomer may therefore be obtained by pumping the monomer through the mass spectrometer as they are formed by vaporization of the liquid and by maintaining a low pressure of trimethylaluminum in the mass spectrometer (attainable in ICR but possibly not in conventional MS sources).

## **Metal Ion CI**

The use of metal and metal-containing ions formed by electron impact on metal carbonyls,  $M(CO)_n$ , as chemical ionization (CI) reagent ions has been suggested previously<sup>20-22</sup>. The ion/molecule reactions between the metal and metal-containing ions and the analyte may provide both molecular weight and structural information. Molecular weight information is obtained from the reaction of metal-containing ions,  $[M(CO)_X]^+$ , with the analyte molecule (P) as shown in reaction 16.

$$[M(CO)_{\mathbf{X}}]^{+} + P \longrightarrow [M(CO)_{\mathbf{X}-\mathbf{a}}P]^{+} + aCO$$
(16)

The neutral molecule P may displace carbonyl ligands which are present on the reactant metal ion. The determination of the product ions and their precursors (using double resonance techniques) can yield information on the molecular weight of the neutral reactant P.

The reactions of metal-containing ions formed by 70 eV electron impact ionization on  $Co(CO)_3NO$  with trimethylaluminum were studied in the ICR in an attempt to determine the molecular weight (and thus evidence for monomer or dimer) of the species present. One ion/molecule reaction product from the reaction of the bare metal,  $[Co]^+$ , with trimethylaluminum was observed at m/z 101 which corresponds to the loss of  $C_2H_6$  (reaction 17).

$$[Co]^+ + Al(CH_3)_3 \longrightarrow [CoAlCH_3]^+ + C_2H_6$$
 (17)

The predicted reaction of the monomer and dimer of trimethylaluminum with  $[Co(CO)_2]^+$ , for example, would yield products indicative of displacement of the monomer and dimer for one or two carbonyl ligands as shown in reactions 18 to 21.

$$[Co(CO)_{2}]^{+} + Al(CH_{3})_{3} - [Co(CO)Al(CH_{3})_{3}]^{+} (m/z \ 159) + CO \ (18)$$

$$= [CoAl(CH_{3})_{3}]^{+} (m/z \ 131) + 2 \ CO \ (19)$$

$$[Co(CO)_{2}]^{+} + Al_{2}(CH_{3})_{6} - [Co(CO)Al_{2}(CH_{3})_{6}]^{+} (m/z \ 231) + CO \ (20)$$

$$= [CoAl_{2}(CH_{3})_{6}]^{+} (m/z \ 203) + 2 \ CO \ (21)$$

A lower limit on the ratio of dimer to monomer could be calculated from the intensities of these product ions as shown in the equation below.

$$\frac{\text{dimer}}{\text{monomer}} = \frac{I([CoAl_2(CH_3)_6]^+) + I([Co(CO)Al_2(CH_3)_6]^+)}{I([CoAl(CH_3)_3]^+) + I([Co(CO)Al(CH_3)_3]^+)}$$

The observed reactions of the cobalt-containing ions with trimethylaluminum are shown in reactions 22 to 27.

$$[CoCO]^+ + Al(CH_3)_3 \longrightarrow [CoAl(CH_3)_3]^+ (m/z \ 131) + CO$$
 (22)

$$[Co(CO)_2]^+ + Al(CH_3)_3 \longrightarrow [Co(CO)Al(CH_3)_3]^+ (m/z \ 159) + CO (23)$$

$$[Co(CO)_2NO]^+ + Al(CH_3)_3 \longrightarrow [Co(NO)Al(CH_3)_3]^+ (m/z \ 161) + 2 \ CO \ (25)$$

$$\sim$$
 [CoCONOAl(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup> (m/z 189) + CO (26)

$$[Co(CO)_{3}NO]^{+} + Al(CH_{3})_{3} \longrightarrow [CoCONOAl(CH_{3})_{3}]^{+} (m/z \ 189) + 2 \ CO \ (27)$$

The monomer,  $Al(CH_3)_3$ , is seen to displace one or two carbonyl ligands from the metal-containing reactant ion. <u>No</u> product ions were observed which would indicate the presence of the dimer,  $Al_2(CH_3)_6$  (reaction 20 or 21).

These results suggest that trimethylaluminum exists only as a monomer in the gas phase at these conditions. It is possible, however, that the dimer may dissociate upon complexation to the metal ion (due to the relatively low dissociation energy) which would prevent the formation of products indicative of the dimer during metal ion chemical ionization.

## **Collision Induced Dissociation Studies**

The collision induced dissociation (CID) spectra for the major ions present in the mass spectrum of trimethylaluminum were obtained using a triple quadrupole mass spectrometer (TQMS). A typical 70 eV electron impact mass spectrum of trimethylaluminum (4.0 x  $10^{-5}$  torr) obtained with the TQMS is listed in Table 3. The TQMS mass spectrum is in good agreement with the ICR spectra and the previously reported spectra.

Daughter ion (CID) spectra were obtained for ions of m/z 42, 57, 72, and 129. Daughter scans of the other ions were not possible due to the low intensity of the parent ions. The CID of  $[AlCH_3]^+$  (m/z 42) yielded m/z 27 ( $[A1]^+$ ) corresponding to a loss of 15 (CH<sub>3</sub>·) as shown in reaction 28.

$$[A1CH_3]^+ \xrightarrow{Ar} [A1]^+ + CH_3$$
 (28)

Daughter ions at m/z 27 ([A1]<sup>+</sup>) and m/z 42 ([A1CH<sub>3</sub>]<sup>+</sup>) (loss of one or two methyl groups) were observed in the CID spectrum of  $[A1(CH_3)_2]^+$  (m/z 57) as shown in reactions 29 and 30.

$$[A1(CH_3)_2]^+ \xrightarrow{Ar} [A1CH_3]^+ + CH_3.$$
(29)

$$[A1]^{+} + 2 CH_{3}$$
 (30)

The molecular ion of the monomer,  $[Al(CH_3)_3]^+$  (m/z 72), undergoes CID to

Table 3.	Typical 70 eV EI mass spectrum of trimethylaluminum
	obtained on the TQMS.

<u>m/z</u>	% rel. int.
27	17.2
28	0.6
29	0.2
42	4.3
43	1.1
57	100.0
72	2.8
99	1.0
113	0.6
129	21.5
145	0.6
149	0.4
203	0.3

yield  $[Al(CH_3)_2]^+$  (m/z 57) (reaction 31) but <u>no</u>  $[AlCH_3]^+$  (m/z 42) (loss of two methyl groups) is observed.

$$[Al(CH_3)_3]^+ - \frac{Ar}{(Al(CH_3)_2)^2} + CH_3 \cdot$$
(31)

The last ion studied was m/z 129 which was proposed to be  $[Al_2(CH_3)_5]^+$ from the ICR studies. This ion undergoes CID to yield m/z 57 ( $[Al(CH_3)_2]^+$ ) at low collision energies ( $\sim 10 \text{ eV}$ ). At higher collision energies ( $\sim 30 \text{ eV}$ ), a small amount of  $[AlCH_3]^+$  is also observed. These processes are shown in reactions 32 and 33.

$$[Al_2(CH_3)_5]^+ \xrightarrow{Ar} [Al(CH_3)_2]^+ + Al(CH_3)_3$$
(32)

$$\rightarrow$$
 [A1CH<sub>3</sub>]<sup>+</sup> + A1(CH<sub>3</sub>)<sub>3</sub> + CH<sub>3</sub>. (33)

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Reaction 32 is not unexpected since the previously reported value of D(Al-C-Al)= 10.2 kcal/mole<sup>4</sup> is relatively small.

All of the CID processes observed for the ions studied here appear to result from the simple cleavage of the Al-CH<sub>3</sub> bonds and the relatively weak bridging Al-C-Al bonds in the  $[Al_2(CH_3)_5]^+$  dimer ion.

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### Appendix D

### **Unsuccessful ICR Studies**

#### Nickel-Containing Anions

In addition to the study of the ion/molecule reactions of iron, chromium, and cobalt-containing anions with polar organic molecules, an attempt was made to study the ion/molecule reactions of nickel-containing anions. The only anion present in the 70 eV electron impact mass spectrum of Ni(CO)<sub>4</sub> is the 17-electron species  $Ni(CO)_3^-$ . This ion was unreactive with the organic molecules studied in this dissertation. Low energy electron impact, which was found to be useful in the iron, chromium, and cobalt studies, does not form a sufficient amount of  $Ni(CO)_2^-$  to allow the study of its ion/molecule Another nickel-containing compound,  $Ni(PF_3)_4$ , was utilized in reactions. an attempt to form nickel-containing non-17 electrom species. The major anions present in the spectrum of  $Ni(PF_3)_4$ , however, are mass fluorine-containing fragments such as  $PF_3^-$ ,  $PF_2^-$  etc. (presumably due to the high electron affinity of fluorine). Nickel-containing anions formed from electron impact on  $Ni(PF_3)_4$  are of relatively low abundance.

### Isomer Analysis Using Metal Ion Chemical Ionization

A study was attempted in which metal and metal-containing positive ions were utilized as chemical ionization (CI) reagent ions to distinguish between two pairs of isomers: cis- and trans-1,2-dichloroethylene and cis- and trans-1,2-cyclohexanediol. The 70 eV electron impact fragment ions from  $Co(CO)_3NO$ ,  $Fe(CO)_5$ , and  $Cr(CO)_6$  were used in this study. It was believed that the differences in the ion/molecule reactions observed between the metal species and the two isomers would provide structural information indicating the type of isomer present. For example,  $Co^+$  has been observed to abstract two chlorine atoms from 1,2-dichloroethane to form  $CoCl_2^+$  25. This product ion may also be expected in the reaction of cis-1,2-dichloroethylene but may not be expected for the trans-1,2-dichloroethylene isomer due to the spatial separation of the chlorine atoms. The ion/molecule reactions observed between the metal ions and the dichloroethylene and cyclohexanediol isomers were nearly identical. No differences were observed in the ion/molecule reactions of the isomers which might provide structural information.

# Studies of Ligand Effects in Metal Ion/Molecule Reactions

The study of ligand effects on metal ion reactivity (metal species formed by electron impact on  $ML_1L_2$  species) has been limited to the presence of carbonyl ligands (from  $M(CO)_n$ ) and nitrosyl ligands (from  $Co(CO)_3NO$ ). This study was initiated in an attempt to determine the effects of the presence of ligands other than CO and NO on metal ion reactivity. These metal-containing ions were reacted with several n-alkanes, n-alcohols, and primary amines to compare the ion/molecule reactions observed with those previously reported with M<sup>+</sup> and MCO<sup>+</sup>.

The ion/molecule reactions of nickel-containing ions from electron impact on Ni(PF<sub>3</sub>)<sub>4</sub> are similar to those observed for Ni<sup>+</sup> and Ni(CO)<sub>x</sub><sup>+</sup>, i.e., the PF<sub>3</sub> ligands were either "spectators" in the ion/molecule reaction or were lost in a ligand substitution process similar to CO loss with Ni(CO)<sub>x</sub><sup>+</sup>. No product ions were observed in which the PF<sub>3</sub> ligand changed the reactivity of the metal ion (i.e., no evidence for active participation of the PF<sub>3</sub> ligand).

Chromyl chloride,  $CrO_2Cl_2$ , was also utilized since a variety of metal species are formed during electron impact (e.g.,  $CrO^+$ ,  $CrCl^+$ ,  $CrOCl^+$  etc.). The major difficulty in the study of chromyl chloride is the presence of neutral-neutral reaction products with the organic molecules due to the extreme

reactivity of chromyl chloride. The use of Fourier transform mass spectrometry and ion ejection techniques would make the study of the ion/molecule reactions of these ions possible.

Tungsten carbonyl  $(W(CO)_6)$  is unique in that a large amount of  $WC^+$  is formed during 70 eV electron impact. This allows the possible study of the effect of the C ligand. No ion/molecule reactions, however, were observed from  $WC^+$  with the organic molecules studied here.

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LIST OF FOOTNOTES AND REFERENCES

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