

$\text{CH}_2\text{Cl}_2$ . This gave 2 (0.39 g, 8.8%) and 4 (0.48 g, 6.8%), in addition to the desired 6. Complex 6 formed metallic orange crystals (1.95 g, 42%): mp 256–258 °C;  $^1\text{H NMR}$  (250 MHz, acetone- $d_6$ )  $\delta$  5.88 (dd, 2 H,  $J = 2.2, 2.1$  Hz), 5.53 (dd, 2 H,  $J = 2.3, 2.3$  Hz), 4.79 (dd, 2 H,  $J = 2.4, 2.3$  Hz), 4.42 (dd, 2 H,  $J = 2.2, 2.1$  Hz); IR (KBr)  $\nu_{\text{CO}}$  2020 (s), 1942 (s), 1935 (s), 1868 (s)  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  309 ( $\epsilon$  15000), 378 (9100), 470 (sh, 880) nm; MS,  $m/e$  465 ( $\text{M}^+$ , 19.6), 438, ( $\text{M}^+ - \text{CO}$ , 15.9), 411 ( $\text{M}^+ - 2\text{CO}$ , 7.0), 381 ( $\text{M}^+ - 3\text{CO}$ , 71.0), 352 ( $\text{M}^+ - 4\text{CO}$ , 16.2), 324 ( $\text{M}^+ - 5\text{CO}$ , 100). Anal. Calcd for  $\text{C}_{15}\text{H}_8\text{O}_5\text{MoRu}$ : C, 38.73; H, 1.73. Found: C, 38.70; H, 1.75.

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## Chemistry of $\text{Co}^+$ and $\text{Co}(\text{ligand})_n^+$ with Mono- and Bisubstituted $n$ -Butanes in the Gas Phase: Using a Simple "Ligand Competition" Model and Collision-Induced Dissociation Analysis To Provide Insights into Product Structures

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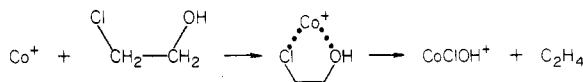
The gas-phase chemistry of ions of the type  $\text{Co}^+$ ,  $\text{Co}(\text{CO})_x^+$ , and  $\text{Co}(\text{CO})_x\text{NO}^+$  with mono- and bisubstituted  $n$ -butanes is discussed. Bifunctional molecules exhibit a much richer chemistry with these metal centers than do the monofunctional compounds. If  $\text{Co}^+$  must "choose" between two groups such as Br and OH, some preference for the halogen is indicated. In such mass spectrometric studies, the mass of a product ion is frequently insufficient for determining what type of reaction actually occurred. This text discusses a model that predicts the relative strengths of metal-ligand interactions. By postulating possible reaction intermediates and using the suggested model to determine which neutrals would be lost from each possible intermediate, information on product ion structures becomes available. Collision-induced dissociation experiments are also used as a probe of ionic product structures. These experiments also yield a lower limit on the  $\text{Co}^+$ -butadiene bond strength of 85.9 kcal/mol.

### Introduction

Investigations in the dynamics of bimolecular ion-molecule reactions under low-pressure conditions in the gas phase have been very productive. With use of ion cyclotron resonance spectrometry<sup>1</sup> and other mass spectrometric methods, the chemistry of metal- and metal-containing ions with organic molecules can be studied in the gas phase, yielding mechanistic, thermodynamic, and kinetic information on the basic processes and driving forces of organometallic chemistry.<sup>2</sup> Also, the specificity with which metal ions react with organic functional groups suggests that metal ion chemical ionization may be a useful mass spectrometric technique.<sup>3</sup>

Most of the work reported to date in this area involves the chemistry of transition-metal ionic species with organic compounds containing one functional group or no functional groups (alkanes). A major research effort in this laboratory is the study of the chemistry of ionic metal

centers with multifunctional compounds.<sup>3b</sup> For an evaluation of the eventual utility of metal ion chemical ionization, it must be determined how the products of the reaction between a metal ion and an organic compound containing more than one functional group are related to the reactant molecule. If  $\text{Co}^+$  reacts with a saturated hydrocarbon skeleton containing, e.g., a Cl and an OH group, one or more of the following may be observed: (1) Products representative of alcohol reactions and products typical of alkyl halide reactions are formed. (2) Products only typical of one functional group are formed (indicating the  $\text{Co}^+$  would show a preference for one functional group over another). (3) Products that are unique to this combination of functional groups are formed. Reactions exemplifying all three possibilities have been observed.<sup>3b</sup> In a previous report from our laboratory,<sup>3b</sup> bifunctional compounds with both groups in close proximity were studied. In this case, the interaction of both functional groups with the reactant metal ion is geometrically accessible and apparently occurs, e.g.



To determine whether  $\text{Co}^+$  would exhibit a preference for one functional group over another, the decision was made to investigate a series of 1,4-bisubstituted  $n$ -butanes. It was initially thought that the four-carbon chain would be

(1) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* 1971, 22, 527.

(2) Publications representative of the groups currently active in this area include: (a) Dietz, T. G.; Chatellier, D. S.; Ridge, D. P. *J. Am. Chem. Soc.* 1978, 100, 4905. (b) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Ibid.* 1981, 103, 4360. (c) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Chem. Phys.* 1982, 76, 2449. (d) Huang, S. K.; Allison, J. *Organometallics* 1983, 2, 883.

(3) See for example: (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* 1980, 52, 1641. (b) Lombarski, M.; Allison, J. *Int. J. Mass Spec. Ion Phys.* 1983, 49, 281.

sufficiently long such that both groups could not easily interact with the metal ion simultaneously (a seven-membered ring intermediate would be involved). Thus, with this goal in mind, we report here the chemistry of the  $\text{Co}(\text{CO})_x^+$  ( $x = 0-2$ ) and  $\text{Co}(\text{CO})_x\text{NO}^+$  ( $x = 0-3$ ) ions derived from electron impact on  $\text{Co}(\text{CO})_3\text{NO}$ , with a series of *n*-butyl halides, 1-butanol, 4-halo-1-butanols, and one 1,4-dihalobutane.

The chemistry of  $\text{Co}^+$  with each compound will be discussed as well as the effects of ligands on the observed chemistry of the metal center. The results will be interpreted by using a model that has been implied in the literature to date, but not extensively used. Also, collision-induced dissociation analysis will be used to provide insights into the structures of several important reaction products.

Of the work done to date concerning the gas-phase organometallic chemistry of transition-metal ions, cobalt has been prominent. Historically, 70-eV electron impact (EI) on  $\text{Co}(\text{CO})_3\text{NO}$  was used because of the copious amounts of  $\text{Co}^+$  formed.<sup>4</sup> Also, EI on this compound was of interest since species such as  $\text{CoCO}^+$  and  $\text{CoNO}^+$  were formed. (CO and NO are both very important ligands in catalytic reactions.) Recently, EI on metal carbonyls has been somewhat replaced by other techniques that only produce one type of ion, the bare metal ion.<sup>2b,5</sup> This approach greatly simplifies interpretation of results but does not facilitate the study of ligand effects.

One of the earliest works involving ionic cobalt reactions was a study of ligand substitution reactions of ions derived from EI on  $\text{Co}(\text{CO})_3\text{NO}$ .<sup>6</sup> Competitive ligand substitution reactions such as

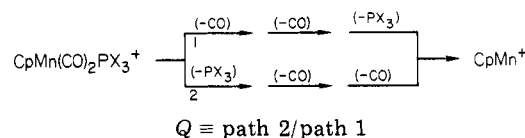


were used to determine the following order of metal-ligand "affinities":  $\text{NO} > \text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{C}_2\text{D}_4 > \text{H}_2\text{O} > \text{CO} > \text{O}_2$ . Three important concepts resulted from this work. First, the order appeared to be independent of the number of ligands on the metal. Second, reactions of the  $\text{CoNO}(\text{X})(\text{Y})^+$  species did not indicate that the strength of the Co-X interaction depended on the identity of Y (at least not in the context of the ligand substitution reactions studied). Third, the trend reported suggests that the proton affinity (PA) of the ligand reflects its metal ion affinity  $D(\text{M}^+\text{-ligand})$  (i.e., the strength of the metal-ligand interaction). (PA is defined in Table III). Thus in the series shown above,  $\text{NH}_3$  has the highest PA (207 kcal/mol) and  $\text{O}_2$  has the lowest (100 kcal/mol). Note that only simple, monodentate ligands were studied. There are two notable exceptions to this rule. The NO molecule has a PA of 120 kcal/mol but has a very high bond strength to  $\text{Co}^+$ . This is expected because NO is (can be) a three-electron donor and cannot be considered in the same category as the other compounds that can only "offer" an electron pair for the interaction with the metal. Also, when  $\text{H}_2\text{O}$  and olefins ( $\text{C}_2\text{H}_4$ ) compete for a site on the metal, preference by the metal for the olefin over  $\text{H}_2\text{O}$  is shown, even though, by the proton affinity rule,  $\text{H}_2\text{O}$  should be a slightly better ligand than an olefin such as ethylene. The trend of metal-ligand bond strengths paralleling proton affinity has been discussed for many other transition-metal and metal-containing ions.<sup>7-10</sup>

(4) Allison, J.; Ridge, D. P. *J. Organomet. Chem.* **1975**, *99*, C11.  
 (5) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819.  
 (6) Weddle, G. H.; Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 105.  
 (7) Corderman, R. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3998.

Thus, the model suggested from gas-phase ion-molecule reactions is as follows: If a complex of the type  $\text{M}(\text{L}_1)(\text{L}_2)(\text{L}_3)^+$  is formed with excess energy, that energy can be used to break metal-ligand bonds. The bonds most readily broken are the weakest bonds. Ligands with the lowest metal-ligand bond strength(s) are preferentially lost. This preference can be predicted with knowledge of the proton affinity of the ligands.

This effect has also been noted in the EI mass spectra of organometallic compounds. In a classic review on early work in this area by Müller,<sup>11</sup> the fragmentation sequence for organometallic compounds containing several different ligands bonded to a central metal is discussed. Ligands are divided into two groups according to their ease of removal. Group 1 ligands (e.g., CO,  $\text{N}_2$ ,  $\text{PF}_3$ ,  $\text{C}_2\text{H}_4$ ) are easily removed. Group 2 (e.g., amines, thioethers, aromatic hydrocarbons) are difficult to remove. Müller discusses these two groups in terms of their donor/acceptor ability.<sup>11</sup> Group 1 represents good acceptor ligands, i.e., species which should exhibit weakened metal-ligand bonds by the presence of a charge on the metal. Group 2 species are good donor ligands. It should be noted that group 1 compounds have lower PA's than group 2. Consider two pathways for fragmentation of  $\text{CpMn}(\text{CO})_2\text{PX}_3$  to form  $\text{CpMn}^+$ :

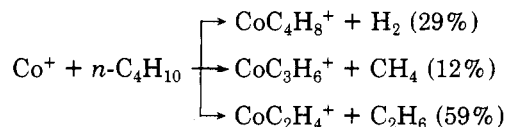


For X = F,  $Q = 5.57$ . For X = H,  $Q = 0.05$ . Thus, as the PA of  $\text{PX}_3$  increases, pathway 1 is favored over pathway 2; i.e., the  $\text{PX}_3$  ligand becomes more difficult to remove.<sup>11</sup>

Thus, the ligand competition model has been established. Proton affinities of monofunctional  $\pi$ - and  $n$ -donor bases appear to provide an indication of the interaction energy between a ligand and a metal ion, with some noted exceptions. The greater the PA of a ligand, the greater the metal ion affinity for that ligand will be. This will be referred to as the "proton affinity rule" in this text. This concept will be used to interpret our results. The evaluation and establishment of such a rule becomes very important in such experiments. As the complexity of reactions in such systems increases, such guidelines will become vital for interpretation of results.

A brief overview of the chemistry of  $\text{Co}^+$  and  $\text{Co}(\text{L})_n^+$  with organic molecules (similar to those which will be discussed here) will put this work in the proper context. It will also provide a basis with which the ligand competition model (proton affinity rule) can be evaluated.

Beauchamp and Armentrout have reported the chemistry of  $\text{Co}^+$  with alkanes such as butane.<sup>12</sup>



(8) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967.

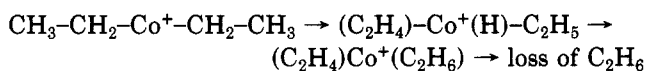
(9) Jones, R. W.; Staley, R. H. *Int. J. Mass Spec. Ion Phys.* **1981**, *39*, 35.

(10) (a) Kappes, M. M.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1813. (b) Kappes, M. M.; Staley, R. H. *Ibid.* **1982**, *104*, 1819. (c) Jones, R. W.; Staley, R. H. *J. Phys. Chem.* **1982**, *86*, 1387. (d) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1235. (e) Uppal, J. S.; Staley, R. H. *Ibid.* **1982**, *104*, 1238.

(11) Müller, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 653.

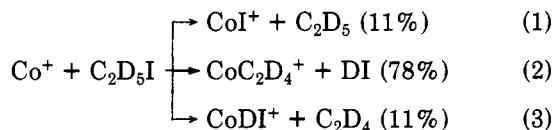
(12) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784.

The major pathway is insertion into the central C-C bond followed by a  $\beta$ -H atom shift:

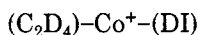


Note that  $\text{Co}^+$  induces the formation of ethylene and ethane from butane. These two molecules then compete as ligands for  $\text{Co}^+$ . Only  $\text{CoC}_2\text{H}_4^+$  is observed ( $\text{C}_2\text{H}_6$  is lost).  $\text{CoC}_2\text{H}_6^+$  would not be an expected product since  $\text{PA}(\text{C}_2\text{H}_4) > \text{PA}(\text{C}_2\text{H}_6)$ ; i.e., it is predicted that ethylene interacts with  $\text{Co}^+$  much more than ethane.

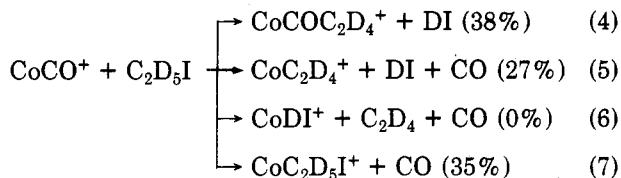
In 1979, Allison and Ridge reported the chemistry of  $\text{Fe}^+$ ,  $\text{Co}^+$ , and  $\text{Ni}^+$  (in various states of coordination) with alkyl halides and alcohols.<sup>13</sup> Reactions were discussed in terms of a metal insertion  $\beta$ -H atom shift sequence that had been proposed.<sup>14</sup> The ions formed by electron impact on  $\text{Co}(\text{CO})_3\text{NO}$  were studied in their reactions with compounds such as ethyl iodide.  $\text{Co}^+$  forms the three products shown in reactions 1-3 with this compound.<sup>13</sup> Reaction



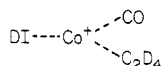
1, halogen abstraction, is usually observed for alkyl halides (a similar process frequently occurs for alcohols). Reaction products in (2) and (3) presumably are formed through a common intermediate:



Since  $\text{PA}(\text{HI}) < \text{PA}(\text{C}_2\text{H}_4)$ , one would predict DI loss to dominate. This pattern is observed. It is interesting to contrast these reactions to those reported for  $\text{CoCO}^+$  with  $\text{C}_2\text{D}_5\text{I}$  (reaction 4-7). If the products in (4)-(6) are formed



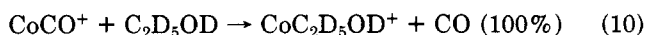
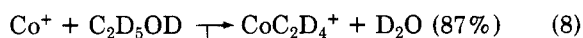
through the common intermediate



the PA order [ $\text{PA}(\text{DI}) < \text{PA}(\text{CO}) < \text{PA}(\text{C}_2\text{D}_4)$ ] would predict products in (4) and (5) to dominate over products in (6), as is observed.

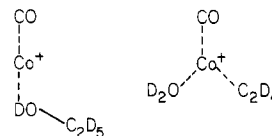
Also, we would assume that reaction 7 is a simple ligand substitution. That is, the product contains  $\text{C}_2\text{D}_5\text{I}$  intact, not as ( $\text{C}_2\text{D}_4$ ) and (DI), since CO should not be eliminated to a large extent with DI retention.

The actual processes that occur for alcohols are not as straightforward. Consider reactions 8-11. Products in



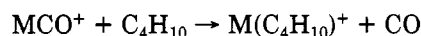
(8) and (9) presumably come from the common intermediate  $\text{Co}(\text{H}_2\text{O})(\text{C}_2\text{H}_4)^+$ . The product distribution does not

reflect the relative PA's of  $\text{H}_2\text{O}$  and  $\text{C}_2\text{H}_4$  (which differ by only 5 kcal/mol) but agrees with the results of Weddle, Allison, and Ridge which specifically indicate  $D(\text{Co}^+ - \text{C}_2\text{H}_4) > D(\text{Co}^+ - \text{H}_2\text{O})$ .<sup>6</sup> Reaction 11 indicates that  $\text{CoL}^+$  can also induce the decomposition of ethanol to ethylene and  $\text{H}_2\text{O}$  (both bound to  $\text{Co}^+$  in the intermediate complex); however, here only  $\text{H}_2\text{O}$  is retained. This preference for  $\text{H}_2\text{O}$  over olefins apparently occurs when an NO is bound to the metal. Reaction 10 could be interpreted as proceeding through either of these two intermediates:

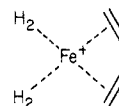


In either case, the PA rule would predict that CO is the most weakly bound ligand and should be lost. Thus, it is not always apparent as to how the metal ion reacts with alcohols (i.e., how the atoms of the alcohol are bound to the metal), due to the relatively high  $D(\text{Co}^+ - \text{H}_2\text{O})$ . This contrasts to reactions in which the metal ion induced rearrangement of alkyl halides to an olefin and HX is obvious due to the low value of  $D(\text{Co}^+ - \text{HX})$ .

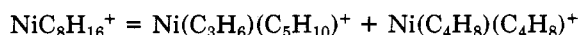
This work will utilize the collision-induced dissociation (CID) process to provide information on product structures. As the name implies, CID involves the energetic collision of an ion with a collision gas to induce fragmentation of the ion. This method of ion structure analysis has been very useful for organic ions<sup>15</sup> and has recently been applied to products of organometallic ion-molecule reaction products. Freas and Ridge<sup>16</sup> reported the high-energy (6-KV collisions with He) CID products of ions of the type  $\text{M}(\text{C}_4\text{H}_{10})^+$  formed by



for  $\text{M} = \text{Fe}$  and  $\text{Cr}$ . Dramatic differences were noted for the two metals and for isomeric butanes. Products such as  $\text{FeC}_2\text{H}_4^+$  were postulated to result from structures such as  $(\text{C}_2\text{H}_6)\text{Fe}(\text{C}_2\text{H}_4)^+$ . Ions such as  $\text{FeC}_4\text{H}_6^+$ , however, are probably not indicative of an  $\text{FeC}_4\text{H}_{10}^+$  structure such as



but rather is the result of a collision-induced reaction (CIR), in which additional energy supplied to  $\text{FeC}_4\text{H}_{10}^+$  on the collision prompts the formation of butadiene. Jacobson and Freiser have done an exhaustive CID analysis of metal-olefin complexes from  $\text{NiC}_4\text{H}_8^+$  through  $\text{NiC}_8\text{H}_{16}^+$ , under "low"-energy conditions in a Fourier transform ion cyclotron resonance mass spectrometer.<sup>17</sup> These results imply that an ion such as  $\text{NiC}_8\text{H}_{16}^+$  may exist as a collection of structures such as



If evidence exists for a  $\text{C}_4\text{H}_8$  ligand bound to a metal ion, CID of that complex always appears to induce  $\text{H}_2$  elimination to form a metal-butadiene product. Jacobson and Freiser point out that caution must be exercised in interpreting CID spectra of such ions, since the products represent a mixture of CID and CIR processes.<sup>17</sup> The CIR problem appears to become significant when additional

(13) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998.

(14) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445.

(15) Cooks, R. G. "Collision Spectroscopy"; Plenum Press: New York, 1978; p 357.

(16) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129.

(17) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736.

reduction of a ligand is possible. For example,  $\text{NiC}_6\text{H}_{12}^+$  appears to actually exist as  $\text{Ni}(\text{C}_3\text{H}_6)_2^+$ . The CID spectrum is simple, consisting of  $\text{NiC}_3\text{H}_6^+$  and  $\text{Ni}^+$ . No further collision-induced reaction for a metal-propene complex would be expected.  $\text{Ni}(\text{C}_4\text{H}_8)^+$  is not as simple since butene can be induced to lose  $\text{H}_2$  and form a metal-butadiene complex. Thus, the utility of CID in such analyses is still being evaluated. (It should be noted that, in the work done to date, CID products, which are most likely CIR products, tend to be of relatively low intensity.) The limitations must be realized. Nonetheless, we present CID results that appear to be interpretable and frequently provide useful information.

### Experimental Section

All experiments were performed on an ion cyclotron resonance (ICR) mass spectrometer<sup>1</sup> of conventional design (used in the "drift mode") which was constructed at Michigan State University and is described elsewhere.<sup>18</sup> A Wavetek Model 144 sweep generator was used as the secondary oscillator in ion cyclotron double-resonance experiments. The compounds used in this work which include tricarbonylnitrosylcobalt (0) (Alfa Inorganics), 1-bromo- and 1-chlorobutane (Chem-Service), 1-butanol, 4-bromo-1-butanol, and 4-chloro-1-butanol (Alfa Products), 4-fluoro-1-butanol and 1-bromo-4-chloro-butane (Columbia Organic Chemicals Co.), and 1-fluoro-butane (Pfaltz and Bauer Inc.) were analyzed for purity and for particular suspected contaminants by gas chromatography and mass spectrometry. All samples were degassed by multiple freeze-pump-thaw cycles and used without further purification.

Ion-molecule reaction products up to  $m/z$  270 were identified, and their precursors were determined by standard double resonance techniques in 1:1 or 1:2 (by pressure) mixtures of  $\text{Co}(\text{CO})_3\text{NO}$ /sample at a total pressure of  $1.0 \times 10^{-5}$  torr. Possible organic reaction products that may also be primary products of EI were also considered. The results of these experiments are listed in Table I. The problems associated with ambiguities in assignment of ionic products have been discussed.<sup>18</sup> This table represents a self-consistent interpretation, with ionic product assignments based on careful analysis of precursors and by cross-correlating similar products from various neutral organic reactants.

Branching ratios in Table I are accurate to within  $\pm 10\%$ . Reported reactions are facile and usually occur within an order of magnitude of the collision frequency. An approximate lower limit for the rate constant for processes not observable in this work is  $5 \times 10^{-11}$   $\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>. In the case of 1-butanol, it should be noted that three minor product ions at  $m/z$  101, 103, and 105 were observed, but their rates of formation were low, approaching the detection limits. Precursors of ions of such low abundance cannot be accurately determined; however, these (possible) products may be important. The ion at  $m/z$  101 would be  $\text{CoCH}_2\text{CO}^+$  but was of such low intensity that no double-resonance analysis could be performed. The ions at  $m/z$  103 and 105, tentatively assigned as  $\text{CoC}_2\text{H}_3\text{OH}^+$  and  $\text{CoC}_2\text{H}_5\text{OH}^+$ , respectively, appear to be formed from reaction of  $\text{Co}^+$  and  $\text{CoCO}^+$ ; however, the accurate contribution due to each precursor cannot be determined, so these are not included in Table I.

Collision-induced dissociation (CID) experiments were performed on an Extranuclear triple quadrupole mass spectrometer. In the (CI) ion source, 1:2 mixtures ( $\text{Co}(\text{CO})_3\text{NO}$ /sample) are admitted to a total pressure of  $3 \times 10^{-4}$  torr (measured outside the source in the source housing). Ion-molecule reaction products 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 is  $3 \times 10^{-3}$  torr). Typical collision energies are in the 10–30 eV (lab) range. The products of collision-induced processes that are formed in the collision chamber are mass analyzed by scanning the third mass filter. The results of these experiments are listed in Tables IV–VII. Under the conditions of these experiments, ions such as  $\text{ArCH}_3^+$  and  $\text{ArOH}^+$  are formed. Such products are not included in the tabulated data.

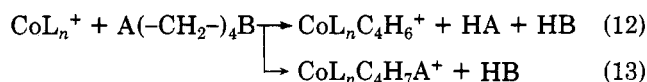
### Discussion

The chemistry of the cobalt and cobalt-containing ions with the *n*-butyl halides will first be discussed. The chemistry of these ions with 1-chloro-4-bromobutane will then be analyzed in light of the butyl halide results. The reactions with 1-butanol will then be discussed and used in the analysis of the halobutanol products.

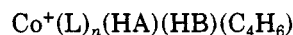
Table II lists some pertinent enthalpy values for selected bond cleavage and elimination processes. Note that, thermodynamically, butanol falls between fluorobutane and chlorobutane. Table II shows that the strength of the C–X bond *decreases* as X becomes larger. Also, the energy required for HX elimination *increases* as X = F → Br.

Table III lists some proton affinities of neutral molecules that will be competing as ligands on  $\text{Co}^+$  in these studies.

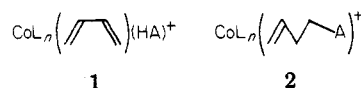
Many of the processes in Table I are expected in the context of the current literature in this area. The proton affinity rule will be used to answer a number of questions concerning structural assignment. Suppose we observe



We would assume that reaction 12 proceeds through an intermediate such as

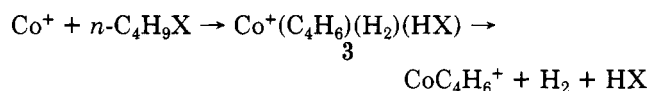


The question is, does the same intermediate lead to the product in (13)? That is, does the product in (13) have the structure 1 or 2? Depending on the nature of L, A,



B, and the value of  $n$ , the proton affinity rule will provide insights into the product structure. Note that, to use this approach, all of the ligands in the reaction must be bound to the metal at some time during the reaction and can *compete*. In some cases, as will be pointed out, reactions will not be able to occur this way but must occur in a stepwise manner. In approaching such questions, the 18-electron rule should presumably not be violated at any point in a proposed mechanism.

**Reactions of *n*-Butyl Halides.** The  $\text{Co}^+$  ion reacts with 1-chloro-, 1-bromo-, and 1-fluoro-*n*-butane to form the butyl cation. Similar results have been reported for other alkyl halides,<sup>13</sup> so this product is not unexpected. The cobalt ion also reacts with each of the three halobutanes to form the metal-butadiene complex  $\text{Co}(\text{C}_4\text{H}_6)^+$ . (The  $\text{Co}^+$  ion reacts with a variety of compounds containing a four-carbon chain to produce the ( $\text{Co}^+$ -butadiene) complex.) The formation of this species from 1-bromo-*n*-butane implies a lower limit on the metal-ligand bond strength,  $D(\text{Co}^+-\text{C}_4\text{H}_6) > 43.3$  kcal/mol. If the reaction occurs through the intermediate 3 in which all products



are bound to the metal, the proton affinity rule for estimating metal-ligand interactions, i.e., ease of ligand loss, would suggest that  $\text{H}_2$  and HX are weakly bound ligands. The bond strengths of *multidentate* ligands such as butadiene have not been studied to date,<sup>19</sup> thus we cannot

(19) Studies of the chemistry of  $\text{Co}^+$  with olefins have suggested 45–60 kcal/mol as the estimate for the bond strength between this metal ion and 1,3-alkadienes: Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1981, 103, 6624.

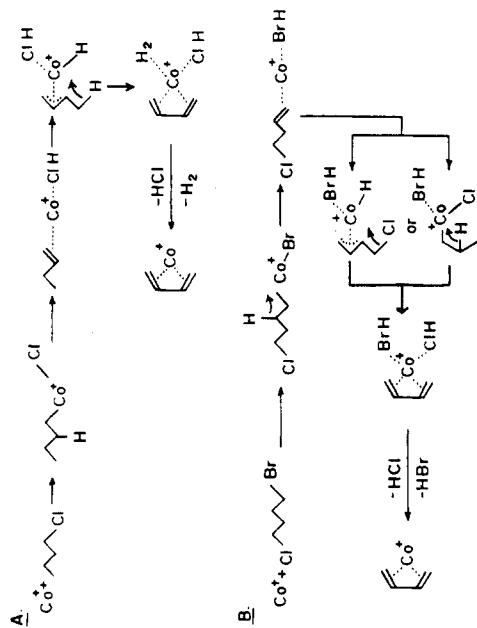
Table I. Reactions of Mono- and Disubstituted *n*-Butanes with Ions Derived from  $\text{Co}(\text{CO})_3\text{NO}^a$ 

reactant neutrals

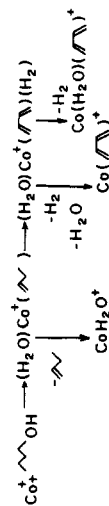
reactant ion	F	Cl	Br	OH	F	Cl	Br	OH	F	Cl	Br	OH	
$\text{Co}^+$	$\text{CoF}$ (0.87)	$\text{CoCl}$ (0.81)	$\text{CoBr}$ (0.87)	$\text{H}_2$ (0.87)	$\text{HF} + \text{H}_2\text{O}$ (0.29)	$\text{HCl} + \text{H}_2\text{O}$ (0.65)	$\text{HBr} + \text{H}_2\text{O}$ (0.59)	$\text{H}_2\text{O}$ (0.52)	$\text{H}_2 + \text{C}_2\text{H}_5\text{F}$ (0.35)	$\text{HCl} + \text{H}_2\text{O}$ (0.65)	$\text{HBr} + \text{H}_2\text{O}$ (0.59)	$\text{H}_2 + \text{C}_2\text{H}_5\text{Cl}$ (0.35)	$\text{HBr} + \text{H}_2\text{O}$ (0.59)
$\text{CoCO}^+$	$\text{HF} + \text{H}_2$ (1.00)	$\text{HCl} + \text{H}_2$ (0.19)	$\text{HBr} + \text{H}_2$ (0.19)	$\text{C}_2\text{H}_8$ (1.00)	$\text{H}_2 + \text{C}_2\text{H}_5\text{F}$ (0.19)	$\text{HCl} + \text{H}_2$ (0.06)	$\text{H}_2 + \text{C}_2\text{H}_5\text{Cl}$ (0.06)	$\text{H}_2 + \text{C}_2\text{H}_5\text{Br}$ (0.06)	$\text{HF}$ (0.06)	$\text{HCl}$ (0.06)	$\text{HBr}$ (0.06)	$\text{H}_2 + \text{C}_2\text{H}_5\text{Br}$ (0.19)	$\text{H}_2 + \text{C}_2\text{H}_5\text{Br}$ (0.09)
$\text{Co}(\text{CO})_2^+$	$\text{HF} + \text{CO}$ (1.00)	$\text{HCl} + \text{CO}$ (1.00)	$\text{HBr} + \text{CO}$ (1.00)	$\text{H}_2 + \text{CO}$ (0.87)	$\text{HF} + \text{CO}$ (0.35)	$\text{HCl} + \text{CO}$ (0.18)	$\text{HBr} + \text{CO}$ (0.53)	$\text{H}_2 + \text{CO}$ (0.10)	$\text{HF} + \text{CO}$ (0.10)	$\text{HCl} + \text{CO}$ (0.09)	$\text{HBr} + \text{CO}$ (0.13)	$\text{H}_2 + \text{CO}$ (0.10)	$\text{HBr} + \text{CO}$ (0.09)
$\text{CoNO}^+$ $\text{CoCONO}^+$	$\text{CO}$ (1.00)	$\text{C}_2\text{H}_8$ (0.40)	$\text{C}_2\text{H}_8$ (0.40)	$\text{CO}$ (1.00)	$\text{C}_3\text{H}_5\text{F} + \text{CO}$ (0.31)	$\text{C}_3\text{H}_5\text{Cl} + \text{CO}$ (0.67)	$\text{C}_3\text{H}_5\text{Br} + \text{CO}$ (0.15)	$\text{CO}$ (0.28)	$\text{C}_3\text{H}_5\text{F} + \text{CO}$ (0.31)	$\text{C}_3\text{H}_5\text{Cl} + \text{CO}$ (0.24)	$\text{C}_3\text{H}_5\text{Br} + \text{CO}$ (0.77)	$\text{CO}$ (0.08)	$\text{HBr} + \text{CO}$ (1.00)
$\text{Co}(\text{CO})_2\text{NO}^+$	$\text{CO}$ (0.31)	$\text{CO}$ (0.69)	$\text{CO}$ (0.14)	$\text{C}_2\text{H}_8 + \text{CO}$ (0.20)	$\text{HF} + \text{CO}$ (0.04)	$\text{HCl} + \text{CO}$ (0.34)	$\text{HBr} + \text{CO}$ (0.82)	$\text{C}_2\text{H}_8 + \text{CO}$ (0.04)	$\text{HF} + \text{CO}$ (0.04)	$\text{HCl} + \text{CO}$ (0.05)	$\text{HBr} + \text{CO}$ (0.07)	$\text{C}_2\text{H}_8 + \text{CO}$ (0.21)	$\text{C}_2\text{H}_8 + \text{CO}$ (0.04)
$\text{Co}(\text{CO})_3\text{NO}^+$	$\text{CO}$ (1.00)	$\text{CO}$ (1.00)	$\text{CO}$ (1.00)	$\text{H}_2 + \text{CO}$ (0.14)	$\text{HF} + \text{CO}$ (0.14)	$\text{HCl} + \text{CO}$ (0.20)	$\text{HBr} + \text{CO}$ (0.45)	$\text{C}_2\text{H}_8 + \text{CO}$ (0.86)	$\text{HF} + \text{CO}$ (0.86)	$\text{HCl} + \text{CO}$ (0.35)	$\text{HBr} + \text{CO}$ (0.29)	$\text{C}_2\text{H}_8 + \text{CO}$ (0.45)	$\text{HBr} + \text{CO}$ (1.00)

<sup>a</sup> Neutral products for observed processes with branching ratios are listed.

Scheme I. The Formation of Metal-Butadiene Complexes



Scheme II



Scheme III

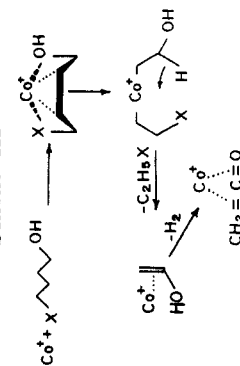


Table II. Rearrangement Energies<sup>a</sup>

reaction	$\Delta H_{\text{rxn}}$ , kcal/mol			
	X = F	OH	Cl	Br
$n\text{-C}_4\text{H}_9\text{X} \rightarrow \text{C}_4\text{H}_9\cdot + \text{X}\cdot$	107.3	94.3	83.0	70.9
$\rightarrow \text{C}_4\text{H}_8 + \text{HX}$	5.1	8.7	13.3	16.9
$\rightarrow \text{C}_4\text{H}_8 + \text{HX} + \text{H}_2$	31.4	35.0	39.7	43.3
$\text{HO}(\text{CH}_2)_4\text{X} \rightarrow \cdot\text{C}_4\text{H}_8\text{X} + \text{OH}\cdot$	90.1		90.1	90.1
$\rightarrow \cdot\text{C}_4\text{H}_8\text{OH} + \text{X}\cdot$	102.8		78.0	63.7
$\rightarrow \text{C}_4\text{H}_8 + \text{H}_2\text{O} + \text{HX}$	76.8		84.5	85.9
$\rightarrow \text{C}_4\text{H}_8\text{OH} + \text{HX}$	5.1		12.8	14.2
$\text{Cl}(\text{CH}_2)_4\text{Br} \rightarrow \text{C}_4\text{H}_6 + \text{HCl} + \text{HBr}$	$\Delta H_{\text{rxn}} = 23.3$			

<sup>a</sup> Thermodynamic data were taken from ref 26–28. In cases where heats of formation were not available, these were estimated by using the group equivalence data in ref 27.

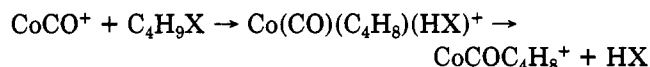
Table III. Pertinent Proton Affinities<sup>a</sup>

ligand	PA, kcal/mol	ref
HF	112	29
HCl	141 ± 3	30
HBr	140 ± 3	30
$\text{C}_4\text{H}_8$	183	31
$\text{H}_2$	101	32
CO	139.0	33
$\text{CH}_2\text{O}$	165 ± 3, 177.2	34, 35
$\text{H}_2\text{O}$	173.0	34
$\text{CH}_3\text{OH}$	184.9	34
$\text{CH}_2\text{CO}$	201 ± 2	36
$\text{CH}_3\text{F}$	151	37
$\text{CH}_3\text{Cl}$	160	37
$\text{CH}_3\text{Br}$	163	37
$\text{C}_2\text{H}_5\text{F}$	163	37
$\text{C}_2\text{H}_5\text{Cl}$	167	37
$\text{C}_2\text{H}_5\text{Br}$	170	37
$\text{C}_2\text{H}_5\text{OH}$	190.3	34

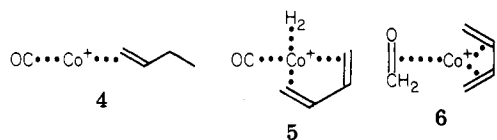
<sup>a</sup> Proton affinity, PA, is defined as follows: for the reaction  $\{\text{A} + \text{H}^+ \rightleftharpoons \text{AH}^+\}$ ,  $\text{PA}(\text{A}) \equiv -\Delta H^\circ$ . (Metal ion affinity has an analogous definition). It should be noted that PA's are frequently reported assuming a particular value for  $\text{PA}(\text{NH}_3)$ . This value has varied by a few kilocalories per mol in recent years. Reference 34 discusses this problem and adjusts previously reported PA's using the value of  $\text{PA}(\text{NH}_3) = 205.0$  kcal/mol.

assume that the  $\text{Co}^+-\text{C}_4\text{H}_8$  interaction is reflected in its PA. Nonetheless, reactions reported here suggest a very strong  $\text{Co}^+-\text{C}_4\text{H}_8$  bond.

The  $\text{CoCO}^+$  ion reacts with the halobutanes to eliminate HX.



The simplest predicted structure of the product of the reaction is structure 4 as a result of HX loss from the



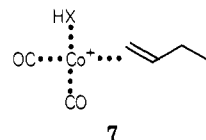
intermediate shown. Structures 5 and 6 result from transfer of two H atoms from  $\text{C}_4\text{H}_8$  to another part of the intermediate complex (i.e., two H atoms can migrate to the metal as an  $\text{H}_2$  ligand or to the CO). Structure 5 is not acceptable since the  $\text{H}_2$  would have been lost preferentially over the HX. Product 6 cannot be ruled out. Here, two H atoms are "stored" on the CO which has become  $\text{CH}_2\text{O}$ . Thermodynamically, this would be a favorable situation, since  $\text{PA}(\text{CH}_2\text{O}) > \text{PA}(\text{CO})$  by more than 25 kcal/mol. That is, transfer of two H atoms to CO produces a more strongly bound ligand. The chemistry of  $\text{CoCO}^+$  with

alkanes also suggests that  $\text{H}_2$  may be "reversibly" stored on a CO ligand by forming  $\text{CH}_2\text{O}$ .<sup>20</sup> This would also explain why reaction 14 is not observed. Since the proton



affinities of the hydrogen halides (HX) are similar to that for CO, CO loss and HX loss may be expected to be competitive processes. If, however, CO and  $\text{C}_4\text{H}_8$  become  $\text{H}_2\text{CO}$  and  $\text{C}_4\text{H}_6$  on the metal, only HX elimination would be expected.

The  $\text{Co}(\text{CO})_2^+$  ion reacts with the halobutanes to form the same products as  $\text{CoCO}^+$  forms. An intermediate such as 7 is reasonable since it does not violate the 18-electron



rule and would predict that the weakly bound ligands are HX and CO. Since two CO's are not lost, a final product structure of 6, again, cannot be ruled out. Structure 6 may explain why  $\text{CoCO}^+$  does not lose CO as a neutral, while  $\text{Co}(\text{CO})_2^+$  reacts only by losing one CO (never two). Again, the formation of butadiene may be the driving force leading to the conversion of CO to formaldehyde.<sup>21</sup>

The  $\text{Co}(\text{CO})_x\text{NO}^+$  ions appear to react only by ligand substitution. There is no evidence that  $\text{C}_4\text{H}_9\text{X}$  is bound to the metal in the reaction products in any way except as the intact molecule. Note that the  $\text{Co}(\text{CO})_x\text{NO}^+$  ions do not react with fluorobutane. When  $\text{Co}(\text{CO})_x\text{NO}^+$  reacts with a haloalkane, an initial complex,  $\text{Co}(\text{CO})_x\text{NO}(\text{XR})^+$ , is formed. If the metal-RX interaction is strong, one or more CO's may be lost or a ligand decomposition may occur. Of the compounds studied, alkyl fluorides have the lowest PA's of the alkyl halides.<sup>22</sup> Thus, the initial metal-alkyl halide interaction should be least for X = F. The  $\text{PA}(\text{C}_4\text{H}_9\text{F})$  should be slightly greater than  $\text{PA}(\text{CO})$ , but this energy difference may not be large enough to overcome any activation barriers that lead to CO loss. (If this would ever be the case, it would occur for alkyl fluorides.)

In summary, the first part of Table I shows that the  $\text{Co}(\text{CO})_x^+$  and  $\text{Co}(\text{CO})_x\text{NO}^+$  ions react with halobutanes to give products similar to those observed for other haloalkanes. The main difference between halobutanes and smaller haloalkanes which have been previously studied is that, when such a molecule contains a four-carbon chain, HX elimination can be followed by  $\text{H}_2$  elimination to form a metal-butadiene complex.

**Reactions of 4-Chloro-1-bromobutane.** The observed chemistry of the metal-containing species under study with this 1,4-dihalobutane parallels, in some respects, the halobutane reactions.  $\text{Co}^+$  reacts by chloride and bromide abstraction but does not abstract both halogens simultaneously (in contrast to, e.g., 1,2-dihaloethanes). This is expected, since the formation of a diradical would accompany a  $\text{CoClBr}^+$  product, which would not be thermodynamically possible. Apparently, interaction with the "Br end" of the molecule is favored over the "Cl end". Both homolytic and heterolytic cleavage of the C-Br bond is

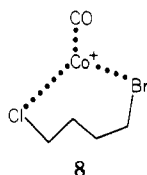
(20) Radecki, B.; Allison, J., unpublished results.

(21) Approximately 25 kcal/mol are required to form butadiene and formaldehyde from 1-butene and CO. The additional metal-ligand binding energies which would result may be the driving force for such a process.

(22) It is assumed here that, for the halobutanes, the PA decreases as X = Br → F. This is apparently the trend for similar molecules (HX,  $\text{CH}_3\text{X}$ ,  $\text{C}_2\text{H}_5\text{X}$ ).

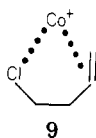
thermodynamically favored over the C-Cl bond, so this behavior may be expected. Note that, when  $\text{Co}^+$  reacts to form, e.g.,  $\text{CoCl}$ , the results  $\text{C}_4\text{H}_8\text{Br}^+$  could be a cyclic halonium ion. Again,  $\text{Co}^+$  induces the formation of a metal-butadiene complex. Scheme I suggests possible differences in mechanism in the formation of butadiene from a 1,4-bisubstituted butane in contrast with a 1-halobutane. Scheme IB suggests that, if HBr elimination occurs first, HCl loss may proceed in two ways. If the next step is formation of an *allyl-type* intermediate, a Cl shift must follow. While,  $\beta$ -halide shifts are typically not observed, allyl intermediates are commonly suggested.<sup>23</sup> Alternatively, insertion into C-Cl followed by a  $\beta$ -H shift may lead to HCl elimination.

The reactions of  $\text{CoCO}^+$  also suggest that reaction at the "Br end" of this compound is favored over reaction at the "Cl end". Again, the formation of  $\text{CoC}_4\text{H}_8^+$  is observed. The reactions of  $\text{CoCO}^+$  may indicate that an initial interaction of both halogens with the metal *may* occur (structure 8). Presumably, the energy required to form



8

$\text{CoCl}$  from  $\text{C}_4\text{H}_9\text{Cl}$  and  $\text{CoCO}^+$  is the same as with  $\text{BrC}_4\text{H}_8\text{Cl}$  as a reactant. Since the reaction only occurs for the dihalo compound, this may suggest the additional interaction shown in 8 that could provide additional energy in the complex to overcome any energy barrier. Since loss of  $\{\text{HCl} + \text{CO}\}$  is not observed as a process competitive with loss of  $\{\text{HBr} + \text{CO}\}$ , we assume that loss of  $\{\text{HBr} + \text{CO}\}$  implies a product with the structure 9. Note that  $\text{CoCO}^+$



9

loses CO in a number of reactions with bromochlorobutane. The loss of CO was not observed in reactions with the halobutanes. This may support the proposal that halobutanes react to form butadiene by "storing"  $\text{H}_2$  on a CO (since there is no evidence suggesting a similar mechanism for bromochlorobutane leading to the formation of butadiene by "storing" HCl on a CO ligand).

The  $\text{Co}(\text{CO})_2^+$  reactions also indicate preferential HBr elimination over HCl elimination.

Presumably, bromochlorobutane reacts with  $\text{CoNO}(\text{CO})_{2,3}^+$  by ligand substitution only. Since the bifunctional butane can displace three CO's, where the halobutanes displace only two CO's, multiple metal-ligand interactions of the type shown in 8 are again suggested.

**Reactions of 1-Butanol.** Fragmentation patterns following metal-induced rearrangements differ for butyl halides and butanol since  $\text{H}_2\text{O}$  and olefins have similar metal ion affinities (whereas hydrogen halides are much weaker in their interaction with metals than are olefins). Also, for many processes, alcohols are (thermodynamically) between chloroalkanes and fluoralkanes (see Table II). This, however, is not the trend for proton affinities. While PA information is not available for the halobutanes and butanol, data on the methyl and ethyl species indicate that the alcohols have much higher PA's than any of the ha-

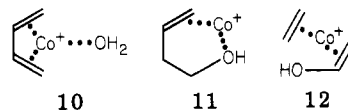
Table IV. CID Results/Ionic Products of  $\text{CoCO}^+$  with Butanol

$$\text{CoCO}^+ + n\text{-C}_4\text{H}_9\text{OH} \begin{cases} \rightarrow \text{CoC}_4\text{H}_{10}\text{O}^+ (m/z 133) + \text{CO} \\ \rightarrow \text{CoCOC}_4\text{H}_8\text{O}^+ (m/z 159) + \text{H}_2 \end{cases}$$

CID products of $m/z$ 133			CID products of $m/z$ 159		
$m/z$	RI	assignt	$m/z$	RI	assignt
59	69.4	$\text{Co}^+$	59	10.2	$\text{Co}^+$
77	34.7	$\text{CoH}_2\text{O}^+$	87	22.5	$\text{CoCO}^+$ and/or $\text{CoC}_2\text{H}_4^+$
87	100	$\text{CoC}_2\text{H}_4^+$	103	5.1	$\text{CoC}_2\text{H}_3\text{OH}^+$
105	39.8	$\text{CoCOH}_2\text{O}^+$ and/or $\text{CoC}_2\text{H}_3\text{OH}^+$	131	100	$\text{CoC}_4\text{H}_8\text{O}^+$
113	19.8	$\text{CoC}_4\text{H}_6^+$			
115	38.7	$\text{CoC}_4\text{H}_8^+$			
131	29.8	$\text{CoC}_4\text{H}_8\text{O}^+$			

lobutanes. This may explain the failure of  $\text{Co}^+$  to form  $\text{CoOH}$  from butanol. The initial  $\text{Co}^+$ -organic interaction will be greatest for butanol. This energy may favor metal insertion instead of having insertion and abstraction compete, as is the case for haloalkanes. Note that  $\text{Co}^+$  does not form  $\text{CoOH}^-$  in its reaction with ethanol (a primary alcohol), but it does with 2-propanol (a secondary alcohol).<sup>13</sup>

One way of explaining the products observed for 1-butanol is shown in Scheme II. Scheme II follows the assumption that the metal first rearranges butanol into butene and  $\text{H}_2\text{O}$  and butene can then be induced to lose  $\text{H}_2$ ; thus, loss of  $\text{H}_2$  as a neutral product implies that  $\{\text{C}_4\text{H}_8\text{O}\}$  on the metal is actually two ligands,  $(\text{C}_4\text{H}_8)(\text{H}_2\text{O})$ . If  $\text{H}_2$  elimination is observed, a number of ionic product complexes can be postulated (10-12).



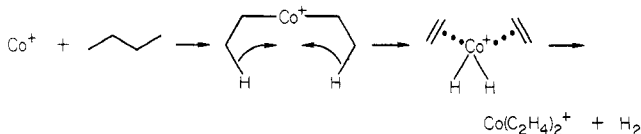
10

11

12

Complex 10 might be preferred since all studies of transition-metal ion reactions with alcohols give  $\text{H}_2\text{O}$  elimination. Thus, one might expect this to always be a first step. A second possible structure, 11, would only involve  $\text{H}_2$  elimination forming a double bond between two skeletal atoms of butanol. There is some evidence in the literature that, as the alkyl chain of monofunctional organic molecules *increases*, alkane-like chemistry is observed in addition to the reactions expected for that functional group.<sup>3b</sup> Thus, we may expect the four-carbon chain to exhibit, to some extent, a chemistry typical for alkanes, such as reaction by  $\text{H}_2$  elimination.

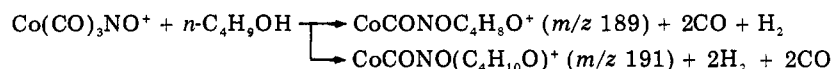
Recent work on alkanes suggests yet another mechanism for  $\text{H}_2$  elimination. A fraction of the  $\text{H}_2$  elimination in the reaction of  $\text{Co}^+$  with *n*-butane appears to follow metal insertion into the central C-C bond:<sup>24</sup>

 $\text{Co}(\text{C}_2\text{H}_4)_2^+ + \text{H}_2$ 

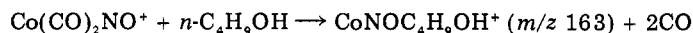
(24) Houriet, R.; Halle, L. F.; Beauchamp, J. L., unpublished results.

(25) The mechanism in Scheme IV may not appear to be one that requires the presence of an alcohol group. That is, the same intermediate may be expected for the halobutanes. However, the OH group significantly effects the strength of the adjacent C-C bond. Consider molecules of the type  $\text{CH}_3\text{CH}_2\text{X}$ . The C-C bond strength is 86-89 kcal/mol for X = H, Cl, F, and Br but drops to 71 kcal/mol for X = OH. Thus, the mechanism shown in Scheme IV makes a (relatively weakened) bond available for insertion. Without the OH present, this bond is less susceptible (thermodynamically) to attack. Thus, the halogen contributes to the reaction mechanistically, and the alcohol contributes thermodynamically.

(23) Allyl intermediates are suggested in ref 19.

Table V. CID Results/Ionic Products of  $\text{Co}(\text{CO})_{2,3}\text{NO}^+$  with Butanol

CID products of <i>m/z</i> 189			CID products of <i>m/z</i> 191		
<i>m/z</i>	RI	assignt	<i>m/z</i>	RI	assignt
87	11.2	$\text{CoCO}^+$	57	12.4	$\text{C}_4\text{H}_9^+$
89	9.1	$\text{CoNO}^+$	107	39.3	$\text{CoNOH}_2\text{O}^+$
161	100	$\text{CoNO}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})^+$	115	2.3	$\text{CoC}_4\text{H}_8^+$
			145	12.0	$\text{CoNOC}_4\text{H}_8^+$
			161	1.5	$\text{CoNOC}_4\text{H}_8\text{O}^+$ (possibly $\text{CoNO}(\text{C}_4\text{H}_8)(\text{H}_2\text{O})^+$ )
			163	100	$\text{CoNOC}_4\text{H}_{10}\text{O}^+$



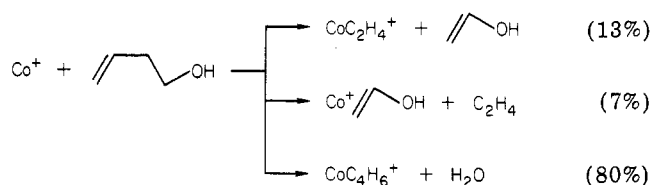
CID products of <i>m/z</i> 163					
<i>m/z</i>	RI	assignt	<i>m/z</i>	RI	assignt
41	8.2	$\text{C}_3\text{H}_5^+$	115	19.7	$\text{CoC}_4\text{H}_8^+$
57	50.4	$\text{C}_4\text{H}_9^+$	135	2.4	$\text{CoNOC}_4\text{H}_8\text{O}^+$
89	37.3	$\text{CoNO}^+$	145	25.5	$\text{CoNOC}_4\text{H}_8^+$
107	100	$\text{CoNOH}_2\text{O}^+$			

Such a mechanism would lead to the structure 12.

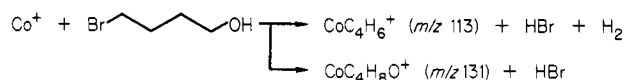
The reaction products of  $\text{CoCO}^+$  could be explained by a mechanism very similar to Scheme II. With use of the proton affinity rule, the only unexpected process is the loss of  $\text{C}_4\text{H}_8$ , which should not be lost in the presence of a CO ligand.

Table IV lists CID results for two ions that were products of  $\text{CoCO}^+$  reaction with butanol.

The CID spectrum of  $\text{CoC}_4\text{H}_{10}\text{O}^+$  implies that it exists as a mixture of  $\text{Co}(\text{C}_4\text{H}_8)(\text{H}_2\text{O})^+$  (which would have as CID products, *m/z* 77, 115, and 113) and  $\text{Co}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_5\text{OH})^+$  (which would form *m/z* 87 and 105 as CID products). The major CID product of  $\text{CoCOC}_4\text{H}_8\text{O}^+$  is  $\text{CoC}_4\text{H}_8\text{O}^+$ , implying that  $\text{H}_2$  elimination occurs leaving the molecular skeleton intact; i.e., the structure is similar to 11. The CID products at *m/z* 87 and 103 may be CIR products of a species similar to 11 since the following reactions have been observed for 3-buten-1-ol<sup>38</sup> with  $\text{Co}^+$ :



That is, evidence suggests that structures 10, 11, and 12 are formed during  $\text{H}_2$  elimination. If 12 is a contributing

Table VI. CID Results/Ionic Products from Reactions of  $\text{Co}^+$  with 4-Bromo-1-butanol

CID products of <i>m/z</i> 113			CID products of <i>m/z</i> 131		
<i>m/z</i>	RI	assignt	<i>m/z</i>	RI	assignt
59	100	$\text{Co}^+$	113	100	$\text{CoC}_4\text{H}_6^+$
			103	13.1	$\text{CoC}_2\text{H}_3\text{OH}^+$
			101	29.0	$\text{CoC}_3\text{H}_6^+$
			89	4.0	$\text{CoCH}_3\text{O}^+$
			87	1.0	$\text{CoC}_2\text{H}_4^+$
			71	41.4	$\text{C}_4\text{H}_7\text{O}^+$
			59	50.5	$\text{Co}^+$

structure, loss of " $\text{C}_4\text{H}_8$ " (56 u) may, instead, be loss of  $\{\text{CO}$  and  $\text{C}_2\text{H}_4\}$ . This possibility is consistent with the PA rule.

The formation of  $\text{CoNOH}_2\text{O}^+$  in the reaction of  $\text{CoNO}^+$  with 1-butanol parallels smaller alcohol reactions with this ion. Selective retention of  $\text{H}_2\text{O}$  over olefins is consistently observed<sup>13</sup> for  $\text{CoNO}^+$ . The same is observed for  $\text{CoCO-NO}^+$ .

The reactions observed for  $\text{Co}(\text{CO})_{2,3}\text{NO}^+$  cannot go through intermediates with all ligands bound to the metal; i.e., reactions must proceed through a series of ligand losses and metal-induced reactions. That is, intermediates such as  $\text{Co}(\text{CO})_3\text{NO}(\text{C}_4\text{H}_8\text{O})(\text{H}_2)^+$  would not be expected.

CID results on some products of  $\text{Co}(\text{CO})_{2,3}\text{NO}^+$  reactions are listed in Table V. The CID spectra of *m/z* 163 and 191 imply that  $\text{C}_4\text{H}_{10}\text{O}$  exists on the metal predominately as  $\{\text{C}_4\text{H}_8$  and  $\text{H}_2\text{O}\}$ . Also, the CID spectrum of the product of *m/z* 189 suggests that  $\text{H}_2$  loss occurs leaving a structure similar to 11.

Thus, in light of the reported chemistry of alcohols with  $\text{CoL}_n^+$  to date, 1-butanol is surprising in its reactivity. The high PA of alcohols suggests a strong initial metal-alcohol interaction. That is, in the formation of the complex  $[\text{CoLn}(\text{RX})]^+$ , a relatively large amount of energy is available in the complex when  $\text{X} = \text{OH}$ . This energy may promote this rich chemistry. CID results are useful in attempting to make structural assignments for product ions.

**Reactions of 4-Halo-1-butanols.** In light of the results for the halobutanes, butanol, and chlorobromobutane, the halobutanols exhibit an unexpected chemistry. Insertion

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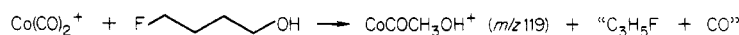
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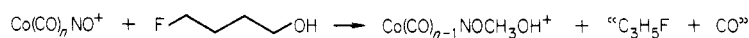
(38) Tzaropoulos, A.; Allison, J., unpublished results.



Table VII. CID Results/Products of Reactions with Fluorobutanol

CID products of  $m/z$  119

$m/z$	RI	assignt
91	39.4	$\text{CoCH}_2\text{OH}^+$
87	100	$\text{CoCO}^+$
59	44.8	$\text{Co}^+$



$$n = 1, m/z 121$$

$$n = 2, m/z 149$$

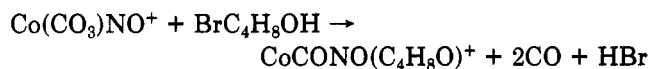
$$n = 3, m/z 177$$

CID products of $m/z$ 121			CID products of $m/z$ 149			CID products of $m/z$ 177		
$m/z$	RI	assignt	$m/z$	RI	assignt	$m/z$	RI	assignt
91	9.1	$\text{CoCH}_2\text{OH}^+$	121	18.4	$\text{CoNOCH}_2\text{OH}^+$	121	53.7	$\text{CoNOCH}_2\text{OH}^+$
89	100	$\text{CoNO}^+$	119	1.5	$\text{CoCOCH}_2\text{OH}^+$	117	8.1	$\text{CoCONO}^+$
59	29.0	$\text{Co}^+$	117	1.3	$\text{CoCONO}^+$	91	9.3	$\text{CoCH}_2\text{OH}^+$
			91	8.2	$\text{CoCH}_2\text{OH}^+$	89	100	$\text{CoNO}^+$
			89	100	$\text{CoNO}^+$	59	13.4	$\text{Co}^+$
			59	19.4	$\text{Co}^+$			

into C-C bonds becomes a major mechanistic step in many cases.

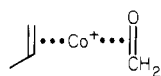
Again, the formation of  $\text{Co}^+$ -butadiene is observed. The fact that this reaction occurs for bromobutanol requires that  $D(\text{Co}^+-\text{C}_4\text{H}_6) \geq 85.9$  kcal/mol. (Note that 85.9 kcal/mol is more than twice the reported  $\text{Co}^+-\text{C}_2\text{H}_4$  bond strength of 37 kcal/mol.<sup>39</sup>) Table VI indicates the CID spectrum of a  $\text{CoC}_4\text{H}_6^+$  product with no evidence for any structure except a simple metal-alkadiene complex.

In the formation of  $\text{Co}^+$ -butadiene, dehydration and dehydrohalogenation occur. The data in Table I suggest that dehydrohalogenation may occur *first*, since it can occur without subsequent dehydration. Consider the reaction of  $\text{Co}(\text{CO})_3\text{NO}^+$  with bromobutanol by loss of  $\{\text{HBr} + 2\text{CO}\}$ .



The  $\text{C}_4\text{H}_8\text{O}$  must exist intact on the metal, since other possibilities such as the combination of ligands  $\{\text{C}_4\text{H}_6$  and  $\text{H}_2\text{O}\}$  would violate the 18-electron rule. Thus, HBr elimination was induced but not  $\text{H}_2\text{O}$  elimination.

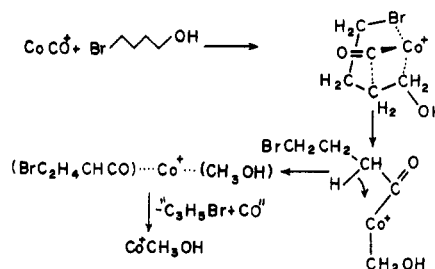
$\text{Co}^+$  reacts with chloro- and bromobutanol by eliminating HX. Again, similar to the assignment problem in butanol alone, a number of product structures could be suggested (10, 11, 12). The CID data in Table VII may be interpreted as evidence for a mixture of all *three* structures, plus, possibly a fourth, 13. The most surprising reaction of  $\text{Co}^+$



13

is the elimination of  $\{\text{C}_2\text{H}_5\text{X} + \text{H}_2\}$  from the three halo-butanol. Note that a similar pathway was not observed for the monofunctional compounds or the dihalobutane in Table I. Apparently, both functional groups (one being an OH) contribute to an intermediate geometry favoring attack of the central C-C bond, presumably following the mechanism shown in Scheme III. Transition-metal ion-alkene complexes have been previously observed as reaction products.<sup>2b,3a</sup> Failure to see the intermediate  $\text{Co}^+$ -allyl

## Scheme IV



alcohol complex is, however, surprising.

The  $\text{CoCO}^+$  ion reacts to form a metal-methanol complex. Note that (a) loss of  $\text{C}_3\text{H}_5\text{X}$  does not occur with  $\text{Co}^+$  or  $\text{CoNO}^+$  as a reactant, (b) the process *only* occurs with CO's present on the metal, (c) one CO is always *lost*, and (d) the process *only* occurs for the bifunctional compounds, where one group is an alcohol.

These observations suggest a mechanism involving insertion of the  $\text{CoCO}$  groups into a C-C bond followed by a  $\beta$ -H shift, leaving a methanol complex. A possible mechanism is given in Scheme IV. The implication in the scheme is that the initial complex is of a geometry such that attack of the C-C(OH) bond is favored.<sup>25</sup>

Table I shows that the mechanism in Scheme IV occurs for fluoro- and chlorobutanol, with  $\text{CoCO}^+$ ,  $\text{Co}(\text{CO})_2^+$ , and  $\text{Co}(\text{CO})_2\text{NO}^+$ . In contrast, the reaction *only* occurs for bromobutanol with  $\text{CoCO}^+$ . Since the C-X bond is weakest for X = Br (of the series of halogens studied), metal insertion leading to HBr elimination may occur much more readily than insertion into C-C bonds.

The  $\text{Co}(\text{CO})_x\text{NO}^+$  reactions with the halo-butanol are fairly straightforward. Note that, while monofunctional compounds appear to react with the  $\text{Co}(\text{CO})_x\text{NO}^+$  ions predominately by ligand *displacement*, bifunctional molecules exhibit a rich chemistry with these ions.

A number of product ions of the type  $\text{Co}(\text{CO})_x\text{CH}_2\text{OH}^+$  and  $\text{CoNO}(\text{CO})_x\text{CH}_2\text{OH}^+$  from reactions of fluorobutanol were analyzed by collision induced dissociation. The results are given in Table VII. These results imply simple complexes containing methanol intact.

## Summary

Reaction products of gas-phase organometallic ion-molecule reactions do not always reflect the extent to

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which organic molecules can be "decomposed" by a metal center into smaller molecules. The proton affinity rule works well in providing insights into mechanisms and ion structures. Metal ions such as  $\text{Co}^+$  react with 1-halobutanes by mechanisms similar to smaller haloalkanes. Such reactants containing a four-carbon chain readily form metal-butadiene complexes. Bifunctional butanes exhibit an unexpected chemistry with metal ions.  $\text{Co}^+$  attacks the central C-C bond of halobutanol while  $\text{CoCO}^+$  prefers to attack the C-C(OH) bond. CID analysis can be very useful but can be difficult to interpret because of the ease with which collision-induced decomposition of ligands occurs.

When  $\text{Co}^+$  is forced to "choose" over the OH and X groups of a 1,4-bisubstituted butane, some preference for the halogen is suggested.

Work is now under way investigating the reactions of  $\text{Co}^+$  with molecules containing three- to six-carbon chains in an effort to shed more light on the mechanisms suggested here.

**Acknowledgment** is made to the NSF (CHE-8023704) and the Dow Chemical Company Foundation for support of this work. Also, the assistance of Dr. Anne Giordani in obtaining CID data was appreciated.

**Registry No.**  $\text{Co}^+$ , 16610-75-6;  $\text{CoCO}^+$ , 28963-35-1;  $\text{Co}(\text{CO})_2^+$ , 28963-34-0;  $\text{CoNO}^+$ , 87616-10-2;  $\text{CoCONO}^+$ , 61816-95-3;  $\text{Co}(\text{CO})_2\text{NO}^+$ , 61816-96-4;  $\text{Co}(\text{CO})_3\text{NO}^+$ , 52309-13-4;  $\text{Co}(\text{CO})_3\text{NO}$ , 14096-82-3;  $n\text{-C}_4\text{H}_9\text{F}$ , 2366-52-1;  $n\text{-C}_4\text{H}_9\text{Cl}$ , 109-69-3;  $n\text{-C}_4\text{H}_9\text{Br}$ , 109-65-9;  $n\text{-C}_4\text{H}_9\text{OH}$ , 71-36-3;  $\text{HO}(\text{CH}_2)_4\text{F}$ , 372-93-0;  $\text{HO}(\text{CH}_2)_4\text{Cl}$ , 928-51-8;  $\text{HO}(\text{CH}_2)_4\text{Br}$ , 33036-62-3;  $\text{Cl}(\text{CH}_2)_4\text{Br}$ , 6940-78-9.

## Syn-Gas Reactions with Co Subgroup Cluster Catalysts. 1. Interaction of $\text{M}_x\text{Co}_{4-x}(\text{CO})_{12}$ ( $\text{M} = \text{Rh}$ , $x = 4, 2-0$ ; $\text{M} = \text{Ir}$ , $x = 4, 2, 0$ ) with Tertiary Amine Functionalized Supports

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The interaction of the series of Co subgroup clusters  $\text{Rh}_x\text{Co}_{4-x}(\text{CO})_{12}$  ( $x = 4, 2-0$ ) and  $\text{Ir}_x\text{Co}_{4-x}(\text{CO})_{12}$  ( $x = 4, 2, 0$ ) with amine-functionalized polystyrene, polyacrylate, or silica has been examined. Infrared studies, extractive separations with quaternary ammonium perchlorate, and plasma emission metal analyses reveal the clusters undergo fragmentation and redistribution to give mononuclear and polynuclear anionic and/or cationic products. The influence of residual  $\text{Cl}^-$  on the functionalized resins has been examined. All evidence points to segregation of the two metals in the products. Although such studies do not allow unequivocal structural assignment for all the products observed, it is clear that different reactivity patterns exist for the different clusters with the different supports.

### Introduction

Homogeneous catalysis by cluster complexes has recently attracted much attention<sup>1-3</sup> as systems have been reported that catalyze commercially important reactions such as hydroformylation,<sup>4</sup> water gas shift,<sup>5</sup> oxidation<sup>6</sup> and  $\text{CO}/\text{H}_2$  to ethylene glycol.<sup>7</sup> Although these catalyst sys-

tems initially contain metal clusters, proving the clusters remain intact and/or are the catalytically active species is always more difficult. Indeed, reports on catalysis of the Fischer-Tropsch reaction by  $\text{Ru}_3(\text{CO})_{12}$ <sup>8</sup> and catalysis of hydroformylation by  $\text{Co}_3(\text{CO})_9(\mu_3\text{-CPh})$ <sup>9</sup> have recently been reinterpreted as catalysis due to mononuclear species.<sup>10,11</sup> The potential of bimetallic clusters in syn-gas catalysis has, in general, been cast into doubt since the reports of Geoffroy et al.<sup>12</sup> indicated that a variety of such

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