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Formation of Ionic Transition-Metal Carbonyl Cluster Fragments by Ion–Molecule Reactions. 3. The Heteronuclear Systems

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Abstract: The ion–molecule reaction chemistry of the $Co(CO)_3(NO)/Ni(CO)_4$, $Co(CO)_3(NO)/Fe(CO)_5$, and $Ni(CO)_4/Fe(CO)_5$ heteronuclear systems is presented. The relative reaction rate and cluster valence electron deficiency of the ionic cluster fragments are used to estimate the bond order of the ionic cluster fragments. The coordination unsaturation of the $Co(CO)_3(NO)/Ni(CO)_4$ system is very similar to the coordination unsaturation of the ionic cluster fragments found in the homonuclear $Cr(CO)_6$, $Fe(CO)_5$, $Co(CO)_3(NO)$, and $Ni(CO)_4$ systems. The ionic cluster fragments formed in the $Co(CO)_3(NO)/Fe(CO)_5$ and $Ni(CO)_4/Fe(CO)_5$ systems seem to follow bonding patterns found in heterometallic systems containing $Fe(CO)_4^{2-}$.

The structure, thermochemistry, ligand stereochemistry, and ligand mobility of transition-metal clusters are very similar to the structure, thermochemistry, stereochemistry, and mobility of metal surfaces and chemisorbed molecules on metal surfaces.[1] Therefore, many analogies have been made between transition-metal clusters and metal surfaces. For example, the core structure of metal clusters is a cubic closed-pack, hexagonal closed-pack, or body-centered-cubic fragment of a bulk metal structure. The geometric features of the bound ligands in a metal cluster are similar to the geometric features of adsorbed molecules on a metal surface. The average metal–ligand and metal–metal binding energies found in transition-metal clusters is also comparable to the average metal–metal binding energies of the metal surface and the binding energies for interactions between metal surfaces and chemisorbed molecules.[1] Ligand migration, which plays an important role in cluster catalysis, can serve as a model for surface mobility of chemisorbed species.[2]

However, the cluster/surface analogy (in terms of chemical properties) begins to break down when the coordination saturation of the transition-metal clusters is considered. Many clusters are stable, coordinatively saturated molecules and obey the 18-electron rule.[3] In many transition-metal clusters the coordination number for metal/ligand interactions is high, and the coordination number for metal/metal interactions is low. Conversely, the high coordination number for metal surfaces is due to the metal/metal interaction. Over the past four years our laboratory has actively pursued the development of synthetic methods for preparing coordinatively unsaturated ionic transition-metal cluster fragments. By using the approach ionic transition-metal cluster fragments having a range of numbers of metal atoms (typically 2–8) and ligands (typically CO) can be prepared. Thus, the chemical and physical properties of these clusters can be studied as a function of cluster size and metal-to-ligand ratio.

We have previously reported on the formation of ionic cluster fragments of $Cr_x(CO)_y^+$, $Fe_x(CO)_y^+$, $Co_x(CO)_y(NO)_z^+$, and $Ni_x(CO)_y^+$.[4] The electron deficiency (based on relative reactivity) of the ionic cluster fragments is used to estimate the bond order of the ionic cluster fragments. Comparison of the $Cr(CO)_6$, $Fe(CO)_5$, $Co(CO)_3(NO)$, and $Ni(CO)_4$ systems shows that the ionic cluster fragments can be divided into two categories: (1) ionic cluster fragments having simple polyhedral structures and (2) ionic cluster fragments which exhibit unusual binding of the ligands and/or metal centers, resulting in a high bond order. These two classes of ionic cluster fragments were then discussed in terms of the interrelationship of the reactivity/electron deficiency model and the cluster valence molecular orbital model (CVMO) developed by Lauher.[5] The electron deficiency model and CVMO model provide insight into the bonding of the ionic cluster fragments, but the CVMO model offers a better understanding of the sequence leading to the formation of the ionic cluster fragments.

To probe further the relationship between the CVMO theory and the reaction sequence of the ionic cluster fragments, we have examined the ion–molecule chemistry of the heteronuclear ionic cluster fragments of the $Co(CO)_3(NO)/Ni(CO)_4$, $Fe(CO)_5/Ni(CO)_4$, and $Fe(CO)_5/Co(CO)_3(NO)$ systems. Owing to the low yield for heteronuclear ionic cluster fragments for the $Cr(CO)_6/Fe(CO)_5$, $Cr(CO)_6/Co(CO)_3NO$, and $Cr(CO)_6/Ni(CO)_4$ systems, studies on these systems are not included in this report.

In this report we present the general ion–molecule reaction sequences for the ionic cluster fragments formed in the $Fe(CO)_5$, $Co(CO)_3NO$, and $Ni(CO)_4$ heteronuclear systems. The heteronuclear ionic cluster fragments are discussed in terms of their relative reactivity and degree of coordination unsaturation. The sequence of reactions leading to formation of the different ionic cluster fragments are then discussed in terms of the CVMO model. The principle objective of these studies is to develop a better understanding of the structure and bond order of these ionic cluster fragments. Such studies combined with studies on metal–metal and metal–ligand bond energies, chemical reactivity (ligand exchange reaction, oxidation, etc.), and electronic spectroscopy will aid in the development of fundamental understanding of metal chemistry, e.g., gas-phase metal ion/metal cluster reactivity and possibly catalysis.

Experimental Procedure

All the experiments described herein were carried out on a standard Nicolet FTMS-1000 equipped with a 3T magnet and a cubic (2.5 cm × 2.5 cm × 2.5 cm) ion cell. This system has been described in our earlier papers.[4] Samples were introduced to the system thru variable leak valves maintained at ambient temperatures. A total sample pressure of ca. 3×10^{-7} Torr, measured with a Granville-Phillips Gauge Controller Series 270, was employed for all studies. Electron impact ionization of the sample was performed by using 50 eV (nominal) ionizing energy and 100 ± – 10 nA of emission current. The ion cell trapping voltage was typically maintained at 1.25 V (16.5 V/m).

In some cases the ion–molecule reaction rate for the formation of the homonuclear ionic cluster fragments was much greater than the rate for formation of the heteronuclear ionic cluster fragments. For example, the

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Scheme I

$$M^+ + M(CO)_x(NO)_y \rightarrow M_2(CO)_{x-z}(NO)_{y-b}^+ \quad (1)$$

$$M^+ + M'(CO)_i(NO)_j \rightarrow MM'(CO)_{i-a}(NO)_{j-t}^+ \quad (2)$$

$$M'^+ + M'(CO)_i(NO)_j \rightarrow M'_2(CO)_{i-a}(NO)_{j-b}^+ \quad (3)$$

$$M'^+ + M(CO)_x(NO)_y \rightarrow M'M(CO)_{x-a}(NO)_{y-t}^+ \quad (4)$$

formation of $Fe_2(CO)_3^+$, a very facile reaction,[4a] dominates the mass spectrum and precludes observation of any heteronuclear ionic cluster fragments in both the $Ni(CO)_4/Fe(CO)_5$ and $Co(CO)_3NO/Fe(CO)_5$ systems. In order to minimize interferences from the $Fe_2(CO)_3^+$ ion, the pressure of $Fe(CO)_5$ was kept 3 times lower than the pressure of $Ni(CO)_4$ or $Co(CO)_3NO$. For the studies of the $Ni(CO)_4/Fe(CO)_5$ systems, the partial pressures of $Ni(CO)_4$ and $Fe(CO)_5$ were 2×10^{-7} and 8.0×10^{-8}, respectively.

Ion-ejection techniques were used to mass-select the reactant ion of interest. The procedures utilized for these studies have been described previously and are analogous to those used for collision-induced dissociation.[6] In all experiments the ion-ejection frequencies were selected so as to minimize the transitional excitation of the reactant ions.[4] The details concerning the ion-ejection procedures are given in our previous papers.[4]

Relative ion–molecule reaction rates and electron deficiencies were calculated as described previously.[4]

Results and Discussion

In this section the ion–molecule reactions of the heteronuclear systems $Co(CO)_3(NO)/Ni(CO)_4$, $Ni(CO)_4/Fe(CO)_5$, and $Fe(CO)_5/Co(CO)_3(NO)$ are discussed. The only reaction observed between $Cr(CO)_6$ and the group VIII–X metals was the reaction of M^+ ion of $Cr(CO)_6$ and $Fe(CO)_5$ to produce $CrFe(CO)_5^+$. Although it is of interest to note that the $CrFe(CO)_5^+$ ion does not react further with either $Cr(CO)_6$ or $Fe(CO)_5$, a good explanation for the stability of this ion must await additional studies. However, it is interesting to note that the $CrFe(CO)_5^+$ ion is isoelectric with $Cr_2(CO)_6^+$, an ion which is also quite unreactive.[4] In the case of $Cr_2(CO)_6^+$ the relative reactivity data are consistent with either a triple or quadruple Cr–Cr bond. Although it is quite plausible that $CrFe(CO)_5^+$ could have similar metal–metal bond, such an assignment is speculation at this time.

For a given mixed metal system, samples were simultaneously introduced to the analyzer. Electron impact ionization (50 eV nominal ionizing energy) of the samples produces a series of metal-containing ions, viz., $M(CO)_m(NO)_n^+$ and $M'(CO)_m(NO)_n^+$ (m = 3–5, n = 0–1). In order to study the ion–molecular chemistry of a specific ion, the reactant ion is mass-selected with use of ion-ejection techniques.[4] Following the mass-selection step a suitable delay time is imposed during which time the ion undergoes reactions with the neutral molecule. Because both metal carbonyl compounds are introduced to the analyzer and ionized simultaneously, it is not always possible to mass-select a particular reactant ion without affecting its transitional energy.[4,6d] For example, in the $Co(CO)_3(NO)/Ni(CO)_4$ mixed metal system there are pairs of ions, e.g., Co^+ and Ni^+, $Co(CO)^+$ and $Ni(CO)^+$, that are separated by only one mass unit. (Both the ^{58}Ni and ^{60}Ni isotopes are present.) In order to avoid translationally exciting the reactant ions no attempts were made to individually select Co^+ or Ni^+.[1,2] Instead both Co^+ and Ni^+ or $Co(CO)^+$ and $Ni(CO)^+$ were mass-selected and studied together.

The major advantage in using ion-ejection techniques to select the primary reactant ions is to obtain relative reactivity data for the various cluster ions, i.e., $M_x(CO)_y(NO)_z^+$, and to follow a specific sequence of reactions leading to cluster formation. However, the reaction schemes for the heteronuclear metal systems are complicated by the presence of both neutral metal carbonyls.

Scheme II

$$Ni^+ + Co(CO)_3(NO) \rightarrow NiCo(CO)_x(NO)^+ \quad (x = 1, 2) \quad (5)$$

$$Co^+ + Ni(CO)_4 \rightarrow NiCo(CO)_y^+ \quad (y = 2, 3) \quad (6)$$

$$NiCo(CO)_3^+ + Co(CO)_3(NO) \rightarrow NiCo_2(CO)_3(NO)^+ \quad (7)$$

$$NiCo(CO)(NO)^+ + Co(CO)_3(NO) \rightarrow NiCo_2(CO)_2(NO)_2^+ \quad (8)$$

$$NiCo(CO)_3^+ + Ni(CO)_4 \rightarrow Ni_2Co(CO)_4^+ \quad (9)$$

$$NiCo(CO)(NO)^+ + Ni(CO)_4 \rightarrow Ni_2Co(CO)_3(NO)^+ \quad (10)$$

$$Ni_2Co(CO)_4^+ + Co(CO)_3(NO) \rightarrow Ni_2Co_2(CO)_z(NO)^+ \quad (z = 4, 5) \quad (11)$$

$$NiCo_2(CO)_2(NO)_2^+ + Ni(CO)_4 \rightarrow Ni_2Co_2(CO)_4(NO)_2^+ \quad (12)$$

$$NiCo_2(CO)_3(NO)^+ + Co(CO)_3(NO) \rightarrow NiCo_3(CO)_4(NO)_2^+ \quad (13)$$

$$Ni_2Co(CO)_3(NO)^+ + Ni(CO)_4 \rightarrow Ni_3Co(CO)_6(NO)^+ \quad (14)$$

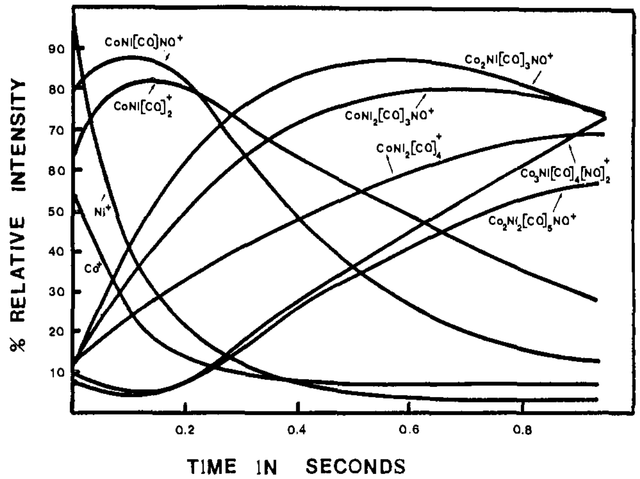

Figure 1. Temporal distribution of ionic cluster fragments formed when Co^+/Ni^+ react with $Co(CO)_3(NO)/Ni(CO)_4$.

For example, after mass-selection the M^+ and M'^+ ions can react with either the $M(CO)_x(NO)_y$ or $M'(CO)_i(NO)_j$ neutral (see reactions 1–4). Formation of both homo- and heterodinuclear species, e.g., $M_2(CO)_{x-a}(NO)_{y-b}^+$, $M'_2(CO)_{i-a}(NO)_{j-b}^+$, $MM'(CO)_{i-s}(NO)_{j-t}^+$, and $M'M(CO)_{x-s}(NO)_{y-t}^+$, complicates the reaction scheme (Scheme I). Because our previous papers described in detail the homonuclear ionic cluster fragments, this paper will deal only with those reactions which lead to formation of the heteronuclear ionic cluster fragments (for further details see the second paragraph of the Experimental Section).

In the following sections a detailed analysis of the cluster sequences for the $Co(CO)_3(NO)/Ni(CO)_4$, $Fe(CO)_5/Ni(CO)_4$, and $Fe(CO)_5/C(CO)_3(NO)$ systems is presented. The cluster sequence for the heteronuclear systems appears to be similar to the cluster sequences for the homonuclear systems, i.e., each successive ionic cluster fragment is formed by the addition of an $M(CO)_a$ moiety which corresponds to adding 14 electrons to the precursor ionic cluster fragments.[4b] The general reaction sequences for the heteronuclear systems have characteristic differences. For example, the ionic cluster fragments of the $Ni(CO)_4/Fe(CO)_5$ and $Co(CO)_3(NO)/Fe(CO)_5$ systems exhibit characteristic differences which we attribute to unusual bonding of the $Fe(CO)_x$ fragment. It appears that these ionic cluster fragments contain an $Fe(CO)_4^{2-}$ moiety which acts as a bulky analogue of an edge bridging carbonyl ligand.[7] Conversely, the ionic cluster fragments of the $Co(CO)_3(NO)/Ni(CO)_4$ system follow the bonding found in the triangular polyhedra of the boron hydrides.

$Co(CO)_3(NO)/Ni(CO)_4$. The largest ionic cluster fragments produced by the reaction of the Co^+ and Ni^+ ions with Co(C-

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[6] (a) For a discussion of ion cyclotron resonance spectrometry double resonance and ion-ejection techniques see: Lehman, T. A.; Bursey, M. N. *Ion Cyclotron Resonance Spectrometry*; Wiley-Interscience: New York, 1976. (b) Gross, M. L.; Rempel, D. L. *Science* **1984**, *226*, 261. (c) Johlman, C. L.; White, R. L.; Wilkins, C. L. *Mass Spectrom. Rev.* **1983**, *2*, 389. (d) Castro, M. E.; Russell, D. H. *Anal. Chem.* **1985**, *57S*, 2290. (e) Armstrong, J. T.; Beauchamp, J. L. *Rev. Sci. Instrum.* **1969**, *40*, 123. (f) Cody, R. B.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 2225.

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Scheme III

$$\mathrm{Ni(CO)^+ + Co(CO)_3(NO) \rightarrow NiCo(CO)_{\mathit{x}}(NO)^+} \quad (x = 2, 3) \tag{15}$$

$$\mathrm{Co(CO)^+ + Ni(CO)_4 \rightarrow NiCo(CO)_4{}^+} \tag{16}$$

$$\mathrm{NiCo(CO)_2(NO)^+ + Ni(CO)_4 \rightarrow Ni_2Co(CO)_{\mathit{y}}(NO)^+} \quad (y = 4, 5) \tag{17}$$

$$\mathrm{NiCo(CO)_4{}^+ + Co(CO)_3(NO) \rightarrow NiCo_2(CO)_{\mathit{y}}(NO)_2{}^+} \tag{18}$$

$$\mathrm{NiCo_2(CO)_5(NO)^+ + Co(CO)_3(NO)} \rightarrow \begin{cases} \mathrm{NiCo_3(CO)_5(NO)_2{}^+} & (19) \\ \mathrm{NiCo_3(CO)_6(NO)^+} & (20) \end{cases}$$

Scheme IV

$$\mathrm{Ni(CO)_2{}^+ + Co(CO)_3(NO) \rightarrow NiCo(CO)_{\mathit{x}}(NO)^+} \quad (x = 3, 4) \tag{21}$$

$$\mathrm{NiCo(CO)_3(NO)^+ + Co(CO)_3(NO)} \rightarrow \begin{cases} \mathrm{NiCo_2(CO)_5(NO)_5{}^+} & (22) \\ \mathrm{NiCo_2(CO)_6(NO)^+} & (23) \end{cases}$$

Scheme V

$$\mathrm{Co^+ + Fe(CO)_5 \rightarrow FeCo(CO)_3{}^+} \tag{24}$$

$$\mathrm{Fe^+ + Co(CO)_3(NO) \rightarrow FeCo(CO)(NO)^+} \tag{25}$$

$$\mathrm{FeCo(CO)(NO)^+ + Fe(CO)_5 \rightarrow Fe_2Co(CO)_3(NO)^+} \tag{26}$$

$$\mathrm{FeCo(CO)_3{}^+ + Fe(CO)_5 \rightarrow Fe_2Co(CO)_3{}^+} \tag{27}$$

$$\mathrm{FeCo(CO)(NO)^+ + Co(CO)_3(NO) \rightarrow FeCo_2(CO)_2(NO)_2{}^+} \tag{28}$$

$$\mathrm{FeCo_2(CO)_2(NO)_2{}^+ + Co(CO)_3(NO)} \rightarrow \begin{cases} \mathrm{FeCo_3(CO)_4(NO)_2{}^+} & (29) \\ \mathrm{FeCo_3(CO)_3(NO)_3{}^+} & (30) \end{cases}$$

O)$_3$(NO) and Ni(CO)$_4$ contain four metal atoms. The major tetranuclear ionic cluster fragments formed are $\mathrm{Co_2Ni_2(CO)_{\mathit{m}}(NO)^+}$ (m = 4, 5), $\mathrm{Co_3Ni(CO)_4(NO)_2{}^+}$, and $\mathrm{Ni_3Co(CO)_5(NO)^+}$. The overall reaction sequence is summarized in Scheme II. Only those ionic cluster fragments of 20% relative abundance or greater are included in Scheme II. The reaction scheme was confirmed by using ion-ejection techniques and by following the temporal distribution of the product ions. A temporal distribution of the various ionic cluster fragments initiated by reaction of the $\mathrm{Co^+}$ and $\mathrm{Ni^+}$ ions is shown in Figure 1. The data in Figure 1 give the relative abundance for each of the ionic cluster fragments, i.e., percent total ion current, vs. time.

The clustering sequence for the $\mathrm{Co(CO)^+/Ni(CO)^+}$ ions is similar to that for the $\mathrm{Co^+/Ni^+}$ ions. For instance, $\mathrm{Co(CO)^+/Ni(CO)^+}$ reacts to form ionic cluster fragments containing four metal atoms. The major tetranuclear ionic cluster fragments formed in this reaction sequence (Scheme III) are $\mathrm{NiCo_3(CO)_5(NO)_2{}^+}$ and $\mathrm{NiCo_3(CO)_6(NO)^+}$. Scheme IV contains the clustering sequence for the $\mathrm{Co(CO)_2{}^+/Ni(CO)_2{}^+}$ ions. The major difference between this scheme and Schemes II and III is the lack of any tetranuclear clusters. However, the relative abundance (RA) of the $\mathrm{Co(CO)_2{}^+}$ and $\mathrm{Ni(CO)_2{}^+}$ ions formed by ionization of $\mathrm{Co(CO)_3NO}$ and $\mathrm{Ni(CO)_4}$ is very low (ca. 10% RA). After mass-selection of these ions, the absolute number of reactant ions is low, thus leading to a sensitivity problem in detecting the larger ionic cluster fragments. Therefore, the relative abundance of the tetranuclear ionic cluster fragments is too low to be detected.

$\mathrm{Co(CO)_3(NO)/Fe(CO)_5}$. The clustering sequence for $\mathrm{Co^+/Fe^+}$ reacting with the $\mathrm{Co(CO)_3(NO)}$ and $\mathrm{Fe(CO)_5}$ neutrals is given in Scheme V. The largest ionic cluster fragments formed contain four metal atoms and include the $\mathrm{FeCo_3(CO)_4(NO_2)^+}$ and $\mathrm{FeCo_3(CO)_3(NO)_3{}^+}$ ions. Schemes VI and VII contain the clustering sequence for the $\mathrm{Co(CO)^+/Fe(CO)^+}$ and $\mathrm{Co(CO)_2{}^+/Fe(CO)_2{}^+}$ ions. In Schemes V–VII there is a lack of ionic cluster fragmetns containing more than two Fe atoms. However, to minimize the production of homonuclear $\mathrm{Fe_{\mathit{x}}(CO)_{\mathit{y}}{}^+}$ ionic cluster fragments the pressure of $\mathrm{Fe(CO)_5}$ is 3 times lower than the pressure of $\mathrm{Co(CO)_3(NO)}$. Since the number of possible collisions with $\mathrm{Fe(CO)_5}$ will be lower, the ratio of iron atoms to cobalt atoms in an ionic cluster fragment will be reduced.

Scheme VI

$$\mathrm{Co(CO)^+ + Fe(CO)_5 \rightarrow FeCo(CO)_4{}^+} \tag{31}$$

$$\mathrm{Fe(CO)^+ + Co(CO)_3(NO) \rightarrow FeCo(CO)_3(NO)^+} \tag{32}$$

$$\mathrm{FeCo(CO)_3(NO)^+ + Fe(CO)_5 \rightarrow Fe_2Co(CO)_3(NO)^+} \tag{33}$$

$$\mathrm{FeCo(CO)_4{}^+ + Fe(CO)_5 \rightarrow Fe_2Co(CO)_4{}^+} \tag{34}$$

$$\mathrm{FeCo(CO)_4{}^+ + Co(CO)_3(NO) \rightarrow FeCo_2(CO)_5(NO)^+} \tag{35}$$

$$\mathrm{FeCo(CO)_3{}^+\ Co(CO)_3(NO) \rightarrow FeCo_2(CO)_3(NO)_2{}^+} \tag{36}$$

Scheme VII

$$\mathrm{Fe(CO)_2{}^+ + Co(CO)_3(NO) \rightarrow FeCo(CO)_4(NO)^+} \tag{37}$$

$$\mathrm{FeCo(CO)_4(NO)^+ + Fe(CO)_5} \rightarrow \begin{cases} \mathrm{Fe_2Co(CO)_4{}^+} & (38) \\ \mathrm{Fe_2Co(CO)_3(NO)^+} & (39) \end{cases}$$

$$\mathrm{FeCo(CO)_4(NO)^+ + Co(CO)_3(NO)} \rightarrow \begin{cases} \mathrm{FeCo_2(CO)_5(NO)^+} & (40) \\ \mathrm{FeCo_2(CO)_5(NO)_2{}^+} & (41) \end{cases}$$

$$\mathrm{FeCo_2(CO)_5(NO)^+ + Fe(CO)_5 \rightarrow Fe_2Co_2(CO)_5(NO)^+} \tag{42}$$

Scheme VIII

$$\mathrm{Ni^+ + Fe(CO)_5 \rightarrow FeNi(CO)_3{}^+} \tag{43}$$

$$\mathrm{FeNi(CO)_3{}^+ + Fe(CO)_5 \rightarrow Fe_2Ni(CO)_5{}^+} \tag{44}$$

$$\mathrm{FeNi(CO)_3{}^+ + Ni(CO)_4 \rightarrow FeNi_2(CO)_5{}^+} \tag{45}$$

Scheme IX

$$\mathrm{Ni(CO)^+ + Fe(CO)_5 \rightarrow FeNi(CO)_4{}^+} \tag{46}$$

$$\mathrm{FeNi(CO)_4{}^+ + Ni(CO)_4 \rightarrow FeNi_2(CO)_{\mathit{x}}{}^+} \quad (x = 4, 6, 7) \tag{47}$$

Scheme X

$$\mathrm{Ni(CO)_2{}^+ + Fe(CO)_5 \rightarrow FeNi(CO)_{\mathit{x}}{}^+} \quad (x = 5, 6) \tag{48}$$

$$\mathrm{FeNi(CO)_5{}^+ + Ni(CO)_4 \rightarrow FeNi_2(CO)_{\mathit{y}}{}^+} \quad (y = 8, 9) \tag{49}$$

$\mathrm{Ni(CO)_4/Fe(CO)_5}$. The clustering sequences for the $\mathrm{Ni(CO)_4/Fe(CO)_5}$ system are given in Schemes VIII–X. The largest ionic cluster fragments formed in this system contain three metal atoms. The three trinuclear ionic cluster fragments formed include $\mathrm{Fe_2Ni(CO)_5{}^+}$ and $\mathrm{FeNi_2(CO)_{\mathit{x}}{}^+}$ (x = 4–9).

Cluster Valence Molecular Orbital Theory (CVMO). In our two previous papers we proposed that the ionic cluster fragments formed in the $\mathrm{Cr(CO)_6}$, $\mathrm{Fe(CO)_5}$, $\mathrm{Co(CO)_3(NO)}$, and $\mathrm{Ni(CO)_4}$ systems can be understood by examining the electron deficiencies of the cluster fragments and comparing the sequence for cluster formation to the CVMO model described by Lauher.[5] Our basic premise is that the electron deficiency of an ionic cluster fragment is an indication of the number of open coordination sites on a metal atom. Ionic cluster fragments with high electron deficiencies will have open coordination sites that are readily available for interaction with the neutral molecule. Therefore, a direct correlation should exist between electron deficiency and relative reactivity.[4,8] A plot of relative reactivity vs. electron deficiency should increase in a monotonic manner.

According to the CVMO model the molecular orbitals of transition-metal clusters are of two types: (i) high-lying antibonding orbitals (HLAO) and (ii) cluster valence molecular orbitals (CVMO). The CVMO are accessible to either ligand or metal electrons, whereas the HLAO are too high in energy to accept electrons from ligands or contain nonbonding electrons. The stoichiometry of a cluster is determined by the geometry of the cluster and not by the identity of the metals or ligands.[9]

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(8) Wronka, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 67.

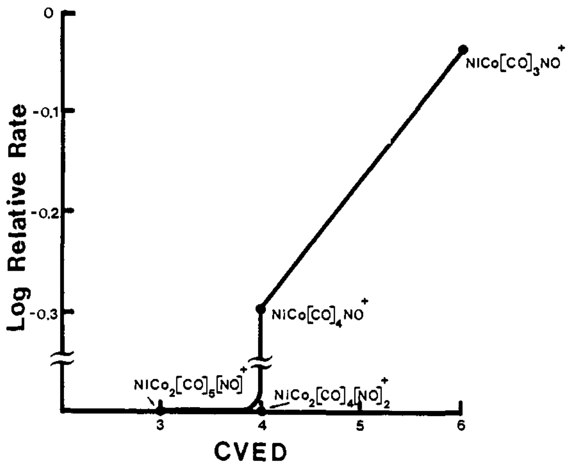

Figure 2. Plot of log of the relative rate vs. cluster valence electron deficiency for the ionic cluster fragments formed when $Co(CO)_2^+/Ni(CO)_2^+$ react with neutral $Co(CO)_3(NO)/Ni(CO)_4$. The rates of the ionic cluster fragments are normalized to the rate of the $Co(CO)_2^+$ ion.

Therefore, a cluster with a particular geometry will have a certain number of CVMO. Each CVMO should contain two cluster valence electrons (CVE). An unsaturated cluster will have a decrease in the number of CVE which could result in a high reactivity.

The basic concepts of the CVMO model and electron deficiency model are consistent. The reactivity of a cluster is determined by either the number of unoccupied CVMO or the electron deficiency. For example, a tetrahedron has 30 CVMO (60 CVE). If the tetrahedron has one unoccupied CVMO (58 CVE), the cluster would tend to add an additional two-electron donor ligand, e.g., a CO ligand, in order to achieve the desired number of CVE. Similarly, an electron deficient ionic cluster fragment would react with additional ligands to satisfy the deficiency. A parallel between the electron deficiency and CVMO model emerges. For both models, the number of electrons present in the ionic cluster fragment is determined by the structure (geometry) of the ionic cluster fragments. Both models also explain the different reactivities of the ionic cluster fragments. However, the electron deficiency model indicates the electron deficiency for the individual metal atoms of an ionic cluster fragment, whereas the CVMO model indicates the electron deficiency of the ionic cluster fragments as a whole. Although both the electron deficiency model and CVMO model can explain the data for the clustering sequence of the homonuclear and heteronuclear systems, the CVMO model provides a higher lever of understanding. Therefore, the data obtained for the heteronuclear systems have been analyzed with the CVMO model.

Because the CVMO model predicts that a coordinatively unsaturated cluster will show unusual reactivity and readily react with additional ligands to achieve the proper number of CVE, a plot of the cluster valence electron deficiency (CVED) vs. relative reactivity should also increase in a monotonic manner. (Here the cluster valence electron deficiency is defined as the number of CVE needed by an ionic cluster fragment of a particular geometry to achieve the proper number of CVE.) Figure 2 contains a plot of relative reactivity vs. CVED for the ionic cluster fragments formed when $Co(CO)_2^+/Ni(CO)_2^+$ react with the neutral $Co(CO)_3(NO)/Ni(CO)_4$ system (Scheme IV). Table I contains the relative reactivity and CVED data for each ionic cluster fragment of the $Co(CO)_3NO/Ni(CO)_4$ system. The relative reactivity data for Scheme IV are consistent with the $Co_2Ni(CO)_6(NO)^+$ ion having a double metal–metal bond possibly between the two cobalt atoms or a four-electron donor carbonyl ligand.

A simplified way of viewing the CVMO model (applicable only to small clusters, e.g., 6 metal atoms or less) is to consider the number of metal–metal bonds in a cluster. With this method the number of CVE can be determined by subtracting the number of metal–metal bonds (*N*) for each metal atom from 18 and multiplying by the number of metal atoms (*X*) present (eq I). For

$$CVE = (18 - N)X \tag{I}$$

example, the number of metal–metal bonds surrounding each metal atom in a tetrahedron is 3. Therefore, eq I would predict that the number of CVE in a tetrahedron would be 60 (eq II).

$$CVE = (18 - 3)4 = 60 \tag{II}$$

However, for a C_{2v} butterfly structure the number of metal–metal bonds surrounding each metal atom is 2 for two of the metal atoms and 3 for the other two metal atoms. The number of CVE needed for a C_{2v} butterfly structure is 62 (eq III). The change in number

$$CVE = (18 - 2)2 + (18 - 3)2 = 62 \tag{III}$$

of CVE on going from a T_d symmetry to a C_{2v} symmetry is a result of a HLAO droping in energy and increasing the number of CVMO. Once the number of CVE for a particular geometry is determined, the CVED of an ionic cluster fragment is determined by summing the actual number of valence electrons present in an ionic cluster fragment and subtracting from the proper number of CVE needed for the particular geometry.

The relationship between relative reactivity and CVED is used to analyze the ionic cluster fragments formed in Schemes II–X. Tables I–III contain the log relative rate and CVED for each ionic cluster fragment. Plots of relative reactivity vs. CVED are helpful in explaining the differences found in the heteronuclear systems.

Bonding of $Fe(CO)_4^{2-}$ in Heterometallic Clusters. As noted above, the heteronuclear systems containing $Fe(CO)_5$ exhibit unusual bonding. The relative reactivity vs. CVED data of the ionic cluster fragments formed in the $Co(CO)_3(NO)/Fe(CO)_5$ and $Ni(CO)_4/Fe(CO)_5$ systems suggest the presence of unusual

Table I. Ionic Cluster Fragments of the $Co(CO)_3(NO)/Ni(CO)_4$ System

ion	log relative[a] reaction rate	CVED[b]
reactant ions = Co^+, Ni^+		
$CoNi(CO)_2(NO)^+$	-0.403	8
$CoNi(CO)(NO)^+$	-0.0985	10
$CoNi(CO)_3^+$	-0.148	9
$CoNi(CO)_2^+$	-0.709	7
$Co_2Ni(CO)_3(NO)^+$	-0.897	7
$Co_2Ni(CO)_2(NO)_2^+$	-0.938	6
$CoNi_2(CO)_4^+$	–	5
$CoNi_2(CO)_3(NO)^+$	–	6
$Co_2Ni_2(CO)_5(NO)^+$	–	5
$Co_2Ni_2(CO)_4(NO)^+$	–	11
$Co_2Ni_2(CO)_4(NO)_2^+$	–	6
$Co_3Ni(CO)_4(NO)_2$	-0.151	9
$CoNi_3(CO)_6(NO)^+$	-0.025	10
reactant ion = $Co(CO)^+$, $Ni(CO)^+$		
$NiCo(CO)_3(NO)^+$	-0.0764	6
$NiCo(CO)_2(NO)^+$	-0.0468	8
$NiCo(CO)_4$	-0.0709	7
$Ni_2Co(CO)_5(NO)^+$	-0.676	4
$Ni_2Co(CO)_4(NO)^+$	–	2
$NiCo_2(CO)_5(NO)^+$	-0.595	5
$NiCo_2(CO)_4(NO)_2^+$	-0.490	6
$NiCo_2(CO)_6(NO)^+$	–	3
$NiCo_2(CO)_5(NO)_2^+$	–	4
$NiCo_3(CO)_6(NO)_2^+$	–	1
$NiCo_3(CO)_7(NO)^+$	–	4
reactant ions = $Co(CO)_2^+$, $Ni(CO)_2^+$		
$NiCo(CO)_4(NO)^+$	-0.294	4
$NiCo(CO)_3(NO)^+$	-0.0325	6
$NiCo_2(CO)_5(NO)^+$	–	3
$NiCo_2(CO)_4(NO)_2^+$	–	4

[a] The reaction rate of the ionic cluster fragments is relative to the rate of the $Co(CO)_x^+$ ion. [b] The column marked CVED refers to the cluster valence electron deficiency which is calculated by subtracting the number of cluster valence electrons of the ionic cluster fragments from the number of cluster valence electrons which are predicted for a particular structure. [c] The log relative rate is defined as – for those ionic cluster fragments which have no discernable rates.

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(9) Lauher, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 2604.

Table II. Ionic Cluster Fragments of the $Ni(CO)_4/Fe(CO)_5$ System

ion	log relative[a] reaction rate	CVED[b]
reactant ions = Ni^+, Fe^+		
$NiFe(CO)_3^+$	−0.640	10
$Ni_2Fe(CO)_4^+$	−0.924	8
$Ni_2Fe(CO)_5^+$	−0.521	12
$NiFe_2(CO)_5^+$	–	0
reactant ions = $Ni(CO)^+$, $Fe(CO)^+$		
$NiFe(CO)_4^+$	−0.231	8
$Ni_2Fe(CO)_4^+$	0.146	10
$Ni_2Fe(CO)_6^+$	0.255	12
$Ni_2Fe(CO)_7^+$	0.0556	10
reactant ions = $Ni(CO)_2^+$, $Fe(CO)_2^+$		
$NiFe(CO)_5^+$	−0.075	6
$NiFe(CO)_6^+$	−0.413	4
$Ni_2Fe(CO)_8^+$	0.149	6
$Ni_2Fe(CO)_9^+$	–	4

[a] The reaction rate of the ionic cluster fragments is relative to the rate of the $Ni(CO)_x^+$ ion. [b] The column marked CVED refers to the cluster valence electron deficiency which is calculated by subtracting the number of cluster valence electrons of the ionic cluster fragments from the number of cluster valence electrons which are predicted for a particular structure. [c] The log relative rate is defined as – for the ionic cluster fragments which have no discernable rates.

Table III. Ionic Cluster Fragments of the $Co(CO)_3(NO)/Fe(CO)_5$ Systems

ion	log relative[a] reaction rate	CVED
reactant ions = Fe^+, Co^+		
$CoFe(CO)_3^+$	−0.272	11
$CoFe(CO)(NO)^+$	−0.288	10
$CoFe_2(CO)_4^+$	−0.455	1
$CoFe_2(CO)_3(NO)^+$	−0.805	0
$Co_2Fe(CO)_2(NO)_2^+$	−0.110	12
$Co_3Fe(CO)_4(NO)_2^+$	+0.0291	13
$Co_3Fe(CO)_3(NO)_3^+$	−0.0743	12
reactant ions = $Fe(CO)^+$, $Co(CO)^+$		
$CoFe(CO)_4^+$	–	5
$CoFe(CO)_3(NO)^+$	–	6
$CoFe_2(CO)_3(NO)^+$	−0.479	13
$CoFe_2(CO)_4^+$	−0.324	14
$Co_2Fe(CO)_3(NO)_2^+$	−0.600	10
$Co_2Fe(CO)_5(NO)^+$	–	9
reactant ions = $Fe(CO)_2^+$, $Co(CO)_2^+$		
$CoFe(CO)_4(NO)^+$	0.173	8
$CoFe_2(CO)_3(NO)^+$	–	4
$CoFe_2(CO)_4^+$	−0.0278	7
$Co_2Fe(CO)_5(NO)_2^+$	−0.101	6
$Co_2Fe(CO)_5(NO)^+$	−0.202	9
$Co_2Fe_2(CO)_5(NO)^+$	–	1

[a] The reaction rate of the ionic cluster fragments is relative to the rate of $Co(CO)_x^+$ ion. [b] The column marked CVED refers to the cluster valence electron deficiency which is calculated by subtracting the number of cluster valence electrons of the ionic cluster fragments from the number of cluster valence electrons which are predicted for a particular structure. [c] The log relative rate is defined as – for the ionic cluster fragments which have no discernable rate.

bonding among some of the ionic cluster fragments. Conversely, the relative reactivities of the $Co(CO)_3(NO)/Ni(CO)_4$ system are consistent with the ionic cluster fragments having structures of the simple polyhedral model.[4] The coordination unsaturation of the ionic cluster fragments of the $Co(CO)_3NO/Ni(CO)_4$ system is very similar to the coordination unsaturation of the ionic cluster fragments found in the homonuclear systems. However, the coordination unsaturation of the $Co(CO)_3(NO)/Fe(CO)_5$ and $Ni(CO)_4/Fe(CO)_5$ systems is considerably different from that of the homonuclear systems. Because the bonding in the $Co(CO)_3(NO)/Fe(CO)_5$ and $Ni(CO)_4/Fe(CO)_5$ systems appears to differ from that of the homonuclear systems, the difference in bonding is attributed to the presence of $Fe(CO)_4$.

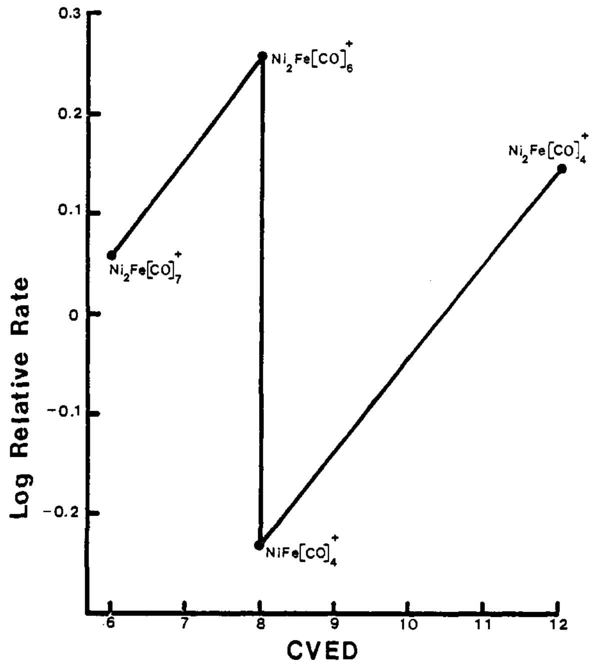

Figure 3. Plot of log of the relative rate vs. cluster valence electron deficiency (CVED) for the ionic cluster fragments formed when $Ni(CO)^+/Fe(CO)^+$ react with $Ni(CO)_4/Fe(CO)_5$. The CVED were calculated assuming the trinuclear ionic cluster fragments have a trigonal-pyramidal structure.

Recent literature reports address the unusual bonding in heterometallic systems containing $Fe(CO)_4^{2-}$ or $Fe(CO)_4^-$. For example, Longoni et al. report a $[Fe_3Pt_3(CO)_{15}]^{2-}$ dianion in which the $Fe(CO)_4$ group acts as a bulky analogue of an edge-bridging carbonyl group.[10] These authors suggest that the dianion be reformulated as $[Pt_3(CO)_3(\mu\text{-}Fe(CO)_4)_3]^{2-}$ and viewed as a stabilized analogue of $[Pt_3(CO)_3(\mu\text{-}(CO)_3)]^{2-}$. Sosinsky and coworkers report on a series of $(Na\{THF_2\}_2)^+[M'(Fe(CO)_4)_2]^{2-}$ complexes (M′ = Zn, Cd, and Hg) where the group 2B-iron bond description varies from near-ionic-distorted T_d $d^{10-\delta}$ $Fe^{2-(\delta+)}$ to near co-valent d^8 Fe^0.[11] Darensbourg et al. have reported on $Et_4N^+Ph_3PAuFeW(CO)_9^-$ which also illustrates the ability of $Fe^{\delta-}$ to dominate metal–metal donor–acceptor bond formation.[7] The structure assigned to $Et_4N^+Ph_3PAuFeW(CO)_9^-$ is best formulated as $Fe(CO)_4^{2-}$ interacting with two metaloelectrophiles; the 16-electron $W(CO)_3$ forms a metal–metal donor–acceptor bond with the iron nucleophile while the 12-electron Ph_3PAu^+ accepts electrons directly from the iron and indirectly from the electron-rich carbonyl carbons.

The presence of $Fe(CO)_5$ in heterometallic clusters has also led to unusual structures. For example, Doyle reports on mixed copper/iron clusters which include a linear Cu–F–Cu triatomic complex, the close-packed planar $Cu_3Fe_3(CO)_{12}^{3-}$, and the novel $Cu_6Fe_4(CO)_{16}^{2-}$ triangular array.[12] Longoni has synthesized and characterized Fe–Pd and Fe–Pt with the formula $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd, Pt).[13] The structure of the two dianions are identical and consist of a rectangularly distorted square-planar coordination of iron atoms around the unique central metal atom. The $[Pt_3Fe_3(CO)_{15}]^{2-}$ mentioned earlier also has a metallic array for its structure.[10]

The relative reactivity vs. CVED data may be explained by considering the formation of dative bonds (partial ionic bonds) between $Fe(CO)_4$ and either a nickel or a cobalt cluster fragment. Unusual bonding in the $Ni(CO)_4/Fe(CO)_5$ and $Co(CO)_3$-

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(10) Longoni, G.; Manassero, M.; Sansoni, M. *J. Am. Chem. Soc.* **1980**, *102*, 7973.

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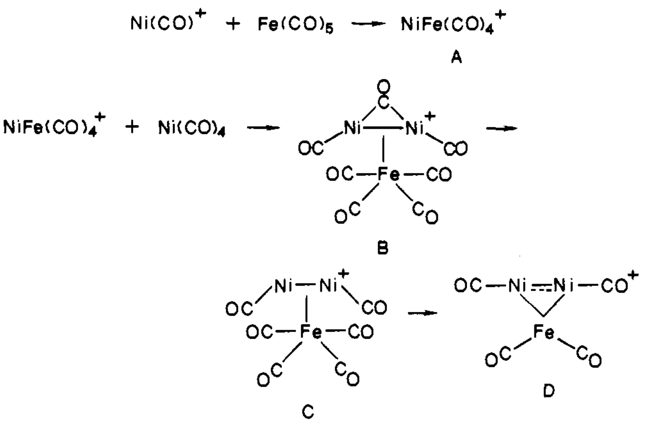
Scheme XI



$(NO)/Fe(CO)_5$ systems is suggested by the relative reactivity vs. CVED data. Figure 3 contains a plot of log of the relative reaction rate vs. CVED for $Ni(CO)^+/Fe(CO)^+$ reacting with $Ni(CO)_4/Fe(CO)_5$ (Scheme IX). The CVED used for plotting this data is based on the trimeric ionic cluster having triangular pyramids. These data suggest that the $NiFe(CO)_4^+$, $Ni_2Fe(CO)_4^+$ and $Ni_2Fe(CO)_6^+$ ionic cluster fragments are more coordinatively saturated than predicted by simple polyhedral models For example, the reactivity for $Ni_2Fe(CO)_6^+$ is relatively high (0.255) which is inconsistent with the low CVED (8) predicted for a simple polyhedral model. The high reactivity for $Ni_2Fe(CO)_6^+$ suggests that the ion is more coordinatively unsaturated than the relative reactivity vs. CVED model would indicate. Doyle suggested that the linear triatomic Cu-Fe heterometallic cluster consists of a triangular Cu_3 core bridged on all three edges by an $Fe(CO)_4$ group.[12] If a linear structure is assumed for the $Ni_2Fe(CO)_7^+$ and $Ni_2Fe(CO)_6^+$ ionic cluster fragments, a plot of log of the relative rate vs. CVED montonically increases (Figure 4). A linear structure would increase the coordination unsaturation of $Ni_2Fe(CO)_7^+$ and $Ni_2Fe(CO)_6^+$ relative to the $NiFe(CO)_4^+$ and $Ni_2Fe(CO)_4^+$ ions. Scheme XI shows a possible mechanism for the formation of the triatomic ionic cluster fragments of the $Ni(CO)^+/Fe(CO)^+$ reaction sequence (Schene IX). The Ni^+ ion reacts with $Fe(CO)_5$ to form the $NiFe(CO)_4^+$ ionic cluster fragment. Thus, the structure of $NiFe(CO)_4^+$ is best rationalized as $[Ni\cdots Fe(CO)_4]^+$ analogous to Ph_3PAu in $Et_4N^+Ph_3PAuFeW(CO)_9^-$.[7] When $NiFe(CO)_4^+$ reacts with $Ni(CO)_4$ the linear $Ni_2Fe(CO)_7^+$ trinuclear ionic cluster fragment is produced, which can be formulated as $[Ni_2(CO)_3\cdots Fe(CO)_4]^+$.

Our previous work showed that the $Ni_2(CO)_3^+$ ionic cluster fragment formed in the homonuclear system is quite unsaturated (electron deficiency of 4.5).[4] $Ni_2(CO)_3^+$ contains only 26 CVE as compared to 34 CVE needed for a dimer. Owing to the coordination unsaturation of the $Ni_2(CO)_3$ moiety, no metal-metal donor bonds are formed between the two nickel atoms and the iron atom. A carbonyl ligand is lost from $Ni_2Fe(CO)_7^+$ to produce $Ni_2Fe(CO)_6^+$, formulated as $[Ni_2(CO)_2\cdots Fe(CO)_4^+]$. Again, owing to the electronic unsaturation, the $Ni_2(CO)_2$ moiety accepts electron density from the $Fe(CO)_4$ group and no metal-metal donor-acceptor bonds are formed between nickel and iron. However, upon loss of two additional carbonyls, the relative reactivity/CVED data suggest that the nickel and iron atoms do form metal-metal donor-acceptor bonds (structure D), i.e., $Ni_2Fe(CO)_4^+$ is more coordinatively saturated. Structure D (Scheme XI) can result from the high coordination unsaturation of the $Ni_2(CO)_2$ moiety. Because of this high coordination unsaturation the two carbonyl ligands would preferentially be lost from the $Fe(CO)_4$ group. The proposed loss of the carbonyl ligands from the $Fe(CO)_4$ group agrees with thermodymamic data which give $D_{Fe-CO} < D_{Ni-CO}$ ($D_{Fe-CO} = 28.1$ kcal/mol, $D_{Ni-CO} = 35.1$ kcal/mol).[14] (However, the loss of the CO ligand from the $Ni_2(CO)_3$ moietv in B to produce C can be rationalized by assuming that $Ni_2(CO)_2$ bonded to $Fe(CO)_4$ is more stable than is $Ni_2(CO)_3$ bonded to $Fe(CO)_3$.) The formation of a double metal-metal bond in $Ni_2Fe(CO)_4^+$ can be a direct result of the electron density given up by the $Ni_2(CO)_2$ moiety when the donor-acceptor bonds are formed with iron. The relative reactivity data of the $Ni_2(CO)_2^+$ ionic cluster fragment formed in the homonuclear systems indicate that $Ni_2(CO)_2^+$ is coordinatively saturated and also contains a double bond.[4]

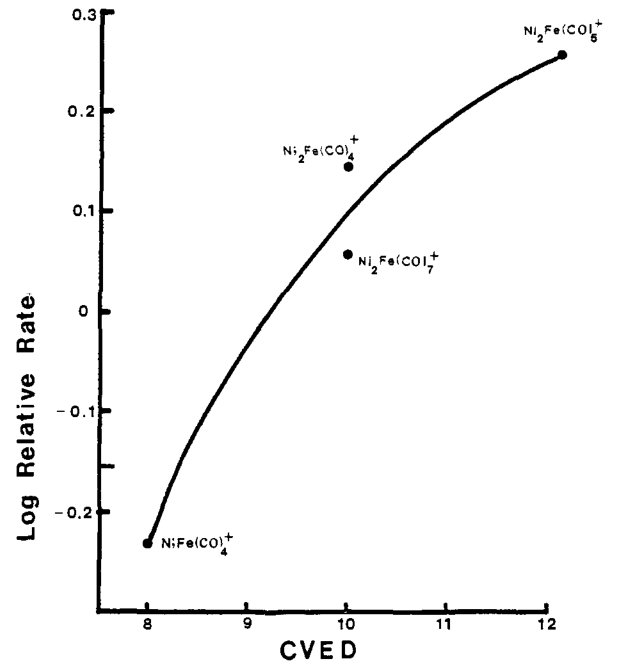


Figure 4. Plot of log of the relative rate vs. cluster valence electron deficiency (CVED) for the ionic cluster fragments formed when $Ni(CO)^+/Fe(CO)^+$ react with $Ni(CO)_4/Fe(CO)_5$. The CVED were calculated assuming linear structures for the trinuclear ionic cluster fragments.

Evidence exists in the relative reactivity vs. CVED data for $Fe(CO)_4$ acting as a bulky analogue of an edge-bridging carbonyl.[7-10] The formation of $CoFe_2(CO)_4^+$ in Scheme V offers an example of $Fe(CO)_4$ acting as a ligand. If $CoFe_2(CO)_4^+$ is considered to be a trimer, the CVED of this ionic cluster fragment would be too high for its relative reaction rate, and the log of the relative reaction rate vs. CVED plot would not show a monotonic increase. However, if $CoFe_2CO)_4^+$ is considered to be a dimer in which a $Fe(CO)_4$ group chelates a Co^+-Fe moiety, the log of the relative reaction rate vs. CVED plot increases monotonically. Owing to the high unsaturation of the Co^+-Fe dimer, this ion accepts electron density directly from the iron atom and indirectly from the carbonyl ligands. As in the case of $Ni_2Fe(CO)_7^+$, the interaction of Co^+-Fe with the $Fe(CO)_4$ group is similar to the interaction of Ph_3PAu with $Fe(CO)_4$.[7] Reformulating $CoFe_2(CO)_4^+$ as $[CoFe(\mu\text{-}Fe(CO)_4)]^+$ also gives a structure very similar to that of $Fe_2(CO)_9$.

$CoFe_2(CO)_4^+$ is also formed in Scheme VI ($Co(CO)^+/Fe(CO)^+$ reacting with $Co(CO)_3(NO)/Fe(CO)_5$). However, in this case the relative reactivity vs. CVED data suggest that this ionic cluster fragment is indeed a trinuclear cluster having three metal-metal donor-acceptor bonds. The difference in reactivity of the $CoFe_2(CO)_4^+$ in Schemes V and VI, and therefore, the difference in structure, could be a result of the added stability of the CO ligand found in the reaction sequence for $Co(CO)^+/Fe(CO)^+$.[4] Now, instead of forming a Co^+-Fe dimer a $Co(CO)^+$-Fe dimer is formed. The lower coordination unsaturation and the lower energy of the $Co(CO)^+$-Fe dimer favors formation of metal-metal donor-acceptor bonds. It should be noted that Ridge has also observed dramatic differences in the chemistry of bare metal dimer ions and ligated dimer ions, specifically Co_2^+ and $Co_2(CO)^+$.[15]

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(15) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 825.

The ionic cluster fragments formed in the $Co(CO)_3(NO)/Ni(CO)_4$ system seem to follow the bonding found in the triangular polyhedra of the boron hydrides. For the trinuclear clusters $Co_2Ni(CO)_3(NO)^+$, $Co_2Ni(CO)_3(NO)_2^+$, $CoNi_2(CO)_4^+$, and $CoNi_2(CO)_3(NO)^+$ found in Scheme II, the relative reactivity vs. CVED data suggest the presence of two double metal–metal bonds. However, it is possible that these ionic cluster fragments have metal–metal bonds which are somewhere between an acceptor bond and a metal–metal donor–acceptor bond, i.e., the metal–metal bonds could be dative bonds. (In this case, a dative bond is defined as a bond in which the cobalt atoms donate both of the electrons in the metal–metal bond.)[16] For example, the nickel atom in $Co_2Ni(CO)_3(NO)^+$ could form two dative metal–metal bonds with the two cobalt atoms. Nickel would then be accepting more electron density from the cobalt atoms than it is donating to the cobalt atoms. Therefore, three metal–metal donor–acceptor bonds are not formed, but more than two metal–metal donor–acceptor bonds are formed. The problem that arises from dative bonds is how to determine the proper number of CVE for the relative reactivity vs. CVED analysis. Since it is impossible to determine the exact number of metal–metal bonds (and therefore, the number of CVMO and CVE) which should be present if dative bonds are formed, double metal–metal bonds are included in the structure of $Co_2Ni(CO)_3(NO)^+$.

Absence of Clustering between $Cr(CO)_6$ and Group VIII–X Metals. As mentioned earlier, the only heteronuclear ionic cluster fragment containing chromium is $CrFe(CO)_5^+$. The lack of cluster formation between chromium and the group VIII–X metals is attributed to a periodic effect. The relative energy of the $(n+1)$s, $(n+1)$p, and nd orbitals varies for a given element.[17] The energy level sequence for an element on the left side of a transition series is $(n+1)s = nd < (n+1)p$. However, for an element on the right side of a transition series, the energy level sequence is $nd < (n+1)s < (n+1)p$.

The bonding for the dimers Fe_2, Ni_2, NiFe, Co_2, Cu_2, and NiCu has been proposed to be due to the 4s molecular orbital.[18-21] Freiser and Jacobsen have also proposed that the diatomic cluster $CoFe^+$ contains a single bond of 4s character.[22] For metal clusters of the type M_xL_y (L = ligand), the strongest interactions between the metal core are between the s and p orbitals due to their higher overlaps.[5] Therefore, if the energy difference between the s orbitals for two different transition metals can decrease the overlap of the s orbital by a significant amount, metal–metal bonds, and hence, metal clusters, cannot be formed. Therefore, chromium does not form ionic cluster fragments with nickel and cobalt because of the difference in energy of the s orbitals.

The s orbitals of chromium and iron are apparently close enough in energy to form the $CrFe(CO)_5^+$ ion. This ionic cluster fragment, however, does not react further. The lack of reactivity of the $CrFe(CO)_5^+$ ionic cluster fragment can be a direct result of high bond order. For example, in the homonuclear $Fe(CO)_5$ system, $Fe_2(CO)_3^+$ did not react to form trinuclear ionic cluster fragments.[4a] It was suggested that the $Fe_2(CO)_3^+$ ion has a triple metal–metal bond and three four-electron donating carbonyls. The unreactive nature of $CrFe(CO)_5^+$ could also be due to the structure of the ionic cluster fragment. For instance, if $CrFe(CO)_5^+$ has a structure analogous to $Fe_2(CO)_3^+$, i.e., a triple metal–metal bond, three four-electron-donating carbonyls, and two terminal carbonyls, the number of CVE of the ionic cluster fragment would be equal to the number of CVE predicted by Lauher's model. Therefore, the $CrFe(CO)_5^+$ ionic cluster fragment would be coordinatively saturated and as a result of the coordination unsaturation unreactive.

Conclusions

In this paper we have expanded the ideas and concepts developed for the $Cr(CO)_6$, $Fe(CO)_5$, $Co(CO)_3(NO)$, and $Ni(CO)_4$ systems to the ionic cluster fragments formed in the $Co(CO)_3(NO)/Ni(CO)_4$, $Fe(CO)_5/Ni(CO)_4$, and $Fe(CO)_5/Co(CO)_3(NO)$ heteronuclear systems. Although the heteronuclear ionic cluster fragments formed in the $Co(CO)_3NO/Ni(CO)_4$ system are similar to those formed in the homonuclear systems, the ionic cluster fragments formed in the $Co(CO)_3(NO)/Fe(CO)_5$ and $Ni(CO)_4/Fe(CO)_5$ systems seem to follow bonding patterns found in heterometallic systems containing $Fe(CO)_4^{2-}$ groups. The $Fe(CO)_4^{2-}$ group has the ability to act as an analogue of an edge-bridging carbonyl and can form acceptor bonds with other transition metals.

The heteronuclear ionic cluster fragments further illustrate the utility of comparing reactivity and coordination unsaturation as a means of providing insight into the bonding and structure of ionic cluster fragments formed by ion–molecule reactions. Furthermore, this study provides a guide based on bond order, structure, and reactivity for additional studies on the ion–molecule chemistry of the ionic cluster fragments.

What is lacking from these studies is an informative structural probe technique sensitive to the structural features of the ionic cluster fragments. Collision-induced dissociation (CID) studies have been performed on selected systems; however, at the collision energies available on our system (up to 100–200 eV) the dominant reactions observed are associative ion–molecule reactions, i.e., the production of large cluster fragments. In cases where CID is observed the most abundant product ions arise by loss of multiple CO ligands, which is not a very structurally informative dissociation channel. On the other hand, preliminary experiments with laser-ion-beam photodissociation are quite encouraging.[23] To date laser-ion-beam photodissociation has been used to study ionic cluster fragments of the type $M_x(CO)_y^+$, where M = Mn ($x = 2$), Fe ($x = 3$), or Co ($x = 2$–4). From these data we have obtained both metal–metal and metal–ligand bond energies. We are hopeful that this method will provide information on both metal–metal and metal–ligand bond energies and some insight as to subtle structural features of novel ionic cluster fragments formed by ion–molecule reaction chemistry such as described in this and previous papers.

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Registry No. Co^+, 16610-75-6; $Co(CO)^+$, 28963-35-1; $Co(CO)_2^+$, 28963-34-0; Ni^+, 14903-34-5; $Ni(CO)^+$, 71837-05-3; $Ni(CO)_2^+$, 69276-23-9; $Co(CO)_3NO$, 14096-82-3; $Ni(CO)_4$, 13463-39-3; Fe^+, 14067-02-8; $Fe(CO)^+$, 35038-14-3; $Fe(CO)_2^+$, 35038-15-4; $Fe(CO)_5$, 13463-40-6.

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