perimental data provide an unambiguous answer in favor of the second alternative; thus, we have to conclude that the isomerization **10** $\rightleftharpoons$ **5a**-Fe$^+$ is rapid in comparison to the production of molecular hydrogen.

The behavior of the $[M - C_2H_4]^+$ species generated from **9a**-Fe$^+$ was also probed by using FTICR. If, for example $Fe(C_2H_4)^+$, generated from Fe$^+$ and C_2H_5Cl, is reacted with $CD_3(CH_2)_2C$-OC_3H_7 (**5c**), the primary reaction products are *m/z* 201 (6%), 173 (36), 171 (43), and 170 (15). The reaction time was 500 ms, the pressure of **5c** $\sim 2 \times 10^{-8}$ mbar, and that of argon $\sim 4 \times 10^{-7}$ mbar. The product distribution is easily explained by dissociation of the ion/molecule complex *m/z* 201, which very likely corresponds to structure **22**; this complex either directly (**22** $\rightarrow$ **10**) or via **21** decomposes to **10** and/or **5a**-Fe$^+$. Loss of H_2/HD from these products occurs in a ratio practically identical with what has been observed for **9b**-Fe$^+$ in the beam experiment.

Acknowledgment. The continuing financial support of our work by the Volkswagen-Stiftung, Fonds der Chemischen Industrie, Deutsche Forschungsgemeinschaft, and Gesellschaft von Freunden der Technischen Universität Berlin is gratefully acknowledged. We are indebted to Karsten Eller and Gregor Czekay for enlightening discussions, to Dr. Thomas Weiske for technical assistance, and to a reviewer for helpful comments.

Ion-Molecule Reaction Chemistry of Ionic Transition-Metal Carbonyl Cluster Fragments. 1. Ligand-Exchange Reactions of $Cr_2(CO)_y^+$ Ions

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Abstract: The ligand-exchange ion-molecule reaction chemistry of $Cr_2(CO)_y^+$ ionic transition metal cluster fragments has been investigated by using a two-section ion cell Fourier transform ion cyclotron resonance mass spectrometer. Simple ligand-exchange reactions involving ligand (L) addition followed by metal-ligand (M---CO) bond cleavage (i.e., an associative ligand-exchange mechanism) as well as ligand exchange involving metal-metal cleavage (i.e., addition of L to $Cr_2(CO)_y^+$ followed by metal-metal bond cleavage) are observed. The branching ratios for reactions involving metal-metal bond cleavage increase as the metal-to-ligand ratio decreases. In addition, the ratio for simple ligand exchange to metal-metal bond cleavage is strongly dependent upon the nature of the reacting ligand (L). These data combined with collision-induced dissociation data for $Cr_2(CO)_y^+$ ionic cluster fragments suggest that the Cr-Cr bond strength decreases as *y* is increased; i.e., the Cr---Cr bond order is strongly dependent upon the ligand environment.

Introduction

Studies of the chemical and physical properties of gas-phase transition-metal ions are a subject of growing research interest.[1] An understanding of the chemical and physical properties of transition-metal ions and unsaturated ionic cluster fragments is fundamental to continued development in several areas of inorganic chemistry. Studies of transition-metal clusters is partially motivated by the similarities between transition-metal clusters and bulk-metal surfaces. Although one can argue the merits of studies aimed toward bridging the gap between atomic/molecular properties and bulk materials, our understanding of "catalysis/surface chemistry" will be enhanced if the factors which alter the chemical and physical properties of transition metal species can be delineated. Thus, the study of transition-metal clusters provides information essential to a complete description of adsorbate-metal surface interactions. The breakdown between transition-metal clusters and metal surfaces lies in the fact that metal surfaces exhibit higher metal/ligand ratios than most saturated transition-metal clusters. Consequently, the current trends in much of cluster chemistry is centered around so-called bare metal clusters.

An important aspect is the study of gas-phase ionic transition-metal clusters is the ability to study highly unsaturated cluster (both cationic and anionic) fragments which have higher metal-to-ligand ratios. Our work is directed toward developing methods for measuring metal-metal and metal-ligand binding energies as a function of cluster size as well as a function of metal-to-ligand ratio.[2] For example, ions of the type $M_x(CO)_y^+$ ($x = 2$-8, $y = 0$-$3x$) can be synthesized and probed by ion-molecule reaction chemistry,[3-5] collisional activation methods,[6-8] and photodissociation.[9-11] Ridge[3] and Russell[12] studied the ion-molecule clustering reactions of anionic and cationic transition-metal species and reported on the formation of highly unsaturated ionic cluster fragments, and proposed that the reactivities of the cluster fragments directly correlate with the electron deficiencies. Because electron deficiency is an indication of the number of open coordination sites of the metal atoms within the cluster fragment, a change in the electron deficiency (number of open coordination sites) is observed as a change in the reactivity.

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The calculated (using the 18-electron rule)[13] electron deficiencies of $Cr_2(CO)_y^+$ (y = 4–6) are 7.5, 6.5, and 5.5, respectively. However, the reactivities of $Cr_2(CO)_6^+$ and $Cr_2(CO)_5^+$ are much lower than that for $Cr_2(CO)_4^+$, suggesting that the cluster fragments have much smaller electron deficiencies, 3.5 and 4.5, respectively.[12a] Because the reactivity of $Cr_2(CO)_6^+$ is low relative to the predicted electron deficiency, it was suggested that higher order metal–metal or metal–ligand bonds could compensate the electron deficiencies.

On the basis of ion–molecule reactivity data, the electron deficiencies of the Cr and Fe ionic cluster fragments are found to be of two types: (i) electron deficiencies that are typical for simple polyhedra structures (e.g., systems that obey the 18-electron rule) and (ii) electron deficiencies that deviate from the 18-electron rule. It was proposed that deviations from the 18-electron rule are attributable to high bond orders for either the metal–metal bond or the metal–ligand interaction(s).[3,12] Such bonding is especially interesting because most clusters differ from surfaces in that metal–metal bond orders for clusters are low. For example, the low electron deficiency of $Cr_2(CO)_6^+$ could be explained by the presence of a Cr–Cr triple bond and/or CO ligands which are four-electron rather than two-electron donors. Consequently, the metal–metal and/or metal–ligand binding energies for $Cr_2(CO)_6^+$ should differ from that for $Cr_2(CO)_4^+$. Furthermore, the chemical properties of cluster fragments such as $Cr_2(CO)_4^+$ and $Cr_2(CO)_6^+$ may be strongly influenced by either structure or metal–metal and metal–ligand bonding.

Ligand-exchange reaction chemistry of unsaturated ionic cluster fragments is of fundamental interest as well as an informative probe of chemical properties. Although addition of ligands to coordinatively unsaturated metal centers might be expected to be rapid and efficient, recent studies show that some ligand-exchange reactions are slow and inefficient. For example, CO addition reactions to coordinatively unsaturated, neutral metal carbonyls have been examined by Weitz et al.[14] Large variations in the reaction rate for CO addition to $Fe(CO)_y$ were observed, and the slow rate for CO addition to $Fe(CO)_4$ was attributed to a spin-forbidden transition: $Fe(CO)_4$ (triplet ground state) + CO → $Fe(CO)_5$ (singlet ground state). Conversely, the rapid rate for CO addition to $Fe(CO)_2$ and $Fe(CO)_3$ suggest these processes are spin-allowed. Thus, the first step in ligand-exchange reactions, e.g., ligand addition as illustrated by reaction 1, and, consequently

$$M_x(CO)_y^+ + L \rightleftarrows [M_x(CO)_y^+\cdots L]^* \rightarrow M_x(CO)_{y-a}L^+ + aCO \qquad (1)$$

the overall rate for ligand exchange, may be exceedingly sensitive to the spin state of the ionic cluster fragment. Similar trends in the rates of ligand-exchange reactions have been observed for gas-phase ionic species. Specifically, Beauchamp and co-workers showed that CO addition reactions for some gas-phase cationic metal species are also quite slow.[15]

Experimental Section

All experiments were carried out by using a Fourier transform ion cyclotron resonance built at TAMU. The system consists of a Nicolet 1280 data system, a 3-tesla Oxford superconducting magnet, a home-built vacuum system, and a two-section ion cell. Samples were introduced into the system with variable leak valves maintained at ambient temperature with typical pressures of 1–3 × 10^{-7} Torr (measured with a Granville Phillips Gauge Controller Series 280). Electron impact ionization of the sample was performed by using a pulsed electron beam (pulse duration 1–3 ms) at 50 eV (nominal) ionizing energy and 200 ± 10 nA emission current. The ion cell trapping voltage was maintained at 4 V.

The ionic cluster fragments studied were formed by ion–molecule reactions as described by Fredeen and Russell.[12] After formation of the ionic cluster fragments ion ejection[16] and/or skimmed partitioning,[17] techniques were used to mass select a particular ionic cluster fragment for ligand-exchange studies. The mass-selected ionic cluster fragment was then partitioned to the analyzer side of the two-section cell which contains the neutral ligand at a static pressure of 1–3 × 10^{-7} Torr. The ligand-exchange products for a particular ionic cluster fragment and a particular ligand was then monitored as a function of time. The complete experimental sequence has been described in detail previously.[18] The data for each reaction are represented as relative total ion intensity versus time to produce temporal plots which can be fitted and used to extract reaction rate constants.

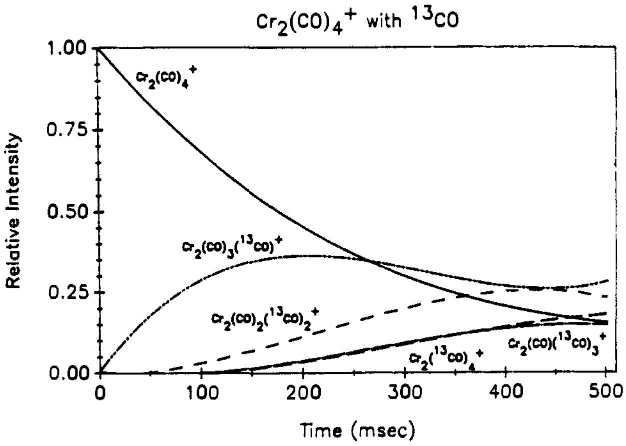

Figure 1. Temporal plot for the ligand-exchange ion–molecule reactions of $Cr_2(CO)_4^+$ with ^{13}CO.

The rate of disappearance of the ionic cluster fragment is defined as $\ln I/I_0 = -\exp(nkt)$ where I is the intensity of the ionic cluster fragment at any time, t, I_0 is the initial intensity of the ionic cluster fragment, n is the number density of neutral molecules, and k is the rate constant for the reaction. Therefore, a plot of [($\ln I/I_0$)] versus time would have a slope of $-nk$, where k is the rate constant for disappearance of the ionic cluster fragments. The number density is calculated using the ideal gas law. The pressure of the neutrals is corrected for the sensitivity of the ionization gauge to the particular ligand (relative to nitrogen) by multiplying the pressure by the sensitivity factors.[19] The reaction rate constants obtained in this manner are good to ±10%, determined by comparing reaction rate constants for $C_2H_4^{\cdot+} + C_2H_4 \rightarrow C_3H_5^+ + CH_3^{\cdot}$ with literature values.[20]

Collision-induced dissociation spectra of the $Cr_2(CO)_y^+$ ions were obtained by using a Kratos MS-50TA tandem mass spectrometer. The instrument and the details of the experiment have been described previously.[21]

Results

This work investigates the ion–molecule ligand-exchange reactions for $Cr_2(CO)_y^+$ (y = 4, 5, 6) ionic cluster fragments with several ligands (^{13}CO, O_2, C_4H_6 (1,3-butadiene), benzene, NH_3, and CH_3OH). The $Cr_2(CO)_y^+$ ionic cluster fragments are formed by ion–molecule reactions of Cr^+ with neutral $Cr(CO)_6$.[12a] The ligand-exchange reactions proceed by an associative reaction mechanism (reaction 2) where L is some ligand. Thus, addition

$$Cr_2(CO)_y^+ + L \rightarrow [Cr_2(CO)_y...L]^* \rightarrow Cr_2(CO)_{y-a}L^+ + a(CO) \qquad (2)$$

of L to $Cr_2(CO)_y^+$ occurs because open coordination sites are available for ligand binding to form a collision complex $[Cr_2(CO)_y^+\cdots L]^*$. Dissociation of the collision complex to the final products, $Cr_2(CO)_{y-a}L^+ + a(CO)$, corresponds to unimolecular dissociation of the ion–molecule collision complex. In the following sections a detailed description of the ligand-exchange reactions for $Cr_2(CO)_4^+$, $Cr_2(CO)_5^+$, and $Cr_2(CO)_6^+$ with several ligands are presented. Although the general ligand-exchange reactions

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Table I. Ion-Molecule Reaction Rate Constants[a] for Disappearance of $Cr_2(CO)_x^+$ for Ligand-Exchange Reactions with Various Ligands

	k (cm^3 molecule^{-1} s^{-1}) × 10^9 for								
	$Cr_2(CO)_4^+$			$Cr_2(CO)_5^+$			$Cr_2(CO)_6^+$		
ligand	exp	induced dipole	ADO	exp	induced dipole	ADO	exp	induced dipole	ADO
^{13}CO	0.5	0.7	0.7	0.4	0.6	0.7		0.6	0.6
oxygen	0.6	0.7	0.7	0.5	0.7	0.7	0.4	0.7	0.7
methanol	0.7	0.8	1.4	0.6	0.8	1.4	0.6	0.8	1.4
ammonia	1.6	0.9	1.6	1.3	0.9	1.6	1.4	0.9	1.6
benzene	0.3	1.0	1.0	0.2	1.0	1.0	0.2	1.0	1.0
1,3-butadiene	0.3	1.1	1.1	0.2	1.1	1.1	0.2	1.0	1.0

[a] Reaction rate constants are reproducible (based on three replicate measurements) to ±10% in each case. See Experimental Section for further discussion on methods.

for the $Cr_2(CO)_y^+$ ions are quite similar, each ionic cluster fragment manifests characteristic differences.

Ligand-Exchange Reactions with ^{13}CO (Thermoneutral Exchange Reactions). $Cr_2(CO)_4^+$ and $Cr_2(CO)_5^+$ react (stepwise) with ^{13}CO to displace all of the ^{12}CO ligands. Figure 1 contains a temporal plot for the ligand-exchange reaction products of $Cr_2(CO)_4^+$ and ^{13}CO. The $Cr_2(CO)_6^+$ ionic cluster fragment does not undergo a ligand-exchange reactions with ^{13}CO. There is no significant amount (<10%) of ^{13}CO ligand-exchange reaction product(s) detected for the $Cr_2(CO)_6^+$ ion for reaction times of up to 800 ms (~20 ion-neutral collisions).

The rate constants for the disappearance of the $Cr_2(CO)_x^+$ ionic cluster fragments by ^{13}CO ligand-exchange reactions are contained in Table I. The rate for the disappearance of $Cr_2(CO)_4^+$ (k = 5 × 10^{-10} cm^3 molecule^{-1} s^{-1}) is approximately 20% faster than that for $Cr_2(CO)_5^+$ (k = 4 × 10^{-10} cm^3 molecule^{-1} s^{-1}). The experimental reaction rates are compared with calculated collision frequencies (Langevin and averaged-dipole orientation theories).[22] Note that in each case the reaction with ^{13}CO is relatively efficient (70-80%). Assuming that all CO ligands of the collision complex are equivalent, loss of both ^{12}CO and ^{13}CO is possible; thus the measured reaction rate will deviate significantly from the calculated collision rate.

Ligand-Exchange Reactions with Oxygen. The ligand-exchange reactions of $Cr_2(CO)_4^+$ and $Cr_2(CO)_5^+$ with O_2 proceed with the displacement of all the CO ligands by a single O_2 ligand (reaction 3).[23] At longer reaction times (reaction times corresponding to

$$Cr_2(CO)_y^+ + O_2 \rightarrow [Cr_2(CO)_yO_2^+]^* \rightarrow Cr_2O_2^+ + y(CO) \qquad (y = 4, 5) \quad (3)$$

5-10 ion-neutral collisions), the $Cr_2O_2^+$ ion reacts with O_2 to form $Cr_2O_3^+$ or $Cr_2O_4^+$. The $Cr_2O_3^+$ and $Cr_2O_4^+$ are both present in low (<20%) relative abundances. Figure 2a contains temporal plots for the ligand-exchange reaction for $Cr_2(CO)_4^+$ reacting with O_2; this temporal plot is representative of both the $Cr_2(CO)_4^+$ and $Cr_2(CO)_5^+$ ions.

The ligand-exchange reaction of $Cr_2(CO)_6^+$ with O_2 is similar to those observed for $Cr_2(CO)_4^+$ and $Cr_2(CO)_5^+$. That is, the initial ligand-exchange reaction yields $Cr_2O_2^+$ ions by displacement of all six CO ligands by a single O_2 ligand (reaction 4; y = 6). Also, the $Cr_2O_2^+$ ion reacts with O_2 to form $Cr_2O_3^+$ or $Cr_2O_4^+$. However, there are significant differences in the ion-molecule reaction rates, as well as the observed ion-molecule products. For example, the relative abundances of $Cr_2O_3^+$ and $Cr_2O_4^+$ are approximately twice that observed for the $Cr_2O_2^+$ ions formed by reaction of $Cr_2(CO)_4^+$ and $Cr_2(CO)_5^+$ with O_2 (Figure 2b). The difference in the product ion yield for $Cr_2O_2^+$ (formed by reactions of $Cr_2(CO)_6^+$ with O_2) is probably due to differences in internal energies of the $Cr_2O_2^+$ ion.[24] In addition, a new product ion, $Cr(CO)_3O_2^+$, which arises by addition of O_2 to $Cr_2(CO)_6^+$ followed by cleavage of the metal-metal bond is formed as the major ion-molecule product. Note that the $Cr(CO)_3O_2^+$ ion-molecule reaction product is not observed for $Cr_2(CO)_4^+$ and $Cr_2(CO)_5^+$.

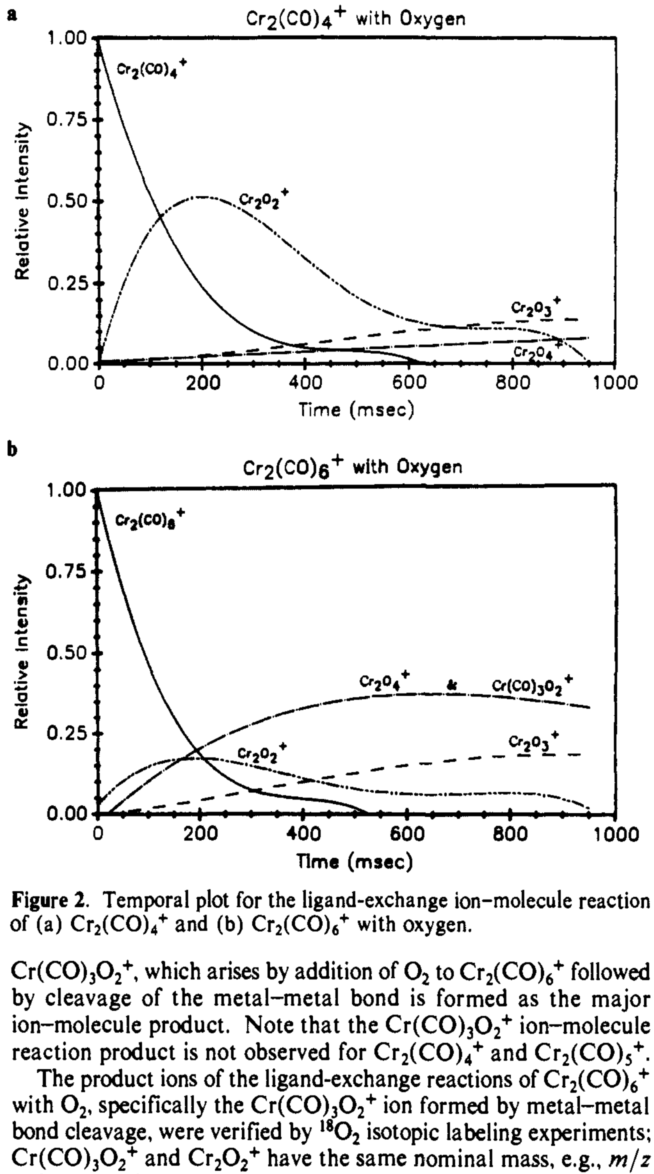
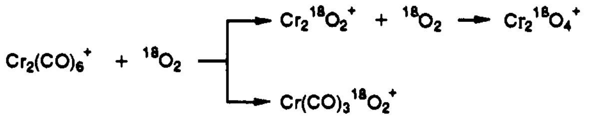


Figure 2. Temporal plot for the ligand-exchange ion-molecule reaction of (a) $Cr_2(CO)_4^+$ and (b) $Cr_2(CO)_6^+$ with oxygen.

The product ions of the ligand-exchange reactions of $Cr_2(CO)_6^+$ with O_2, specifically the $Cr(CO)_3O_2^+$ ion formed by metal-metal bond cleavage, were verified by $^{18}O_2$ isotopic labeling experiments; $Cr(CO)_3O_2^+$ and $Cr_2O_2^+$ have the same nominal mass, e.g., m/z 168. All of the O_2 ligand-exchange reaction products from $Cr_2(CO)_4^+$ and $Cr_2(CO)_5^+$ (e.g., $Cr_2O_2^+$, $Cr_2O_3^+$, and $Cr_2O_4^+$) increased in mass by $2n$, where n is the number of oxygen atoms contained in the product ions. For the $Cr_2(CO)_6^+$ ligand-exchange reaction products, reactions with $^{18}O_2$ gave products which also increased in mass by $2n$; however, the product ion observed at m/z 168 using unlabeled O_2 is shifted to m/z 176 ($Cr_2{}^{18}O_4^+$), and a signal at m/z 172 ($Cr(CO)_3{}^{18}O_2^+$) is also observed (reactions 4 and 5).



$$Cr_2(CO)_6^+ + {}^{18}O_2 \rightarrow Cr_2{}^{18}O_2^+ + {}^{18}O_2 \rightarrow Cr_2{}^{18}O_4^+ \quad (4)$$

$$Cr_2(CO)_6^+ + {}^{18}O_2 \rightarrow Cr(CO)_3{}^{18}O_2^+ \quad (5)$$

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It is of interest to note that the $Cr(CO)_3O_2{}^+$ product ion is not observed as an ion–molecule product at short reaction times, but at reaction times of greater than ~300–400 ms the $Cr_2{}^{18}O_4{}^+$ and $Cr(CO)_3{}^{18}O_2{}^+$ product ions are of comparable abundances. This result suggests that the $Cr_2(CO)_6{}^+$ ion must undergo some relaxation process (either collisional or radiative) before the $Cr(CO)_3O_2{}^+$ reaction channel becomes competitive. Also, the efficiency of the ion–molecule reaction is low (exp/calc reaction rate ≃60%), which also suggest that not all ion–molecule collisions yield product ions. The details of this process are being studied further.

The rate constants for the disappearance of the $Cr_2(CO)_x{}^+$ ionic cluster fragments with oxygen are shown in Table I. Note that the rate of $Cr_2(CO)_4{}^+$ ($k = 1.1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) reacting with oxygen is approximately 25% faster than that for $Cr_2(CO)_5{}^+$ ($k = 9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) and ca. 40% faster than that for $Cr_2(CO)_6{}^+$ ($k = 7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}).

Ligand-Exchange Reactions with Methanol. $Cr_2(CO)_4{}^+$ reacts with CH_3OH to displace one or two CO ligands (reactions 6 and 7). The ligand-exchange product ions react to displace two additional CO ligands, yielding $Cr_2(CO)(CH_3OH)_2{}^+$ or $Cr_2(CH_3OH)_2{}^+$.

$$Cr_2(CO)_4{}^+ + CH_3OH \rightarrow$$

$$[Cr_2(CO)_4(CH_3OH)^+]^* \rightarrow Cr_2(CO)_3CH_3OH^+ + CO \qquad (6)$$

$$[Cr_2(CO)_4(CH_3OH)^+]^* \rightarrow C_2(CO)_2CH_3OH^+ + 2(CO) \qquad (7)$$

The $Cr_2(CO)_5{}^+$ ionic cluster fragment undergoes ligand-exchange reactions with CH_3OH by displacement of one CO ligand to form $Cr_2(CO)_4(CH_3OH)^+$ (reaction 8). The $Cr_2(CO)_4(CH_3OH)^+$ product ion reacts with CH_3OH to displace another CO ligand, yielding $Cr_2(CO)_3(CH_3OH)_2{}^{\bullet +}$, but this ion does not react further. In addition, the $Cr_2(CO)_5{}^+$ ionic cluster fragment reacts with CH_3OH to yield metal–metal bond cleavage products, e.g., $CrCH_3OH^+$ (reaction 9), and the $Cr(CH_3OH)^+$ ion reacts with CH_3OH to yield $Cr(CH_3OH)_2{}^+$. Presumably the neutral formed in reaction 9 is $Cr(CO)_5$.

$$Cr_2(CO)_5{}^+ + CH_3OH \rightarrow$$

$$[Cr_2(CO)_5(CH_3OH)^+]^* \rightarrow Cr_2(CO)_4(CH_3OH)^+ + CO \qquad (8)$$

$$[Cr_2(CO)_5(CH_3OH)^+]^* \rightarrow Cr(CH_3OH)^+ + Cr(CO)_5 \qquad (9)$$

The $Cr_2(CO)_6{}^+$ ionic cluster fragment reacts with CH_3OH to displace one CO ligand, but this ligand-exchange product does not react further with methanol. The dominant ion–molecule products observed for $Cr_2(CO)_6{}^+$ with CH_3OH correspond to metal–metal cleavage products, e.g., $Cr(CH_3OH)^+$, and this ion reacts with CH_3OH to form $Cr(CH_3OH)_2{}^+$.

The rate constants for reaction of the $Cr_2(CO)_x{}^+$ ionic cluster fragments with methanol are given in Table I. The rate of $Cr_2(CO)_4{}^+$ ($k = 7 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) reacting with methanol is approximately 15% faster than those observed for $Cr_2(CO)_5{}^+$ ($k = 6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) and $Cr_2(CO)_6{}^+$ ($k = 6 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}).

Ligand-Exchange Reactions with Ammonia. $Cr_2(CO)_4{}^+$ reacts with NH_3 to displace one or two CO ligands (reactions 10 and 11). $Cr_2(CO)_yNH_3{}^+$ ($y = 2$–3) reacts with NH_3 to displace one or two CO ligands, and these product ions react to displace the remaining CO ligands to yield $Cr_2(NH_3)_3{}^+$. The ligand-exchange reaction between $Cr_2(CO)_4{}^+$ and NH_3 also yields products which correspond to metal–metal cleavage of the ionic cluster fragment to form $CrNH_3{}^+$ and $Cr(NH_3)_2{}^+$. The temporal distribution for the ligand-exchange reaction products for $Cr_2(CO)_4{}^+$ with NH_3 is shown in Figure 3a.

$$Cr_2(CO)_4{}^+ + NH_3 \rightarrow$$

$$[Cr_2(CO)_4(NH_3)^+]^* \rightarrow Cr_2(CO)_3(NH_3)^+ + CO \qquad (10)$$

$$[Cr_2(CO)_4(NH_3)^+]^* \rightarrow Cr_2(CO)_2(NH_3)^+ + 2(CO) \qquad (11)$$

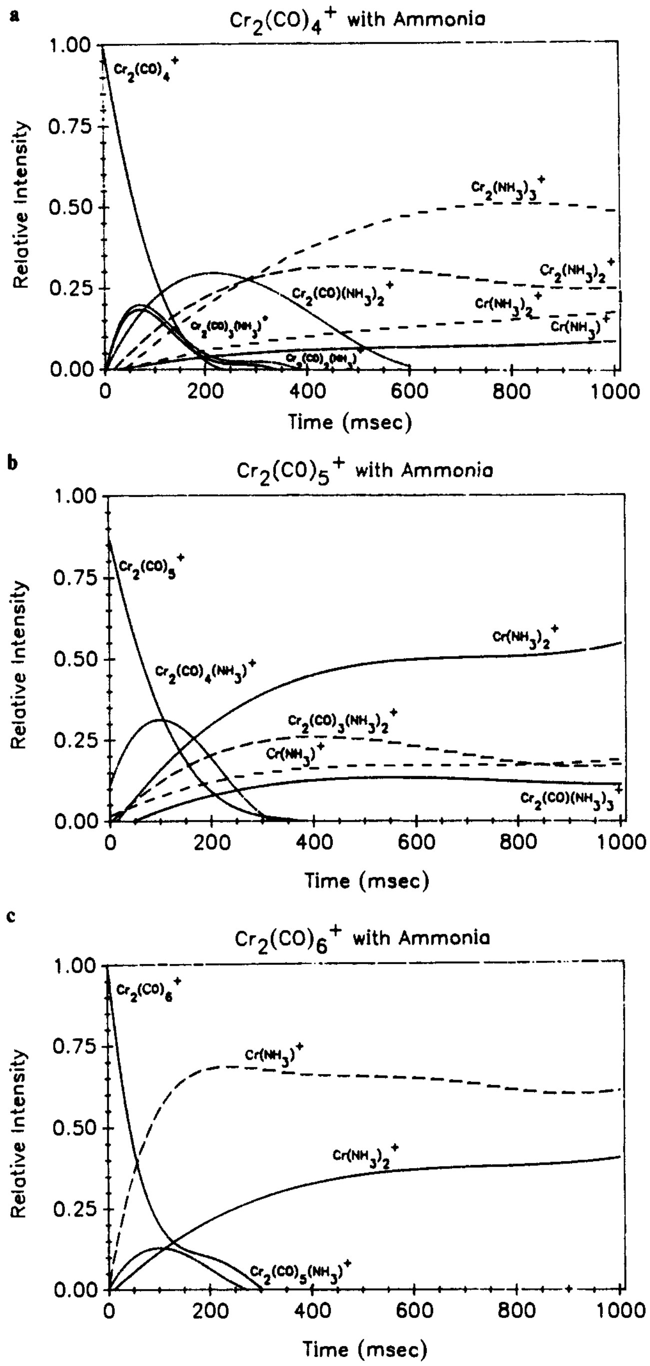

Figure 3. Temporal plot for the ligand-exchange ion–molecule reaction of (a) $Cr_2(CO)_4{}^+$ (b) $Cr_2(CO)_5{}^+$, and (c) $Cr_2(CO)_6{}^+$ with ammonia.

The ligand-exchange reactions of $Cr_2(CO)_5{}^+$ are very similar to that for $Cr_2(CO)_4{}^+$. For the $Cr_2(CO)_5{}^+$ ion ligand exchange proceeds with the displacement of one or two CO ligands by one NH_3 ligand. A stepwise reaction continues until all the CO ligands are exchanged, final product ions being $Cr_2(NH_3)_2{}^+$ and $Cr_2(NH_3)_3{}^+$. The $Cr_2(CO)_5{}^+$ ion also forms products corresponding to metal–metal cleavage. The yield of product ions formed by metal–metal cleavage for $Cr_2(CO)_5{}^+$ is approximately twice that observed for the $Cr_2(CO)_4{}^+$. Figure 3b contains the temporal distribution for the ligand-exchange reaction products between $Cr_2(CO)_5{}^+$ and NH_3.

The $Cr_2(CO)_6{}^+$ undergoes a ligand-exchange reaction by displacement of one CO ligand by one NH_3 ligand, but additional stepwise ligand-exchange reactions are not observed. The $Cr_2(CO)_6{}^+$ ion also forms products corresponding to metal–metal cleavage (note: the metal–metal cleavage products are the dominant ligand-exchange reaction for the $Cr_2(CO)_6{}^+$ ionic cluster fragment). Figure 3c contains the temporal distribution for the ligand-exchange reaction products between $Cr_2(CO)_6{}^+$ and ammonia.

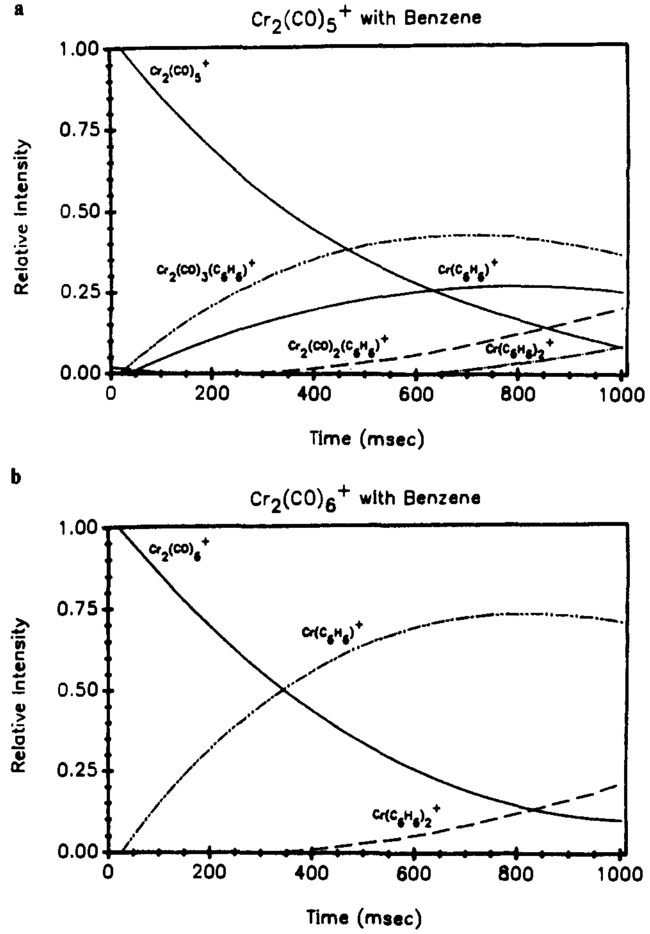

Figure 4. Temporal plot for the ligand-exchange ion–molecule reaction of (a) $Cr_2(CO)_5^+$ and (b) $Cr_2(CO)_6^+$ with benzene.

The rate constants for the disappearance of the $Cr_2(CO)_x^+$ ionic cluster fragments for the ligand-exchange reaction with ammonia are shown in Table I. The rate of $Cr_2(CO)_4^+$ ($k = 1.6 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) reacting with ammonia is approximately 20% greater than that for $Cr_2(CO)_5^+$ ($k = 1.3 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) and ca. 10% faster than that for $Cr_2(CO)_6^+$ ($k = 1.4 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}).

Ligand-Exchange Reactions with Benzene and 1,3-Butadiene. $Cr_2(CO)_4^+$ reacts with benzene or 1,3-butadiene to displace two CO ligands (reaction 12). The $Cr_2(CO)_2L^+$ ion reacts with C_6H_6

$$Cr_2(CO)_4^+ + L \rightarrow [Cr_2(CO)_4L^+]^* \rightarrow Cr_2(CO)_2L^+ + 2(CO) \quad (12)$$

$$[L = C_6H_6 \text{ or } C_4H_6]$$

or C_4H_6 to displace two additional CO ligands to yield $Cr_2(L)_2^+$. The temporal plots for the reaction between $Cr_2(CO)_4^+$ and benzene or 1,3-butadiene are similar to those previously presented for the $Cr_2(CO)_4^+$ ionic cluster fragment.

The $Cr_2(CO)_5^+$ ionic cluster fragment undergoes ligand-exchange reaction to form the same products as the $Cr_2(CO)_4^+$ ion; i.e., the ligand-exchange reaction proceeds by displacement of two CO ligands by a C_6H_6 or C_4H_6 ligand and then stepwise displacement of one to three molecules of CO by a second C_6H_6 or C_4H_6 ligand. However, the $Cr_2(CO)_5^+$ ionic cluster fragment also reacts to form metal–metal cleavage product ions, i.e., $CrC_6H_6^+$ and $Cr(C_6H_6)_2^+$ or $CrC_4H_6^+$ and $Cr(C_4H_6)_2^+$. Branching ratios for simple ligand-exchange and metal–metal cleavage reactions can be estimated from the temporal plots provided in Figure 4a.

The $Cr_2(CO)_6^+$ ionic cluster fragment does not undergo simple ligand-exchange reactions with benzene, but it reacts with 1,3-butadiene to displace one CO ligand. The dominant (see Figure 4b) ion–molecule reaction products observed for $Cr_2(CO)_6^+$ with benzene or 1,3-butadiene correspond to metal–metal cleavage reactions analogous to those products observed for $Cr_2(CO)_5^+$ with benzene and 1,3-butadiene.

The rate constants for the disappearance of the $Cr_2(CO)_x^+$ ionic cluster fragments for ligand-exchange reactions with benzene and 1,3-butadiene are given in Table I. The rate of $Cr_2(CO)_4^+$ ($k = 3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) reacting with benzene is approximately 25% faster than those for $Cr_2(CO)_5^+$ ($k = 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) and $Cr_2(CO)_6^+$ ($k = 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). The rate of $Cr_2(CO)_4^+$ ($k = 3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) reacting with 1,3-butadiene is approximately 10% faster than that for $Cr_2(CO)_5^+$ ($k = 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) and that for $Cr_2(CO)_6^+$ ($k = 2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}).

Discussion

In order for an ionic transition metal cluster fragment to undergo a ligand-exchange reaction, an open coordination site must be available to the incoming ligand, i.e., formation of an associative collision complex (reaction 1). The ion–molecule collision complex $[M_x(CO)_y^+\text{---}L]^*$ contains excess internal energy, and some fraction of the excess energy can be dissipated by expulsion of other ligands. Therefore, the exothermicity of the reaction and the number of CO ligands displaced by the incoming ligand (L) depends upon the relative binding energies of the ligands to the metal cluster. Steric effects may influence the overall rate of reaction, but it is unlikely that such effects (where L is a small molecule) will play a very important role for the $M_x(CO)_y^+$ species. Conversely, geometric relaxation (e.g., structural rearrangement and/or changes in the metal–metal or metal–ligand bond order) of the ion–molecule collision complex may be important. That is, addition of a ligand (L) to $M_x(CO)_y^+$ may significantly alter the nature of the metal–metal bond or even the metal–CO bonding. The photodissociation data for the $M_x(CO)_y^+$ ionic species clearly show that metal–CO bond energies are sensitive to the metal-to-ligand ratio,[2] a result consistent with studies of metal–CO bond energies of mono-metal species.[14,25]

The thermoneutral ligand-exchange reactions with ^{13}CO provide an indication of the ligand lability for the $Cr_2(CO)_y^+$ ions. The ligands of $Cr_2(CO)_4^+$ and $Cr_2(CO)_5^+$ ions are very labile and readily exchange with the ^{13}CO; conversely, the $Cr_2(CO)_6^+$ ions do not undergo ligand exchange with ^{13}CO. There are several factors which may influence the thermoneutral ligand-exchange reaction between ^{13}CO and $Cr_2(CO)_6^+$ ions: (i) the ligands of the $Cr_2(CO)_6^+$ are very strongly bound and the geometric relaxation[26] required to accommodate the incoming ligand is associated with a high activation (either kinetic or thermodynamic) barrier; (ii) the $Cr_2(CO)_6^+$ ion does not have an open coordination site to accept bonding electrons from the incoming CO ligand. In our original work on $Cr_x(CO)_y^+$ ionic cluster fragments, we suggested that the electron deficiency of $Cr_2(CO)_6^+$ is low (e.g., 3.5); an electron deficiency of 3.5 suggests that there are open (1.75 per Cr atom) coordination sites for attachment of the incoming ligand. Therefore, it seems unlikely that the reactivity of $Cr_2(CO)_6^+$ with CO can be attributed to the lack of an open coordination site.

It is interesting to compare the rates for the ligand-exchange reactions of $Cr_2(CO)_y^+$ with ^{13}CO and the electron deficiencies for the ionic cluster fragments. For example, the rate of the ion–molecule reactions with ^{13}CO (ligand lability) increases as the electron deficiency of the ionic cluster fragments increases. The electron deficiency for $Cr_2(CO)_4^+$ is ca. 7.5, and the electron deficiencies for $Cr_2(CO)_5^+$ and $Cr_2(CO)_6^+$ are 4.5 and 3.5, respectively.[2] Although the rates of reactions for the $Cr_2(CO)_y^+$ ($y = 4, 5, 6$) ion are different, specifically $Cr_2(CO)_4^+ > Cr_2(CO)_5^+ > Cr_2(CO)_6^+$, the differences appear smaller than expected based on an electron deficiency argument. In general, the $Cr_2(CO)_5^+$ and $Cr_2(CO)_6^+$ ions have roughly the same reaction rates except for ligand-exchange reactions with ^{13}CO and oxygen where the $Cr_2(CO)_5^+$ ion is more reactive. Comparisons of the experimental reaction rate constants with Langevin and averaged-dipole ori-

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entation theories show that ligand exchange does not occur for every ion–neutral collision, e.g., 70% and 80% for $Cr_2(CO)_5^+$ and $Cr_2(CO)_4^+$, respectively. Thus, the reaction efficiency may result from a strong orientation dependence on the reaction. But the reaction efficiency may also be due to a preference for loss of the incoming ^{13}CO ligand upon dissociation of the collision complex, e.g., $[Cr_2(CO)_y^+ \cdots {}^{13}CO]^* \rightarrow Cr_2(CO)_y^+ + {}^{13}CO$. That is, at early stages in the reaction the ligands are nonfluxional and the ligand identity is preserved.

Issues related to ligand fluxionality were examined in separate experiments. Kerley and Russell examined the extent of ^{13}CO retention by $Fe_x(CO)_y^+$ formed by reaction of $Fe(^{13}CO)_+$ with $Fe(CO)_5^+$.[27] The results of these studies suggest that geometric relaxation of the $[(^{13}CO)Fe^+ \cdots Fe(CO)_5]$ collision complex occurs by rearrangement within the initial neutral moiety. That is, the extent of label retention in the $Fe_2(CO)_4^+$ and $Fe_2(CO)_5^+$ product ions is low, less than a few percent, which suggests preferential elimination of ^{13}CO from the collision complex. There may, however, be fundamental differences in the dynamics of addition of L to $M_x(CO)_y^+$ and addition of $(^{13}CO)Fe^+$ to $Fe(CO)_5$. For example, the initial interaction between $(^{13}CO)Fe^+$ and $Fe(CO)_5$ occurs via the Fe^+ and the CO ligands of $Fe(CO)_5$, whereas, the initial interaction between L and $M_x(CO)_y^+$ probably involves addition of L to the metal center.

Beauchamp recently suggested that variations in the rates for ligand-exchange reactions of mono-metal ionic species arise due to the spin-forbidden nature of the ligand addition reaction.[14] We interpreted data from photodissociation reactions in mono-metal ionic species in a similar fashion;[2] however, we have not observed such effects for metal dimer or trimer ions. Presumably, the metal dimer and trimer ions promote spin–orbit coupling through a heavy atom effect; this interpretation is consistent with the photochemistry of $Fe(CO)_yX^+$ species, X = I, Br, Cl.[28] $Fe(CO)_y^+$ (y = 1–3, 5) ions do not photodissociate between 514.5 and 458 nm, presumably because $Fe(CO)_y^+ \rightarrow Fe(CO)_{y-1}^+$ is spin-forbidden, but the $Fe(CO)_yX^+$ ions readily photodissociate to $Fe(CO)_{y-1}X^+$ and $Fe(CO)_{y-2}X^+$.

In our original work on the formation of ionic cluster fragments by ion-molecule reactions, we explained the clustering sequence in term of the addition of a 14-electron metal carbonyl fragment (L′) to $M_x(CO)_y^+$ to form $[M_x(CO)_y^+ \text{---} L']^*$ which subsequently rearranges to a stable $M_{x+1}(CO)_y^+$ ion.[12b] The transformation $[M_x(CO)_y^+ \text{---} L']^*$ to $M_{x+1}(CO)_y^+$ corresponds to a complete reorganization of the electronic structure, or, in terms of Lauher's model of the cluster bonding, a complete restructuring of the cluster valence molecular orbital (CVMO).[29] An important factor which emerges from this model is that the reactivity (as measured by the disappearance of the reactant ion or the appearance of the ion–molecule product ion) of the ionic cluster fragment will be strongly dependent upon the (relative) strength of the interaction between the reacting ion and the neutral. For example, if the interaction between the reacting ion and the neutral is weak, relative to the metal–metal and metal–ligand binding energy of the reacting species, the collision complex will simply dissociate to re-form the reactants. However, a strong interaction between the ionic and neutral reactants will lead to displacement of ligands of the ionic or neutral reactants and formation of a new product ion.

Formation of an associative ligand-exchange collision complex can be viewed in a similar manner. That is, L (CO, O_2, etc.) reacts with $M_x(CO)_y^+$ to form $[M_x(CO)_y^+ \text{---} L]^*$, and CO ligands are expelled to form $M_x(CO)_{y-a}L^+$. If formation of $M_x(CO)_{y-a}L^+$ is strongly exothermic, several CO ligands may be displaced from $[M_x(CO)_y^+ \text{---} L]^*$ upon addition of L. Because the exothermicity of the reaction may be due to geometric relaxation or rearrangement of the $[M_x(CO)_y^+ \text{---} L]^*$ collision complex as well as differences in the bond energies of the in-coming and out-going ligands, bracketing of ligand bond energies is not a straightforward problem. For example, such rearrangements are suggested when competitive reaction channels are involved; e.g., CH_3OH reacts with $Cr_2(CO)_4^+$ to yield $Cr_2(CO)_3(CH_3OH)^+$ and $Cr_2(CO)_2(CH_3OH)^+$. Clearly, there must be relaxation channels available to the collision complex in addition to simple ligand expulsion.

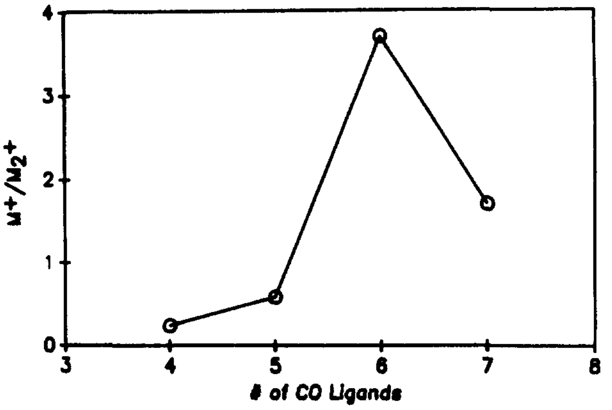

Figure 5. Plot of the M^+/M_2^+ branching ratio from collision-induced dissociation reactions versus the number of CO ligands (y) of the $Cr_2(CO)_y^+$ (y = 4–7) ionic cluster fragment.

The occurrence of metal–metal cleavage ion–molecule reactions follows a general trend which can be explained in terms of metal–metal and metal–ligand bond energies. For example, the fraction of ions which react by Cr–Cr cleavage increases with decreasing electron deficiencies, (e.g., $Cr_2(CO)_6^+ > Cr_2(CO)_5^+ > Cr_2(CO)_4^+$). Also, Cr–Cr cleavage product ions follow the general trend, $NH_3 > C_4H_6 \sim CH_3OH \sim C_6H_6 > O_2$). Although accurate metal–ligand bond energies for $Cr_2^+ \text{---} L$ species (L = CO, O_2, CH_3OH, etc.) are not known, preliminary studies[30] suggest that $Cr_2^+ \text{---} L$ bond energies roughly parallel those reported for mono-metal ions.[31] That is, the metal–ligand bond energies for the ligands examined approximate the trend observed for metal–metal bond cleavage reactions of the $Cr_2(CO)_y^+$ ions; $D°(Cr_2^+ \text{---} L)$ values are $NH_3 > C_4H_6 \sim C_6H_6 > CH_3OH > O_2 > CO$. On the basis of the observed reactivity, for example, $Cr_2(CO)_4^+$ undergoes metal–metal bond cleavage only with NH_3, whereas, $Cr_2(CO)_5^+$ undergoes metal–metal bond cleavage with ligands having bonds energies greater than that of O_2. On the basis of preliminary estimates of metal–ligand bond energies,[32] we estimate that the metal–metal bond of $Cr_2(CO)_4^+$ is ca. 12–15 kcal/mol stronger than that for $Cr_2(CO)_5^+$.

Questions concerning the metal–metal bond of the Cr_2 dimer are of importance to the general area of metal clusters and cluster chemistry. Smalley et. al. reported a Cr–Cr bond length of 1.68 Å.[33] Such a short bond length is consistent with the view that Cr_2 involves a sextuple bond. Although chromium carbonyl species do not generally bond together to form clusters, the stability of small $Cr_x(CO)_y^+$ ionic species suggests that such species are not intrinsically unstable. In fact, collision-induced dissociation of $Cr_x(CO)_y^+$ ions suggest that the Cr–Cr bond in dimers, trimers, and tetramers is quite substantial. For example, collisionally activated $Cr_x(CO)_y^+$ ions favor dissociation by loss of CO over cleavage of the Cr–Cr bond, and the collision-induced dissociation spectra can be used to estimate the relative Cr---Cr bond strengths for the ions. The branching ratios for formation of M^+ and M_2^+ product ions from collisionally activated $Cr_2(CO)_y^+$ ions should be sensitive to the metal–metal bond energy. Figure 5 contains a plot of the ratio of M^+/M_2^+ versus the number of CO ligands contained in the $Cr_2(CO)_y^+$ ionic cluster fragment. Note that for y = 4 the M^+/M_2^+ ratio is 0.25; whereas for y = 6 the

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M^+/M_2^+ ratio is 3.7. The collision-induced dissociation data are interpreted as evidence that the Cr–Cr bond strength is directly influenced by the M/L ratio. That is, the metal–metal bond strength follows the order $Cr_2(CO)_6^+ < Cr_2(CO)_5^+ < Cr_2(CO)_4^+$. The CID data have also been obtained for the $Cr_3(CO)_y^+$ (y = 6, 7) ionic cluster fragments and the M^+/M_3^+ ratio is 1/12 for y = 6 and 1/10 for y = 7; whereas the M_2^+/M_3^+ ratio is 1/6 for y = 6 and 1/5 for y = 7, suggesting a very strong metal–metal interaction for the chromium trimer center. The general utility of the collision-induced dissociation experiment for probing the metal–metal bond order is now being examined on larger Cr-containing clusters as well as clusters containing Fe, Co, and Ni.

Conclusions

The reactivities of $Cr_2(CO)_y^+$ (y = 4, 5, 6) with small neutral molecules do not parallel that observed for reactions with $Cr(CO)_6$. That is, reaction rates for $Cr_2(CO)_y^+$ ions with $Cr(CO)_6$ differ considerably and the reactivity can be explained by an electron deficiency argument, but the variations in reaction rate for the $Cr_2(CO)_y^+$ ions with the small neutral molecules are rather small, e.g., 10–40%. In each case the ion–molecule reaction efficiency (determined by comparing theoretical collision frequency with the experimental reaction rate) is quite high and approaches unity.

The CO ligands of $Cr_2(CO)_4^+$ and $Cr_2(CO)_5^+$ are quite labile and readily undergo thermoneutral ligand exchange with ^{13}CO, whereas the CO ligands of $Cr_2(CO)_6^+$ are nonlabile and do not undergo exchange reactions with ^{13}CO. Ligand-exchange reactions of $Cr_2(CO)_6^+$ with other ligands (e.g., CH_3OH and NH_3) further illustrate the nonlability of this system. For example, both CH_3OH and NH_3 react to displace one CO ligand to form $Cr_2(CO)_5L^+$ (L = CH_3OH or NH_3), but this ion does not react further by ligand exchange.

A very interesting aspect of the observed ion–molecule reactions of the $Cr_2(CO)_y^+$ ions is the variation in the ratio of cleavage of the Cr---CO bond versus Cr---Cr bond upon addition of neutral ligand as the metal-to-ligand ratio decreases. The strong preference for metal–metal bond cleavage for $Cr_2(CO)_6^+$ suggests that the Cr---Cr bond in this ion is relatively labile. In addition, similar conclusions can be made on the basis of the abundance of Cr_2^+ (relative to Cr^+) in the collision-induced dissociation spectrum of $Cr_2(CO)_y^+$ (y = 4–7) ions. That is, the ratio Cr^+/Cr_2^+ varies from 0.25 for y = 4 to 3.7 for y = 6. It is surprising, therefore, that the Cr^+/Cr_2^+ ratio for $Cr_2(CO)_7^+$ is also low, e.g., 1.75, suggesting that the metal–metal bond orders for $Cr_2(CO)_7^+$ and $Cr_2(CO)_6^+$ are quite different. Our current objectives in this area are to obtain accurate metal–metal and metal–ligand bond energies for the $Cr_2(CO)_y^+$ (y = 4–7) ionic cluster fragments.

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Ligand Fluxionality and the Formation of Cationic Iron Carbonyl Clusters

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Abstract: The clustering gas-phase reactions of $Fe(^{13}CO)^+$ with $Fe(CO)_5$ to form $Fe_x(^{13}CO)_r(CO)_s^+$ (x = 1–3; r = 0, 1; s = 4–8) are studied by Fourier transform ion cyclotron resonance mass spectrometry. It was found that the binary cluster cations formed by these reactions have a strong tendency to lose the ^{13}CO ligand during cluster formation. Label preference ratios varied only slightly from 0.56 ± 0.06 to 0.7 ± 0.1 indicating a clear preference for loss of the labeled carbonyl ligand. This preferential loss is indicative of the nonfluxional nature of these systems. Nonfluxionality in the cationic iron carbonyl clusters results from a decrease in back-bonding to the 2π orbital of the carbonyl ligands.

Introduction

Ligand fluxionality is commonly observed for coordinatively and electronically saturated iron carbonyl compounds.[1] For example, $Fe_3(CO)_{12}$ exists in solution as a continuum of structures ranging from the symmetrically bridged C_{2v} to the nonbridged D_{3h} structure. The activation energy for going from one structure to the other is estimated at <5 kcal mol^{-1}, giving rise to the observation of only a single ^{13}C NMR resonance at −150 °C.[2] The concept of ligand fluxionality has been successfully employed for prediction of structures of binary carbonyl clusters.[3,4] In this procedure, carbonyl ligands are assumed to be equivalent such that the repulsions between ligands ultimately determine their arrangement around a bare metal cluster. The solid-state C_{2v} structure of $Fe_3(CO)_{12}$ can be rationalized by this method if one considers the 12 carbonyl ligands to form an icosahedron with an Fe_3 triangle placed inside. Further, the D_{3h} structure of the isovalent $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ species can be explained by realizing that the interstice of the icosahedral carbonyl arrangement cannot support these larger homologues, causing the icosahedron to expand to an anticubooctahedron.

The amphoteric nature of the carbonyl ligand gives rise to the fluxional behavior observed for iron carbonyl compounds. Ligands with occupied σ orbitals and unoccupied π orbitals can act as both Lewis bases (σ donors) and Lewis acids (π acids). A number of transition metal atoms (especially those in groups 6–8) display a complementary amphoterism. The d orbitals of iron lie intermediate in energy between the 5σ and the 2π orbitals of CO, maximizing overlap for both the σ-donating and π-back-bonding bonding modes. If the sum of the σ- and π-bonding components remains constant as a carbonyl ligand moves from terminal to bridging for a given cluster nucleus, then CO fluxionality should occur. As the coordinative saturation or electronic charge (electronic saturation) of a cluster is changed, the tendency for

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