plane of sodium β'' alumina. Nonetheless, the luminescence spectra show that not only is the uranyl ion incorporated in the conduction plane but also that it is a sensitive probe of the environment in the conduction plane. This result suggests that it may be feasible to use various molecules to probe the local structural environment of solid ionic conductors and provide greater insight concerning the structure/property relationship in these materials.

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Activation of Nitric Oxide by Dimeric Cobalt Ions in the Gas Phase

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Transition-metal clusters containing nitrosyl ligands are the focus of increasing interest due to their rich and diverse chemistry compared with binary carbonyl compounds.[1,2] For example, the nitrosyl ligand is susceptible to electrophilic attack,[3,4] reduction with molecular hydrogen,[4,5] and deoxygenation yielding nitrido clusters.[6-8] This latter process results in the conversion of CO to CO_2 by oxygen transfer, process 1. The mechanisms of these

$$M_x(CO)_y(NO) \rightarrow M_x(CO)_{y-1}N + CO_2 \tag{1}$$

oxygen transfers are quite speculative. For example, oxide transfer may proceed by (1) initial dissociation of a CO ligand followed by insertion of NO yielding a nitrido-oxide cluster with subsequent oxide transfer to free CO or (2) by a concerted oxide transfer to a coordinated CO from an intact NO ligand resulting in CO_2 elimination.[7] Gas phase ion techniques, however, may provide unique insights into the above process. In this communication the formation of cobalt-cluster-nitrido cations in the gas phase by oxide transfer to carbon monoxide from cobalt cluster nitrosyls is described.

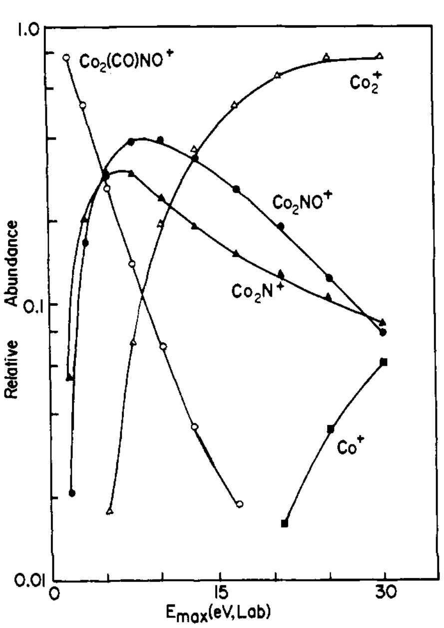

Figure 1. Variation of ion abundances as a function of kinetic energy for dissociation of collisionally activated $Co_2(CO)NO^+$ with argon as the collision gas at a pressure of 1×10^{-5} Torr. The relative ion intensities are taken as a fraction of the initial $Co_2(CO)NO^+$ intensity (no excitation). The sum of ion abundances totals slightly less than unity at high kinetic energy due to ion ejection from the cell.

All experiments were performed on a Nicolet FTMS-1000 Fourier transform mass spectrometer equipped with a 5.08-cm cubic-trapping cell immersed in a 3.0-T magnetic field.[9] The theory, instrumentation, and methodology of conventional ion cyclotron resonance (ICR)[9,10] and Fourier transform mass spectrometry (FTMS)[11] have been discussed at length elsewhere. The cobalt-cluster cations were generated by rapid condensation of fragment ions (formed from electron impact on $Co(CO)_3NO$) with $Co(CO)_3NO$.[12] For example, $Co_2(CO)_2NO^+$, $Co_2(CO)NO^+$, and $Co_3(CO)NO^+$ are formed by reactions 2-4. The highly unsaturated clusters, Co_2NO^+ and Co_3NO^+, were generated by collisional activation (CA)[13,14] of $Co_2(CO)_2NO^+$ and $Co_3(CO)NO^+$ which were subsequently isolated by swept double resonance ejection techniques.[11] Argon was used as the target gas for collisional activation at a pressure of 1×10^{-5} Torr and also serves to collisionally cool the daughter ions prior to studying their reactivity. $Co(CO)_3NO$ was admitted into the vacuum chamber via a pulsed solenoid inlet valve[15] allowing it to be removed from the chamber within 500 ms permitting these studies to be performed without complicating side reactions with $Co(CO)_3NO$.

$$Co^+ + Co(CO)_3NO \xrightarrow{80\%} Co_2(CO)_2NO^+ + CO \tag{2}$$

$$Co^+ + Co(CO)_3NO \xrightarrow{40\%} Co_2(CO)NO^+ + 2CO \tag{3}$$

$$Co_2^+ + Co_3(CO)_3NO \longrightarrow Co_3(CO)NO^+ + 2CO \tag{4}$$

The variation of ion abundances as a function of kinetic energy for dissociation of collisionally activated $Co_2(CO)NO^+$ is illustrated in Figure 1 with facile elimination of CO and CO_2 observed, processes 5 and 6. This is in stark contrast to the binary metal-carbonyls which yield exclusively facile elimination of the

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$$[Co_2(CO)NO]^{+*} \xrightarrow{CA} \begin{cases} Co_2NO^+ + CO & (5) \\ Co_2N^+ + CO_2 & (6) \end{cases}$$

carbonyls as the only fragmentation processes.[16] Formation of Co_2N^+, process 6, may also proceed by successive elimination of CO and O. The direct elimination of CO_2 from activated $Co_2(CO)NO^+$ was confirmed by directly observing the dissocation of Co_2NO^+, formed in process 5, where facile elimination of nitrosyl was the only process observed, reaction 7. The formation

$$[Co_2NO]^{+*} \xrightarrow{CA} Co_2^+ + NO \qquad (7)$$

of transition-metal cluster nitrides from transition-metal cluster-nitrosyl-carbonyl complexes is found to be facile for large saturated or nearly saturated species.[2a] Collisional activation of $Co_2(CO)_2NO^+$ yields initial loss of a carbonyl followed by either elimination of CO or CO_2, vide supra.

Co_2NO^+ reacts with CO yielding Co_2N^+ exclusively, process 8, with linear first-order kinetics giving a rate constant of 3.3 ±

$$Co_2NO^+ + CO \rightarrow Co_2N^+ + CO_2 \qquad (8)$$

0.7×10^{-11} cm^3 molecule^{-1} s^{-1}. Comparison with the corresponding collision rate of 6.9×10^{-10} cm^3 molecule^{-1} s^{-1} indicates that decarboxylation occurs on only one of every 21 collisions.[17] In addition $Co_2(CO)NO^+$ is unreactive with CO in accord with the collisional activation results for $Co_2(CO)_2NO^+$. This slow rate of decarboxylation, process 8, is surprising since it is competitive with direct CO elimination for collisional activation of $Co_2(CO)NO^+$ at low collision energy, Figure 1. These results suggest a kinetic barrier for oxygen transfer to CO from Co_2NO^+ which may result from spin restrictions in the intermediate complex.[18] Such a kinetic barrier has previously been inferred for the absence of oxygen abstraction from N_2O by both atomic[19] and small bare transition-metal cluster ions,[20] and this barrier was attributed to spin multiplicity differences. It appears that $Co_2(CO)NO^+$ has achieved an electronic configuration favorable for oxygen transfer to CO prior to collisional activation. Finally, observation of reaction 8 implies $D°(Co_2N^+–O) < 127.2$ cal/mol.[21] For comparison $D°(N–O) = 151$ kcal/mol[21] and $D°(Co_2^+–O) > 119$ kcal/mol.[20] In contrast to the above results collisional activation of $Co_3(CO)NO^+$ yields exclusively loss of CO as its primary fragmentation with *no* Co_3N^+ formation observed. In addition Co_3NO^+ is unreactive with carbon monoxide. The inert behavior of $Co_2(CO)NO^+$ and Co_3NO^+ with CO clearly shows that both the degree of saturation as well as cluster size are critical for NO activation.

The mechanism of the above oxygen transfer is unclear at this time. Since only the highly unsaturated dimeric species participates suggests that dissociation of NO forming an oxide-nitrido species may precede oxygen transfer to CO. This is supported by the observation that nitric oxide generally dissociates on clean metal surfaces at low coverages while at higher coverages molecular absorption becomes more favorable.[22] In addition stable oxide-nitrido clusters have recently been characterized.[8,23] We are currently attempting to determine if dissociation of NO precedes oxide transfer for $Co_2(CO)NO^+$.

The above results demonstrate that unsaturated metal cluster nitrosyls exhibit a rich and varied chemistry compared with their corresponding binary carbonyl systems. Clearly additional work in this area should yield equally exciting results.

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Organometallic Coordination Chemistry of Aluminum. Synthesis and Molecular Structure of $[Al(CH_3)]_2[C_8H_{20}N_6][Al(CH_3)_2]_2$: A Novel Example of a Neutral Organoaluminum Complex Containing Two Five-Coordinate Aluminum Atoms in Square Pyramidal Environments

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The reaction of aluminum alkyls with amines is perhaps one of the most celebrated reactions in organoaluminum chemistry. Investigations may be traced to 1930 when Krause and Dittmar[1] reported the synthesis of $(H_3N)Al(p\text{-tolyl})_3$ and $(H_3N)Al(Ph)_3$. In terms of contemporary organoaluminum chemistry, the most definitive work in the area has concerned poly(*N*-alkyliminoalanes)[2-16] and aluminum–nitrogen oligomers.[17-25] The coordination

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