

Figure 2. Orbital interactions of $M-\mu_4\text{-CO}$ in $\text{Cp}_4\text{Mo}_2\text{Ni}_2\text{S}_2(\text{CO})$.

Both overlap population and energy matrix analysis from EHMO calculations indicated significant bonding interactions between Ni and CO. The overlap population between Ni and CO is 19% of the total overlap population (1.267) between the metals and the carbonyl carbon. Two unusual bonding features of Ni-CO interactions, related to the electronic saturation on the Ni atoms, were observed. First, bonding molecular orbitals between Ni and CO having Ni 4s and 4p character were found. This is difficult from our calculational results on $\text{Cp}_2\text{Mo}_2\text{M}_{2,3}\text{S}_{3,2}\text{L}_n$ clusters, in which metal d orbitals only contribute to bonding.¹² Second, two filled Ni-CO orbitals with Ni-C antibonding interactions were calculated.

The orbital interactions of the $\mu_4\text{-CO}$ are demonstrated in Figure 2. Type a, σ bonding in nature, and type b, multicenter bonding with the CO π -system, are about equally important in the Mo-CO interactions. Types b and b' (distinguished only by the composition of the Ni atomic orbitals) are dominant (overlap population $a:(b + b') < 1:3$) in the Ni-CO interactions. The Ni-CO bonding is best described as a dative bond from Ni to the π^* orbitals of the $\mu_4\text{-CO}$. The low C-O overlap population (0.95 vs ca. 1.2 for terminal C-O ligands) reflects this additional electron donation into the C-O antibonding orbitals and is consistent with the low ν_{CO} observed.

The framework of **2** may also be viewed as a pentagonal bipyramid in which five atoms (C, Ni, S, S, Ni) are unevenly spread around the Mo-Mo axis. Other clusters having the same framework geometry include $\text{Cp}_4\text{Cr}_2\text{Ni}_2\text{S}_2(\mu_4\text{-S})$,¹³ $\text{Cp}_2\text{Mo}_2\text{Fe}_2\text{S}_2(\mu_4\text{-S})(\text{CO})_6$,⁸ $\text{Cp}_2\text{Mo}_2\text{Co}_3\text{S}_2(\text{CO})_7$,⁵ and $(\text{RCp})_2\text{Mo}_2\text{Co}_2\text{S}_2(\mu_4\text{-S})(\text{CO})_4$.^{5,7} A comparison of these clusters shows that the dihedral angle between the MMM' (M = hinge metal, M' = wingtip) and the $\text{MM}(\mu_4\text{-X})$ planes is rather variable, suggesting a soft potential for deformation of the hinge angle or the $M'-\mu_4\text{-X}$ distance. Thus, it is unlikely that the relatively long Ni- $\mu_4\text{-CO}$ distance is caused by steric crowding in the $\text{M}_2\text{M}'_2$ pocket. A series of EHMO calculations in which the CpNiS units were rotated around the Mo-Mo axis showed a shallow-bottomed well with a minimum corresponding to a Ni- $\mu_4\text{-CO}$ distance of ca. 2.25 Å. Below ca. 2.0 Å, the energy rises rapidly, but no single bonding or antibonding interaction could be identified as the cause of the rapid increase in energy.

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Supplementary Material Available: Tables IS-VIS and VIIS (list of dihedral angles, crystallographic data, fractional atomic coordinates, thermal parameters, bond distances and angles, and EHMO parameters for **2**) and Figure 1S (labeled ORTEP plot of entire molecule of **2**) (10 pages); Table VIIS (listing of structure factors F_o vs F_c for **2**) (6 pages). Ordering information is given on any current masthead page.

Investigation of Isomeric Intermediates: Co^+-NH_3 and $\text{H-CO}^+-\text{NH}_2$

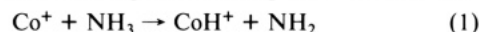
D. E. Clemmer and P. B. Armentrout*[†]

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

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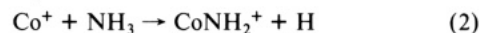
One of the prime distinctions between studies of gas-phase and condensed-phase chemistry is that chemical intermediates are rarely isolated in the former, whereas they are routinely studied in the latter. Because of this, gas-phase-ion chemists have resorted to a variety of *indirect* means to study and characterize proposed intermediates in a chemical reaction. These include collision-induced,¹ photon-induced,² and metastable³ dissociations, kinetic energy "sampling",⁴ and chemical reactivity studies.^{2,5} In this work, we describe the surprising *direct* observation of a long-lived chemical intermediate in a five-atom reaction system, $\text{Co}^+ + \text{NH}_3$.

Figure 1 shows results obtained by using guided ion beam mass spectrometry to study the reaction of ammonia with Co^+ (as produced by surface ionization at 2300 K, and therefore primarily in the a^3F state). Details of the technique and methods for analyzing the energy dependence of the cross sections can be found elsewhere.^{6,7} The dominant product is CoH^+ . Analysis of this cross section, $\sigma(\text{CoH}^+)$, leads to a threshold of 2.79 ± 0.12 eV. This is within experimental error of the threshold expected for reaction 1, 2.67 ± 0.06 eV, given $D^\circ(\text{NH}_2\text{-H}) = 4.69$ eV⁸ and



$D^\circ(\text{Co}^+\text{-H}) = 2.02 \pm 0.06$ eV.⁹ This agreement verifies that reaction 1 has no large barriers in excess of the endothermicity.

Below the threshold for reaction 1, formation of CoNH_2^+ is the most favorable process and must be due to reaction 2. While



the logarithmic scale of Figure 1 makes the threshold for this process appear to be near 1 eV, analysis of $\sigma(\text{CoNH}_2^+)$ (which accurately accounts for the kinetic and electronic energy distributions of the reactants) shows that the true threshold is 2.0 ± 0.1 eV. This value leads to $D^\circ(\text{Co}^+\text{-NH}_2) = 62 \pm 2$ kcal/mol,

[†] NSF Presidential Young Investigator, 1984-1989; Alfred P. Sloan Fellow; Camille and Henry Dreyfus Teacher-Scholar, 1988-1993.

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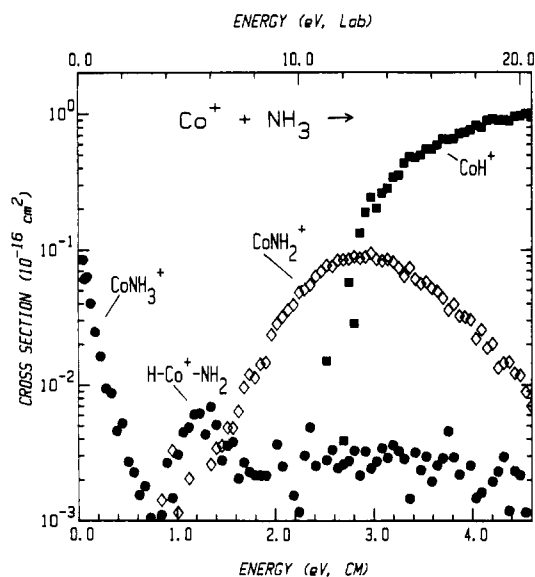


Figure 1. Variation of product cross sections for reaction of ammonia (at a pressure of 0.14 mTorr) with Co^+ (produced by surface ionization) as a function of translational energy in the center-of-mass frame (lower scale) and laboratory frame (upper scale).

in agreement with the value 65 ± 8 kcal/mol obtained from bracketing measurements.¹⁰ Above 2.8 eV, $\sigma(\text{CoNH}_2^+)$ declines. This cannot be due to product dissociation since formation of $\text{Co}^+ + \text{NH}_2 + \text{H}$ requires 4.69 eV. An alternative explanation is that reaction 1 depletes the intermediate precursor to reaction 2. This is strongly suggested by the coincidence between the peak in $\sigma(\text{CoNH}_2^+)$ and the onset of CoH^+ formation. Similar observations have been made for the reactions of other transition-metal ions with ammonia^{7,11} and methane.¹² The common intermediate is presumably $\text{H-Co}^+-\text{NH}_2$, I, the result of oxidative addition of the N-H bond to the metal center. It is well-known that Co^+ activates C-H and C-C bonds of saturated alkanes,^{13,14} so the formation of I is certainly plausible.

At the lowest energies, we observe the formation of CoNH_3^+ . The most striking aspect of $\sigma(\text{CoNH}_3^+)$ is that it contains two features. Below 0.8 eV, the cross section increases monotonically with decreasing energy, establishing that the process is a barrierless exothermic reaction. The magnitude of this feature is found to depend linearly upon pressure, establishing that the CoNH_3^+ formed at these energies results from stabilizing secondary collisions. Analysis of this pressure dependence by a previously outlined method¹⁵ leads to a lifetime for CoNH_3^+ of $\sim 0.2 \mu\text{s}$ at our lowest energies (~ 0.05 eV).

The second feature of $\sigma(\text{CoNH}_3^+)$ appears at ~ 0.8 eV and peaks at ~ 1.4 eV. The magnitude of this feature is independent of pressure. Thus the CoNH_3^+ produced at these energies must live long enough to reach the detector, $\sim 60 \mu\text{s}$ at 1.4 eV. Since this is a very long lifetime for a five-atom molecule, we confirmed the observation by studying the reaction of $\text{Co}^+ + \text{ND}_3$. Nearly identical cross sections are obtained for all three deuterated products.

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To explain these observations regarding $\sigma(\text{CoNH}_3^+)$, we assign different structures to the two features observed. The exothermic reaction must form Co^+-NH_3 , the simple adduct in which the lone pair of electrons on N is donated to the cation. This exothermicity is consistent with $D^\circ(\text{Co}^+-\text{NH}_3) = 2.5$ eV.¹⁶ Furthermore, formation of Co^+-NH_3 is unlikely to have a barrier since the long-range part of the potential is the very attractive ion-dipole interaction. We assign the second, endothermic feature to the structure $\text{H-Co}^+-\text{NH}_2$, I. Since reaction 2 depletes this intermediate, this assignment explains why $\sigma(\text{CoNH}_3^+)$ peaks at the onset for reaction 2. This structure also allows a reasonable explanation of the long lifetime of this species, since reformation of reactants should proceed via a tight transition state needed for reductive elimination of NH_3 . The lifetime of this species could be appreciable if I lies in a potential well below the ~ 0.8 -eV barrier required for its formation. Indeed, this well is ~ 0.8 eV deep, assuming that $D^\circ(\text{HCo}^+-\text{NH}_2) \approx D^\circ(\text{Co}^+-\text{NH}_2)$.

The observation of the long-lived HCoNH_2^+ intermediate can probably be attributed to the balance of several factors. Compared with alkane systems, the lone-pair electrons on ammonia help stabilize the ionic intermediate. Compared with several other metal ions, Co^+ is less reactive with ammonia,^{7,11,17} and in these cases, such intermediates rapidly dissociate to products. The prospect of making similar observations in other systems is of current interest in our laboratories.

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Pd-Catalyzed Synthesis of Macrocycles. A Total Synthesis of (-)-Aspochalasin B

Barry M. Trost,* Masayuki Ohmori, Steven A. Boyd, Hideki Okawara, and Steven J. Brickner

Departments of Chemistry
Stanford University, Stanford, California 94305-5080
University of Wisconsin, Madison, Wisconsin 53706

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The extraordinary effects of the cytochalasins on mammalian cell membranes affecting transport across the membrane, cell mobility, among others, have made these important tools in cell research attractive synthetic targets.¹⁻⁴ An examination of the

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