Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

Chapter 18

Gas-Phase Chemistry of First-Row Transition Metal Ions with Nitrogen-Containing Compounds

Theoretical and Experimental Investigations

A. Mavridis[1], K. Kunze[2], J. F. Harrison[2], and J. Allison[2]

[1]Chemistry Department, University of Athens, 13a Navarinou Street, Athens 10680 Greece
[2]Department of Chemistry, Michigan State University, East Lansing, MI 48824

The rich gas phase chemistry of first row transition metal (+1) ions with ammonia, and organic compounds (R-X where X=NH_2, CN, NO_2) is discussed. Ongoing theoretical investigations into the Sc^+/NH_3 system are presented, which provide some insights into the bonding and energetics of a variety of MNH_x^+ complexes.

There are a number of mass spectrometric techniques that have been developed for the study of the low pressure gas phase reactions of ionic species with organic molecules. The earliest experiments involving ion/molecule reactions involved chemical ionization mass spectrometry, and the most recent utilize ion beam and Fourier transform ion cyclotron resonance methods. The earliest studies were predominantly organic in nature. More recently, these methods have been used to study organometallic chemistry in the gas phase. The various ionization techniques available in mass spectrometry allow for the generation of unique gas phase species including bare transition metal ions (such as Co^+, Ni^+) and ligated species (such as $CoCO^+$, $CoNO^+$, $NiPF_3^+$, $NiC_5H_5^+$). Their chemistry with small molecules and a variety of larger molecules containing the functional groups of organic chemistry has been extensively studied in the past 15 years(1). The earlier studies were largely mechanistic in nature, to gain an understanding of how product ions were formed. Recently, combined experimental and theoretical efforts have provided important insights into how these reactions occur. These insights will become, we believe, the basis for a fresh evaluation of the reactivity of inorganic and organometallic species that are studied and utilized in condensed phases.

0097–6156/90/0428–0263$06.00/0
© 1990 American Chemical Society

Both polar and nonpolar organic compounds exhibit a rich chemistry with bare transition metal ions(1). Small polar compounds react with ions such as Fe^+ and Co^+, in a single, bimolecular step to form a metal-olefin complex, reaction (1).

$$Co^+ + C_3H_7X \rightarrow CoC_3H_6^+ + HX \qquad (1)$$

Such reactions have been reported for X=Cl, Br, OH, SH, OR and even for X=H and R (R=alkyl substituent). The mechanism by which these products are formed was proposed by Allison and Ridge in 1979(2), and is shown in reaction (2). The reactants first form a complex (a), which may be simply electrostatically bound. In (b), the transition metal ion inserts into the polar C-X bond (formal "oxidative addition"), followed by the shift of a H

$$\begin{array}{lll} Co^+ + C_3H_7X \rightarrow & C_3H_7X^{\cdot}\ \cdot\ \cdot Co^+ \rightarrow & C_3H_7 - Co^+ - X \\ \qquad\qquad (a) & \qquad\qquad (b) & \qquad\qquad (c)\downarrow \\ & & (C_3H_6)Co^+(HX) \qquad (2) \\ & & \qquad\qquad (d)\downarrow \\ & & CoC_3H_6^+ + HX \end{array}$$

atom that is on a C which is β to the metal (β-H shift), across the metal onto X, resulting in the degradation of the molecule into two smaller, stable species that reside as ligands on the metal. The last step (d) is a competitive ligand loss. In this process, it appears that the ligand that is more weakly bound to the metal is preferentially lost(3). In some cases, two products result from this dissociation. For example, Co^+ reacts with propanol to form both CoH_2O^+ and $CoC_3H_6^+$(2). While studies of series of, e.g., alcohols, and labeling studies provided some insights into the mechanisms that are operative in the chemistry, many important questions are difficult to approach experimentally. To understand the chemistry, it is certainly important to understand the bonding of the molecules and fragments involved to the transition metal and the strengths of these bonds. Many features such as the distribution of the charge in the various intermediates may also be important in controlling the types of products that are formed. Thus, theoretical studies are necessary to understand the "driving forces" that dominate these reactions and lead to the rich chemistry.

The chemistry of polar compounds containing many types of functional groups and multifunctional organic compounds, with bare transition metal ions has been

Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

reported. The richest chemistry certainly involves those functional groups that contain nitrogen, and a few examples will be provided here.

Stepnowski and Allison(4) reported the chemistry of a variety of transition metal ions with a series of alkyl cyanides. While ions such as Fe^+ and Co^+ insert into the C-X bond in many polar compounds, they do not appear to do so for -X = -CN. Instead, C-C bonds are cleaved, as shown for the Co^+/n-propyl nitrile system in reactions (3) and (4).

$$Co^+ + n\text{-}C_3H_7CN \rightarrow CoCH_3CN^+ + C_2H_4 \quad (3)$$

$$\rightarrow CoC_2H_4^+ + CH_3CN \quad (4)$$

The reactivity of nitriles may be dominated by a number of aspects of the chemistry including the fact that C-CN bond dissociation energy (BDE) is substantially larger than the BDE's for C-Cl and C-OH bonds(4). Also, there is evidence that the geometry of the initial complex has a dramatic effect - an "end-on" interaction of the metal ions with the nitrile group may make insertion into the C-CN bond geometrically inaccessible(5).

Another interesting functional group containing nitrogen is the nitro group. The chemistry of Co^+ with a series of nitroalkanes has been reported by Cassady et al.(6). Consider the Co^+/n-$C_3H_7NO_2$ system. Fourteen different products were reported. Product ions such as $Co(C_3H_6)^+$ and $Co(HNO_2)^+$ suggested that Co^+ inserted into the C-NO_2 bond. Other product ions such as $CoC_3H_7O^+$ and $CoNO^+$ suggest that RNO_2 may be converted, in part, to RO- and NO- on the metal center. Thus the -NO_2 group actively interacts with the metal. The chemistry of organometallic anions with nitroalkanes has also been reported(7).

The chemistry of NO with transition metal ions has also received some attention, and deserves comment here. One of the first ways in which Co^+ ions were generated for mass spectrometric study was by electron impact ionization of the volatile compound $Co(CO)_3NO$. In addition to Co^+, ions such as $CoCO^+$ and $CoNO^+$ were formed. While Co^+ and $CoCO^+$ ions frequently react with organic molecules in the gas phase, $CoNO^+$ is unreactive(8). The reason for this change in chemistry upon change of ligand was unclear, since there was only "traditional" bonding-schemes to consider at the time. However, theoretical studies show that the CO ligand is not bonded to first row transition metal ions via the Dewar-Chatt model, but is electrostatically bound(8,9) - thus it's presence does not change the electronic structure of the metal. Presumably NO acts as a 1 or 3-electron donor with Co^+ (which has a $3d^8$ ground state configuration), so the $CoNO^+$ ion has a single unpaired

Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

electron on the metal, and should not participate in reactions that require an insertion step. We also note that the NO ligand does appear to be reactive when bound to Co_2^+. Jacobson(10) reported the observation of reaction (5) involving CO.

$$Co_2NO^+ + CO \rightarrow Co_2N^+ + CO_2 \quad (5)$$

There have been a number of studies reported involving metal ion reactions with amines and ammonia. The first of these involved Co^+ with a series of amines, reported by Radecki and Allison in 1984(11). Reactions (6-9) were observed for the $Co^+/n\text{-}C_3H_7NH_2$ system.

$$Co^+ + n\text{-}C_3H_7NH_2 \rightarrow CoC_3H_7N^+ + H_2 \quad (6)$$

$$\rightarrow CoC_3H_5N^+ + 2\ H_2 \quad (7)$$

$$\rightarrow CoCH_5N^+ + C_2H_4 \quad (8)$$

$$\rightarrow C_3H_8N^+ + CoH \quad (9)$$

These results were certainly surprising since insertion into the $C\text{-}NH_2$ bond was not observed, although the reaction (10)

$$Co^+ + C_3H_7NH_2 \rightarrow CoC_3H_6^+ + NH_3 \quad (10)$$

should be exothermic. It was proposed that H_2 elimination occurred by initial insertion into the N-H bond. While Co^+ did not insert into the $C\text{-}NH_2$ bond of primary amines, it does appear to insert into the C-N bond in the tertiary amine, $(C_2H_5)_3N$, and in allyl amine. To explain the failure to observe reaction (10) it was proposed that there was a barrier along the reaction channel - that the insertion intermediate was energetically inaccessible for thermal energy reactions, which could only be due to a weak $Co^+\text{-}NH_2$ bond. The BDE would have to be unusually small, < 20 kcal/mol. It has since been shown, as discussed below, that this is not the case. Another explanation may be that Co^+ does react with, e.g., propyl amine, to form propene and ammonia, but there is a barrier to the dissociation step of $(C_3H_6)Co^+(NH_3)$ - which cannot be distinguished in the mass spectrum from the complex containing the intact molecule, $Co^+(C_3H_7NH_2)$. The gas phase chemistry of a number of metal ions with amines has been studied. Babinec and Allison(12) reported the chemistry of Cr^+, Mn^+, Fe^+, Ni^+, Cu^+ and Zn^+ with n-propyl amine. Only Fe^+ clearly inserted into the C-N bond, as evidenced by the observation of the two products $FeNH_3^+$ and $FeC_3H_6^+$. Mn^+ (with a half-filled d-shell, $3d^5 4s^1$ ground state) and Zn^+ (with a filled

Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

d-shell, $3d^{10}4s^1$ ground state) were unreactive with propyl amine. In contrast, Cr^+($3d^5$ ground state) and Cu^+($3d^{10}$ ground state) were both observed to induce H_2 elimination only. Sigsworth and Castleman(13) studied the reactions of Ag^+ and Cu^+ with methyl amine, dimethyl amine and trimethyl amine. In these studies, hydride abstraction was observed to yield the (amine-H)$^+$ ion and the MH neutral product.

In 1987, Buckner and Freiser(14) showed that Co^+ does form a strong bond to NH_2, and did so as follows. In an FTMS instrument they formed $CoOH^+$, which reacts with ammonia, reaction (11).

$$CoOH^+ + NH_3 \rightarrow CoNH_2^+ + H_2O \qquad (11)$$

They also found that the NH_2 group can be displaced from Co^+ by benzene, but not by acetonitrile. With this information, they concluded that the BDE for Co^+-NH_2 is 65 ± 8 kcal/mol. In this same work they reported the chemistry of MNH_2^+ with some hydrocarbons. They also found that FeO^+ reacts with ammonia to form $FeNH^+$, and reported some chemistry for this ionic species. Their work suggested that the BDE for $FeNH^+$ was > 41 kcal/mol and < 81 kcal/mol. This work was extended in a report by Buckner, Gord and Freiser in 1988(15). They found that a variety of metal ions including Sc^+, Ti^+ and V^+ react with ammonia in an exothermic process by reaction (12), which suggests that these M^+-NH bonds are stronger than 93 kcal/mol. The BDE for V^+-NH was determined to be 101 ±7 kcal/mol, and the BDE for Fe^+-NH to be lower, 54 ± 14 kcal/mol.

$$M^+ + NH_3 \rightarrow MNH^+ + H_2 \qquad (12)$$

They also reported a number of reactions for MNH^+ with neutral molecules. A variety of mechanisms for reaction (12) was discussed, including dehydrogenation via direct decomposition of the intermediates $(H)_2M^+$=NH and/or H-M^+-NH_2.

The Reaction of Sc^+ with NH_3

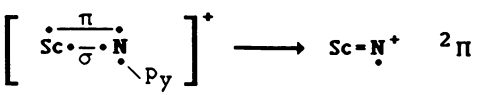
Our intent is to gain theoretical insights into the initial interaction of M^+ with a polar molecule, the insertion step and reductive elimination by a systematic study of the interaction of M^+ with NH_3. We begin here with Sc^+ because it has only two valence electrons and thus its theoretical description and its calculated interaction with NH_3 and its fragments will be more reliable than with the latter transition elements. We will first describe the ScN^+ core and then build up the various intermediates by adding hydrogens. Specific fragments to be studied include $ScNH^+$, $ScNH_2^+$, $HScNH_2^+$ and $ScNH_3^+$. The calculations will include all electrons and will use both MCSCF and

Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

CI techniques. The basis sets used and the general approach have been described previously(16).

ScN$^+$

The relative energies of the low lying states of Sc^+, N, NH and NH_2 are collected in Figure 1. Because the excited states of N are much higher in energy than those of Sc^+ we will consider the states of ScN^+ which correlate to the ground state of N and the sd and d^2 configuration of Sc^+(16). As Sc^+ in an sd configuration approaches N we can imagine forming a σ bond between the 4s electron on Sc^+ and a 2p σ electron on N and a π bond between the $3d_{xz}$ and $2p_x$ electrons. This leaves an unpaired electron on N in the $2p_y$ orbital and results in a $^2\Pi$ state represented by



It is only at large ScN separations that the Sc electron in the σ bond is pure 4s. As the bond forms other orbitals on Sc of σ symmetry mix into the bonding orbital. This is seen most vividly in Figure 2a which shows the occupancies of various atomic orbitals in the $^2\Pi$ state of ScN^+ as a function of separation. At equilibrium the atomic orbitals in the σ bond have the occupancy

$$(4s^{0.0}\ 4p_\sigma^{0.0}\ 3d_\sigma^{\ 0.66})_{Sc}(2p_\sigma^{1.28})_N$$

and the 4s orbital has gone from an occupancy of 1 to 0. Interestingly the π bond occupancy is equal to that of the σ bond

$$(3d_{xz}^{0.66})_{Sc}(2p_x^{1.28})_N$$

while the unpaired electron remains essentially localized on N.

$$(3d_{yz}^{0.07})_{Sc}(2p_y^{0.91})_N$$

The net result is that Sc^+ looses 0.49 electrons to N resulting in the charge distribution

$$^{+1.51}Sc\ N^{-0.49}.$$

If we break the π bond in this state and place the high spin electron on Sc in a $d\delta_\pm$ orbital we will form a $^4\Delta_\pm$ state.

Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

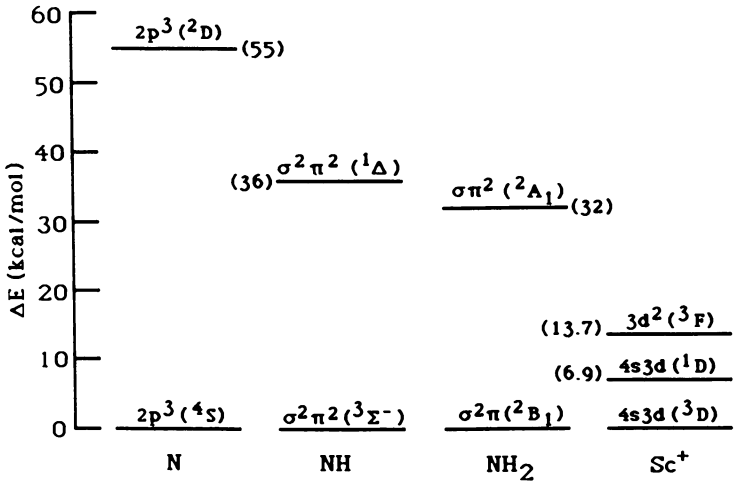


Figure 1. Relative Energy Levels (kcal/mol^{-1}) of N(19), NH(20), NH_2(21) and Sc^+(19).

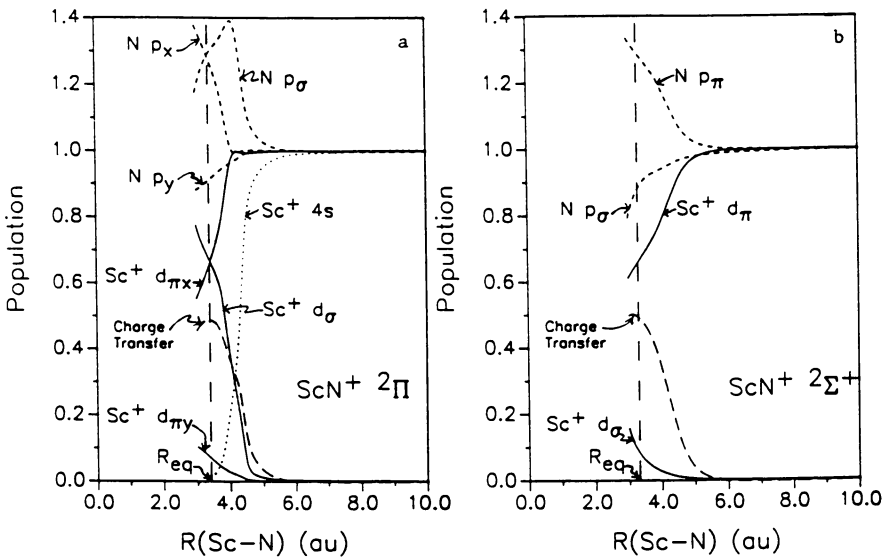
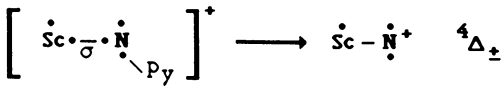
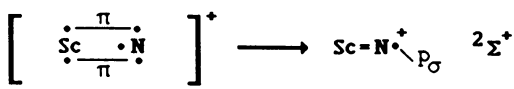


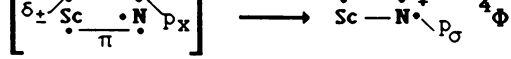
Figure 2. Orbital occupancy as a function of internuclear distance for ScN^+ in the a) $^2\Pi$ and b) $^2\Sigma^+$ states.



In a similar way we can consider states of ScN^+ which correlate to the d^2 (excited) state of Sc^+. For example the $^2\Sigma^+$ state has a π, π double bond and an unpaired electron on N in the σ system

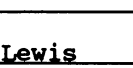
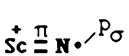
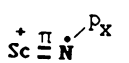
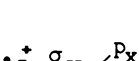


If we break a π bond in this structure and place the then uncoupled $d\pi$ electron in a $d\delta_{\pm}$ orbital we have ScN^+ in a $^4\Phi$ state held together by a single π bond



Configuration interaction calculations on these four states result in the potential curves shown in Figure 3. The orbital populations in the $^2\Sigma^+$ state are shown in Figure 2b and the properties of all four states are summarized in Table I.

Table I. Calculated Properties of Several States of ScN^+

State	Lewis	D_e(kcal/mol)	R_e(Å)	ω_e(cm^{-1})	Q(Sc)
$^2\Sigma^+(d^2)$		63.0	1.738	871	+1.51
$^2\Pi_x(sd)$		55.3	1.804	811	+1.51
$^4\Delta(sd)$		26.8	2.101	534	+1.46
$^4\Phi(d^2)$		21.1	1.979	674	+1.47

Note that all D_e's are reported relative to the ground states of $Sc^+(^3D)$ and $N(^4S)$. Most interestingly, the ground state is the $^2\Sigma^+$ which contains two π bonds and which correlates with the excited d^2 configuration of

Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

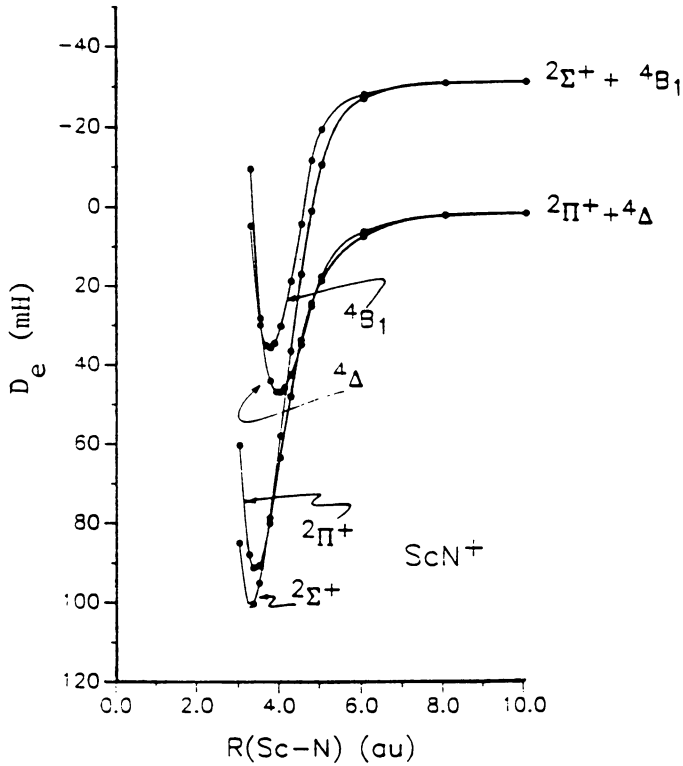


Figure 3. Potential Energy Curves for 4 States of ScN^+.

Sc^+. It is also noteworthy that the charge on Sc^+, Q, is independent of the number and type of formal bonds in the molecule.

<u>ScNH</u>+

We can imagine $ScNH^+$ being formed by addition of a H to either the $^2\Sigma^+$ or $^2\Pi$ state of ScN^+.

$$Sc = N\bullet^{+}_{\diagdown p_\sigma}\,[^2\Sigma^+] + \bullet H\,[^2S] \longrightarrow Sc = N - H^+\,[^1\Sigma^+]$$

or

$$Sc = \overset{p_\pi}{N}\bullet^{+}\,[^2\Pi] + \bullet H\,[^2S] \longrightarrow Sc = \overset{H}{\overset{|}{N}}{}^{+}\,[^1A']$$

Optimizing the structure of this system at the CI level results in the linear structure with a ^+ScN-H dissociation energy of 118.5 kcal/mol (Kunze, K.L. and Harrison, J.F., MSU, unpublished results). This is a remarkably strong NH bond (free NH has a D_e of 80 kcal/mol and we require 108 kcal/mol to break the first N-H bond in NH_3).

The reason for this enhanced NH bond strength is apparent when one analyzes the electron distribution in the $ScNH^+$ molecule and compares it with ScN^+ and NH. This analysis shows that when H bonds to ScN^+ the N 2s orbital loses 0.45 electrons, the H 1s loses 0.17e and the N $2p_\sigma$ orbital gains 0.30 electrons. If, for bookkeeping purposes, we assume all of the electrons lost by H go into the N $2p_\sigma$ and that the remaining gain in the N $2p_\sigma$ comes from the N 2s, then we can allot the remaining 0.32 electrons lost by the N 2s to the σ orbitals on Sc^+. This accounts nicely for the increase of 0.33 electrons in the Sc^+ σ system and suggests that the enhanced N-H bond strength in $ScNH^+$ is due to a significant dative bond formed between Sc and the N 2s electron pair. Alternatively, we may imagine forming $ScNH^+$ via the lowest state (^3F) of the excited d^2 configuration.

$$Sc^+\ (^3F) + NH\ (^3\Sigma^-) \rightarrow ScNH^+\ (^1\Sigma^+)$$

The Sc^+ - NH bond strength is calculated to be 105.9 kcal/mol relative to the ground state fragments (Kunze, K.L. and Harrison, J.F., MSU, unpublished results), which should be compared with recent results by Armentrout et al. (Armentrout, P., Univ. of Utah, private communication, 1989) suggesting a Sc^+-NH bond strength of 118 kcal/mol. This Sc^+-NH calculated bond strength is 43 kcal/mol stronger than the 63 kcal/mol calculated for the ScN^+ bond in the $^2\Sigma^+$ state. Note that the calculated N-H bond strength in ScN^+-H is also 43 kcal/mol stronger than the 75.5 kcal/mol calculated

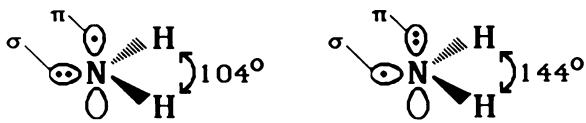
Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

bond strength in NH. This symergistic relationship between the N-H and Sc-N bonds in $ScNH^+$ is a consequence of the freedom given to the σ system by the unusual π, π double bond between the metal and N. As H bonds to the pσ electron on N considerable 2s character is mixed into the NH bonding orbital. This hybridization not only strengthens the N-H bond but the companion orbital which points toward the Sc simultaneously stabilizes the ScN bond by a dative interaction. The $^2\Sigma^+$ state represented above is more accurately written as

$$^+Sc \leftarrow N\text{-}H\ (^1\Sigma^+)$$

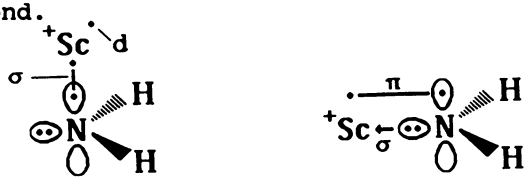
<u>$ScNH_2$</u>$^+$

The ground state of NH_2 is of $^2B_1$ symmetry and is characterized by a $\sigma^2\pi^1$ electronic configuration and an NH_2 angle of 104°, whereas, the first excited state is of $^2A_1$ symmetry and is 32 kcal/mol above the ground $^2B_1$. It is characterized by a $\sigma^1\pi^2$ electronic configuration and an angle of 144°

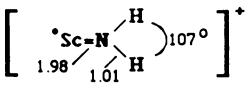


We may imagine the ground state of NH_2 reacting with either the ground or excited state of Sc^+ to form a doublet with a nonplanar structure in which the bonding electron on Sc^+ is formally either 4s or 3dσ.

Alternatively we can imagine the ground state of NH_2 reacting with the $3d^2$ configuration of Sc^+ to form the planar molecule having a π bond and a (dative) σ bond. The unpaired electron on Sc would most likely be in a $\delta_\pm$ orbital to optimize the ability to form a π and dative σ bond.



All electron multireference single and double CI calculations (Mavridis, A.; Herrera, F.; and Harrison, J.F., MSU, unpublished work) predict that the ground state of $ScNH_2^+$ is of $^2A_2$ symmetry and that it is planar with the geometry



Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

Only small energies are required to deviate from the planar structure. Our calculations suggest that 0.3 kcal/mol is required to move Sc 10° out of plane and 0.9 kcal/mol to move it 20°.

The electron distribution at equilibrium suggests that Sc has a total charge of +1.51 having lost 0.49 electrons to the NH_2 group. The electrons remaining on Sc are distributed as follows

$$4s^{0.06}4p_{\sigma}^{0.0}4p_{x}^{0.07}3d_{\sigma}^{0.16}3d\pi_{x}^{0.22}3d_{\delta}^{1.00}$$

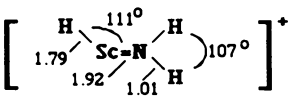
We calculate the $^{+}Sc{=}NH_2$ bond dissociation energy for the $^2A_2$ state to be 79 kcal/mol which compares favorably with the 85 kcal/mol recently determined by Armentrout et al. (Armentrout, P.B., Univ. of Utah, private communication, 1989). The lowest $^2A_1$ state has the unpaired electron in a δ_+ orbital and is essentially degenerate with the ground $^2A_2$ state. The lowest $^2B_2$ state has a D_e of 70 kcal/mol and results when the unpaired electron is in a $d\pi_y$ orbital. Placing the unpaired electron in a $d\pi_x$ orbital results in the $^2B_1$ state which is 22 kcal/mol above the $^2A_2$ ground state. We have also investigated several quartet states which are bound by ~30 kcal/mol, primarily by charge-dipole interactions.

<u>$ScNH_3^+$</u>

Three isomers with this formula are relevant. The first is a charge-dipole complex in which NH_3 is intact. This complex is bound relative to ground state fragments by 36.8 kcal/mol.

The second isomer is the insertion product $H\text{-}Sc\text{-}NH_2^+$. Generalized Valence Bond calculations on this system suggest that it is bound relative to Sc^+ + NH_3 by 16 kcal/mol.

The geometry is



The third isomer is the electrostatic complex $(H_2)ScNH^+$ that is bound relative to Sc^+ + NH_3 by 14 kcal/mol. Interestingly the H_2 molecule is bound to the $ScNH^+$ ion by 5 kcal/mol.

<u>Summary of Energetics</u>

The relative energies of the various products of the reaction of Sc^+ (^3D) with NH_3 are collected in Figure 4. This figure was constructed using the energies discussed in the previous section as well as binding energies of ScH^+ and ScH_2^+(<u>18</u>) reported earlier. Energies determined experimentally are shown in parentheses.

Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

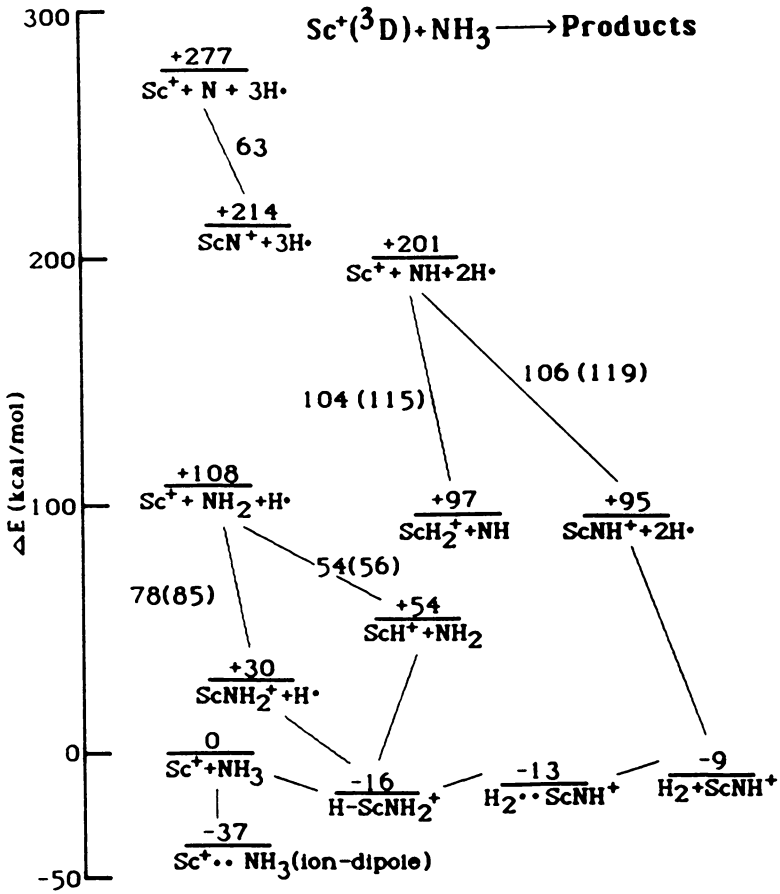


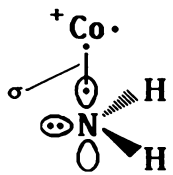
Figure 4. Summary of Energetics for $Sc^+ + NH_3$.

These calculations suggest that both the insertion product $H\text{-}Sc\text{-}NH_2^+$ and the complex $H_2 \cdots ScNH^+$ are exothermic products of the reaction of Sc^+ with NH_3. The insertion product is formed exothermically because the $Sc\text{-}NH_2$ bond strength and the Sc-H bond strength are large and able to overcome the 108 kcal/mol required to break a N-H bond in NH_3. Our calculations suggest that the $^+Sc\text{-}NH_2$ bond is strong because:

1. The NH_2 group donates charge to the transition metal ion via the σ^2 pair on N. This dative interaction is optimized when there are no 4s or $3d\sigma$ electrons on the metal.
2. The metal donates charge to the π orbital of the NH_2 group. This transfer is optimized when there is one $d\pi$ electron in the π system being coupled with the NH_2 π orbital.

Interfering with either of these mechanisms will reduce the metal - NH_2 bond strength and consequently the potential for an exothermic $H\text{-}M\text{-}NH_2^+$ insertion product. Likewise reducing the metal-H bond strength would also reduce the possibility of an exothermic insertion product.

For example, Co^+ is a d^8 system and regardless of the configuration of the electrons in the ground ^3F state one will always have at least one electron, in a $d\sigma$ orbital. Consequently the planar configuration is not obviously better than the singly bonded non planar structure



and, as a result, the $M\text{-}NH_2$ bond strength will be smaller for Co than Sc. So while Sc^+ and Co^+ both have two singly occupied d orbitals Co^+ is less energetically favored to react with NH_3 to form

$$H - Co - NH_2^+.$$

Similar considerations apply to the exothermic products $H_2 + ScNH^+$. In this case the exothermicity results from the strong M-NH bond which arises from:

1. Each $2p_\pi$ electron on N bonding to a singly occupied orbital on Sc^+ and
2. The lone pair on N bonding to the empty 4s, 3d orbitals on Sc.

Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

It is not possible for Co^+ to satisfy both of these conditions simultaneously and consequently, $CoNH^+$ should have a relatively weak Metal-NH bond strength. The process

$$Co^+ + NH_3 \rightarrow Co{=}NH^+ + H_2$$

will be less exothermic if the $Co{=}NH^+$ bond strength is less than 90 kcal/mol.

Acknowledgments

This work was partially supported under NSF Grants CHE8519752 (JFH) and CHE8722111 (JA), as well as a NATO Grant CRG890502 to A. Mavridis and J. F. Harrison. The Electron Structure codes provided by the Argonne Theory group have been indispensable to this work.

Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018

Literature Cited

1. Allison, J. Prog. Inorg. Chem. vol. 34, S.J. Lippard, Ed. **1986**, p. 627.
2. Allison, J.; Ridge, D.P. J. Am. Chem. Soc. **1979**, 101, 1332.
3. Tsarbopoulos, A.; Allison, J. Organometallics **1984**, 3, 86.
4. Stepnowski, R.M.; Allison, J. Organometallics **1988**, 7, 2097.
5. An end-on interaction of the metal ion with the CN group results in reactions that are remote from the site of complexation. Such reactions are also discussed in: Tsarbopoulos, A.; Allison, J. J. Am. Chem. Soc. **1985**, 107, 5085.
6. Cassady, C.J.; Freiser, B.S.; McElvany, S.W.; Allison, J. J. Am. Chem. Soc. **1984**, 106, 6125.
7. McElvany, S.W.; Allison, J. Organometallics **1986**, 5, 1219.
8. Allison, J.; Mavridis, A.; Harrison, J.F. Polyhedron. **1988**, 16/17, 1559.
9. Mavridis, A.; Harrison, J.F.; Allison, J. J. Am. Chem. Soc. **1989**, 111, 2482.
10. Jacobson, D.B.; J. Am. Chem. Soc. **1987**, 109, 6851.
11. Radecki, B.D.; Allison, J. J. Am. Chem. Soc. **1984**, 106, 946.
12. Babinec, S.J.; Allison, J. J. Am. Chem. Soc. **1984**, 106, 7718.
13. Sigsworth, S.W.; Castleman, Jr., A.W. J. Am. Chem. Soc. **1989**, 111, 3566.
14. Buckner, S.W.; Freiser, B.S. J. Am. Chem. Soc. **1987**, 109, 4715.
15. Buckner, S.W.; Gord, J.R.; Freiser, B.S. J. Am. Chem. Soc. **1988**, 110, 6606.
16. Kunze, K.L. and Harrison, J.F. J. Phys. Chem. **1989**, 93, 2983.
17. Alvarado Swaisgood, A.E. and Harrison, J.F. J. Phys. Chem. **1985**, 89, 5198.

18. Sunderlin, L.; Aristov, N and Armentrout P.B. J. Am. Chem. Soc. **1987**, 109, 78
19. Moore, C. E., "Atomic Energy Levels; Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. Circular 35, Washington, DC, **1971**, Vol. I and II.
20. Huber, K.P. and Herzberg, G., "Moleculear Spectra and Molecular Structure", Van Nostrand Reinhold Co., New York, **1979**.
21. Johns, J.W.C.; Ramsay, D.A. and Ross, S.C., Can. J. Phys., **1976**, 54, 1804.

RECEIVED December 19, 1989

Downloaded by NORTH CAROLINA STATE UNIV on May 3, 2015 | http://pubs.acs.org
Publication Date: June 25, 1990 | doi: 10.1021/bk-1990-0428.ch018