

Figure 6. Reaction scheme for the radical attack to saturated Si atoms in the bulk.

reactions. Reaction via radical species, i.e., a chain reaction, has been mainly studied, and the order of ease of bond formations by chain reactions has been predicted as Si-Si > Si-C > C-C. Namely, it has been predicted that a Si-Si bond is more favorable to form than a Si-C bond, and a C-C bond is most unfavorable to form, which is consistent with the experimental results. Reactions via silylene species and direct reaction have also been examined and compared with the chain reaction. It has been found that a chain reaction should be considered a favorable pathway in pyrolytic SiC formation. A reaction path for the formation of silyl radical from silylene has also been proposed.

It has been verified theoretically that a Si-Si bond is more likely to form than a Si-C bond. This suggests that the Si rather than the SiC phase is preferentially formed during pyrolytic SiC CVD,

which is consistent with the experimental result. Since the surface of the Si phase may have many dangling bonds, molecules containing carbon such as CH<sub>4</sub> can readily react to form a Si-C bond. Moreover, CH<sub>3</sub> can react even with saturated Si atoms to form a Si-C bond: see Figure 6. This is because the orbital pattern for a saturated Si atom is different from that for a saturated C atom, which has been shown in Figure 2: the LUMO of SiH<sub>4</sub> is extended much more than that of CH<sub>4</sub>.

Our model reaction systems are so small that a further extended approach should be performed in order to get a comprehensive picture of the complex reaction systems. Our approach is considered a preliminary step for a real understanding of the SiC formation mechanism.

**Acknowledgment.** This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan, for which we express our gratitude. The numerical calculations were carried out at the Data Processing Center of Kyoto University and the Computer Center of the Institute for Molecular Science (IMS), and we are grateful for their generous permission to use FACOM M-780 and VP-400, and HITAC M-680H and S-820 computer systems, respectively.

Registry No. SiH<sub>4</sub>, 7803-62-5; CH<sub>4</sub>, 74-82-8; SiC, 409-21-2.

## Electronic and Geometric Structures of <sup>+</sup>ScNH<sub>2</sub> and <sup>+</sup>ScNH<sub>3</sub>

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The electronic and geometric structures of <sup>+</sup>ScNH<sub>2</sub> and three isomers of <sup>+</sup>ScNH<sub>3</sub> have been studied by ab initio MCSCF and CI techniques. All three isomers of <sup>+</sup>ScNH<sub>3</sub> are calculated to be exothermic products relative to Sc<sup>+</sup> and NH<sub>3</sub>, and the ion-dipole complex Sc<sup>+</sup>...NH<sub>3</sub> is the most exothermic. The Sc<sup>+</sup>-NH<sub>2</sub> bond energy is calculated to be 79 kcal/mol, in good agreement with a recent experimental result of 85 kcal/mol. The nature of the bonding in <sup>+</sup>ScNH<sub>2</sub> is analyzed, and the structure and energetics of various insertion products of Sc<sup>+</sup> and NH<sub>3</sub> are discussed.

### Introduction

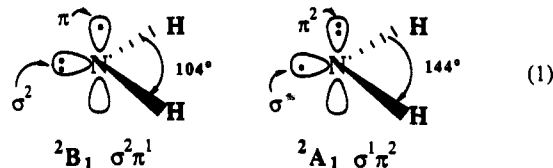
The rich gas-phase chemistry of transition metal ions with amines and ammonia is being explored by several groups.<sup>1-6</sup> These studies have produced accurate bond strengths for several intermediates and considerable insight into the mechanism of the various observed reactions. We believe that a detailed understanding of the electronic and geometric structures of these intermediates is central to an understanding of these reaction mechanisms, and we have been studying these properties for various fragments which arise from the interaction of M<sup>+</sup> with NH<sub>3</sub>.<sup>7-9</sup> This study is concerned with the fragments <sup>+</sup>ScNH<sub>2</sub>, the insertion product H-Sc<sup>+</sup>NH<sub>2</sub>, and the electrostatic complex Sc<sup>+</sup>...NH<sub>3</sub>. Sc<sup>+</sup> was selected as the metal in these computational studies because its two valence electrons permit accurate calculations of the geometry, electron distribution, and bond energies for a variety of low lying states.

After characterizing the fragments Sc<sup>+</sup> and NH<sub>2</sub>, we describe the results of our calculations on <sup>+</sup>ScNH<sub>2</sub>, HSc<sup>+</sup>NH<sub>2</sub>, and <sup>+</sup>Sc...NH<sub>3</sub>. We conclude with some observations on the effect of replacing Sc<sup>+</sup> with another first-row transition-metal ion, M<sup>+</sup>. Details of the calculations are collected in the appendix.

### ScNH<sub>2</sub><sup>+</sup>

**Preliminaries.** The 4s3d electronic configuration of Sc<sup>+</sup> gives rise to a <sup>3</sup>D ground state and a <sup>1</sup>D state 6.9 kcal/mol higher.<sup>10</sup>

The lowest state of the 3d<sup>2</sup> configuration is of <sup>3</sup>F symmetry and is 14 kcal/mol above the <sup>3</sup>D. NH<sub>2</sub> has a <sup>2</sup>B<sub>1</sub> ground state and an excited <sup>2</sup>A<sub>1</sub> state which is 32 kcal/mol higher in energy.<sup>11</sup>



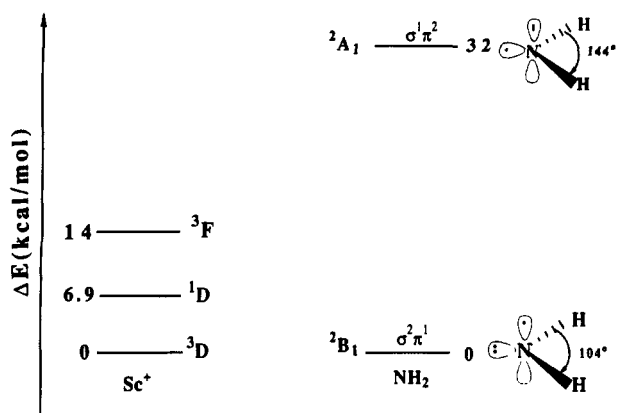
These energy levels are shown in Figure 1.

The doublet states of NH<sub>2</sub> can combine with the triplet states of Sc<sup>+</sup> to form doublets and quartets and with the singlet states

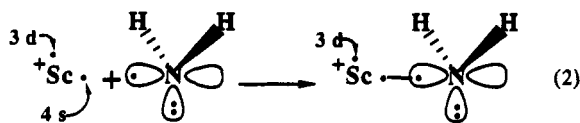
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<sup>†</sup>National and Kapodistrian University of Athens.

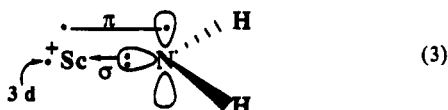
<sup>‡</sup>Michigan State University.

Sc<sup>+</sup> & NH<sub>2</sub> PRELIMINARIESFigure 1. Low-lying electronic energy levels of Sc<sup>+</sup> and NH<sub>2</sub>.

of Sc<sup>+</sup> to form only doublets. Since the unpaired electron in the  $^2B_1$  state of NH<sub>2</sub> is in a  $\pi$  orbital, we may imagine ground-state Sc<sup>+</sup> reacting to form a nonplanar molecule as in



Sc<sup>+</sup> in a  $3d^2$  configuration can react to form the planar molecule



with a formal covalent bond in the  $\pi$  system and a dative bond in the  $\sigma$  system. The remaining  $3d$  electron could be of  $\sigma$ ,  $\pi$ , or  $\delta_+$  symmetry.

Alternatively, the ground  $^2B_1$  can be bound electrostatically to the  $^3D$  or  $^3F$  states to form a quartet in which we have the same number of unpaired electrons as in the separated fragments.

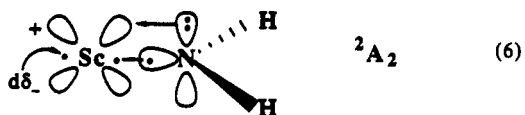


Of course, the  $^1D$  can also form an electrostatic complex with the doublets of NH<sub>2</sub> to form a molecule of doublet spin symmetry. These states would not be distinguishable from the covalently bonded doublets formed from the Sc<sup>+</sup>  $^3D$  state.

**Results for Doublet States.** A molecular state of  $^2A_2$  symmetry results when NH<sub>2</sub> in its  $^2B_1$  state ( $\sigma^2\pi^1$ ) interacts with an excited  $d\pi, d\delta_-$  configuration of Sc<sup>+</sup>. Formally, we form a dative bond in the  $\sigma$  system and a covalent bond in the  $\pi$  system, leaving the unpaired electron in a  $\delta_-$  orbital on Sc<sup>+</sup>.



Alternatively, we may form this state from the excited  $^2A_1$  state of NH<sub>2</sub> ( $\sigma\pi^2$ ) and the ground state of Sc<sup>+</sup> ( $4s3d\delta_-$ ). In this scenario we form a covalent bond in the  $\sigma$  system and a dative bond in the  $\pi$  system.



Generalized valence bond<sup>12</sup> calculations in which the NH bonds as well as the two bonds between N and Sc are correlated were

TABLE I: Electron Population in Various Atomic Orbitals in  $^+ScNH_2$  in the  $^2A_2$  State<sup>a</sup>

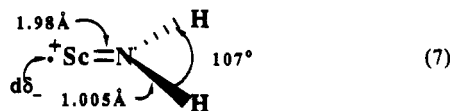
atom	orbital	Sc-N distance		population difference	
		3.75 au	20.00 au		
Sc	4s	0.06	0.00	+0.06	
	3d $\sigma$	0.16	0.00	+0.16	
	3d $\delta_+$	0.00	0.00	0	
	3d $\pi_x$	0.22	1.00	-0.78	
	3d $\pi_y$	0.00	0.00	0	
	3d $\pi_z$	1.00	1.00	0	
	4p $_z$	0.00	0.00	0	
	4p $_x$	0.07	0.00	+0.07	
	4p $_y$	0.00	0.00	0	
	total Sc	1.51	2.00	-0.49	
N	2s	1.46	1.65	-0.19	
	2p $_z$	1.41	1.57	-0.16	
	2p $_x$	1.66	0.97	+0.69	
	2p $_y$	1.14	1.12	+0.02	
	total N	5.67	5.31	+0.36	
H <sub>1</sub>	s + p	0.86	0.84	+0.02	
	H <sub>2</sub>	s + p	0.86	0.84	+0.02
		total H	1.72	1.68	+0.04

<sup>a</sup>The Sc-N  $\sigma$  bond lies along the  $z$  axis, and  $x$  is perpendicular to the molecular plane.

TABLE II: Energies of the Lowest  $^2A_2$  State of  $^+ScNH_2$ 

calculation	$R = 3.75$ au	$R = 20.00$ au
GVB(4/8)	-815.236 576	-815.091 536
GVB(4/8)+1+2	-815.405 876	-815.240 213

carried out for this  $^2A_2$  symmetry. These (GVB(4/8)) calculations predict the geometry



GVB(4/8) calculations were also carried out for the nonplanar structure (2) as a function of the angle between Sc<sup>+</sup> and the NH<sub>2</sub> plane. The molecule is planar but requires only 0.3 kcal/mol to move the Sc<sup>+</sup> 10° out of plane and 0.9 kcal/mol to move it 20°. The electron distribution is shown in Table I and is compared with the asymptotic fragments Sc<sup>+</sup>( $3d\pi_x, 3d\delta_-$ ) and NH<sub>2</sub>( $^2B_1$ ). Note that the  $\pi$  orbital on N gains 0.69 e while the  $\pi$  orbital on Sc<sup>+</sup> loses 0.71 e. Simultaneously, the  $\sigma$  orbitals on Sc<sup>+</sup> gain 0.22 e while the 2s, 2p<sub>y</sub>, and 2p<sub>z</sub> orbitals on N lose 0.33 e. This picture of a large charge transfer in the  $\pi$  system is supported by the electron density contours shown in Figure 2, where we subtract the density of the noninteracting fragments from the molecular density. Figure 2 shows a cut in both the molecular plane and perpendicular to the molecular plane. The solid lines represent an increase in electron density, and the dashed, a decrease in electron density. Clearly, there has been a large electron shift from the Sc<sup>+</sup>( $d\pi_x$ ) to the N( $\pi$ ) orbital.

To estimate the Sc-NH<sub>2</sub><sup>+</sup> bond energy in the  $^2A_2$  state, we carried out a GVB(4/8)+1+2 configuration interaction calculation at Sc<sup>+</sup>-NH<sub>2</sub> separations of 3.75 and 20 au. This calculation consisted of 190 000 configuration state functions (CSFs), separated to the  $^3F$  state of Sc<sup>+</sup> and the  $^2B_1$  state of NH<sub>2</sub>, and gave the energies shown in Table II. The difference between these two energies is 166 millihartrees (1 millihartree = 0.62751 kcal/mol) and corresponds to a bond energy of 106 kcal/mol. Our calculated  $^3D$ - $^3F$  separation in Sc<sup>+</sup> is 18.6 kcal/mol, so relative to *ground state fragments*, we calculate a bond energy of 87 kcal/mol. To estimate the size consistency error, we calculated the SCF+1+2 energy of Sc<sup>+</sup> ( $^3F$ ) and the GVB(3/6)+1+2 energy of NH<sub>2</sub>( $^2B_1$ ). These energies sum to -815.255 97 au, which is 15 millihartrees lower than the CI energy at 20 au, shown in Table II. This 15 millihartrees represents a rather conservative estimate for the size consistency error, which reduces the calculated bond energy by 9.6 kcal/mol to ~77 kcal/mol. Additional calculations in which an STO-3G representation<sup>13</sup> of an f orbital ( $\alpha = 2.6$  for

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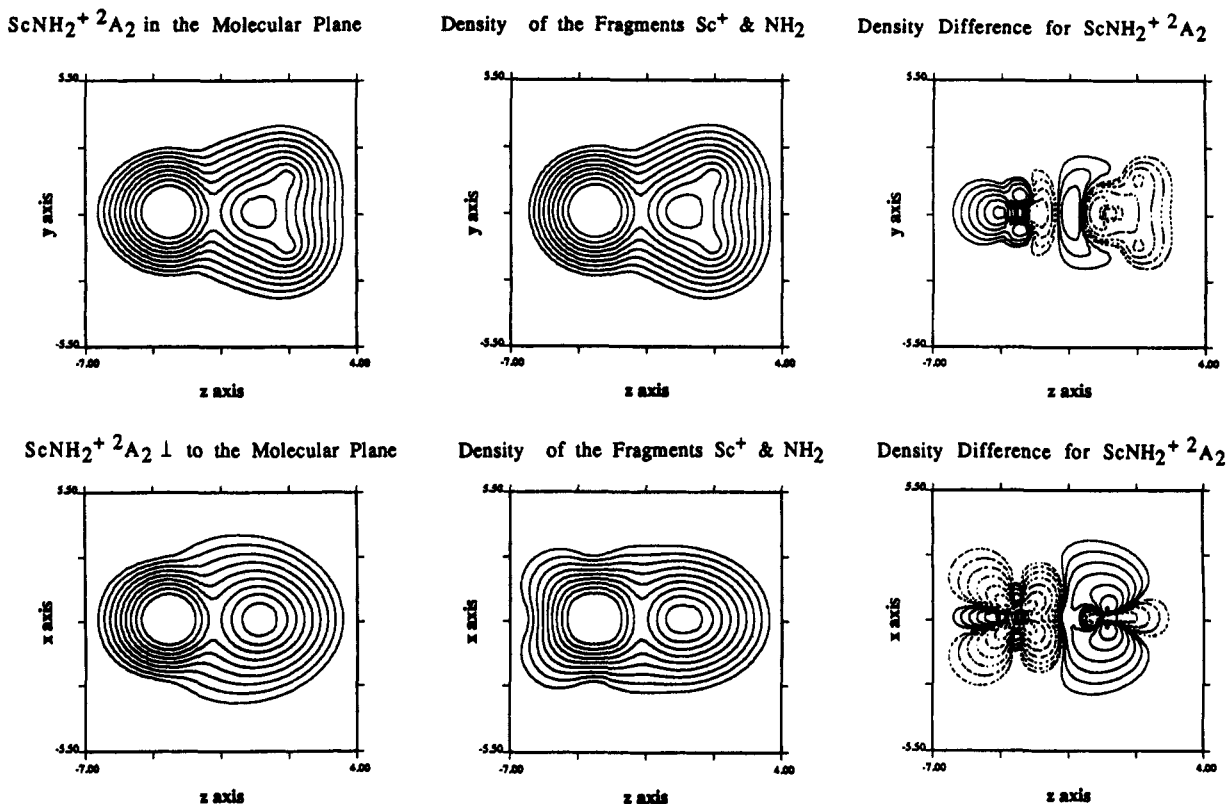


Figure 2. Electron density contours of  ${}^2A_2(\text{ScNH}_2^+)$  in the molecular plane and perpendicular to the molecular plane. Also presented are the density contours of the superimposed fragments and the corresponding density difference.

each component) was added to the  $\text{Sc}^+$  basis predicts a differential lowering of the molecule relative to the separated fragments of 2 kcal/mol, bringing our calculated bond energy to  $\sim 79$  kcal/mol.

GVB(4/8) calculations on the  ${}^2A_1$  ( $d\delta_+$ ),  ${}^2B_1$  ( $d\pi_x$ ), and  ${}^2B_2$  ( $d\pi_y$ ) states predict the order

$${}^2A_2 \leq {}^2A_1 (\sim 0) < {}^2B_2 (7.8 \text{ kcal/mol}) < {}^2B_1 (21.3 \text{ kcal/mol})$$

with the energy separation from the  ${}^2A_2$  in parentheses. All states have similar geometries, with an Sc-N separation of  $\sim 2.00$  Å and an  $\text{NH}_2$  angle of  $\sim 107^\circ$ .

While the bonding electron distribution in the  ${}^2A_1$  and  ${}^2B_2$  states is very similar to that in the  ${}^2A_2$  state, the  ${}^2B_1$  differs significantly. By symmetry the  ${}^2B_1$  state should have three  $\pi_x$  electrons and therefore a significantly decreased opportunity for charge transfer via the  $\pi$  system. In addition, the in situ, asymptotic state of  $\text{NH}_2$  should be the  ${}^2A_1$ .

The equilibrium atomic orbital population in  ${}^2B_1$  is

$$4s^{0.073}d_\sigma^{0.173}d_{xz}^{1.04}4p_x^{0.17} \text{ on Sc}$$

and

$$2s^{1.46}2p_z^{1.39}2p_y^{1.13}2p_x^{1.73} \text{ on N}$$

Clearly, the 4s electron has been transferred to the N( $\sigma$ ) orbital (a mixture of 2s,  $2p_z$ , and  $2p_y$ ). If we compare this with the electron distribution in the  ${}^2A_2$  state

$$4s^{0.063}d_\sigma^{0.163}d_{xz}^{0.223}d_\pi^{1.00} \text{ on Sc}$$

and

$$2s^{1.46}2p_z^{1.41}2p_y^{1.14}2p_x^{1.66} \text{ on N}$$

we see very little change on N and essentially the same number of electrons on Sc in the two states. We suspect that the 22 kcal/mol bond energy difference between the  ${}^2A_2$  and  ${}^2B_1$  is an artifact of referring both to the ground state of  $\text{Sc}^+$  and  $\text{NH}_2$ . For example, when the  ${}^2A_2$  is referred to the fragments  $\text{Sc}^+(d^2) +$

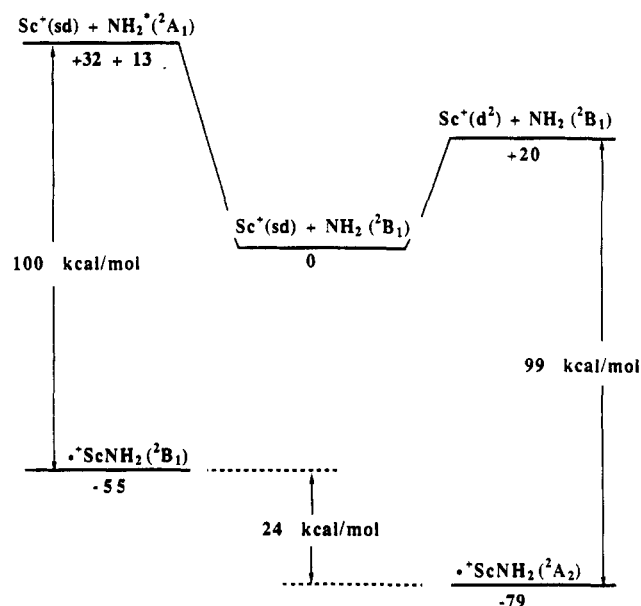


Figure 3. Comparison of  ${}^+\text{Sc-NH}_2$  bond energies in the  ${}^2A_2$  and  ${}^2B_1$  states.

$\text{NH}_2({}^2B_1)$ , we must augment the calculated bond energy of 79 kcal/mol of the  $\text{Sc}^+(sd)\text{-Sc}^+(d^2)$  excitation energy of 20 kcal/mol. This results in a bond energy of 99 kcal/mol relative to the "natural" asymptote. The calculated bond energy of 55 kcal/mol for the  ${}^2B_1$  state should be augmented by the energy required to excite the  ${}^2B_1(\text{NH}_2)$  to  ${}^2A_1(\text{NH}_2)$  or 32 kcal/mol and the 13 kcal/mol required to close the  $\text{NH}_2$  angle in the  ${}^2A_1$  state from  $144^\circ$  to  $104^\circ$ . This results in a bond energy of 100 kcal/mol, in substantial agreement with the  ${}^2A_2$  number of 99 kcal/mol. These energies are shown in Figure 3.

**Quartet States.** Quartet states obtain when the two valence electrons on  $\text{Sc}^+$  and the one unpaired electron on  $\text{NH}_2$  are all kept high spin. For  $\text{Sc}^+$  in the  ${}^3D$  state we have high-spin electrons in a 4s and a 3d orbital while for  $\text{NH}_2$  in the  ${}^2B_1$  the high-spin

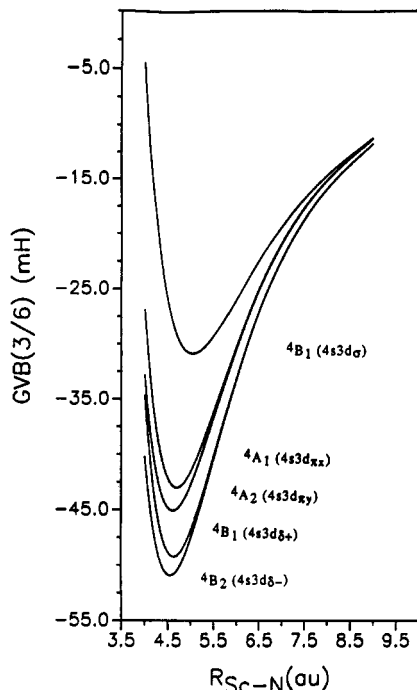
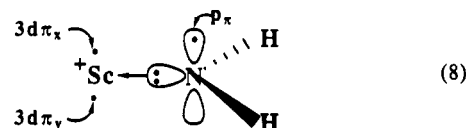


Figure 4. Potential energy curves of various quartet states of  $^+ScNH_2$  calculated at the GVB(3/6) level.

electron is in the  $\pi$  or  $b_1$  orbital. The symmetry of the resulting molecular state, in  $C_{2v}$ , is determined by the symmetry of the singly occupied 3d orbital. Specifically, we have  $^4B_1$  ( $3d_{\sigma}$  or  $3d_{\delta+}$ ),  $^4A_1$  ( $3d_{xz}$ ),  $^4A_2$  ( $3d_{zy}$ ), or  $^4B_2$  ( $3d_{xy}$ ). The potential energy of these four states at the GVB(3/6) level are shown in Figure 4. Examination of the population analysis confirms that there is no electron transfer in these states. The electron density plot shown in Figure 5 suggests however that there has been considerable mutual polarization of the  $NH_2$  and  $Sc^+$ . Figure 5 shows a contour map of the difference between the electron density of the  $^4B_2$  state

of  $^+ScNH_2$  and the separated fragments placed at the equilibrium separation. The solid contours represent an increase in density in the molecule relative to the separated fragments. The increase on  $Sc^+$  is a consequence of  $4s \rightarrow 3d$  promotion, required to compact the density on  $Sc^+$ . The increase on  $NH_2$  is a result of the polarization of the electrons due to the positive charge on  $Sc^+$ . Note that the difference maps are very similar regardless of whether the cut contains the molecular plane or is perpendicular to it. Note that the singly occupied  $3d_{xy}$  electron does not contribute in either plane.

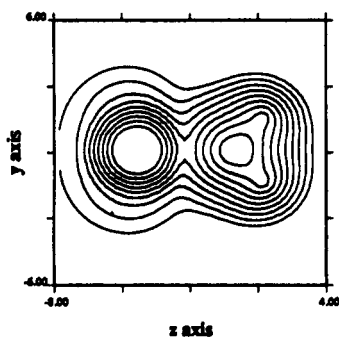
The electrostatic interaction of  $Sc^+$  in the  $3d\delta_+, 3d\delta_-$  configuration with  $NH_2(^2B_1)$  was evaluated and found to be very similar to the interaction with  $Sc^+(4s3d)$ . This is somewhat surprising in that we expected the lone pair on  $NH_2$  to bond by forming a dative bond with the empty  $Sc(4s\sigma)$  system.



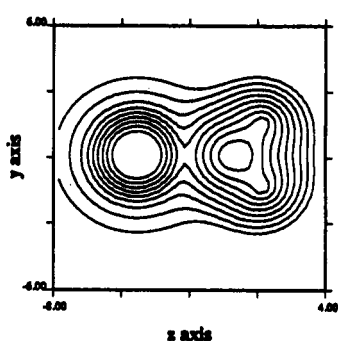
However, for this to happen the  $Sc^+$  would have to receive some electron density, and with the d electrons high spin coupled, there was no mechanism available to  $Sc^+$  to keep its +1 charge. Apparently, the Coulombic energy the molecule would lose was not to be made up by the dative bond.

These results are summarized in Figure 6. Note that the quartet states shown arise from the interaction of the two ground-state fragments,  $^3D(Sc^+)$  and  $^2B_1(NH_2)$ . A set of doublet electrostatic states will of course result from the  $^1D(Sc^+)$  and  $^2B_1(NH_2)$ . Since the  $^3D-^1D$  separation is only 7 kcal/mol and the  $^1D$  and  $^3D$  states of  $Sc^+$  should have the same electrostatic interaction with  $NH_2$ , we expect the lowest electrostatically bound  $^2B_1$  state to be  $\sim 27$  kcal/mol below the ground-state asymptotes. This means that the electrostatic doublets and quartets will be interleaved. Obviously, a similar argument holds for the quartets arising from the  $^3F$  and  $^2B_1$  asymptotes. This congestion of electronic potential surfaces with their associated vibrational levels produces a virtual continuum of states, which is in contrast to the

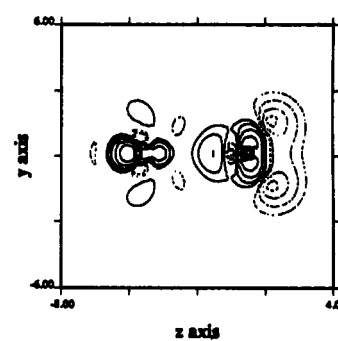
$ScNH_2 + ^4B_2$  in the Molecular Plane



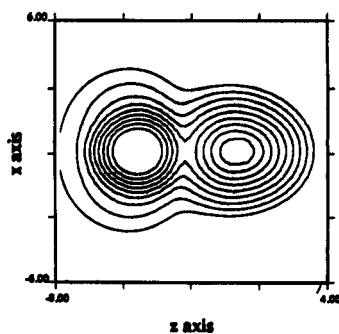
Density of the Fragments  $Sc^+$  &  $NH_2$



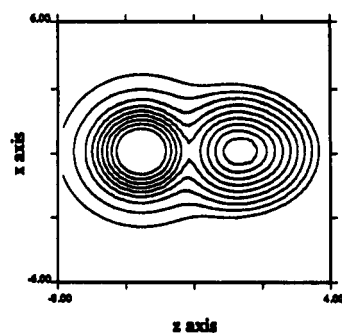
Density Difference for  $ScNH_2 + ^4B_2$



$ScNH_2 + ^4B_2 \perp$  to the Molecular Plane



Density of the Fragments  $Sc^+$  &  $NH_2$



Density Difference for  $ScNH_2 + ^4B_2$

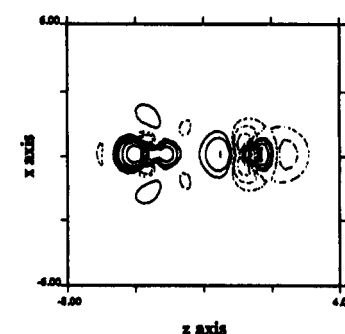


Figure 5. Electron density contours of the  $^4B_2$  state of  $^+ScNH_2$  in the molecular plane and perpendicular to the molecular plane. Also presented are the density contours of the superimposed fragments and the corresponding density difference.

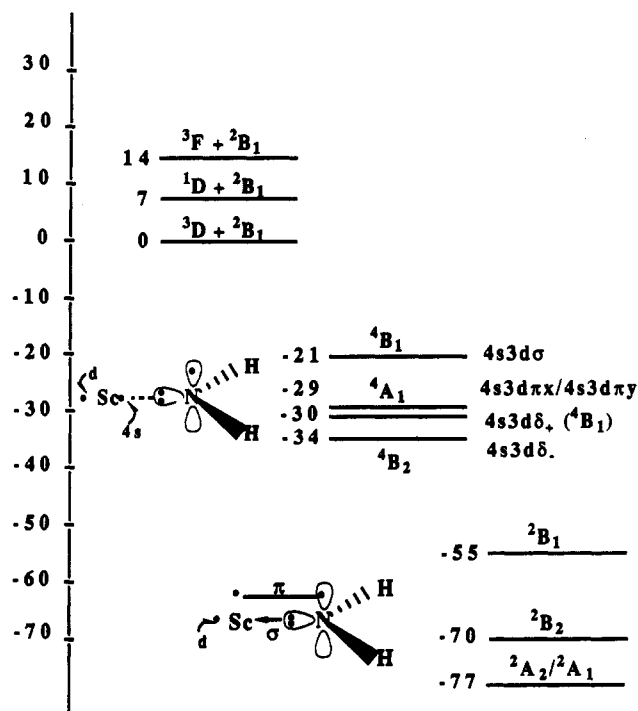


Figure 6. Summary of the relative energies of the low-lying states of  $^+ScNH_2$ .

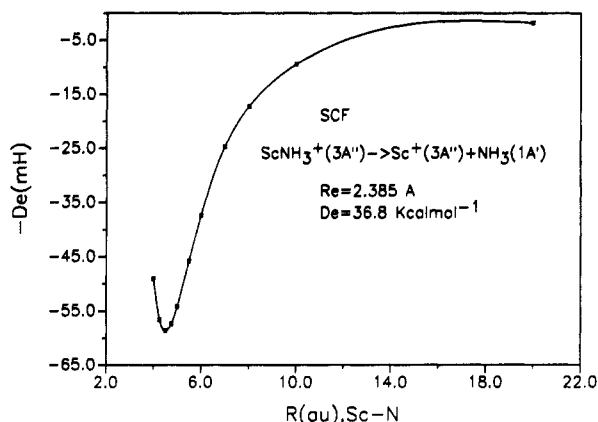


Figure 7. Potential energy of  $Sc^+$  interacting with  $NH_3$ .

relatively granular spacing of the covalently bound doublets.

### $ScNH_3^+$

Three isomers with the above formula are relevant. The first is the electrostatic or charge-dipole complex in which  $NH_3$  is bound, intact to  $Sc^+$ . The interaction energy for  $Sc^+(^3D; 4s3d)$  plus  $NH_3$  is shown as a function of distance in Figure 7. This curve was constructed at the SCF level and results in a bond length of 2.39 Å and a bond energy of 36.8 kcal/mol. This bond energy is due primarily to charge-dipole and charge-induced dipole interactions. Most interestingly, this is the ground state of all  $ScNH_3^+$  isomers studied. The interaction energy of  $Sc^+$  in the  $3d\pi_x, 3d\pi_y$  configuration with  $NH_3$  is calculated as 30.5 kcal/mol, and the bond length is 2.48 Å. Interestingly, the removal of the 4s electron from  $Sc^+$  does not permit the  $NH_3$  to approach as closely as it does when in the  $4s3d_{xy}$  configuration. The two  $3d\pi$  orbitals both have a component in the direction of the incoming  $NH_3$ , and both are more extended<sup>14</sup> than the d electrons in the  $4s3d$  configuration.

The second isomer is the insertion product  $H-ScNH_2^+$ . The geometry of this molecule was optimized at the GVB(5/10) level

(14) Botch, B. H. Dunning, T. H.; Harrison, J. F. *J. Chem. Phys.* 1981, 75, 3466.

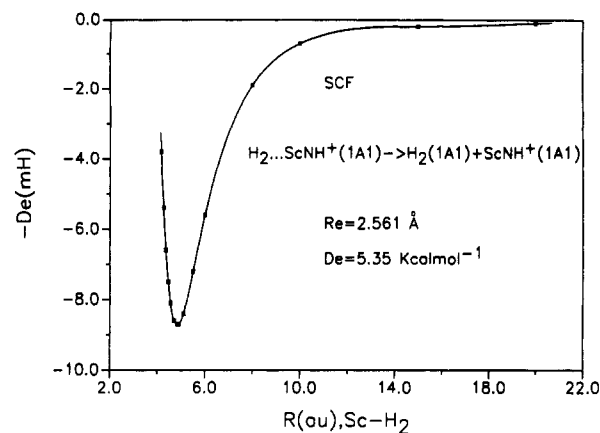
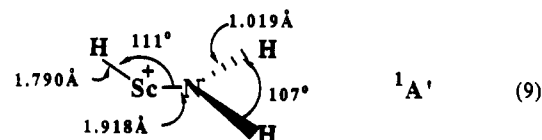
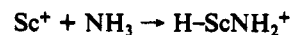


Figure 8. Potential energy of  $^+ScNH$  interacting with  $H_2$ .

in which all bonds and the nitrogen lone pair were correlated. The resulting geometry is

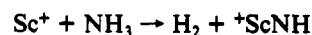


and the  $H-ScNH_2^+$  bond strength was calculated to be 45.5 kcal/mol—a typical  $Sc-H$  bond strength.<sup>15</sup> Combining this with our results on  $ScNH_2^+$  suggests that the reaction



is exothermic by at least 16 kcal/mol.

The third isomer is the electrostatic complex of  $ScNH^+$  with  $H_2$ . The  $Sc-NH^+$  bond energy is calculated<sup>9</sup> to be 106 kcal/mol (experimental<sup>6</sup> = 119 kcal/mol) while the  $ScN-H^+$  bond is calculated<sup>9</sup> to be 118.5 kcal/mol. These exceptionally strong bonds result in the reaction



being exothermic by 9 kcal/mol. The subsequent electrostatic attraction between the products (Figure 8) lowers the energy by an additional 5.5 kcal/mol, resulting in the complex



being bound relative to  $Sc^+$  and  $NH_3$  by 14 kcal/mol. Note that  $H_2$  is perpendicular to the  $^+ScNH$  axis.

**Summary of Energetics.** The relative energies of the various products of the reaction of  $Sc^+$  and  $NH_3$  are shown in Figure 9. This figure was constructed by using the previously calculated energies<sup>15</sup> for  $ScH^+$  and  $ScH_2^+$  as well as the various fragment energies discussed earlier. Experimental numbers,<sup>6,16</sup> where available, are in parentheses. These results agree with the experimental observation<sup>6</sup> that  $ScNH^+$  is formed exothermically but also suggest that the insertion product and the electrostatic complex involving intact  $NH_3$  are also formed exothermically. The insertion product is formed exothermically because the  $Sc-NH_2^+$  bond strength and the  $Sc-H$  bond strength are large and able to overcome the 108 kcal/mol required to break an  $N-H$  bond in  $NH_3$ . The  $Sc-NH_2^+$  bond is strong because of the following: (1) The  $NH_2$  group donates charge to the transition-metal ion via the  $\sigma^2$  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  $\pi$  orbital of the  $NH_2$  group. This transfer is optimized when there is one d $\pi$  electron in the  $\pi$  system being coupled with the  $NH_2(\pi)$  orbital.

(15) Alvarado-Swaigood, A. E.; Harrison, J. F. *J. Phys. Chem.* 1985, 89, 5198.

(16) Sunderlin, L.; Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* 1987, 109, 78. Armentrout, P. B. In *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; ACS Symposium Series 428, American Chemical Society: Washington, DC, 1990; Chapter 2.

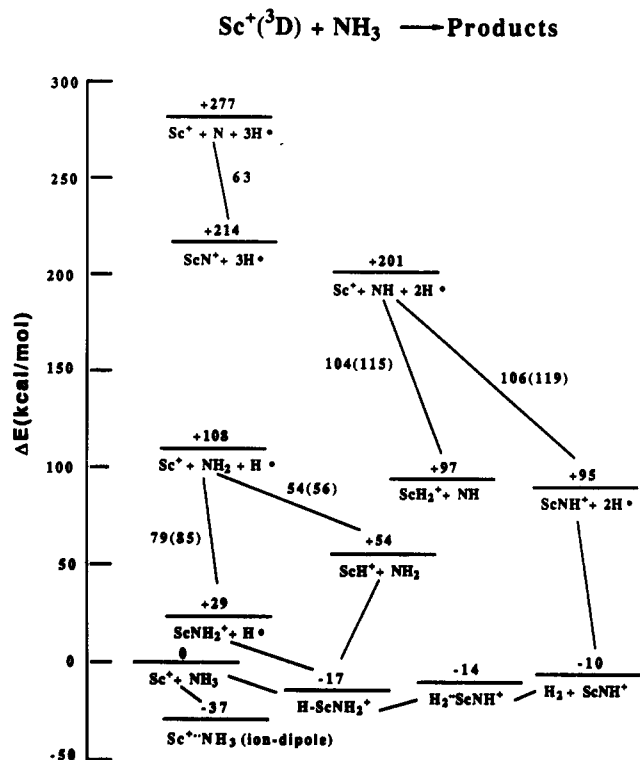


Figure 9. Summary of the relative energies of  $Sc^+ + NH_3$  in various low-lying electronic states.

Interfering with either of these mechanisms will reduce the metal-NH<sub>2</sub> bond strength and consequently the potential for an exothermic H-M-NH<sub>2</sub><sup>+</sup> insertion product. Likewise, reducing the metal-H bond strength would also reduce the possibility of an exothermic insertion product.

For example, Cr<sup>+</sup> is a d<sup>5</sup> system and the ground <sup>6</sup>S state one will always have at least one electron in a dσ orbital. Consequently, the planar configuration is not obviously better than the singly bonded nonplanar structure, and as a result, the M-NH<sub>2</sub> bond strength will be smaller for Cr<sup>+</sup> than Sc<sup>+</sup>.

Similar considerations apply to the exothermic products H<sub>2</sub> + ScNH<sup>+</sup>. In this case, the exothermicity results from the strong M-NH bond which arises from (1) each 2p<sub>x</sub> electron on N bonding to a singly occupied orbital on Sc<sup>+</sup> and (2) the lone pair

on N bonding to the empty 4s and 3d orbitals on Sc. It is not possible for Cr<sup>+</sup> to satisfy both of these conditions simultaneously, and consequently, CrNH<sup>+</sup> should have a relatively weak metal-NH bond strength.

**Acknowledgment.** This work was partially supported under NSF Grant CHE8519752 (J.F.H.), as well as NATO Grant GRE890502 to A.M. and J.F.H. The electronic structure codes provided by the Argonne theory group have been indispensable to this work. The advice and interest of John Allison are gratefully acknowledged.

#### Appendix

The scandium basis set used in this study consists of the (14s,9p,5d) basis from Wachters,<sup>17</sup> augmented with two diffuse p functions (Dunning)<sup>18</sup> and a diffuse d function as recommended by Hay.<sup>19</sup> This set was contracted to (5s,4p,3d) following Raffanetti.<sup>20</sup> The nitrogen basis set was the 5s,4p,2d ANO set of Almlöf and Taylor.<sup>21</sup> The hydrogen basis set was Huzinaga's<sup>22</sup> 4s contracted to 2s and augmented with a set of p functions (α = 1.0).

All ab initio calculations were done on an FPS-164 jointly supported by the Michigan State University Chemistry Department and the Office of the Provost by using the Argonne National Laboratory collection of Quest-164 codes. The integrals were calculated by using the program ARGOS written by Pitzer;<sup>23</sup> the SCF and MCSCF calculations were done by using GVB164 written by Bair<sup>24</sup> and the UEXP program and related utility codes written by Shepard.<sup>25</sup> The configuration interaction calculations were performed by using the program UCI (and related utility codes) written by Lischka et al.<sup>26</sup>

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(18) Dunning, T. H., Jr. Private communication.

(19) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377.

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(21) Duijneveldt, F. B. IBM Technical Research Report No. RJ-945; IBM Research Laboratory: San Jose, CA, 1971.

(22) Huzinaga, S. *Approximate Atomic Functions II*; Research Report, Division of Theoretical Chemistry; Department of Chemistry, The University of Alberta, 1971.

(23) The ARGOS integral program was developed by R. M. Pitzer (The Ohio State University).

(24) The GVB164 program was written by R. Bair (Argonne National Laboratory).

(25) A description of the UEXP program is given in: Shepard, R.; Simons, J.; Shavitt, I. *J. Chem. Phys.* **1982**, *76*, 543.

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