Silicon Surfaces as Electron Acceptors: Dative Bonding of Amines with Si(001) and Si(111) Surfaces

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Abstract: The bonding of the trimethylamine (TMA) and dimethylamine (DMA) with crystalline silicon surfaces has been investigated using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy, and density-functional computational methods. XPS spectra show that TMA forms stable dative-bonded adducts on both Si(001) and Si(111) surfaces that are characterized by very high N(1s) binding energies of 402.2 eV on Si(001) and 402.4 eV on Si(111). The highly ionic nature of these adducts is further evidenced by comparison with other charge-transfer complexes and through computational chemistry studies. The ability to form these highly ionic charge-transfer complexes between TMA and silicon surfaces stems from the ability to delocalize the donated electron density between different types of chemically distinct atoms within the surface unit cells. Corresponding studies of DMA on Si(001) show only dissociative adsorption via cleavage of the N−H bond. These results show that the unique geometric structures present on silicon surfaces permit silicon atoms to act as excellent electron acceptors.

Introduction

While the mechanistic chemistry of molecules based upon the group IV elements carbon, silicon, and germanium has been placed on a firm foundation by more than 100 years of intense study, much less is understood about the reactivity of these elements when present as pure crystalline solids. The (001) surfaces of Si, Ge, and diamond are important model systems because of their technological relevance. These surfaces share a particularly simple bonding motif in which pairs of atoms bond together in dimers. The two atoms within each dimer are formally held together with both a strong σ and a weak π bond,[1−3] making them somewhat analogous to the C═C bonds of organic alkenes and the Si═Si bonds of silenes.

Recent studies of the interaction of unsaturated organic molecules with dimerized surfaces of silicon,[4−7] carbon (diamond),[8,9] and germanium[10,11] have suggested that electron donation from C═C π orbitals to these surfaces plays an important role in controlling the overall reaction chemistry. More generally, the ability of silicon to act as an electron acceptor has been implicated in the interaction of molecules based on group V elements, such as ammonia[12−19] and phosphine,[20] with silicon surfaces. For example, ammonia reacts with the Si(001) and Si(111) surfaces via cleavage of an N−H bond, producing chemisorbed H atoms and NH_2 fragments.[12−19] Computational studies have indicated that this reaction proceeds through a mechanism in which the nitrogen lone-pair electron interacts at the edge of a Si═Si dimer via a kind of transient dative bond, which in turn weakens the N−H bond and leads to dissociative adsorption.[21,22] A similar process has been proposed for aniline (C_6H_5−NH_2), which also interacts with Si(001) via cleavage of one N−H bond, leaving chemisorbed Si−NH(C_6H_5) fragments and chemisorbed H atoms.[23−26]

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These previous studies have suggested that dative-bonded intermediates play an important role in the decomposition pathway of ammonia and other small molecules. Under most conditions, however, these species lead a fleeting existence and are difficult to observe. Experimental studies have shown that the phosphorus analogue, phosphine (PH_3), can form a stable dative-bonded adduct,[27−29] especially when dissociation is sterically hindered.[27,28] Similarly, the existence of dative-bonded amines has been inferred from detailed analysis of C−H stretching vibrations of organic amines.[30] However, these studies have not directly observed the significant changes in electron structure and charge distribution that lie at the core of chemical bonding. In this paper, we report experimental and computational investigations of the adsorption of trimethylamine (TMA) on the Si(001)−(2 × 1) and Si(111)−(7 × 7) surfaces. Our experimental and computational studies show that TMA forms a dative-bonded adduct, which has a surprisingly high degree of ionic character. These results suggest that the ability to form these stable dative-bonded adducts is strongly connected with the ability of these surfaces to transfer charge between different types of chemically inequivalent Si atoms.

Experimental Section

The experiments described here were performed in several different ultrahigh vacuum (UHV) chambers, each having a base pressure of $<1 \times 10^{-10}$ Torr. The silicon samples were rinsed in methanol and then cleaned of residual carbon contamination by exposure to ozone for ~15 min. The samples were degassed at ~850 K overnight in the chamber and then annealed to 1400 K to remove the oxide layer, producing clean silicon surfaces. Atoms at semiconductor surfaces frequently undergo characteristic rearrangements (reconstructions) to optimize their coordination and minimize the surface energy. On samples with a (001) crystal orientation, the above procedure yields surfaces exhibiting a well-ordered (2 × 1) reconstruction, while on a (111)-oriented sample the surfaces exhibit a (7 × 7) reconstruction.[2] Highly doped samples (0.01−0.02 Ω•cm, Sb-doped Si(001) and 0.005 Ω•cm, As-doped Si(111)) were used for the X-ray photoelectron spectroscopy (XPS) experiments, while lightly doped samples (15 Ω•cm, B-doped) were used in the IR experiments.

XPS data were obtained using a Physical Electronics system with monochromatized Al Kα radiation (1486.6 eV). Sample temperatures were determined using an infrared pyrometer (for T >750 K), by measuring the power applied to the sample during the experiment and later by calibrating with an thermocouple attached directly to the sample surface (for T <750 K); temperatures are believed accurate to with 50 K. The Si(2p) peaks were measured and used as an internal standard for both energy and intensity. All of the spectra reported here have been adjusted to yield a constant 99.4-eV binding energy for the bulk Si($2p_{3/2}$) line. XPS spectra were analyzed using standard curve-fitting procedures in which the quality of fit was evaluated through a "quality-of-fit" parameter, based on a reduced χ^2.[31] In general, a smaller value of quality of fit represents a better fit, with values of less than 1, indicating that the fit and the data are indistinguishable within the experimental noise.

Fourier transform infrared (FTIR) absorption spectra were obtained using 8 mm × 20 mm × 0.7 mm pieces cut from a 15 Ω•cm Si(001) wafer polished on the large (001) faces. The 8 mm × 0.7 mm edges were polished for use as a multiple internal reflection prism. Infrared radiation from a Mattson RS-1 FTIR spectrometer was coupled to a UHV chamber via BaF_2 windows and focused onto the narrow polished edge of the sample; the light exiting from the other end of the sample was collected with an InSb detector cooled to 77 K. Spectra were acquired with 4-cm^{-1} resolution.

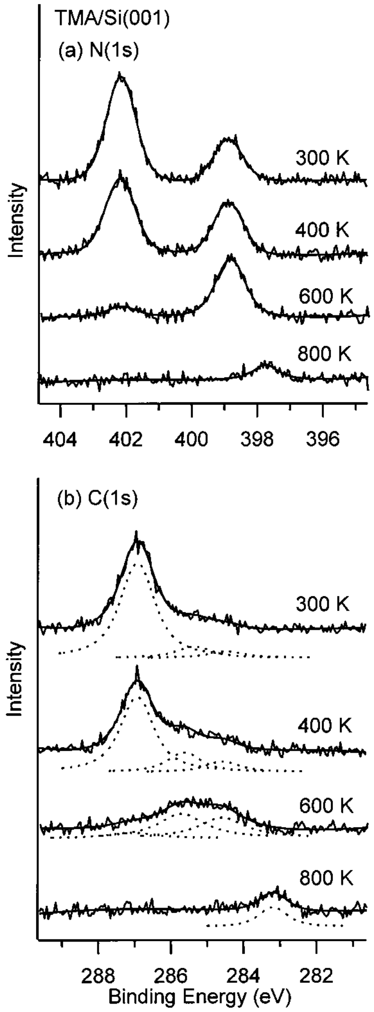

Figure 1. N(1s) (a) and C(1s) (b) XPS spectra of a Si(001) surface exposed to 20 L of trimethylamine at 300 K and subsequently annealed at elevated temperatures. All spectra were obtained after cooling the sample back to 300 K.

All amines were purchased from Aldrich with 99% purity. They were further purified through freeze−pump−thaw cycles. Purity was verified with mass spectrometers in the XPS and FTIR chambers. The compounds were introduced to the UHV chambers through variable leak valves. While the rise in chamber background pressure was used as an indicator for overall dose, the actual exposures at the surface are higher due to the chamber geometry. All exposures were given in Langmuirs (1 Langmuir ≡ 1 L ≡ 1×10^{-6} Torr•s).

Results

A. Photoemission Results for TMA and Dimethylamine (DMA) on Si(001). (1) Core-Level Photoemission of TMA/Si(001).

Figure 1 show the N(1s) and C(1s) XPS data obtained after exposing a Si(001) sample to 20 L (5.0×10^{-8} Torr for 400 s) of TMA at 300 K and the same sample after subsequently annealing to higher temperatures. After each heating cycle, the sample was returned to 300 K for XPS characterization. Immediately after dosing at 300 K, Figure 1a shows that there are two peaks in the N(1s) XPS spectrum at 402.2 and 398.9 eV, with the 402.2-eV peak comprising ~85% of the total area. The corresponding C(1s) spectrum (Figure 1b) is dominated by single sharp peak, with a broader asymmetric tail on the low-

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binding-energy side. Curve-fitting analysis yields a large peak at 286.9 eV (~85% of the total C(1s) area) and two smaller peaks with smaller binding energies of 284.6 and 285.7 eV.

The XPS data show that ~85% of the TMA molecules bond initially into a configuration yielding the 402.2-eV N(1s) and 286.9-eV C(1s) peaks. Upon heating, the largest N(1s) peak at 402.2 eV and the largest C(1s) peak at 286.9 eV both decrease. There is a small increase in area of the N(1s) peak at 398.9 eV and the C(1s) peaks at 284.6 and 285.7 eV, but the total area of the N(1s) and C(1s) features decreases by ~70%. Heating to 800 K leads to a N(1s) peak at 397.7 eV and a C(1s) peak at 283.2 eV, which are characteristic of silicon nitride,[13,23,32−35] and silicon carbide,[23,32,33] respectively. In other experiments (not shown), we find that adsorption onto a surface held at ~190 K yields only a *single* N(1s) peak at 402.2 eV and a single C(1s) peak at 286.9 eV. When dosed at 300 K, however, ~15% of the molecules dissociate upon adsorption, leading to the N(1s) and C(1s) peaks at lower binding energy. When further heated above 300 K, the decrease in total area of both N(1s) and C(1s) indicates that most molecules desorb from the surface instead of dissociating.

The XPS spectra are also slightly dependent on the total amount of TMA to which the surface has been exposed. Figure 2 shows the N(1s) and C(1s) spectra after different doses between 0.1 and 20 L. At low exposures (≤2 L), the N(1s) and C(1s) spectra are each dominated by a single peak, at 402.2 and 286.9 eV, respectively. As the exposure is increased beyond 2 L, the N(1s) peak at 402.2 eV and C(1s) peak at 286.9 eV decrease in intensity and broaden slightly, while the N(1s) peak at 398.9 eV and C(1s) peaks at 284.6 and 285.7 eV increase slightly. The overall integrated intensities of the N(1s) and C(1s) spectra are nearly constant for exposures of ≥5 L, indicating the spectra obtained after a 20-L exposure are characteristic of the saturated surface.

Analysis of peak areas shows that the ratio of total N(1s) to Si(2p) peak areas (A_{N1s}/A_{Si2p}) after saturation is 1.59. For comparison, we measured the corresponding spectrum (not shown) produced by adsorption of ammonia on the Si(001) surface and found a single N(1s) peak at 399.1 eV and an area ratio A_{N1s}/A_{Si2p} of 3.35 for a saturated surface. Since previous studies have established that the saturation N coverage is ~0.5 monolayer (ML) (1 nitrogen atom per Si═Si dimer),[36] we can estimate the saturation N coverage from TMA to be ~0.24 ML or ~1 TMA molecule per 2 Si═Si dimers.

The most striking result showing in Figure 1 is the presence of N(1) and C(1s) peaks at very high binding energies. In particular, the 402.2-eV N(1s) binding energy is much higher than the values of 398.5−399.5 eV observed for typical amines.[13,16,23,24,34,37] These high binding energies suggest a very electron-deficient environment around the nitrogen and carbon atoms and suggest that the TMA molecules may be in an environment similar to the tetramethylammonium ion. For comparison, we also obtained an XPS spectrum of ammonium chloride deposited onto a silicon substrate (as an internal standard); the resulting N(1s) binding energy was 403.2 eV. Similarly, previous studies of tetraalkylammonium salts have reported binding energies of 402.5 eV for $(CH_3)_4NCl$[38] and 401.6 eV for $(CH_3)_4NBr$.[39,40] Thus, we conclude that the binding energy of 402.2 eV we observed for TMA on Si(001) is very close to that expected for a nitrogen atom present as a molecular cation (ammonium ion) with a formal charge of +1. As will be shown later by comparison with DMA (vide infra), the smaller XPS features at 398.9 eV (N(1s)) and 284.6 and 285.7 eV (C(1s)) arise from dissociation fragments produced via cleavage of N−C bonds.

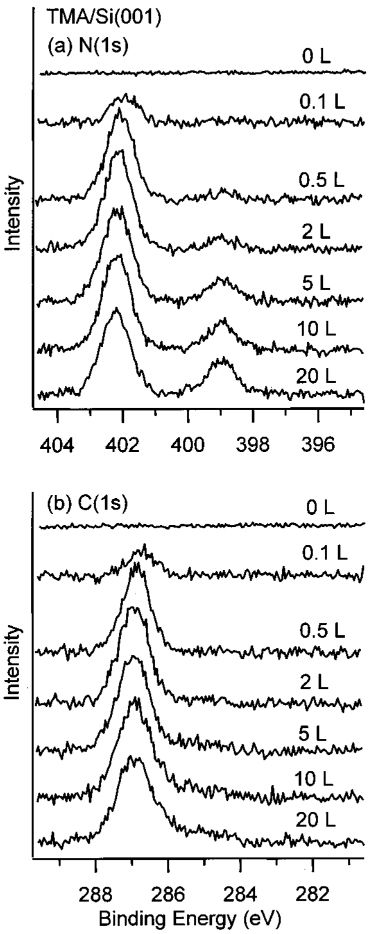

Figure 2. N(1s) (a) and C(1s) (b) XPS spectra of a Si(001) surface exposed to different doses of trimethylamine at 300 K.

(2) Core-Level Photoemission of DMA/Si(001). The above results suggest that TMA bonds into a configuration yielding unusually high N(1s) and C(1s) binding energies. For comparison, we performed analogous experiments on DMA. Figure 3 show the N(1s) and C(1s) XPS data obtained by exposing a Si(001) surface to 10 L (5.0×10^{-8} Torr for 200 s) of DMA at 300 K. This sample was then sequentially heated to each of the indicated temperatures for 10 min and returned to 300 K for XPS analysis. The N(1s) XPS data at temperatures ≤600 K show only a single peak at 398.9 eV with a fwhm of 0.87 eV ($\chi^2 = 1.0$), close to the overall resolution of our XPS instrument. Similarly, the C(1s) spectra obtained after exposure at temperatures ≤600 K show a single, narrow peak at 286.0 eV (fwhm = 0.90 eV, $\chi^2 = 1.0$). Heating to >400 K leads to a uniform decrease in N(1s) and C(1s) intensities, indicating that most molecules desorb from the surface without further dissociation.

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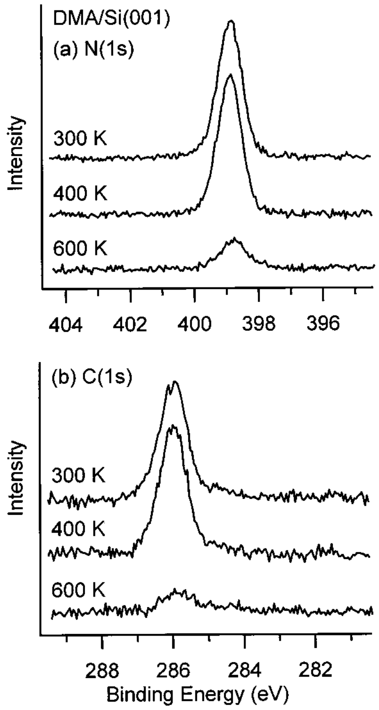

Figure 3. N(1s) (a) and C(1s) (b) XPS spectra of a Si(001) surface exposed to 10 L of dimethylamine at 300 K and subsequently annealed at elevated temperature. All spectra were obtained after cooling the sample back to 300 K.

The narrow width and low χ^2 suggest that there is only one chemically distinguishable form of nitrogen and carbon on the surface. The 398.9-eV N(1s) binding energy is close to the 398.5−399.1-eV N(1s) binding energies of dissociatively adsorbed ammonia,[13,16,34] pyrrolidine, and aniline on Si(001) surfaces.[23,24] Since in all these compounds adsorption occurs via cleavage of an N−H bond, leaving the N atom with a coordination number of three, it is likely that DMA also bonds with cleavage of an N−H bond. Since there is little difference in electronegativity between H and C, however, it is not clear from the N(1s) data alone whether DMA cleaves N−H or N−C bonds when adsorbing to the Si(001) surface. Analysis of the C(1s) data clarifies the situation. Cleavage of an N−C bond would be expected to produce methyl fragments bonded to the silicon surface (i.e., Si−CH_3 species). Methyl groups can also be prepared by exposing a Si(001) surface to methyl iodide, which is known to cleave the C−I bond to produce methyl groups (Si−CH_3 species) and iodine atoms (Si−I species) on the surface.[41−43] We exposed a Si(001) surface to methyl iodide and found that the resulting XPS spectrum (not shown) yields a single C(1s) peak at 284.1 eV from Si−CH_3 species. In contrast, the C(1s) spectrum for DMA shows only a single peak with a binding energy of 286.0 eV, nearly 2 eV higher than that of the Si−CH_3 species. Because silicon (Pauling electronegativity, 1.90) is a better electron donor than nitrogen (electronegativity, 3.04) is, carbon atoms bonded to an N atom are normally expected to have a higher binding energy than those bonded to Si. Thus, the XPS data suggest that adsorption of DMA onto Si(001) leaves all N−C bonds intact and, therefore, indicates that that DMA adsorbs to the surface by cleaving an N−H bond, leaving Si−$N(CH_3)_2$ species and Si−H species on the surface.

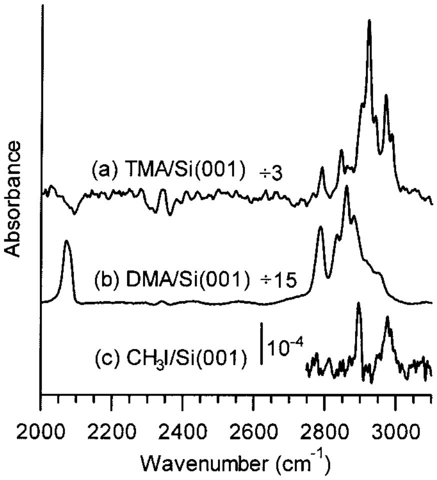

Figure 4. FTIR spectrum of Si(001) surfaces exposed to (a) 5 L of trimethylamine, (b) 10 L of dimethylamine, and (c) 10 L of methyl iodide at 300 K.

B. Infrared Spectroscopy of TMA and DMA on Si(001). To help confirm identification of the surface-bonded species, we obtained infrared spectra of trimethylamine, dimethylamine, and methyl groups on Si(001). Figure 4a show an infrared spectrum of a Si(001) surface after exposure to 5 L (2.0×10^{-8} Torr for 250 s) of TMA at 300 K. The spectrum is dominated by a large, sharp peak at 2919 cm^{-1} and weaker peaks at 2789, 2842, 2900, 2940, 2969, and 2989 cm^{-1}. The most notable feature in this spectrum, however, is the absence of any peaks in the 2080−2100-cm^{-1} region, where Si−H stretching vibrations are found.[44] Since the Si−H infrared transition dipole is much larger than that for C−H bonds, the absence of any detectable Si−H vibrations indicates that TMA bonds to Si(001) with little or no cleavage of C−H bonds.

While the FTIR spectrum for TMA on Si(001) shows no evidence for Si−H vibrations, the situation for DMA is rather different. Figure 4b shows an infrared spectrum of a Si(001) surface exposed to 10 L (5.0×10^{-8} Torr for 200 s) of DMA at 300 K. The spectrum shows a strong, sharp peak at 2072 cm^{-1}, in the region where the Si−H stretching vibrations are typically observed. Large peaks are observed at 2787, 2831, 2861, and 2883 cm^{-1}, in the spectral region usually associated with alkane C−H vibrations. No significant absorption is detected in the region above 3000 cm^{-1}, where unsaturated C−H vibrations and N−H modes typically are observed. The presence of Si−H vibrational features and the absence of N−H features in the FTIR spectrum strongly indicate that DMA cleaves the N−H bond upon bonding, producing Si−$N(CH_3)_2$ and Si−H species.

As a further check for the presence of Si−CH_3 species, we obtained an infrared spectrum of a Si(001) surface exposed to 10 L (5.0×10^{-8} Torr for 200 s) of methyl iodide (CH_3I). The spectrum shows that the surface-adsorbed methyl groups (Si−CH_3 species) give rise to a strong peak at 2895 cm^{-1}, a second, slightly weaker peak with a maximum at 2976 cm^{-1}, and possible shoulders at 2951 and 2987 cm^{-1}. These features are similar to those reported previously[43] and are very distinct from the vibrational features observed for DMA, again indicating that there is no evidence for N−C bond cleavage for DMA.

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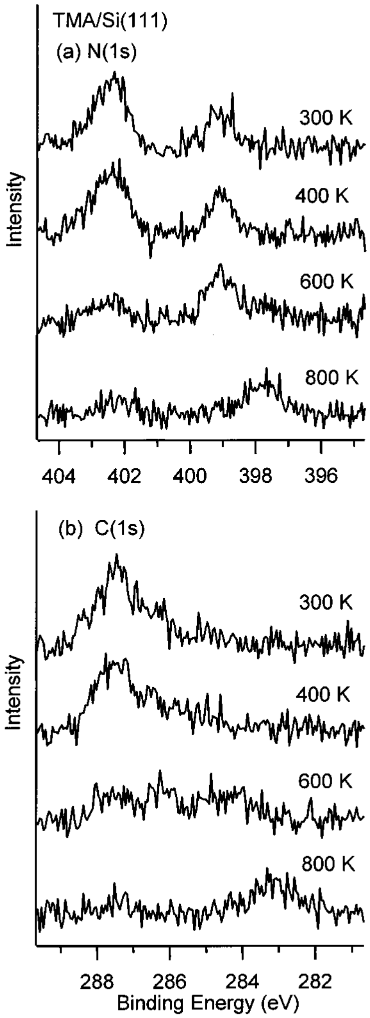

Figure 5. N(1s) (a) and C(1s) (b) XPS spectra of a Si(111) surface exposed to 20 L of trimethylamine at 300 K and subsequently annealed at elevated temperature. All spectra were obtained after cooling the sample back to 300 K.

However, the 2895- and 2976-cm^{-1} features due to methyl groups agree well with two peaks observed in the spectrum of Si(001) exposed to TMA. This correspondence supports the idea that there is some cleavage of C−N bonds upon TMA adsorption, producing Si−N(CH$_3$)$_2$ and Si−CH$_3$ species in addition to the major product.

Comparison with the Si(111)−(7 × 7) Surface. While the Si(001) surface adopts a very simple surface structure,[45] the Si(111) surface undergoes a very complex rearrangement that leads to the Si(111)−(7 × 7) reconstruction, as discussed in more detail below. Figure 5 shows the N(1s) and C(1s) XPS data obtained by exposing a Si(111)−(7 × 7) surface to 20 L (5.0 × 10^{-8} Torr for 400 s) of TMA at 300 K. Also included are the spectra obtained by subsequently heating the sample for 10 min to the temperatures indicated in the figure and then cooling to 300 K for XPS analysis. Immediately after dosing at 300 K, the N(1s) spectrum (Figure 5a) shows a large peak with a binding energy of 402.4 eV and a smaller peak at 399.1 eV. The corresponding C(1s) spectrum (Figure 5b) shows one predominant peak at 287.5 eV. Annealing to 600 K almost eliminates the N(1s) peaks at 402.4 eV and the C(1s) peak at 287.5 eV C(1s), with a small increase in the N(1s) peak at 399.1 eV.

The overall behavior on Si(111)−(7 × 7) is similar to that observed on the Si(001) surface. On both surfaces, the TMA molecules bind primarily into a molecularly bonded configuration yielding very high N(1s) and C(1s) binding energies, with some minor dissociation producing Si−N(CH$_3$)$_2$ and Si−CH$_3$ species. The most significant difference between TMA on the Si(001) and Si(111) surfaces is that quantitative analysis of the N(1s) and C(1s) peak areas yields an A_{N1s}/A_{Si2p} ratio of 0.78 on Si(111)−(7 × 7), compared with the value of 1.59 measured on the Si(001) surface. Thus, the number of TMA molecules per unit area on that bond to the Si(111)−(7 × 7) surface is only about half that of the Si(001) surface.

D. Theoretical Calculations. To better understand the bonding on TMA on silicon surfaces, we performed calculations of the geometry and electronic structure of TMA−silicon adducts, using the Gaussian 98 program.[46] Results reported here were performed using density functional theory with the 6-31+G* basis set and the Becke3LYP hybrid density functional,[47] because a previous study[48] of the H$_3$B−NH$_3$ system showed that density functional theory under similar conditions yielded highly accurate geometries, dative bond energies, and dipole moments. Additional calculations (not reported here) were performed using a larger basis set to check the effect of basis set size, with insignificant differences. We note, however, that because of the diradical nature of the Si(001) surface, single-determinant wave functions may not always properly describe the energetics, particularly at transition states, and that multiconfiguration wave functions may be needed for quantitative comparison with experiment.[5]

The Si$_9$H$_{12}$ cluster shown in Figure 6a was used to simulate the Si(001) surface; this cluster has seven “bulklike” Si atoms, has two more “surfacelike” Si atoms in a dimer configuration similar to that of a single dimer on the Si(001) surface, and has been used extensively in previous studies.[5,11,22,30,49] Figure 6b depicts the optimized geometry when TMA is bonded at the dimer edge.

The molecular bonding of TMA and the dissociative bonding of DMA are readily explained from computational results. The quaternary-bonded TMA−Si(001) adduct (Figure 6b) has an energy 104 kJ/mol lower in energy than the separated reactants. A similar calculation shows that dissociation to produce Si−N(CH$_3$)$_2$ and chemisorbed methyl groups (on the same dimer) is 248 kJ/mol lower in energy than the separated reactants. Thus, thermodynamics clearly favors dissociation. However, the high-symmetry transition state involved in cleaving an N−C bond to product Si−N(CH$_3$)$_2$ and Si−CH$_3$ species produces a barrier 107 kJ/mol *higher* than the energy of the separated reactants. Consequently, the TMA−Si(001) molecular complex is only metastable toward dissociation, but the barrier is sufficiently large that the molecularly bonded adduct can be easily observed at room temperature. Analogous calculations for dimethylamine show that the molecularly bonded adduct is 113 kJ/mol lower in energy than the separated reactants. The final products of N−C bond cleavage (Si−N(CH$_3$)H and Si−CH$_3$ species) are 263 kJ/mol lower than the reactants, while those produced by N−H bond cleavage (Si−N(CH$_3$)$_2$ and Si−H species) are only 212 kJ/mol lower than the reactants. However, while the transition state for N−C cleavage is again high (96 kJ/mol above the reactants), the transition state for N−H cleavage is 27 kJ/mol *below* the energy of the separated reactants. Thus, for DMA, the calculations predict that dissociation should occur in a facile

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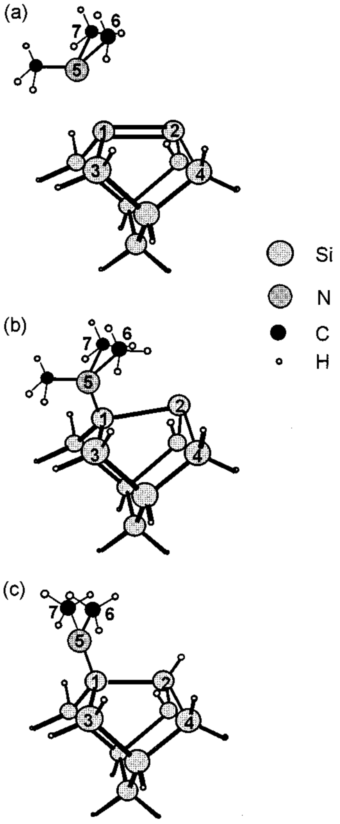

Figure 6. Representations of molecular geometries as described in text. (a) Si_9H_{12} cluster representing Si(001) surface, and TMA molecule. (b) Si_9H_{12}−TMA adduct with N in quaternary configuration (dative-bonded). (c) Si_9H_{12} + $N(CH_3)_2$ + H, produced by DMA dissociation.

manner via N−H bond cleavage leading to the product depicted in Figure 6c, and the molecular configuration, although a likely transient intermediate, is not likely to be observed at room temperature. Similar conclusions have been reached in previous computational studies of ammonia[21,22] and a very recent study of methylamines[30] interacting with the Si(001) surface.

While both experimental and computational results indicate that TMA forms a stable molecular complex on the Si(100) surface, the experimental data also show that formation of the interaction of TMA with Si(001) and Si(111) surfaces is accompanied by large changes in electronic structure, evidenced by the large core-level shifts in our XPS measurements. These features point toward an unusually ionic bond between TMA and the Si(001) surface.

The high ionicity of the TMA−Si(001) adduct suggests that there is a high degree of electron donation from N to Si. This suggests that the electronic interaction between N and Si is highly asymmetric, with the N atom acting as an electron donor and the Si acting as an electron acceptor. Such highly asymmetric bonding is one of the features often associated with *dative* bonds. "Dative" bonding, (or the now-preferred term, "dipolar bonding")[50] is often loosely described as a bond in which both electrons originate from one of the two bonded species. A more specific definition is that a dative (dipolar) bond is a bond in which the minimum-energy pathway for bond cleavage produces neutral species in their lowest energy state.[50,51] To confirm that the N−Si bond in the TMA−Si(001) adduct meets this definition, we performed a series of calculations in which the electronic structure of the TMA−Si_9H_{12} was minimized as the N−Si bond was gradually lengthened; this calculation confirmed that the bond cleavage was indeed heterolytic, with the dissociation products consisting of the neutral Si_9H_{12} cluster and the neutral TMA molecule. Analogous calculations show that the neutral Si_9H_{12} and $N(CH_3)_3$ molecules are lower in energy than the ion pair $N(CH_3)_3^+$ + $Si_9H_{12}^-$. Thus, our calculations show that the N−Si bond in the TMA−Si(001) adduct meets the technical definition of a *dative* bond.

A second characteristic feature of dative bonding is that dative bonds are unusually long. To illustrate the physical changes that accompany bonding to the surface, Table 1 lists a number of the selected bond lengths and angles for the clean Si(001) surface, for the free TMA molecule, and for the TMA−Si(001) dative-bonded complex. In Table 1, the atomic number coincides with the atoms labeled in Figure 6. The dative-bonded complex in Figure 6b has a Si−N bond length of 2.03 Å. This is 0.27 Å longer than the1.76-Å Si−N bond length calculated for Si−$N(CH_3)_2$ species produced by dissociative adsorption of TMA and DMA and for Si−NH_2 species produced from dissociative bonding of ammonia. Bonding of TMA to the surface lengthens the N−C bonds slightly (from 1.46 to 1.50 Å) and decreases the C−N−C bond angle slightly from 109.4 to 108.8°, leaving the N atom close to ideal tetrahedral coordination.

Formation of the dative-bonded complex also causes very strong changes in the underlying Si substrate. While the Si=Si "dimer bond" of the starting surface has an unusually short length of 2.22 Å (reflecting a partial double-bond character), formation of the dative-bonded complex lengthens this to 2.38 Å, slightly longer than the value of 2.35 Å calculated for "bulklike" Si−Si bonds (and the experimental value of 2.35 Å for bulk Si). The most pronounced effect of the dative bond, however, is the strong dimer tilting of that is induced, as the Si=Si dimer axis is tilted 8.1° with respect to the plane established by the four first-layer atoms to which the dimer is connected. This dimer tilting results in the bond angle $\angle 312$ increasing from 106.6 to 114.2° as the silicon atom labeled "1" adopts a more planar configuration, while the bond angle $\angle 124$ decreases from 106.6 to 94.0°, as the Si atom labeled "2" becomes more pyramidal.

These changes in structure are accompanied by significant changes in charge distribution within the molecule. To analyze the charge distributions, we used the natural population analysis (NPA) method.[52] In NPA, the populated molecular orbitals are decomposed into their individual atomic orbital components, permitting assignment of charge to individual atomic centers. Table 2 shows the resulting charges on selected atoms (in units of the fundamental electron charge, $\sim 1.602 \times 10^{-19}$ C), along with the total charge on the TMA moiety. Analogous calculations on other molecular and dissociative adducts are shown for comparison. Most notable is that the effective charge on the TMA fragment is +0.23 when dative-bonded to the Si(001) surface. This charge is close to the +0.28 value we calculate for the TMA−BF_3 complex, a well-studied dative-bonded complex, and is quite distinct from the charge on NH_2 and $N(CH_3)_2$ groups in more conventional adducts. For example, the total charge on the $N(CH_3)_2$ group bonded to the Si_9H_{12} cluster (like that produced by dissociative adsorption of DMA on Si(001)) is −0.51, while a similar calculation for the NH_2 group (produced by dissociative adsorption of ammonia) yields

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Table 1. Selected Bond Lengths (Å) and Angles (deg)

	R_{12} Si−Si	R_{13} Si−Si	R_{24} Si−Si	R_{15} Si−N	R_{56} N−C	∠312	∠124	∠657	∠651
Si_9H_{12}	2.222	2.346	2.346			106.6	106.6		
TMA					1.456			109.4	
molecular TMA/Si_9H_{12} (Figure 6b)	2.377	2.372	2.392	2.033	1.496	114.2	94.0	108.8	108.9
dissociative DMA/Si_9H_{12} (Figure 6c)	2.423	2.378	2.368	1.757	1.459	103.4	105.5	112.0	120.5

[a] Atom labels are indicated in Figure 6.

Table 2. NPA Charges on N-Containing Fragments and on Selected Individual Atoms[a]

	N-containing fragment	N atom	Si_1 atom	Si_2 atom
Si_9H_{12} cluster			−0.11	−0.11
Si_9H_{12}−TMA (molecular complex, Figure 6b)	0.23 ($N(CH_3)_3$)	−0.62	+0.32	−0.39
Si_9H_{12} + $N(CH_3)_2$ + CH_3 (TMA dissociation product, Figure 6b)	−0.51 ($N(CH_3)_2$)	−0.93	0.00	+0.29
Si_9H_{12}+ NH_2 + H (NH_3 dissociation product)	−0.49 (NH_2)	−1.3	+0.55	−0.02
TMA−BF_3	+0.28 ($N(CH_3)_3$)	−0.57		

[a] Atom numbers are indicated in Figure 6.

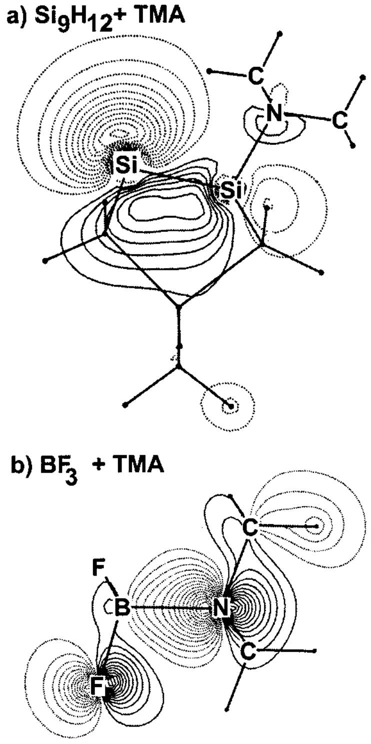

Figure 7. Contour plot of HOMO orbitals of dative-bonded complexes. Outermost contours is at a value of 0.025; spacing between contours is 0.025. (a) HOMO orbital of Si_9H_{12}−TMA dative-bonded adduct. (b) HOMO orbital of TMA−BF_3 dative-bonded adduct.

a charge of −0.49. There are also correspondingly large changes in the charge on the underlying silicon dimers, discussed in more detail below.

These unusual charge distributions arise from the transfer of electron density from the TMA molecule to the silicon atoms. In Figure 7 we present contour plots of the highest occupied molecular orbital (HOMO) for the TMA−Si_9H_{12} adduct (Figure 7a) and for the well-studied TMA−BF_3 dative-bonded complex (Figure 7b). The TMA−BF_3 adduct has a HOMO that is essentially an sp^3-hybridized orbital centered on the N atom. However, the HOMO orbital of the TMA−Si_9H_{12} cluster has a completely different appearance. There is comparatively little change along the Si−N bond, but instead the HOMO orbital is essentially a lone-pair orbital (occupation = 1.8 electrons) centered on the Si atom that is *not* bonded to the TMA adduct.

Discussion

A. Experimental Bonding Configurations.

(1) DMA on Si(001). The presence of a strong Si−H peak in FTIR clearly shows that DMA bonds to the surface by breaking the N−H bond, while the absence of Si−CH_3 groups (which would have C(1s) binding energies of ∼284.1 eV) shows that there is no significant N−C bond cleavage. Thus, both XPS and FTIR indicate that DMA bonds almost *exclusively* via N−H bond cleavage to produce Si−$N(CH_3)_2$ and Si−H species on the surface. This is further supported by the fact that the 398.9-eV N(1s) binding energy for DMA on Si(001) is close to the 398.5−399.1-eV N(1s) binding energies of dissociatively adsorbed ammonia,[13,16,34] pyrrolidine, and aniline on Si(001) surfaces.[23,24] We therefore conclude the DMA bonds to the Si(001) surface by cleaving the N−H bond and that the Si−$N(CH_3)_2$ product gives rise to the N(1s) at 398.9 eV and the C(1s) feature at 286.0 eV. Our conclusion that DMA bonds to Si(001) via N−H bond cleavage contradicts a recent study in which it was concluded that DMA bonds via C−N cleavage.[53] In that paper, however, the surface species were inferred from the decomposition products detected during thermal desorption experiments. We believe that the XPS and FTIR data presented here clearly show that the N−H bond cleavage is by far the predominant decomposition pathway.

The above behavior is in full agreement with a number of theoretical studies as well as a recent experimental study using infrared spectroscopy.[30] It is known that although the N−H bond is stronger than the N−C bond for neutral amines, any increase in positive charge on the N atom preferentially decreases the strength of the N−H bond.[54−57] Consequently, for cations such as $(CH_3)_3NH^+$, cleavage of the N−H bonds is facile and occurs with virtually no barrier, while cleavage of the N−C bonds requires surmounting a significant barrier. Our calculations presented here, along with other theoretical studies of amines[30] and ammonia,[21] indicate that similar factors control the behavior on silicon surfaces.

(2) TMA on Si(001). While the adsorption of DMA is primarily dissociative, the adsorption of TMA onto the Si(001) surface is primarily molecular in nature. The largest N(1s) peak at 402.2 eV and the largest C(1s) peak at 286.9 eV are correlated with one another and represent ∼85% of the total N(1s) and

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C(1s) area, respectively. Since the smaller N(1s) feature at 398.9 eV and the C(1s) features at 285.7 and 284.6 eV are not observed at all when Si(001) is exposed to TMA at low temperatures and their intensity increases after thermal annealing, we conclude that these features arise from minor dissociation products.

The 402.2-eV binding energy of the main N(1s) peak is close to the value of ∼403 eV that is characteristic of ammonium salts and is also more than 3 eV higher than that the typical N(1s) binding energies of 398.5−399.1 eV produced by dissociative adsorption of DMA, NH_3, pyrrolidine, and aniline on the Si(001) surface.[13,16,23,24,34] We therefore conclude that the primary N(1s) peak, at 402.2 eV, arises from an adduct in which nitrogen atom of TMA forms a dative bond with surface silicon atom, producing a quaternary nitrogen similar to that found in the ammonium ion. Since the binding energy of the 286.9-eV C(1s) peak is unusually high, and since the intensity of this peak is strongly correlated with the intensity of the 402.2-eV N(1s) peak, we likewise attribute the C(1s) peaks at 286.9 eV to the C atoms in this dative-bonded adduct.

Identification of the minor dissociation products of TMA is also straightforward. The absence of any detectable Si−H stretching vibration in the FTIR spectrum (Figure 4a) indicates that there is no significant C−H bond cleavage, so that any dissociation must arise from N−C bond cleavage. Indeed, the 398.9-eV energy of the small N(1s) peak produced by TMA is identical to that of the main N(1s) peak produced by dissociative adsorption of DMA. Likewise, the C(1s) peak at 285.7 eV from dissociation of TMA is very close to that observed for DMA (286.0 eV) and attributed to the C atoms in $Si-N(CH_3)_2$, and the C(1s) peak at 284.6 eV is close to that observed for $Si-CH_3$ groups.

Thus, the data are completely consistent with ∼15% dissociation to produce $Si-N(CH_3)_2$ and $Si-CH_3$ species. More importantly, however, is that the vast majority of TMA molecules form a dative-bonded adduct on Si(001) that can be readily observed via XPS.

(3) TMA on Si(111)−(7 × 7). The behavior of TMA on the Si(111) surface appears to be similar to that on the (001) surface. The interaction of TMA with the Si(111) surface yields N(1s) and C(1s) peaks that are slightly higher in energy than those attributed to the dative-bonded adduct on the Si(001) surface (402.4 and 399.1 eV on Si(111) compared with 402.2 and 398.9 eV on Si(001)), but the differences are much less than the inherent line width (∼1 eV) of the N(1s) features. The high N(1s) binding energy and the similarities with the (001) surface demonstrate that TMA also bonds nondissociatively on the Si(111) surface via formation of a dative bond. The appearance of weak N(1s) peaks at 399.1 eV and C(1s) peaks at 284.5−286.5 eV indicates a small fraction of molecule cleaving an N−C bond to produce $Si-N(CH_3)_2$ and $Si-CH_3$ species. However, most molecules form a dative-bonded adduct.

B. Charge Transfer in Dative Bonding on Silicon Surfaces. Our results above show that TMA bonds to Si(001) and Si(111) via a dative bond in which some of the electron density of the nitrogen "lone pair" is used to form a bond with the Si=Si dimer. The XPS results show that the N(1s) binding energy for the quaternary nitrogen in the dative-bonded adduct (the $Si-N(CH_3)_3$ species) is 3.3 eV higher than that for the ternary nitrogen in species such as $Si-N(CH_3)_2$. Likewise, the C(1s) binding energies are also ∼1.2 eV higher in the $Si-N(CH_3)_3$ than in the $Si-N(CH_3)_2$ species. Most notable is that the absolute N(1s) binding energies of 402.2 (TMA/Si(001)) and 402.4 eV (TMA/Si(111)) are only slightly smaller than the energy of 403.2 eV we measured for ammonium chloride, which is usually described as an ionic salt with the N atom in a formal oxidation state of +1.

The very high degree of ionic character in bonding of TMA to Si(001) is in full agreement with the NPA charge analysis presented in Table 2. In the NPA analysis, the total change in natural charge of the TMA molecule (i.e., the sum of the charges of all 13 atoms in the TMA moiety) is used to quantify the amount of charge transfer; similar results are shown for the $N(CH_3)_2$ and NH_2 fragments produced by DMA and NH_3 dissociative adsorption on the Si_9H_{12} cluster and from TMA in the well-studied $TMA-BF_3$ complex. The population analysis of TMA interacting with BF_3 complexes and with Si surfaces predicts that the electron transfer from TMA to the corresponding acceptor is ∼0.28 electron for the $TMA-BF_3$ adduct, while it is calculated to be 0.23 electron for the TMA−Si(001) adduct. This result is consistent with the fact that the experimental N(1s) binding energies we find for dative-bonded TMA is close to those measured previously for $TMA-BX_3$ complexes.[58] The high N(1s) binding energies and the calculated charge transfers show that the Si(001) and Si(111)(7×7) surfaces both act as strong electron acceptors (Lewis acids) toward adduct formation with TMA.

Consequently, our results show that the dative bonding of TMA to Si(001) and Si(111) surfaces is highly ionic, with a high degree of electron transfer from N to Si.

C. Electrophilic Nature of Silicon Surfaces. (A) Si(001) Surface. The strong electron transfer from N to Si is somewhat surprising, since nitrogen (Pauling electronegativity, 3.04) is significantly more electronegative than Si (electronegativity, 1.90). It is widely known that the individual Si=Si dimers of the Si(001) surface can tilt out of the surface plane and that this dimer tilting is accompanied by transfer of electron density from the "down" atom to the "up" atom in each dimer, resulting in ionic character.[45] Examination of the equilibrium structure obtained from the electronic structure calculations (Figure 6b) shows that Si−Si dimer bond is tilted by 8.1°. This tilting places the "down" atom into a geometry that is closer to a trigonal planar geometry such as the CH_3^+ or SiH_3^+ ions and places the "up" atom into a pyramidal geometry like the CH_3^- ions. Thus, the dimer tilting permits the electron density from the nitrogen lone pair to be transferred to the "up" atom of the tilted dimer.

The high electron density at the Si "dangling bond" location is clearly evident from an NPA charge analysis, which shows that the Si at the dangling bond position has a natural charge of −0.39 eV, while the Si atom directly bonded to the TMA molecule has a natural charge of +0.32 eV.

The origin of the surprising stability of the TMA−Si(001) dative-bonded complex is more clearly evident from a comparison of the HOMO orbital of the $TMA-Si_9H_{12}$ cluster, in Figure 7a, with the HOMO orbital of the well-studied $TMA-BF_3$ complex, shown in Figure 7b. In Figure 7a, the HOMO orbital is completely occupied and is essentially a "lone-pair" orbital on the remaining Si atom. The LUMO orbital (not shown) is essentially a classical σ^* orbital formed from coaxial p-like orbitals on the N and Si atoms. In contrast, the HOMO orbital of the $TMA-BF_3$ complex is very much like an sp^3-hybridized orbital centered on the N atom, with the orbital density highly concentrated along the N−Si bond. Our results indicate that the stability of the TMA−surface adduct is closely connected with the fact that the atomic structure of the Si(001)

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surface permits the electron density to be transferred to the adjacent Si atom, thereby permitting the electron density to be delocalized to a greater degree than in normal saturated compounds. This is also supported by calculations indicating that if charge transfer to the second atom is restricted (by putting a hydrogen atom onto that Si atoms so that it achieves 4-fold coordination), the ability of the adjacent Si dimer atom to form a dative bond to TMA is eliminated.

(2) Si(111)−(7 × 7) Surface. Although the Si(111)−(7 × 7) surface is characterized by a very complicated structure, we believe that similar considerations hold. Starting with 49 unsaturated “dangling bonds” per bulk-truncated unit cell of (7 × 7) dimensions, the Si(111) surface undergoes a very complex reconstruction which reduces the number of 3-coordinate Si atoms in each unit cell from 49 to 19, divided into six “rest atoms”, 12 “adatoms, and one “corner hole". Formation of the (7 × 7) unit cell is also accompanied by redistribution of the 19 electrons such that 14 electrons are localized on the 6 “rest atoms” and the 1 corner hole, leaving 5 electrons to be distributed among the 12 adatoms. Each “rest atom” has a formal charge of -1, while each adatom has an electron occupancy of only $^5/_{12}$ instead of 1 electron, leading to a formal charge of approximately $^7/_{12}$ ($\sim$+0.58). This positive charge on the adatoms gives the adatoms of the Si(111)−(7 × 7) surface a significant Lewis acid character, while the “rest atoms” have filled lone-pair orbitals that make them Lewis bases. Thus, we anticipate that the adatoms will be the most favorable sites for TMA dative bonding. Previous studies of ammonia interacting with the Si(111)−(7 × 7) surface have shown that dissociation is again facile and have proposed that the adatoms act as electrophilic reactive sites.[35,59] While there are 12 electrophilic adatoms in each unit cell, our measurements of the total TMA coverage indicate that at saturation coverage only ∼6 TMA molecules are able to bond in each unit cell. While this limit could arise from steric constraints, it may also be due to charge transfer between adatoms that may limit the total density of dative-bonded adducts.[59]

Our experimental and computational results show that the ability of the Si(001) and Si(111) surfaces to undergo dative bonding with trimethylamine is a direct consequence of the ability of the Si(001)−(2 × 1) and Si(111)−(7 × 7) surfaces to delocalize the electronic charge associated with charge transfer from the N atom to the surface Si atoms.

Conclusions

Our results show that TMA can form stable, highly ionic dative bonds with both Si(001) and Si(111) surfaces at 300 K. The formation of these dative-bonded adducts transfers electron density from the N lone-pair electrons of trimethylamine to the surface silicon atoms, which act as facile electron acceptors. The computational results show that the presence of the Si═Si double bond on the Si(001) surface is crucial for formation of the stable dative bond by permitting the electronic charge to be delocalized onto the second atom in the dimer. The formation of dative bonds as transient intermediates is likely important in controlling reactions of amine with silicon. The preferential cleavage of the N−H rather than N−C bonds during adsorption of dimethylamine on Si(001) is consistent with the formation of a transient dative-bonded complex, since increasing positive charge on the N atom preferentially weakens the N−H bond.

Overall, our results show that while silicon is widely considered to be electron-donating,[60] silicon atoms present at extended surfaces show a remarkable ability to act as strong electron acceptors. This unusual ability is directly connected with the unusual geometry and coordination of surface atoms, which provides them with unusual chemistry.

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