A particularly novel approach to the detosylation of protected amines was also demonstrated. Low-temperature NaNap reductive cleavage of amine–sulfonamide bonds *in the presence of alcohol* was found to be quite efficient and quantitative. In addition, preservation of the diastereomeric integrity of the detosylated species was maintained, and no oxidation of the vulnerable phosphine atoms was observed. Several Ni^{II}, Pd^{II}, and Pt^{II} complexes were prepared and characterized. A subsequent paper will demonstrate that two metals may be incorporated within the azaphosphands to create Pt–Cu bimetallic species.[50]

Acknowledgment. This work was supported by grants from the National Science Foundation. We thank R. B. Klassen for assistance.

Supplementary Material Available: Listings of hydrogen atom positional and thermal parameters (Tables S1 and S5) and non-hydrogen atom thermal parameters (Tables S2 and S4) for $\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$ and *anti*-$\langle P_2PdCl_2|O_5\rangle$ and ORTEP diagrams for *anti*-$\langle P_2NiCl_2|N_3\rangle Ts_3$ and *anti*-$\langle P_2PdCl_2|N_3\rangle Ts_3 \cdot CH_3CN \cdot H_2O$ (Figures S1 and S2) (6 pages); listings of observed and calculated structure factors (Tables S3 and S6) for $\langle P_2Ni(NCS)_2|H_2N_3\rangle(NCS)_2$ and *anti*-$\langle P_2PdCl_2|O_5\rangle$ (25 pages). Ordering information is given on any current masthead page.

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Infrared Matrix Isolation Studies of Molecular Interactions: Complexes of Trichlorosilane, HSiCl$_3$, with Selected Bases

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The matrix isolation technique and twin-jet deposition have been employed to isolate and characterize the reaction products of the codeposition of trichlorosilane with bases containing nitrogen and oxygen donor atoms. The infrared spectra of these initial reaction products indicate that a complex is formed in which the donor atom of the base interacts with the silicon center on HSiCl$_3$. These complexes were characterized by a blue shift of the Si–H stretching mode and red shifts for the Cl–Si–H bending and Si–Cl stretching modes. In addition, the Si–N stretching mode in the complex was identified near 700 cm^{-1} for the amine complexes. Also, when the amines were codeposited with HSiCl$_3$, a red-shifted and broadened Si–H stretching mode was detected, providing tentative evidence for a second, isomeric form of the complex. In this complex, the nitrogen of the base is weakly hydrogen-bonded to the Si–H bond of HSiCl$_3$. Attempts to isolate analogous complexes of CH$_3$SiCl$_3$ were unsuccessful, in accord with the results of earlier studies.

Introduction

The chemical reactions of trichlorosilane, HSiCl$_3$, are very sensitive to the solvent.[1] Consequently, there is interest in a complete characterization of the intermolecular interactions of this species with electron donors. By analogy with chloroform, which is well-known[2-5] to serve as a proton donor in hydrogen-bonding interactions with strong bases, one might anticipate hydrogen-bond formation involving the Si–H bond. Also, several studies have demonstrated the stability of the SiCl$_3^-$ anion in both the gas phase and in solution.[6,7] Consequently, trichlorosilane may have some ability to act as a proton donor, although the increased metallic character and lower electronegativity of silicon relative to carbon weakens this analogy. In any event, the role of the Si–H bond in hydrogen bonding is not well established, although this bond is a very important moiety in organosilicon chemistry.

Voronkov and Lebedeva[8,9] have investigated the intermolecular interactions in solutions of halosilane hydrides. In these binary systems, three types of interactions were found: (1) the formation of a hydrogen bond involving the Si–H bond to ethers and ketones; (2) coordination of the solvent molecules to the silicon center on the silane; (3) dipole–dipole interactions. It is known[10-12] that HSiCl$_3$ is able to form complexes with nitrogen-containing bases in solution, and researchers have preferred[13-15] to invoke a three-center interaction rather than formation of a coordinate bond or a hydrogen bond. In addition, it has been reported that a number of halosilanes[16,17] serve as Lewis acids and form five-coordinate complexes with medium-to-strong bases. The interaction of a strong base with HSiCl$_3$ might be through hydrogen bonding to the Si–H bond, coordination to the central Si, or formation of a three-center interaction.

Infrared spectroscopy has emerged as one of the most effective experimental tools for the study of hydrogen bonding, in that hydrogen-bond formation gives rise to distinct, readily identifiable spectral features.[2] The matrix isolation technique[18-20] has been used often for the study of weakly bound, intermediate complexes,[21-23] including hydrogen-bonded complexes.[24-29] Matrix

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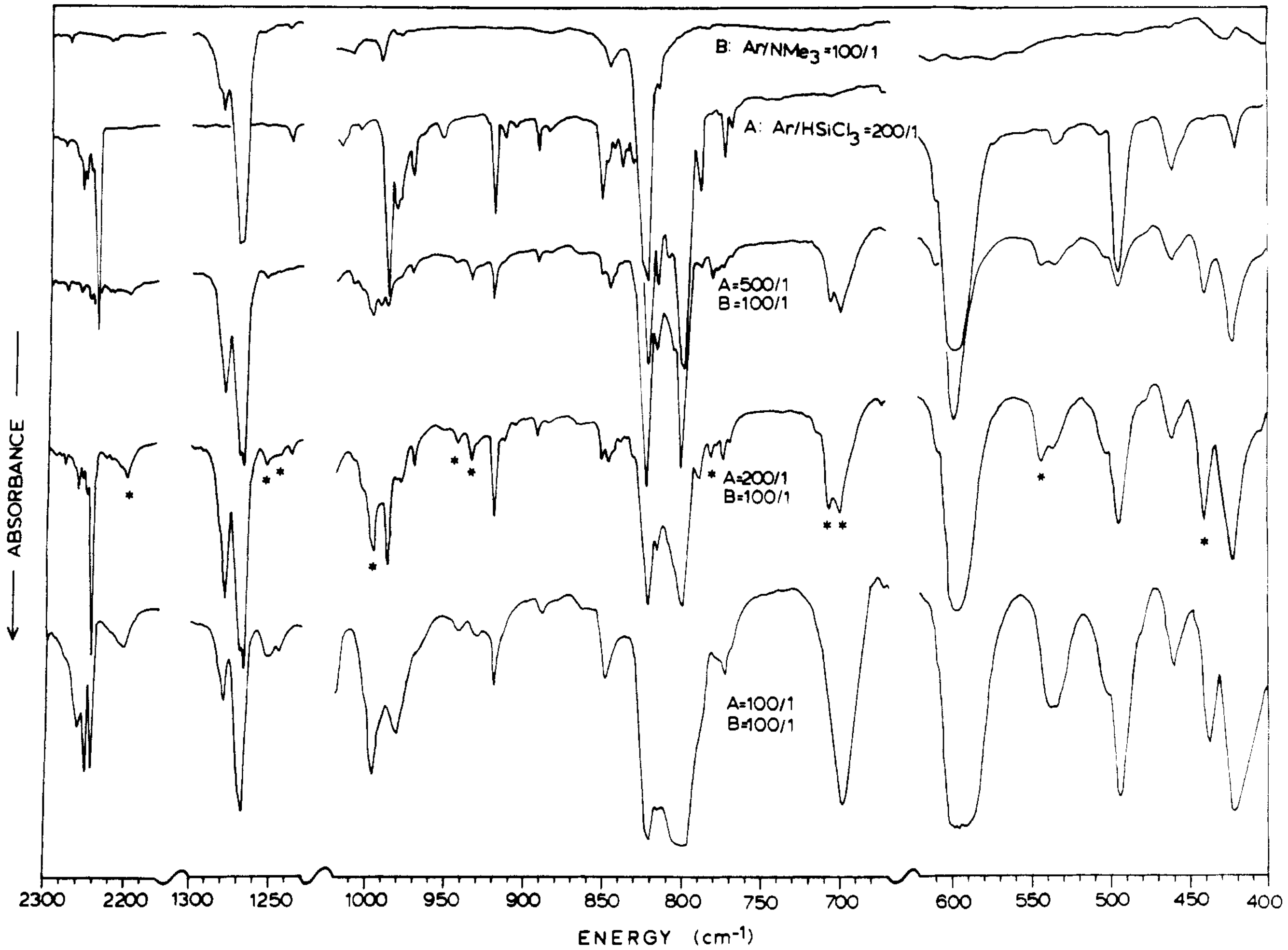

Figure 1. Infrared spectra, over selected spectral regions, of the products arising from the twin-jet codeposition of $HSiCl_3$ with $(CH_3)_3N$ into argon matrices, compared to blank spectra of each reagent along in solid argon. Peaks denoted with an asterisk are due to reaction products.

isolation should be an effective approach to examine isolated complexes of $HSiCl_3$ and determine the mode(s) of interactions, free from complications arising from solvent effects.

Experimental Section

A conventional matrix isolation apparatus was used for all of the experiments in this study and has been described previously.[30] The two reactants were each diluted with argon or nitrogen in separate vacuum lines and codeposited onto the 17 K cold window for 20–24 h at a rate of approximately 2 mmol/h from each line. Final spectra were recorded on a Perkin Elmer 983 infrared spectrometer at 2-cm^{-1} resolution.

The reagents employed in this study were trichlorosilane ($HSiCl_3$, Aldrich), methyltrichlorosilane (CH_3SiCl_3, PCR), $(CH_3)_3N$, $(CH_3)_2NH$, NH_3, $(CH_3)_2O$ (all Matheson), $(CH_3)_2CO$ (Baker), and CH_3CN (Fisher). $HSiCl_3$ and CH_3SiCl_3 were purified by vacuum distillation and transferred to a sample tube containing activated 4A molecular sieves to eliminate traces of water. All reagents were subjected to one or more freeze–thaw cycles at 77 K prior to sample preparation. Argon and nitrogen were used as the matrix gases throughout and were used without further purification.

Results

For most of the bases employed in this study, blank or background spectra had already been recorded in earlier studies in this laboratory.[31] Additional blank experiments at different concentrations were conducted when needed. Blank experiments were carried out on trichlorosilane, methyltrichlorosilane, and dimethylamine, and the resulting spectra were in good agreement with literature spectra.[32-35]

$HSiCl_3$ + $(CH_3)_3N$. These reagents were codeposited from separate vacuum lines in a number of experiments over a wide range of concentrations. Codeposition of a sample of Ar/$HSiCl_3$ = 500 with a sample of Ar/$(CH_3)_3N$ = 500 gave rise to new, weak features at 439, 706, 781, 934, and 1253 cm^{-1}, with the 706-cm^{-1} band being somewhat broader than the other absorptions. Increasing the concentration of the $(CH_3)_3N$ sample to 200/1 or 100/1 while holding the concentration of the $HSiCl_3$ sample constant led to an increased yield of the above product bands, along with a number of additional peaks. A weak, broad absorption was observed at 2200 cm^{-1}, as well as a moderately intense band at 996 cm^{-1} with a shoulder at 998 cm^{-1}. In addition, weak bands were detected at 542 and 944 cm^{-1}, and the region near 700 cm^{-1} now appeared as a strong doublet at 700, 706 cm^{-1}. When the concentrations of both reagents were increased simultaneously, an intensification of all product absorptions was noted. This pair of reagents was then codeposited, each at a concentration of 100/1 in argon. A similar set of product absorptions was observed, except that a very strong, broad singlet was observed at 700 cm^{-1}, instead of the 700-, 706-cm^{-1} doublet seen in the more dilute experiments. In addition, a considerable decrease in intensity of the 783-cm^{-1} product band was noted. Figure 1 shows representative infrared spectra of matrices containing this pair of reagents at different concentrations.

As a test of the behavior of this system in the limit of no matrix material, pure $HSiCl_3$ was deposited with pure $(CH_3)_3N$ from separate vacuum lines onto the 17 K CsI cold window. The resulting spectrum contained two features of medium intensity at 2162 and 2215 cm^{-1}, along with a band at 1404 cm^{-1}, a doublet at 1235, 1245 cm^{-1}, and a weak broad absorption at 1116 cm^{-1}.

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In addition, a strong band was observed at 984 cm^{-1}, with a shoulder at 998 cm^{-1}, which overlapped a parent band at 975 cm^{-1}, as well as a band at 933 cm^{-1}, which overlapped a parent absorption at 928 cm^{-1}. Finally, a very strong band was detected at 690 cm^{-1} along with several moderately intense features at 428, 515, and 526 cm^{-1}. Variation in the intensity of some of the parent absorptions was also observed, such as the great increase in intensity of the bands at 460 and 1060 cm^{-1} compared to blank spectra of $HSiCl_3$ and $(CH_3)_3N$, respectively (also in the absence of argon). The disappearance of the 1270-cm^{-1} absorption of parent $(CH_3)_3N$ was also noted. This sample was then warmed to room temperature and additional spectra recorded. Several bands were absent in the room-temperature spectrum, namely the peaks at 428, 515, 526, 690, 1235, 2162, and 2215 cm^{-1}.

$HSiCl_3$ was also codeposited with $(CD_3)_3N$ in four experiments at different concentrations. This resulted in the observation of a strong band at 440 cm^{-1}, a band at 706 cm^{-1} with satellites at 700 and 697 cm^{-1}, and weaker features at 542, 723, 864, 1009, 1071, and 1075 cm^{-1}. Increasing the concentration of both reagents led to greater overall intensity and a more distinguishable doublet at 1071, 1075 cm^{-1}, along with an additional weak band at 1084 cm^{-1}.

$HSiCl_3$ + $(CH_3)_2NH$. The twin-jet codeposition of a sample of Ar/$HSiCl_3$ = 500 with a sample of Ar/$(CH_3)_2NH$ = 200 led to a weak new feature at 2271 cm^{-1} along with a very weak adsorption at 2199 cm^{-1}. In addition, a weak sharp band was noted at 782 cm^{-1} with a shoulder at 785 cm^{-1}. A moderately intense band was observed at 706 cm^{-1} with a shoulder at 694 cm^{-1} as well as a weak band at 544 cm^{-1} which overlapped a parent band of $HSiCl_3$ at 534 cm^{-1}. Finally, a strong, very broad feature was noted at 440 cm^{-1}. When the concentration of the $HSiCl_3$ sample was increased to 200/1 while that of $(CH_3)_2NH$ was held constant, a similar set of product bands was observed, with the broad band at 2199 cm^{-1} being more distinct. The multiplet near 700 cm^{-1} was now quite intense. An additional, very broad feature was also observed at 889 cm^{-1}, overlapping a parent adsorption at 893 cm^{-1}, as well as a weak broad absorption at 512 cm^{-1}. Also, the intensity of the 440-cm^{-1} absorption was considerably increased, while the intensity of the 2271-cm^{-1} band was not. Increasing the concentration of the Ar/$(CH_3)_2NH$ sample to 100/1 while maintaining Ar/$HSiCl_3$ = 200 gave rise to the same set of product bands with growth in intensity of each band except the peak at 2271 cm^{-1}. The infrared spectra of this pair of reagents at different concentrations are shown in Figure 2.

$HSiCl_3$ + NH_3. Codeposition of $HSiCl_3$ with NH_3, both at 500/1 in argon, resulted in weak, sharp new features at 784, 1003, and 2271 cm^{-1}, along with very weak bands at 442 and 706 cm^{-1}. When the $HSiCl_3$ concentration was increased to 100/1 while keeping Ar/NH_3 = 500, the above product bands were intensified and a more distinct doublet was observed at 706 and 694 cm^{-1}, along with two additional weak features at 687 and 714 cm^{-1} and a shoulder at 450 cm^{-1}. Diluting the $HSiCl_3$ sample and increasing the NH_3 concentration led to a slight decrease in the intensities of the 784-, 1003-, and 2271-cm^{-1} bands, while the 442-cm^{-1} band was broadened and intensified. Additional experiments were carried out at yet higher concentrations of both samples, up to 100/1 for each, and led to the appearance of several additional bands that could not be detected at lower concentrations. These included a very broad band with maximum at 2210 cm^{-1}, a doublet at 2125 and 2143 cm^{-1}, a strong multiplet at 658, 666, and 673 cm^{-1}, and a broad feature at 515 cm^{-1}. This pair of reagents was also codeposited into nitrogen matrices and led to a weak feature at 2297 cm^{-1}, along with strong band at 445 and 772 cm^{-1} and a shoulder at 440 cm^{-1}. Representative spectra of matrices containing this pair of reactants are shown in Figure 3.

$HSiCl_3$ + $(CH_3)_2O$. Samples of Ar/$HSiCl_3$ and Ar/$(CH_3)_2O$ were codeposited over a wide range of concentrations and led to a number of product absorptions. These included a strong, sharp band at 2275 cm^{-1}, a weak, broad feature at 945 cm^{-1}, a weak, sharp band at 900 cm^{-1} and a strong, sharp absorption at 783 cm^{-1}. In addition, a band was noted at 582 cm^{-1}, overlapping somewhat the $HSiCl_3$ parent absorption at 596 cm^{-1}.

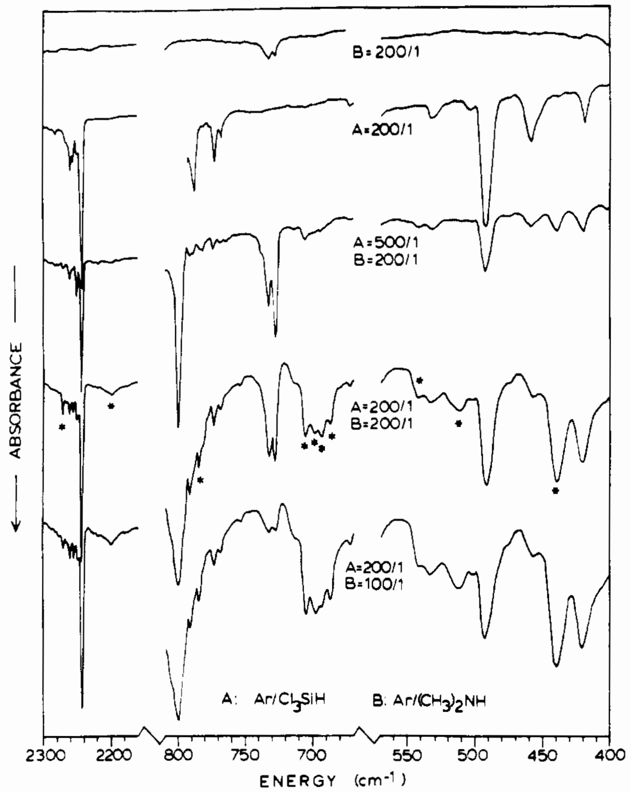

Figure 2. Infrared spectra of the products of the twin-jet codeposition of $HSiCl_3$ with $(CH_3)_2NH$ into an argon matrix, compared to appropriate blank spectra. Peaks marked with an asterisk are due to reaction products.

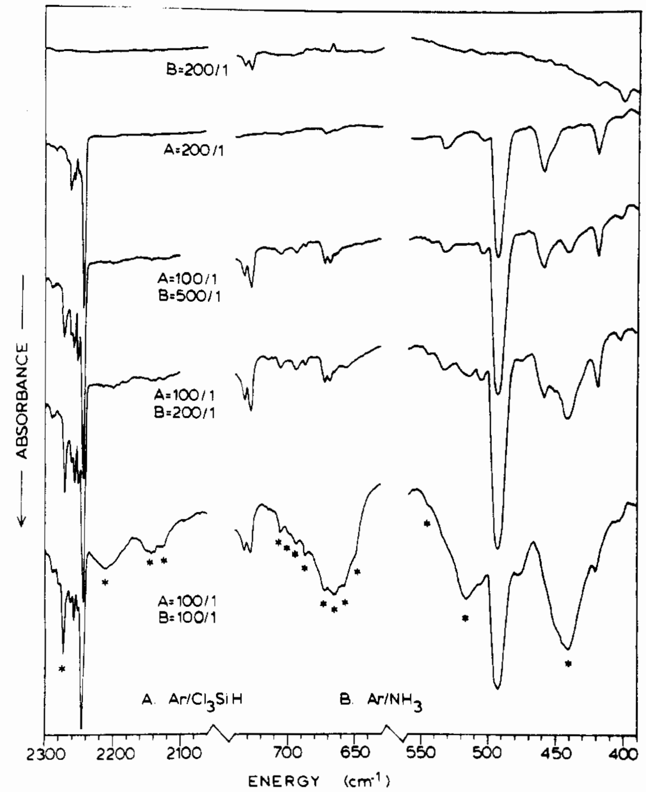

Figure 3. Infrared spectra obtained after the codeposition of $HSiCl_3$ with NH_3 into an argon matrix at 17 K, compared to blank spectra of each reagent alone in solid argon. Peaks marked with an asterisk are due to reaction products.

For comparison, samples of Ar/$HSiCl_3$ were also codeposited with samples of Ar/$(CH_3)_2CO$ and Ar/CH_3CN over a wide range of concentrations. No distinct product bands were observed in these experiments. Table I summarizes all of the product band

Table I. Band Positions (cm^{-1}) and Assignments for the Complexes of $HSiCl_3$ with Selected Bases

band positions					
$(CH_3)_3N$	$(CD_3)_3N$	$(CH_3)_2NH$	NH_3	$(CH_3)_2O$	assign[a,d-h]
		2271	2271	2275	species A, Si–H str
2200		2200	2210		species B, Si–H str
			2134[b]		species, C, Si–H str
1249[b]					species A, C–N str
	1073[b]				species A, C–N str
	1009				species A, C–N str
			1003		species A, NH_3 sym def
939, 997[b]					species A, CH_3 rock
				945	species A, C–O–C str (?)
				900	species A, C–O–C sym str
		889			species A, C–N str
783		782	785	784	species A, Cl–Si–H bend
	864, 723				species A, CD_3 rock
703[b]	703[b]	697[c]	700[c]		species A, Si–N str
			666[c]		species C, Si–N str
542	542	544	543	582	species A, Si–Cl str
		512	515		species C, Si–Cl str
438	440	440	442		species A, Si–Cl str

[a] Species A: 1/1 coordination complex. Species B: 1/1 hydrogen-bonded complex. Species C: 2/1 complex; see text. [b] Average of doublet. [c] Average of multiplet. [d] Corresponding parent band positions for the $(CH_3)_3N$–$HSiCl_3$ system at 493, 594, 800, 918, 990, 1269, and 2243 cm^{-1}. [e] Corresponding parent bond positions for the $(CD_3)_3N$–$HSiCl_3$ system at 493, 594, 796, 800, 831, 999, 1094, and 2243 cm^{-1}. [f] Corresponding parent band positions for the $(CH_3)_2NH$–$HSiCl_3$ system at 493, 594, 800, 1037, and 2243 cm^{-1}. [g] Corresponding parent band positions for the H_3N–$HSiCl_3$ system at 493, 594, 800, 970, and 2243 cm^{-1}. [h] Corresponding parent band positions for the $(CH_3)_2O$–$HSiCl_3$ system at 594, 800, 928, and 2243 cm^{-1}.

positions for the above codeposition experiments with $HSiCl_3$.

CH_3SiCl_3 + $(CH_3)_3N$. The twin-jet codeposition of a sample of Ar/CH_3SiCl_3 = 500 with a sample of Ar/$(CH_3)_3N$ = 200 gave rise to a single weak absorption at 422 cm^{-1}. Increasing the concentrations to 200/1 and 100/1, respectively, led to an additional new feature at 1248 cm^{-1} and a decrease in the intensity of the CH_3SiCl_3 parent band at 1238 cm^{-1}. No significant change was noted in the 422-cm^{-1} absorption. A further increase in concentration of either CH_3SiCl_3 or $(CH_3)_3N$ led to a disappearance of the parent band at 1238 cm^{-1} as well as the parent band of $(CH_3)_3N$ at 990 cm^{-1}. A weak feature at 414 cm^{-1} was noted, which overlapped the 422-cm^{-1} absorption. Finally, the intensities of parent bands of CH_3SiCl_3 at 329 and 896 cm^{-1} were significantly decreased while peaks at 576, 760, and 920 cm^{-1} were broadened.

CH_3SiCl_3 + NH_3. The coedeposition of these two reagents at concentrations of up to 200/1 each in argon resulted in the observation of a very weak band at 1006 cm^{-1}. No new absorptions could be found in any other spectral region.

Discussion

The twin-jet codeposition of trichlorosilane with both amines and dimethyl ether into argon or nitrogen matrices gave rise to a number of new infrared absorptions that cannot be assigned to either parent species. Many of these were relatively weak but did grow upon an increase in the concentration of either reagent. The product absorptions can be broadly classified into three groups, those that fell near vibrational modes of $HSiCl_3$, those that fell near certain vibrational modes of the base, and, for the amines, an additional strong band near 700 cm^{-1}. Finally when either NH_3 or $(CH_3)_2NH$ was employed, a fourth set of bands was found at high concentrations of the base. The bands in this last set were broader than the initial absorptions and, given their concentration dependence, are probably due to aggregate species. The initial absorptions, formed at lower concentrations, are due to the isolated reaction product(s) involving one molecule of $HSiCl_3$ and one molecule of the base. The lack of observation of the fourth set of bands for $(CH_3)_3N$ under comparable conditions is consistent with earlier reports that only a 1/1 complex of $(CH_3)_3N$ with halosilanes could be formed.[36] The inability to form a distinct 2/1 species was thought to be due to the steric hindrance of this larger amine. In any event, the initial or primary product bands are best assigned to a reaction product with overall 1/1 reaction stoichiometry.

The fact that the majority of the primary product absorptions (all except the 700-cm^{-1} band) fell near an absorption of either trichlorosilane or the base indicates formation of a molecular complex in which the two subunits are perturbed but retain their basic structural integrity.[37] Consequently, these product absorptions may be attributed to one or more molecular complexes with 1/1 stoichiometry. Upon formation of a 1/1 molecular complex, regardless of its structure (see below), three translational and three rotational degrees of freedom are lost and become vibrational modes of the complex. These include the stretching vibration of one subunit against the other, as well as torsional modes of the two subunits. The strong product absorption near 700 cm^{-1} for each of the amine complexes of $HSiCl_3$ does not fall near a vibrational mode of either the amine or trichlorosilane and must have its origin in one of these intermolecular vibrational modes.

For the complexes of $HSiCl_3$ with NH_3 and $(CH_3)_2NH$, two distinct new Si–H stretching modes were observed, one near 2270 cm^{-1} and the other near 2200 cm^{-1}. The Si–H stretch of parent $HSiCl_3$ falls between these two, at 2243 cm^{-1}. Consequently, both a red-shifted Si–H stretch and a blue-shifted Si–H stretch were observed. Since a given 1/1 complex can only contain one Si–H bond, these observations suggest formation of two different 1/1 complexes, i.e. two different structural isomers. On the other hand, for $(CH_3)_2O$ and $(CH_3)_3N$, only a single Si–H stretch was observed, blue-shifted very distinctly for the $(CH_3)_2O$ complex and red-shifted for the complex of $HSiCl_3$ with $(CH_3)_3N$. This argues that, for these bases, only a single complex was formed and isolated, although given the low intensities in the Si–H region the second isomeric form could have been obscured or been sufficiently weak as to escape detection.

The observation of two isomeric complexes for certain bases and at least one for other bases leads to the question of what types of interactions might occur. Three different types of interactions between $HSiCl_3$ and bases have been reported: (1) the formation[10-12,38] of coordination complexes with creation of a Si–N coordinate bond; (2) the formation[8,9] of a hydrogen bond between the hydrogen of $HSiCl_3$ and the lone electron pair on the base; (3) the formation of a three-center interaction[13-15] involving the Si and H atoms of the silane with the donor atom of the base. These three modes of interaction should give rise to distinctly different spectral features. For example, coordination of the silicon through its vacant d orbitals with the lone electron pair on the base should lead to a blue shift of the Si–H stretching mode, and red shifts of the Cl–Si–H bending mode and the Si–Cl stretching modes.[9] In this interaction, the base should be sufficiently perturbed that shifted vibrational modes of the base, particularly skeletal stretching vibrations, should be observable. The spectral characteristics of hydrogen bonding are well-known[2] and involve primarily a red shift and intensification of the Si–H stretching mode, as well as a blue shift of the Cl–Si–H bending mode, withiout significant intensification. Also, because there is no rehybridization or geometry change for the silane or the base in a hydrogen-bonding interaction, perturbed vibrational modes of the silane or base subunits will not likely be observed, other than those modes involving the Si–H bond, as noted above. The third alternative, a three-center interaction, is the most difficult to predict but at the very least should involve significant weakening of the Si–H bond and, in the limiting case, rupture of this bond.

Most of the product bands observed here, for all of the basis for which product was observed, can be readily attributed to a coordination complex (species A in Table I and Figure 4) involving

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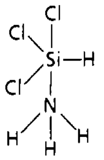
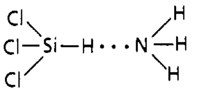


SPECIES A



SPECIES B

Figure 4. Proposed structures for species A, the 1/1 coordination complex of $HSiCl_3$ with NH_3, and species B, the hydrogen-bonded complex between $HSiCl_3$ and NH_3.

formation of a coordinate bond to the silicon. The blue-shifted Si–H stretch observed near 2270 cm^{-1}, the red-shifted Cl–Si–H bending mode observed near 785 cm^{-1}, and the red-shifted Si–Cl stretching modes all are indicative of this type of interaction. Boal and Ozin[38] have isolated the 1/1 complex of $HSiCl_3$ with $(CH_3)_3N$ at low temperatures in the absence of a matrix and invoked this structure for the complex. They obtained Raman spectra up to 600 cm^{-1} and were able to observed three distinctly perturbed SiCl stretching modes; unfortunately, they did not report spectra at higher energies, including the Si–H stretching region. In the present study, several new, intense absorptions were noted in the Si–Cl stretching region, to the red of the parent $HSiCl_3$ modes. Due to the breadth and overlap of these bands and the parent absorptions, the number of product bands in this region could not be accurately determined. For the amine complexes, at least two and possibly three such bands were detected.

Observation of the strong product absorption near 700 cm^{-1} for all of the amine complexes is consistent with the formation of a coordination complex. Of the new intermolecular vibrations created upon formation of a complex, most should lie at very low energies. However, the intermolecular, Si–N stretching mode is expected to lie in a spectroscopically accessible region, and has been placed by other authors[39–42] anywhere from 200 to 900 cm^{-1}. This mode should be relatively intense and should not shift significantly upon deuteration of the base subunit. This is in accord with the $(CD_3)_3N$ experiments, supporting assignment of this band to the stretching mode of the coordinate Si–N bond. This vibration is sensitive to the strength of interaction, which should be similar for the three amines and substantially less for $(CH_3)_2O$. No counterpart absorption was noted for the dimethyl ether complex in accord with the expectation that this mode will lie at much lower energy and be lower in intensity. That the dimethyl ether complex is substantially less strongly bound is also shown by the much smaller shift in the antisymmetric Si–Cl stretching mode in the $(CH_3)_2O{\cdot}HSiCl_3$ complex compared to the amine complexes. Certainly, in a hydrogen-bonded complex, there would be no direct analogue of the Si–N stretching mode. The heavy-atom stretch of the hydrogen bond should lie at very low energies; for the very strongly bound, centrosymmetric HCl_2^- anion, the symmetric heavy-atom stretching mode has been observed[43] near 250 cm^{-1}. Consequently, assignment of the 706-cm^{-1} band to the intermolecular Si–N stretching mode in a 1/1 coordination complex is made.

Several product bands were detected near absorptions of the parent base, such as the 900-cm^{-1} absorption of the $(CH_3)_2O{\cdot}HSiCl_3$ complex. This lies 25 cm^{-1} to the red of the symmetric C–O–C stretching mode of the parent dimethyl ether; this is precisely the mode that is perturbed and red-shifted most significantly in coordination complexes involving dimethyl ether. While this mode is also red-shifted in hydrogen-bonded complexes,[24] the shift is typically only 2–5 cm^{-1}. Product bands at 944, 996, 1245, and 1253 cm^{-1} were detected for the $(CH_3)_3N$ complex with $HSiCl_3$ and shifted to lower energies upon deuteration of the base. The latter two fall in the C–N stretching region, while the former two fall in the region where CH_3 rocking modes occur. These are modes that are particularly sensitive to complexation and are assigned to these modes of the $(CH_3)_3$ subunit in the $(CH_3)_3N{\cdot}HSiCl_3$ complex.

While the blue-shifted Si–H band characteristic of coordination complexes was observed for most of the complexes reported here, it was not seen for the $(CH_3)_3N$ complex with $HSiCl_3$. Nonetheless, the strong band near 700 cm^{-1}, the substantially perturbed Si–Cl stretching modes, and the shifted modes of $(CH_3)_3N$ provide ample evidence that such a complex is formed. The absence of the blue-shifted Si–H band may be due to a combination of low intensity with spectral congestion in the region 2250–2320 cm^{-1} ($(CH_3)_3N$ has several weak absorptions in this region, along with strong absorptions due to $HSiCl_3$). For the $(CH_3)_2O$ complex with $HSiCl_3$, distinct and strongly blue-shifted Si-H stretching and red-shifted Cl–Si–H bending modes were observed, but only one perturbed band in the Si–Cl stretching region. While, in principle, three perturbed Si–Cl stretches would be expected, similar results have been observed[21] for complexes of oxygen donors with SiF_4. The weaker interaction with $(CH_3)_2O$ does not as strongly shift the parent stretching modes, and the apparent missing bands may lie within the intense envelope of the parent absorption. Nonetheless, the detection of several product bands, and their locations, points to the formation of a complex of $(CH_3)_2O$ that is structurally similar to the amine complexes.

For 1:1 complexes of amines with halosilanes, a trigonal-bipyramidal structure has been determined in each case[16,17,44–46] and verified by ab initio calculations. Within this basic structural framework, the base may occupy either an axial or equatorial position. A number of literature reports[16,17,44,45] all indicate that the base preferentially occupies an axial position; this is precisely the geometry Ozin et al. determined for the $(CH_3)_3N{\cdot}HSiCl_3$ complex. Theoretical calculations[46] support this structure as well. Consequently, the two structures in which the base is in an axial position will be considered. In one, the hydrogen is in an equatorial position (hereafter I), and in the other the hydrogen is in the second axial position (hereafter II). For the bases NH_3 and $(CH_3)_3N$, which maintain a C_3 axis, I will have C_s symmetry, while II will have C_{3v} symmetry, with Si–Cl stretching modes of A_1 and E symmetry. In II, when NH_3 is replaced by $(CH_3)_2NH$, the E mode should split into a doublet as has been seen previously for complexes of SiF_4. On the other hand, for I, no significant changes are anticipated when $(CH_3)_2NH$ is substituted for either NH_3 or $(CH_3)_3N$. The fact that the spectra in the Si–Cl stretching region were nearly identical for all three bases points to structure I. Using similar arguments with Raman spectra in this region, Ozin et al.[38] determined that I was the correct structure for the $(CH_3)_3N{\cdot}HSiCl_3$ complex as the low-temperature solid. The experiments conducted here in which pure $HSiCl_3$ was codeposited with pure $(CH_3)_3N$ at 17 K without argon led to three bands in the Si–Cl stretching region, matching the number Ozin et al. observed (although somewhat shifted). This, too, supports structure I. Consequently, structure I is the preferred structure for the 1/1 coordination complex of each of the bases studied here with $HSiCl_3$ (see Figure 4, species A).

One significant spectral feature in the amine experiments remains that cannot be accounted for by the simple formation of a coordination complex. As noted above, two perturbed Si–H stretches were observed, one blue-shifted with respect to the parent and the other red-shifted. The blue-shifted band was assigned above to the Si–H stretch in the coordination complex; the red-shifted band remains unassigned. A shift to lower energy and broadening and intensification are all characteristic of hydro-

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gen-bond formation.[2] Moreover, several groups[8,9,47] have reported hydrogen bonding between $HSiCl_3$ and oxygen bases, although the evidence presented is rather sketchy. Certainly, several hydrogen-bonded complexes of the carbon analogue, chloroform, have been isolated and characterized in argon matrices.[3,48] Hence, the possibility of a weak hydrogen bond involving the Si–H bond and the lone electron pair on the base is present, and the spectral data near 2200 cm^{-1} support this. It is noteworthy that a red-shifted Si–H band was not observed when $(CH_3)_2O$ was codeposited with $HSiCl_3$. Dimethyl ether is a weaker base than the amines,[49] and hydrogen-bond formation would be energetically less favored.

One would also expect that the Cl–Si–H bending mode to blue shift as has been seen for many other hydrogen-bonded complexes. However, the intensity of the bending mode is usually much less than that of the stretching mode. Since the red-shifted stretching mode was itself quite weak, the blue-shifted bending mode might well escape detection. The remaining acid and base modes in a weak hydrogen-bonding interaction are generally very weakly perturbed and would not be observed here. Consequently, the red-shifted Si–H stretching mode suggests formation of a second isomeric complex in which a hydrogen bond is formed between the Si–H group and the amine (species B in Figure 4). However, lack of observation of the perturbed bending mode makes this assignment tentative.

The observation, at least tentatively, of two different complexes between the amine bases and $HSiCl_3$ suggests that there are at least two local minima on the complete potential energy surface for the complex. Whether there is a barrier to interconversion between the two isomers in the gas phase or in solution is not clear; Ozin et al.[38] only reported a single structure. However, the argon matrix environment, which condenses rapidly around the complex during the deposition process, could well stabilize both isomers and prevent isomerization to the more stable form, presumably the coordination complex.

In the $NH_3/HSiCl_3$ experiments, additional bands were observed at high NH_3 concentrations and assigned to a larger aggregate. Most likely, this is a 2/1 complex, which can be envisioned as forming through the addition of a second NH_3 to the initial 1/1 complex. It is difficult to determine the structure of the 2/1 complex, which might either be cis or trans octahedral or involve the two sites of coordination seen for the two different 1/1 complexes. The study[11,12] of the 2/1 complex of pyridine with $HSiCl_3$ showed a strongly red-shifted Si–H stretch, and a strongly blue-shifted Cl–Si–H bending mode, indicative of hydrogen bonding (although the authors did not make this suggestion). It may well be that one pyridine coordinates to the silicon and the second pyridine is hydrogen-bonded to the Si–H group. If so, a similar structure might be suggested for the 2/1 complex observed here, but the data do not permit a more definitive conclusion.

Previous studies have all demonstrated that substitution of a methyl group on silicon significantly reduces its reactivity and ability to form complexes.[16,17,44] The experiments here involving codeposition of CH_3SiCl_3 with either NH_3 or $(CH_3)_3N$ led to very little, if any, product formation, consistent with this view. Likewise, codeposition of $HSiCl_3$ with acetone and with acetonitrile did not lead to the formation of a detectable product, which is probably due to their lower basicities, particularly for CH_3CN.

Summary

The codeposition of a series of bases containing nitrogen and oxygen donor atoms with $HSiCl_3$ has led to the formation of isolated 1/1 molecular complexes. In each case, evidence pointed to the formation of coordination complexes, in which the donor atom of the base interacts with the silicon center on $HSiCl_3$. These complexes were characterized by a distinct blue shift of the Si–H stretching mode, a red shift of the Cl–Si–H bending mode, and red shifts of the Si–Cl stretches. These complexes appear to be trigonal bipyramidal around the central silicon, with the base in an axial position and the hydrogen in an equatorial position. In addition, when amines were codeposited with $HSiCl_3$, evidence was found to tentatively indicate that a second, isomeric form of the complex was isolated, in which the base hydrogen bonded to the Si–H bond. These complexes were characterized by a distinct red shift and broadening of the Si–H stretching mode.

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Magnetic Properties of $[Co(NH_3)_6][FeCl_6]$: A Quasi-Ideal fcc Structure with Antiferromagnetic Ordering

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We report the magnetic properties of $[Co(NH_3)_6][FeCl_6]$, a bimetallic salt showing an fcc antiferromagnetic frustrated lattice. The temperature dependence of the ac magnetic susceptibility, measured on a single crystal, indicates antiferromagnetic ordering at $T_c = 0.50 \pm 0.05$ K, with a maximum at 0.80 ± 0.01 K. The analysis of the data gives values of $J_{nn}/k = -0.068 \pm 0.001$ K for the first-neighbor interactions and $J_{nnn}/k = 0.005 \pm 0.001$ K for the second-neighbor ones.

Introduction

Complex bimetallic salts have proved to be important sources of new, interesting magnetic model materials.[1] Indeed, when both complex counterions are of comparable size, the crystalline structures of the corresponding compounds are expected to be highly isotropic. Then, it is feasible to use complex ions as building blocks of a rather symmetric crystalline lattice. When those ions are chosen carefully, it is possible to arrive at a material that exhibits magnetic ordering. Moreover, the chemistry of these compounds is quite flexible, permitting the use of a variety of

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