

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 10-07-2006		2. REPORT TYPE Journal Article		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Synthesis and Characterization of Silyldichloramines, their Reactions with F ⁻ Ions, Stability of N ₂ Cl ₂ and NCl ₂ ⁻ , and Formation of NCl ₃ (PREPRINT)				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Stefan Schneider & Thorsten Schroer (ERC); Michael Gerkin, Ralf Haiges, & Karl O. Christe (USC); Jerry Boatz (AFRL/PRSP)				5d. PROJECT NUMBER	
				5e. TASK NUMBER 23030423	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRSP 10 E. Saturn Blvd. Edwards AFB CA 93524-7680				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-PR-ED-JA-2006-237	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-PR-ED-JA-2006-237	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited (AFRL-ERS-PAS-2006-184A)					
13. SUPPLEMENTARY NOTES Submitted to the journal Inorganic Chemistry					
14. ABSTRACT Only two silyldichloramines, (C ₆ H ₅) ₃ SiNCl ₂ and (CH ₃) ₃ SiNCl ₂ , have been reported in the literature. The synthesis of the former was successfully repeated, and its structure was established by single crystal X-ray diffraction and vibrational spectroscopy. Attempts to prepare (CH ₃) ₃ SiNCl ₂ were unsuccessful, however, a new trialkylsilyldichloramine, <i>t</i> -BuMe ₂ Si-NCl ₂ , was prepared and characterized by Raman and multinuclear NMR spectroscopy. The reaction of <i>t</i> -BuMe ₂ SiNCl ₂ with (CH ₃) ₄ NF in CHF ₃ solution at -78 °C, followed by removal of all volatile products at -30 °C, produced the expected <i>t</i> -BuMe ₂ SiF by-product and a white solid consisting of NCl ₃ absorbed on Me ₄ NCl. The NCl ₃ could be reversibly desorbed from the substrate and was identified as a neat liquid at room temperature by Raman spectroscopy. The observed final reaction products are consistent with the formation of an unstable N(CH ₃) ₄ ⁺ NCl ₂ ⁻ intermediate which decomposes to N(CH ₃) ₄ ⁺ Cl ⁻ and NCl molecules which can dimerize to N ₂ Cl ₂ . Theoretical calculations confirm that NCl ₂ ⁻ can readily lose Cl ⁻ and that N ₂ Cl ₂ also possesses a low barrier towards loss of N ₂ to give chlorine atoms and, thus, can account for the formation of NCl ₃ .					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT A	18. NUMBER OF PAGES 33	19a. NAME OF RESPONSIBLE PERSON Dr. Scott A. Shackelford
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) N/A

Synthesis and Characterization of Silyldichloramines, their Reactions with F⁻ Ions, Stability of N₂Cl₂ and NCl₂⁻, and Formation of NCl₃ (PREPRINT)

Stefan Schneider,^{*†§} Michael Gerken,^{†¶} Ralf Haiges,[†] Thorsten Schroer,^{†§} Jerry A. Boatz,[‡]
Karl O. Christe,^{*†}

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089, and Air Force Research Laboratory, Edwards AFB, California 93524

Abstract: Only two silyldichloramines, (C₆H₅)₃SiNCl₂ and (CH₃)₃SiNCl₂, have been reported in the literature. The synthesis of the former was successfully repeated, and its structure was established by single crystal X-ray diffraction and vibrational spectroscopy. Attempts to prepare (CH₃)₃SiNCl₂ were unsuccessful, however, a new trialkylsilyldichloramine, *t*-BuMe₂Si-NCl₂, was prepared and characterized by Raman and multinuclear NMR spectroscopy. The reaction of *t*-BuMe₂SiNCl₂ with (CH₃)₄NF in CHF₃ solution at -78 °C, followed by removal of all volatile products at -30 °C, produced the expected *t*-BuMe₂SiF by-product and a white solid consisting of NCl₃ absorbed on Me₄NCl. The NCl₃ could be reversibly desorbed from the substrate and was identified as a neat liquid at room temperature by Raman spectroscopy. The observed final reaction products are consistent with the formation of an unstable N(CH₃)₄⁺NCl₂⁻ intermediate which decomposes to N(CH₃)₄⁺Cl⁻ and NCl molecules which can dimerize to N₂Cl₂. Theoretical calculations confirm that NCl₂⁻ can readily lose Cl⁻ and that N₂Cl₂ also possesses a low barrier towards loss of N₂ to give chlorine atoms and, thus, can account for the formation of NCl₃.

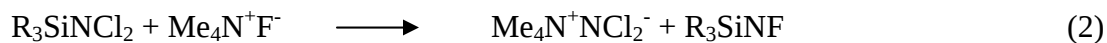
Introduction

Chloramines are important intermediates in the industrial production of hydrazine by the Raschig process and hold potential as precursors for the synthesis of azidamines. However, neat chloramines are highly unstable and often can decompose explosively. Therefore, relatively little is known about these compounds. Chloramine chemistry had its ominous beginning in 1811 when Dulong lost three fingers and an eye during the discovery of NCl_3 . Almost a century later in 1908, a second nitrogen chloride, chlorine azide, was observed by Raschig when he added acetic acid to equimolecular amounts of sodium azide and sodium hypochlorite in aqueous solution. Another 12 years went past before Marckwardt and Wille added NH_2Cl to the nitrogen chloride family, followed by the synthesis of NHCl_2 in 1929 by Chapin.^{1,2} It is noteworthy that almost another half a century went by until in 1977 and 1990 the first nitrogen chloride ions, ONCl_2^+ and NCl_4^+ , were reported,^{3,4} but so far the synthesis of neither one of these two compounds has been confirmed.

Very recently we reported the syntheses and characterization of $\text{NH}_3\text{Cl}^+\text{M}^-$ salts ($\text{M} = \text{BF}_4, \text{AsF}_6, \text{SbF}_6$) in which the explosiveness and thermal instability of the parent molecule NH_2Cl were circumvented by using an organosilicon derivative, $(\text{Me}_3\text{Si})_2\text{NCl}$, as starting material.⁵ Generally, covalent $\text{R}_3\text{Si-X}$ bonds can be readily cleaved by strong acids and nucleophiles, such as fluoride ions. In the case of $(\text{Me}_3\text{Si})_2\text{NCl}$, the silicon nitrogen bond was cleaved by anhydrous HF in the presence of Lewis acids, resulting in the formation of the desired NH_3Cl^+ salts (eq 1).



In this paper, we describe a modification of this approach which has the potential of generating nitrogen chloride anions instead of cations by using the strongly basic fluoride anion in place of the HF/MF₅ super-acid system as the cleaving agent (eq 2).



Although the chlorination of amine complexes of platinum (IV+) affords covalently bonded NCl₂ ligands,⁶ and numerous free pseudo-halide amide anions, NX₂⁻ (X = SO₂F,⁷ SO₂CF₃,⁸ SO₂Cl,⁹ CF₃,¹⁰ SF₅,¹¹ TeF₅,¹² CN¹³), are known, the free NCl₂⁻ anion is unknown.

Surprisingly, little was known about the required triorganylsilyldichloramines starting materials. To the best of our knowledge, only two examples of this class of compounds, triphenylsilyldichloramine¹⁴ and trimethylsilyldichloramine,¹⁵ have previously been reported. Therefore, the synthesis of these compounds was reexamined.

Experimental Section

Caution! Neat chloramines are highly unstable and often can decompose explosively. They should be handled on a small scale with appropriate safety precautions. ***Especially, the handling of neat NCl₃ has led in the past to serious injuries!***

Materials and Apparatus. Reactions were carried out in Teflon-FEP ampules that contained Teflon coated magnetic stirring bars and were closed by stainless steel valves. The valves were attached to the ampules through stainless steel T-fittings. The valve was attached to the horizontal part of the T and the top end of the T was closed by a removable stainless steel cap allowing the addition of solids or liquids to the ampule under dry nitrogen conditions. Volatile materials were handled on a Pyrex glass vacuum line equipped with grease-free Kontes glass-Teflon valves. Nonvolatile solids were handled in the dry nitrogen atmosphere of a glove box.

Infrared spectra were recorded on a Midac M Series FT-IR spectrometer using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded in the range 4000-80 cm^{-1} on a Bruker Equinox 55 FT-RA 106/S spectrometer using a Nd-Yag laser at 1064 nm. Pyrex melting point capillaries, glass NMR or 9 mm Teflon-FEP tubes were used as sample containers. Nuclear magnetic resonance spectra were recorded unlocked on a Bruker AMX 500 NMR spectrometer at room temperature. The ^1H , ^{13}C , ^{29}Si (^{14}N) NMR spectra were referenced to external samples of neat TMS, (neat nitromethane).

The $\text{Ph}_3\text{SiNCl}_2$ was prepared using the literature method.¹⁴ Diethylether was dried over sodium. NH_3 (Aldrich, anhydrous, 99.99%), CF_3H (Matheson Co.), Ph_3SiNH_2 (Aldrich, 97%), *tert*- BuMe_2SiCl (Aldrich, 97%) and *tert*- BuOCl (TCI, 98%) were used without further purification. Tetramethylammonium fluoride tetrahydrate (Aldrich, 98%) was dehydrated by a literature method.¹⁶

Crystal Structure Determination of $\text{Ph}_3\text{SiNCl}_2$. (a) Collection and Reduction of X-ray Data. The crystal used in this study had the dimensions $0.155 \times 0.152 \times 0.106 \text{ mm}^3$. X-ray diffraction data were collected using a Bruker 3-circle platform diffractometer, equipped with a SMART APEX CCD (charge coupled device) detector with the χ -axis fixed at 54.74° (using the program SMART¹⁷), and using MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) from a fine-focus tube. The diffractometer was equipped with a cryo-cooler from CRYO Industries for low-temperature data collection using controlled liquid nitrogen boil off. Cell constants were determined from 60 ten-second frames at 130 °K. A complete hemisphere of data was collected up to a resolution of 0.75 $\text{\AA}$. Processing was carried out by using the program SAINT,¹⁸ which applied Lorentz and polarization correction to three-dimensionally integrated diffraction spots. The program

SADABS¹⁹ was used for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections.

(b) Solution and Refinement of the Structure. All data were processed using the SHELXTL package (version 5.1)²⁰ for structure determination, refinement, and molecular graphics. The XPREP program was used to confirm the unit cell dimensions and the crystal lattices. The structure was solved by the direct method. Successive difference Fourier synthesis revealed all atoms. The structure was refined by the least squares method on F^2 . All atoms except hydrogen were refined anisotropically. For the anisotropic displacement parameters, the $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Raman data for $\text{Ph}_3\text{SiNCl}_2$ in cm^{-1} (rel. Int.). 3174 (3), 3134 (6), 3054 (100), 2998 (3), 2978(3), 2958 (4), 2894 (1), 2851 (1), 2820 (<0.5), 2773 (<0.5), 2685 (<0.5), 2596 (1), 2524 (1), 2424 (1), 1589 (42), 1568 (9), 1482 (1), 1429 (2), 1336 (2), 1309 (1), 1188 (8), 1160 (11), 1115 (1), 1102 (11), 1071 (1), 1028 (28), 999 (87), 986 (1), 923 (1), 858 (2), 828 (14), 745 (1), 715 (3), 688 (16), 678 (2), 619 (6), 513 (11), 446 (12), 437 (4), 399 (<0.5), 391 (<0.5), 329 (10), 308 (23), 250 (3), 238 (17), 220 (6), 212 (2), 179 (1), 169 (32), 121 (3), 95 (83), 79 (7).

Preparation of $t\text{-BuMe}_2\text{SiNH}_2$. In a variation of the published literature methods,^{21,22} a solution of 15.79g (119.48 mmole) of $t\text{-BuMe}_2\text{SiCl}$ in ca. 50 mL diethylether was pressurized in a 200 mL flask with excess anhydrous ammonia and stirred overnight at room temperature to ensure the completion of the reaction. The reaction mixture was then cooled to -196°C , and the volatile products, solvent and $t\text{-BuMe}_2\text{SiNH}_2$, were separated by fractional condensation by pumping them, on warm-up to room temperature, through two cold traps kept at -24°C (CCl_4 slush bath) and -196°C . A glass-wool plug was placed inside the connector between the reaction vessel and the -24°C cold-trap, ensuring that none of the NH_4Cl by-product was swept from the reactor into the

cold trap. The -24 °C trap contained the desired *t*-BuMe₂SiNH₂ as a white, crystalline solid in better than 90% yield. The purity of the *t*-BuMe₂SiNH₂ was verified by Raman and NMR spectroscopy.

Preparation of *t*-BuMe₂SiNCl₂. By analogy with the method published for the preparation of Ph₃SiNCl₂,¹⁴ *t*-BuOCl (15.914g, 146.58 mmol) was added drop-wise in the dark to an ice-cooled stirred solution of *t*-BuMe₂SiNH₂ (8.776g, 66.38 mmol) in dry diethylether. The solution turned immediately yellow, but no precipitate was formed as in the case of Ph₃SiNCl₂, because, contrary to Ph₃SiNCl₂, *t*-BuMe₂SiNCl₂ is soluble in diethylether. The solvent was pumped off between -78 and -30 °C. Because the volatilities of *t*-BuMe₂SiNCl₂ and *t*-BuOH, the by-product formed in the reaction, are similar, further pumping on the residual *t*-BuMe₂SiNCl₂/*t*-BuOH mixture at RT was required for the isolation of pure, highly viscous *t*-BuMe₂SiNCl₂ (13.18 mmol, ~20 %). Most of the product was lost during this procedure, indicating that *t*-BuOH has only a slightly higher volatility than *t*-BuMe₂SiNCl₂. The isolated yield of *t*-BuMe₂SiNCl₂ could certainly be improved by the use of better separation techniques. The purity of the product was continuously monitored by Raman and NMR spectroscopy.

Raman data for *t*-BuMe₂SiNCl₂ in cm⁻¹ (rel. Int.). 2964 (57), 2931 (64), 2905 (100), 2864 (68), 2781 (10), 2713 (7), 1464 (14), 1445 (12), 1409 (5), 1401 (5), 1365 (3), 1256 (3), 1213 (14), 1184 (5), 1013 (3), 1005 (3), 941 (7), 832 (9), 819 (16), 779 (11), 745 (3), 676 (22), 578 (26), 463 (27), 438 (17), 399 (7), 365 (7), 354 (9), 332 (19), 305 (17), 218 (24), 168 (12), 148 (11), 123 (11), 83 (15).

Reaction of *t*-BuMe₂SiNCl₂ with Me₄NF and Generation of NCl₃. In a typical experiment, *t*-BuMe₂SiNCl₂ (0.607g, 3.03 mmol) was loaded with a pipette into one of the above described Teflon-FEP ampules. To exclude moisture, this operation was carried out in dry

nitrogen streams, which were passed through the *t*-BuMe₂SiNCl₂ storage vessel and the Teflon ampule. The ampule was then cooled to -196 °C, evacuated, and a layer of CF₃H was condensed in at this temperature on the vacuum line. An equimolar amount of Me₄NF was added to the frozen mixture in a stream of dry nitrogen, followed by an additional layer of CF₃H. The mixture was then warmed to -78 °C and vigorously stirred. The reaction was stopped when the yellow color of *t*-BuMe₂SiNCl₂ had disappeared. The solvent CF₃H was pumped off at -78 °C, and a stoichiometric amount of *t*-BuMe₂SiF was removed between -30 and -20 °C. At this temperature, the solid residue consisted only of NCl₃ absorbed on Me₄NCl. Warming the solid to room temperature resulted in the slow reversible release of NCl₃.

Results and Discussion

Synthesis and Properties of Ph₃SiNCl₂. Of the two previously reported triorganylsilyldichloramines, triphenylsilyldichloramine¹⁴ and trimethylsilyldichloramine¹⁵, only the latter would be volatile enough to allow easy low-temperature product separation from other nonvolatile reaction products. However, our efforts were unsuccessful to repeat the previously described¹⁴ preparation of this compound. Instead of the required unstable (CH₃)₃SiNH₂ intermediate, only [(CH₃)₃Si]₂NH was formed which, upon chlorination, produced [(CH₃)₃Si]₂NCl.⁵ Therefore, the preparation of the triphenylsilyldichloramine was reexamined (eq 3).



The compound was successfully prepared and characterized by its X-ray crystal structure (Figure 1, Tables 1-3) and Raman spectrum (Figure 2) because previously only its melting point and proton NMR spectrum had been reported.¹⁴

Ph₃SiNCl₂ crystallizes in the triclinic space group *P*-1. The most interesting part of the molecule (Figure 1) is the nitrogen environment, which is close to tetrahedral with Cl-N-Cl and Cl-N-Si bond angles of 108.4(1) and 112.1(1) °, respectively. The increased repulsion from the bulky phenyl groups and the sterically active, free valence electron pair on the nitrogen atom are responsible for the relatively long silicon-nitrogen distance of 181.2(2) pm. The N-Cl bond lengths of 173.8(2) and 175.4(2) pm are similar to those found in CH₃C₆H₄SO₂NCl₂ and CH₃SO₂NCl₂.^{23, 24} The bond distances and angles of the triphenylsilyl group are as expected.

No attempt was made to completely assign the Raman spectrum because of its complexity due to the triphenylsilyl group. However, a comparison between the Raman spectra of the Ph₃SiNH₂ starting material and the Ph₃SiNCl₂ product (Figure 2) demonstrates that, upon chlorination, the following very intense, new bands at 688, 513, 446, and 437 cm⁻¹ appear in the region of the SiNCl₂ stretching vibrations. Based on our theoretical calculations and normal coordinate analysis, these skeletal modes are strongly mixed. The 688 cm⁻¹ mode is a mixture of Si-N and antisymmetric NCl₂ stretching and the 513 and 446/437 cm⁻¹ modes are out-of-phase and in-phase combinations, respectively, of Si-N and symmetric NCl₂ stretching. For highly characteristic NCl₂ vibrations, the expected frequency separation between antisymmetric and symmetric NCl₂ stretching would be much smaller and be of the order of 20-40 cm⁻¹.

Synthesis and Properties of *t*-BuMe₂SiNCl₂. Since our repeated efforts to duplicate the reported¹⁵ preparation of trimethylsilyldichloramine failed, and the corresponding triphenylsilyl compounds were not volatile enough for our purposes, the previously unknown *tert*-butyl-dimethylsilyldichloramine was prepared according to eq 3.



Unfortunately, the volatility of the dichloramine is similar to that of the by-product *t*-BuOH, rendering the separation of the two compounds difficult and resulting in low isolated yields. At room-temperature, the moisture sensitive *t*-BuMe₂SiNCl₂ is a tacky yellow solid with a very intense odor and mp of ~25-30 °C. It cannot be distilled without decomposition. Storage for a prolonged period of time at RT, especially under the influence of light, resulted in the formation of *t*-BuMe₂SiCl. Its purity was ascertained by Raman and NMR spectroscopy. The ¹H, ¹³C, ²⁹Si and ¹⁴N NMR spectroscopic data of neat *t*-BuMe₂SiNCl₂ are listed in Table 4. The ¹H, ¹³C and ²⁹Si NMR chemical shifts are located in the region expected for the *t*-BuMe₂Si group. The broad ¹⁴N resonance for -NCl₂ at -280 ppm ($\Delta\nu_{1/2}$ = 770 Hz) lies within our expectations.²⁵

The Raman spectra of *t*-BuMe₂SiNCl₂ (upper) and of *t*-BuMe₂SiNH₂ (lower trace) are shown in Figure 3. While the *t*-BuMe₂Si-skeleton results again in complex vibrational spectra, a comparison of the two spectra reveals for the NCl₂ compound strong Raman bands at 676, 463 and 438 cm⁻¹. These are attributed, similarly to Ph₃SiNCl₂, to NCl₂ motions which are strongly coupled to the skeletal Si-NC₃ modes. In support of this interpretation, a normal coordinate analysis was carried out for the most simple, but unknown, silyldichloramine, H₃SiNCl₂. The calculated structure is shown in Figure 4, and the results from the normal coordinate analysis are summarized in Table 5. It can be seen from the potential energy distribution that, even in this relatively simple molecule, the skeletal modes are strongly mixed. For example, the maximum contribution from symmetric NCl₂ stretching (S7) to any single mode does not exceed 38% and that from antisymmetric NCl₂ stretching (S12) is even smaller with 18%. This analysis demonstrates the fallacy of assigning, for these compounds, characteristic NCl₂ bands.

Reaction of *t*-BuMe₂SiNCl₂ with Tetramethylammoniumfluoride. The cleavage of the Si-N bond in *t*-BuMe₂SiNCl₂ by Me₄NF (eq 2) was studied in CHF₃ solution¹⁶ at -78 °C. The solvent was pumped off at this temperature, and the *t*-BuMe₂SiF by-product, which was formed in quantitative yield, was removed at -25 °C. The latter was identified by mass-balance and IR, Raman and NMR spectroscopy. The low-temperature Raman spectrum (Figure 5) of the solid residue showed bands due to Me₄NCl and intense new bands at 635, 617, 611, 540, 356, and 276 cm⁻¹. Clearly, the number and frequencies of these bands were incompatible with the presence of an NCl₂⁻ anion which, based on our theoretical predictions at the CCSD(T)/cc-pvtz level, should exhibit only three bands with frequencies of about 579, 526, and 258 cm⁻¹. The identity of the species, absorbed on the Me₄NCl, was established by warming the solid to room temperature and collecting the volatiles at -196 °C. Based on their Raman spectra, the solid residue consisted of Me₄NCl, while the volatile product, a yellow liquid at room temperature, was pure NCl₃.²⁶⁻²⁹ Our Raman spectrum of liquid NCl₃ (Figure 6) is the first well defined spectrum of the neat substance. Previously, only a partial spectrum of poor quality had been reported by Hendra and Mackenzie.²⁷ All these Raman data together with their assignments are listed in Table 6. To clarify the composition of the species absorbed on Me₄NCl at -25°C, the collected NCl₃ was condensed back onto the Me₄NCl, and the low-temperature Raman spectrum was rerecorded. The spectrum was identical to the initial one and shows that the absorbed species is indeed NCl₃ and that the absorption and desorption are reversible. The marked differences in the spectra of absorbed and neat NCl₃ are attributed to crystal splittings and solid state effects.

A plausible explanation for the overall process which led to the formation of Me₄NCl and NCl₃ is given by the following equations:



The proposed sequence of reactions is supported by theoretical calculations. Although the NCl_2^- anion is vibrationally stable, its energy barrier toward the loss of a chloride ion is predicted to be low. The thermodynamically most favorable dissociation path for NCl_2^- is the loss of a Cl^- ion and spin-forbidden formation of ground state ($^3\Sigma^-$) NCl , whereas the lowest energy spin-allowed pathway leads to formation of excited state ($^1\Delta$) NCl . Full valence complete active space self-consistent field (CASSCF) calculations³⁰ with the 6-311+G(2df) basis set³¹ were performed to map out the lowest dissociative singlet and triplet potential energy surfaces and to determine the point at which they intersect. These calculations, which include nondynamical correlation but omit dynamical correlation effects, show that formation of excited ($^1\Delta$) NCl plus chloride is endothermic by 16.5 kcal mol⁻¹, whereas formation of ground state ($^3\Sigma^-$) NCl + chloride is exothermic by 15.1 kcal mol⁻¹. At the point where the lowest singlet and triplet potential energy surfaces intersect, the partially dissociated NCl_2^- species has N-Cl bond distances of 1.727 and 2.177 angstroms and a Cl-N-Cl bond angle of 105.6 degrees, and is 6.9 kcal/mol higher in energy than the NCl_2^- local minimum. Therefore, assuming the presence of sufficient spin-orbit coupling in the vicinity of the intersection, intersystem crossing from the

initial singlet state to the triplet electronic state could lower the effective barrier to dissociation to 6.9 kcal mol⁻¹.

These results are *qualitatively* similar to the previous calculations by Milburn, Rodriques and Hopkinson³² at the MP2/6-311++G(2df,p) and QCISD(T)/6-311++G(2df,p) levels (which include dynamical correlation but do not explicitly include effects of nondynamical correlation), for which the endothermicities toward Cl⁻ loss are only 37.5 and 7.3 kcal mol⁻¹ on the spin allowed singlet surface (with formation of excited (¹Δ) NCl) and spin-forbidden triplet surface (with formation of ground state (³Σ⁻) NCl,) respectively.

Out of the three possible isomers of N₂Cl₂, only the *cis*- and the *trans*- isomers are vibrationally stable, while the *iso*- isomer is not a minimum on the potential energy surface. As has been shown in a previous high level study by Tschumper, Heaven and Morokuma,³³ the *cis*- and the *trans*- isomers of N₂Cl₂ also have very low predicted barriers to dissociation of only 7-8 kcal mol⁻¹ at the CCSD(T) level and of ≤1.5 kcal mol⁻¹ at the CASPT2 level and are barely bound. For comparison, we have also calculated the structures and vibrational spectra of the NCl₄⁺ and NCl₂⁻ ions and the N₂Cl₄ and NCl₃ molecules at the CCSD(T)/cc-pvtz and MP2/6-31+G(d) levels of theory. Whereas the agreement between the CCSD(T) and MP2 calculations was quite good for all the geometries and the vibrational frequencies of the relatively well bound NCl₃ and NCl₄⁺ species, there were large discrepancies between the CCSD(T) and MP2 vibrational frequencies for the N₂Cl₂ isomers and NCl₂⁻, indicating that the frequency predictions for these weakly bound species require very careful high level calculations.

Conclusions. Only two silyldichloramines, (CH₃)₃SiNCl₂ and (C₆H₅)₃SiNCl₂, had previously been reported. Out of these, only the synthesis of (C₆H₅)₃SiNCl₂ could be duplicated, and its crystal structure was determined. The new silyldichloramine, *t*-BuMe₂SiNCl₂, was

prepared and characterized. It is shown that in these triorganylsilyldichloramines and the yet unknown H_3SiNCl_2 the NCl_2 stretching modes strongly couple to the skeletal modes, thus making it impossible to assign characteristic stretching frequencies to the NCl_2 group. The reaction of $t\text{-BuMe}_2\text{SiNCl}_2$ with $[\text{N}(\text{CH}_3)_4]^+\text{F}^-$ provides indirect evidence for the formation of the unstable intermediates, $[\text{N}(\text{CH}_3)_4]^+\text{NCl}_2^-$ and N_2Cl_2 , giving rise to $[\text{N}(\text{CH}_3)_4]^+\text{Cl}^-$ and NCl_3 as the final products. The latter two compounds reversibly form a loose adduct, exhibiting a Raman spectrum which deviates significantly from that of pure NCl_3 . Also, a reliable Raman spectrum of highly explosive, neat liquid NCl_3 has been recorded for the first time. Theoretical calculations for NCl_2^- , NCl_3 , N_2Cl_4 , NCl_4^+ , and the different isomers of N_2Cl_2 , support the inferred instabilities of NCl_2^- and N_2Cl_2 and demonstrate the difficulties involved in making reliable stability and property predictions for very weakly bound systems.

Acknowledgements

The authors thank the National Science Foundation, the Air Force Office of Scientific Research and the Office of Naval Research for financial support. We thank Prof. G. A. Olah and the Loker Research Institute for their steady support and hospitality and Irina Tsyba for her help with the crystal structure determination.

Supporting Information Available

CCDC 253436 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

References

* To whom correspondence should be sent.

E-mail: kchrste@usc.edu; stefan.schneider@edwards.af.mil.

† University of Southern California

‡ Air Force Research Laboratory

§ Present address: Air Force Research Laboratory, Edwards AFB, California 93524

¶ Present address: Department of Chemistry and Biochemistry, The University of Lethbridge, Alberta, T1K 3M4, Canada

- (1) Holleman, A. F.; Wiberg, N., *Inorganic Chemistry*, Academic Press, San Diego, California, 2001.
- (2) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, Second Edition, Butterworth-Heinemann, Oxford, 1998.
- (3) a) Dehnicke, K.; Aeissen, H; Koelmel, M.; Straehle, J. *Angew. Chem. Int. Ed. Engl.* **1977**, 16, 545; b) Minkwitz, R.; Bernstein, D.; Sawodny, W.; Haertner, H. *Z. anorg. Allg. Chem.* **1990**, 580, 109.
- (4) Minkwitz, R.; Bernstein, D.; Sawodny, W. *Angew. Chem. Int. Ed. Engl.* **1990**, 29, 181.
- (5) Schneider, S.; Haiges, R.; Schroer, T.; Boatz, J.; Christe, K. O. *Angew. Chem.* **2004**, 43, 5213.
- (6) a) Kukushkin, Y. N. *Zh. Neorg. Khim.* **1957**, 2, 2371; b) Kukushkin, Y. N. *Zh. Neorg. Khim.* **1959**, 4, 2460; c) Kukushkin, Y. N. *Zh. Neorg. Khim.* **1960**, 5, 1943; c) Kukushkin, Y. N. *Zh. Neorg. Khim.* **1961**, 6, 1762; d) Kukushkin, Y. N. *Zh. Neorg. Khim.* **1962**, 7,

- 769; e) Kukushkin, Y. N. *Zh. Neorg. Khim.* **1962**, 7, 1795; f) Kukushkin, Y. N. *Zh. Neorg. Khim.* **1965**, 10, 601; g) Varshavskii, Y. S.; Kukushkin, Y. N. *Zh. Neorg. Khim.* **1965**, 10, 1332.
- (7) Ruff, J. K. *Inorg. Chem.* **1965**, 4, 1446.
 - (8) Foropoulos, Jr., J.; DesMarteau, D. *Inorg. Chem.* **1984**, 23, 3720.
 - (9) Becke-Goering, M.; Hormuth, B. *Z. anorg. Allg. Chem.* **1969**, 369, 105.
 - (10) Minkwitz, R; Liedtke, A. *Inorg. Chem.* **1989**, 28, 1627.
 - (11) a) Hoefer, R.; Glemser, O. *Z. Naturforsch.* **1975**, 30b, 458; b) Waterfeld, A.; Mews, R. *Angew. Chem. Int. Ed. Engl.* **1982**, 21, 354.
 - (12) Thrasher, J. S.; Seppelt, K. *Angew. Chem. Int. Ed. Engl.* **1983**, 22, 789.
 - (13) a) Starynowicz, P. *Acta Cryst.* **1991**, C47, 2198 ; b) Bu, X.; Coppens, P. *Acta Cryst.* **1992**, C48, 1560.
 - (14) Wiberg, N. Raschig, F. *J. Organometal. Chem.* **1967**, 10, 15.
 - (15) Wiberg, N.; Uhlenbrock, W. *Chem. Ber.* **1971**, 104, 2643.
 - (16) Christe, K. O.; Wilson, W. W.; Wilson, R. D.; Bau, R.; Feng, J. *J. Am. Chem. Soc.* **1990**, 112, 7619.
 - (17) SMART V 5.625, Software for the CCD Detector System, Bruker AXS, Madison, WI, 2001.
 - (18) SAINT V 6.22, Software for the CCD Detector System, Bruker AXS, Madison, WI, 2001.
 - (19) SADABS, Program for absorption correction for area detectors, Version 2.03, Bruker AXS, Madison, WI (2001).

- (20) SHELXTL 6.10 for Windows NT, Program library for Structure Solution and Molecular Graphics, Bruker AXS, Madison, WI (2000).
- (21) Kraus, C. A.; Rosen, R. *J. Am. Chem. Soc.* **1925**, 47, 2739.
- (22) Dugat, D.; Just, G.; Sahoo, S. *Can. J. Chem.* **1987**, 65, 88.
- (23) Minkwitz, R.; Garzarek, P.; Preut, H. *Z. Naturforsch.* **1997**, 52b, 88.
- (24) Minkwitz, R.; Garzarek, P.; Neikes, F.; Kornath, A.; Preut, H. *Z. anorg. Allg. Chem.* **1997**, 623, 333.
- (25) Wrackmeyer, B. *Spectrochim. Acta* **1987**, 43, 1187.
- (26) Moore, G. E.; Badger, R. M. *J. Am. Chem. Soc.* **1952**, 74, 6076.
- (27) Hendra, P.J.; Mackenzie, J.R. *Chem. Comm.* **1968**, 760.
- (28) Bayersdorfer, L.; Engelhardt, U.; Fischer, J.; Hoehne, K.; Jander, J. *Z. anorg. Allg. Chem.* **1969**, 366, 169.
- (29) Gilbert, J. V.; Smith, L. J. *J. Phys. Chem.* **1991**, 95, 7278.
- (30) The NCl_2^- full valence CASSCF wavefunction is a linear combination of configurations generated by distributing the 20 valence electrons among the 12 valence orbitals in all possible ways which are consistent with the overall space and spin symmetry of the molecular electronic state. See, for example, a) Schmidt, M.W.; Gordon, M.S. *Ann. Rev. Phys. Chem.* **1998**, 49, 233; b) Roos, B.O., in "Methods in Computational Molecular Physics", G.H.F. Diercksen and S.Wilson; eds., D. Reidel Publishing, Dordrecht, Netherlands, 1983, pp 161-187.
- (31) a) Krishnan, R.; Binkley, J.S.; Seeger, R.; Pople, J.A. *J. Chem. Phys.* **1980**, 72, 650-654.; b) Frisch, M.J.; Pople, J.A.; Binkley, J.S. *J. Chem. Phys.* **1984**, 80, 3265.; c) Clark, T.; Chandrasekhar, J.; Spitznagel, G.W.; Schleyer, P. von R. *J. Comput. Chem.* **1983**, 4, 294.

- (32) Milburn, R. K.; Rodriguez, C. F. ; Hopkinson, A. C. *J. Phys. Chem. B* **1997**, *101*, 1837.
- (33) Tschumper, G. S.; Heaven, M. C.; Morokuma, K. *Chem. Phys. Lett.* **2003**, *370*, 418.

Table 1. Crystal Data for Ph₃SiNCl₂.

chemical formula	C18 H15 Cl2 N Si
fw	344.30
T, K	85(2)
space group	P-1 Triclinic
<i>a</i> , Å	9.073(2)
<i>b</i> , Å	9.797(2)
<i>c</i> , Å	10.1333(2)
α , deg	107.983(4)
β , deg	102.954(4)
γ , deg	96.174(4)
<i>V</i> , Å ³	819.6(3)
<i>Z</i>	2
ρ_{calc} , g cm ⁻³	1.395
μ , mm ⁻¹	0.464
<i>R</i> 1, ^a <i>wR</i> 2 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0391, 0.0939
<i>R</i> 1, ^a <i>wR</i> 2 ^b (all data)	0.0453, 0.0973

^a *R*1 = $(\sum(F_o - F_c)/F_o)$. ^b *wR*2 = $[\sum(w(F_o - F_c)^2)/\sum(wF_o^2)]^{1/2}$.

Table 2. Selected Bond Lengths [Å] and Angles [°] for Ph₃SiNCl₂.

bond lengths [pm]		bond angles [°]	
Si(1)-N(1)	181.3(2)	N(1)-Si(1)-C(1)	100.53(8)
Si(1)-C	185.7(2)-186.2(2)	N(1)-Si(1)-C(13)	104.77(8)
N(1)-Cl(1)	173.8(2)	N(1)-Si(1)-C(7)	113.84(8)
N(1)-Cl(2)	175.4(2)	C(7)-Si(1)-C(13)	111.33(8)
		C(7)-Si(1)-C(1)	113.42(8)
		C(1)-Si(1)-C(13)	112.22(8)
		Cl(1)-N(1)-Cl(2)	108.43(9)
		Cl(1)-N(1)-Si(1)	112.07(9)
		Cl(2)-N(1)-Si(1)	112.10(9)

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ph}_3\text{SiNCl}_2$.

	x	y	z	U(eq) ^a
Si(1)	3696(1)	1371(1)	3032(1)	14(1)
N(1)	2559(2)	2103(2)	1794(2)	19(1)
C(1)	3041(2)	-621(2)	2029(2)	16(1)
C(2)	4077(2)	-1586(2)	1894(2)	18(1)
C(3)	3562(3)	-3067(2)	1114(2)	22(1)
C(4)	2008(2)	-3607(2)	453(2)	22(1)
C(5)	958(2)	-2671(2)	575(2)	21(1)
C(6)	1466(2)	-1197(2)	1355(2)	19(1)
C(7)	5810(2)	1992(2)	3440(2)	15(1)
C(8)	6570(2)	1792(2)	2350(2)	21(1)
C(9)	8158(2)	2237(2)	2685(2)	23(1)
C(10)	9017(2)	2895(2)	4106(2)	23(1)
C(11)	8295(2)	3094(2)	5198(2)	23(1)
C(12)	6708(2)	2639(2)	4869(2)	19(1)
C(13)	3020(2)	1976(2)	4689(2)	15(1)
C(14)	2201(2)	937(2)	5080(2)	17(1)
C(15)	1705(2)	1349(2)	6327(2)	19(1)
C(16)	2011(2)	2803(2)	7195(2)	21(1)
C(17)	2827(2)	3853(2)	6840(2)	20(1)
C(18)	3331(2)	3441(2)	5603(2)	18(1)
Cl(1)	2933(1)	4003(1)	2426(1)	31(1)
Cl(2)	2871(1)	1488(1)	79(1)	27(1)

^a U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 4. ^1H , ^{13}C , ^{29}Si and ^{14}N NMR Spectra of *t*-BuMe₂SiNCl₂.

chem shift, δ ppm);			$\Delta\nu_{1/2}$ (Hz)
^1H	C(CH) ₃	2.25 (s)	
	(CH ₃) ₂	1.53 (s)	
^{13}C	C(<u>C</u> H) ₃	27.15 (s)	
	<u>C</u> (CH) ₃	19.96 (s)	
	(CH ₃) ₂	5.81 (s)	
^{29}Si		39.8 (s)	
^{14}N		-280 (s)	770

Table 5. Vibrational Frequencies (cm^{-1}), calculated at the MP2/6-31G(d) Level, of H_3SiNCl_2 with C_s symmetry, and Mode Description derived from a Normal Coordinate Analysis.

symmetry coordinate	calcd freq	potential energy distribution (%)
S1 ν sym SiH_3 in phase	$a' \nu_1$ 2362	88(1), 12(2)
S2 ν sym SiH_3 out of phase	ν_2 2331	89(2), 10(1)
S3 δ umbrella SiH_3	ν_3 988	54(4), 46(3)
S4 δ sciss SiH_2	ν_4 973	98(4)
S5 ν SiN	ν_5 883	55(5), 28(7), 12(9), 5(8)
S6 δ rock SiH_3	ν_6 703	96(6), 2(8), 1(9)
S7 ν sym NCl_2	ν_7 485	38(7), 25(5), 22(8), 11(9), 3(6)
S8 δ sciss NCl_2	ν_8 299	89(8), 5(6), 3(9), 2(5)
S9 δ Si-N= Cl_2	ν_9 206	67(9), 24(8), 6(6), 1(7)
S10 ν asym SiH_3	$a'' \nu_{10}$ 2375	100(10)
S11 δ as SiH_3	ν_{11} 995	63(11), 35(15)
S12 ν asym NCl_2	ν_{12} 779	43(13), 29(15)(5), 18(12), 9(14)
S13 δ wag SiH_3	ν_{13} 653	81(13), 10(12), 7(15), 1(14)
S14 δ twist NCl_2	ν_{14} 218	92(15), 7(14)
S15 τ Si-N	ν_{15} 171	89(15), 10(14)

Table 6. Raman spectra of solid Me₄NCl, Me₄NCl“·1/3(NCl₃)” and neat, liquid NCl₃.

Me ₄ NCl at RT		Me ₄ NCl·NCl ₃ at -25°C		NCl ₃ at RT		assignments	
						Me ₄ N ⁺ (^a)	NCl ₃
3026	(95)	3026	(51)			} νCH_3 and combination bands	
3018	(100)	3017	(71)				
2950	(83)	2952	(51)				
		2926	(31)				
		2898	(18)				
2877	(30)	2877	(15)				
		2827	(6)				
		2821	(7)				
		2813	(5)				
2788	(14)	2786	(7)				
1482	(32)	1483	(21)			ν_{15}	
1477	(30)	1477	(24)			ν_6	
1455	(15)	1455	(22)			ν_2	
1401	(13)	1399	(7)			ν_{16}	
1287	(13)	1288	(15)			ν_{17}	
1191	(1)	1191	(2)			ν_7	
1181	(5)	1181	(5)			ν_{11}	
948	(36)	947	(27)			ν_{18}	
803	(1)						
759	(29)	753	(16)			ν_3	
		732	(5) ^(b)				
		635	(11)				$\nu_2 + \nu_4 (b_2)^c$
		617	(49)	640	(19)		$\nu_3 (b_2)^c$
		611	(61)				
565	(3)						
		550	(6)				
		540	(100)	539	(86)		$\nu_1 (a_1)$
458	(13)	458	(7)			ν_{19}	
		452	(7)				
388	(5)	387	(5)			ν_8	
375	(3)	372	(5)			ν_8 or ν_{12}	
360	(3)						
		356	(70)	351	(100)		$\nu_2 (a_1)$
		338	(5)				
		276	(61)	260	(69)		$\nu_4 (b_2)$
109	(1)	108	(15)				
85	(9)	74	(41)	73	(11)		

(^a) Based on refs 15 and 28. (^b) Teflon-FEP band from the sample container. (^c) Fermi resonance.

Figure Captions

Figure 1. Structure of the $\text{Ph}_3\text{SiNCl}_2$ molecule. Thermal ellipsoids are shown at the 50% probability level.

Figure 2. Raman spectra of $\text{Ph}_3\text{SiNCl}_2$ (upper) and Ph_3SiNH_2 (lower trace).

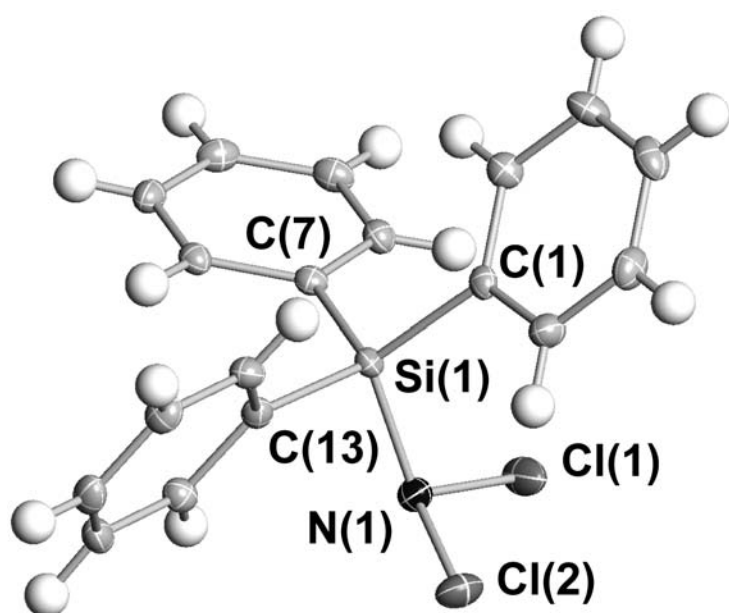
Figure 3. Raman spectrum of $t\text{-BuMe}_2\text{SiNCl}_2$ (upper) and $t\text{-BuMe}_2\text{SiNH}_2$ (lower trace).

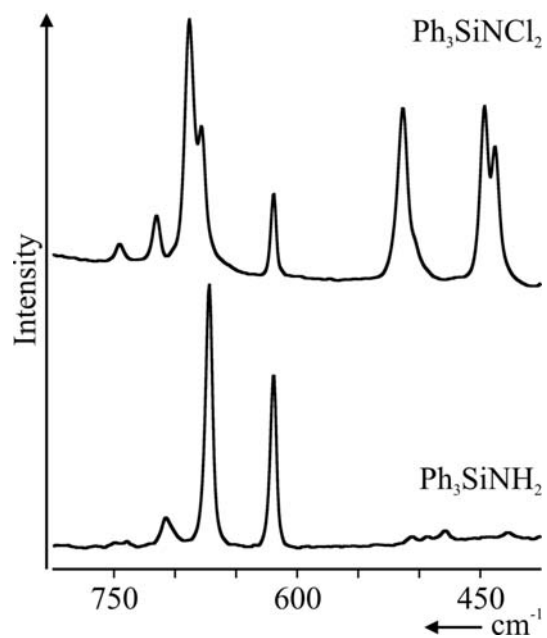
Figure 4. Geometry of H_3SiNCl_2 , calculated at the MP2/6-31G(d) level; bond lengths in Å, angles in degrees.

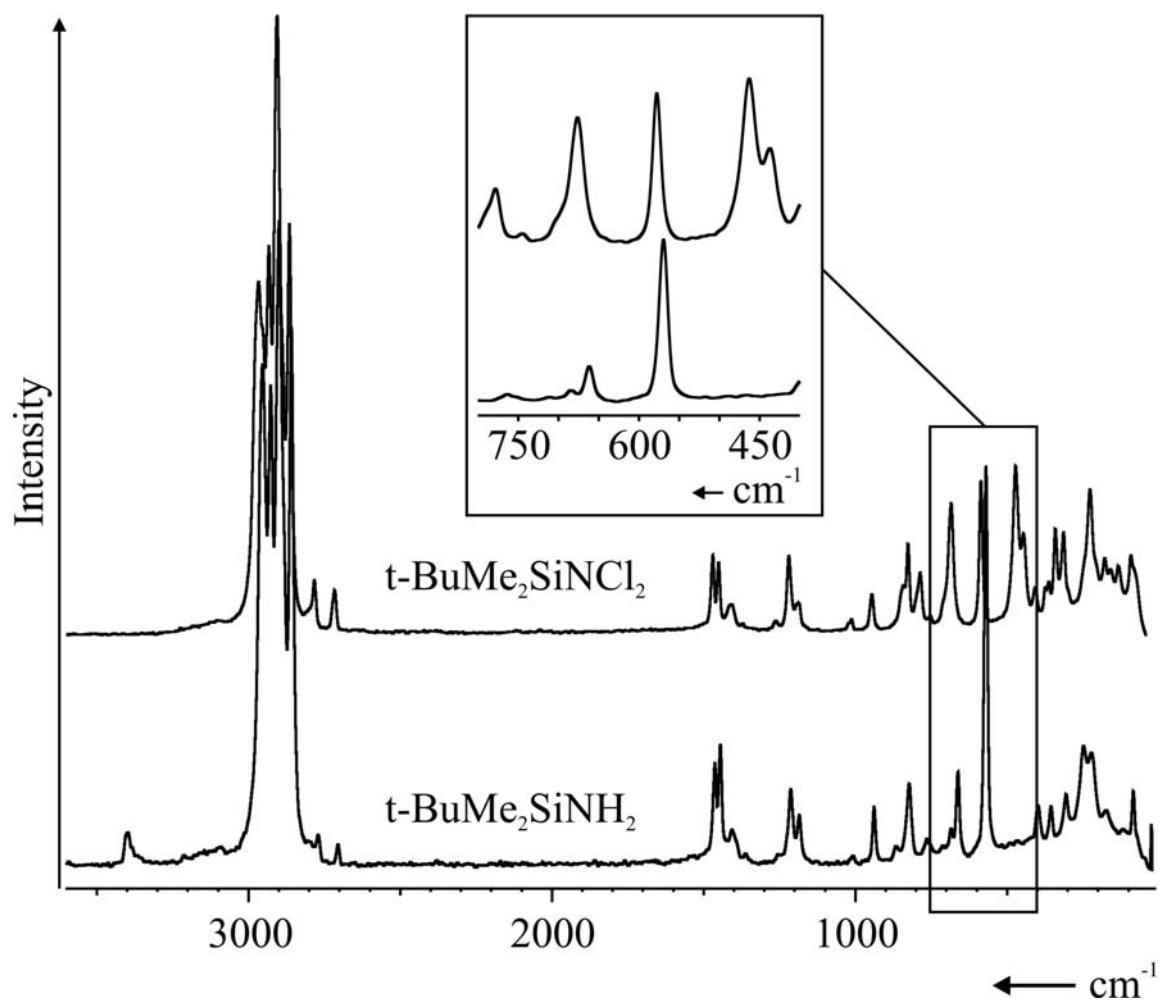
Figure 5. Raman spectrum of solid $\text{Me}_4\text{NCl} \cdot \frac{1}{3}(\text{NCl}_3)$.

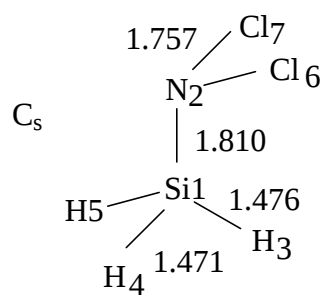
Figure 6. Raman spectrum of neat NCl_3 .

Figure 7. Calculated CCSD(T)/cc-pvtz geometries of NCl_2^- , NCl_3 , NCl_4^+ , *cis*- N_2Cl_2 , *trans*- N_2Cl_2 , *iso*- N_2Cl_2 , and N_2Cl_4 ; numbers in parentheses are the MP2/6-311+G(d) values and numbers in brackets are experimental values; bond lengths are in Å, angles in degrees.

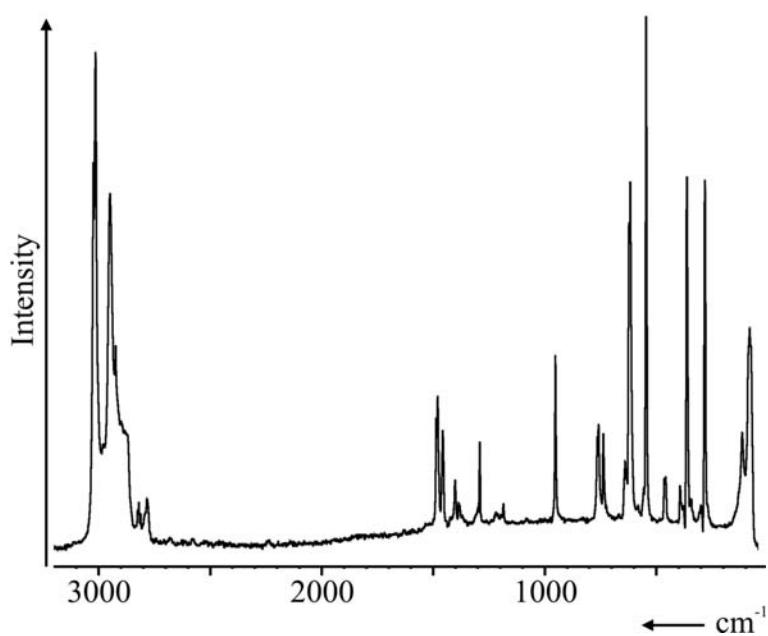


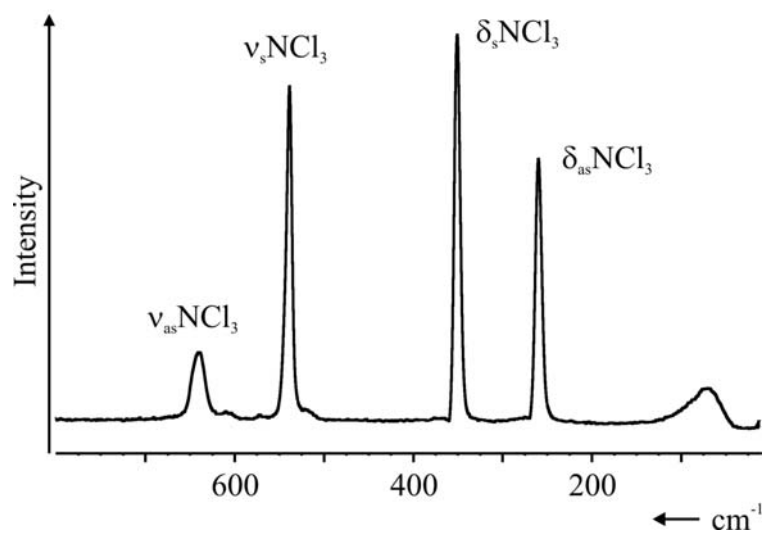


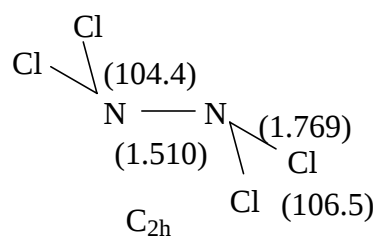
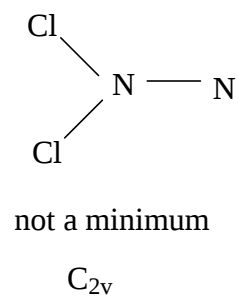
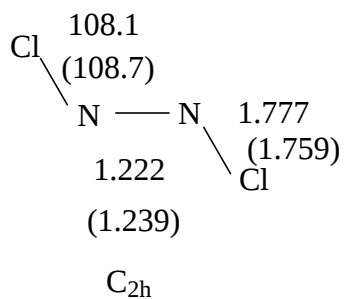
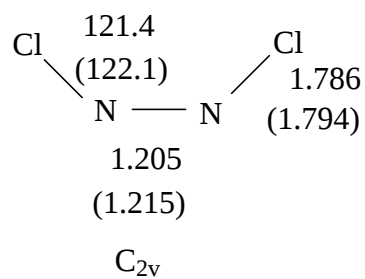
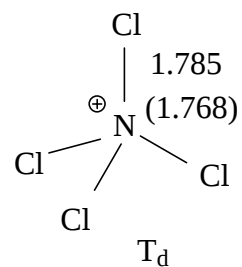
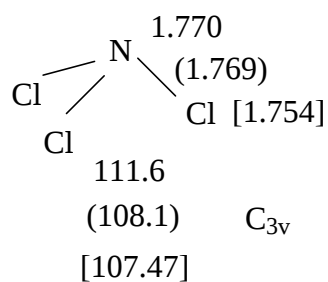
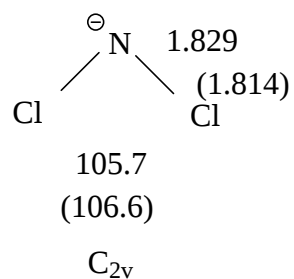




3-1-2 112.0; 4-1-2 104.9; 1-2-6 110.2;
 6-2-7 110.4; 4-1-5 112.3; 4-1-3 111.2 deg







Synthesis and Characterization of Silyldichloramines, their Reactions with F⁻ Ions, Stability of N₂Cl₂ and NCl₂⁻, and Formation of NCl₃

Stefan Schneider*, Michael Gerken,
Ralf Haiges, Thorsten Schroer, Jerry A.
Boatz, Karl O. Christe*

The reaction of previously unknown *tert*-butyldimethylsilyldichloramine with Me₄NF results in the formation of *t*-BuMe₂SiF, Me₄NCl and surprisingly NCl₃. The generation of NCl₃ can be explained by the formation and decomposition of the unstable intermediates NCl₂⁻ and N₂Cl₂.

