of nearly 3 T is needed to clearly show an effect. Since the internal intratrimeric magnetic field is about 0.8 T and the material is a metamagnetic, it is possible that these effects are associated with a Zeeman effect due to both the magnitude and direction of the internal and external fields.

Conclusions

The value of the ground-state exchange parameter J was found to be about 1 cm^{-1}. Since the total spread of this multiplet is $55J$, this value is consistent with the small change in slope of the susceptibility vs. $1/T$ curve at about 20 K[1] and the more pronounced changes in the low-temperature EPR behavior which set in the 20–30 K range.[4] The intensity-producing mechanism contains both electric dipole and magnetic dipole components. Finally, nonlinear Zeeman effects were noted in the low-temperature optical spectra.

Registry No. $Mn(OAc)_2\cdot 4H_2O$, 6156-78-1.

References and Notes

(1) R. B. Flippen and S. A. Friedberg, *Phys. Rev.*, **121**, 1591 (1961).
(2) I. Tsujikawa, *J. Phys. Soc. Jpn.*, **18**, 1407 (1963).
(3) R. D. Spence, *J. Chem. Phys.*, **62**, 3659 (1975).
(4) H. Abe and H. Moriyali, "Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1960", W. Low, Ed., Academic Press, New York, 1963, p 567.
(5) R. Gaura, G. Kokoszka, and P. Szydlik, *J. Magn. Reson.*, in press.
(6) P. Burlet, P. Burlet, and E. F. Bertaut, *Solid State Commun.*, **14**, 665 (1974).
(7) D. Tranqui, P. Burlet, A. Filhol, and M. Thomas, *Acta Crystallogr., Sect. B*, **33**, 1357 (1977).
(8) A. Mehra and P. Venkateswarlu, *J. Chem. Phys.*, **48**, 4381 (1968).
(9) D. S. McClure, *NATO Adv. Study Inst. Ser., Ser. B*, **8**, 259 (1975).
(10) J. Catterick and P. Thornton, *Adv. Inorg. Chem. Radiochem.*, **20**, 291 (1977).
(11) J. Ferguson, *Prog. Inorg. Chem.*, **12**, 159 (1970).

Contribution from the Department of Chemistry,
Lake Forest College, Lake Forest, Illinois 60045

Silyl Group Exchange between Chlorosilane and *N*-Methyldisilazane

Martin L. Thompson

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A good deal of evidence has been presented in recent years affirming the electron-accepting powers of the silyl (SiH_3) group. In the case where silicon is already bound by a σ bond to another atom, an additional dative bond of the $p\pi$–$d\pi$ type may be formed by utilizing one of the vacant silicon d-orbitals. Where the attached atom is one belonging to group 5 or 6 normally possessing marked electron-donating properties, these properties will be weakened after attachment to a silyl group. This effect explains why the basic properties of the following series of compounds toward Lewis acids increase as shown:[1-3] $(SiH_3)_3N < (SiH_3)_2NCH_3 < SiH_3N(CH_3)_2 < N(CH_3)_3$. Further evidence of the relative basicities of the former two amines is presented as a result of the rapid silyl group exchange between chlorosilane and *N*-methyldisilazane.

Experimental Section

Apparatus and Equipment. All chemical reactions were carried out by using conventional high-vacuum techniques.[4] Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer, Model 137. The samples were confined in a 5-cm gas cell with NaCl windows. Proton NMR spectra were obtained at 60 MHz with a Varian DP60 or Varian A-60A spectrometer equipped with a standard variable-temperature control. Mass spectra were obtained with an MS-10 mass spectrometer.

Reagents. All solvents were reagent grade and were dried by standard methods. Chlorosilane was prepared from silane and hydrogen chloride in the presence of an aluminum chloride catalyst[5,6] and purified by fractional condensation to give a vapor pressure of 50 torr at −78 °C. Chlorosilane-d_3 was synthesized from silane-d_4 and DCl in a similar manner. The preparation of trisilylazane by the ammonolysis of chlorosilane has been described previously.[1,2,7] The vapor pressure of the purified material was 109 torr at 0 °C (lit. 109[7] and 110 torr[2]). *N*-Methyldisilazane was prepared from chlorosilane and methylamine[2,5] and purified to give a vapor pressure of 188 torr at 0 °C (lit. 192[5] and 193 torr[2]).

Exchange Reaction between Chlorosilane and *N*-Methyldisilazane. a. Infrared Studies. In a typical experiment chlorosilane-d_3, 0.45 mmol, and 0.23 mmol of *N*-methyldisilazane were mixed together and allowed to remain in the gas phase in a U-tube for 10 min at room temperature at a total pressure of 0.12 atm. No association could be detected in the gas phase. The gases were separated by passage into a −112 °C trap, and the distillate (chlorosilane fraction) was sampled for an infrared spectrum. All absorbances could be accounted for by assuming a mixture of SiH_3Cl and SiD_3Cl; there was no evidence for the pressure of any mixed species such as SiH_2DCl and $SiHD_2Cl$. (The broad doublet in the 10–15 μm range characteristic of the SiX_3 deformation is uniquely defined in each of the four isotopically different compounds: SiH_3Cl, 950 cm^{-1};[8] SiH_2DCl, 890 cm^{-1}; $SiHD_2Cl$, 845 cm^{-1}; SiD_3Cl, 700 cm^{-1} [9]).

For determination of the extent of silyl group exchange, a calibration curve was constructed wherein the differences between the optical densities of the Si–D and Si–H stretching frequencies were plotted vs. the mole percentage of silyl-d_3 groups in known mixtures of SiD_3Cl and SiH_3Cl. The difference in the optical densities of the two stretching frequencies was chosen as a parameter in preference to that of either frequency alone to minimize the error caused by slight pressure variations in the cell when proceeding from one experiment to the next. The pressure employed in the cell was 40 ± 1 torr. The resulting linear plot was refined by the method of least squares to give $m = 0.0173$, $b = -0.880$, and $\sum r_i^2 = 0.0086$.

The percentage of deuterated silyl groups initially present in the mixture was 49%. By reference to the calibration curve, the percentage found in the chlorosilane fraction after exchange was also 49%, confirming complete equilibration of silyl groups.

b. NMR Studies. It seemed possible that exchange was occurring so rapidly that an NMR spectrum of a mixture of SiH_3Cl and $(SiH_3)_2NCH_3$ might yield only one observable Si–H resonance absorption. The proton resonances (vs. Me_4Si) of each compound were obtained in CS_2: $\delta = -4.66$ for SiH_3Cl; $\delta = -4.38$ (Si–H) and -2.62 (C–H) for $(SiH_3)_2NCH_3$. The observed chemical shifts of a 2:1 molar mixture in CS_2 were identical, showing no tendency toward coalescence. The separations between the two Si–H resonances did not change (within experimental error) as the temperature was raised in 20 °C intervals to 100 °C.

In a second series of experiments SiD_3Cl and $(SiH_3)_2NCH_3$ in a 2:1 molar ratio were separately condensed into an NMR tube, as was CS_2, and the tube was sealed under vacuum. The sample was not allowed to warm above −50 °C; the spectrum was scanned repeatedly at this temperature in an attempt to follow the exchange process. It was expected than an initially small peak at −4.66 ppm would increase as the silyl group exchange occurred and that the peak at −4.38 ppm would decrease. The −4.66 ppm resonance due to SiH_3Cl was unexpectedly intense initially. No changes in relative peak areas occurred as a function of time. Analysis of all three peak areas showed that silyl group scrambling was complete at this temperature in a matter of minutes.

c. Mass Spectral Studies. For determination of whether the liquid phase is required for silyl group exchange, 0.241 mmol of $(SiH_3)_2NCH_3$ and 0.516 mmol of SiD_3Cl were separately sealed into glass tubes joined by a 4-mm stopcock. The two gas phases were allowed to equilibrate, and the mixture sampled for a mass spectrum without condensation. The spectrum was consistent with silyl group exchange, with a strong peak at m/e 97 due to $(SiD_3)_2NCH_3^+$ and minor higher peaks up to 100 due to small amounts of silicon-29 and -30.

Exchange Reaction between Chlorosilane and Trisilazane. In a typical experiment, SiD_3Cl and $(SiH_3)_3N$ in a molar ratio of 3:1 were transferred to an all-glass reaction bulb. After being sealed, the bulb and its contents were immersed in a constant-temperature bath for a given period of time. The bulb was quenched with liquid nitrogen and opened on the vacuum system. The gases were fractionated by a single pass through a −112 °C trap, and the distillate (the chlorosilane

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fraction) was sampled for an infrared spectrum.

Results and Discussion

The infrared studies show that silyl group exchange between chlorosilane and *N*-methyldisilazane is complete within 10 min at ambient temperature. No convergence of silyl group resonances is detectable in the NMR spectrum of a mixture of the two, allowing a lower limit of the half-time of exchange to be calculated according to the formula[10]

$$t_{1/2} = \frac{2^{1/2}}{2\pi(\nu_A - \nu_B)} \quad \text{(valid when resonances coalesce)}$$

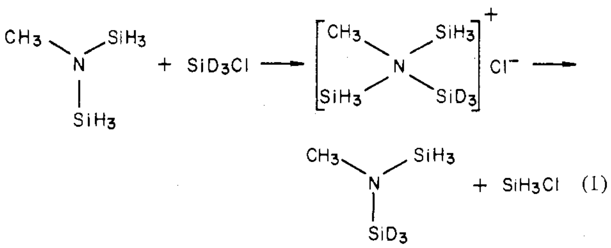
Since $\nu_A - \nu_B = 16.4$ Hz, the half-time of exchange at 40 °C is greater than 0.01 s.

An NMR spectrum of a mixture of SiD_3Cl and $(SiH_3)_2NCH_3$ showed immediate equilibration of silyl groups at −50 °C. However, no tendency toward coalescence of silyl group resonant frequencies was detectable at even 100 °C, indicating a very low activation energy for the exchange process.

In the $SiD_3Cl–(SiH_3)_3N$ system, no exchange of any type was detected at room temperature after 1 week at 25 °C. At elevated temperatures (73–93 °C) exchange was slow, and analysis of the infrared spectra of the chlorosilane fractions indicated the presence of partially deuterated species, suggesting hydrogen exchange. The possibility of silyl group transfer cannot be dismissed, however, as it was found in separate experiments that SiD_3Cl and SiH_3Cl slowly undergo hydrogen scrambling at comparable temperatures, as do $(SiD_3)_3N$ and $(SiH_3)_3N$. Thus silyl group exchange between SiD_3Cl and $(SiH_3)_3N$ could lead to a statistically scrambled mixture of partially deuterated chlorosilane moieties via either or both of the above routes.

The marked difference in the rates of silyl group exchange of chlorosilane with the two amines is further evidence for the increased basicity of$(SiH_3)_2NCH_3$ over $(SiH_3)_3N$. Any intermediate or transition-state complex involving a tetravalent nitrogen would require a lower activation energy in the case of $(SiH_3)_2NCH_3$ than in $(SiH_3)_3N$ if the lone pair of electrons on the nitrogen atom in the amines is involved in internal dative bonding to the 3d orbitals of the silicon atoms. The planarity of the Si_3N skeleton in $(SiH_3)_3N$[11] confirms the existence of such Si–N dπ–pπ bonding. The presence of three silyl groups would allow a more effective withdrawal of this electron density than would two, suggesting a greater energy of hybridization to form a tetravalent nitrogen atom.

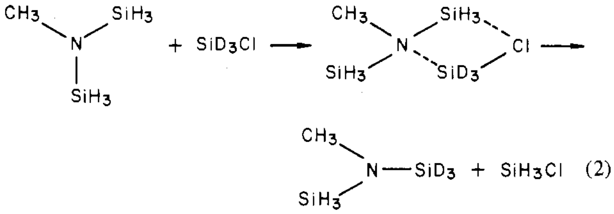
A mechanism involving the formation of a quaternary intermediate is conceivable (eq 1). Quaternary ammonium type compounds containing only one or two silyl groups such as silyltrimethylammonium iodide and disilyldimethylammonium chloride have been obtained,[5,12] although the disilyl-substituted species is unstable and decomposes readily.



(1)

Another possible mechanism would involve a four-center transition state followed by an unsymmetrical withdrawl (eq 2). Bimolecular complexes of $(SiH_3)_2NCH_3$ molecules involving five-coordinate Si and four-coordinate N atoms have been hypothesized[13] in the base-catalyzed decomposition of $(SiH_3)_2NCH_3$.

The former mechanism ought to be favored in a polar solvent. When deuterated acetonitrile was used as a solvent in a 2:1 mixture of SiH_3Cl and $(SiH_3)_2NCH_3$, the NMR spectrum again showed no tendency toward coalescence of the silyl hydrogen resonances.[14]



(2)

The mass spectral results show that the liquid phase is not necessary for silyl group exchange, in sharp contrast to a number of redistribution and elimination reactions involving compounds containing the silyl group attached to a group 5A element.[15-19]

These latter two factors both indicate a preference for the second mechanism. The rapidity of the exchange plus the lack of any detectable association in the gaseous phase shows the kinetic and thermodynamic instability of either proposed complex.

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Registry No. Chlorosilane-d_3, 13637-82-6; *N*-methyldisilazane, 4459-06-7; trisilazane, 13862-16-3.

References and Notes

(1) A. B. Burg and E. S. Kuljian, *J. Am. Chem. Soc.*, **72**, 3103 (1950).
(2) S. Sujishi and S. Witz, *J. Am. Chem. Soc.*, **76**, 4631 (1954).
(3) S. Sujishi and S. Witz, *J. Am. Chem. Soc.*, **79**, 2447 (1957).
(4) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, 1969.
(5) H. J. Emeleus and N. Miller, *J. Chem. Soc.*, 819 (1939).
(6) A. Stock and C. Somieski, *Ber. Dtsch. Chem. Ges.*, **52**, 695 (1919).
(7) A. Stock and C. Somieski, *Ber. Dtsch. Chem. Ges.*, **54**, 740 (1921).
(8) C. Newman, J. K. O'Loane, S. R. Polo, and M. K. Wilson, *J. Chem. Phys.*, **25**, 855 (1956).
(9) C. Newman, S. R. Polo, and M. K. Wilson, *Spectrochim. Acta*, 793 (1959).
(10) J. A. Pople, W. G. Schneider, and J. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, 1959, p 223.
(11) K. Hedburg, *J. Am. Chem. Soc.*, **77**, 6491 (1955).
(12) B. J. Aylett, H. J. Emeleus, and A. G. Maddock, *J. Inorg. Nucl. Chem.*, **1**, 187 (1955).
(13) B. J. Aylett and M. J. Hakim, *J. Chem. Soc. A*, 1788 (1969).
(14) An interesting process that does occur in this solvent is the disproportionation of chlorosilane to silane and dichlorosilane.
(15) R. L. Wells and R. Schaeffer, *J. Am. Chem. Soc.*, **88**, 37 (1966).
(16) B. J. Aylett and M. J. Hakim, *Inorg. Chem.*, **5**, 167 (1966).
(17) B. J. Aylett and M. J. Hakim, *J. Chem. Soc. A*, 639 (1969).
(18) W. M. Scantlin and A. N. Norman, *Inorg. Chem.*, **11**, 3081 (1972).
(19) A. D. Norman and W. L. Jolly, *Inorg. Chem.*, **18**, 1594 (1979).

Contribution from the Laboratoire de Chimie Quantique,
E.R. No. 139 du CNRS, Université Louis Pasteur,
67000 Satrsbourg, France

A Molecular Orbital Analysis of the Oxidative Addition of Hydrogen to the Chlorotris(triphenylphosphine)rhodium(I) Complex

A. Dedieu* and A. Strich

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The oxidative addition of molecular hydrogen to four-coordinate d^8 square-planar transition-metal complexes is an important reaction per se as well as in connection with homogeneous hydrogenation.[1,2] Spectroscopic results and kinetic

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