The spin distribution data combined with the spectral data suggest that the low-temperature form is a high symmetry penta- or hexacoordinate species in which the unpaired electron resides principally in a metal orbital which does not overlap with the N-oxide's annular π system. The high-temperature form may be a pentacoordinate species of low symmetry or alternatively a "tetrahedral" structure in which one TFAA acts as a monodentate group with the other coordination site being occupied by an N-oxide. Either of these alternatives would be favored at high temperatures by entropy considerations and is consistent with some fraction of an unpaired electron being located in metal orbitals which allow delocalization into the π system of the N-oxide.

From the observed line widths a mechanism for the nuclear spin relaxation can be deduced. Thus the transverse relaxation time of the proton, T_2, which is inversely related to the line width is given by eq 1,[13] in which ω_s is the electronic Larmor precession frequency.

$$\frac{1}{T_2} = \frac{S(S + 1)g^2\beta^2\gamma_I{}^2}{15r^6}\left[7\tau_c + \frac{13\tau_c}{1 + \omega_s{}^2\tau_c{}^2}\right] + \frac{S(S + 1)A^2}{3h^2}\left[\tau_e + \frac{\tau_e}{1 + \omega_s{}^2\tau_e{}^2}\right] \qquad (1)$$

Under conditions for which the broadening due to spin delocalization is small the second term involving A, the hyperfine coupling constant, can be neglected. The correlation time τ_c is defined by the relationship $\tau_c{}^{-1} = \tau_s{}^{-1} + \tau_r{}^{-1}$, where τ_r is the rotational correlation time. This quantity can be independently approximated for a spherical particle by the Debye expression, $\tau_r = 4\pi\eta r^3/3kT$, where η is the viscosity of the solution and r is the effective radius of the sphere. Since $\tau_s \cong 10^{-8}$ sec was independently determined by an esr experiment, τ_c can be evaluated and compared with the magnitudes of its components. Using the line-width data taken from the system described in Figure 1 (for the γ-CH_3 protons in a pure 1:1 complex $(\langle r^1\rangle_{av}{}^{1/6} = 7.13$ A, $1/T_2 = 270$ sec^{-1}, $T = 284$°K) a value of $\tau_c = 3.4 \times 10^{-10}$ is calculated. This compares with $\tau_r = 3.2 \times 10^{-10}$ for a particle of radius 5.5 A calculated using the Debye equation. As this radius is approximately that of the β-diketone ring system, these calculations strongly indicate that nuclear relaxation is effected by the fluctuating magnetic field seen by the proton caused by the tumbling of the complex in solution. Such a mechanism is also supported by the increase in line width with decrease in solution temperature. These data contrast with the nuclear relaxation mechanism previously postulated for Ni(II) and Co(II) complexes[14] which have much shorter electron spin relaxation times.

Corrections for pseudo-contact shifts cannot be made because the exact geometry of the complex for which delocalization is being observed is unknown. However, using the geometric factors for the 2:1 Ni(AA)$_2$–N-oxide complex[2] and the g tensor anisotropy found for the solid Cu(TFAA)$_2$–γ-picoline N-oxide complex, pseudo-contact shifts of -5, -6, and -3 cps can be estimated at 39° for the α, β, and γ-CH_3 protons of this ligand coordinated along the fourfold axis of a square pyramid.

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[13] This and other equations are discussed in the review by D. R. Eaton and W. D. Phillips in "Advances in Magnetic Resonance," Vol. 1, J. S. Waugh Ed., Academic Press Inc., New York, N. Y., 1965, p 103. This equation neglects the g tensor anisotropy which can also contribute to the relaxation of the proton spin: H. Sternlicht, *J. Chem. Phys.*, **42**, 2250 (1965). However, for systems with small anisotropies the contribution from this mechanism is small and can be ignored.

[14] G. N. LaMar, *J. Am. Chem. Soc.*, **87**, 3567 (1965).

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The Alkali Metal Salt Catalyzed Disproportionation Reactions of Alkyldisilanes

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The alkali metal salt catalyzed disproportionation reactions of disilane in 1,2-dimethoxyethane have been recently investigated.[1] The first step in these reactions is a base-catalyzed disproportionation similar to those found for other silyl compounds[2–5]

$$x\mathrm{Si_2H_6} \xrightarrow{\text{salt}} x\mathrm{SiH_4} + (1/x)(\text{-}\mathrm{SiH_2}\text{-})_x \qquad (1)$$

The relative catalytic effectiveness for the disilane disproportionations were KH > LiD > LiCl. For the metal hydride reactions a second, slower reaction also occurred (M = K or Li)

$$(1/x)(\mathrm{SiH_2})_x + \mathrm{MH} \longrightarrow \mathrm{MSiH_3} \qquad (2)$$

This reaction was faster with KH than with LiD.

In this note we report the extension of these reactions to a number of alkyldisilanes.

Experimental Section

The cleavage reactions were carried out at room temperature in 100-ml round-bottom flasks which were fitted with either Teflon needle valves or stopcocks and ground joints to allow for transfer of reactants and volatile products between standard vacuum systems and the reaction vessels. The reaction vessels were also fitted with a side tube through which the solid catalysts could be added.

The solvent, 1,2-dimethoxyethane, was dried over potassium sand at −78° until the ether was a dark blue. The solvent was then distilled, *in vacuo*, to the reaction vessel.

The alkyldisilanes used were prepared as described by Bolduc and Ring[6] or by Groschwitz, Ingle, and Ring.[7] These reactants

[1] J. A. Morrison and M. A. Ring, *Inorg. Chem.*, **6**, 100 (1967).

[2] R. L. Wells and R. Schaeffer, *J. Am. Chem. Soc.*, **88**, 37 (1966).

[3] A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **25**, 1934 (1963).

[4] A. G. MacDiarmid and T. Yoshioka, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 5M.

[5] G. Urry, *J. Inorg. Nucl. Chem.*, **26**, 409 (1964).

[6] W. J. Bolduc and M. A. Ring, *J. Organometal. Chem.* (Amsterdam), **6**, 202 (1966).

[7] E. A. Groschwitz, W. M. Ingle, and M. A. Ring, *ibid.*, in press.

were identified and checked for purity by comparing their infrared spectra and vapor pressures with those reported in the literature.[6-9]

Infrared spectra were obtained in 10-cm gas cells fitted with KBr windows on a Perkin-Elmer Model 337 spectrophotometer. All separations were made by trap-to-trap distillations through standard slush baths.

Reactions with LiCl.—Lithium chloride (excess) was placed in a reaction vessel which was then evacuated. The reaction vessel was heated to 120° for 2 hr under dynamic vacuum. Then, about 4 ml of 1,2-dimethoxyethane and an alkyldisilane were condensed onto the dried salt. After 18 hr, the system was analyzed. No reaction was observed with methyldisilane, ethyldisilane, 1,2-dimethyldisilane, or 1,1-dimethyldisilane. Since disilane reacts under these conditions,[1] our alkyldisilanes were free from disilane contamination.

Reactions with LiD.—The products from the following reactions were isolated and identified as previously described.[7]

(1) Methyldisilane (0.21 mmole) and about 1 ml of 1,2-dimethoxyethane were distilled onto excess lithium deuteride. After 10 hr, silane (0.082 mmole), methylsilane (0.049 mmole), and methyldisilane (0.083 mmole) were found. The infrared spectra of these compounds did not contain the strong Si–D stretching band. After all of the volatile materials were distilled from the reaction vessel, excess hydrogen chloride was condensed onto the solid. No reaction was observed with the solid indicating the lack of anion formation during the cleavage reaction.

(2) A sample of ethyldisilane (0.28 mmole) whose infrared spectrum had a very weak absorbance at 713 cm^{-1} (assigned to trisilane) was added to 1 ml of 1,2-dimethoxyethane. The infrared spectrum of a vapor sample of this mixture retained the 713-cm^{-1} absorption. This mixture was then condensed onto excess lithium deuteride. After 30 min, the volatile products found were silane (0.019 mmole), ethylsilane (0.014 mmole), and disilane (0.005 mmole). The 713-cm^{-1} absorption was now absent from an infrared spectrum of the remaining ethyldisilane. Since the 713-cm^{-1} absorption of trisilane is stronger than any ethyldisilane band, the remaining ethyldisilane was free from trisilane contamination. This ethyldisilane and solvent were recondensed onto the solid in the reaction vessel and the reaction was allowed to proceed. At about 45-min intervals, the volatile products were removed and analyzed. This procedure was continued until the reaction had run for 3 hr. Each time the mixture was examined, silane, ethylsilane, and disilane were observed while trisilane was never observed. For this reaction, the total yield of products consisted of 0.08 mmole of silane, 0.06 mmole of ethylsilane, and 0.02 mmole of disilane. No reaction was observed between the solid product and hydrogen chloride. The infrared spectra of the volatile compounds from the above experiment did not contain an observable Si–D stretching frequency.

(3) The reaction between lithium deuteride and 1,1-dimethyldisilane or 1,2-dimethyldisilane was carried out as described above. No reaction was observed after 18 hr in either case. These results demonstrate that both dimethyldisilanes were free from methyldisilane contamination.

Reactions with KH.—The potassium hydride (a 50% slurry in Bayol-85 obtained from Metal Hydrides) was washed with the solvent to remove the oil. Then the alkyldisilane and fresh solvent were condensed onto the free potassium hydride.

(1) Methyldisilane (0.24 mmole) and about 1 ml of 1,2-dimethoxyethane were condensed onto excess potassium hydride. After a 9-min reaction, methylsilane (0.15 mmole) and silane (0.11 mmole) were found. These products and the solvent were distilled off, and hydrogen chloride (0.5 mmole) was condensed onto the solid. The products from this reaction were silane (0.06 mmole) and disilane (0.01 mmole).

(2) The reaction between ethyldisilane (0.51 mmole) and excess potassium hydride was carried out as described above. After 15 min, the products found were ethylsilane (0.29 mmole) and silane (0.19 mmole). The products from the reaction of excess hydrogen chloride and the solid product were silane (0.11 mmole) and a trace of disilane and ethylsilane.

(3) The reaction between 1,1-dimethyldisilane and potassium hydride was carried out as described above. The volatile product from a 20-min reaction with 0.24 mmole of 1,1-dimethyldisilane was 0.25 mmole of dimethylsilane; silane was not observed. The reaction between the solid product and hydrogen chloride yielded only a trace of silane. For an 8-hr reaction with 0.22 mmole of 1,1-dimethyldisilane, 0.21 mmole of dimethylsilane was obtained. When the solid product from this reaction was treated with excess hydrogen chloride, 0.045 mmole of silane and 0.011 mmole of disilane were obtained.

(4) The reaction of 1,2-dimethyldisilane was carried out as described above. The volatile product from the 1-hr reaction with 0.16 mmole of 1,2-dimethyldisilane was 0.19 mmole of methylsilane. No reaction was observed between hydrogen chloride and the solid product. The solid product from a similar reaction run for 21 hr did react with hydrogen chloride to produce methylsilane in an 8% yield based on the 1,2-dimethyldisilane consumed.

Discussion

While the disproportionation of disilane to silane and a polymer is catalyzed by lithium chloride, lithium deuteride, or potassium hydride,[1] under the same conditions, the disproportionation of monoethyl- (or methyl-) disilane is only catalyzed by the latter two salts while the disproportionation of both dimethyldisilanes was only catalyzed by potassium hydride. Since hexaphenyldisilane reacts with phenyllithium,[10] steric factors do not appear to be important in these systems. Therefore, we feel that the changes in reactivity between disilane and the alkyldisilanes are due primarily to inductive effects. It has been suggested that alkyl groups release electrons (relative to hydrogen atoms) toward silicon more easily than toward carbon.[11]

The formation of small quantities of disilane from the lithium deuteride catalyzed ethyldisilane disproportionation is consistent with our previously proposed mechanism of the salt-catalyzed reactions of disilane where the formation of silenes followed by their insertion into silicon–hydrogen bonds was proposed.[1] However, our attempts to trap silenes have not been successful. Since ethane was never observed as a product from the ethyldisilane reactions with either lithium deuteride or potassium hydride, it is unlikely that the disilane arises from carbon–silicon bond rupture. We propose that the ethyldisilane disproportionation proceeds through the formation of ethylsilane and ethyltrisilane (possibly *via* silene transfer) (eq 3). Cleavage of the silicon–silicon bonds in ethyltrisilane together with a hydride transfer would result in the formation of silane, ethyldisilane, and disilane. The fact that the initial products of the potassium

$$2C_2H_5Si_2H_5 \xrightarrow{\text{Lewis base}} C_2H_5SiH_3 + C_2H_5Si_3H_7 \qquad (3)$$

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[8] A. D. Craig and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **24**, 161 (1962).

[9] M. Abedini and A. G. MacDiarmid, *Inorg. Chem.*, **5**, 2040 (1966).

[10] B. J. Gaj, reported by H. Gilman and H. J. S. Winkler, "Organometallic Chemistry," H. Zeiss, Ed., American Chemical Society Monograph Series, No. 147, American Chemical Society, Washington, D. C., 1960, p 294.

[11] V. N. Krishnamurthy and S. Soundararajan, *J. Inorg. Nucl. Chem.*, **27**, 2341 (1965).

hydride catalyzed disproportionation of 1,1-dimethyldisilane were dimethylsilane and a polymer suggests that a hydride transfer occurs with silicon–silicon bond rupture.

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Reactions of Coordinated Ligands. XVI. The Reactions of the Chloroacetate Anion with Mercapto Groups in Nickel(II) Complexes of Mercaptoamines

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Reports of alkylation reactions occurring at the sulfur atoms of coordinated mercaptide groups have appeared in the scientific literature since 1888. However, only recently have the full utility and scope of such reactions been demonstrated.[1,2] The known reactions can be conveniently classified as follows: (1) reactions using monofunctional alkylating agents which simply transform the mercaptide group to a thioether moiety and (2) reactions using difunctional alkylating agents which lead the concomitant formation of two thioether groups and a chelate ring joining them. The reaction of the nickel(II) complex of 2-aminoethanethiol with methyl iodide serves as an example of the first type (Figure 1, reaction 1), whereas the reaction of the same nickel complex with α,α'-dibromo-*o*-xylene illustrates the second (Figure 1, reaction 2).

We present here an extension of the classes of reactions of coordinated mercaptides to include those in which the alkylating agent contains a functional group which can complex with the nickel ion. The chloroacetate anion meets these requirements and can be employed with nickel(II) complexes of mercaptoamines to generate pseudo-octahedral complexes containing two tridentate ligands each of which possesses three dissimilar donor atoms, nitrogen, sulfur, and oxygen (Figure 1, reaction 3).

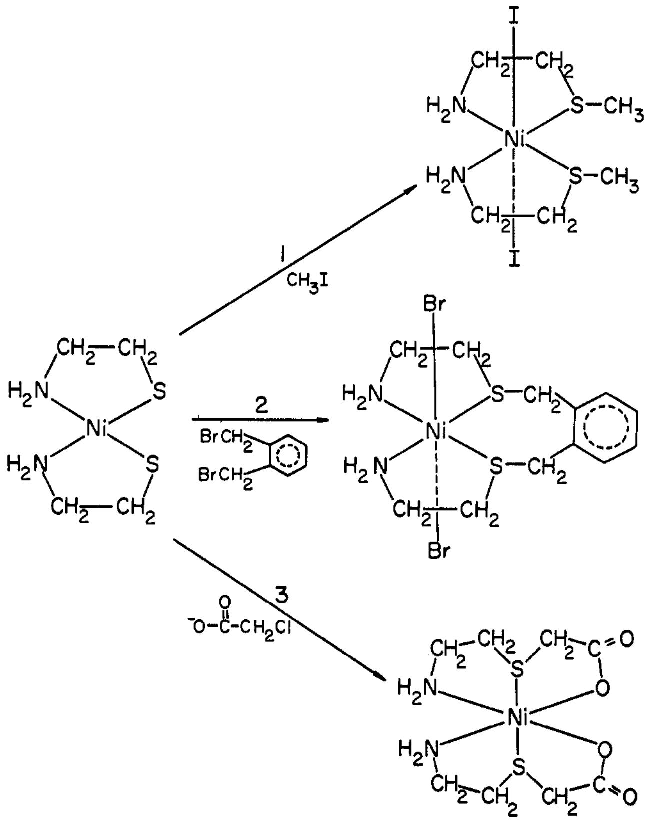

Figure 1. Alkylation reactions of the coordinated mercaptide group. Specific isomers are indicated as products; however, no information is available concerning the isomers of the complexes.

The reactions of the $Ni(RR'NCH_2CH_2S)_2$ complexes with the chloroacetate anion proceed smoothly in hot water over a period of 1–5 hr. In the case of the R = R' = H complex, the reaction is performed in boiling water and is characterized by the simultaneous disappearance of the insoluble, green mercaptoamine complex and appearance of a blue solution. Blue crystals are readily obtained by recrystallization from hot water of the solid deposited from the reaction mixture.

Both the molecular weight and magnetic susceptibility data for the R = R' = H compound support the proposed structure. The molecular weight in water, 300 (theory 327), suggests that the complex exists predominantly as undissociated monomers in this solvent. The six-coordinate nature of the nickel in the crystals is supported by a measured magnetic moment of 3.04 BM, a value similar to six-coordinate amine–thioether complexes previously reported and generally typical of spin-free octahedral nickel(II) complexes.[1,2]

Although it is impossible for the complexes in question to exhibit strictly octahedral symmetry, their electronic spectra can best be interpreted as though the metal ions were in an octahedral site. Apparently the real noncubic field components are small compared with the approximately cubic field because the bands in the electronic spectra can be assigned with the octahedral model as follows: ν_1 to $^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$; ν_2 to $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$; ν_3 to $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ (see Table II). In the solid phase the R = R' = H complex shows a split second band which is also common to octahedral complexes of nickel(II) with water and with some amides.[3,4] In each of the aqueous spectra a shoulder at approximately 11,700 cm^{-1} occurs on the high-energy side of the first band. This band may arise from a spin-forbidden triplet to singlet transition.

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