

Figure 2.—Effect of temperature on the spectrum of Ni(II) in molten LiI-36.8 mol % KI. Each spectrum is labeled with the temperature at which it was measured.

We conclude that nickel entities in the LiBr-KBr system are quite similar to those in the LiCl-KCl system. The principal difference is a displacement of the conformational equilibrium more strongly toward tetrahedral geometry in the bromide system as compared with the chloride system.

Figure 2 shows the experimental results for the iodide melt. These spectra correspond to essentially tetrahedral coordination.<sup>5</sup> There are no bands that cannot be accounted for in terms of this geometry but the charge-transfer absorption is so strong in the region where the strongest octahedral band is expected that we cannot exclude the possibility of a small amount of nickel in octahedral coordination. Nevertheless, the results are in line with the supposition that at a given temperature, nickel(II) in LiX-KX (X = Cl, Br, or I) with about 40 mol % KX occurs in a tetrahedral-octahedral conformational equilibrium that is shifted increasingly toward tetrahedral in going from chloride through bromide to iodide. This effect is plausibly attributed to the increasing size of the halide ion, which would tend to destabilize octahedral geometry owing to crowding of adjacent halides.

Further evidence for the importance of this steric effect comes from a recent potentiometric study<sup>8</sup> of the over-all formation constants of the tetrahalonickel(II) ions in molten dimethyl sulfone at 125°. The stability was found to follow the order Br > Cl > I, whereas the normal order for metal halide complexes with  $d\pi$  bonding is I > Br > Cl. This reversal in stability is reasonably attributed to the large size of the iodide ions packed around the relatively small nickel(II) ion. In dimethyl sulfone there is no evidence, either potentiometric<sup>8</sup> or spectrophotometric,<sup>5</sup> for nickel halide species with a coordination number greater than 4, and in molten halide salts with large organic cations, the tetrahedral  $NiX_4^{2-}$

complexes are the only appreciable species even at comparatively low temperatures.<sup>5</sup> The presence of octahedral coordination at low temperatures in LiCl-KCl mixtures as solvents has been accounted for in terms of the polarization of halide ions by outer-shell lithium ions,<sup>3</sup> and Mg<sup>2+</sup> has been shown to play a similar role in MgCl<sub>2</sub>-KCl mixtures as solvents.<sup>9</sup> Although the order of polarizability is I<sup>-</sup> > Br<sup>-</sup> > Cl<sup>-</sup>, the present results show that the effectiveness of outer-shell Li<sup>+</sup> in inducing octahedral coordination of nickel(II) is greatest for molten chlorides and least for molten iodides. We conclude that the steric effect is of overriding importance in producing this reversal.

(9) J. Brynestad and G. P. Smith, *J. Chem. Phys.*, **47**, 3190 (1967).

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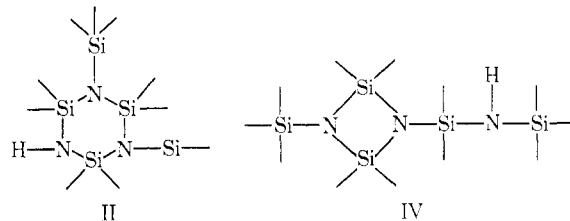
## Anionic Rearrangement of a Cyclotrisilazane to a Cyclodisilazane

BY L. W. BREED

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We published a method for preparing N-trimethylsilylhexamethylcyclotrisilazane (I) by the condensation of N-sodiohexamethylcyclotrisilazane with chlorotrimethylsilane<sup>1</sup> after Fink had reported that N,N'-bis(trimethylsilyl)hexamethylcyclotrisilazane (II) could be prepared in high yield from N,N'-dilithiohexamethylcyclotrisilazane and chlorotrimethylsilane at 160°, but that I, prepared from N-lithiohexamethylcyclotrisilazane and chlorotrimethylsilane, disproportionated to II and hexamethylcyclotrisilazane (III) at 160°. <sup>2,3</sup> We cited data and questioned the structural assignment of II by Fink on the basis of boiling points, refractive indices, the densities of the series III, I, II, and an inconsistent proton magnetic spectrum of II.<sup>1</sup>

We now wish to report that the compound originally assigned structure II can be unequivocally identified as N-trimethylsilyl-N'-1-(1,1,3,3-pentamethyldisilazanyl)-tetramethylcyclodisilazane (IV). (All unfilled val-

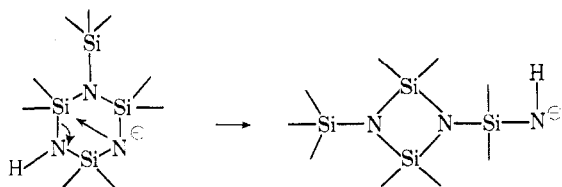


ences are methyl groups here and throughout the rest of the paper.) The formation of structure IV under the conditions of the experiment can be explained on the basis of an anionic rearrangement accompanied by ring contraction

(1) L. W. Breed and R. L. Elliott, *Inorg. Chem.*, **2**, 1069 (1963).

(2) W. Fink, *Helv. Chim. Acta*, **45**, 1081 (1962).

(3) German Patent 1,187,615 (Feb 25, 1965).



Anionic rearrangements in silicon-nitrogen compounds have been reported by others.<sup>4</sup>

Particularly strong evidence for the newly assigned structure is found in the infrared spectra of IV and related compounds. The spectra of both I and III show a strong Si<sub>2</sub>N asymmetric stretch frequency at 925–935 cm<sup>-1</sup> and are similar in other respects except for bands that can be accounted for on the basis of the trimethylsilyl group.<sup>5</sup> Compound IV, however, also shows strong absorption in the 880–895- and 1025–1030-cm<sup>-1</sup> regions. Recent work here, a portion of which has been published,<sup>6</sup> revealed that the infrared absorption band for the Si<sub>2</sub>N frequency in a series of about 15 functional cyclodisilazane derivatives did not occur in the 900–950-cm<sup>-1</sup> region, but shifted to 875–900 cm<sup>-1</sup>. A second strong band also always occurred at 1020–1040 cm<sup>-1</sup>. Similar observations have been made by Buerger.<sup>7</sup> The spectrum of compound IV showed a strong absorption band in each of the three regions, 875–900, 900–950, and 1020–1040 cm<sup>-1</sup>, and is similar in every necessary respect to the spectrum of N-(dimethyldimethylaminosilyl)-N'-1-(3-dimethylamino-1,1,3,3-tetramethyldisilazanyl)tetramethylcyclodisilazane, which has been prepared here by a different method.<sup>8</sup> Structure IV has also been confirmed by its nmr spectrum.<sup>9</sup> Chemical shifts were observed at  $\tau$  9.77, 9.95, 9.98, and 10.00 with an integrated area ratio of 4:3:2:3. The required proton ratio for structure IV is 4:3:2:3 while II requires 3:2:1. The chemical shift that is usually observed for silylmethyl protons attached to a cyclodisilazane ring is  $\tau$  9.76–9.79.

It should be pointed out that the cyclodisilazane structure is isomeric with the cyclotrisilazane structure and that the elemental analyses and molecular weight originally reported for the compound by Fink are equally correct for II and IV.

Structure IV could be readily formed under the experimental conditions from N,N'-dilithiohexamethylcyclotrisilazane after the substitution of the first lithium by a trimethylsilyl group by ring contraction of the intermediate anion. The formation of a cyclodisilazane structure under these conditions is not too surprising in view of the great ease with which functional trisilylamines form cyclodisilazanes. For example, pentamethyl-N-trimethylsilylcyclodisilazane<sup>10</sup>

(4) For a leading reference see R. West, M. Ishikawa, and R. E. Bailey, *J. Am. Chem. Soc.*, **89**, 4072 (1967).

(5) In ref 1, a weak band was reported at 1030 cm<sup>-1</sup> for I. This band has since been found to be absent when the compound is pure.

(6) L. W. Breed, W. L. Budde, and R. L. Elliott, *J. Organometal. Chem.* (Amsterdam), **6**, 876 (1966).

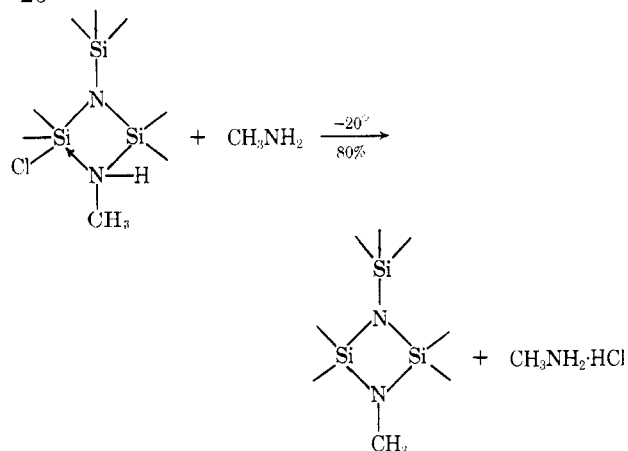
(7) H. Buerger, E. Bogusch, and P. Geymayer, *Z. Anorg. Allgem. Chem.*, **349**, 124 (1967).

(8) Unpublished data.

(9) The 100-Mc spectrum used cyclohexane as an internal standard. The 60-Mc spectrum was reported in ref 1.

(10) L. W. Breed and R. L. Elliott, *J. Organometal. Chem.* (Amsterdam), **11**, 447 (1968).

can be obtained in yields up to 80% from methylamine and bis(chlorodimethylsilyl)trimethylsilylamine at -20°<sup>11</sup>



A confirmation of this mechanism was obtained by heating I and III with butyllithium. When 0.035 mol of pure I was treated with 0.035 mol of butyllithium in hexane, the hexane was distilled out, the mixture was heated at 160°, and the strong infrared band was observed at 1032 and at 880 cm<sup>-1</sup> in the spectrum of the product indicating the formation of the cyclodisilazane ring. A similar ring contraction did not occur when III was heated with butyllithium under similar conditions. The role of the trisilylamine structure seems to be essential for the ring closure, and these results are parallel to the earlier finding that while bis(chlorodimethylsilyl)trimethylsilylamine readily forms a cyclodisilazane with methylamine, 1,3-dichloropentamethyldisilazane gives only the bis-methylamino derivative.<sup>10</sup>

With the recognition that an anionic rearrangement can occur during the condensation and that N-lithiohexamethylcyclotrisilazane is probably polymeric owing to the ability of lithium to act as a bridging atom between silyl-substituted nitrogen atoms after the manner described by Wannagat,<sup>12</sup> a reasonable explanation can be offered for Fink's finding that equimolar quantities of III and IV are formed when N-lithiohexamethylcyclotrisilazane is treated with chlorotrimethylsilane. (See Scheme I.)

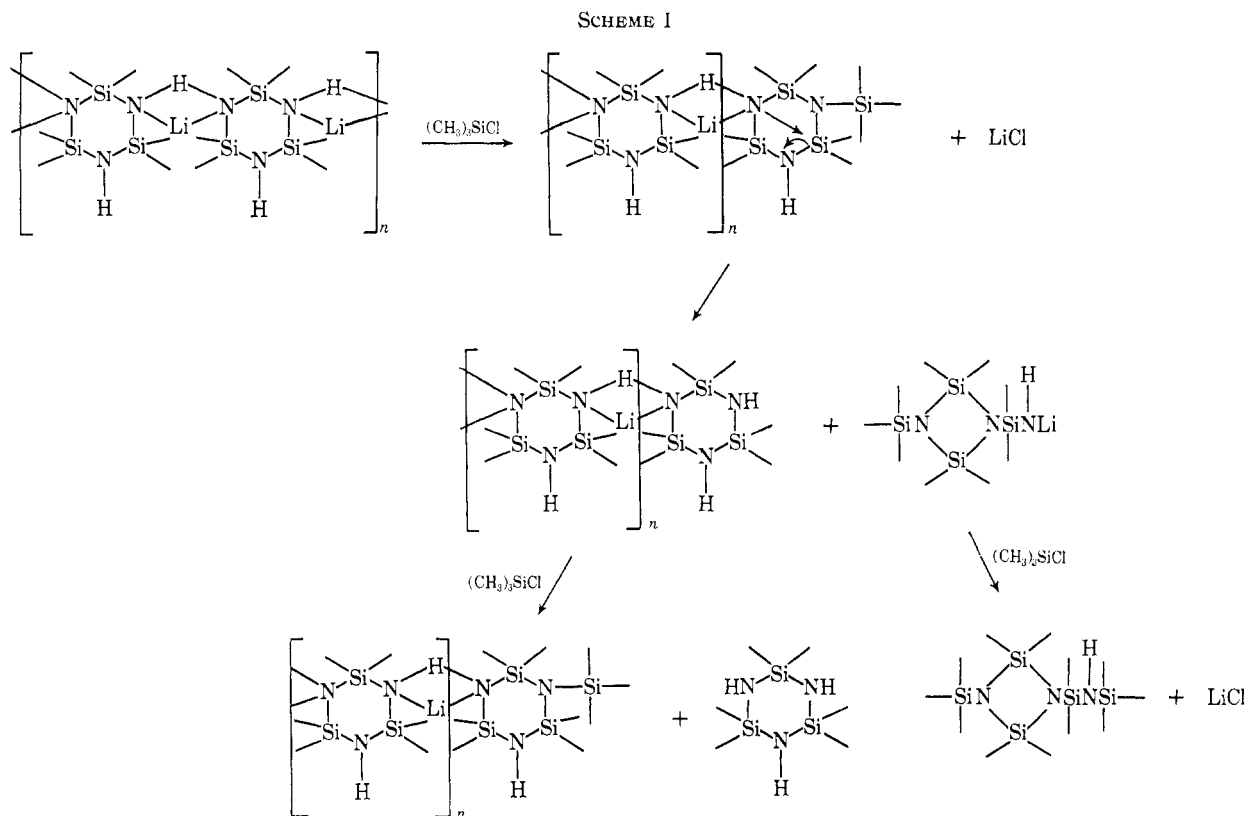
#### Experimental Section

**N-Trimethylsilyl-N'-1-(1,1,3,3,3-pentamethyldisilazanyl)tetramethylcyclodisilazane.**—After a solution of 43.8 g (0.20 mol) of hexamethylcyclotrisilazane in 100 ml of hexane was treated with 256 ml (0.30 mol) of 1.6 M butyllithium in hexane during 45 min, the mixture was heated 2 hr and 155 ml of solvent was allowed to distil. The mixture was cooled, treated with 43.6 g (0.40 mol) of chlorotrimethylsilane during 30 min, transferred to a 2-l. autoclave, and heated under autogenous pressure for 6 hr. After the lithium salts were filtered off, fractional distillation gave 33.0 g (46%) of N-trimethylsilyl-N'-1-(1,1,3,3,3-pentamethyldisilazanyl)tetramethylcyclodisilazane, bp 122–123° (6 mm),  $n_D^{20}$  1.4427 (lit.<sup>2</sup> bp 81.0–82.7° (2 mm),  $n_D^{20}$  1.4422, yield 83.9%).

**Acknowledgment.**—This work was supported in part by the United States Army under Contract DA-23-

(11) The high conversion is obtained only when the by-product methylamine hydrochloride is removed at low temperature before the cyclodisilazane is purified.

(12) U. Wannagat, *Chem. Eng. News*, **46**, 38 (Feb 19, 1968).



07200RD-1687, monitored by the United States Army Weapons Command, Rock Island, Ill., and in part by the United States Air Force under Contract AF 33(615)-

3126, monitored by the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

## Correspondence

### $\sigma$ and $\pi$ Effects of Phosphines, Pyridines, and Amines in $\text{LW}(\text{CO})_5$ Complexes

Sir:

In a recent paper Graham<sup>1</sup> has defined inductive ( $\sigma$ ) and resonance ( $\pi$ ) effects of a ligand or group L in terms of the effect of L on  $\nu_{\text{CO}}$  of  $\text{LM}(\text{CO})_5$  complexes (M = Mn, Mo). Using eq 1 and 2 relative  $\sigma$  and  $\pi$  parameters were derived for various L groups from the differences between the CO stretching force constants<sup>2,3</sup> of the compound  $\text{LM}(\text{CO})_5$  and a reference compound  $\text{RM}(\text{CO})_5$ . A positive value of the  $\sigma$  (or  $\pi$ ) parameter

$$\Delta k_1 = \sigma + 2\pi \quad (1)$$

$$\Delta k_2 = \sigma + \pi \quad (2)$$

implies that L is a  $\sigma$  (or  $\pi$ ) acceptor, while a negative  $\sigma$  (or  $\pi$ ) parameter implies that L is a  $\sigma$  (or  $\pi$ ) donor com-

pared to the reference group R, for which  $\sigma = \pi = 0$ .

From the similar decrease in carbonyl stretching frequencies and force constants with increasing  $\text{p}K_{\text{a}}$  of L in  $\text{LW}(\text{CO})_5$  complexes (L = amine, pyridine, or phosphine) it has been suggested earlier that only changes in W-L  $\sigma$  bonding affect the CO stretching force constants,<sup>4</sup> though for at least the phosphine ligands this would seem to be a controversial conclusion in view of earlier studies.<sup>5</sup> We wish to observe here that these published data on  $\text{LW}(\text{CO})_5$  complexes can be evaluated using Graham's method. This treatment of these data assumes that both inductive and resonance effects are operative in determining carbonyl band positions and hence contradicts the suggestion that  $\sigma$  bonding alone is influential in these spectra. As a result of this treatment one sees the difference in  $k_1$  between the phosphine and amine complexes appears to reflect the  $\pi$  component of M-L bonding. While application of this model<sup>1</sup> is not a proof, *a priori*, that  $\pi$  bonding plays a significant part in determining this observed effect of a ligand, one

(1) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968).

(2) CO stretching force constants are those obtained from the Cotton-Kraihanzel method;<sup>3</sup>  $k_1$  is the force constant associated with the CO group *trans* to L and  $k_2$  is the force constant of the CO groups *cis* to L.

(3) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(4) R. J. Angelici and M. D. Malone, *Inorg. Chem.*, **6**, 1731 (1967).

(5) W. D. Horrocks, Jr., and R. C. Taylor, *ibid.*, **2**, 723 (1963); F. A. Cotton, *ibid.*, **3**, 702 (1964), and references therein.