

N-METALLATED SILICON-NITROGEN DERIVATIVES: PREPARATION, STRUCTURE AND REACTIONS

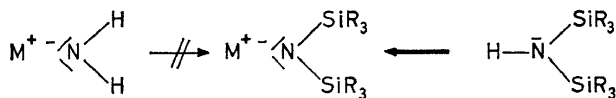
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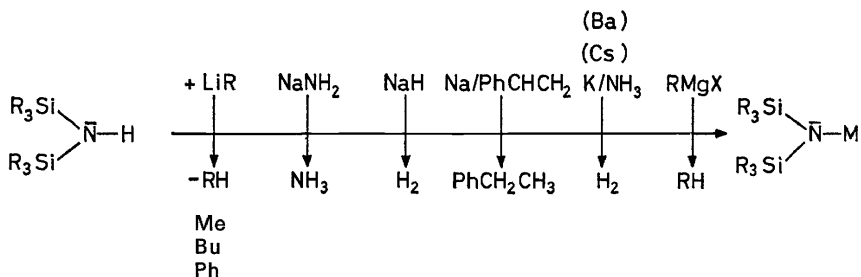
Ten years ago N-metallated silicon-nitrogen compounds were still unknown. Today the lithium as well as the sodium derivative of hexamethyl-disilazane belong—second only to hexamethyldisilazane itself—to the most investigated of SiN-compounds.

In 1959 we metallated for the first time the triorganylsilyl derivatives of ammonia and hydrazine with phenyllithium. The resulting N-substituted lithium compounds could be isolated. They were of interest to us primarily with respect to their transformation into multiple silylsubstituted derivatives of ammonia and of hydrazine. Later we noticed that they presented an extraordinary variety of preparative problems, and their physical properties turned out to be unusual and unpredictable. The more involved we became with the structure of these compounds the more enigmatic they seemed. Even today we can only describe many of them and explain little. In each new investigation they bring more surprising results, and the possibilities for their synthesis seem far from exhaustion.

Well to the fore of interest are SiN-compounds substituted on the N-atom by alkali metals, and here again the doubly silylsubstituted amides have become the most important. It is not possible to prepare them by substitution of the H-atoms of the alkali amides. One must start with disilazanes and metallate them:



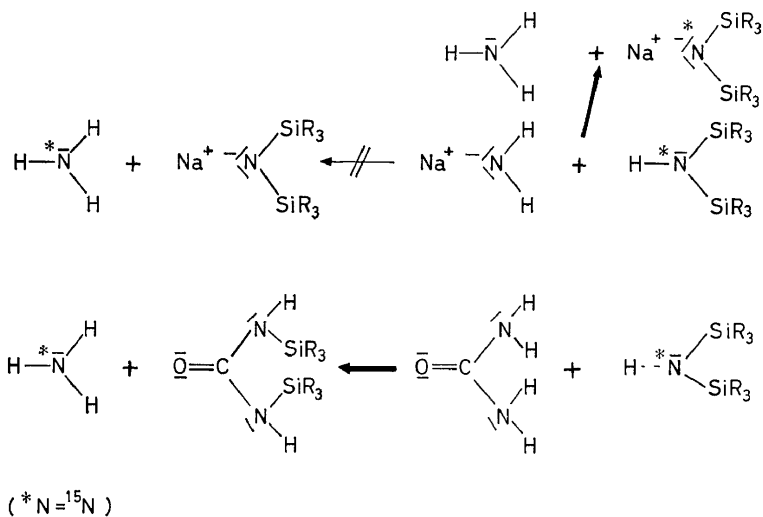
Organolithium compounds were the first to be used successfully in these metallation reactions. For the preparation of the sodium derivatives heating of the disilazanes with sodium amide, finely suspended in aliphatic hydrocarbons, proved to be effective. Next to this reagent sodium hydride or metallic sodium in vinylbenzene are practicable. The derivatives of potassium, rubidium and caesium are best prepared via the amides of those metals in liquid ammonia, but one can also start in this solvent with the metals themselves. Grignard reagents react in a way comparable to the organolithium compounds:



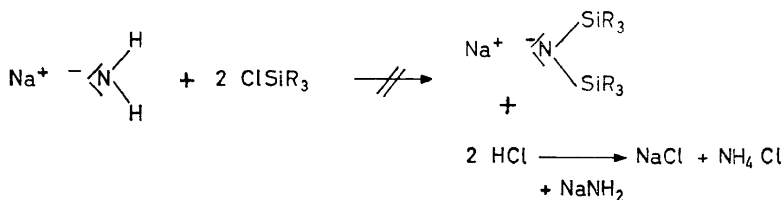
Looking at the reactions with sodium amide we were interested in the source of the escaping ammonia. If the ammonia nitrogen stems from the amide ion, the reaction is a true metallation process. (This process might be looked upon also as a neutralisation process in the ammonia system, between the weak acid hexamethyldisilazane and the strong, but not dissolved base sodium amide in an organic solvent, comparable to a reaction of acetic acid with sodium hydroxide in boiling toluene). The alternative is a silylation reaction with hydrogen substitution at the amide ion. In this case the ammonia would be formed by the disilazane nitrogen.

Investigations with ^{15}N (in the diagram = *N) proved without doubt, that the ^{15}N is completely transferred to the sodium bis(trimethylsilyl)amide, and that the escaping ammonia is free from ^{15}N .

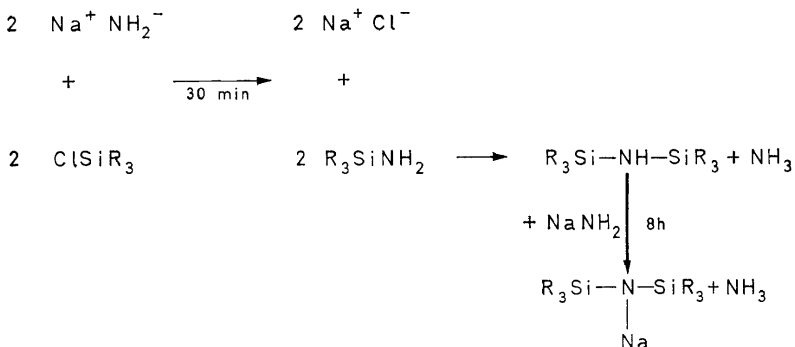
This is not such a matter of course as it seems. In the analogous reaction of carbonyldiamide (urea) the alternative process occurs: the escaping ammonia contains all the ^{15}N -atoms, so the NH_2 -group must have been silylated.



If special conditions at the start are observed, sodium amide even reacts with trimethylchlorosilane to give sodium bis(trimethylsilyl)amide. But here again no double silylation of the amide ion takes place:

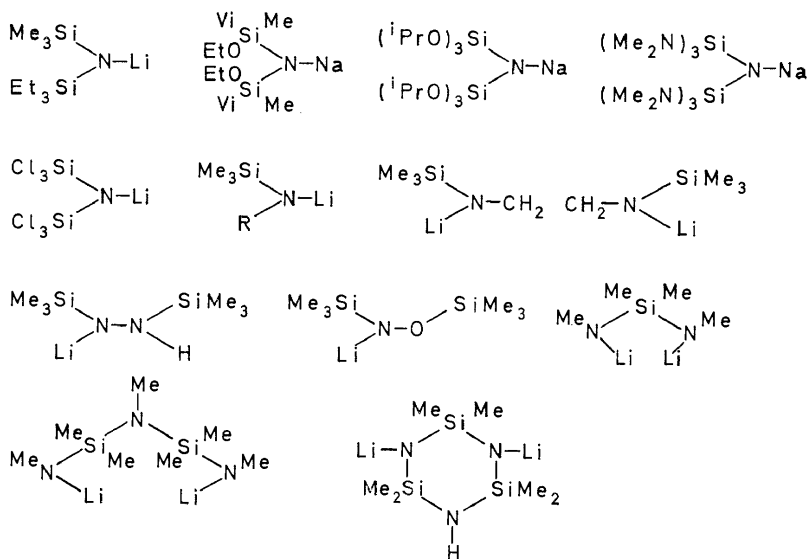


This reaction proceeds via hexamethyldisilazane. The first step of the reaction, the exchange of Cl by NH₂, proceeds at a moderate rate, the condensation of the trimethylsilylamine is very fast, and only the metallation requires a longer time.



Silylsubstituted alkali amides are not limited to the derivatives of hexamethyldisilazane. It is possible to prepare silylsubstituted alkali amides with two different triorganysilyl groups, or with silyl groups in which all three substituents at the silicon atoms are varied, for example methyl and vinyl and ethoxy, or with groups which are bound to the silicon atom only via oxygen or nitrogen atoms. Even completely inorganic substances of this class of compounds are known, such as lithium bis(trichlorosilyl)amide.

In addition metallated derivatives of single silylsubstituted organylamides are still more easily prepared. Here lithium trimethylsilyl-methyl-amide (in the next diagram, R = methyl) became very successful in the hands of Scherer, the dilithium derivative of the N,N'-bis(trimethylsilyl)ethylene-diamine in the school of Rochow. We ourselves were also able to perform metallation reactions at nitrogen derivatives, in which the nitrogen atom has oxidation numbers higher than (-3), in silylsubstituted hydrazines (oxidation number -2), and in hydroxylamines (oxidation number -1). They tend to anionic rearrangements according to the experiments of West. The double lithium metallated derivatives of bis(methylamino)-dimethylsilane and of 1,3-bis(methylamino)pentamethyl-disilazane were used for many syntheses of cyclic SiN-compounds by Rochow, Fink and by our own school. The metallation of cyclosilazanes and their following reactions were successful in a lot of examples as shown by Fink and later by Breed.

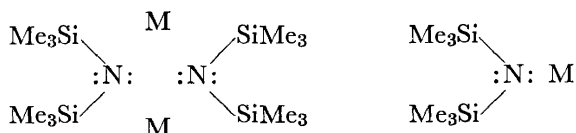


Most of the metallated derivatives mentioned were prepared only in solution and reacted from those solutions without isolation. Some of them were isolated but not characterized. But today the metallation of a Si-NH-unit has become one of the most important operations in silicon-nitrogen chemistry, in all the cases in which the H-atom of this Si-NH-unit is to be replaced by other groups. This metallation reaction has been successful in hundreds of examples.

But let us return to the alkali bis(trimethylsilyl)amides. They are obtained by the preparation methods mentioned earlier in well shaped crystals. Their melting points are comparatively sharp, but sensitive to the presence of impurities. It still remains a mystery why the compounds prepared from ethereal solutions melt 20 and more degrees lower than those from hydrocarbon solutions without showing differences in other properties or analytical composition. It may be that traces of remaining ether are responsible for it. They are all readily soluble in ether, the sodium and lithium compounds as well as in non polar aromatic hydrocarbons: 100 g of xylene dissolve 140 g of the lithium compound at 30°. The lithium and the sodium compounds are distillable *in vacuo* without decomposition. Their boiling points at 1 and 2 mm are 115° and 202°, respectively. Cryoscopic and ebullioscopic measurement of the molecular weights in different solvents indicates dimeric molecules of the lithium and the sodium compounds, whereas the potassium, rubidium and caesium derivatives are insoluble in hydrocarbons and more saltlike in character. By mixing solutions of the lithium compound with the sodium or potassium compound, respectively, new mixed compounds are formed. They have their own melting points and X-ray diagrams, different from those of the starting material. The molecular weights are in agreement with the dimeric type of molecules. All these pure and mixed alkali silylamides show their own characteristic wave numbers of the asymmetric SiNSi stretching vibration. In the same manner as the lithium and the sodium

N-METALLATED SILICON-NITROGEN DERIVATIVES

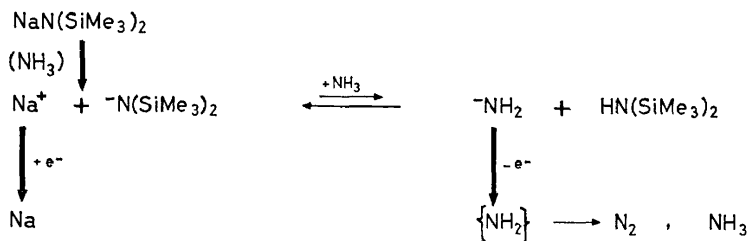
Table 1. Physical data of dimeric and salt-like alkali bis (trimethylsilyl) amides



M	Li	Li	Li	Na	K	Rb	Cs
m.p.	87°	181°	202° (from ether)	183°	165°	178°	195°
b.p. (torr)	115° 1			202° 2			
ν_{as} SiNSi (cm ⁻¹)	973	1042	1071	1035	1085	1106	1095

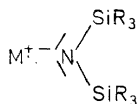
bis(trimethylsilyl)amides, many analogous alkali silylamides with different substituents at the silicon atoms are dimeric.

The constitution of these dimeric compounds was and still remains somewhat mysterious. They show no electrical conductivity, either in solution or in the melt, so they cannot have ionic structures. But they dissolve in liquid ammonia with dissociation. On electrolysis of these solutions the cathode region immediately displays the blue colour of the alkali metal/ammonia system, and at the anode nitrogen is evolved. With mercury as the cathode material the whole Na-amount of the dissolved sodium bis(trimethylsilyl)amide is recovered in the sodium-mercury alloy; analysis of the hexamethyldisilazane amount nearly quantitatively confirms the next equation.

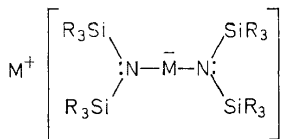


From solutions in ammonia the sodium bis(trimethylsilyl)amide recrystallizes nearly undecomposed. So solutions of this compound in ammonia may be compared with those of sodium acetate in water, in which are found OH⁻ ions and free CH₃CO₂H, but from which pure CH₃CO₂Na is regained.

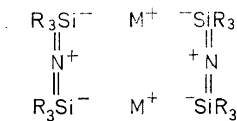
Since the dimeric molecules of the sodium and lithium derivatives are not ionic in character, the formulae (a), (b) and (c) below are only hypothetical. A dimerization as noted in formula (d) is ruled out by spectroscopic investigations. So the assumption is justified that both electron pairs of a single nitrogen atom will form donor bonds to the metal atoms, but even this model (e) does not reflect the true state.



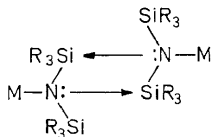
(a)



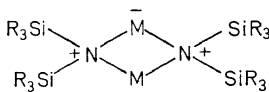
(b)



(c)

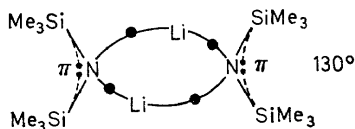


(d)



(e)

In view of the results of the spectroscopic group of our institute, headed by Dr Buerger, we think the following proposal of N—Li—N three centre bonds in the dimeric molecules of lithium bis(trimethylsilyl)amide in solution harmonizes in the best way with all our measurements and observations. A single signal in the ${}^7\text{Li}$ nuclear magnetic resonance spectrum shows that both the lithium atoms are equivalent. Infrared and Raman spectroscopy point to SiNSi bond angles near 130° . One of the lone nitrogen electron pairs gives fairly strong π -bonds with the neighbouring silicon atoms; the silicon-nitrogen stretching force constant (only 2.9 mdynes/Å for a single σ —SiN—bond according to calculations of Gordy), is strengthened to 3.7 mdynes/Å. By interpretation of the vibrational spectra from the ${}^6\text{Li}$ as well as from the ${}^7\text{Li}$ compounds, we discovered the lithium-nitrogen vibrations. They are relatively weak. The stretching force constant corresponds—with 0.7 mdynes/Å—to a bond order of 0.6 . So on average only four electrons bind the two lithium and two nitrogen atoms, analogous to diborane or to the dimeric trimethylalane.



Li—N	$f = 0.7$	mdynes / Å
Si—N	\curvearrowright	3.7
Si—N	$\ddot{\cdot}$	2.9

Figure 1 shows a refined model (a) of this dimeric lithium bis(trimethylsilyl)amide in solution. There is sp^2 -hybridisation at the nitrogen atoms implying the calculated SiNSi bond angles of 120 – 130° . The vertical p -orbitals of the N-atoms allow for $(p \rightarrow d)_\pi$ -bonds to the silicon atoms. From the increase of the SiN stretching force constant of all the SiN bonds (3.7

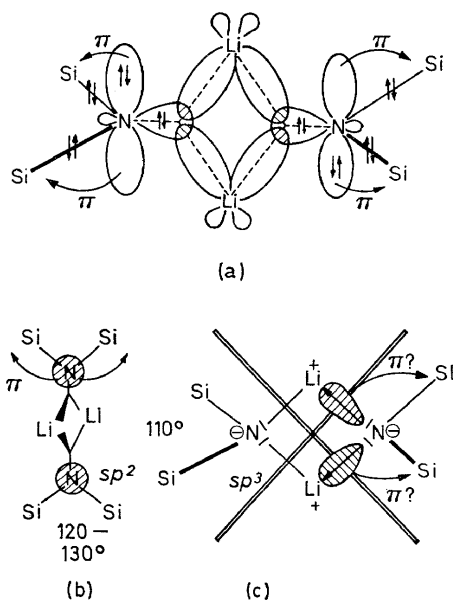


Figure 1. Refined model of the dimeric lithium bis(trimethylsilyl) amide molecule in solutions.

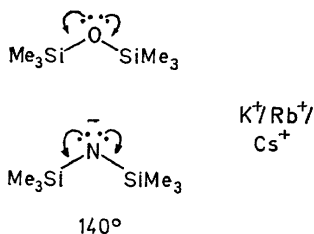
mdynes/Å), exceeding the 2.9 mdynes/Å value of the SiN single bond by 30 per cent, one may conclude that a large portion of these p -orbitals of the N-atoms is absorbed by such ($p \rightarrow d$) π bonds to the silicon atoms.

This same configuration, seen from above and turned through 90° , is shown in Figure 1(b).

The alternative model (c) requires sp^3 -hybridisation at the nitrogen atom, SiNSi bond angles of 110° , and LiN bonds stronger than those observed. Furthermore it does not show how the big increase of the SiN stretching force constant would occur. So we have to reject it in favour to model (a)/(b).

From a structure model of the dimeric lithium bis(trimethylsilyl)amide composed from balls according to the suggestions of Sanderson, the SiNSi as well as the NLiN connections can be recognized. The molecule appears extraordinarily compact, but this is in accordance with its excellent solubility and its low boiling point of 115° at 1 mm.

The bis(trimethylsilyl)amides of the potassium, rubidium and caesium are much more saltlike in character. They do not dissolve in hydrocarbons, and only to a moderate amount in ether. The vibration spectroscopic analysis of the solid compounds shows the typical spectrum of a bis(trimethylsilyl)amide ion: there is a complete analogy to the isoelectronic hexamethyldisiloxane. As both of the lone nitrogen electron pairs are free for π -bonding to silicon, the SiN stretching force constant is still more strengthened to 4.3 mdynes/Å. So the SiN bonds are here 50 per cent stronger than in a single σ -SiN bond.



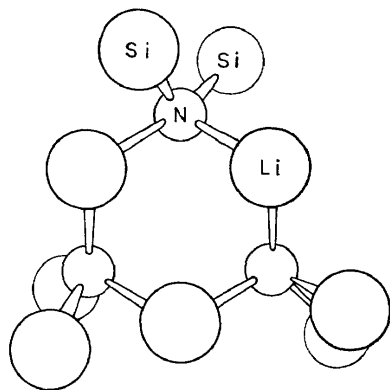
Normally the transformation of a hydrogen compound into its anion by deprotonation brings about a decrease of the stretching force constants or of the wave numbers of the remaining bonds, as can be seen from the examples of water and ammonia. But in the neighbourhood of atoms with vacant *d*-orbitals, such as chlorine, phosphorus or silicon, an increase of the force constants or wave numbers takes place instead. This can only be interpreted by assuming (*p*—*d*)_{*n*} bonds—in our case by SiN (*p* → *d*)_{*n*} donor bonds.

Table 2. Evidence of (*p* — *d*) π bonds in SiN⁻ and SiO⁻ units from force constants and wave numbers.

	f (mydn/Å)			$\bar{\nu}$	(cm ⁻¹)
HN	H ₂ N—H	6.54	HO	HO—H	3707
	H ₂ N ⁻	5.76		HO ⁻	3635
SiN	(Me ₃ Si) ₂ N—H	3.8	SiO	Me ₃ SiO—H	880
	(Me ₃ Si) ₂ N ⁻	4.3		Me ₃ SiO ⁻	985

The vibration spectra of dissolved and solid lithium bis(trimethylsilyl) amide are different, the solid spectrum somewhat resembling the one of the solid potassium derivative. So we hoped, by an X-ray structure analysis of the key substance lithium bis(trimethylsilyl)amide, to detect the transition state between the dimeric and saltlike species of alkali bis(trimethylsilyl) amides. The lithium compound was recrystallized from petrolether and its structure solved from more than 3000 photographic Weissenberg data in the X-ray structure laboratory of our institute, headed by Prof. Mootz. The lithium compound crystallizes monoclinic in a rather large unit cell with dimensions *a* = 8.827, *b* = 31.875, and *c* = 12.312 Å, β = 104.90° and the cell volume 3347.6 Å³. The space group is P 2₁/c. The unit cell contains 12 lithium bis(trimethylsilyl)amide formula units which seem to be contracted to four blocks of three molecules.

The evaluation of the X-ray data for the structural parameters, which were only recently refined, was very surprising: we did not find either an ionic structure or a dimeric compound, but a trimeric unit, in which the three molecules are combined in a LiN six-membered ring. The SiNSi bond angle with its 119° points to the usual *sp*² hybridisation of the N atom attached to two silicon atoms, and the SiN bond distance, on average 1.74 Å, is no shorter than in all the other SiN compounds investigated by X-ray analysis, rather a little longer.



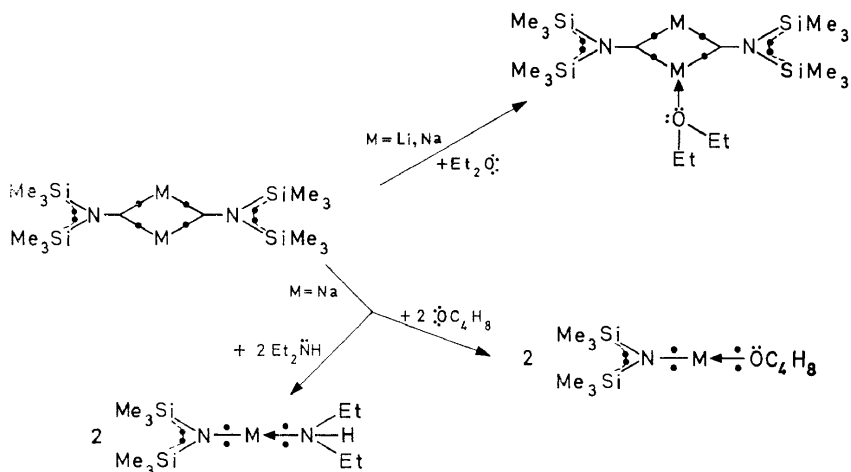
SiNSi	119°
Si-N	1.74 Å
NLiN	148°
LiNLi	92°
Li-N	2.01 Å

Figure 2 Parameters of the solid, trimeric lithium bis(trimethylsilyl) amide.

We know from other six-membered rings that the data of vibrational spectroscopy point to spectroscopic independent groups (in this case Si_2N groups), whereas four-membered rings give skeleton vibrations of the whole ring system. So in this way we may explain the similarity of the infrared spectrum of this solid trimeric lithium bis(trimethylsilyl)amide with the spectrum of the saltlike potassium derivative with its bis(trimethylsilyl)anion. This may also explain the nonconductivity of this lithium compound in the melt and its high solubility in nonpolar organic liquids. But we do not know why this trimeric molecule reduces to a dimeric molecule in solution. After these surprising X-ray results we repeated, somewhat irritated, our molecular weight determinations in several different solvents. But the results confirmed once more the dimeric units. Unfortunately until now we were unable to obtain a mass spectroscopic molecular weight for the solid lithium compound: the operators always hydrolyzed it before introducing it into the spectrometer.

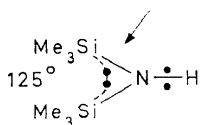
The dimeric molecules behave like electron deficient compounds. So they react with electronpair donors under cleavage of the LiN rings. But even here the dimeric units survive in certain cases. With diethylether the lithium as well as the sodium bis(trimethylsilyl)amide forms adducts of the composition $[\text{MN}(\text{SiMe}_3)_2]_2 \cdot \text{OEt}_2$. In boiling ether their molecular weights correspond to the calculated values for the dimers. But tetrahydrofuran or diethylamine form monomers, in agreement with their elemental analysis and their molecular weights. In the adducts—the dimers as well as the monomers—the ν_{as} SiNSi stretching vibrations are shifted to higher wave numbers: from 1035 cm^{-1} in the dimeric sodium bis(trimethylsilyl)amide to 1065 cm^{-1} in its dimeric ether adduct, to 1065 cm^{-1} in the monomeric tetrahydrofuran adduct and to 1060 cm^{-1} in the diethylamine adduct. This indicates

that the N-electrons are occupied to a lower extent by the metal atoms, owing to the participation of the metal atoms in the electron pairs of the ether and amine donors. In the adducts the bis(trimethylsilyl)amino groups approach to a certain degree the state of the bis(trimethylsilyl)amide anions.

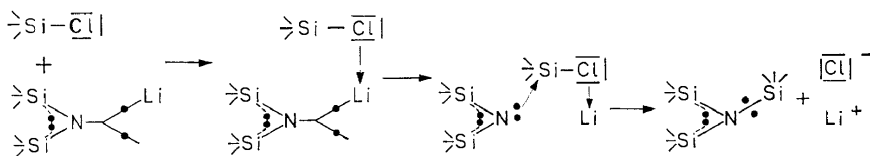
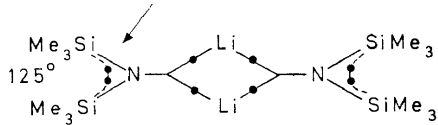


The alkali bis(trimethylsilyl)amides have become very useful reagents in preparative inorganic chemistry. Readily soluble in ether and in aromatic hydrocarbons, they easily react with other compounds. In most cases they react as if they possessed free, strong nucleophilic bis(silyl)amide anions. But from this point of view alone one cannot understand why they are so much more effective than the hexamethyldisilazane itself. In this compound as well as in its lithium derivative the N atoms are sp^2 hybridized, the SiNSi bond angles 125° and the values of the SiN stretching force constants $3.7/3.8$ m dynes/ \AA . I think it is the metal atom which starts the reaction by attack on a free electron pair of the reactant, according to the formation of the adducts mentioned above. The three-centre bond electrons now return to the N-atom of the bis(silyl)amino group, which then acts like a strong nucleophilic bis(silyl)amide ion and adds—in our example—to the silicon atom of the reactant.

$$f = 3.8 \text{ m dynes / \AA}$$

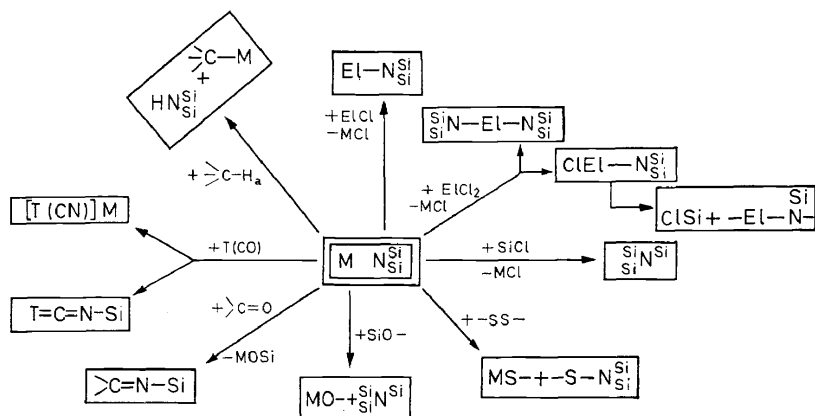


$$f = 3.7 \text{ m dynes / \AA}$$



M-METALLATED SILICON-NITROGEN DERIVATIVES

Let us look on the most important reactions of the alkali bis(trimethyl silyl)amides. They transform many chlorides of non-metals, and even of transition metals, into their double silylsubstituted amines. With dichlorides, both the chlorine atoms may be substituted. But if there is only substitution of a single chlorine atom, the detachment of chlorosilane may follow in certain cases, and the element-nitrogen-silicon fragment polymerize or, for example with boron, join to four- or six-membered rings. With chlorosilanes, tris(silyl)amines are formed. Sulphur-sulphur bonds are cleaved, as detected by Schmidt and Scherer, giving mercaptides and silylsubstituted sulphenic acid amides. Even silicon-oxygen bonds may be cleaved. Organic carbonyl groups are transformed into silylsubstituted ketimines. Transition



Si = Si (CH₃)₃

metal carbonyls form silylisocyano or even cyanide complexes. Organic compounds with active hydrogen are metallated; acetonitrile may be transformed according to Krueger and Rochow into the mono-, di or tri sodium compound, and with heavy water, the N-deuterated hexamethyldisilazane is obtained. The alkali bis(silyl)amides have also served well in many cases as basic compounds in Claisen, Stobbe or Wittig reactions.

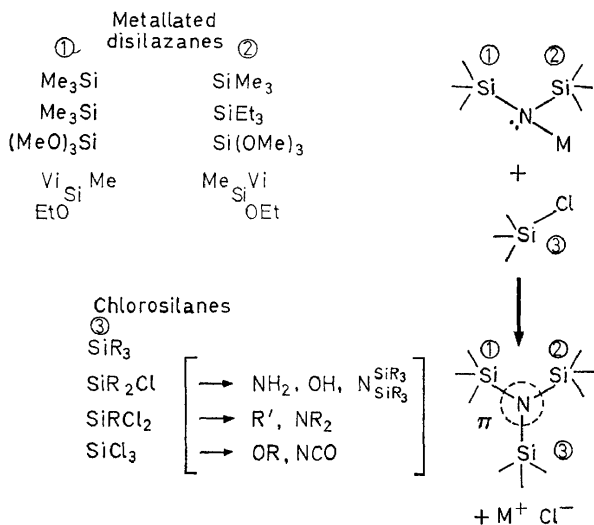
A survey on all elements from which compounds with bis(trimethylsilyl)-amino groups are known—prepared via metallation reactions of hexamethyldisilazane, or by following reactions of the alkali bis(trimethylsilyl)amides according to the last diagram, is shown in *Figure 3*. There are only a few

Figure 3. Survey of compounds $EIN \begin{smallmatrix} Si \\ Si \end{smallmatrix}$ or $EIN \begin{smallmatrix} Si \\ Me \end{smallmatrix}$

H																		He	
Li	Be													B	C	N	O	F	Ne
Na	Mg													Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		

among the representative elements (for example calcium, strontium, gallium, indium, thallium and fluorine), which have not been investigated or which have so far resisted such experiments. The transition metal derivatives from chromium to copper are extremely sensitive to moisture and oxygen, and must be examined in more detail. Compounds of the elements shown in shading were first prepared by our own school. A few of them (B, Al, P, S) were already known in the composition EI—NH—Si by cleavage reactions of hexamethyldisilazane with the element halogenides. In all other cases the combination EINSi was obtained for the first time. In the discovery of the halogen derivatives mainly West and Wiberg were engaged. Scherer synthesized the derivatives of the block of elements down the line from germanium to selenium, but some are only known with trimethylsilyl-methyl-amino groups.

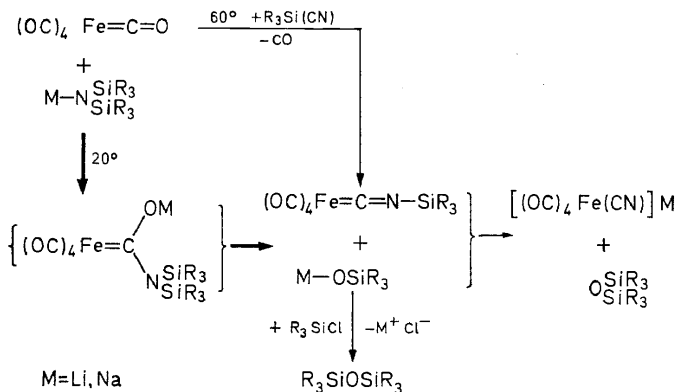
Let me give a few of the reactions of the alkali bis(trimethylsilyl)amides in more detail. Chlorosilanes may represent the reactions with element halides. These lead to tris(silyl)amines. We can vary both of the silyl groups in the amides; we may take the same or different trialkylsilyl groups, or take methoxy groups instead of alkyl groups; or we may even use three different substituents on the silicon atoms. On the other hand, we can employ



chlorosilanes with functional groups and transform them later into amino-hydroxy, alkyl or cyanato groups. So it was possible to construct nearly all the tris(silyl)amines we wished to have. Ten years ago there existed only the trisilylamine $\text{N}(\text{SiH}_3)_3$ of Stock. Today we know more than a hundred compounds with a Si_3N -unit.

Remember that alkali bis(silyl)amides substitute the oxygen atoms in organic carbonyl groups and transform them into silylsubstituted ketimines. With carbon monoxide, reacted in a sealed vessel, they give alkali cyanides and disiloxane. They also react very vigorously with metal carbonyls: cyanocarbonylmetallates are the reaction products. There are hundreds of experi-

ments in which substitution reactions on metal carbonyls proceed by displacement of carbon monoxide. Here we have the first example in which only an oxygen atom is substituted whereas the metal-carbon bonds remain fixed. The proof was possible by isolation of the trimethylsilylisocyanotetracarbonyl-iron in high yield as intermediate in the reaction of pentacarbonyl-iron with lithium or sodium bis(trimethylsilyl)amide, if the simul-

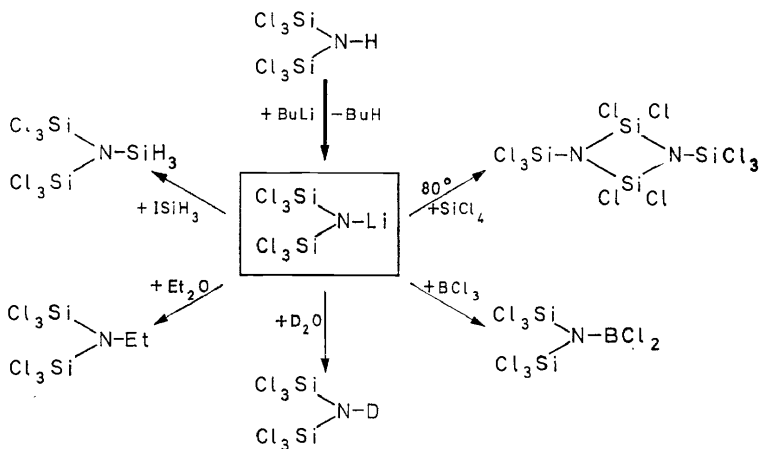


taneously formed alkali silanolate was destroyed by addition of chlorosilane. If we add the silanolate to the pure isocyanocarbonyliron compound, we obtain the cyanocarbonylferrate and hexamethyldisiloxane. The key substance trimethylsilylisocyanotetracarbonyl-iron was first prepared by Seyferth(MIT); but he displaced a CO molecule by trimethylsilylcyano at temperatures above 60°. However, we excluded the possibility of the Seyferth reaction during our process, and proved in many other cases the O-substitution in metal carbonyls without cleaving the metal-carbon bond.†

The symbol of this symposium is C_{Si} . So I hope I am not mistaken if I interpret the term "organosilicon" in the classical meaning: chemistry of non silicatic compounds, of volatile, covalent silicon compounds comparable to the volatile compounds of carbon. Accordingly I should like to tell you at the end of my lecture something about lithium bis(trimethylsilyl)amide, a sole inorganic SiN compound. It can easily—and in high yield—be prepared by the reaction of hexachlorodisilazane with butyllithium, and no Cl substitution on the silicon takes place during this reaction. It is only slightly soluble in organic liquids, but it reacts in many cases from its suspensions giving new and unknown inorganic compounds and classes of compounds.

With iodosilane it furnishes silyl-bis(trimethylsilyl)amine, m.p. - 50°, b.p. 91°/33 mm. Silicon tetrachloride, however, does not supply the analogous tris(trimethylsilyl)amine, but the four-membered ring compound of decachloro-N, N'-bis(trimethylsilyl)cyclodisilazane, m.p. 66°. The same compound is formed by heating lithium bis(trimethylsilyl)amide to 80° and by reacting

† Cf. Paper presented by my coworker, G. Schirawski in the discussion lectures at the Second International Symposium of the Chemistry of Organosilicon Compounds held Bordeaux, July 1968, *Resumes des communications*, p. 194.



it with silicon tetrabromide or with germanium tetrachloride, so it must originate from the fragments of the amide after displacement of lithium chloride. With ether no adduct was formed, but N-ethyl bis(trichlorosilyl)-amine, b.p. 205°. Heavy water cleaves only the LiN, not the SiCl bonds: the N-deuterated hexachlorodisilazane results. Boron trichloride is transformed into the dichloroboryl-bis(trichlorosilyl)amine, b.p. 210°. This compound shows the weakest boron nitrogen stretching force constant ever observed, with 5 instead of the normal 7 mdynes/Å of a BN bond. The opposite "world record" of the strongest silicon nitrogen bond is held by lithium bis(trichlorosilyl)amide itself: 5.0 mdynes/Å, nearly 60 per cent above the value of the SiN single bond. So this compound has opened a wide field in synthesizing new inorganic compounds, and we still expect much from it.