

The Silicon Effect in Metallic Silylamides

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Summary: The alkoxy-silazane $t\text{BuO-SiMe}_2\text{-N(H)-CMe}_3$ (1), which has a tert-butyl substituent at nitrogen and the corresponding trimethylsilyl derivative $t\text{BuO-SiMe}_2\text{-N(H)-SiMe}_3$ (2) can be transformed to amides of divalent transition metals. While $(t\text{BuO-SiMe}_2\text{-N-CMe}_3)_2\text{Ni}$ is blue and has a paramagnetism of 3.25 B.M., the corresponding $(t\text{BuO-SiMe}_2\text{-N-SiMe}_3)_2\text{Ni}$ is red and has a paramagnetism of 2.41 B.M. If Ni is substituted by Co the differences in B.M. of the two derivatives are even greater (4.05 B.M. versus 1.86 B.M.). The dithium salt $\text{Me}_2\text{Si(NCMe}_3)_2\text{Li}_2$ reacts smoothly with PbCl_2 to yield the metallacycle $\text{Me}_2\text{Si(NtBu)}_2\text{Pb}$, while in the case of the more silicon-rich amide $\text{Me}_2\text{Si(NSiMe}_3)_2\text{Li}_2$ a hetero-metallic amide $[\text{Me}_2\text{Si(NSiMe}_3)_2\text{PbLi}_2]$ is obtained from the reaction with PbCl_2 . The latter procedure may be used to synthesize similar heterometallic silylamides. If in hexamethyldisilazane two of the methyl groups are substituted by *t*-butoxy-groups, an alkoxy-silazane $(t\text{BuO})\text{SiMe}_2\text{-N(H)-SiMe}_2\text{(OtBu)}$ originates, which has chelating capabilities. A number of divalent metallic elements can be bound to the nitrogen, replacing hydrogen. All derivatives of the general formula $[\text{M}_2\text{Si(OtBu)}]_2\text{N-M-N}[(\text{OtBu})\text{SiMe}_2]_2$, $\text{M} = \text{Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Ba}$, behave as molecular compounds with no further organic base linked to the metallic element M. A comparison of different structures shows that the ligand $[\text{Me}_2\text{Si(OtBu)}]_2\text{N}$ can adopt quite different chemical bonding.

Introduction

If a carbon-nitrogen bond is compared to a silicon-nitrogen bond, important differences appear as summarized in Figure 1. Generally speaking, the Si-N bond is more polar because of the greater differences in electronegativity and covers a greater range of bond lengths in crystal structures compared to C-N. Semiempirical methods [1] show that the charge on the nitrogen atom is considerably higher in the Si-N case compared to C-N. Roughly speaking, the partial negative charge at nitrogen is almost doubled if a carbon atom adjacent to the nitrogen is replaced by a silicon atom. From these findings, it is obvious that silylamido groups should be better ligands for metallic elements than organylamido groups. As a matter of fact, simple metal salts of hexamethyldisilazane are known with a great variety of metallic elements and have the common property of enabling low coordination numbers at the electropositive element. Thus, $\text{LiN}(\text{SiMe}_3)_2$ forms a trimer with a planar six-membered Li_3N_3 ring, the lithium atoms displaying mainly two bonds to the adjacent nitrogen atoms [2]. Another well known example of a low-coordinated metallic element is found in $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_3$, the iron atom being in the center of a trigonal

planar arrangement [3]. It seemed interesting to us to explore further properties of metal silylamides in order to promote understanding of the bonding. In the following article, several pairs of metal amides will be described which differ only in one atom (a silicon atom is situated in the place of the carbon atom attached to nitrogen). Furthermore we will show that a special alkoxy-silylamido group can be used in order to coordinate very electropositive elements very efficiently.

$\text{>Si-N} \begin{matrix} \diagup \\ \diagdown \end{matrix} \begin{matrix} \text{M} \\ \text{M} \end{matrix}$	Si-N	C-N
$\text{>C-N} \begin{matrix} \diagup \\ \diagdown \end{matrix} \begin{matrix} \text{M} \\ \text{M} \end{matrix}$	1.70 - 1.83	1.44 - 1.49
	Bond length [Å]	304.6
	Bond energy [kJ/Mol]	335
	Δ EN	1.14
	+I	→
	-I	←
The silicon substituted nitrogen atom is the more appropriate ligand for metals		

Figure 1. Comparison between silicon and carbon substituted amides

1 Ni and Co Derivatives of Two Alkoxy-silazanes Differing only in C and Si in One Position

Displacement of amino-hydrogen atoms by lithium can be accomplished when $t\text{Bu-O-SiMe}_2\text{-N(H)-CMe}_3$ (1) or $t\text{Bu-O-SiMe}_2\text{-N(H)-SiMe}_3$ (2) is allowed to react with butyllithium [4]. The lithium salts which are well soluble in organic solvents can be further reacted with NiCl_2 or CoCl_2 in a diphasic system yielding lithium chloride and the oxygen- and water-sensitive nickel (3a, 3b) and cobalt (4a, 4b) salts.

As can be seen from Table 1, not only the spectral data are quite different between pairs of compounds, but also the paramagnetism is decreasing when the carbon atom attached to the nitrogen is replaced by silicon, all other atoms being equal. As we have not been able to determine the molecular structures of the compounds until now, we cannot ascribe the change in properties to a definite change in structure. Nevertheless it seems obvious that the carbon or silicon atom in β -position to the metal must have an important impact on the orbital-splitting at the transition element.

Table 1. Comparison of Pairs of Ni- and Co-Salts

$[t\text{Bu-O-SiMe}_2\text{-N-CMe}_3]_2\text{Ni}$ 3a	$[t\text{Bu-O-SiMe}_2\text{-N-SiMe}_3]_2\text{Ni}$ 3b
UV: 572 nm ($\epsilon = 192$) 630 nm (112)	UV: 554 nm ($\epsilon = 213$)
B.M.: 3.25	B.M.: 2.41
$[t\text{Bu-O-SiMe}_2\text{-N-CMe}_3]_2\text{Co}$ 4a	$[t\text{Bu-O-SiMe}_2\text{-N-SiMe}_3]_2\text{Co}$ 4b
UV: 502 nm (49) 566 nm (94) 666 nm (103)	UV: 472 nm (55) 560 nm (80) 615 nm (80) 640 nm (84) 663 nm (80)
B.M.: 4.05	B.M.: 1.86

2 Reactivities of Two Types of Lithium Salts

H. Bürger and coworkers have been able to show that $\text{Me}_2\text{Si(NCMe}_3)_2\text{Li}_2$ is dimeric in solution and in the solid with a distorted tetrahedral arrangement of the lithium atoms. All lithium atoms are equivalent and have three contacts to nitrogen atoms [5]. The corresponding $\text{Me}_2\text{Si(NSiMe}_3)_2\text{Li}_2$, which differs from the former compound only in a C/Si substitution at nitrogen, is also dimeric but has a completely different structure, with lithium atoms displaying in pairs either two or three nitrogen contacts [6]. The difference in structures between the two lithium salts is nicely reflected by their different reaction behavior towards PbCl_2 , as may be deduced from Figure 2.

The synthesis of this new compound can be accomplished by a route which is depicted in Eq. (1) [10].



The new silazane **5** may be reacted with activated metals, organometallic compounds or simple metal amides, or may first be transformed to its lithium salt and then reacted with metal(II) chlorides [11]. In all these cases, metal derivatives of **5** are obtained with the general formula $[\text{Me}_2(\text{tBuO})\text{Si}]_2\text{N}_2\text{M}$, which have no further base coordinated to the metal. So far we have synthesized amides with $\text{M} = \text{Ca}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Sr}, \text{Ba}$, all elements in oxidation state +2. X-ray structure determinations have been performed on the calcium, manganese, iron, zinc, and barium derivatives.

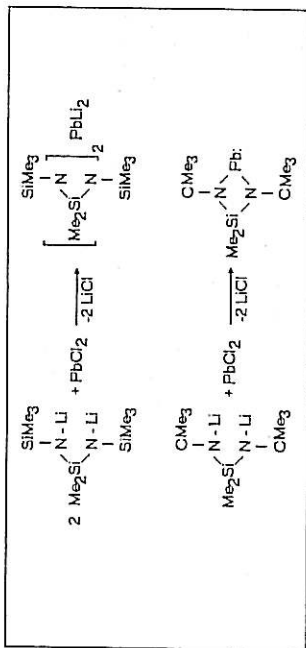


Figure 2. The different reactions of two lithium salts with PbCl_2

While in the case of the *t*-butyl derivative the metallacycle $\text{Me}_2\text{Si}(\text{NCMe}_2)_2\text{Pb}$ can be obtained in high yields [7], in the trimethylsilyl derivative only two of the four lithium atoms are displaced by lead, the amide formed incorporating two lithium and one lead atoms. This type of reaction may be used in order to access a whole variety of heterometallic silylamides (*omts* = octamethyltrisilylazyl) = $\text{Me}_2\text{Si}(\text{Me}_3\text{SiN})_2$: (*omts*) $_2\text{AlLi}$, (*omts*) $_2\text{InLi}$, (*omts*) $_2\text{FeLi}$, (*omts*) $_2\text{PbLi}_2$, (*omts*) $_3\text{Cd}_2\text{Li}_2$ [8]. Also, other monovalent metallic elements may be used in place of lithium, pushing the variety of molecules even further: (*omts*) $_2\text{InNa}$, (*omts*) $_2\text{InK}$, (*omts*) $_2\text{InIn}$, (*omts*) $_2\text{InTi}$ [8].

3 Chelating Properties of a Special Alkoxy-silazane

As stated in the introduction, hexamethyldisilazyl can be used to coordinate electropositive elements in a very efficient way. Nevertheless, with divalent metallic elements it is often found that further organic bases are coordinated to the metal: thus, in $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Cr}(\text{THF})_2$ the chromium atom is linked to two nitrogen and two oxygen atoms [9]. Such compounds tend to dissociate in the gas phase which makes them less appropriate for reactions controlled by pressure and temperature, as in MO-CVD processes.

We have overcome this problem by a very simple approach, formally replacing one of the methyl groups at each silicon in hexamethyldisilazane by an alkoxy group like *tert*-butoxy:

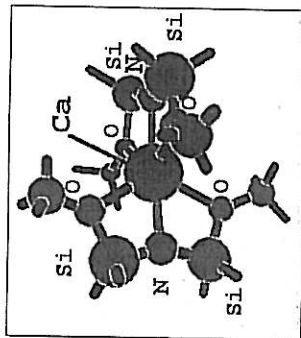


Figure 3. A sketch of the molecular skeleton of $[(\text{Me}_2(\text{tBuO})\text{Si})_2\text{N}_2]\text{Ca}$ as derived from X-ray analysis

In Figure 3 a rough sketch of the structure of the Ca compound is drawn. As can be seen, the metal is coordinated by two nitrogen and four oxygen atoms in a very distorted octahedral fashion. The other derivatives display similar structures, the two oxygen and the nitrogen atoms of the $[\text{Me}_2(\text{O}t\text{Bu})\text{Si}]_2\text{N}_2$ ligand being situated together with the silicon atoms in one plane. A plot of the Si-O and Si-N distances versus the M-N distances (as displayed in Figure 4) is very relevant: the more the interaction between the metal and nitrogen becomes weak (longer M-N distances), the more the Si-N bond becomes strong. On the other hand the correlation between the M-N distance and the Si-O distance is just the opposite, the Zn derivative displaying a very short Si-O bond. The dependence is linear from Zn to Ca, but then the line deviates from linearity as it continues to Ba. These findings may be interpreted by a more important bonding of the oxygen atoms to the metallic elements as the radii are increasing. In the calcium derivative this bonding seems to attain a saturation as the barium derivative has a shorter Si-O bond.

Another interesting plot is given in Figure 5. Here the radii of the metallic ions M^{2+} are correlated with the M-O and M-N distances. Again, the two dependences are in opposite direction (at least in the series Zn-Fe-Mn-Ca) with the exception of the barium compound.

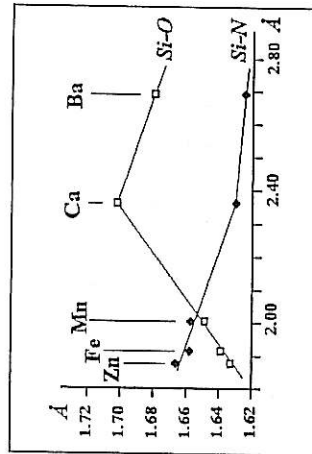


Figure 4. The Correlation between the M-N bond length (x-Axis) and the Si-O bond lengths (y-Axis) in $[(Me_2(rBuO)Si)_2N]_2M$, M = Zn, Fe, Mn, Ca, Ba.

The more the cation becomes larger, the more the M-O and M-N distances become closer together. This means that with small cations the M-N bond is dominant while with larger cations the oxygen atoms seem to take over the bonding at the expense of the M-N bond. This should of course have a direct impact on the bonding of the nitrogen to silicon.

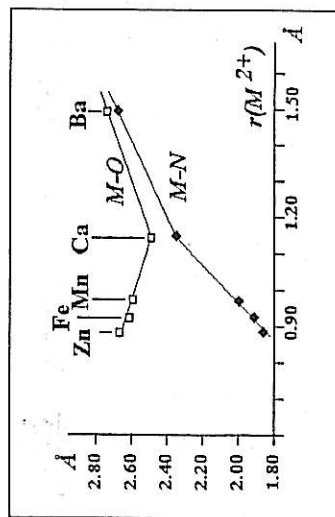


Figure 5. The Correlation between the ionic radii of the M^{2+} cations (x-axis) and the M-N and M-O distances (y-axis) in $[(Me_2(rBuO)Si)_2N]_2M$

As a matter of fact this can easily be visualized when the structures are superimposed one upon the other. In Figure 6 this has been done with the Zn, Ca and Ba derivatives (only one side of the

coordination at the metal is shown). The Si-N-Si angle within this series is dramatically changing from $137.3(3)^\circ$ (Zn) to $153.5(5)^\circ$ (Ca) and $151.9(6)^\circ$ (Ba). This situation is somewhat similar to the transition of a disilanimido group to a disilamido group as found in $[Li(12-crown-4)]_2[Ph_3Si-N-SiPh_3] \cdot THF$ [12].

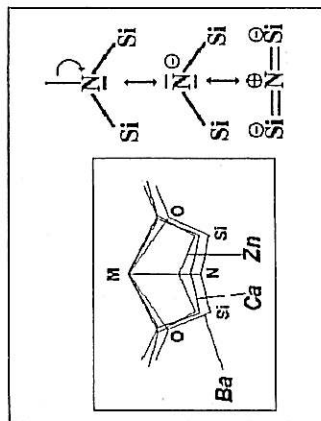


Figure 6. Superposition of molecular structures of $[(Me_2(rBuO)Si)_2N]_2M$, M = Zn, Ca, Ba and mesomeric structures for the Si-N-Si part

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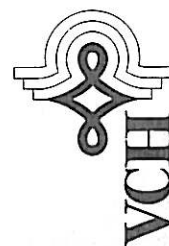
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