

# Fully Chlorinated *N*-Silyl Amides of Titanium and Tungsten – Crystal Structure of $\text{Cl}_3\text{SiNW}(\text{Cl}_3)\text{N}(\text{SiCl}_3)_2$

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The reaction of hexachlorodisilazanyllithium ( $\text{Cl}_3\text{Si}_2\text{NLi}$  (**1**), with  $\text{TiCl}_4$  leads selectively to the novel fully chlorinated amides ( $\text{Cl}_3\text{Si}_2\text{NTiCl}_3$  (**2**) or  $[(\text{Cl}_3\text{Si})_2\text{N}]_2\text{TiCl}_2$  (**3**), respectively, depending on the molar ratio of the starting materials. The analogous reaction of **1** with  $\text{WCl}_6$  yielded the amide imide  $\text{Cl}_3\text{SiN}=\text{W}(\text{Cl}_3)\text{N}(\text{SiCl}_3)_2$  (**5**) by elimination of  $\text{SiCl}_4$ . The relative amounts of the starting materials had no effect

on the formation of **5**.  $^{14}\text{N}$ - and  $^{29}\text{Si}$ -NMR data on the starting materials and products show significantly different effects, when compared with those of analogous *N*-trimethylsilyl derivatives, due to the lower energy of the electrons in the *N*-Si and *N*-M  $\sigma$  bonds. The crystal structure of **5** (triclinic, space group  $P\bar{1}$ ) was determined by X-ray structure analysis.

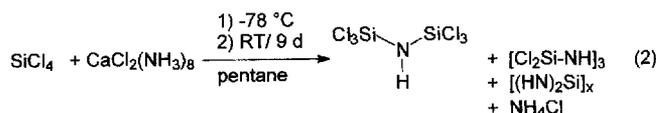
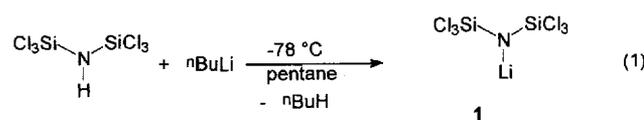
Fully chlorinated *N*-silylamido or -imido compounds are promising candidates for molecular preorganization leading to novel polymer, and highly crosslinked, silicon-nitrogen networks. For example  $\text{SiPN}_3$ <sup>[1]</sup> has been synthesized via the molecular precursor  $\text{Cl}_3\text{Si}-\text{N}=\text{PCl}_3$ , which already contains the required structural element of two vertex-sharing tetrahedra centered by, respectively, a phosphorus or a silicon atom, which are connected through a common nitrogen atom. Ammonolysis of this precursor, followed by thermal condensation, preserves this structural element and directly yields the highly crosslinked crystalline ceramic compound  $\text{SiPN}_3$ , which contains a network structure of corner-sharing  $\text{SiN}_4$  and  $\text{PN}_4$  tetrahedra<sup>[1]</sup>. A similar approach has been used for the synthesis of the non-crystalline ceramic  $\text{Si}_3\text{B}_3\text{N}_7$ <sup>[2]</sup>.

In the context of a systematic investigation of nitrido bridges between main-group elements and transition metals, we are now targeting molecular precursor compounds which might be valuable for the synthesis of ternary nitrides, or nanocomposites, in the system *Ti*-*Si*-*N* and *W*-*Si*-*N*. As in the synthesis of  $\text{SiPN}_3$ , fully chlorinated *N*-silylamido or -imido compounds of *Ti* and *W* seem to be appropriate candidates for this synthetic approach.

Several *N*-trimethylsilyl amides or imides with a large number of transition metals and main-group elements exist. Their synthesis by the reactions of metal halides with hexamethyldisilazane or with hexamethyldisilazanyllithium have been extensively studied in the literature<sup>[3–8]</sup>. In contrast there are only a few compounds reported with nitrogen-bearing trichlorosilyl groups instead of trimethylsilyl groups<sup>[9–11]</sup>, and *Zn* is the only transition metal reported so far<sup>[11]</sup> in these systems.

Wannaget et al. have already investigated the preparation and the reactivity of hexachlorodisilazane and showed that *N*-lithiation is readily achieved by treatment with *n*BuLi

in pentane to give hexachlorodisilazanyllithium (**1**; see Equation 1)<sup>[9]</sup>. Recently, Burgdorf et al. described an improved synthesis of chlorodisilazanes starting from  $\text{CaCl}_2(\text{NH}_3)_8$ <sup>[12]</sup> (see Equation 2). Reactions of **1** were carried out with boron and silicon halides and the possibility of substitution reactions was shown in principle<sup>[10]</sup>.

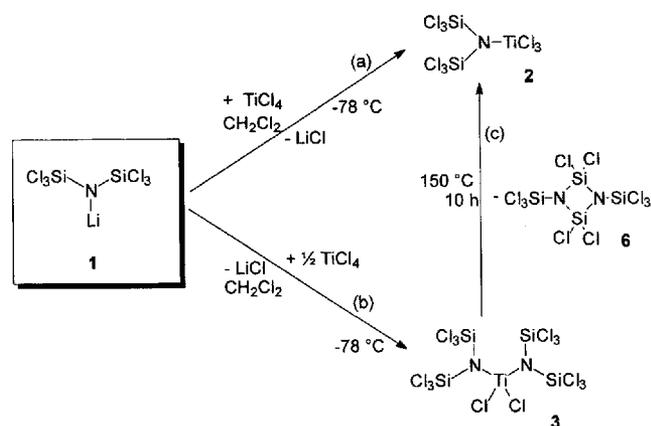


Here we report on the synthesis and characterization of fully chlorinated *N*-silylamides obtained by the reaction of **1** with  $\text{TiCl}_4$  and  $\text{WCl}_6$ .

## Results and Discussion

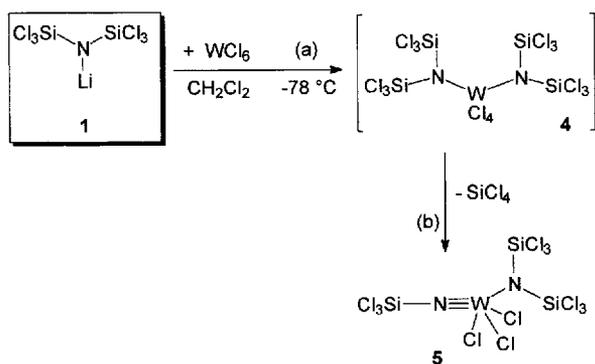
The reactions of **1** with  $\text{TiCl}_4$  are summarized in Scheme 1. The mono-substituted product **2** is obtained in high yield by the reaction of **1** with  $\text{TiCl}_4$  in a molar ratio of 1:1 (Scheme 1a). It is a yellowish solid which gives bright yellow solutions in organic solvents. The treatment of **1** with  $\text{TiCl}_4$  in a molar ratio of 2:1 (Scheme 1b) gives the corresponding diamide **3**. On heating, **3** decomposes to **2** and the well-characterized 4-membered ring **6**<sup>[9b, 13]</sup> (Scheme 1c).

Scheme 1



The reaction of **1** with  $\text{WCl}_6$  (Scheme 2) leads directly to the amide imide **5** which can be recrystallized from pentane to give yellow crystals (vide infra). Solutions of **5** in aromatic solvents exhibit a dark brown color. The formation of **5** can be explained by the elimination of  $\text{SiCl}_4$  from the proposed intermediate **4**, resulting in a  $\text{W}\equiv\text{N}$  multiple bond (Scheme 2b). This type of reaction is well known for the analogous *N*-trimethylsilyl derivatives, e.g. with tantalum as the central atom<sup>[4a]</sup>. The relative amounts of the starting materials **1** and  $\text{WCl}_6$  may be varied across a wide range without any effect on the formation of **5**. Obviously, a monosubstitution product analogous to **2** is much more reactive towards **1** than  $\text{WCl}_6$  itself.

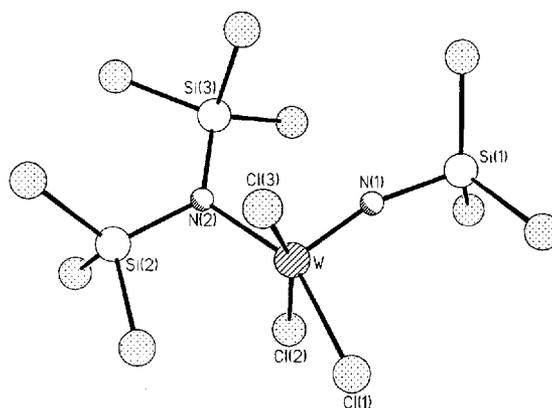
Scheme 2



### Crystal Structure of **5**<sup>[4a]</sup>

Details of the X-ray structure analysis of **5** are summarized in Table 1. The tungsten amide imide  $\text{Cl}_3\text{SiN}\equiv\text{W}(\text{Cl}_3)\text{N}(\text{SiCl}_3)_2$  is monomeric. There are no significantly short intermolecular atomic distances. The coordination sphere of the central atom of **5** is best described to be of pseudo-square-pyramidal geometry, with the imido group at the apex. The  $\text{SiCl}_3$  groups [Cl<sub>3</sub>Si(3)] and [Cl<sub>3</sub>Si(1)] show rotational disorder. The imido group is nearly linear [angle  $\text{W}\equiv\text{N}-\text{Si}$  165.4(6)°] and the imido nitrogen atom can be viewed as *sp*-hybridized. The coordination of the amido nitrogen atom is trigonal planar. The two bonds between W and N differ by nearly 30 pm [ $\text{W}\equiv\text{N}$  171.8(9),  $\text{W}-\text{N}$

200.7(8) pm] which is significantly larger than the value found for the comparable dimeric tantalum compound  $[\text{Me}_3\text{SiN}\equiv\text{Ta}(\text{Br}_2)\text{N}(\text{SiMe}_3)_2]_2$ <sup>[4a]</sup>. The bond lengths  $\text{W}-\text{N}$  are in the same range as those found for other tungsten amides and imides<sup>[15–17]</sup>. In contrast to the tantalum derivative  $[\text{Me}_3\text{SiN}\equiv\text{Ta}(\text{Br}_2)\text{N}(\text{SiMe}_3)_2]_2$ , the hybridization of the nitrogen atoms in **5** has no effect on the  $\text{N}-\text{Si}$  bond lengths (average value 171.5 pm) which correspond to those of a normal  $\text{Si}-\text{N}$  single bond<sup>[13]</sup> which also holds for the  $\text{W}-\text{Cl}$  bond lengths<sup>[18]</sup>. The bond lengths  $\text{Si}-\text{Cl}$  of the Si(2)Cl<sub>3</sub> group are as expected<sup>[13]</sup> (bond lengths in the rotationally disordered groups were fixed).

Figure 1. Molecular structure of **5**<sup>[a]</sup>

<sup>[a]</sup> Selected bond lengths [pm] and angles [°]:  $\text{W}-\text{Cl}1$  229.8(3),  $\text{W}-\text{Cl}2$  231.4(3),  $\text{W}-\text{Cl}3$  230.5(3),  $\text{N}1-\text{Si}1$  171.1(9),  $\text{N}2-\text{Si}2$  171.4(8),  $\text{N}2-\text{Si}3$  172.5(10);  $\text{N}1-\text{W}-\text{N}2$  104.0(4),  $\text{N}1-\text{W}-\text{Cl}1$  102.5(3),  $\text{N}2-\text{W}-\text{Cl}1$  153.5(3),  $\text{N}1-\text{W}-\text{Cl}2$  98.5(3),  $\text{Cl}2-\text{W}-\text{Cl}3$  162.1(1),  $\text{W}-\text{N}1-\text{Si}1$  165.4(6).

Table 1. Crystallographic data of **5**

Empirical formula	$\text{Cl}_{12}\text{N}_2\text{Si}_3\text{W}$
Crystal system, space group	triclinic, $P\bar{1}$
Unit-cell dimensions [pm] [°]	$a = 879.8(2)$ $b = 888.5(2)$ $c = 1318.4(2)$ $\alpha = 99.14(2)$ $\beta = 98.10(2)$ $\gamma = 100.55(2)$
Unit-cell volume $V$ [ $10^6$ pm <sup>3</sup> ]	985.0(3)
Z	2
Density (calcd.) [g/cm <sup>3</sup> ]	2.433
Diffractometer, radiation	Siemens P4, Mo- $K_\alpha$ , $\lambda = 71.073$ pm
Temperature [K]	296
2 $\theta$ range [°]	2.0–55.0
Reflections collected	5391, $\omega$ scan
Independent reflections	4509 ( $R_{\text{int}} = 0.0423$ )
Observed reflections	4181 with $F_o \geq 2.0 \sigma(F_o)$
Absorption correction	semi-empirical ( $\nu$ scans)
Min./max. transmission factors	0.0282/0.0575
Solution	direct methods
Number of parameters refined	162
Program	Siemens SHELXTL PLUS (VMS)
$R/wR$ [ $w^{-1} = \sigma^2(F_o)$ ]	0.0583/0.0571

Crystalline **5** shows a reversible phase transition between room temperature and  $-100^\circ\text{C}$ , associated with an enlargement of the unit cell without destruction of the single crystal.

## NMR Spectroscopic Results

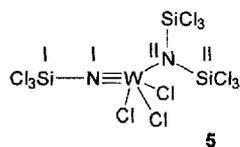
The measured NMR data of hexachlorodisilazane and of the compounds **1–6** are listed in Tables 2 and 3. All NMR data of the compounds **2** and **3** are consistent with the proposed structures. Because of the absence of any protons which could be used for polarization transfer only direct  $^{29}\text{Si}$ -NMR measurements were possible. The  $^{29}\text{Si}$  nuclei of the transition-metal derivatives are shielded by 4–8 ppm when compared with hexachlorodisilazane; this is caused by the replacement of the proton by a transition-metal halide group. In contrast, the  $^{29}\text{Si}$  nuclei of  $(\text{Me}_3\text{Si})_2\text{N}-\text{TiCl}_3$ , the methyl analogue of **2**, are deshielded with respect to hexamethyldisilazane<sup>[19]</sup>. The replacement of a second chlorine atom at the titanium center against a bis(trichlorosilyl)amido group leads to further  $^{29}\text{Si}$  shielding by 1.8 ppm. The trichlorosilyl groups at the imido nitrogen atoms of **5** give signals with a high shielding at  $\delta = -59.8$ . This significantly high shielding of the ring Si nuclei in **6** to a value of  $\delta = -39.8$  is typical of 4-membered rings, and is probably a result of the short transannular Si...Si distance of 246.3 pm<sup>[13]</sup> which is comparable to a covalent Si–Si single bond length of 234 pm<sup>[20]</sup>.

Table 2.  $^{14}\text{N}$ - and  $^{29}\text{Si}$ -NMR data<sup>[a]</sup> of hexachlorodisilazane, compounds **1–3**, and **6**

Compound	Hexachloro- disilazane <sup>[b]</sup>	<b>1</b>	<b>2</b>	<b>3</b>	<b>6</b>
$\delta^{14}\text{N}$ ( $\nu_{1/2}$ )	-313 (430)	-283 (250)	-117 (160)	-140 (510)	-283 (220)
$\delta^{29}\text{Si}$	-25.5	-43.5	-29.6	-31.4	-30.2 (SiCl <sub>3</sub> ) -39.8 (SiCl <sub>2</sub> )

[a]  $\text{C}_6\text{D}_6$ , 25°C. – [b]  $\delta^1\text{H} = 2.82$ ;  $^1J[^{15}\text{N}, ^1\text{H}] = 71.9$  Hz;  $^1J[^{29}\text{Si}, ^{15}\text{N}] = 28.8$  Hz.

Table 3.  $^{14}\text{N}$ - and  $^{29}\text{Si}$ -NMR data<sup>[a]</sup> of compound **5**

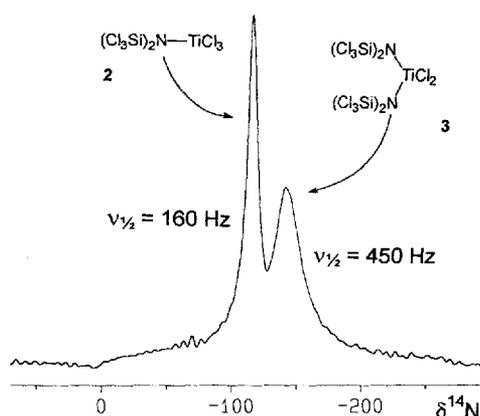


$\delta^{14}\text{N}$ ( $\nu_{1/2}$ ) (N-I)	$\delta^{14}\text{N}$ ( $\nu_{1/2}$ ) (N-II)	$\delta^{29}\text{Si}$ (Si-I)	$\delta^{29}\text{Si}$ (Si-II)
93 (110)	-167 (310)	-59.8	-33.1

[a]  $\text{C}_6\text{D}_6$ , 25°C.

The most instructive information on the product distribution, and on the progress of the reactions, is obtained by  $^{14}\text{N}$ -NMR spectroscopy. Previously, only a few  $^{14/15}\text{N}$  chemical shifts of transition-metal amides and imides were measured<sup>[17]</sup>, most of them by  $^{15}\text{N}$ -NMR spectroscopy of samples enriched with  $^{15}\text{N}$ <sup>[17,21]</sup>. Our investigations on  $^{14}\text{N}$ -NMR spectroscopy show that the resonances of transition-metal amides and imides are surprisingly easy to observe (see Figure 2).

Figure 2. 18.1-MHz  $^{14}\text{N}$ -NMR spectrum of a 1:1 mixture of the compounds **2** and **3**



The substitution of the proton of hexachlorodisilazane against lithium in **1** leads to a  $^{14}\text{N}$  deshielding of 30 ppm and to a sharpening of the  $^{14}\text{N}$ -NMR signal. The  $\delta^{14}\text{N}$  values of the compounds **2** ( $\delta^{14}\text{N} = -117$ ) and **3** ( $\delta^{14}\text{N} = -140$ ) can be explained by the lower acidity of the  $\text{TiCl}_2$  group when compared with that of the  $\text{TiCl}_3$  group. In a mixture, the increase of the line width of the  $^{14}\text{N}$ -NMR signal due to the higher molecular weight of **3** (Figure 2) is also indicative. The low  $^{14}\text{N}$  shielding, together with a sharp  $^{14}\text{N}$ -resonance signal for the imido-nitrogen atom of **5**, is typical of sp-hybridized  $^{14}\text{N}$  atoms<sup>[17,21,22]</sup>.

The marked  $^{14}\text{N}$  deshielding in metal amides or imides, if the metal is an early transition element in a high oxidation state, may be explained by the contribution to the paramagnetic shielding term  $\sigma_p$  of  $B_0$ -induced mixing of ground and electronic excited states. This concerns in particular the electrons in the M–N  $\sigma$  bond, the nitrogen lone pair of electrons, and the presence of unoccupied metal d-orbitals. The comparison between  $\delta^{14}\text{N}$  of **2** ( $\delta^{14}\text{N} = -117$ ) and  $(\text{Me}_3\text{Si})_2\text{NTiCl}_3$  ( $\delta^{14}\text{N} = +30$ )<sup>[19]</sup> indicates the influence of the electronegative chloro substituents. The energy of electrons in the N–Si and also in the M–N  $\sigma$  bonds, as well as that of the lone pairs of electrons, is lower in **2** than in  $(\text{Me}_3\text{Si})_2\text{NTiCl}_3$ . Therefore, the mean  $\Delta E$  is larger in **2** and paramagnetic contributions become smaller<sup>[23]</sup> i.e.  $^{14}\text{N}$ -nuclear shielding increases. The same arguments explain the high shielding of the  $^{29}\text{Si}$  nuclei. However, in comparison with amines, the effect of the neighboring metal center still dominates the  $^{14}\text{N}$  deshielding but not the  $^{29}\text{Si}$  shielding in **2**, **3**, and **5**.

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## Experimental Section

All preparative work and handling of the samples was carried out under pure  $\text{N}_2$  using dry glassware and dry solvents.

$\text{CaCl}_2(\text{NH}_3)_8$ <sup>[12]</sup> and hexachlorodisilazanyllithium (**1**)<sup>[9b]</sup> were prepared as described. The preparation of hexachlorodisilazane is analogous to literature procedures<sup>[12]</sup>.  $\text{SiCl}_4$ ,  $\text{TiCl}_4$ ,  $\text{WCl}_6$ , and  $n\text{BuLi}$  in hexane (1.6 M) were commercial products and used without further purification. – IR spectra: Bruker IFS 66v; KBr pellets. – NMR spectra: Bruker ARX 250 ( $^1\text{H}$ ,  $^{14}\text{N}$ ,  $^{15}\text{N}$ ,  $^{29}\text{Si}$ ); chemical shifts are given with respect to  $\text{Me}_4\text{Si}$  [ $\delta^1\text{H}$  ( $\text{C}_6\text{D}_6$ ) = 7.15;  $\delta^{29}\text{Si}$ :  $\Xi(^{29}\text{Si})$  = 19.867184 MHz] and neat  $\text{MeNO}_2$  [ $\delta^{14}\text{N}$ :  $\Xi(^{14}\text{N})$  = 7.223656 MHz;  $\delta^{15}\text{N}$ :  $\Xi(^{15}\text{N})$  = 10.136767 MHz].

$(\text{Cl}_3\text{Si})_2\text{NH}$ : To a cooled ( $-78^\circ\text{C}$ ) solution of 400 g of  $\text{SiCl}_4$  (2.4 mol) in 500 ml of pentane, 40 g of  $\text{CaCl}_2(\text{NH}_3)_8$  (0.16 mol  $\approx$  1.28 mol of  $\text{NH}_3$ ) was added in one portion. Then the mixture was stirred at room temp. for 8 d. After that, the reaction mixture was filtered, and pentane and  $\text{SiCl}_4$  were removed from the filtrate by distillation. Distillation of the residue at reduced pressure gave 60 g (18%) of hexachlorodisilazane as a colorless, extremely moisture-sensitive liquid (b.p.  $81^\circ\text{C}/40$  Torr).

$(\text{Cl}_3\text{Si})_2\text{N}-\text{TiCl}_3$  (**2**) and  $[(\text{Cl}_3\text{Si})_2\text{N}]_2\text{TiCl}_2$  (**3**): To a solution of 0.7 g of **1** (2.4 mmol) in 20 ml of  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$ , 0.5 g (2.4 mmol) or 0.25 g (1.2 mmol) of  $\text{TiCl}_4$ , respectively, were added in one portion. After the mixture was warmed to room temp., it was stirred for 4 h. Then the mixture was filtered. Removal of the solvent from the filtrate gave 1.0 g of **2** (95%; m.p.  $190^\circ\text{C}$ ) or 0.8 g of **3** (97%; m.p.  $140^\circ\text{C}$  under decomposition), as yellowish solids. – **3**: IR:  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 1405, 985, 815, 746, several vibrations between 400 and 630.

$\text{Cl}_3\text{SiN}\equiv\text{W}(\text{Cl}_3\text{N})(\text{SiCl}_3)_2$  (**5**): A solution of 0.7 g of **1** (2.4 mmol) in 10 ml of  $\text{CH}_2\text{Cl}_2$  was added carefully to a stirred solution of 0.5 g of  $\text{WCl}_6$  (1.3 mmol) in 20 ml of  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$ . The mixture was allowed to warm up. At a temperature of  $0^\circ\text{C}$  the color changed from dark brown to yellow and  $\text{LiCl}$  began to precipitate. After stirring for 1 h at room temp., the reaction mixture was filtered. Removal of the solvent in vacuo from the filtrate gave an orange oil. Recrystallization from pentane gave 0.5 g of **5** (58%) as yellow platelets (m.p.  $115^\circ\text{C}$ ). – IR:  $\tilde{\nu}$  [ $\text{cm}^{-1}$ ] = 1403, 1178 [ $\nu\text{W}\equiv\text{N}$ ], 1083, 964, 772, 624, several vibrations between 400 and 600.

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