Synthesis and Structural Characterization of Novel Aluminum, Gallium and Indium Compounds with Silylamide Ligands

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Dedicated to my father – आबा - तुकाराम माने

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Abstract (English)

The synthesis of Group III coordination compounds containing silylamide ligands is interesting due to their potential use as Single Source Molecular Precursors. These precursors can be useful in the preparation of technologically important Group III nitride semiconductor materials MN (M = Al, Ga and In). Silylamide ligands like $R_2Si(NHR')_2$ and $RSi(NHR')_3$ (R and R' = alkyl or aryl groups) have been synthesized by standard procedures. The reactions of MCl_3 (M = Al, Ga and In) with $R_nSi(NLiR')_{(4-n)}$ (n = 1, 2; R = Me, Et or Ph and R' = Ph, Mes or Cy) lead to different coordination compounds. To achieve increased kinetic stability in the final metal group III complexes, it was necessary to use bulky R and R' groups attached to Si and N atoms of the aminosilanes such as $R_nSi(NHR')_{(4-n)}$, because the Si-N bond is weak. In case of difunctional silylamide ligands ionic spirocyclic coordination compounds were obtained while neutral coordination compounds were isolated for trifunctional silylamide ligands. These Single Source Molecular Precursors can be useful to obtain group III nitrides either in the form of nanoparticles or as bulk material using sol-gel chemistry and thermal degradation.

Keywords: Aluminum / Gallium / Indium / Coordination Compounds / Single Source Molecular Precursors / Cluster Compounds / Silylamide Ligands / X-ray Crystal Structure Determination / NMR Spectroscopy

Abstract (Deutsch)

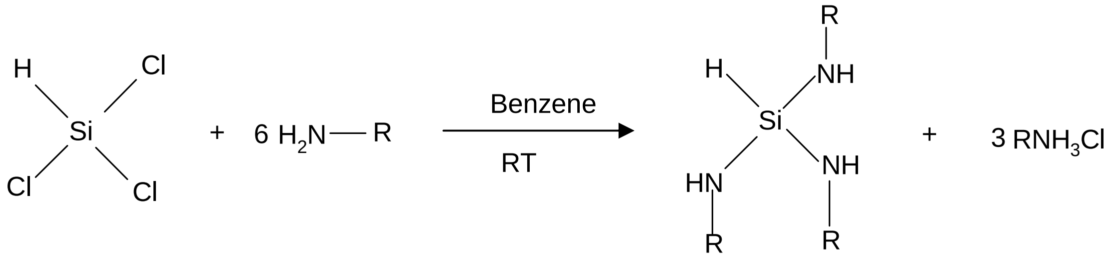
Silylamide von Elementen der III. Hauptgruppe sind als Precursor-Moleküle zur Synthese von Nitriden MN (M = Al, Ga und In) von Interesse. Silazan-Liganden wie z.B. $R_2Si(NHR')_2$ und $RSi(NHR')_3$ (R und R'= Alkyl oder Aryl) konnten mittels einer Standardsynthese hergestellt werden. Die Reaktion von MCl_3 (M = Al, Ga und In) mit $R_nSi(NLiR')_{(4-n)}$ (n = 1, 2; R = Me, Et oder Ph und R' = Ph, Mes oder Cy) führt zu verschiedenen Koordinationsverbindungen. Um die kinetische Stabilität der Zielverbindungen zu erhöhen, wurden Silazan-Liganden mit sperrigen Resten R und R' (R = Me, Et oder Ph und R' = Ph, Mes oder Cy) eingesetzt. Im Fall von bifunktionalen Silylamid-Liganden wurden ionische spirocyclische Koordinationsverbindungen erhalten. Im Fall der trifunktionalen Silylamid-Liganden wurden neutrale Cluster-Verbindungen erhalten. Die synthetisierten Substanzen können als Precursor-Moleküle zur Synthsese von Al-, Ga- und In-Nitiriden in nanodisperser Form oder als Bulk-Materalien Verwendung finden.

Keywords: Aluminum / Gallium / Indium / Koordinationsverbindungen / Einzelmolekül Precursor / Cluster-Verbindungen / Silylamid-Liganden / Kristallstrukturanalyse / NMR-Spektroskopie

1. Introduction

1.1 Amino silanes of the type $R_2Si(NHR')_2$ and $RSi(NHR')_3$ and their applications in coordination chemistry

The first synthesis of an aminosilane was carried out by O. Ruff *et al.* in 1909 [1]. Primary amines such as aniline react with $HSiCl_3$ in benzene as a solvent at room temperature to form aminosilanes as shown in the following general reaction equation 1. Excess of primary amine was used to abstract HCl which is generated during the reaction to form an amine salt (RNH_3Cl).



(1)

In order to prepare triaminosilanes and substituted aminosilanes Anderson *et al.* used the above mentioned general reaction and heated the reaction mixture at reflux temperature using an excess of primary amine [2]. Towards the end of 1969 Takiguchi *et al.* came with a new reaction in a single step for the synthesis of difunctional and trifunctional aminosilanes. Advantage of this method over the Anderson method was the use of triethylamine as a base instead of primary amine which gives higher yields of aminosilanes and with different substitution [3].

$$R_nSiCl_{(4-n)} + (4-n)\ R'NH_2 + (4-n)\ NEt_3 \longrightarrow R_nSi(NHR')_{(4-n)} + (4-n)\ [HNEt_3]Cl \qquad (2)$$

(n = 1, 2; R = Me, Et or Ph and R' = Ph, Mes and Cy)

These reactions were carried out in THF, hexane or toluene as solvent. When bulkier groups are present both on Si as well as on N-atoms for example Ph and Mes, the above general reaction equations 1 and 2 could not be applied. In these cases the aminolysis of R_2SiCl_2 or $RSiCl_3$ stops at the stage of $R_2SiClNHR'$ or $RSiCl(NR')_2$. These aminolysis products e.g.

$R_2SiClNHR'$ or $RSiCl(NHR')_2$ were reacted with lithium amides such as R'NHLi to remove the Cl atom to obtain the aminosilanes $R_2Si(NHR')_2$ and $RSi(NHR')_3$. This method allows the synthesis of mixed bisaminosilanes like [Ph_2Si(NH*t*-Bu)(NH*i*-Pr)] which were studied by Nöth *et al.* [5].

R_2SiCl_2 and $RSiCl_3$ can be treated directly with R'NHLi to obtain the corresponding aminosilanes as shown in the following general reaction equations 3 and 4.

$$R'NH_2 \quad + \quad n\text{-}BuLi \quad \longrightarrow \quad R'NHLi \quad + \quad n\text{-}BuH \qquad (3)$$

$$R_nSiCl_{(4-n)} \; + \; (4-n)\; R'NHLi \quad \longrightarrow \quad R_nSi(NHR')_{(4-n)} \; + \; (4-n)\; LiCl \qquad (4)$$

(Where n = 1, 2; R = Me, Et, or Ph and R' = Ph, Mes and Cy).

The lithium amide method was first invented by Fink *et al.* for the synthesis of bisaminosilanes $R_2Si(NHR')_2$ [7]. The first step was the lithiation of primary amine (mesitylamine or aniline), which was strictly carried out at -78 ^{o}C. The completion of the reaction was achieved by a gradual warming of the reaction mixture to room temperature. In the second step the lithium amide so formed was reacted with di or trichlorosilanes to obtain corresponding $R_2Si(NHR')_2$ and $RSi(NHR')_3$ aminosilanes in THF or toluene [7, 8].

1.2 Lithiated aminosilanes as intermediate products

Usually lithiated aminosilanes are prepared by the reaction of $R_2Si(NHR')_2$ or $RSi(NHR')_3$ with n-BuLi in hexane or pentane solvent at -78 ^{o}C. One of the first examples of a dilithio derivative was [{*t*-BuNLi}$_2$SiMe$_2$]$_2$ which was mentioned by Fink [7]. [{*t*-BuNLi}$_2$SiMe$_2$]$_2$ was generated (but not isolated) during the synthesis of cyclodisilazanes of type $R_4Si_2(NR')_2$.

Brauer and Bürger synthesized and isolated [{*t*-BuNLi}$_2$SiMe$_2$]$_2$ and [{*t*-BuNLi}$_3$SiPh]$_2$ for the first time. [{*t*-BuNLi}$_2$SiMe$_2$]$_2$ and [{*t*-BuNLi}$_3$SiPh]$_2$ were prepared by lithiation of (*t*-BuNH)$_2$SiMe$_2$ and (*t*-BuNH)$_3$SiPh using n-BuLi in hexane. The solid state structures of these compounds were dimeric with crystallographic $\bar{1}$ symmetry. From the X-ray crystallographic studies it is known that these compounds tend to form dimeric structures in the solid state as represented in Figures 1 and 2 simultaneously [9].

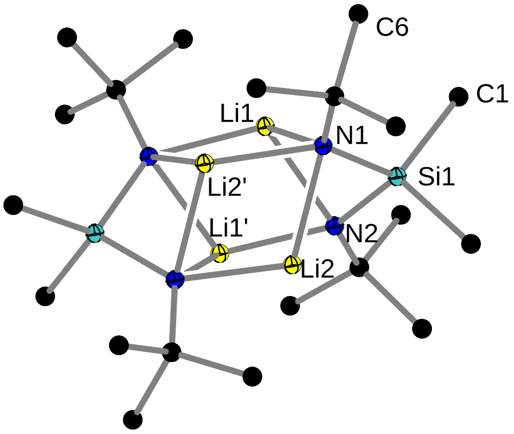


Fig. **1**. Molecular structure of $[\{(t\text{-BuNLi})_2\text{SiMe}_2\}_2]$

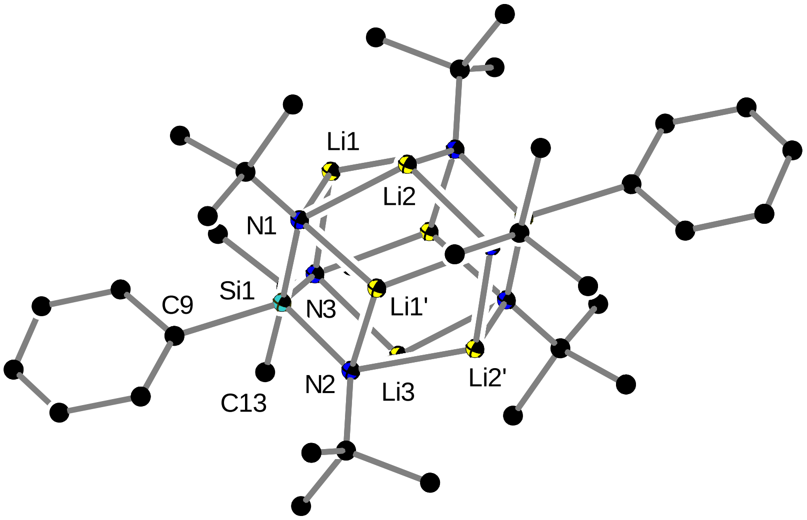


Fig. **2**. Molecular structure of $[\{(t\text{-BuNLi})_3\text{SiPh}\}_2]$

One of the ladder like structure of $[\{\text{LiOEt}_2\text{Me}_2(\text{SiNPh})(\text{NHPh})\}_2]$ was formed by the reaction of $\text{Me}_2\text{Si}(\text{NHPh})_2$ with n-BuLi at -78 ^{o}C. This compound forms a centrosymmetric dimeric molecule in which two Li atoms form a Li_2N_2 ring with the coordination of one Et_2O solvent molecule [10].

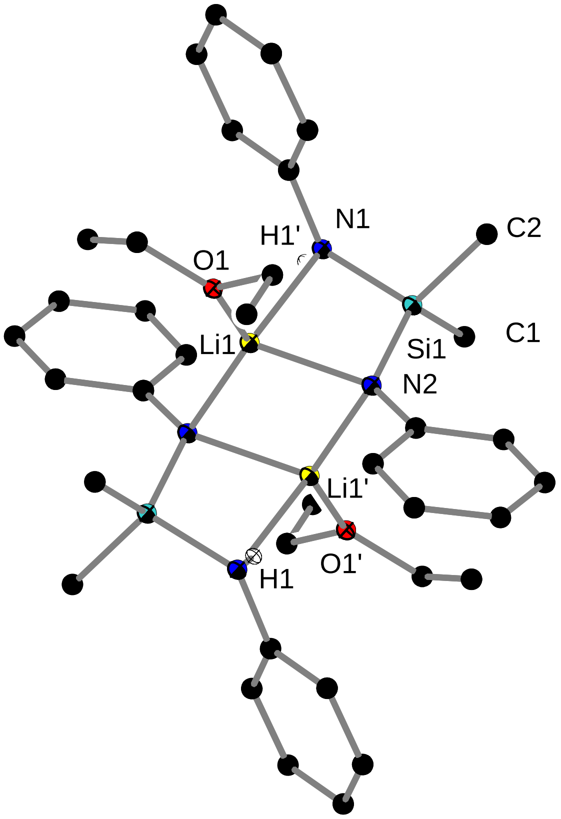


Fig. **3**. Molecular structure of [$\{LiOEt_2Me_2(SiNPh)(NHPh)\}_2$]

1.3 Transition and main group metal derivatives

In the literature there are a number of reports on main group and transition metal derivatives with silylamide ligands mainly because of the property of silylamides to stabilize the electron deficiency at the metal centre most efficiently. This effect is well outlined to the electron-donating properties of silylamide ligands in a review by Lappert and Power *et al*. [11]. In 1978 Veith studied the reaction of [$Me_2Si(NLi$*t*-Bu$)_2]_2$ with $SnCl_4$ for the formation of [$\{Me_2Si(NLi$*t*-Bu$)_2\}_2Sn$]. This compound was spirocyclic in nature as represented in Figure 4 [12, 13].

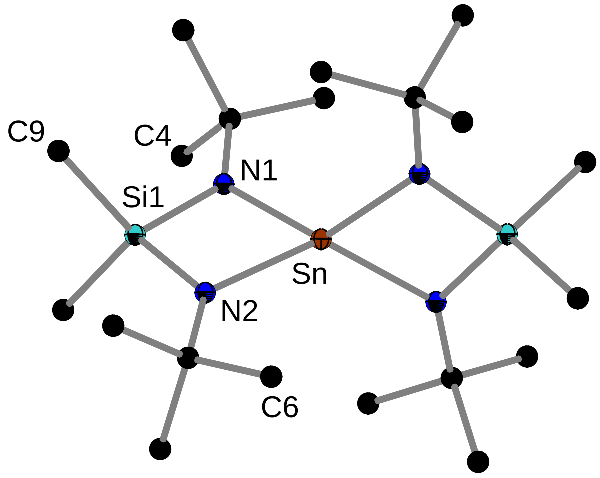


Fig. **4**. Molecular structure of [{$Me_2Si(N$*t*-$Bu)_2\}_2Sn$]

Subsequently Brauer and Bürger also used an analogous reaction strategy for the synthesis and characterization of the spirocyclic titanium derivative [{$Ph_2Si(NSiMe_3)_2\}_2Ti$] from [$Ph_2Si(NLiSiMe_3)_2$] and $TiCl_4$ as shown in Figure 5 [14].

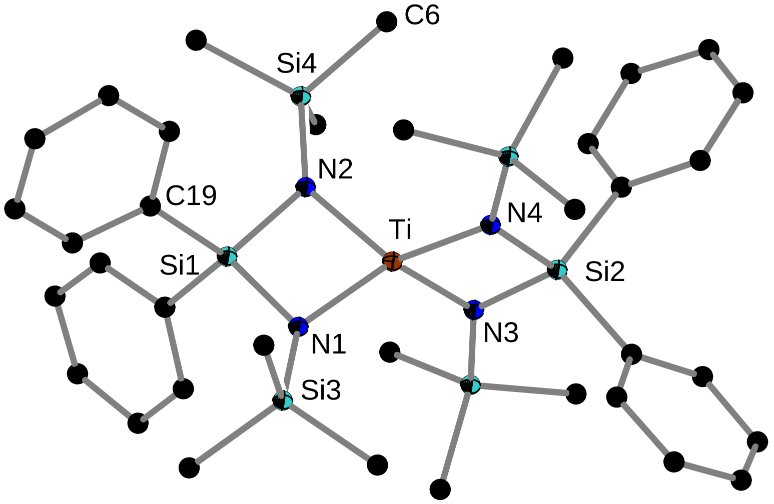


Fig. **5**. Molecular structure of [{$Ph_2Si(NSiMe_3)_2\}_2Ti$]

Alternatively aminosilanes can be reacted directly with metal alkyls like $AlMe_3$ and $AlEt_3$ to form metal cluster complexes. The reaction of a stable triaminosilane such as $2,6\text{-}^{i}Pr_2C_6H_3NSiMe_2{}^{i}PrSi(NH_2)_3$ with trialkyls of group III metals e.g. $AlMe_3$ leads to the formation of a cage compound $[2,6\text{-}^{i}Pr_2C_6H_3NSiMe_2{}^{i}PrSi(NH)_3Al_2Me_3]_2$ represented in Figure 6. This cage molecule can be described as a bitruncated square bipyramid [15].

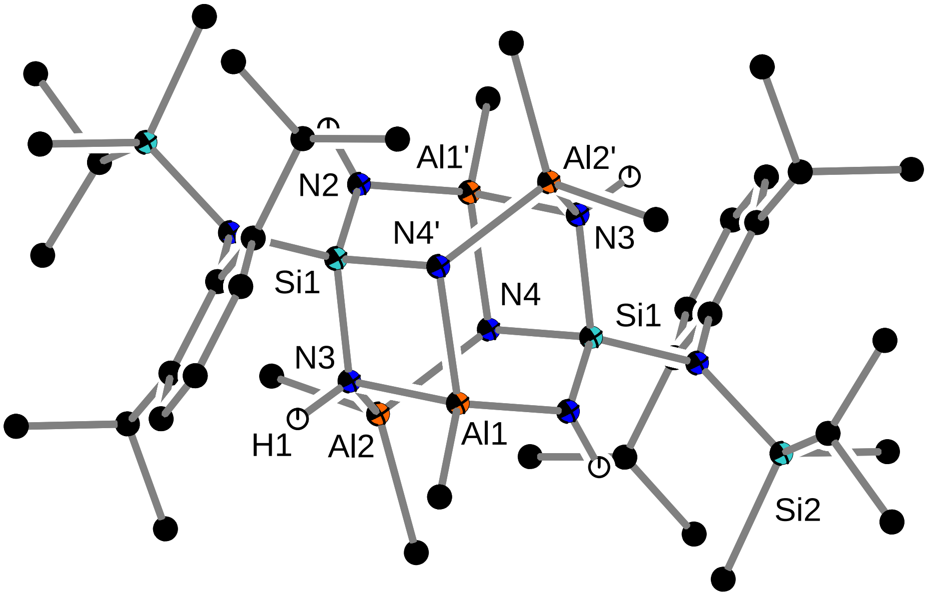


Fig. **6**. Molecular structure of $[\{2,6\text{-}^{i}Pr_2C_6H_3NSiMe_2{}^{i}PrSi(NH)_3Al_2Me_3\}_2]$

Another interesting example of a cage compound is $[EtAl(\mu\text{-}NHEt)(\mu\text{-}NEt)_2Si(NHEt)]_2$ which was studied by Kaskel *et al*. [16]. The reaction between tetrakis(ethylamino)silane $Si(NHEt)_4$ and $AlMe_3$ leads to the formation of $[MeAl(\mu\text{-}NHEt)(\mu\text{-}NEt)_2Si(NHEt)]_2$. The basic structural characteristic of this compound is a heterocyclic eight membered ring composed of alternating Al, N and Si atoms. Two additional NHEt groups, bridge one pair of Si and Al atoms to produce a tricyclic ring system as illustrated in Figure 7.

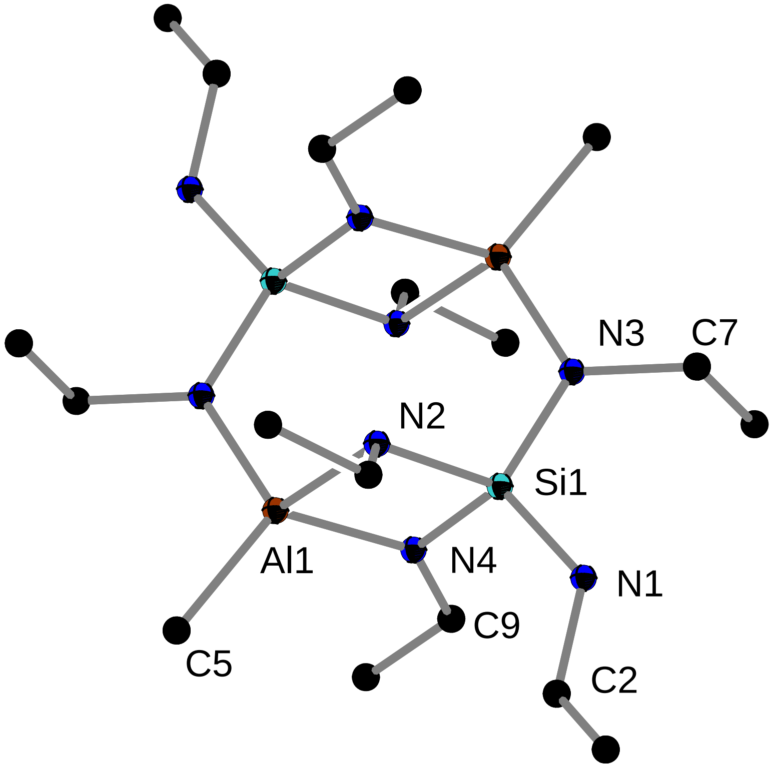


Fig. **7**. Molecular structure of [{MeAl(μ-NHEt)(μ-NEt)$_2$Si(NHEt)}$_2$]

Kroke and Roewer *et al*. reported compounds of titanium, germanium and tin which were prepared from 1,1,3,3,5,5-hexamethylcyclotrisilazane H$_3$(HMCTS) as a ligand and titanium, germanium and tin tetrachlorides [17].

[(Me$_2$Si)$_6$N$_3$(NH)$_3$TiCl] exhibits a Ti atom at the centre surrounded by the cyclohexasilazane ring system as shown in Figure 8. The titanium atom is coordinated by three nitrogen atoms and one chlorine substituent exhibiting a tetrahedral geometry. These complexes were used as single-source precursors for ceramic materials of the quaternary SiCNTi and SiCNGe systems.

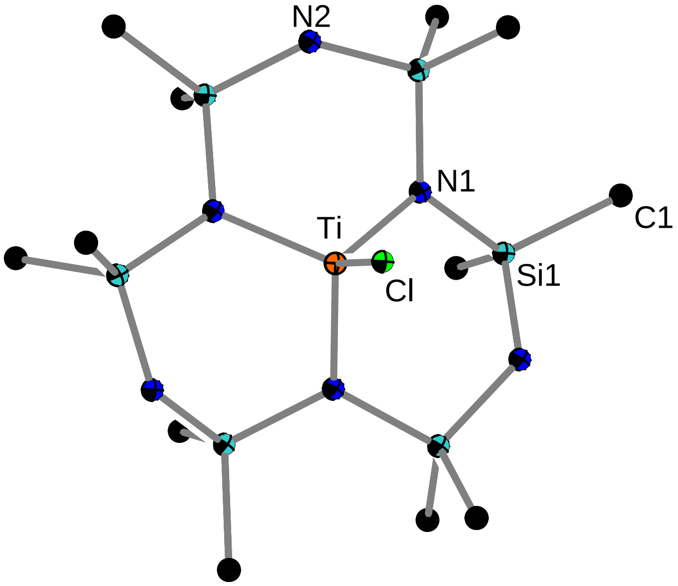


Fig. 8. Molecular structure of [$(Me_2Si)_6N_3(NH)_3TiCl$]

1.4 General comment on molecular structures group III silylamides and their use as semiconductor precursors

Silylamides $[R_2Si(NR')_2]^{2-}$ or $[RSi(NR')_3]^{3-}$ as ligands have been used to prepare several group III derivatives. Group III compounds can be used as precursors for semiconductor materials. These molecular precursors are quite demanding in the semiconductor industry and nanotechnology research area for the preparation of nitrides [18-20]. Since the last 20 years semiconductors have become virtually indispensable in many aspects of daily life. Even people who do not own or use a computer are likely to use semiconductor memory in one way or another. Many of the fantastic capabilities of modern world are possible through the semiconductor materials only. Nitrides of Al, Ga and In have characteristic band gap properties [20-21]. Metal nitrides find diverse applications ranging from refractory ceramics (AlN, TiN…) wear resistant coatings (TiN, ZrN, CrN, Zr_3N_4) industrial catalysis (VN) to the semiconductor devices for optoelectronics (GaN, InN) [22-29].

2. Objective of the research work

Present research work is focused on the synthesis and characterization of group III metal compounds which contain silylamides as supporting ligands. Difunctional aminosilanes $R_2Si(NHR')_2$ and trifunctional aminosilanes $RSi(NHR')_3$ can be prepared by standard techniques. After lithiation of aminosilanes with n-BuLi the corresponding lithium silylamides $R_2Si(NLiR')_2$ and $RSi(NLiR')_3$ are obtained.

The synthetic procedure for group III metal complexes consists of two steps:

a) Synthesis of difunctional aminosilanes $R_2Si(NHR')_2$ and trifunctional aminosilanes $RSi(NHR')_3$ by standard techniques.

b) Metalation of the aminosilanes by n-BuLi and subsequent reactions of the lithiated silylamides such as $R_2Si(NLiR')_2$ or $RSi(NLiR')_3$ with MCl_3 (M = Al, Ga and In).

Variation in the R and R' groups of silylamide ligands and synthetic conditions are attempted in order to obtain different group III metal complexes. The characterization of the products are mainly done by X-ray single crystal diffraction and spectroscopic methods like IR spectroscopy, ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. The last part of the investigation is concerned with the potential applications of group III silylamides as precursors for III-V semiconductor compounds. Group III silylamide complexes are appealing candidates as single source precursors for group III nitrides due to the relatively weak Si-N bond.

3. Results and discussion

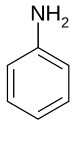
3.1 Synthesis and structural characterization of silylamines of the type $R_2Si(NHR')_2$ and $RSi(NHR')_3$ (*Part-I*)

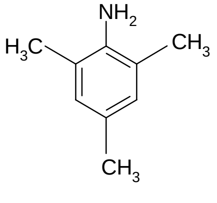
3.1.1 Introduction:

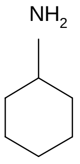
The distinctive properties of difunctional silylamides of the type $[R_2Si(NR')_2]^{2-}$ for the stabilization of low coordination numbers of main group and transition elements are well known in literature [9-12]. Aminosilanes such as $Me_2Si(NH\textit{t}\text{-}Bu)_2$ have been comprehensively used as ligands in organometallic chemistry, as it favors different (low) coordination numbers in metal complex formation, such as for magnesium compounds $[\{Me_2Si(N\textit{t}\text{-}Bu)_2\}(AlMe_2)(MgI)]_2$ (Mg, c. n. 4) and $[Mg\{Me_2Si(N\textit{t}\text{-}Bu)_2AlMe_2\}_2]$ (Mg, c. n. 2) [30-32]. Such a coordination behavior for manganese is followed by Power *et al.* for preparation of $[Li(Mn\{N(Mes)\}_2SiMe_2)_2N(SiMe_2)_2]$ (Mn, c. n. 2) and $[Mn\{N(Dipp)CH_2CH_2NHDipp\}_2]$ (Dipp = 2,6-$\textit{i}\text{-}Pr_2C_6H_3$) (Mn, c. n. 4) compounds by using bulky bidentate diamines [33]. Compounds like $[\{Me_2Si(N\textit{t}\text{-}Bu)_2\}_2Sn]$ and other group IV derivatives are studied extensively with their crystal structure determination by Veith *et al.* using the diamido ligand $[Me_2Si(N\textit{t}\text{-}Bu)_2]^{2-}$ cited in literature [12-13 and 30-32].

There are a number of reports about preparation of aminosilanes. As the time progresses there are more reports about improvements regarding the yield, selectivity and complete characterization of aminosilanes. However there are very few reports on their crystal structure determinations and some crystal structures of aminosilanes have been studied for the first time. In the next section a survey of the synthesis of aminosilanes by various methods are discussed.

3.1.2 Amines: Primary amines as aniline, mesitylamine and cyclohexylamine are used for the synthesis of aminosilanes of the type $R_2Si(NHR')_2$ and $RSi(NHR')_3$.







Generally aminosilanes which are also called as silazanes are prepared by using different synthetic routes as outlined below by various methods using auxiliary base or without base.

3.1.3 Synthesis of diaminosilanes of the type $R_2Si(NHR')_2$ and triaminosilanes $RSi(NHR')_3$ by various methods

[Method 1]: Synthesis of aminosilanes by aminolysis of organochlorosilanes: The history of the synthesis of amiosilanes begins with the aminolysis reactions of organochlorosilanes with primary amines in THF or toluene under elimination of salt to form aminosilanes (silazanes) as represented in general reaction equation 5. The excess of amine acts here as a base to form an amine hydrochloride salt [1].

$$RSiCl_3 + 6\,R'NH_2 \xrightarrow{\Delta T} 3R'NH_3Cl + RSi(NHR')_3 \qquad (5)$$

[Method 2]: Synthesis of aminosilanes from organochlorosilanes and primary amines in the presence of triethylamine as auxiliary base: With respect to aminosilane synthesis there are number of reports in literature about the use of triethylamine as an auxiliary base as shown in general reaction equation 6 [3]. In this case NEt_3 is used as a base to capture HCl which is generated during the reaction. These reactions are carried out in THF, hexane or toluene as solvent. The use of triethylamine leads to better yields as compared with the aminolysis method 1.

$$R_nSiCl_{(4-n)} + (4-n)\,R'NH_2 + (4-n)\,NEt_3 \longrightarrow R_nSi(NHR')_{(4-n)} + (4-n)\,[HNEt_3]Cl \qquad (6)$$

(Where n = 1, 2; R = Me, Et or Ph and R' = Ph, Mes or Cy)

[Method 3]: Synthesis of aminosilanes by using lithium amides: There are quite few reports about the synthesis of silazanes using lithium amides. As discussed in above general reactions 5, 6 are not applicable when bulkier groups are (e.g. mesityl) attached to nitrogen. The aminolysis reaction or base reaction in presence of triethylamine stops after the formation of $R_2SiCl(NHR')$ and $RSiCl(NHR')_2$. One Cl atom remains unreacted even though an excess of primary amine is used. To overcome such a difficulty, lithiation method is employed in two steps as shown in general reaction equations 7 and 8. The first step is the lithiation of primary amine (mesitylamine or aniline), which is strictly carried out at -78 ^{o}C. Completion of the reaction is achieved by a gradual warming of the reaction mixture to room temperature. In the second step the lithium amides so formed are reacted with di or trichlorosilanes to obtain corresponding $R_2Si(NHR')_2$ and $RSi(NHR')_3$ aminosilanes in THF or toluene (Table 1) [5-8].

$$R'NH_2 \quad + \quad n\text{-}BuLi \longrightarrow R'NHLi \quad + \quad n\text{-}BuH \qquad (7)$$

$$R_nSiCl_{(4-n)} \ + \ (4\text{-}n)\ R'NHLi \longrightarrow R_nSi(NHR')_{(4-n)} \ + \ (4\text{-}n)\ LiCl \qquad (8)$$

(Where n = 1, 2; R = Me, Et or Ph and R' = Ph, Mes or Cy).

Table 1. Preparation methods of aminosilanes with different R and R'.

Compound (number)	**R**	**R'**	**Preparation Method**	**Literature reference no.**
$Me_2Si(NHPh)_2$ **(1)**	Me	Ph	2	Nöth *et al.*[5]
$Me_2Si(NHCy)_2$ **(2)**	Me	Cy	2	Mansfeld *et al.* [4]
$Ph_2Si(NHPh)_2$ **(3)**	Ph	Ph	2	Nöth *et.al.* [5]
$Me_2Si(NHMes)_2$ **(4)**	Me	Mes	3	Power *et al.* [9]
$Ph_2Si(NHMes)_2$**(5)**	Ph	Mes	3	Murugavel *et al.* [8]
$PhSiCl(NHMes)_2$ **(6)**	Ph	Mes	2	This work
$Ph_2SiCl(NHMes)$ **(7)**	Ph	Mes	2	This work
$MeSi(NHPh)_3$ **(8)**	Me	Ph	2	This work
$MeSi(NHMes)_3$ **(9)**	Me	Mes	3	This work
$EtSi(NHMes)_3$ **(10)**	Et	Mes	3	This work
$PhSi(NHPh)_3$ (**11)**	Ph	Ph	2	Lämmer, thesis [6]
$PhSi(NHMes)_3$ **(12)**	Ph	Mes	3	This work

All the silylamine compounds except **2 (**which is semisolid) are white crystalline powders. The yields are in between 65-70 % depending on the di or trichlorosilane used for the synthesis of aminosilanes by method 2 whereas for method 3 it is in between 80-85%. The synthesis of **1**, **2**, **3**, **4**, **5**, **8** and **11** is already well described in the literature [2-5]. **6** and **7** are synthesized by using method 2 and **9**, **10** and **12** are synthesized using method 3 and fully characterized by using single crystal XRD, ^{1}H and ^{29}Si NMR, IR and mass spectroscopy for the first time. The crystal structure of compounds **3**, **5** and **8** are studied in this research work even though their synthesis is already known since a long time.

3.1.4 Discussion of the spectroscopic data of diaminosilanes and triaminosilanes

A comparative study of the aminosilanes is outlined below in Table 2. The first characteristic feature of these compounds is the N-H stretching vibration from the IR spectra, in the range of 3363-3388 cm^{-1} and the C-N-H bending absorption around 1450 cm^{-1}. Si-N stretching around 900 cm^{-1} is observed for each aminosilane. All the aminosilanes give a very sharp signal for the NH groups in ^{1}H NMR in between 2.42-3.19 *ppm* depending on the nature of substituent on nitrogen. Aromatic protons of phenyl or mesityl groups are observed in between 6.78-7.15 *ppm*. Ortho and para methyl protons of mesityl are observed in the range of 2.10 and 2.18 *ppm* with meta protons at 6.67 *ppm*. The ^{29}Si NMR spectra of some of these aminosilanes have been studied for the first time and its shifts are outlined in Table 2. These values were compared with the known values of the aminosilanes from the literature [5, 8]. When silazanes are studied by ^{29}Si NMR spectra, it is found that their signals are very sharp and shifted upfield as we move from phenyl to cyclohexyl to mesityl groups on the N atoms and methyl/ethyl to phenyl on Si atoms. The upfield shifts of the ^{29}Si NMR spectra are correlated with the NH shifts in ^{1}H NMR spectra. These results are further confirmed by mass spectroscopy, melting point determination and elemental analysis. Aminosilanes are stable in air and moisture at room temperature and can be stored under inert atmosphere for years. Stable amines or amides of silicon invariably have the element in oxidation state +4 and a four coordinate environment. They are among the most commonly studied amides for all the elements in last century.

Table 2. ^{1}H and ^{29}Si NMR shifts and (N-H stretching) of aminosilanes bearing bulky substituents on nitrogen.

Compound (number)	**IR *v* (N-H) (cm^{-1})**	**^{1}H NMR (N-H) (ppm)**	**^{29}Si NMR (ppm)**	**Literature reference no.**
$Me_2Si(NHPh)_2$ **(1)**	3367	3.19	-11.09	Nöth *et al.* [5]
$Me_2Si(NHCy)_2$ **(2)**	3365	2.66	-12.462	Marga *et al.* [4]
$Ph_2Si(NHPh)_2$ **(3)**	3368	3.96	-30.07	Nöth *et.al.* [5]
$Me_2Si(NHMes)_2$ **(4)**	3388	2.42	-7.86	Power *et al.* [9]
$Ph_2Si(NHMes)_2$**(5)**	3363	3.22	-30.03	Murugavel *et al.* [8]
$PhSiCl(NHMes)_2$ **(6)**	3378	2.82	-28.47	This work
$Ph_2SiCl(NHMes)$ **(7)**	3363	2.98	-12.84	This work
$MeSi(NHPh)_3$ **(8)**	3367	3.53	-29.91	This work
$MeSi(NHMes)_3$ **(9)**	3364	2.59	-31.10	This work
$EtSi(NHMes)_3$ **(10)**	3367	2.54	-31.33	This work
$PhSi(NHPh)_3$ (**11)**	3371	3.66	-41.47	Lämmer, thesis [6]
$PhSi(NHMes)_3$ **(12)**	3364	2.99	-44.85	This work

3.1.5 Crystal structures of $Ph_2Si(NHPh)_2$ (3), $Ph_2Si(NHMes)_2$ (5), $PhSiCl(NHMes)_2$ (6) and $Ph_2SiCl(NHMes)$ (7)

Single crystals suitable for single crystal X-ray diffraction studies were grown at 0 to -10 °C over a period of 48 hours by diffusion of hexane/pentane in a toluene. Compounds **3**, **6** and **7** crystallize triclinic in the space group $P\bar{1}$ with two formula units per unit cell where as compound **5** crystallizes monoclinic in the space group $P\,2_1/c$ with four formula units per unit cell. The perspective view of the molecular structures of the compounds **3**, **5**, **6** and **7** are shown in Figures 9, 10, 11 and 12 respectively. Selected structural parameters for all these compounds are listed in Table 3.

Table 3. Selected bond lengths (Å) and angles (°) for compounds **3, 5, 6** and **7**.

Bond lengths (Å)	**3**	**5**	**6**	**7**
Si-N	1.716(2) - 1.727(2)	1.726(1) - 1.727(1)	1.700(3) - 1.709(3)	1.715(2)
Si-C	1.871(2) - 1.873(2)	1.877(2) - 1.884(2)	1.868(4) -----	1.857(2) - 1.863(2)
Si-Cl	-----	-----	2.086(1)	2.081(1)
N-H	0.86(2)	0.84(3)	0.837(1)	0.788(2)
Bond angles (°)				
N-Si-N	106.88(9)	108.79(8)	105.85(17)	-----
N-Si-C	102.90(9) - 132.83(1)	100.99(7) - 115.46(7)	104.07(12) - 120.16(16)	106.96(1) - 113.28(1)
C-Si-C	112.68(9)	111.81(8)	-----	113.58(1)
C-Si-Cl	-----	-----	105.69(13)	104.31(7) - 107.12(7)

In case of **3** and **5** two N-atoms and two C-atoms are coordinated to the silicon atom whereas in the case of **6** there are two N-atoms, one C-atom, one Cl-atom and for **7** two C- atoms one N-atom and one Cl-atom respectively in a nearly tetrahedral manner.

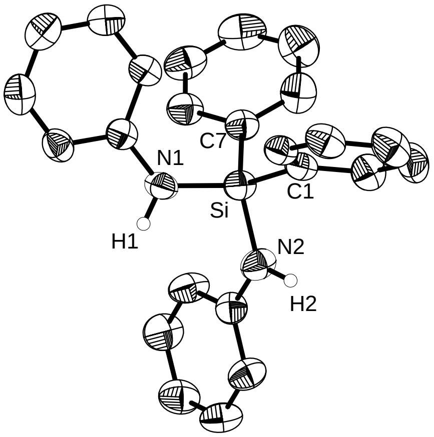


Fig. 9: Molecular structure of $Ph_2Si(NHPh)_2$ **(3)** in the crystal (50% probability level, only H-atoms attached to N are shown)

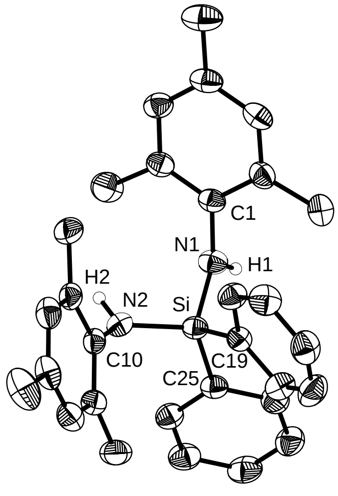


Fig. 10: Molecular structure of $Ph_2Si(NHMes)_2$ **(5)** in the crystal (50% probability level, only H-atoms attached to N are shown)

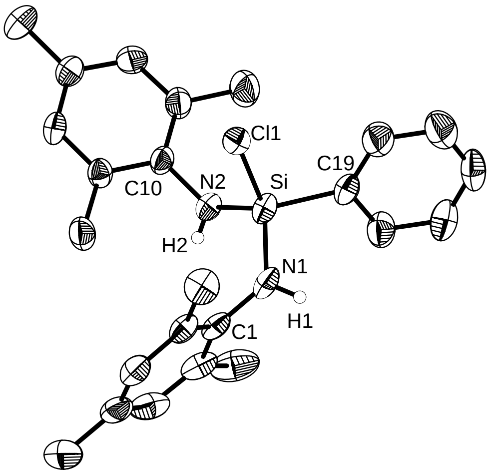


Fig. 11: Molecular structure of $PhSiCl(NHMes)_2$ **(6)** in the crystal (50% probability level, only H-atoms attached to N are shown)

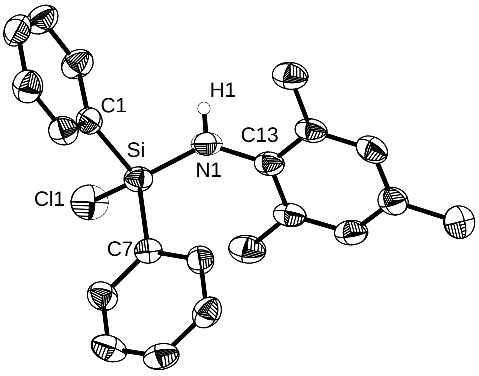


Fig. 12: Molecular structure of $Ph_2SiCl(NHMes)$ **(7)** in the crystal (50% probability level, only H-atoms attached to N are shown)

The arrangement of phenyl or mesityl groups (aromatic rings) around the Si atom looks like a propeller with radiating blades which are arranged in a certain manner. For all the compounds the average Si-N bond length is in the range of 1.700(3)-1.727(2) (Å), Si-C is in the range of 1.87(2)-1.877(2) (Å) and N-H is in the range of 0.706(1)-0.86(2) (Å) with only small deviations. This is in good agreement with literature values reported by Nöth *et al.* and others for diaminosilanes (Si-N 1.700(2)(Å) and Si-C 1.861(1) (Å)).

The bond angles in compound **3** are N(2)-Si(1)-N(1) of 106.88(9)°, N(1)-Si(1)-C(7) of 107.55(9)°; and N(2)-Si(1)-C(1) of 102.90(9)° with a slight flattening of the tetrahedron by wider angle C(7)-Si(1)-C(1) of 112.68(9)° giving a nearly tetrahedral geometry. A similar trend was observed for **5**, **6** and **7** and its values are outlined in Table 3 for the comparison with other compounds. The interplanar angle between the two phenyl groups of compounds **3**, **5**, **6** and **7** are 69.79(2)°, 89.07(1)°, 82.56(3)° and 86.12(2)° respectively. The N atoms in all the compounds are in trigonal planar coordination having no intermolecular N-H----N interactions in the solid state. The sum of bond angles at the nitrogen atoms is close to 360° that indicates trigonal planar coordination.

3.1.6 Crystal structures of $MeSi(NHPh)_3$ (8), $MeSi(NHMes)_3$ (9), $EtSi(NHMes)_3$ (10) and $PhSi(NHMes)_3$ (12)

Colorless X-ray quality single crystals of compounds **8**, **9**, **10** and **11** were obtained after 3 days at -10 °C by the diffusion of hexane/pentane in a toluene. Compound **8** crystallizes monoclinic in the space group I 2/a and compound **9** orthorhombic in the space group P can with eight formula units per unit cell. Whereas **10** and **12** crystallize triclinic in the space group $P\bar{1}$ with two formula units per unit cell. In all compounds the Si atom at the centre is coordinated nearly tetrahedrally by three nitrogen atoms and one C atom. Si atoms with phenyl or mesityl groups (aromatic rings) arrangement looks like a propeller. There is slight flattening of the tetrahedron by wider angles up to 120° and values of the angles are depicted in Table 4. Perspective views of the molecular structure are shown in Figures 13, 14, 15 and 16 respectively. Selected bond lengths and bond angles in the range are listed in Table 4.

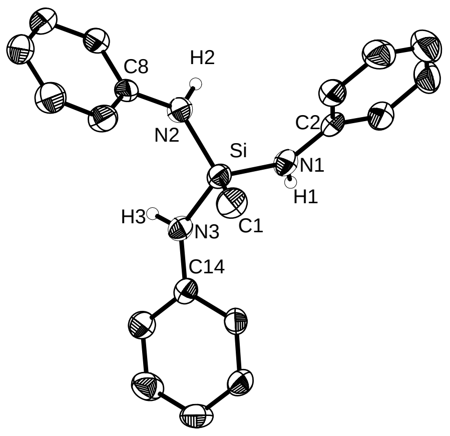


Fig. 13: Molecular structure of MeSi(NHPh)$_3$ **(8)** in the crystal (50% probability level, only H-atoms attached to N are shown)

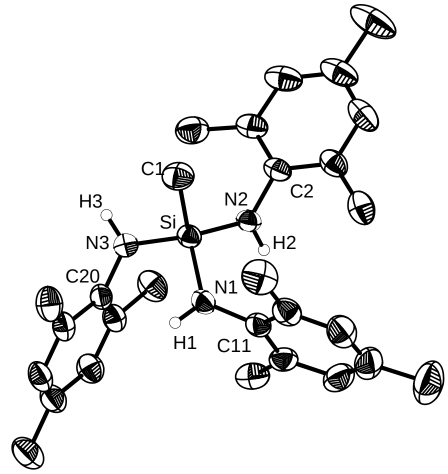


Fig. 14: Molecular structure of MeSi(NHMes)$_3$ **(9)** in the crystal (50% probability level, only H-atoms attached to N are shown)

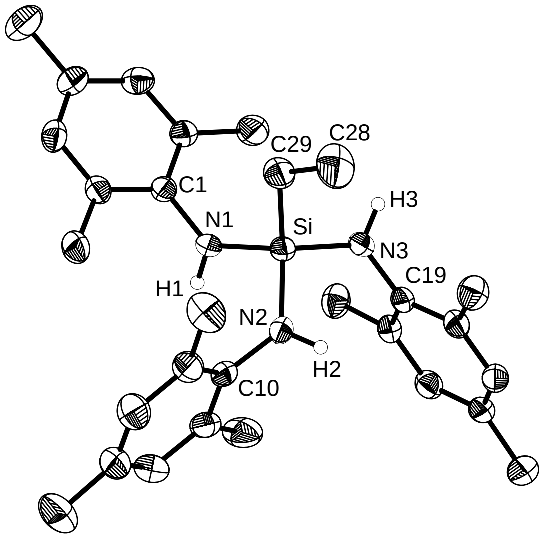


Fig. 15: Molecular structure of EtSi(NHMes)$_3$ **(10)** in the crystal (50% probability level, only H-atoms attached to N are shown)

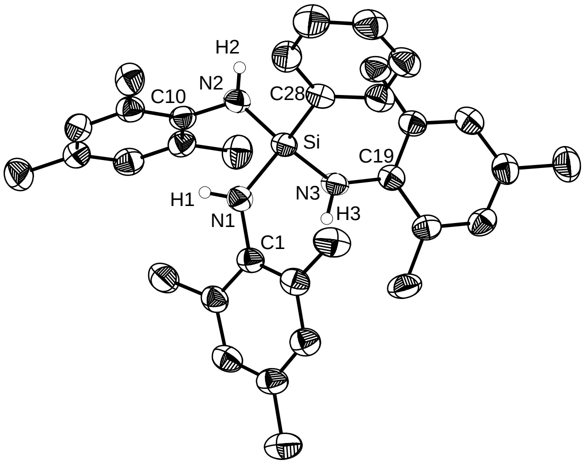


Fig. 16: Molecular structure of PhSi(NHMes)$_3$ **(12)** in the crystal (50% probability level, only H-atoms attached to N are shown)

Table 4. Selected bond lengths (Å) and angles (°) for compounds **8, 9, 10** and **12**.

Bond lengths (Å)	**8**	**9**	**10**	**12**
Si-N	1.724(3) - 1.731(2)	1.720(1) - 1.727(2)	1.731(4) - 1.733(4)	1.706(2) - 1.735(2)
Si-C	1.403(4) - 1.415(3)	1.422(3) - 1.437(3)	1.429(6) - 1.435(6)	1.420(3) - 1.446(3)
N-H	0.86(1)	0.86(1)	0.86(3)	0.77(3) - 0.82(3)
Bond angles (°)				
N-Si-N	105.18(11) - 107.26(12)	103.50(9) - 119.96(9)	103.07(19) - 120.79(18)	102.43(9) 118.55(9)
N-Si-C	111.07(14) - 113.93(14)	104.92(10) 118.97(10)	105.00(2) - 120.50(2)	105.53(10) 115.42(10)

The average Si-N bond length in all compounds is in the range of 1.706(2)-1.735(2) Å which is slightly longer than those observed for $Ph_2Si(NR')_2$ reported by Nöth *et al.* (ave. Si-N bond length 1.70 Å) and Murugavel *et al.* for difunctional aminosilanes of type $Ph_2Si(NHMes)_2$ [5, 8]. This lengthening of Si-N bond length is analogous to effect observed by R. Murugavel *et al.* for compounds which have sterically demanding substituents attached to N such as $(2,6\text{-}^iPr_2C_6H_3NH)_2SiPh_2$ and $(2,6\text{-}Et_2C_6H_3NH)_2SiPh_2$. This Si-N ave. bond length range 1.706(2)-1.735(2) Å of all the compounds **3-12** discussed here, can be compared with the following compounds Si-N bond lengths.

Compound	**Si-N (Å)**	**References**
$N(SiH_3)_3$	1.736	[38]
$[ClSi(NMe_2)_3]$	1.715	[37]
$[(2,4,6\text{-}Me_3C_6H_2NH)_2SiMe_2]$	1.730	[5]
$(Me_2SiNSiMe_3)_3$	1.74	[35]
$Me_2Si(NHMes)_2$	1.730	[33]
$[(Me_2Si)_2Si(NSiMe_3)_4]$	1.74	[36]

The Si-C and N-H bond lengths are normal in the range of 1.403(4)-1.446(3) Å and 0.77(3)-0.86(1) Å as observed for diaminosilanes described in 3.1.5.

Bond angles of compounds **8-12** are similar to compound **3** described in the earlier case with a slight flattening of the tetrahedron by wider angles giving a nearly tetrahedral geometry and its values are outlined in above Table 4. The interplanar angle between phenyl/mesityl groups of compounds **8**, **9**, **10** and **12** are 85.85(2)°, 87.70(2)^o, 79.53(2)° and 75.20(2)^o respectively. All the aromatic rings in molecules are nearly identical with their interplanar angles. Therefore the major conclusion is that in case of triaminosilanes as we move from alkyl (methyl/ethyl) chain to the bulkier group such as phenyl or mesityl, the interplanar angle between two planes becomes smaller. This could be due to the steric effect on the Si atom which is at the centre of the molecule. The sum of bond angles at the nitrogen atoms is close to 360^{o}C which indicate trigonal planar coordination and there are no intermolecular N-H-----N interactions in the solid state.

3.2 Reactions of difunctional silylamides with group III halides $AlCl_3$, $GaCl_3$ and $InCl_3$ (*Part-II*)

3.2.1 Introduction:

The synthesis of difunctional $R_2Si(NHR')_2$ and trifunctional aminoslianes $RSi(NHR')_3$ which are also called as bidentate and tridentate ligands is well described in *section 3.1* of silylamines. The next step involves the lithiation of aminosilanes using n-BuLi to form lithium silylamido compounds like $R_2Si(NLiR')_2$ and $RSi(NLiR')_3$. The intermediate lithiated compounds are reacted with group III halides such as $AlCl_3$, $GaCl_3$ and $InCl_3$ to form metal complexes. Three examples of the isolated lithium silylamide complexes are characterized by ^1H, ^{13}C, ^{29}Si and ^7Li NMR spectroscopy and single crystal XRD. And for other cases of lithiated amidosilanes, the anhydrous metal trichloride in Et_2O is added dropwise *in situ* for the preparation of the desired group III silylamido compounds.

3.2.2 Lithiated silylamide compounds of difunctional aminosilanes $R_2Si(NHR')_2$

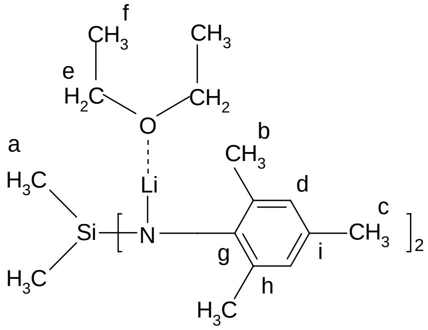
3.2.3 Synthesis of [{$Me_2Si(NLiMes)_2(OEt_2)$}$_2$] (13)

Aminosilanes are reacted with n-BuLi in hexane at -78 °C to form lithiated amidosilanes. In a typical reaction $Me_2Si(NHMes)_2$ reacts with n-BuLi at -78 °C to form a lithiated product. The reaction mixture is refluxed in a boiling hexane for one hour to obtain the product. The product is recrystallized from Et_2O at -15 °C within 48 hrs.

$$Me_2Si(NHMes)_2 + 2\ n\text{-}BuLi \xrightarrow{+\ 2\ Et_2O} \underset{\textbf{(13)}}{[Me_2Si(NLiMes)_2OEt_2]} + 2\ n\text{-}BuH \qquad (7)$$

[$Me_2Si(NLiMes)_2(OEt_2)$] **(13)** is characterized by ^1H, ^{13}C, ^{29}Si, ^7Li NMR spectroscopy and IR spectroscopy. In the ^1H NMR spectrum of **13** (in C_6D_6) methyl protons of the silane ligands are present at 0.33 *ppm* as a sharp *singlet.* The methyl *ortho, para* protons of mesityl group give a sharp peak at 2.31 and 2.33 *ppm* and the signals of the aromatic protons are observed at 6.68 *ppm*. Methyl protons of the coordinated Et_2O solvent are at 0.88 *ppm* as a *triplet* and methylene protons as a *multiplet* at 3.03 *ppm*.

The ratio of the integrated intensities of methyl protons of silylamide ligand to methyl protons of coordinated Et_2O solvent molecule is approx. 1:2. In ^{29}Si NMR (C_6D_6) of **13** a sharp *singlet* is observed at -23.06 *ppm* which was shifted upfield as compared to $Me_2Si(NHMes)_2$ peak (-7.86 *ppm*). In ^{7}Li NMR, there are two peaks at 1.47 *ppm* and at 1.91 *ppm* respectively which indicates that there are two different types of Li atoms present in the compound.



NMR	13	4	Proton assignment
^{1}H		2.42 ppm	H (N-H)
	0.33 ppm	0.12 ppm	H^a
	2.33ppm	2.16 ppm	H^b
	2.31ppm	2.18 ppm	$H^{c,}$
	6.68 ppm	6.65 ppm	H^d
	0.88 ppm		H^f
	3.03 ppm		H^e
^{29}Si	-23.06 ppm	-7.86 ppm	
^{7}Li	1.47 and 1.91 ppm		

3.2.4 Crystal structure of $[\{Me_2Si(NLiMes)_2(OEt_2)\}_2]$ (13)

Compound **13** was recrystallized by diffusion of Et_2O in a toluene solution at -25°C. After four days suitable crystals were obtained for the single crystal XRD measurement. **13** crystallizes triclinic in the space group $P\bar{1}$ with two formula units per unit cell. The molecular structure is shown in Fig. 17 (50% probability level). Selected structural parameters are listed in Table 5.

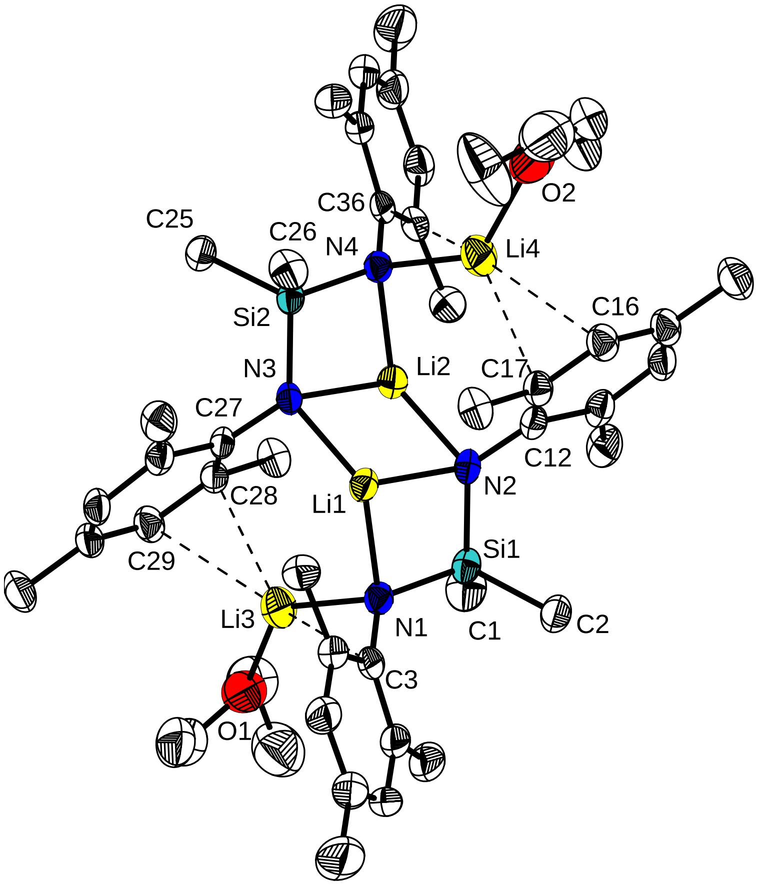


Fig. 17: Molecular structure of [{$Me_2Si(NLiMes)_2(OEt_2)$}$_2$] **(13)** in the crystal (at 50% probability level, and H-atoms are omitted)

In **13** two [$Me_2Si(NLiMes)_2$] units forms a dimer with a ladder like structure. Two [$Me_2Si(NMes)_2$]$^{2-}$ units are linked by four Li^+ cations. Additionally there are two Et_2O molecules attached to Li atoms. The centre of the dimer consists of a four membered Li_2N_2 ring. The Li_2N_2 ring is attached to two four memberd N_2SiLi rings of silylamides at the edges to form a $Li_2Si_2N_4$ core that looks like a ladder. This $Li_2Si_2N_4$ core is attached to $LiOEt_2$ units at the terminal N atoms to give a nearly centrosymmetric structure.

In the Li_2N_2 four membered ring of **13**, Li(1) and Li(2) are coordinated with three N atoms having a distorted trigonal planar coordination. Whereas Li(3) and Li(4) are connected to only one N-atom of the silylamide and one Et_2O molecule. Li(3) has a very close interaction with two C-atoms (C(28) and C(29)) of the one silylamine ligand and one C-atom (C(3)) of another silylamine ligand of mesityl groups as shown by dotted lines in Figure 17. A similar observation is made for Li(4) atom also and shown in the Figure 17 with dotted lines.

Table 5. Selected bond lengths (Å) and angles (^{o}) for compound **13**

Bond lengths (Å)

Li-N	1.966(6)-2.060(5)	Si-N	1.717(3)-1.732(2)
Li-C	2.579(7)-2.765(7)	Li-O	1.930(7)-1.966(6)

Bond angles (^{o})

C-N-Li	100.7(2)-129.4(3)	N-Li-C	32.39(14)-144.0(3)
N-Si- N	52.43(14)-127.68 (17)	Li-N-Li	73.3(2)-97.0(3)
N-Li-N	82.90(2)-131.60(3)		

The Li-N average bond length for Li(1) is 2.04(6) Å and for Li(3) is 1.96(6) Å. The bond length Li(3)-C(3) is 2.579(7) Å of the same silane ligand molecule. In case of the second silane ligand molecule the lengths are 2.536(7) Å for C(28)-Li(3) and 2.765(7) Å for C(29)-Li(3) respectively. These Li-C bond lengths are comparable to the values observed for [(2,6-$Et_2C_6H_3NH$)(2,6-$Et_2C_6H_3NLi$)$SiPh_2$] [34] studied by Murugavel *et al.* and references there in.

The crystal structure of the solvent free [$Me_2Si(NLiMes)_2$]$_2$ has been studied by Power *et al.*. Like **13**, [$Me_2Si(NLiMes)_2$]$_2$ is dimeric in nature but it has exactly crystallographic $\bar{1}$ symmetry. Two Li atoms are exactly over the centroid of the mesityl ring of the silazane [33]. The ave. Li-C distance of the mestiyl C-atoms is 2.382(9) Å in [$Me_2Si(NLiMes)_2$]$_2$. This distance is approximately 0.30 Å shorter than for **13** studied in this work.

A remarkable feature of compound **13** in this study is that two Li cations are coordinated by Et_2O. This observation is in agreement with the two different Li shifts at 1.47 and 1.91 *ppm* observed in ^{7}Li NMR spectra which indicate different coordination behavior of Li atoms. This resemble that **13** has a similar structure in solid state as well as in deuterated benzene solution.

Similar like this $[\{Li(N(SiMe_3)CH_2CH_2NSiMe_3\}Li(Et_2O)]_2$ lithium etherate complex of Li_4N_4 ladder core with ethylene linkages is well studied by Raston *et al.*[40].

In literature it is known that some of the lithumsilylamide compounds lead to aggregation. Most of the studied lithiated compounds were either monomeric or dimeric in nature. Very few of them were polymeric in nature. The ave. Li-N bond length 1.966(6)-2.060(5) Å of **13** is comparable with the Li-N bond length of the different compounds that are already known in the literature.

Compound	**Li-N (Å)**	**Reference**
$[\{t\text{-}BuNLi\}_2SiMe_2]_2$	2.036(6)	[9]
$[\{t\text{-}BuNLi\}_3SiPh_2]_2$	2.030(4)	[9]
$[MeSi(N^t\text{-}Bu)_2LiOEt_2]_2$	2.18(3)	[43]
$[Me_2Si(NLiMes)_2]_2$	2.015(8)	[33]
$[\{Li(N(SiMe_3)CH_2CH_2NSiMe_3\}Li(Et_2O)]_2$	2.06(2)	[40]
$[\{H_2C(CH_2)_3NLi\}_3.PMDTA]_n$	2.04(3)	[42]

The Li-O bond length is 1.940(7) Å. This Li-O bond length is in the range of the organolithium etherate complex $[\{Li(Et_2O)(2,4,6\text{-}(CHMe_2)_3C_6H_2)\}_2]$ (ave. Li-O 1.930(3) Å) [39] and $[Li(OC_6H_2Me\text{-}4\text{-}^tBu_2\text{-}2,6)(OEt_2)]_2$ (ave. Li-O 1.962(1) Å) [41]. To conclude **13** is dimeric in nature and coordinated by one molecule of Et_2O and shows a similar framework of ladder type monolithiated amide structures of compounds studied by Veith and Armstrong *et al.* [43-44].

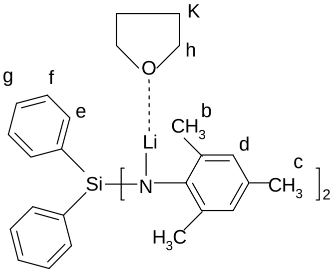
3.2.5 Synthesis of [$Ph_2Si(NLiMes)_2(OC_4H_8)_4$] (14)

n-Butyllithium was added to the suspension of $Ph_2Si(NHMes)_2$ in hexane at -78 °C over a period of 45 min as shown in general reaction equation 8. After complete addition the reaction mixture was heated at 70 °C for 2 hrs. Subsequently the lithiated compound was precipitated as a yellow solid. After the suspension was cooled to room temperature 20 mL of Et_2O and 5 mL of THF were added to make it completely soluble. After 4 days colorless needle like crystals of product **14** were obtained and characterized by single crystal XRD, ^1H, ^{13}C, ^7Li and ^{29}Si NMR spectroscopy and IR spectroscopy.

$$Ph_2Si(NHMes)_2 + 2\ n\text{-}BuLi \xrightarrow{THF} \underset{\textbf{(14)}}{[Ph_2Si(NLiMes)_2(OC_4H_8)_4]\cdot 2THF} + 2\ n\text{-}BuH \quad (8)$$

In the ^1H NMR (in C_6D_6) spectrum of **14** the methyl protons of the mesityl ring are present as singlet at 2.20 *ppm* (*ortho* CH_3) and 2.30 *ppm* (*para* CH_3). These peaks are shifted downfield as compared to the corresponding signals of $Ph_2Si(NHMes)_2$, from 2.07 and 2.09 *ppm* respectively. All other aromatic protons are observed at the same shift (6.67-7.66 *ppm*) as in the starting compound. The signals of the THF used for the recrystallization is observed at 1.81 and 3.69 *ppm* respectively.

In the ^{29}Si NMR spectrum (in C_6D_6) of **14** a sharp singlet is observed at -43.87(*s*) *ppm*. Compared to $Ph_2Si(NHMes)_2$ here is an up field shift of 13 *ppm*. In ^7Li NMR, there are three different peaks at 0.46(*s*), 1.17(*s*) and at 1.91 (*s*) *ppm*. In contrast to **13** it has three different Li peaks in ^7Li NMR even though **14** is also difunctional aminosilane. This observation indicates that **14** has a different arrangement of Li atoms in a molecule. To get better insight of **14** it was decided to study its single crystal XRD analysis.



NMR	14	5	Proton assignment
^{1}H	2.20 ppm	2.07 ppm	H^{b}
	2.30 ppm	2.09 ppm	H^{c}
	6.67 ppm	6.67 ppm	H^{d}
	3.69 ppm		H^{h}
	1.81 ppm		H^{k}
	7.05-7.66 ppm	7.05-7.66 ppm	$H^{e,f,g}$ (*Broad multiplet*)
^{29}Si	-43.87 ppm	-30.03 ppm	
^{7}Li	0.46, 1.71 and 1.89 ppm.		

3.2.6 Crystal structure of $[(Li(OC_4H_8)_4][Li_3\{Ph_2Si(NMes)_2\}_2]\cdot 2THF$ (14)

Compound **14** was recrystallized by diffusion of THF in a toluene solution at -15 °C. After eight days suitable crystals for the single crystal XRD measurement were obtained. It crystallizes monoclinic in the space group P 2_1/n with four formula units per unit cell. The molecular representation of cation and separated anion is shown in Figures 18 and 19 (50% probability level) respectively. Selected structural parameters are listed in Table 6.

In the solid state **14** consists of well separated $[Ph_2Si(NMes)_2\ Li_3]^-$ anions and $[Li(THF)_4]^+$ cations. The anion of **14** consists of two $Ph_2Si(NMes)_2$ fragments with three Li atoms. Li(1) and Li(2) are coordinated by three N atoms giving a distorted trigonal planar geometry. Whereas Li(3) present in the anion is coordinated by one N atom of each $Ph_2Si(NMes)_2$ molecule and two C-atoms of aromatic ring on neighboring N-atoms. This leads to form a $Li_3N_4Si_2$ cluster core approximately with a twofold symmetry axis.

Table 6. Selected bond lengths (Å) and angles (°) for compound **14**.

Bond lengths (Å)

Li-N	1.960(5)-2.095(5)	Si-N	1.702(2)-1.714(2)
Li-C	2.607(5)-2.771(6)	Li-O	1.925(7)-1.955(8)

Bond angles (°)

C-N-Li	105.7(2)-126.3(2)	N-Li-C	30.13(11)-155.2(3)
N-Si-N	101.590(1)-101.840(1)	Li-N-Li	70.97(19)-91.1(2)
N-Li-N	79.27(18)-129.4(2)		

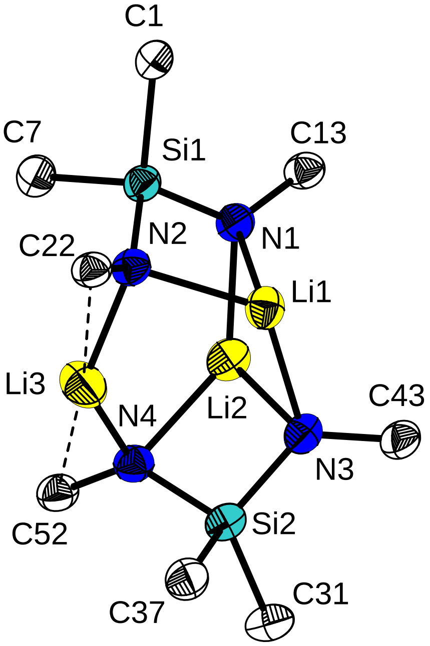


Fig. 18. Molecular structure of $[Li_3\{Ph_2Si(NMes)_2\}_2]^-$ anion of **(14)** in the crystal (50% probability level, phenyl and mesityl groups are represented by the ipso C-atoms and H-atoms are omitted)

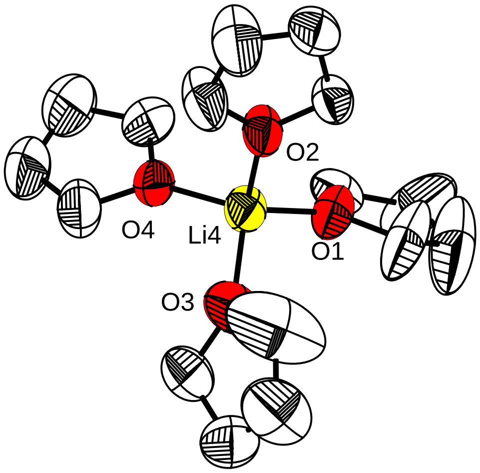


Fig. 19: Molecular structure of $[Li(THF)_4]^+$ cation of **(14)** in the crystal (50% probability level, and H-atoms are omitted)

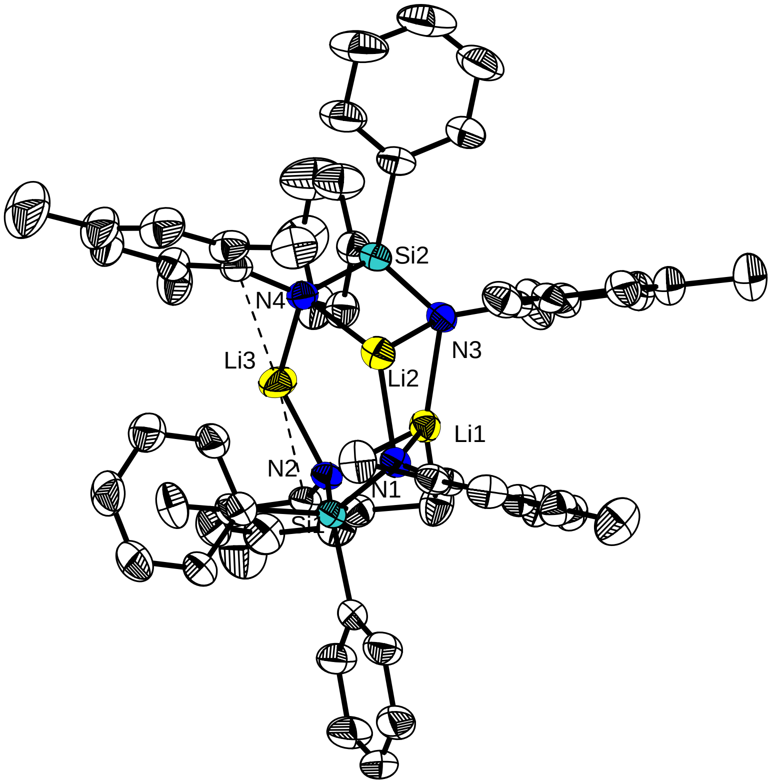


Fig. 20. Molecular structure of $[Li_3\{Ph_2Si(NMes)_2\}]^-$ anion of **(14)** in the crystal (50% probability level, H-atoms are omitted)

The anion is much larger than the cation. It is composed of two silylamine ligands and 3 Li atoms. More bulky groups are attached to Si and N atom to give a totally different configuration than cluster compound **13**. The Li-N average bond length is 2.095(5) Å. The bond distances Li(3)-C(22) of (2.607(1) Å) and Li(3)-C(52) of (2.705(5) Å) indicate that there is an interaction between Li(3) and C(22) and C(52) C-atoms of the aromatic ring. For other C-atoms of the aromatic ring the distance is longer than for C(22) and C(52). These distances are in the range of **13** described earlier. Therefore Li(1) and Li(2) which have similar coordination of three N-atoms are nearly equivalent. Li(3) has different coordination with two N-atoms of each silylamine and one C-atom of each mesityl ring. Thus Si, N and Li atoms in the core of an anion has approximately C_2 symmetry. The ^{7}Li NMR spectrum shows three different signals at 0.46 *ppm*, 1.71 *ppm* and 1.89 *ppm* respectively. It can be assumed that the structure of **14** is retained in the solution. The signal at 0.46 *ppm* corresponds to $[Li(THF)_4]$ cation well separated from anion.

Lithium atoms in the anion have a distorted trigonal planar coordination with a small bond angle N(3)-Li(2)-N(4) of 79.27(18)° and larger bond angle N(1)-Li(2)-N(4) of 129.4(2)°.

The Si-N and Si-C bond lengths are nearly same as in $Ph_2Si(NHMes)_2$ (**5**) with small deviation when it gets coordinated to the Li atom and its values are outlined in Table 6. All the bond distances of **14** can be compared to **13** and references there in. Si atom has a tetrahedral coordination whereas N atoms are having a trigonal pyramidal coordination.

14 shows a counter ion $[Li(THF)_4]^+$ which often occurs in the lithiated compounds. This is also observed in lithiated silylamide compounds. Li(4) in **14** has a tetrahedral coordination of four THF solvent molecules and its Li-O ave. bond length is (1.925(7) Å). The Li-N (2.095(5) Å) and Li-O (1.925(7) Å) bond lengths of **14** are comparable to lithiated ionic compound $[\{(SiMe_2(NC(Ph)N(2,6^{i}\text{-}Pr_2Ph)_2\}_2Li_3\}][Li(THF)_4]$ studied by Liu *et al.*[45].

These average bond lengths Li-N and Li-O are comparable to **13** earlier described. Li-O bond length is comparable with the cations present in the ionic compounds of difunctional silylamides in the forthcoming section. It is also comparable with following different lithiated compounds from the literature.

Compound	**Li-N**	**Li-O**	**Reference**
$[\{Li(N(SiMe_3)CH_2CH_2NSiMe_3\}Li(Et_2O)]_2$	2.060(2)	1.918(1)	[40]
$[\{(SiMe_2(NC(Ph)N(2,6^{i}\text{-}Pr_2Ph)_2\}_2Li_3\}][Li(THF)_4]$	2.052(8)	1.909(1)	[45]
$[NH(Ph)SiMe_2N(Ph)Li(Et_2O)]_2$	2.053(4)	1.988(4)	[45]

3.3 Reactions of lithiated difunctional silylamides with group III halides $AlCl_3$, $GaCl_3$ and $InCl_3$ (*Part-III*)

3.3.1 Synthesis and characterization of aluminum silylamide compounds

The next step is to react these lithiated amidosilanes $R_2SiN(LiR')_2$ with group III halides such as $AlCl_3$, $GaCl_3$ and $InCl_3$. First the synthesis and characterization of aluminum compounds with difunctional silylamides is discussed. Generally the synthesis of aluminum compounds takes place in two steps as shown in the general reactions 9-11.

$$R_2Si(NHR')_2 + 2\ n\text{-}BuLi \longrightarrow R_nSi(NLiR')_2 + 2\ n\text{-}BuH \qquad (9)$$

$$2\ R_2Si(NLiR')_2 + AlCl_3 \begin{array}{l} \xrightarrow{+\,3\ Et_2O} [Li(OEt_2)_3][\{R_2Si(NR')_2\}_2Al] + 3\ LiCl \quad (10) \\ \xrightarrow{+\,4\ THF} [Li(OC_4H_8)_4][\{R_2Si(NR')_2\}_2Al] + 3\ LiCl \quad (11) \end{array}$$

15-18

(R = Me, Ph; R' = Ph, Mes or Cy; M = Al)

In a typical experiment $Me_2Si(NHPh)_2$ was lithiated using n-BuLi at -78 °C in hexane to form $Me_2Si(NLiPh)_2$ as an intermediate product. $Me_2Si(NLiPh)_2$ was treated with $AlCl_3$ dissolved in Et_2O in a molar ratio 2:1. The addition of $AlCl_3$ was carried out at -20 °C and a clear reaction solution was formed in the hexane-Et_2O mixture. Upon warming to room temperature LiCl precipitates together with the aluminum silylamide compound within one hour. Such type of a reaction is more favorable in Et_2O-hexane mixture. When other solvents are tried for the preparation of aluminum silylamide compounds, oily reaction products or starting material is obtained. Reaction mixture is stirred at room temperature for 18 hours. Reaction suspension is allowed to settle down and filtered through a Schlenk line filter. Product is extracted in a warm toluene which upon cooling at -10 °C forms white needle like crystals. The yield of the product was 70% with respect to $Me_2Si(NHPh)_2$. These crystals were sensitive to air and moisture and remain stable under inert atmosphere for a several months in a refrigerator. In a similar way compounds **16-18** are synthesized by using different R and R' groups with the same experimental procedure. Details of the compounds **15-18** are outlined in Table 7. Compounds are further characterized by ^{1}H, ^{13}C, ^{29}Si NMR spectroscopy and IR spectroscopy. The data is outlined in experimental part chapter 5 and EDX measurement.

Table 7. Aluminum silylamide compounds **15-18.**

Compound	R	R’	Recrystallization solvent	Yield based on silylamine
$[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Al]\cdot Tol$ **(15)**	Me	Ph	Et_2O	70 %
$[Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2Al]\cdot 3THF$ **(16)**	Ph	Ph	THF	62 %
$[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2Al]$ **(17)**	Ph	Mes	Et_2O	64 %
$[Li(OEt_2)_3][\{Me_2Si(NCy)_2\}_2Al]$ **(18)**	Me	Cy	Et_2O	70 %

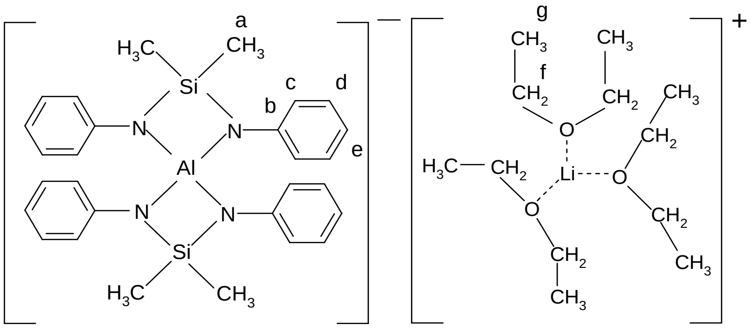
The first hand information of compounds **15-18** was studied by IR spectroscopy, ^1H and ^{13}C NMR spectroscopy. Further these complexes are characterized by ^{29}Si NMR spectroscopy and the values were compared with the data of starting silylamines. The ^{29}Si NMR shifts are outlined in Table 8. It is observed that when Al gets coordinated to the N atoms of the silylamido ligand there is an upfiled shift in the ^{29}Si NMR signals compared to the starting aminosilanes except for **17** which has shifted to downfield.

Table 8. ^{29}Si NMR shifts of compounds **15-18** and aminosilanes.

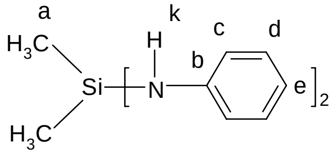
Compound	δ ^{29}Si (ppm)	Starting silylamine	δ ^{29}Si (ppm)
$[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Al]\cdot Tol$ **(15)**	-4.14	$Me_2Si(NHPh)_2$ **(1)**	-11.09
$[Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2Al]\cdot 3THF$ **(16)**	-28.59	$Ph_2Si(NHPh)_2$ **(3)**	-30.07
$[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2Al]$ **(17)**	-33.84	$Ph_2Si(NHMes)_2$ **(5)**	-30.03
$[Li(OEt_2)_3][\{Me_2Si(NCy)_2\}_2Al]$ **(18)**	-6.56	$Me_2Si(NHCy)_2$ **(2)**	-12.46

Presence of Et_2O or THF solvent which was used for the recrystallization is observed in ^1H as well in as ^{13}C NMR spectra and its data is outlined in experimental chapter for **15-18.**

The ^{1}H, ^{13}C and ^{29}Si NMR data of [Li(OEt$_2$)$_3$][{Me$_2$Si(NPh)$_2$}$_2$Al] (**15**) are discussed in detail with respect to starting aminosilane Me$_2$Si(NHPh)$_2$ (**1**) as one of the examples of an ionic aluminum compound.



[Li(OEt$_2$)$_3$][{Me$_2$Si(NPh)$_2$}$_2$Al] **(15)**



Me$_2$Si(NHPh)$_2$ (**1**)

NMR	**15**	**1**	**Proton assignment**
^{1}H	0.67 ppm	0.87 ppm	H^{a}
		3.19 ppm	H^{k}
	6.62 ppm	6.64 ppm	H^{c}
	6.76 -7.08 ppm	6.73 - 7.05 ppm	H^{e} H^{d} } Broad multiplet of aromatic protons
	2.92 ppm		H^{f}
	0.86 ppm		H^{g}
^{29}Si	-4.14 ppm	-11.33 ppm	

In the ^{1}H NMR spectrum (in C$_6$D$_6$**)** of **15** the methyl protons of silylamide are observed as *singlet* at 0.67 *ppm* which is shifted upfield from 0.87 *ppm* of Me$_2$Si(NHPh)$_2$. The Et$_2$O methyl protons peak is present as *triplet* at 0.86 *ppm* and methylene protons as *quartet* at 2.92 *ppm*. From the integrated intensities of the signals, it is found that the ratio of methyl protons of silylamide to the methyl protons of Et$_2$O is 1:1.5. The coordination of Et$_2$O is observed in ^{1}H as well as in ^{13}C NMR spectra at 14.65 (CH$_3$) and 66.00 (CH$_2$) *ppm*.

In ^{29}Si NMR (C_6D_6) of **15** a sharp singlet peak is observed at -4.14(*s*) *ppm*. This corresponds to a downfield shift by 6 *ppm* compared to $Me_2Si(NHMes)_2$ (-11.33 *ppm*). The presence of only one Si signal indicates that only one type of Si coordination is present in the molecule. As NMR spectroscopy data was not sufficient to get all the information about molecular structure of **15** a single crystal analysis was carried out. The content of the Al metal is studied by EDX and the peak was found at 1.48 KeV.

3.3.2 Crystal structures of [Li(OEt$_2$)$_3$][{Me$_2$Si(NPh)$_2$}$_2$Al]·Tol (15) and [Li(OC$_4$H$_8$)$_4$][{Ph$_2$Si(NPh)$_2$}$_2$Al]·3THF (16)

Single crystals suitable for single crystal X-ray diffraction studies were grown at 0 to -20 °C over a period of two days by diffusion of Et_2O and THF in a toluene solution for **15** and **16**. **15** crystallizes monoclinic in the space group P 2_1/n with four formula units per unit cell. Whereas compound **16** crystallizes triclinic in the space group P$\bar{1}$ with two formula units per unit cell. The molecular structures are shown in Figures 13 and 14 and selected structural parameters are listed in Table 9.

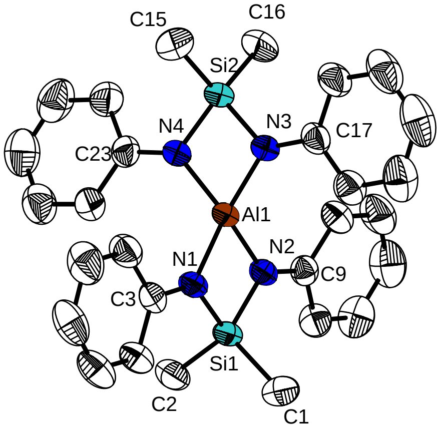


Fig. 13: Molecular structure of the [{$Me_2Si(NPh)_2$}$_2$Al]$^-$ anion **(15)** in the crystal (50% probability level and H-atoms are omitted)

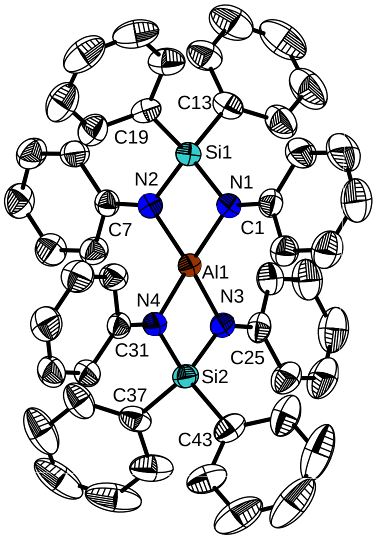


Fig. 14: Molecular structure of the [{$Ph_2Si(NPh)_2$}$_2$Al]$^-$ anion of **(16)** in the crystal (50% probability level and H-atoms are omitted)

Compound **15** is an ionic compound and it consists of $[\{Me_2Si(NPh)_2\}Al]^-$ anions and solvated Li^+ cations whereas in **16** $[\{Ph_2Si(NPh)_2\}Al]^-$ anions and solvated Li^+ cations are observed. Additionally one toluene and two THF non coordinating solvent molecules are observed in case of **15** and **16** simultaneously. In **15** and **16** the Al atom at the centre is coordinated by four N atoms of two chelating diamido $[R_2Si(NR')_2]^{2-}$ ligands. Thus it forms two AlN_2Si four membered rings which are perpendicular to each other. This leads to a spirocyclic Si_2N_2Al core in the anion. Al is having a distorted tetrahedral coordination with a smaller two endocyclic angles N(2)-Al(1)-N(1) of 81.98(9)^o, N(3)-Al(1)-N(4) of 82.05(9)^o and a four exocyclic angles are N(3)-Al(1)-N(1) of 130.63(10)^o, N(3)-Al(1)-N(2) of 123.69(9)^o, N(2)-Al(1)-N(4) of 121.94(10)^o, N(4)-Al(1)-N(1) of 122.23(9)^o. These angles deviate from its ideal value as Al is a part of a four membered ring. A similar pattern is observed in case of **16** and outlined in Table 9. The negative charge of the anion is balanced by the solvated Li^+ cations; such as $[Li(OEt_2)_3]^+$ and $[Li(THF)_4]^+$ in **15** and **16** respectively.

Table 9. Selected bond lengths (Å) and angles (^{o}) for compounds **15** and **16**.

Bond lengths (Å)	**15**	**16**
Al-N	1.865(2)-1.869(2)	1.864(2)-1.866(2)
Si-N	1.732(2)-1.738(2)	1.725(2)-1.729(2)
Si-C	1.866(3)-1.874(3)	1.879(3)-1.885(3)
Bond angles (^{o})		
N(3)-Al(1)-N(4)	82.05(9)	82.26(10)
N(2)-Al(1)-N(1)	81.98(9)	82.10(9)
N(3)-Al(1)-N(2)	123.69(9)	125.05(11)
N(2)-Al(1)-N(4)	121.94(10)	123.27(9)
N(3)-Al(1)-N(1)	130.63(10)	125.01(9)
N(4)-Al(1)-N(1)	122.23(9)	125.10(10)
N-Si-C	113.30(12) - 116.16(12)	113.48(12) - 114.95(12)
N-Si-N	89.84(9) - 89.95(10)	90.23(10) - 90.31(10)
C-Si -C	108.24(16) - 108.31(13)	106.97(13) - 109.42(13)

The dihedral angle between the two four membered AlN_2Si ring planes for **15** is 87.46(4)^{o} and for **16** is 89.04(6)^{o}. The dihedral angles are close to the ideal value 90^{o} which is a characteristic of spirocyclic compound. The Si atom is having a tetrahedral coordination whereas N-atoms have a trigonal planar coordination and the sum of the bond angles is close to 360^{o}.

The Al-N bond length is in the range of 1.864(2)-1.869(2) Å. Si-N and Si-C bond lengths are in the range of respective silylamide compounds discussed in earlier in *section 3.1*. The Al-N bond length of 1.865(2) Å and bond angles of four member ring inside (smaller) N(2)-Al(1)-N(1) of 81.98(9)^{o}; outside (larger) N(3)-Al(1)-N(1) of 130.63(10)^{o} of **15** as well as **16** can be compared with the similar spirocyclic $[Li(THF)_2\{Al[SO_2(N^tBu)_2]_2\}]_\infty$ compound studied by Chievers *et al.* [47]. It has ave. Al-N bond length of (1.844(4) Å) and endocyclic bond angle 77.7^{o} whereas exocyclic bond angle is 127.3^{o}. The spirocyclic anion $[Al\{SO_2(N\textit{t}\text{-}Bu)_2\}_2]^-$ is linked through one of the oxygen atoms by the bis-solvated cation $Li(THF)_2^+$ to give a ionic compound similar to **15-16**.

The ave. Al-N bond lengths of 1.864(2) Å **15** and **16** are within the limits of the Al-N bond lengths of various aluminum compounds known in the literature.

Compound	**Al-N (Å)**	**Reference**
$[ArN(SO_2\text{-}p\text{-}Tol)AlEt_2]$	1.944(3)	[48]
$[Li(Al(NH^tBu)_4]_2$	1.894(4)	[49]
$[Li(THF)_4][\{(NCH_2Ph)_3\}_4Al]$	1.853(3)	[50]
$[Li(THF)_4][H(NPh_2)_3Al]$	1.868(3)	[51]
$[Li(DME)_3][\{(NCH_2Ph_2)_3HAl]$	1.836(3)	[51]
$[Li(THF)_2][(NMe_2)_4Al]$	1.85	[52]
$[Li(THF)_2][\{N(CH_2)_5)_4Al]$	1.83	[53]
$[\{Li(THF)\}\{(NHDipp)_4Al]$	1.85(3)	[54]
$[Li(OEt_2)_3][(HAl)_4(NPh)_6\{Li(OEt_2)_3\}]$	1.901(7)	[55]
$[Li(THF)_4][Li_6\{EtAl(NOMeC_6H_4)_3\}_2]$	1.887(1)	[56]

Very few ionic Al-N spirocyclic compounds are reported in the literature. To conclude new spirocyclic aluminum compounds from difunctional silylamide ligand have been synthesized and their single crystal structure is determined by XRD.

3.4 Reactions of difunctional silylamides with Gallium trichloride ($GaCl_3$)

3.4.1 Synthesis of gallium silylamide compounds (19-21) and characterization

Difunctional silylamines $R_2Si(NHR')_2$ were synthesized according to method 2 or 3 [2, 4]. Aminosilanes are lithiated using n-BuLi. The next step is to react $R_2Si(NLiR')_2$ with group III halides such as $GaCl_3$. It was assumed that these experiments should also give similar results as they were obtained in aluminum compounds studied **15-18**. To compare whether gallium compounds show similar or different behavior, similar reaction pathway was followed as described for the aluminum complexes in *section 3.2.1*. The general reaction pathway for gallium silylamido compounds is shown in reaction equations 12-14.

$$R_2Si(NHR')_2 + 2\ \text{n-BuLi} \longrightarrow R_nSi(NLiR')_2 + 2\ \text{n-BuH} \qquad (12)$$

$$2\ R_2Si(NLiR')_2 + GaCl_3 \left. \begin{array}{ll} \xrightarrow{+3\ Et_2O} [Li(OEt_2)_3][\{R_2Si(NR')_2\}_2Ga] + 3\ LiCl & (13) \\ \xrightarrow{+4\ THF} [Li(OC_4H_8)_4][\{R_2Si(NR')_2\}_2Ga] + 3\ LiCl & (14) \end{array} \right.$$

(19-21)

(R = Me, Ph; R' = Ph, Mes; M = Ga)

The general reaction behavior of Ga complexes is similar to that of aluminum. In a typical experiment a solution of $GaCl_3$ in Et_2O is added dropwise *in situ* to the suspension of lithiated compound $R_2Si(NLiR')_2$, the reaction mixture becomes soluble at -20 ^{o}C. Upon warming up to room temperature within an hour a precipitate of LiCl and gallium compound is obtained in Et_2O-hexane mixture. After that the reaction mixture is stirred overnight at room temperature. The product is isolated in toluene or THF by extraction. White crystals are obtained after one week at -20 ^{o}C. The overall yield is in the range of 62-70 % with respect to the silylamine. Depending on the R and R' substitution of silylamine $R_2Si(NR')_2$ from methyl to mesityl different gallium silylamide compounds **(19-21)** are obtained and their specifications are given below in Table 10.

Compounds $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Ga]$ **(19)** $[Li(OEt_2)_4][\{Me_2Si(NMes)_2\}_2Ga]$ **(20)** and $[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2Ga]$ **(21)** are characterized by ^{1}H, ^{13}C, NMR spectroscopy, IR spectroscopy and EDX measurement. Detailed parameters are outlined in Table 10. Further these complexes, **19-21** are characterized by ^{29}Si NMR spectroscopy and its shifts are compared with the starting silylamine compounds as outlined in Table 11.

As observed in aluminum compounds **15-18**, Ga atom gets coordinated to the N atoms of silylamido ligand and due to the coordination, in ^{29}Si NMR spectra there is a small upfield or downfiled shift by 6-10 *ppm* compared to the starting aminosilane. Analogous to aluminum compounds the presence of Et_2O or THF coordinated to Li^+ cation solvent molecules is clearly observed in ^{1}H and ^{13}C NMR spectra.

Table 10. Gallium silylamide compounds **19-21.**

Compound	R	R'	Recrystallization solvent	Yield based on silylamine
$[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Ga]$ **(19)**	Me	Ph	Et_2O	68 %
$[Li(OEt_2)_4][\{Me_2Si(NMes)_2\}_2Ga]$ **(20)**	Me	Mes	Et_2O	70 %
$[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2Ga]$ **(21)**	Ph	Mes	THF	67 %

The ratio of the integreated intensities of coordinated methyl protons of solvent molecule to methyl protons of silylaminde is 1:1.5 and 1:2 in **19** and **20** respectively. When Et_2O is coordinated ^{13}C NMR signals are observed around 14.68 (CH_3) and 66.15 (CH_2) *ppm* and in case of THF they are at 24.67 and 65.54 *ppm*. And all other aromatic C-atoms resonances in ^{13}C NMR signals are from 125-148 *ppm*. The content of Ga metal is studied by EDX measurement and its peak was found at 1.12 KeV.

Table 11. The ^{29}Si NMR shifts of compounds **19-21** and aminosilanes.

Compound	δ ^{29}Si (ppm)	Starting silylamine compound and no.	^{29}Si (ppm)
$[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Ga]$ **(19)**	-11.16	$Me_2Si(NHPh)_2$ **(1)**	-11.09
$[Li(OEt_2)_4][\{Me_2Si(NMes)_2\}_2Ga]$ **(20)**	-1.10	$Me_2Si(NHMes)_2$ **(4)**	-7.86
$[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2Ga]$ **(21)**	-40.78	$Ph_2Si(NHMes)_2$ **(5)**	-30.03

3.4.2 Crystal structures of $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Ga]$ (19) and $[Li(OEt_2)_4][\{Me_2Si(NMes)_2\}_2Ga]$ (20)

Single crystals suitable for single crystal X-ray diffraction studies were grown at -20 °C over a period of one week by diffusion of Et_2O/THF in a toluene solution. Compound **19** crystallizes monoclinic in the space group $P\ 2_1/n$ with four formula units per unit cell whereas compound **20** crystallizes orthorhombic in the space group $P\ 2_1\ 2_1\ 2_1$ with four formula units per unit cell. Perspective view of the molecular structures has been illustrated in Figures 15, 17 and 18 respectively. Perspective view of cation of **19** is shown in Figure 16. Selected structural parameters are listed in Table 12.

Table 12. Selected bond length (Å) and angles (°) for compounds **19**, **20** and **21**.

Bond lengths (Å)	**19**	**20**
Ga-N	1.923(2)-1.931(2)	1.935(4)-1.947(4)
Si-N	1.722(3)-1.732(2)	1.714(5)-1.715(5)
Si-C	1.866(3)	1.876(7)
Li-O	1.899(6)-1.930(6)	1.990(14)-2.026(16)
Bond angles (°)		
N(2)-Ga(1)-N(1)	79.42(10)	79.5(2)
N(4)-Ga(1)-N(3)	79.55(11)	79.58(18)
N(2)-Ga(1)-N(4)	132.70(11)	124.6(2)
N(4)-Ga(1)-N(1)	125.35(10)	125.96(19)
N(2)-Ga(1)-N(3)	123.76(10)	124.78(17)
N(1)-Ga(1)-N(3)	122.67(11)	129.44(19)
N-Si-C	113.48(12)-114.95(12)	112.8(3)-117.1(3)
N-Si-N	90.31(10)	92.5(2)
C-Si-C	109.42(13)	103.7(4)

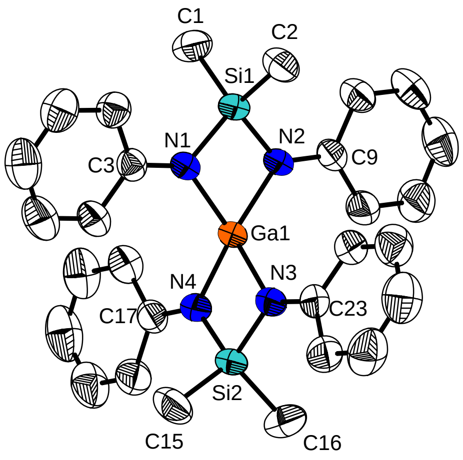


Fig. 15: Molecular structure of the $[\{Me_2Si(NPh)_2\}_2Ga]^-$ anion **(19)** in the crystal (50% probability level and H-atoms are omitted)

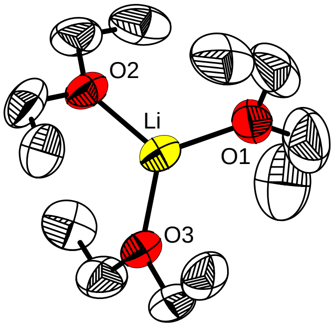


Fig. 16: Molecular structure of the $[Li(OEt_2)_3]^+$ cation **(19)** in the crystal (50% probability level and H-atoms are omitted)

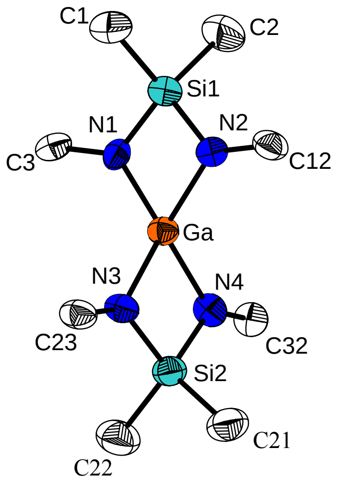


Fig. 17: Molecular structure of the $[\{Me_2Si(NMes)_2\}_2Ga]^-$ anion of **(20)** in the crystal with ipso-C atoms on N (50% probability level and H-atoms are omitted)

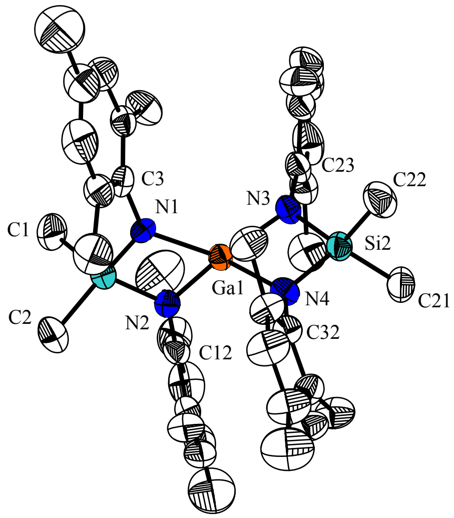


Fig. 18: Molecular structure of the $[\{Me_2Si(NMes)_2\}_2Ga]^-$ anion of **(20)** in the crystal (50% probability level and H-atoms are omitted)

Compounds **19-20**, consist of $[\{R_2Si(NR')_2\}_2Ga]^-$ anions and solvated Li^+ cations. Similar to the aluminum compounds in **19-21** Ga atom at the centre is tetrahedrally coordinated by four N atoms of two chelating diamido $[R_2Si(NR')_2]^{2-}$ ligands. It forms two GaN_2Si four membered rings which are nearly perpendicular to each other. This gives rise to a spirocyclic Si_2N_2Ga core in the anion. The dihedral angles between the two GaN_2Si four membered ring planes of **19-20** are 87.70(3)^o, and 88.50(2)^o respectively which are close to 90^o.

The Ga atom shows a distorted tetrahedral coordination. In case of **19** the smaller endocyclic bond angle for N(2)-Ga(1)-N(1) is 79.42(10)^o and larger exocyclic bond angle for N(2)-Ga(1)-N(4) is 132.70(11)^o. Also similar trend of the bond angles are observed for **20** and its endocyclic and exocyclic values are outlined in Table 12. Therefore **19** and **20** have Si_2N_4Ga cores of two chelating silylamido ligands forming a complete spirocyclic molecule. The charge of the anion is balanced by counter ions such as $[Li(OEt_2)_3]^+$ in **19** and $[Li(OEt_2)_4]^+$ in **20** respectively.

Such type of solvated Li cations which are separated from the anion and coordinated by THF solvent molecules are rarely observed in case of gallium spirocyclic compounds for example $[Li(THF)_4][\{N(CH_2Ph)_2\}_4Ga]$ and $[Li(THF)_4][\{PhB(\mu\text{-N}t\text{-Bu})_2\}GaCl_2GaCl_3]$ [50, 57]. The arrangement of cations and anions of **19** in a packing of the unit cell along a-axis are shown Figure 19.

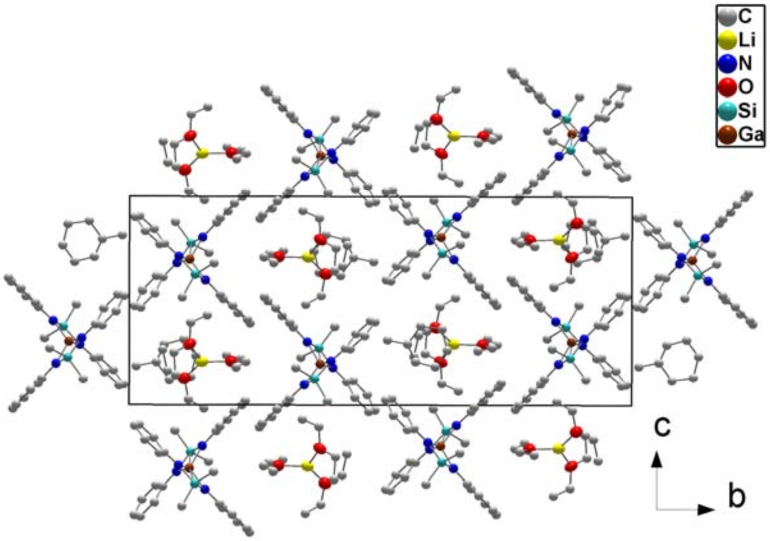


Fig. 19: Packing diagram of the arrangement of cations and anions in the unit cell along a-axis of $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Ga]$ (**19**)

The Li atom is coordinated with three molecules of Et_2O to give a trigonal planer coordination. Similar solvated Li counter ions have been observed by Neumüller *et al.* and Chivers *et al.* in case of ionic compounds [50, 57]. The Li-O bond length of 1.930(6) Å is in the range of other ionic compounds e.g. $[Li(THF)_4][\{N(CH_2Ph)_2\}_4Ga]$ (1.96(2) Å) and $[Li(THF)_4][\{PhB(\mu\text{-}N^t\text{-}Bu)_2\}GaCl_2GaCl_3]$ (1.923(2) Å) [50, 58]. The Li-O bond length is also comparable with **13** discussed in earlier section and references therein.

The Ga-N ave. bond length is in the range of 1.923(2)-1.949(4)Å. Ga-N bond length of compounds **19-20** is greater than the ave. range of Al-N bond length (1.865(2)-1.869(2) Å) of **15-16** because of the larger covalent radius of gallium atom (1.26 Å) compared to aluminum (1.18 Å).

The ave. Ga-N bond length 1.94(4) Å of **19-20** can be compared to the various compounds already known in the literature.

Compound	**Ga-N (Å)**	**Reference**
$[Li(THF)_4][\{N(CH_2Ph)_2\}_4Ga]$	1.927(8)	[50]
$[Li(THF)_4][\{PhB(\mu\text{-}N^t\text{-}Bu)_2\}GaCl_2GaCl_3]$	2.0478	[58]
$[\mu\text{-}Li(OEt_2)\{PhB(\mu\text{-}N^tBu)_2\}_2Ga]$	1.923(2)	[52]
$[(PhGa)_4(NH^iBu)_4(N^iBu)_2]$	2.004(4)	[59]
$[(NMe_2)_3Ga]_2$	2.005(2)	[60]
$[Ga\{N(H)t\text{-}Bu\}_3]_2$	2.008(8)	[60]
$[GaCl_2\{(\mu\text{-}NHSiMe_2Ph\}_2]$	1.988(4)	[61]
$[PhGa\{(\mu\text{-}N(SiMe_2Ph)_2\}(\mu\text{-}Cl)]_2$	1.850(3)	[62]

Compared to the starting silylamines there are only small deviations in Si-N and Si-C bond lengths. Average Si-N bond length is in between 1.707(5)-1.732(2) Å and for Si-C 1.866(3)-1.889(6) Å. Si atom has a nearly tetrahedral coordination, whereas N-atom has a trigonal planar coordination and sum of the bond angles is close to 360°.

3. 5 Reactions of difunctional silylamides with Indium trichloride $InCl_3$

3.5.1 Synthesis of indium silylamide compounds (22-24) and characterization

Here the synthesis and characterization of indium compounds of difunctional silylamides $R_2Si(NHR')_2$ is discussed to compare with aluminum and gallium compounds. The synthesis and work up strategy is the same as for aluminum and gallium compounds **15-21**. Below is the general reaction pathway for indium silylamide synthesis as shown in reaction equations 15-17.

$$R_2Si(NHR')_2 + 2\ n\text{-}BuLi \longrightarrow R_nSi(NLiR')_2 + 2\ n\text{-}BuH \qquad (15)$$

$$3\ MeSi(NLiPh)_2 + InCl_3 + 3\ Et_2O \longrightarrow \underset{\mathbf{22}}{[\{Li(OEt_2)Me_2Si(NPh)_2\}_3In]} + 3\ LiCl \qquad (16)$$

$$2\ R_2Si(NLiR')_2 + InCl_3 + 4\ THF \longrightarrow \underset{\mathbf{23\text{-}24}}{[Li(OC_4H_8)_4][\{R_2Si(NR')_2\}_2In]} + 3\ LiCl \qquad (17)$$

(R = Me, Ph; R' = Ph, Mes; M = In)

The products are isolated from the insoluble residue by extraction in toluene or THF. Colorless crystals are obtained after 48 hrs at -20 °C. The overall yield is in the range of 58-64 % with respect to the silylamine. Depending on the R and R' substitution in the silylamine $R_2Si(NHR')_2$ (R = Me or Ph and R' = Ph or Mes) different indium silylamide compounds **(22-24)** are obtained and their specifications are given below in Table 13.

Table 13. Indium silylamide compounds **22-24**.

Compound	R	R'	Recrystallization solvent	Yield based on silylamine
$[\{Me_2Si(NPh)_2Li(OEt_2)\}_3In]$ (**22**)	Me	Ph	Et_2O	65 %
$[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2In]$ **(23)**	Ph	Mes	THF	64 %
$[Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2In]\cdot 2THF$ **(24)**	Ph	Ph	THF	58 %

Compounds of the type [{$Me_2Si(NPh)_2Li(OEt_2)$}$_3$In] (**22**), [$Li(OC_4H_8)_4$][{$Ph_2Si(NMes)_2$}$_2$In] **(23)** and [$Li(OC_4H_8)_4$][{$Ph_2Si(NPh)_2$}$_2$In **(24)**·2THF are prepared and characterized by ^{1}H, ^{29}Si NMR spectroscopy, IR spectroscopy and EDX measurement. Detailed parameters are outlined in Table 14. In ^{29}Si NMR spectra shifts of compounds **22-24** are compared with the ^{29}Si NMR shifts of starting compounds. In case of **22** the shift difference is marginal whereas for **23** the signal occurs at -43.43 *ppm*, compared to $Ph_2Si(NHMes)_2$ **(5)** there is a downfield shift from -30.03 *ppm*. For **24** the resonance is at -26.23 *ppm* with an upfiled shift compared to $Ph_2Si(NHPh)_2$ **(3)**.

In the ^{1}H NMR spectrum of **22** (in C_6D_6**)** it is observed that the resonances of the methyl protons of the silylamide at 0.57 *ppm* and methyl of Et_2O signals are overlapping. The methyl proton signal of the silylamide has an upfield shift with respect to 0.87 *ppm* of $Me_2Si(NHPh)_2$. CH_2 protons of Et_2O gives a *quartet* at 2.64 *ppm*.

The integrated intensities ratio of the signals of methyl protons of silylamide and OEt_2 together to CH_2 signal of Et_2O is 1:3. All other aromatic protons are observed at 6.68-7.29 *ppm*. The presence of Et_2O is observed in ^{13}C NMR spectra with signals at 14.12 (CH_3) and 65.27 (CH_2) *ppm* respectively. Whereas for **23-24** the ^{13}C signals for the THF carbon are present at 22.41 and 65.54 *ppm*. The resonances of the remaining aromatic C-atoms are observed in between 125-148 *ppm*. The content of the indium metal is studied by EDX and the peak was found at 3.28 KeV.

Table 14. The ^{29}Si NMR peak shifts of compounds **22-24** and aminosilanes.

Compound	δ ^{29}Si NMR (ppm)	Startingsilylamine	^{29}Si NMR (ppm)
[{$Me_2Si(NPh)_2Li(OEt_2)$}$_3$In] (**22**)	-11.16	$Me_2Si(NHPh)_2$ **(1)**	-11.09
[$Li(OC_4H_8)_4$][{$Ph_2Si(NMes)_2$}$_2$In] **(23)**	-43.43	$Ph_2Si(NHMes)_2$ **(5)**	-30.03
[$Li(OC_4H_8)_4$][{$Ph_2Si(NPh)_2$}$_2$In]·2THF **(24)**	-26.23	$Ph_2Si(NHPh)_2$ **(3)**	-30.07

3.5.2 Crystal structure of [{$Me_2Si(NPh)_2Li(OEt_2)$}$_3$In] (22)

Single crystals suitable for single crystal X-ray diffraction study are obtained by the diffusion of Et_2O at -20 ^{o}C over a period of 5 days. Compound **22** crystallizes trigonal in the space group $R\,\overline{3}c$ with six formula units per unit cell. Perspective view of the molecular structure of **22** is shown (50% probability level and ipso C-atoms on N-atoms without hydrogen atoms) in Figure 20. Selected structural parameters are listed in Table 15.

In **22** indium as well as Si, Li and O atoms reside at special positions. At the special residing position of the In (2/3, 1/3, 0.0833) a threefold and three twofold crystallographic axes are crossing. They are shown by color lines in Fig. 20. Additionally Si, Li and O lie on twofold axes. Threefold axis is perpendicular to the three twofold axes resulting in a D_3 symmetry. All other atoms reside at their general positions. An asymmetric unit of the molecule is highlighted by dark filled bonds and generated atoms by symmetry operation are marked by faint bonds as illustrated in Figure 20.

Table 15. Selected bond lengths (Å) and angles (^{o}) for compound **22.**

Bond lengths (Å)

In-N	2.305(2)	Li-N	2.062(5)
Si-N	1.726(3)	Si-C	1.886(3)
N-C	1.393(4)	Li-O	1.906(8)

Bond angles (^{o})

N(1)-In(1)-N(1)^{I}	103.48(7)	N(1)-In(1)-N(1)^{III}	67.59(12)
N(1)-In(1)-N(1)^{IV}	168.34(11)	N(1)^{IV}-In(1)-N(1)^{III}	103.480(12)
N(1)-In(1)-N(1)^{II}	103.48(7)	N(1)-In(1)-N(1)^{IV}	67.59(12)
N-Si-N	95.94(17)	N(1)-Li(1)-C(4)^{II}	119.9(3)
N-Si-C	112.27(13) - 114.37(13)	N-Li-N	99.8(3)

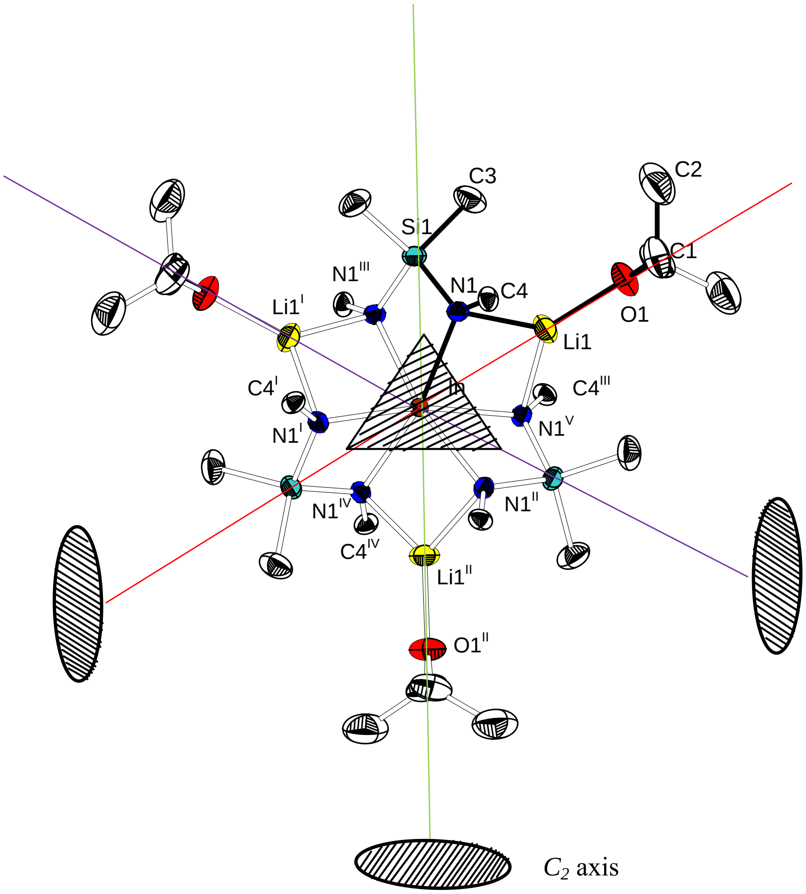


Fig. 20: Molecular structure of $[\{Me_2Si(NPh)_2Li(OEt_2)\}_3In]$ **(22)** along the direction C_3 axis (phenyl groups are represented by the ipso C-atoms and H-atoms are omitted)

In **22** the central In atom is surrounded by three $[Me_2Si(NPh)_2]^{2-}$ units. In contrast to the aluminum silylamide (**15**) and gallium silylamide (**19**) described previously the Li atoms are not separated but coordinated by two nitrogen atoms of two silylamides with a Li-N bond distance of 2.062(5) Å to form three LiN_2In four membered rings which are perpendicular to InN_2Si three four membered rings. Thus it leads to the formation of a 12 membered $Li_3Si_3N_6$ cluster core around the indium atom of $[In\{Me_2Si(NPh)_2\}_3]$ (**22**) .

Thus **22** can be described as a compound which consists of anions $[\{Me_2Si(NPh)_2\}_2In]^{3-}$ in which the indium atom at the centre has an octahedral coordination by three chelating ligands $[\{Me_2Si(NPh)_2\}_3]^{3-}$. The negative charge of the anion is balanced by the solvated Li^+ cations; such as $[Li(OEt_2)]^+$. Li has a coordination of two N atoms and one oxygen of Et_2O solvent.

Solvated $[Li(OEt_2)]^+$ has very close interactions with anions and is not separated in the form of cations as previously observed in the case of **15** and **19**.

Spirocyclic compounds of Al (**15)** and Ga (**19)** of the $[Me_2Si(NPh)_2]^{2-}$ ligand have coordination number 4. In contrast to **15** and **19** indium compound **22** of the same difunctional silylamide ligand has a higher coordination number 6. This coordination number 6 is highest among all the compounds studied so far in this research work. It could be due to the higher covalent radius of indium (1.44 Å) than Al (1.18 Å) and Ga 1.26 Å. And the nature of R (methyl group present on Si atom in ($Me_2Si(NPh)_2$) smaller group in aminosilane. Coordination number of indium is reduced to 4 like other spirocyclic compounds studied in **23** and **24** when the aromatic (bulky group phenyl is present on Si atom in ($Ph_2Si(NMes)_2$) in aminosilane. And these compounds are explained in detail in the coming section.

Indium atom is octahedrally coordinated by 6 N-atoms of 3 silylamide ligands through two different types of four membered InN_2Si and InN_2Li rings attached in the opposite direction. The four membered ring InN_2Si has a smaller endocyclic N(1)-In(1)-N(1)^{III} bond angle of 67.59(12)°. Whereas in the case of InN_2Li four membered ring larger exocyclic bond angle N(1)-In(1)-N(1)^{V} of 86.311(2)° is observed. Its polyhedral representation is illustrated in Figure 21. One can have a look on different endocyclic and exocyclic bond angles in the four membered ring, how they are reduced when the covalent radius increases from Al to In atom in a third row of the periodic table.

	15 (Al)	**19 (Ga)**	**22 (In)**
(Endocyclic Bond angle N- M- N)	82.05(9)	79.42(10)	67.59(12)°
(Exocyclic Bond angle N-M-N)	130.63(10)	132.70(11)	86.311(2)°

(Where M= Al, Ga and In)

The In-N bond length for **22** is 2.305(2) Å. This is larger than all the compounds studied so far for Al and Ga using difunctional silylamide ligands. Si atom is coordinated by two N-atoms and two C-atoms and its angles are in the range of 95.94(17)° to 114.37(13)° which also shows the distorted tetrahedral coordination. The Li atoms have a coordination of two

N-atoms and one O-atom of the coordinating Et_2O solvent molecule giving a trigonal planar coordination. **22** has some resemblance to $[Li^+\{In\{Me_2Si(NSiMe_3)_2\}_2\}^-]$ cluster which is the only indium lithium cluster of silylamide reported by Veith *et al.* in literature [63]. They noticed that Li has coordination with two N-atoms having a bond distance 2.064(6) Å which is comparable with **22** having a Li-N bond distance of 2.062(5) Å. This Li-N bond length of **22** is comparable to the lithiated silylamides **13** and **14** of difunctional amidosilanes described in earlier section *3.2*.

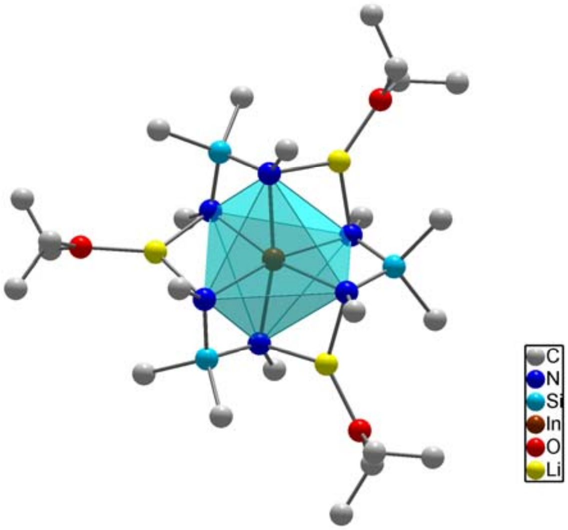


Fig. 21: Polyhedral representation of $[\{Me_2Si(NPh)_2Li(OEt_2)\}_3In]$ **(22)** in the crystal (50% probability level, phenyl groups are represented by the ipso C-atoms and H-atoms are omitted)

3.5.3 Crystal structures of $[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2In]$ (23) and $[Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2In]\cdot 2THF$ (24)

Single crystals suitable for single crystal X-ray diffraction studies were grown at -20 °C over a period of one week by diffusion of THF in a toluene solution. Compound **23** crystallizes orthorhombic in the space group P 2_1cn whereas compound **24** crystallizes monoclinic in the space group P 2_1/c with four formula units per unit cell. The molecular structures are shown (50% probability level without hydrogen atoms) in the Figures 22 and 23 and selected structural parameters are listed in Table 16. **23** and **24** are ionic compounds which consist of well separated $[\{R_2Si(NR')_2\}_2In]^-$ anions and solvated Li^+ cations.

In compounds **23** and **24** indium has a coordination number 4 like other compounds studied of Al and Ga. The indium atom at the centre is tetrahedrally coordinated by four nitrogen atoms of two chelating diamido $[R_2Si(NR')_2]^{2-}$ ligands. Thus it forms two InN_2Si four membered rings which are nearly perpendicular to each other. This leads to spirocyclic Si_2N_4In core in anion as it was observed in case of Al and Ga silylamide compounds before.
Indium atom exhibits distorted tetrahedral geometry with smaller endocyclic bond angle in the InN_2Si four membered ring N(2)-In-N(1) of 73.79(11)^o. And a larger exocyclic bond angle in the InN_2Si four membered ring N(3)-In-N(1) of 145.46(11)^o. The other exocyclic and endocyclic angles are outlined in Table 16 for **23** and **24**.

The negative charge of the anion is balanced by the solvated Li^+ cations, such as $[Li(THF)_4]^+$ to give $[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2In]$ (**23**) and $[Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2In]$ (**24**). Additionally two non coordinationg THF molecules are observed in the case of **24**. Products are recrystallized from a THF polar solvent. Whereas in case of less polar solvents (e.g. Et_2O, toluene and CH_2Cl_2) amorphous powders are formed.

Table 16. Selected bond lengths (Å) and angles (^{o}) for compounds **23** and **24.**

Bond lengths (Å)	**23**	**24**
In-N	2.128(3)-2.157(3)	2.122(3)-2.127(2)
Si-N	1.708(3)-1.710(3)	1.720(3)-1.738(3)
Si-C	1.893(4)	1.877(4)
Bond angles (^{o})		
N(3)-In(1)-N(4)	73.79(11)	73.26(10)
N(2)-In(1)-N(1)	73.86(10)	73.15(10)
N(2)-In(1)-N(3)	126.56(10)	131.85(11)
N(3)-In(1)-N(1)	145.46(11)	132.57(10)
N(2)-In(1)-N(4)	122.32(10)	124.30(11)
N(1)-In(1)-N(4)	122.10(10)	131.47(11)
N-Si-C	111.13(16)-115.76(15)	111.81(15) -114.49(15)

N-Si-N	97.00(13)	94.26(12)
C-Si-C	105.89(17)	108.63(16)

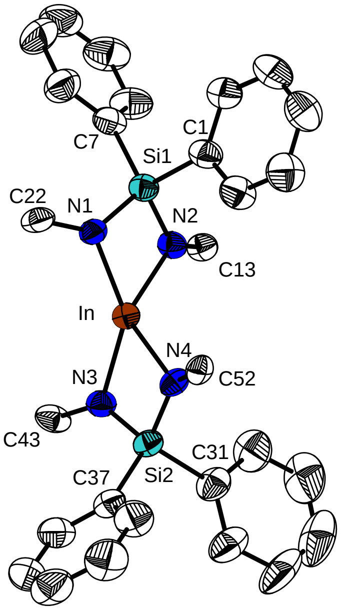


Fig. 22 Molecular structure of the $[\{Ph_2Si(NMes)_2\}_2In]^-$ anion **(23)** in the crystal (50% probability level, mesityl groups are represented by ipso C-atoms and H-atoms are omitted)

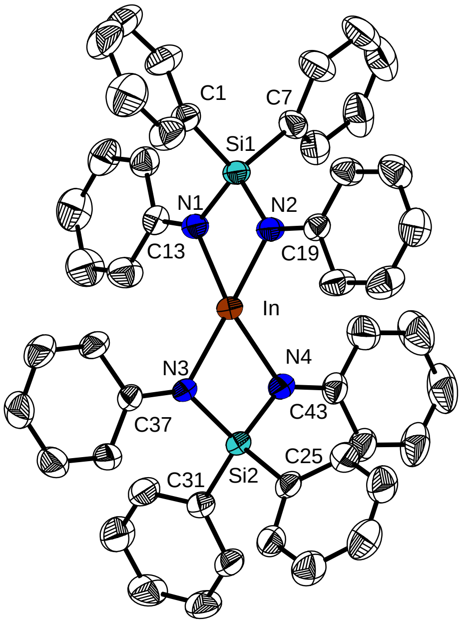


Fig. 23: Molecular structure of the $[\{Ph_2Si(NPh)_2\}_2In]^-$ anion of **(24)** in the crystal (50% probability level and H-atoms are omitted)

The dihedral angle between the two four membered InN_2Si ring planes for **23** is 83.22(4)^o and for **24** it is 86.04(2)^o. The dihedral angle deviates comparatively more from the ideal 90^o up to 83.22(4)^o in case of **23** than all the compounds studied so far this could be due to the reasons that: a) Nature of the mesityl (bulky group steric effect) present on N atoms of silylamide and b) All the N atoms have a slight pyramidalization. And sum of the bond angles around N atom is 358.14^o compared to near trigonal planar coordination.

The average In-N bond length for the compounds **23-24** is in the range of 2.122(3)-2.157(3) Å. M-N bond length has a correlation with covalent radius of the group III metals (M = Al, Ga and In) as shown in the following Table.

Atomic no.	Metal (M)	Covalent radius (Å)	Bond Length (M-N)
13	Al	1.18	1.865(2) Å
31	Ga	1.26	1.931(2) Å
49	In	1.44	2.147(2) Å

As one can move from Al to In (top to the bottom of the periodic table) the covalent radius increases which is directly proportional to the increase in M-N bond length. The ave. M-N bond length increases from Al-N 1.865(2) Å to 1.931(2) Å for Ga-N and followed by In-N 2.147(3) Å respectively. The ave. In-N bond length of 2.147(2) Å for **23-24** is also comparable with following indium compounds from the literature.

Compound	In-N (Å)	Reference
$[Li(OEt_2)_4][\{PhB(NDipp)_2\}_2In]$	2.132(3)	[65]
$[LiCl][InLi\{Te(NtBu)_3\}_2]$	2.154(3)	[66]
$[Me_3In(\mu\text{-}NH(^tBu)]$	2.363(8)	[67]
$[\{N(SiMe_3)NMe_2\}_3In]$	2.0812(15)	[68]
$[LiN(SiMe_3)_2NH\textit{t}\text{-}BuInMe]$	2.178(3)	[69]
$[In_4Cl_4(N^tBu)_4]$	2.178(3)	[77]

The ave. Si-N bond length is in the range of 1.708(3)-1.738(3) Å and for Si-C 1.877(4) -1.893(4) Å with small deviations from the corresponding silylamines studied in section *3.1*.

3.6 Reactions of trifunctional amidosilanes $RSi(NLiR')_3$ with aluminum and indium trichlorides (M = Al and In) (*Part-IV*)

3.6.1 Introduction

In the previous section, the reactions of difunctional amidosilanes with group III metal chlorides were discussed. With the same analogy, the difunctional amidosilanes have been replaced by trifunctional amidosilanes and reacted with aluminum and indium trichlorides to form the derivatives of the group III silylamido complexes. Their synthesis and structural characterization is discussed in this *part-IV*.

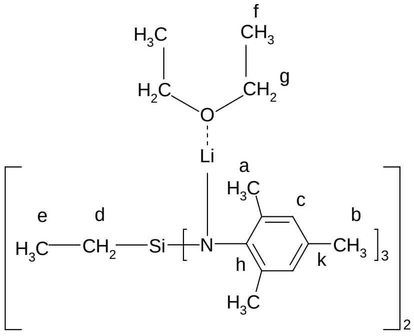
3.6.2 Synthesis and characterization of $[Li(OEt_2)_3][Li_5\{EtSi(NMes)_3\}_2]$ (25)

Lithiated amidosilanes ($RSi(NLiR')_3$ are used as intermediate products for the formation of derivatives of the group III compounds. Trifunctional silylamines $RSi(NHR')_3$ are prepared according to method 3 [3, 6]. Lithiation of $RSi(NHR')_3$ with n-BuLi in hexane at -78 °C leads to the compound $RSi(NLiR')_3$. One of the lithiated trisamidosilane $[Li(OEt_2)_3][Li_5\{EtSi(NMes)_3\}_2]$ **(25)** is prepared from $EtSi(NHMes)_3$ and n-BuLi in hexane at -78 °C as represented in general reaction equation 18. Reaction mixture is allowed to come to the room temperature within one hour. Once it attains room temperature, it is refluxed at 70 °C for 3 hours and a lithiated yellow product precipitated in hexane. Additional 15 mL of Et_2O is added to make it completely soluble in the mixture of Et_2O-hexane.

$$EtSi(NHMes)_3 + 3\ n\text{-}BuLi \xrightarrow{+3\ Et_2O} \underset{\mathbf{(25)}}{[Li(OEt_2)_3][Li_5\{EtSi(NMes)_3\}_2]} + 3\ n\text{-}BuH \quad (18)$$

Crystals of the product were obtained at -20 °C after 4 days by diffusion of toluene in Et_2O solution. The product $[Li(OEt_2)_3][Li_5\{EtSi(NMes)_3\}_2]$ **(25)** is characterized by ^1H, ^{13}C , ^{29}Si, ^7Li NMR spectroscopy, and IR spectroscopy. In the ^1H NMR spectrum (in C_6D_6) it is found that the shifts are nearly the same as compared to $EtSi(NHMes)_3$ **(10)**. The coordination of Et_2O to Li is observed in both ^1H and ^{13}C NMR spectroscopy and its shifts are given below.
In ^{29}Si NMR spectrum only one *singlet* peak is observed at -21.72 *ppm* that is shifted downfield as compared to the $EtSi(NHMes)_3$ **(10)** (-31.33 *ppm*). The observation of only one

Si signal indicates that all Si atoms in the molecule have the same coordination. In the ^{7}Li NMR spectra four peaks are observed with the intensity ratio of 1:2:2:1. Their shifts are at 1.39 *ppm*, 1.75 *ppm*, 3.00 *ppm* and 3.52 *ppm*. To get more insight about the molecular structure of **25** single crystal structure has also been investigated.



NMR	**25**	**10**	**Proton assignment**
^{1}H	0.78 ppm	0.78 ppm	H^d
	1.06 ppm	1.06 ppm	H^e
	2.14 ppm	2.14 ppm	H^a
	2.16 ppm	2.18 ppm	H^b
	6.71 ppm	6.65 ppm	H^c
^{29}Si	-21.72 ppm	-31.33 ppm	
^{7}Li	1.39, 1.75, 3.00 and 3.52 ppm.		

3.6.3 Crystal structure of $[Li(OEt_2)_3][Li_5\{EtSi(NMes)_3\}_2]$ (25)

Single crystals suitable for single crystal XRD are obtained by diffusion of a toluene solution in Et_2O at -20 °C over a period of 48 hours. **25** crystallizes monoclinic in the space group P 2_1/c with four formula units per unit cell. The perspective view of the molecular structure is shown in the Figure 24. Selected bond lengths and bond angles are shown in Table 17.

Complex **25** consists of $[Li_5(EtSi(NMes)_3)_2]^-$ anions and solvated Li^+ cations. The anion of **25** is composed of two $EtSi(NMes)_3$ fragments coordinated to 5 Li atoms. Li atoms are coordinated by three N atoms of two chelating $EtSi(NMes)_3$ units to form a $Li_5Si_2N_6$ cluster core. The cluster core of the anion possesses nearly mirror plane symmetry.

Li(1) and Li(5) as well as Li(2) and Li(3) are present in the same coordination environment. Whereas Li(4) has a different coordination behavior. Thus the anion shows a $Li_5Si_2N_6$ cluster core that is closely related to a distorted rhombic dodecahedron with one vertex removed as shown in Figure 25. The negative charge of the anion is balanced by solvated $[Li(OEt_2)_3]^+$ cations which are well separated from the anion giving an ionic compound $[Li(OEt_2)_3][Li_5\{EtSi(NMes)_3\}_2]$ (**25**). The anion is having a combination of five four-membered $LiSiN_2$ rings and four four-membered Li_2N_2 rings of atoms to give 9 rhombic faces of a polyhedron. The bond angles N-Li-N have a large deviation in their values from 81.49(18)° to 144.3(3)°. In case of Li(4) there is a significant pyramidalization. And sum of the bond angles (N-Li(4)-N) around Li(4) is 298.53°. This implies that all the Li atoms are in a distorted trigonal pyramidal coordination.

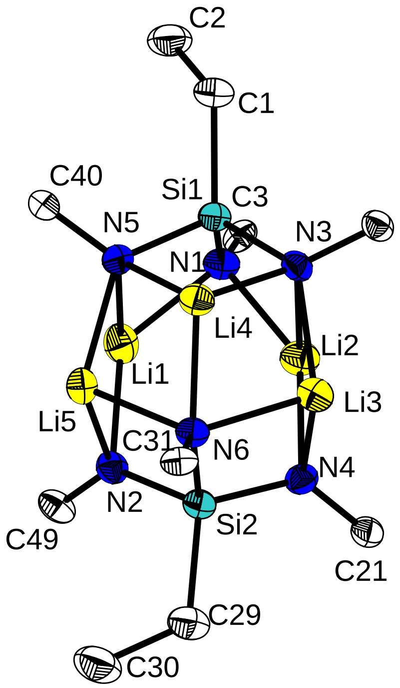


Fig. 24: Molecular structure of the $[Li_5\{EtSi(NMes)_3\}_2]^-$ anion of **25** in the crystal and mesityl groups are represented by the ipso C-atoms and H atoms are omitted

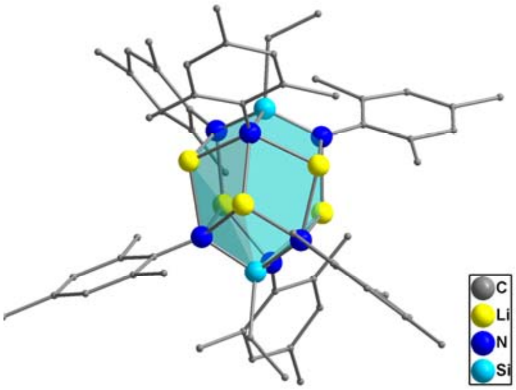


Fig. 25: Polyhedral representation of $[Li_5\{EtSi(NMes)_3\}_2]^-$ anion of **(25)** (H-atoms and one vertex is removed)

Si atom has a tetrahedral coordination whereas N atoms are having a distorted tetrahedral coordination and its bond angle values are outlined in Table 17. Different coordination behavior of Li atoms observed in solid state is retained in the solution and studied by ^7Li NMR spectroscopy. It gives four different peaks at 1.39, 1.75, 3.00 and 3.52 *ppm* respectively of the anion and cation. The intensity ratio of the four different peaks is 1:2:2:1.

Table 17: Selected bond lengths (Å) and angles (°) for compound **25**.

Bond lengths (Å)

Li(1)-N(1)	2.013(5)	Li(2)-N(1)	2.022(5)
Li(1)-N(2)	2.070(6)	Li(2)-N(4)	2.030(5)
Li(1)-N(5)	2.188(5)	Li(2)-N(3)	2.247(5)
Li(3)-N(4)	1.971(5)	Li(4)-N(5)	1.997(5)
Li(3)-N(6)	2.045(5)	Li(4)-N(3)	2.012(5)
Li(3)-N(3)	2.061(5)	Li(4)-N(6)	2.017(5)
Li(5)-N(2)	1.950(5)	Li(6)-O(1)	1.903(7)
Li(5)-N(6)	2.053(5)	Li(6)-O(1)	1.911(7)
Li(5)-N(5)	2.059(5)	Li(6)-O(3)	1.877(7)
Si-N	1.721(2) - 1.765(2)	Si-C	1.890(3) - 1.892(3)

Bond angles (°)

N-Li-N	81.49(18)-144.3(3)	Li-N-Li	68.63(18)-122.00(2)
N-Si-N	102.59(11)-106.55(11)	N-Si-C	109.23(12)-119.15(12)

The Li-N bond lengths range from Li(5)-N(2) of (1.950(5) Å) to higher one Li(2)-N(3) of (2.247(5) Å) due to the pyramidalization of Li atoms and N atoms have a distorted tetrahedral coordination. Approximately 0.25 (Å) deviation is there in the Li-N bond length of **25**. The Si-N and Si-C bond lengths are nearly same as to the $EtSi(NHMes)_2$ (**10**) with small deviation when it gets coordinated to the Li atom.

Li-N bond length in compound **25** is higher than that of **14**, Li-N bond length of 2.095(5) Å and references cited therein. It is also in the range of different lithiated compounds already described in the literature.

Compound	**Li-N (Å)**	**Reference**
$[Li(Et_2O)_3][(HAl)_4(NPh)_6\{Li(O\ Et_2)_3\}]$	2.227(15)	[70]
$[MeSi(NLi\text{-}t\text{-}Bu)_3]_2$	2.07(1)	[71]
$[Me(NLi\text{-}t\text{-}Bu)_3]_2$	2.05(2)	[9]
$[PhSi(NLi\text{-}t\text{-}Bu)_3]_2$	2.030(5)	[9]
$[\{Li(N(SiMe_3)CH_2CH_2NSiMe_3\}Li(Et_2O)]_2$	2.06(2)	[40]
$[\{NSiMe_2(NC(Ph)N(2,6^{i}\text{-}Pr_2Ph)_2\}_2Li_3\}][Li(THF)_4]$	2.04(6)	[45]
$[NH(Ph)SiMe_2N(Ph)Li(Et_2O)]_2$	2.053(4)	[45]

Similar to the $[Li(THF)_4]$ cation of **14**, compound **25** has $[Li(OEt_2)_3]$ cation. Li(6) has a trigonal planar coordination of O atoms of Et_2O. The Li-O ave. bond length 1.895(7) Å which is in the range of ave. 1.925(7) Å bond length in **14**. It is also comparable to different cations of the following compounds from the literature.

Compound	**Li-O (Å)**	**Reference**
$[\{Li(N(SiMe_3)CH_2CH_2NSiMe_3\}Li(Et_2O)]_2$	1.918(1)	[40]
$[\{(SiMe_2(NC(Ph)N(2,6^{i}\text{-}Pr_2Ph)_2\}_2Li_3\}][Li(THF)_4]$	1.909(1)	[45]
$[NH(Ph)SiMe_2N(Ph)Li(Et_2O)]_2$	1.988(4)	[45]
$[Li(Ph_2\text{-}MeGeBPh_3\}$	2.083(1)	[46]
$[Li(Et_2O)_3][(HAl)_4(NPh)_6\{Li(O\ Et_2)_3\}]$	1.929(14)	[70]

3.6.4 Reactions of lithiated triamidosilanes $RSi(NLiR')_3$ with aluminum trichloride

The reactions of $RSi(NLiR')_3$ with $AlCl_3$ are carried out in a similar way to the reactions described for difunctional lithiated silylamides $RSi(NLiR')_2$. Preparation of aluminum trisilylamide compounds takes place in two steps

1) Lithiation of the trifunctional silylamine using n-BuLi at -78 °C in hexane to form a silylamido intermediate product as shown in reaction equation 19.
2) Intermediate silylamido compound is treated with $AlCl_3$ in Et_2O solvent in a molar ratio 1:1, depicted in general reaction 20.

$$RSi(NHR')_3 + 3\ n\text{-}BuLi \longrightarrow RSi(NLiR')_3 + 3\ BuH \qquad (19)$$

$$2\ [RSi(NLiR')_3] + 2\ AlCl_3 + 2\ Et_2O \xrightarrow{+\ 2\ Tol} [\{RSi(NR')_3(AlOEt_2)\}_2]\cdot 2Tol + 6\ LiCl \qquad (20)$$

(26-27)

By changing R in $RSi(NHR')_3$ from phenyl to methyl of triaminosilane different derivatives of aluminum **(26-27)** are obtained with moderate yield.

Compound	**R**	**R'**	**Yied**
$[\{PhSi(NPh)_3(AlOEt_2)\}_2]\cdot 2Tol$ **(26)**	Ph	Ph	68 %
$[\{MeSi(NPh)_3(AlOEt_2)\}_2]\cdot 2Tol$ **(27)**	Me	Ph	70 %

A similar reaction behavior is observed like earlier discussed for compounds **15-24** during the progress of the reaction. When the addition of $AlCl_3$ is in progress, the reaction mixture becomes soluble in mixture of Et_2O-hexane at -20 °C. Once the addition is completed the reaction mixture is allowed to come to the room temperature. Upon warming to room temperature LiCl is precipitated with product within 40 minutes simultaneously. Then this reaction slurry is stirred for 16 hours at room temperature. LiCl and desired products are separated by filtration and are extracted in a warm toluene solvent. Colorless crystals are obtained by diffusion of Et_2O in a toluene solution at -10 °C after one week. These compounds are sensitive to air and water. $[PhSi(NPh)_3Al(OEt_2)]_2\cdot 2Tol$ **(26)** and $[\{MeSi(NPh)_3(AlOEt_2)\}_2]\cdot 2Tol$ **(27)** are characterized by ^1H, ^{13}C, ^{29}Si, spectroscopy, IR spectroscopy and EDX measurement. In the ^{1}H NMR (in C_6D_6) spectra for **26** and **27** very similar shifts are observed for the aromatic protons. The signals of the methyl protons of **27** occur as *singlet* at 0.33 *ppm*. **26** and **27** contain Et_2O that is coordinated to aluminum. The signals of Et_2O occur at 0.73 *ppm triplet* of CH_3 and 2.85 *ppm quartet* of CH_2. The presence of aromatic protons is from 6.57-7.72 *ppm* as a *broad* signal. From the integrated intensities signal, of methyl protons of silylamine in **27** to methyl protons of Et_2O is 1:2. The coordination of Et_2O is also confirmed by ^{13}C NMR resonances of Et_2O found at 15.53 *ppm* and 65.45 *ppm* respectively. All other resonances of aromatic C-atoms occurred in between 117-145 *ppm*.

26 and **27** are further characterized by ^{29}Si NMR spectroscopy. For both of the compounds ^{29}Si NMR signals are sharp singlets with shift of -41.67(*s*) and -29.77(*s*) *ppm* which is close to the shifts of the starting compounds. This indicates that all Si atoms should have a similar surrounding. Al content is studied by EDX measurement and its peak value is found at 1.48 KeV.

Compound	**δ^{29}Si NMR**	**δ ^{29}Si NMR starting compound**
26	-41.67(*s*)	-41.47(*s*) for $PhSi(NHPh)_3$
27	-29.77(*s*)	-29.91 *(s)* for $MeSi(NHPh)_3$

3.6.5 Crystal structure of $[PhSi(NPh)_3Al(OEt_2)]_2\cdot 2Tol$ (26) and $[MeSi(NPh)_3Al(OEt_2)]_2\cdot 2Tol$ (27)

Single crystals suitable for single crystal XRD are obtained by diffusion of Et_2O in a toluene solution at -10 ^{o}C after one week. Compounds **26** and **27** crystallize triclinic in the space group $P\bar{1}$ with one formula units per unit cell with two toluene non coordinated molecules. Perspective views of the molecular structures are shown in Figures 26 and 27. Selected bond lengths and bond angles are outlined in Table 18.

From X-ray crystallographic study it is found that the molecules of aluminum compounds **26** and **27** exhibit crystallographic $\bar{1}$ symmetry. **26** and **27** consist of two $RSi(NR')_3$ units coordinated to two Al atoms. The extra coordination of the Al-atom is fulfilled by one Et_2O solvent molecule.

Thus there are two four membered AlN_2Si rings that are bridged by one N atom of each silane unit to form complete tricyclic structures of [{PhSi(NPh)$_3$(AlOEt$_2$)}$_2$]•2Tol **(26)** and [{MeSi(NPh)$_3$(AlOEt$_2$)}$_2$]•2Tol (**27**).

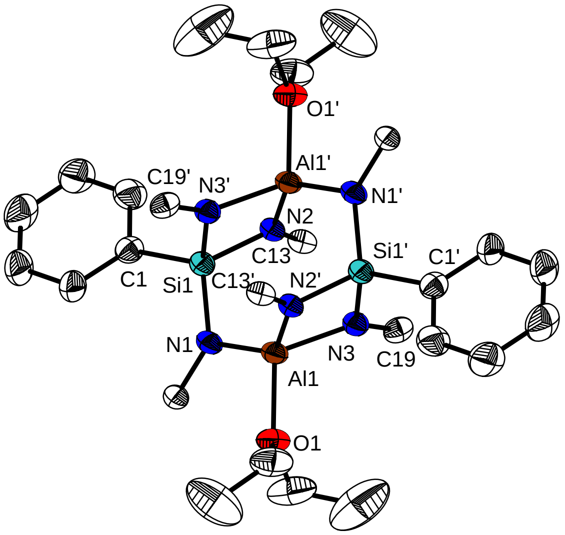


Fig. 26: Molecular structure of [{PhSi(NPh)$_3$(AlOEt$_2$)}$_2$]•2Tol (**26**) (phenyl groups on N atoms are represented by ipso C-atoms and H-atoms are omitted)

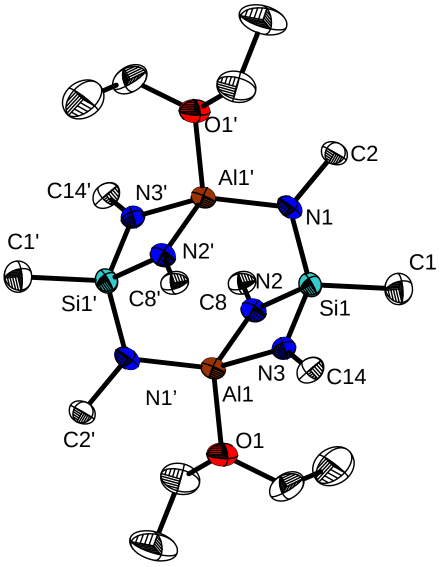


Fig. 27: Molecular structure of [{MeSi(NPh)$_3$(AlOEt$_2$)}$_2$]•2Tol (**27**) (phenyl groups on N atoms are represented by ipso C-atoms and H-atoms are omitted)

Reactions of triaminosilanes with $AlCl_3$ were carried out in a similar manner to that of diaminosilanes. The aluminum derivatives obtained of trissilylamide are neutral whereas for disilylamides they are (**15-16**) ionic. Al atoms have a tetrahedral coordination with three N-atoms and one O atom of Et_2O solvent molecule. The Al atoms are parts of four membered AlN_2Si rings such as Al(1)N(2')N(2)Si(1') and Al(1')N(2)N(3')Si(1) respectively.

The endocyclic bond angle in the four membered AlN_2Si ring of **26** is N(3)-Al(1)-N(2') of 83.06(14)°. And exocyclic bond angle N(1)-Al(1)-N(3) of (117.11(16)° and other bond angles are depicted in Table 18. The N atom which is a bridging atom of two four membered rings is having a largest bond angles of 128.91(15)^{o} for N(1)-Al-N(2'), and other bond angles are outlined in Table 18.

These bond angles have a large deviation from 83.06(14)^{o}-128.91(15)^{o} of an ideal tetrahedron. Similar observation is made for **27** with small bond angle N(2)-Al(1)-N(3) of (82.97(10)^{o}) and larger bond angle N(1')-Al(1)-N(3) of (124.78(10)^{o}).

Table 18. Selected bond lengths (Å) and angles (^{o}) for compounds **26** and **27**.

Bond lengths (Å)	**26**	**27**
Al-N(1)	1.842(3)	1.824(2)
Al-N(2)	1.855(3)	1.840(2)
Al-N(3)	1.845(3)	1.847(2)
Si-N(2)	1.747(3)	1.744(2)
Si-N(3)	1.736(3)	1.744(2)
Si-C	1.874(4)	1.867(3)
Al-O	1.876(3)	1.878(2)
Bond angles (^{o})		
N(3)-Al-N(2')	83.06(14)	82.97(10)
N(1)-Al-N(3)	117.11(16)	124.78(10)
N(1)-Al-N(2')	128.91(15)	121.14(10)
N(1)-Al-O	106.05(14)	106.41(10)
N(3)-Al-O	113.35(14)	110.69(10)
N(2')-Al-O	107.00(15)	109.11(10)
N-Al-O	106.05(14) - 113.35(14)	106.41(10) - 110.69(10)
N-Si-C	112.78(18) - 114.28(16)	111.41(12) - 115.80(13)

The range of the Al-N bond lengths is between 1.842(3)-1.855(3) Å and 1.824(2)-1.847(2) Å for **26** and **27** respectively, which is comparable to the bond length of cages like $[MeAl(\mu\text{-}NHEt)(\mu\text{-}NEt)_2Si(NHEt)]_2$ (ave. Al-N 1.85(3)Å) and

$[EtAl(\mu\text{-}NHEt)(\mu\text{-}NEt)_2Si(NHEt)]_2$ (ave. Al-N 1.84(2) Å) compounds studied by Kaskel *et al.* [16]. And $[2,6\text{-}{}^{i}Pr_2C_6H_3NSiMe_2{}^{i}PrSi(NH)_3Al_2Me_3]_2$ compounds studied by Roesky *et al.*[15]. It is also in the range of spirocyclic compounds (**15**-**16**) described in *section 3.2* and references cited there in.

Si-N and Si-C bonds lengths are normal as observed for triaminosilanes. The distance Al-O is 1.876(3) Å which corresponds to the Al-O bond lengths from 1.899(2)-1.905(2) Å for $[Me_2Al\{n^2\text{-}t\text{-}BuNCR(\mu\text{-}O)\}]_2$ (R= alkyl or aryl groups) reported by Huang *et al.* [72]. In conclusion the above two aluminum cluster compounds are neutral.

The Al-N and Al-O bond lengths are comparable to the following compounds known in the literature.

Compound	**Al-N(Å)**	**Al-O(Å)**	**Reference**
$[Li(Et_2O)_3][(HAl)_4(NPh)_6\{Li(O\ Et_2)_3\}]$	1.914(16)	----	[70]
$[MeSi(t\text{-}BuNAlMe_2)_3]$	2.014(6)	----	[71]
$[\{1,8\text{-}(Me_3SiN)_2C_{10}H_6\}AlH(NMe_3)]$	1.88(2)	----	[73]
$[Al_2(CH_3)_4(C_6HF_5N)_2]$	1.991(14)	----	[75]
$[\{1,8\text{-}(Me_3SiN)_2C_{10}H_6\}Al(Me).THF]$	1.831(12)	1.920(11)	[73]
$[Me_2Si(N\text{-}tBu)_2AlO\text{-}tBu)]_2$	1.819(3)	1.857(2)	[74]
$[Me_2Si(N\text{-}tBu)_2AlOSiMe_3]_2$	1.800(4)	1.861(4)	[74]

3.6.6 Reactions of lithiated amidosilanes $RSi(NLiR')_3$ with $InCl_3$

Trifunctional silylamines $RSi(NHR')_3$ are prepared according to method 2 or 3 [5, 8]. $PhSi(NHPh)_3$ is used as a starting compound for the two step synthesis of an indium silylamide complex.

1) Lithiation of $PhSi(NHPh)_3$ using n-BuLi at -78 °C in hexane to form $[PhSi(NLiPh)_2(NHPh)]$ intermediate product as shown in reaction equation 21.
2) Intermediate lithium silylamido compound is treated in situ with $InCl_3$ in Et_2O solvent depicted in general reaction equation 22.

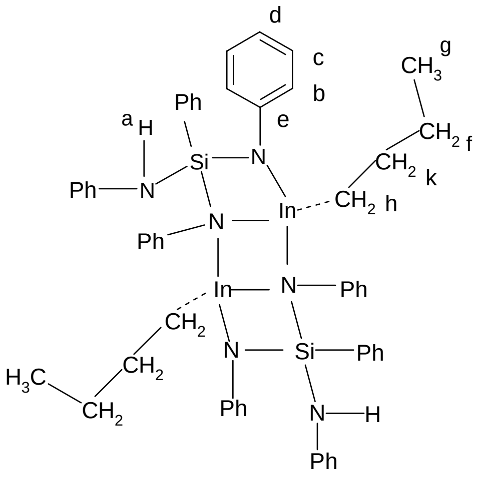
$$[PhSi(NHPh)_3] + 3\ n\text{-}BuLi \longrightarrow [PhSi(NLiPh)_2(NHPh)] + 2\ BuH + n\text{-}BuLi \qquad (21)$$

$$2\ [PhSi(NLiPh)_2(NHPh)] + 2\ InCl_3 + 2\ n\text{-}BuLi \longrightarrow [\{PhSi(NPh)_2(NHPh)(n\text{-}BuIn)\}_2]\cdot Tol + 6\ LiCl \qquad (22)$$

(28)

$[\{PhSi(NPh)_2(NHPh)(n\text{-}BuIn)\}_2]\cdot Tol$ **(28)** is isolated in toluene by extraction as described for earlier compounds in 65 % yield with respect to $PhSi(NHPh)_3$. It is recrystallized from toluene at -15 °C. $[\{PhSi(NPh)_2(NHPh)(n\text{-}BuIn)\}_2]\cdot Tol$ **(28)** is characterized by ^{1}H, ^{29}Si NMR spectroscopy, IR spectroscopy and EDX measurement.

In the ^{1}H-NMR spectrum (400 MHz, in C_6D_6) of **28** two NH protons are observed as a broad peak at 3.76 *ppm* which signifies the presence of unreacted NH on the Si atom of the triaminosilane. It indicates that the reaction is not completed. This is totally in contrast to the earlier compounds prepared and characterized. It is observed that in the first step lithiation is not complete and one mole of n-BuLi remains unreacted as shown in equation 21. This unreacted n-BuLi is carried forward in the second step *in situ*. Then $InCl_3$ is added dropwise to the reaction mixture. n-BuLi takes part in the second step to react with $InCl_3$ and forms an In-butyl unit. The signals of the n-butyl protons are observed from 0.62 *ppm* to 1.46 *ppm* and are well separated from each other. This is a remarkable feature of **28** which is completely different from other indium compounds studied. All other aromatic protons occurred in between 7.04-7.70 *ppm*. In ^{13}C NMR the resonances of aromatic carbon atoms present on Si as well as N atoms are overlapping. In ^{29}Si NMR a *singlet* is observed at -41.47 *ppm.* In content is studied by EDX measurement and its peak value is found at 3.28 KeV.



NMR	**28**	**11**	**Proton assignment**
^{1}H	3.76 ppm	3.66 ppm	H^{a}
	6.77 ppm	6.70 ppm	H^{b}
	7.57-7.70 ppm	6.99-7.76 ppm	$H^{c,d,e}$ (Broad multiplet)
	1.03 -1.10 ppm		$H^{f,k}$ (Broad multiplet)
	0.62 ppm		H^{g}
	1.46 ppm		H^{h}
^{13}C	15.53 ppm		C^{g}
	28.19 ppm		C^{f}
	29.53 ppm		C^{k}
	65.85 ppm		C^{h}
	117.65 ppm		C^{b}
	119.68 ppm		C^{d}
	129.37 ppm		C^{c}
	145.50 ppm		C^{e}
^{29}Si	-41.47	-41.45 ppm	

3.6.7 Crystal structure of [{PhSi(NPh)$_2$(NHPh)(n-BuIn)}$_2$]·Tol (28)

Single crystals suitable for single crystal XRD are obtained by diffusion of hexane in a toluene solution at -10 °C after one week. **28** crystallizes monoclinic in the space group P 21/c with four formula units per unit cell. The perspective view of the molecular structure is shown in Figure 28. Selected bond lengths and bond angles are shown in Table 19. **28** forms a centrosymmetric molecule which consists of two units of [PhSi(NPh)$_2$(NHPh)] and In-Bu with crystallographic $\bar{1}$ symmetry. The In atom has a tetrahedral coordination with three N-atoms and one C atom of the n-butyl chain which is also observed in ^{1}H and ^{13}C NMR study. Indium at the centre forms a square like In$_2$N$_2$ ring to which two four membered InN$_2$Si rings are attached in the opposite direction. Thus **28** has a Si$_2$N$_4$In$_2$ cluster core which looks like a ladder.

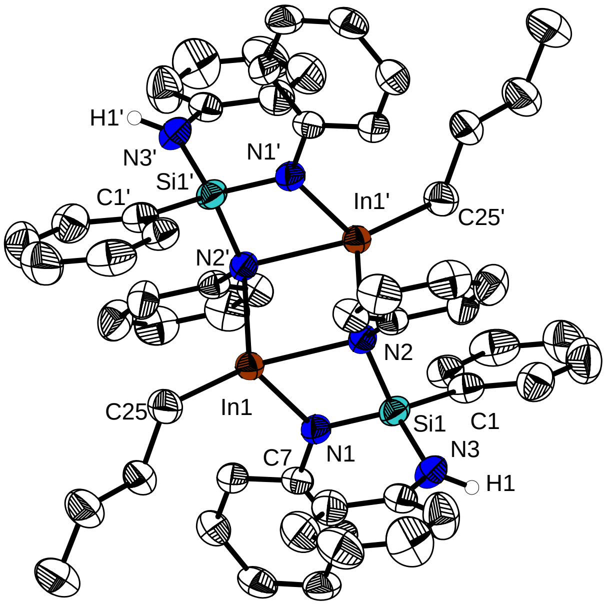


Fig. 28: Molecular structure of [{PhSi(NPh)$_2$(NHPh)(n-BuIn)}$_2$]·Tol **(28)** in the crystal (50% probability level, H-atoms on N-atoms are shown and rest are omitted)

Overall two BuIn fragments and two PhSi groups are connected by four μ_2-bridging NPh groups to give a ladder like Si$_2$N$_4$In$_2$ cluster core. Additionally, there are two terminal HNPh groups attached to silicon which are not coordinated to Indium to give a complete molecule [{PhSi(NPh)$_2$(NHPh)(n-BuIn)}$_2$] **(28)**.

Table 19. Selected bond lengths (Å) and angles (^{o}) for compound **28**.

Bond lengths (Å)			
In(1)-N(1)	2.136(7)	Si(1)-N(3)	1.793(7)
In(1)-N(2)	2.266(6)	In(1)-C(25)	2.159(10)
In(1)-N(2’)	2.237(6)	N(3)-H(1)	0.86(2)
Bond angles (^{o})			
N(25)-In-N(2’)	103.1(3)	N(1)-In-C(25)	124.1(3)
N(25)-In-N(2)	71.6(2)	C(25)-In-N(2’)	123.3(3)
N(2’)-In-N(2)	87.7(2)	C(9)-In-N(2)	133.1(3)
N(1)-Si-N(3)	118.4(4)	N(3)-Si-N(2)	94.8(3)
N(1)-Si-N(2)	109.7(4)	N(3)-Si-C(1)	113.5(4)
N(2)-Si-C(1)	105.5(4)	N(1)-Si-C(1)	115.1(3)

Indium and Si atoms are in the tetrahedral coordination. Indium atom has a coordination of two N-atoms of the same ligand and one N from second molecule with one C-atom of n-butyl chain nearly giving a tetrahedral coordination. Analogous to this, Si atom is also coordinated by three N-atoms and one carbon atom forming a tetrahedral coordination.

The endocyclic bond angle in the In_2N_2 four membered ring N(2’)-In(1)-N(2) of 87.7(2)^{o} and exocyclic C(7)-In(1)-N(2) of 71.08(3)^{o}. For Si it starts from N(3)-Si(1)-N(2) with 94.8(3)^{o} to N(1)-Si(1)-N(3) with 118.4(4)^{o}. Other bond angles are outlined in Table 19. Nitrogen (N2) which is a bridging atom of two indium atoms has a tetrahedral coordination whereas other N-atoms are having a trigonal planar coordination and sum of the bond angle is equal to 360^{o}. There are no intermolecular N-H----N interactions in the solid state.

The In-N bond length is in the range of 2.136(7)-2.266(6) Å. It was found that the N-atom which is a bridge between the two In atoms has a longer bond length of 2.267(7) Å. The In-C bond length is 2.159(1) Å. And other bond lengths such as Si-N (1.793(7) Å) and N-H (0.86(2) Å) are normal for the starting silylamine compound.

Similar to **28** the ladder type molecules $[Me_2Si(N\text{-}^tBu)_2InMe]_2$ and $[Me_2Si(N\text{-}^tBu)_2GaMe]_2$ centrosymmetric were studied by Veith *et al*. by using diaminosilane $Me_2Si(NH\text{-}t\text{-}Bu)_2$ [76]. In these compounds, it is noticed that indium and gallium atoms are in a tetrahedral coordination of three N atoms and one C atom. The In-N bond length of (2.217(4) Å) and the In-C bond length of (2.135(5) Å) are quite analogous to **28**. In-N bond length is also in the range of indium nitrogen heterocubane $[In_4Cl_4(N^tBu)_4]$ (ave. In-N of 2.178(3) Å) cluster compound studied by Merzweiler *et al.*[77].

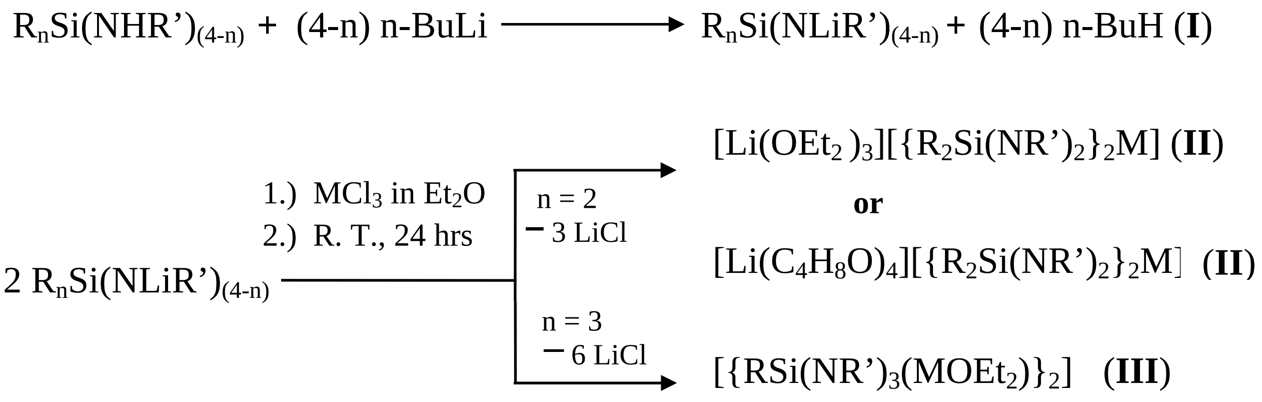
The In-N bond length can be compared with various compounds that are known in literature

Compound	**In-N(Å)**	**Reference**
$[In_4Cl_4(N^tBu)_4]$	2.178(3)	[76]
$[Me_3InNH_2(^tBu)]$	2.215(3)	[47]
$[LiCl][InLi\{Te(NtBu)_3\}_2]$	2.154(3)	[66]
$[Me_3In(\mu\text{-}NH(^tBu)]$	2.363(8)	[67]
$[\{N(SiMe_3)NMe_2\}_3In]$	2.0812(15)	[68]
$[LiN(SiMe_3)_2NHt\text{-}BuInMe]$	2.178(3)	[69]
$[C_6F_5NInMe]_4$	2.197(1)	[78]
$[(4\text{-}C_6H_4F)NInMe(THF)]_4$	2.181(5)	[79]
$[t\text{-}BuNInMe]_4$	2.191(3)	[80]

By using a variety of silylamides as ligands different derivatives of aluminum, gallium and indium are well studied and characterized by using single crystal XRD, from the group three elements. In the future work silylamide as ligands will be used for the preparation of transition element compounds. These compounds could be used for the preparation of nanoparticles by using sol-gel chemistry. They could also be used for the preparation of thin films by using atomic layer deposition techniques [81-83].

4. Summary and Conclusion

The present thesis provides an outline about the synthesis and structural characterization of novel group III silylamide compounds. Compounds containing $[R_2Si(NHR')_2]^{2-}$ and $[RSi(NHR')_3]^{3-}$ ligands are synthesized from diaminosilanes $R_2Si(NHR')_2$ and triaminosilanes $RSi(NHR')_3$. General synthesis of group III amides is carried out by lithiation of aminosilanes in the first step and subsequently addition of anhydrous metal trichloride as shown in general reaction Scheme 1.



Scheme. 1: General reaction scheme for the synthesis of group III silylamides.

Aminosilanes of type $R_nSi(NHR')_{(4-n)}$ are prepared by standard techniques according to the general reaction Scheme 2. Aminosilanes are white crystalline solids which melt to clear liquids. They are stable towards air and moisture at room temperature.

$$R_nSiCl_{(4-n)} + (4-n)\ R'NH_2 + (4-n)\ NEt_3 \longrightarrow R_nSi(NHR')_{(4-n)} + (4-n)\ [HNEt_3]Cl \quad \textbf{(1)}$$

or

$$R_nSiCl_{(4-n)} + (4-n)\ R'NHLi \longrightarrow R_nSi(NHR')_{(4-n)} + (4-n)\ LiCl \quad \textbf{(2)}$$

(n= 1, 2; R = Me, Et or Ph and R'= Ph, Mes or Cy)

Scheme. 2: General reaction scheme for the synthesis of aminosilanes.

To achieve increased kinetic stability in the final metal group III complexes, it is necessary to use bulky R and R’ groups attached to Si and N atoms of the aminosilanes $R_nSi(NHR')_{(4-n)}$ as the Si-N bond is weak.

Some of the lithiated silylamides are isolated and characterized by ^1H, ^{13}C, ^{29}Si, ^7Li NMR spectroscopy and IR spectroscopy as well as by single crystal X-ray diffraction. $[Me_2Si(NLiMes)_2(OEt_2)]_2$ (**13**) along with $[Li(OEt_2)_3][Li_5\{EtSi(NMes)_3\}_2]$ (**25**) are prepared from $Me_2Si(NHMes)_2$ (**4**) and $EtSi(NHMes)_3$ (**10**) using n-BuLi. Complex **13** forms a dimer with ladder like structure as illustrated in Figure 29. The Li, N and Si atoms of anion **25** form a polynuclear distorted rhombic dodecahedron with one vertex removed in cluster represented in Figure 30.

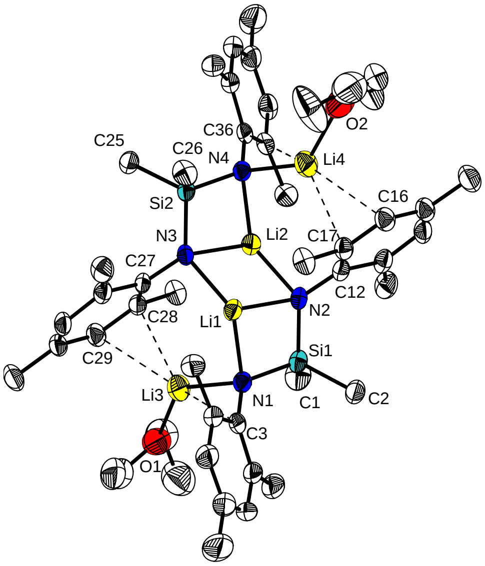


Fig. 29: Molecular structure of $[Me_2Si(NLiMes)_2(OEt_2)]_2$ **(13)** in the crystal (at 50% probability level, and H-atoms are omitted)

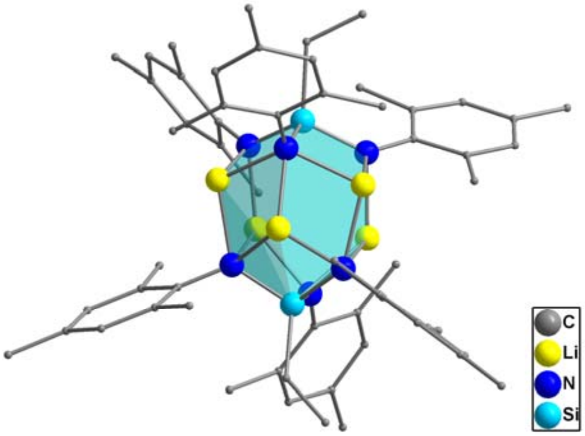


Fig. 30. Polyhedral representation of $[Li_5\{EtSi(NMes)_3\}_2]^-$ anion of **25** (H-atoms are omitted)

Lithiated silylamides $[R_2Si(LiR')_2]$ and $[RSi(LiR')_3]$ are treated with group III halides such as $AlCl_3$, $GaCl_3$ and $InCl_3$ in a 2:1 molar ratio to form corresponding metal compounds. These compounds are divided into two categories such as difunctional and trifunctional group III silylamides depending on the functionality of silylamine.

1) **Difunctional group III silylamide compounds:** $Me_2Si(NHPh)_2$ is lithiated using n-BuLi and *in situ* reacted with anhydrous $AlCl_3$ and $GaCl_3$ according to general reaction Scheme 1 to form $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Al]\cdot Tol$ **(15)** and $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Ga]$ **(19)**. These are ionic compounds with tetrahedral coordination at the metal centre of two chelating silylamide ligands $[\{Me_2Si(NPh)_2\}_2]^{2-}$ which leads to the spirocyclic cores Si_2N_4Al and Si_2N_4Ga as represented in Figures 31 and 32 respectively. The negative charge of the anions is balanced by $[Li(OEt_2)_3]^+$ cations.

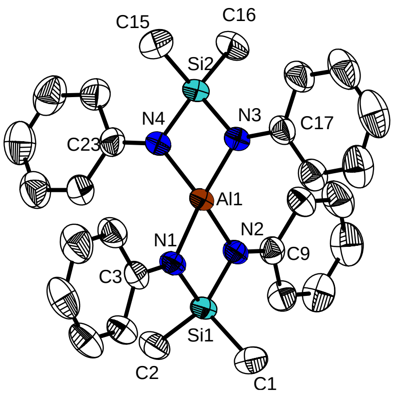


Fig. 31: Molecular structure of $[\{Me_2Si(NPh)_2\}_2Al]^-$ anion of **(15)** in the crystal (50% probability level and H-atoms are omitted)

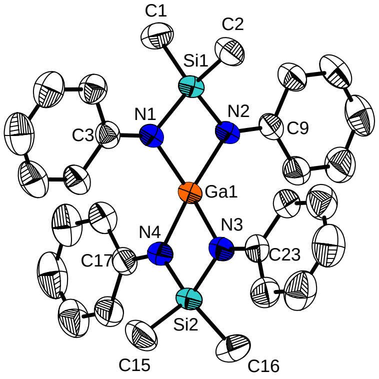


Fig. 32: Molecular structure of $[\{Me_2Si(NPh)_2\}_2Ga]^-$ anion of **(19)** in the crystal (50% probability level and H-atoms are omitted)

When $Me_2Si(NLiPh)_2$ is treated with $InCl_3$ in 2:1 ratio a different coordination behavior is observed in **22** as compared to **15** and **19**. $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_3In]$ (**22**) consists of anions $[\{Me_2Si(NPh)_2\}_3In]^{3-}$ in which the indium atom at the centre has an octahedral coordination by three chelating ligands $[\{Me_2Si(NPh)_2\}_3]^{3-}$. The negative charge of the anion is balanced by three solvated Li^+ cations which are in close contact with anions in contrast to **15** and **19**.

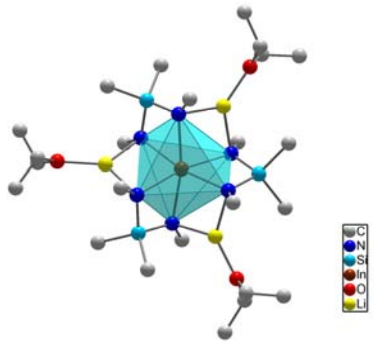


Fig. 33: Polyhedral representation of $[[Li(OEt_2)_3]\{Me_2Si(NPh)_2\}_3In]$ **(22)**

This leads to the formation of a 12 membered $Li_3Si_3N_6$ ring around the central indium atom as shown in Figure 33. Additionally the coordination sphere of the Li cations is completed by OEt_2 molecules.

2) **Trifunctional group III silylamide compounds:** Triaminosilanes RSi(NHR')$_3$ are lithiated to form RSi(NLiR')$_3$ and *in situ* reacted with $AlCl_3$ and $InCl_3$ simultaneously. It leads to the formation of silylamide derivatives like [{PhSi(NPh)$_3$(AlOEt$_2$)}$_2$]·2Tol (**26**) and [{MeSi(NPh)$_3$(AlOEt$_2$)}$_2$]·2Tol (**27**) of aluminum and [{PhSi(NPh)$_2$(NHPh)(n-BuIn)}$_2$]·Tol (**28**) of indium as outlined in general reaction Scheme 1.

    a) [{MeSi(NPh)$_3$(AlOEt$_2$)}$_2$]·2Tol **(27)** is obtained from MeSi(NLiPh)$_3$ and $AlCl_3$. It consists of two Al atoms and two MeSi units which are connected by μ_2-bridging NPh groups to give a tricyclic $Si_2N_6Al_2$ cluster core of the molecule as shown in Figure 34. Extra coordination of the Al atom is fulfilled by one molecule of Et_2O solvent.
    b) [{PhSi(NPh)$_2$(NHPh)(n-BuIn)}$_2$]·Tol **(28)** is prepared from [{PhSi(NLiPh)$_2$(NHPh)}], n-BuLi and $InCl_3$. It consists of two BuIn fragments and two PhSi groups that are connected by four μ_2-bridging of NPh groups to give a ladder like $Si_2N_4In_2$ cluster core of **(28)** illustrated in Figure 35.

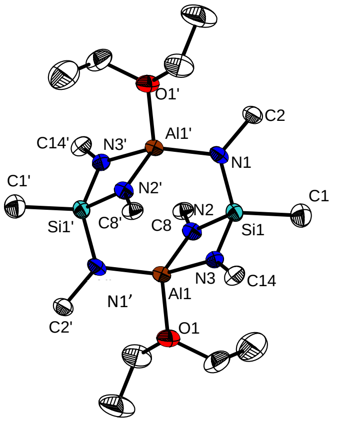


Fig. 34: Molecular structure of the [{MeSi(NPh)$_3$(AlOEt$_2$)}$_2$]·2Tol of (**27**) (phenyl groups on N atoms are represented by ipso C-atoms and H-atoms are omitted)

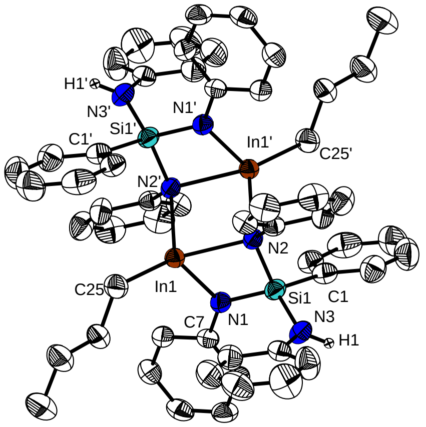
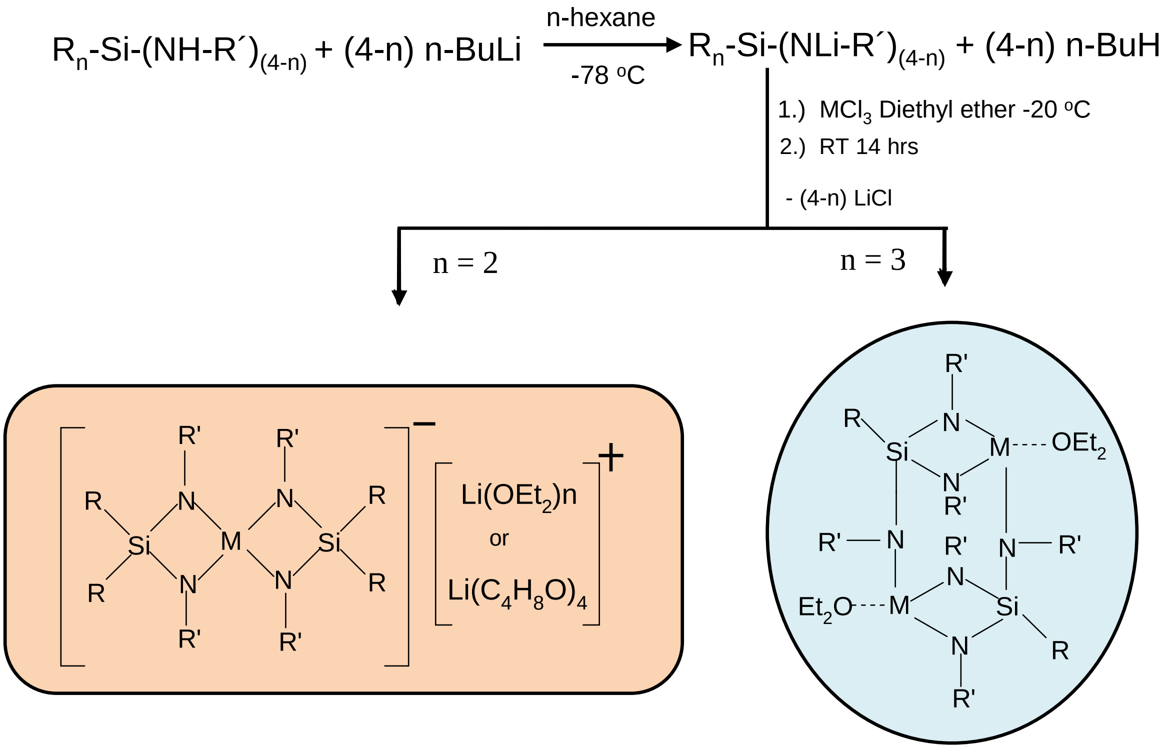


Fig. 35: Molecular structure of [{PhSi(NPh)$_2$(NHPh)(n-BuIn)}$_2$]·Tol **(28)** in the crystal (H-atoms on N-atoms are shown and rest are omitted)

Additionally there are two terminal HNPh groups attached to Si which are not coordinated to indium in a centrosymmetric molecule. It is one of the first crystal structures examples of indium coordinated to alkyl (n-butyl) chain studied so far in this research work.

Overall this research work describes the chemistry of aluminum, gallium and indium silylamides. These compounds are distinct and well defined. And from the present study it can be summarized that in case of difunctional silylamide ionic compounds are obtained while neutral compounds are isolated for trifunctional silylamides as shown in the following Scheme 3 flowchart.



Scheme 3: Flow chart of group III silylamide compounds.

Conclusion

These compounds are potential molecular precursors for preparation of group III nitrides. As an outlook their decomposition behavior can be studied under certain conditions in order to obtain nitrides either in the form of nanoparticles using sol-gel chemistry or thin films by atomic layer deposition technique. These compounds could be used in spintronics for the generation of electronic appliances after doping with other elements such as Fe and Zn.

5. Experimental

5.1 General procedure

All manipulations were performed under an argon atmosphere by standard Schlenk techniques or in an M. Braun Lab master glove box maintained at or below 1 ppm of O_2 and H_2O. Glasswares were dried at 100 °C overnight. All solvents used in the anaerobic syntheses were dried under argon according to the well-known procedures and freshly distilled prior to use. THF, toluene and diethyl ether were distilled over sodium benzophenone; hexane and pentane were dried over $LiAlH_4$. Other solvents were freshly distilled using appropriate drying agents as described in the literature.

5.1.1 NMR Spectroscopy

The ^1H, ^{13}C, ^7Li and ^{29}Si NMR spectra were recorded on Varian Gemini 200, Varian VXR 400 and Varian Unity 500 NMR spectrometers using 5 mm tunable probe at 27 ^oC temperature. Chemical shifts in the ^1H, ^7Li and ^{29}Si NMR spectra are relative to C_6D_6 (δ 7.15) and C_4D_8O (δ 1.73 and 3.58). Deuterated solvents C_6D_6 and C_4D_8O (THF-*d*) were dried using an alloy of Na/K (23% Na, 77 % K metal) and freshly distilled before use. For ^7Li NMR LiCl (1.00 M sol. in D_2O was used as an external standard.)

5.1.2 IR Spectroscopy

The IR spectra were recorded on a Bruker Tensor 27-FT-IR-Spectrometer ATR on a diamond crystal in the range of 4000 to 200 cm^{-1}.

5.1.3 Microanalysis

Microanalyses (C, H, N) were performed at the microanalytical laboratory at the University of Halle using CHNS-932 (LECO) and Vario EL (Elementar Analysensysteme) elemental analyzers. The content of chlorine was determined by burning the substance in oxygen with platinum contact and subsequent titration with mercury nitrate towards diphenylcarbazide.

5.1.4 Mass Spectroscopy

Mass spectra were measured using an Intectra AMD 202 mass spectrometer.

5.1.5 Thermogravimetry

Thermogravimetric measurements were performed on a NETZSCH STA 409C/CD thermal analyser. The samples contained within Al_2O_3 crucibles were heated at a rate of 10 °C per min. from room temperature to 800 °C in static air or in the atmosphere of argon.

5.1.6 EDX measurement

EDX measurements were performed on a Jeol JSM-6701F Field emission Scanning Electron Microscope, with a Bruker EDX (Energy Dispersive X-ray) detector attached.

5.1.7 X-ray crystal structure analysis

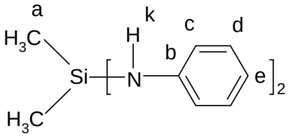
Intensity data were collected on a STOE-IPDS diffractometer with Mo-K_α radiation (0.71073 Å, graphite monochromator) at 220 K. The structures were solved by direct methods with SHELXS-97 and SIR 97 and refined using full-matrix least-square routines against F^2 with SHELXL-97 [85, 86]. Non hydrogen atoms were refined with anisotropic displacement parameters. Details of the crystallographic data collection and refinement parameters are given in appendix at the end of the thesis.

5.2 Experimental synthesis

5.2.1 Synthesis of Dimethylbis-(phenylamino)-silane $Me_2Si(NHPh)_2$ (1)

$$Me_2SiCl_2 + 2\,NEt_3 + 2\,PhNH_2 \longrightarrow Me_2Si(NHPh)_2 + 2\,NEt_3HCl$$

This substance was synthesized according to [1, 2] and was characterized further using spectroscopy techniques. It was prepared from aniline (51.10 g, 0.548 mol) and triethyl amine (55.52 g, 0.548 mol) in the ratio 1:1 in dry THF (250 mL) and dimethyl dichlorosilane (35.36 g, 0.274 mol) giving a white crystalline product.



Yield: 35.45 g (52.79 % based on Me_2SiCl_2) and Mp. = 60 ^oC

Analysis: Molecular Formula: $C_{14}H_{18}N_2Si$ Formula weight: 242.40 g/mol

IR (cm^{-1}): 3367 (m), 3045 (w), 1601 (sh), 1389 (s), 1321 (w), 1288 (s), 1256 (w), 1182 (m), 1156 (w), 1075 (m), 1029 (s), 996 (s), 909 (br), 831 (m), 790 (s), 749 (sh), 724 (w), 688 (m), 657 (w), 613 (w), 465 (w), 375 (m), 292 (m) 245 (w).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 3.19 (*s*, 2H, NH^k), δ 0.087 (*s*, 6H, CH_3^a), δ 6.64 (*d*, *o*- $4H^c$ of Ph), δ 7.05 (*t*, *m*- $4H^d$ of Ph) and δ 6.73 (*t*, *p*- $2H^e$ of Ph).

^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -11.09 (*s*).

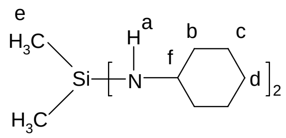
Elemental analysis: Found: C 65.11 %, H 7.46 %, N 10.832 % and calc.: C 69.37 %, H 7.48 %, N 11.56 %

Mass Spectra: 242 m/z (M^+ of $C_{14}H_{18}N_2Si$), 227 m/z (M^+ - CH_3), 149 m/z (M^+ - C_7H_9), 134 m/z (M^+ - C_8H_{12}), 120 m/z (M^+ - $C_8H_{12}N$) and 93 m/z (M^+ - $C_8H_{12}NSi$).

5.2.2 Synthesis of Dimethylbis-(cyclohexylamino)-silane $Me_2Si(NHCy)_2$ (2)

$$Me_2SiCl_2 + 2\,NEt_3 + 2\,CyNH_2 \longrightarrow Me_2Si(NHCy)_2 + 2\,NEt_3HCl$$

$Me_2Si(NHCy)_2$ (**2**) was synthesized according to [1, 2] from cyclohexylamine (38.80 g, 0.351 mol) and triethyl amine (55.52 g, 0.548 mol) in the ratio 1:1 in dry THF (250 mL) and dimethyldichlorosilane (35.36 g, 0.274 mol) giving a thick liquid product.



Yield: 34.45 g (60.00 % based on Me_2SiCl_2)

Analysis: Molecular Formula: $C_{14}H_{30}N_2Si$ Formula weight: 230.40 g/mol

IR (cm^{-1}): 3378 (m), 3045 (w), 1600 (sh), 1392 (s), 1321 (w), 1288 (s), 1259 (w), 1182 (m), 1156 (w), 1075 (m), 1025 (s), 996 (s), 909 (br), 831 (m), 790 (s), 749 (sh), 724 (w), 688 (m), 657 (w), 613 (w), 465 (w), 375 (m), 292 (m), 245 (w).

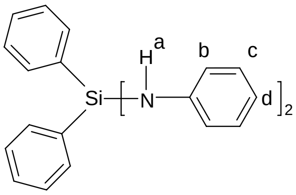
^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 2.66 (*br*, 2H, NH^f), δ 1.406 (*m*, 2H, NH^a), δ 0.046 (*s*, 6H, CH_3^e), δ 0.040 - 1.05 (*b*r, 8H, $CH_3^{b,c,d}$) and δ 1.440 - 2.68 (*b*r, 8H, $CH_3^{b,c,d}$).

^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -12.46 (*s*).

5.2.3 Synthesis of Diphenylbis-(phenylamino)-silane $Ph_2Si(NHPh)_2$ (3)

$$Ph_2SiCl_2 + 2\ NEt_3 + 2\ PhNH_2 \longrightarrow Ph_2Si(NHPh)_2 + 2\ NEt_3HCl$$

Compound $Ph_2Si(NHPh)_2$ (**3**) was synthesized from aniline (40.88 g, 0.438 mol) and triethyl amine (32.67 g, 0.438 mol) in the ratio 1:1 in dry THF (200 mL) and diphenyldichlorosilane (55.45 g, 0.219 mol) as described in [1, 2] giving a white crystalline product.



Yield: 55.15 g (64.87 % based on $PhSiCl_2$) and Mp. = 104 °C

Analysis: Molecular Formula: $C_{24}H_{22}N_2Si$ Formula weight: 366.53 g/mol

IR (cm^{-1}): 3368 (sh), 3068 (w), 3045 (w), 3008 (w), 1598 (sh), 1496 (sh), 1472 (sh), 1424 (s), 1389 (w), 1377 (s), 1325 (w), 1282 (br), 1235 (w), 1182 (w), 1160 (w), 1110 (s), 1079 (m), 1028 (m), 996 (m), 908 (br), 890 (sh), 830 (w), 760 (s), 738 (sh), 698 (br), 617 (w), 583 (m), 569 (m), 522 (w), 499 (m), 477 (br), 454 (br), 426 (w), 409 (m), 299 (w), 280 (w), 266 (w), 233 (m), 211 (m).

^{1}H-NMR (500 MHz, $CDCl_3$ ppm): δ 3.96 (*s*, 2H, NH^a), δ 6.81 (*d*, *o*- 4H^b of Ph), δ 7.034 (*t*, *p*- 2H^d of Ph) and δ 7.77 (*t*, *m*- 4H^c of Ph).

^{29}Si-NMR (100 MHz, $CDCl_3$ ppm): δ -30.07 (*s*).

Elemental analysis: Found: C 77.97 %, H 6.91 %, N 7.41 % and calc.: C 78.65 %, H 6.05 %, N 7.41 %

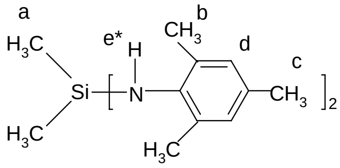
Mass Spectra: 366 m/z (M^+ of $C_{24}H_{22}N_2Si$), 273 m/z ($M^+ - C_6H_6N$), 196 m/z ($M^+ - C_{12}H_{11}N$), 105 m/z ($M^+ - C_{12}H_{17}N_2$) and 77 m/z ($M^+ - C_{12}H_{17}N_2Si$).

5.2.4 Synthesis of Dimethylbis-(mesitylamino)-silane $Me_2Si(NHMes)_2$ (4)

$$MesNH_2 + n\text{-}BuLi \longrightarrow MesNHLi + n\text{-}BuH \qquad \textbf{(I)}$$

$$Me_2SiCl_2 + 2\ MesNHLi \longrightarrow Me_2Si(NHMes)_2 + 2\ LiCl \qquad \textbf{(II)}$$

The synthesis of $Me_2Si(NHMes)_2$ (**4**) is based on [6] from mesitylamine (38.52 g, 0.284 mol), n-BuLi (113.95 mL, 0.284 mol, from a 2.5 M solution in hexane) and dimethyldichlorosilane (18.32 g, 0.142 mol) giving a white crystalline product.



Yield: 23.57 g (49 % based on $PhSiCl_2$) and Mp. = 82 °C

Analysis: Molecular Formula: $C_{20}H_{30}N_2Si$ Formula weight: 326.56 g/mol

IR (cm^{-1}): 3388 (sh), 3010 (w), 1610 (w), 1481 (m), 1444 (w), 1369 (w), 1353 (m), 1303 (m), 1251 (s), 1222 (s), 1158 (m), 1014 (br), 960 (w), 890 (br), 804 (s), 733 (m), 687 (w), 635 (m), 576 (w), 569 (w), 508 (m), 484 (w), 411 (w), 377 (m), 280 (w), 227 (w).

^{1}H-NMR (400 MHz, C_6D_6 ppm): δ 2.427 (*s*, 2H, NH^{e*}), δ 0.124 (*s*, 6H, $CH3^a$), δ 2.16 (*s, o*-12H, of CH_3^b on Mes), δ 2.18 (*s*, *p*-6H, of CH_3^c on Mes) and δ 6.65(*s*, *m*- $4H^d$ of Mes).

^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -7.86 (*s*).

Elemental analysis: Found: C 71.07 %, H 9.34 %, N 7.97 %, and calc.: C 71.756 %, H 9.26 %, N 8.58 %

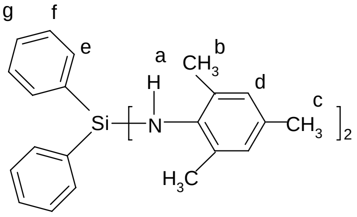
Mass Spectra: 326 m/z (M^+ of $C_{20}H_{30}N_2Si$), 191 m/z (M^+ - $C_9H_{12}N$), 176 m/z (M^+ - $C_{10}H_{15}N$), 162 m/z (M^+ - $C_{11}H_{17}N$) and 135 m/z (M^+ - $C_{11}H_{17}NSi$).

5.2.5 Synthesis of Diphenylbis-(phenylamino)-silane $Ph_2Si(NHMes)_2$ (5)

$$MesNH_2 + n\text{-}BuLi \longrightarrow MesNHLi + n\text{-}BuH \qquad \textbf{(I)}$$

$$Ph_2SiCl_2 + 2\,MesNHLi \longrightarrow Ph_2Si(NHMes)_2 + 2\,LiCl \qquad \textbf{(II)}$$

Compound $Ph_2Si(NHMes)_2$ **(5)** was synthesized according to [6] and was characterized further by using spectroscopy techniques. It was prepared from mesitylamine (48.15 g, 0.356 mol), n-BuLi (142.4 mL, 0.356 mol, from a 2.5 M solution in hexane) and diphenyl dichlorosilane (45.06 g, 0.178 mol) giving a white crystalline product.



Yield: 39.85 g (50 % based on Ph_2SiCl_2) and Mp. = 123 ^oC

Analysis: Molecular Formula: $C_{30}H_{34}N_2Si$ Formula weight: 450.68 g/mol

IR (cm^{-1}): 3363 (m), 3073 (w), 3010 (w), 1616 (w), 1480 (sh), 1428 (m), 1382 (w), 1306 (s), 1281 (w), 1245 (w), 1224 (s), 1158 (m), 1111 (m), 1020 (w), 964 (w), 915 (w), 852 (br), 769 (w), 754 (w), 740 (m), 698 (br), 658 (w), 622 (w), 590 (s), 570 (w), 560 (w), 519 (w), 510 (w), 478 (br), 424 (w), 398 (w), 386 (w), 329 (w), 229 (w).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 3.225 (*s*, 2H, NH^a), δ 2.07 (*s*, *o*-12H, of CH_3^b on Mes), δ 2.09 (*s*, *p*-6H, of CH_3^c on Mes), δ 6.67 (*s*, *m*- $4H^d$ of Mes) and δ 7.05-7.66 (br, $10H^{e,f,g}$ Ph).

^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -30.03 (*s*).

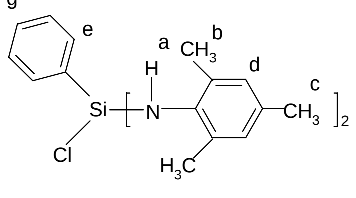
Elemental analysis: Found: C 79.42 %, H 7.66 %, N 6.03 % and calc.: C 79.67 %, H 7.60 %, N 6.22 %

Mass Spectra: 450 m/z (M^+ of $C_{30}H_{34}N_2Si$), 315 m/z (M^+ - $C_9H_{12}N$), 238 m/z (M^+ - $C_{15}H_{17}N$), 160 m/z (M^+ - $C_{21}H_{22}N_2$) and 134 m/z (M^+ - $C_{21}H_{22}N_2Si$).

5.2.6 Synthesis of Chlorophenylbis-(mesitylamino)-silane $PhSiCl(NHMes)_2$ (6)

$$PhSiCl_3 + 3\ NEt_3 + 3\ MesNH_2 \longrightarrow PhSiCl(NHMes)_2 + 2\ NEt_3HCl$$

The method of synthesis of $PhSiCl(NHMes)_2$ (**6**) is the same as that of $Me_2Si(NHPh)_2$ (**1**) using mesitylamine (38.52 g, 0.284 mol) and triethyl amine (28.73 g, 0.284 mol) in the ratio 1:1 in dry THF (200 mL) and phenyltrichlorosilane (20.02 g, 0.94 mol) giving a white crystalline product. Here only two moles of mesitylamine reacted to form $PhSiCl(NHMes)_2$ (**6**) and one chlorine atom remained unreacted.



Yield: 55.05 g (62.16 % based on Ph_2SiCl_2) and Mp. = 85 ^oC

Analysis: Molecular Formula: $C_{24}H_{29}N_2SiCl$ Formula weight: 409.03 g/mol

IR (cm^{-1}): 3378 (m), 3348 (m), 3073 (w), 3022 (w), 1594 (w), 1519 (w), 1484 (sh), 1430 (m), 1376 (w), 1349 (w), 1308 (br), 1249 (w), 1224 (s), 1192 (w), 1158 (w), 1115 (m), 1024 (w), 961 (m), 917 (w), 889 (m), 855 (s), 769 (w), 754 (w), 740 (m), 698 (br), 682 (w), 577 (br) 515, (s) 484, (w), 460 (w), 424 (w), 393 (br), 339 (w), 305(w), 281 (w), 255 (w).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 2.82 (*s*, 2H, NH^a), δ 2.12 (*s*, *o*-12H, of CH_3^{b} on Mes), δ 2.14 (*s*, *p*-6H, of CH_3^{c} on Mes), δ 6.67 (*s*, *m*- 4H^d of Mes) and δ 7.07-7.91 (br, 10H^{e,f,g} Ph).

^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -28.47 (*s*).

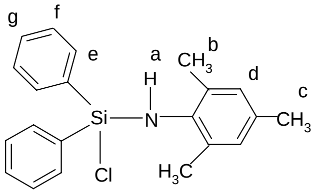
Elemental analysis: Found: C 69.57 %, H 7.24 %, N 6.47 % and calc.: C 70.47 %, H 7.15 %, N 6.85 %

Mass Spectra: 408 m/z (M^+ of $C_{24}H_{29}N_2SiCl$), 273 m/z (M^+- $C_9H_{12}N$), 238 m/z (M^+- $C_9H_{12}NCl$) and 135 m/z (M^+- $C_{15}H_{17}NClSi$).

5.2.7 Synthesis of Chlorodiphenyl-(mesitylamino)-silane $Ph_2SiCl(NHMes)$ (7)

$$Ph_2SiCl_2 + 2\ NEt_3 + 2\ MesNH_2 \longrightarrow Ph_2SiCl(NHMes) + NEt_3HCl$$

Aminosilane $Ph_2SiCl(NHMes)$ (**7**) was synthesized from mesitylamine (41.40 g, 0.306 mol) and triethyl amine (30.99 g, 0.306 mol) in the ratio 1:1 in dry THF (200 mL) and phenyldichlorosilane (38.73 g, 0.153 mol) as described for $Me_2Si(NHPh)_2$ (**1**). The product was white crystalline. Here only one mole of mesitylamine reacted to form $Ph_2SiCl(NHMes)$ (**7**) and one chlorine atom remained unreacted.



Yield: 20.30 g (37.25 % based on Ph_2SiCl_2) and Mp. = 74 ^oC

Analysis: Molecular Formula: $C_{21}H_{22}NSiCl$ Formula weight: 351.94 g/mol

IR (cm^{-1}): 3363 (m), 3087 (w), 3052 (w), 3014 (w), 1591 (m), 1518 (w), 1486 (s), 1444 (w), 1425 (s), 1385 (br), 1329 (w), 1304 (m), 1272 (m), 1250 (m), 1225 (s), 1192 (w), 1161 (w), 1112 (s), 1065 (w), 1028 (w), 997 (w), 960 (m), 900 (br), 861 (s), 752 (m), 735 (s), 718 (m), 698 (br), 619 (w), 587 (m), 573 (m), 516 (br), 496 (w), 477 (w), 411 (br), 393 (br), 348 (w), 301 (w), 290 (w).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 2.98 (*s*, 1H, NH^a), δ 2.17 (*s, o*-6H, of CH_3^b on Mes), δ 2.06 (*s, p*-3H, of CH_3^c on Mes), δ 6.67 (*s, m*- 2H^d of Mes) and δ 7.05-7.72 (br, 10H^{e,f,g} Ph).

^{29}Si-NMR (500 MHz, C_6D_6 ppm): δ -12.84 (*s*).

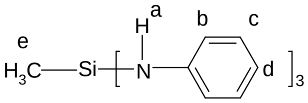
Elemental analysis: Found: C 71.64 %, H 6.51 %, N 3.84 % and calc.: C 71.67 %, H 6.30 %, N 3.98 %

Mass Spectra: 351 m/z (M^+ of $C_{21}H_{22}NSiCl$), 217 m/z (M^+ - C_6H_6N), 181 m/z (M^+ - $C_9H_{12}NCl$) and 135 m/z (M^+ - $C_{15}H_{17}NClSi$).

5.2.8 Synthesis of Methyltris-(phenylamino)-silane MeSi(NHPh)$_3$ (8)

$$MeSiCl_3 \;+\; 3\,NEt_3 \;+\; 3\,PhNH_2 \longrightarrow MeSi(NHPh)_3 \;+\; 3\,NEt_3HCl$$

MeSi(NHPh)$_3$ (**8**) was synthesized according to [3, 6] and was characterized further using spectroscopy techniques. It was prepared from aniline (40.88 g, 0.438 mmol), triethylamine (44.41 g, 0.438 mol) in the ratio 1:1 in dry THF (150 mL) and methyltrichlorosilane (21.78 g, 0.146 mol) giving a white crystalline product.



Yield: 30 g (65.21 % based on $MeSiCl_3$) and Mp. = 78 °C

Analysis: Molecular Formula: $C_{19}H_{21}N_3Si_1$ Formula weight: 319.48 g/mol

IR (cm^{-1}): 3367 (m), 3040 (w), 1598 (m), 1479 (s), 1377 (s), 1322 (w), 1305 (w), 1274 (br), 1186 (w), 1158 (w), 1073 (w), 1032 (m), 998 (w), 964 (w), 896 (sh), 855 (w), 783 (w), 749 (m), 688 (m), 620 (w), 572 (m), 511 (w), 432 (w), 405 (w), 336 (w), 384 (w), 279 (w).

^{1}H-NMR (400 MHz, C_6D_6 ppm): δ 3.53 (*s*, 3H, NH^a), δ 0.34 (*s*, 3H^e, of CH_3), δ 6.64 (*d, o*-6H^b of Ph), δ 7.05 (*t, m*- 6H^c of Ph) and δ 6.73 (*t, p*- 3H^d of Ph).

^{29}Si-NMR (400 MHz, C_6D_6 ppm): δ -29.91 (*s*).

Elemental analysis: Found: C 69.76 %, H 6.96 %, N 12.64 % and calc.: C 71.43 %, H 6.63 %, N 13.15 %

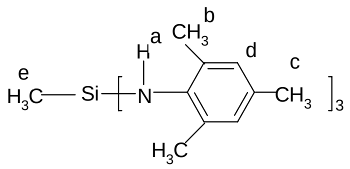
Mass Spectra: 319 m/z (M^+ of $C_{19}H_{21}N_3Si$), 226 m/z (M^+ - C_6H_6N), 134 m/z (M^+ - $C_{12}H_{12}N_2$) and 93 m/z (M^+ - $C_{13}H_{13}N_2Si$).

5.2.9 Synthesis of Methyltris-(mesitylamino)-silane $MeSi(NHMes)_3$ (9)

$MesNH_2$ + n-BuLi $\longrightarrow$ MesNHLi + n-BuH **(I)**

$MeSiCl_3$ + 3 [MesNHLi] $\longrightarrow$ $MeSi(NHMes)_3$ + 3 LiCl **(II)**

The aminosilane $MeSi(NHMes)_3$ (**9**) was synthesized from mesitylamine (48.15 g, 0.356 mol), n-BuLi (142.40 mL, 0.356 mol, from a 2.5 M solution in hexane) and methyltrichlorosilane (17.73 g, 0.118 mol) as described for $MeSi(NHPh)_3$ (**8**).



Yield: 29.10 g (57.00 % based on $MeSiCl_3$) and Mp. = 102 °C

Analysis: Molecular Formula: $C_{28}H_{39}N_3Si$ Formula weight: 445.71 g/mol

IR (cm^{-1}): 3364 (m), 3004 (vw), 1614 (w), 1481 (sh), 1435 (w), 1375 (w), 1331 (s), 1305 (m), 1257 (br), 1240 (br), 1158 (s), 1028 (w), 964 (w), 907 (br), 847 (sh), 778 (w), 760 (m), 731 (w), 695 (w), 658 (w), 581 (m), 567 (s), 509 (w), 424 (m), 376 (m), 306 (w), 384 (w),241 (w).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 0.346 (*s*, 3H^e of CH_3), δ 2.59 (*s*, 3H, NH^a), δ 2.12 (*s*, *o*-18H, of CH_3^b on Mes), δ 2.16 (*s*, *p*-9H, of CH_3^c on Mes) and δ 6.74 (*s*, *m*- 6H^d of Mes).

^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -31.10 (*s*).

Elemental analysis: Found: C 74.39 %, H 9.01 %, N 9.02 % and calc.: C 75.45 %, H 8.82 %, N 9.43 %

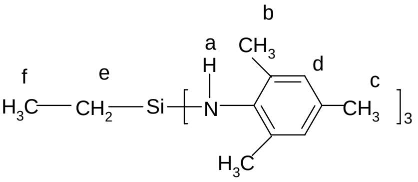
Mass Spectra: 445 m/z (M^+ of $C_{28}H_{39}N_3Si$), 310 m/z (M^+ - $C_9H_{12}N$), 176 m/z (M^+ - $C_{18}H_{24}N_2$) and 134 m/z (M^+ - $C_{19}H_{27}N_2Si$).

5.2.10 Synthesis of ethyltris-(mesitylamino)-silane $EtSi(NHMes)_3$ (10)

$MesNH_2$ + n-BuLi $\longrightarrow$ MesNHLi + n-BuH **(I)**

$EtSiCl_3$ + 3 MesNHLi $\longrightarrow$ $EtSi(NHMes)_3$ + 3 LiCl **(II)**

The method of synthesis of $EtSi(NHMes)_3$ (**10**) is the same as that of $Ph_2Si(NHMes)_2$ **(5)** with mesitylamine (48.15 g, 0.356 mol), n-BuLi (142.40 mL, 0.356 mol, from a 2.5 M solution in hexane) and ethyltrichlorosilane (19.40 g, 0.118 mol) giving a white crystalline product.



Yield: 33.75 g (62.44 % based on $EtSiCl_3$) and Mp. = 156 °C

Analysis: Molecular Formula: $C_{29}H_{41}N_3Si$ Formula weight: 459.74 g/mol

IR (cm^{-1}): 3367 (m), 3009 (w), 2956 (w), 1584 (w), 1480 (sh), 1460 (w), 1346 (m), 1305 (s), 1269 (w), 1244 (w), 1123 (sh), 1155 (s), 1020 (w), 979 (w), 959 (m), 932 (w) 895 (br), 853 (sh), 768 (w), 747 (w), 709 (w), 691 (w), 649 (w), 585 (br), 510 (m), 470 (w), 430 (m), 386 (w), 281(w), 267 (w).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 2.54 (*s*, 3H, NH^a), δ 1.06 (*t*, 3H^f, CH_3), δ 0.784 (*q*, 2H^e of CH_2), δ 2.14 (*s*, *o*-18H, of $CH_3{}^b$ on Mes), δ 2.16 (*s*, *p*-9H, of $CH_3{}^c$ on Mes) and δ 6.65 (*s*, *m*-6H^d of Mes).

^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -31.33 (*s*).

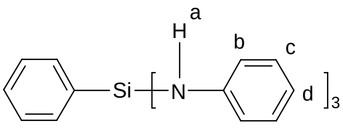
Elemental analysis: Found: C 74.64 %, H 9.01 %, N 8.69 % and calc.: C 75.76 %, H 8.99 %, N 9.14 %

Mass Spectra: 459 m/z (M^+ of $C_{29}H_{41}N_3Si$), 324 m/z (M^+ - $C_9H_{12}N$), 190 m/z (M^+ - $C_{18}H_{24}N_2$) and 134 m/z (M^+ - $C_{20}H_{29}N_2Si$).

5.2.11 Synthesis of Phenyltris-(phenylamino)-silane PhSi(NHPh)$_3$ (11)

$$PhSiCl_3 + 3\ NEt_3 + 3\ PhNH_2 \longrightarrow PhSi(NHPh)_3 + 3\ NEt_3HCl$$

Trisaminosilane PhSi(NHPh)$_3$ (**11**) was synthesized from aniline (12.77 g, 0.137 mol), triethylamine (13.88 g, 0.137 mol) in 1:1 ratio in dry THF (150 mL) and phenyltrichlorosilane (9.66 g, 0.45 mol) in THF (50 mL) as derscribed for $Me_2Si(NHPh)_2$ **(1)**



Yield: 12.50 g (71.75 % based on $PhSiCl_3$) and Mp. = 130 °C

Analysis: Molecular Formula: $C_{24}H_{23}N_3Si$ Formula weight: 381.5 g/mol

IR (cm^{-1}): 3371 (m), 3050 (w), 3013 (w), 1599 (sh), 1496 (sh), 1478 (sh), 1432 (w), 1380 (sh), 1278 (sh), 1243 (w), 1173 (w), 1122 (m), 1077 (s), 1028 (w), 995 (m), 928 (s), 913 (sh), 890 (sh), 830 (w), 780 (w), 751(sh), 744 (sh), 691(sh), 617 (s), 587 (s), 563 (w), 537 (w), 488 (sh), 433 (w), 398 (w), 274 (w), 232 (w).

^{1}H-NMR (400 MHz, C_6D_6 ppm): δ 3.665 (*s*, 3H, NH^a), δ 6.70 (*d*, *o*-6H, CH^b), δ 6.99 (*t*, *p*-3H CH^d) and δ 7.76 *(t, m*-6H CH^c).

^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -41.47 (*s*).

Elemental analysis: Found: C 73.39 %, H 6.33 %, N 10.70 % and calc.: C 75.55 %, H 6.08 %, N 11.01 %

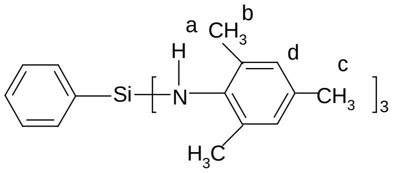
Mass Spectra: 381 m/z (M^+ of $C_{24}H_{23}N_3Si_1$), 288 m/z (M^+ - C_6H_7N), 196 m/z (M^+ - $C_{12}H_{11}N_2$), 120 m/z (M^+ - $C_{18}H_{17}N_2$) and 93 m/z (M^+ - $C_{18}H_{17}N_2Si$).

5.2.12 Synthesis of Phenyltris-(mesitylamino)-silane PhSi(NHMes)$_3$ (12)

$MesNH_2$ + n-BuLi $\longrightarrow$ MesNHLi + n-BuH (**I**)

$PhSiCl_3$ + 3 MesNHLi $\longrightarrow$ $PhSi(NHMes)_3$ + 3 LiCl **(II)**

The procedure of synthesis of PhSi(NHMes)$_3$ (**12**) is the same as that of EtSi(NHMes)$_3$ (**10**) from aniline (48.15 g, 0.356 mol, n-BuLi (142.40 mL, 0.356 mol, from a 2.5 M solution in hexane) and phenyltrichlorosilane (25.10 g, 0.118 mol).



Yield: 44.85 g (74.81 % based on $PhSiCl_3$) and Mp. = 158 °C

Analysis: Molecular Formula: $C_{33}H_{41}N_3Si$ Formula weight: 507.78 g/mol

IR (cm^{-1}): 3364 (m), 3070 (vw), 3012 (w), 1590 (w), 1480 (sh), 1432 (m), 1385 (w), 1303 (s), 1246 (br), 1159 (m), 1109 (m), 1035 (br), 967 (m), 934 (w), 913 (m), 877 (br), 850 (sh), 770 (w), 756 (w), 740 (m), 698 (sh), 658 (w), 592 (s), 569 (w), 525 (w), 481 (m), 420 (w), 400 (w), 384 (w), 292 (w).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 2.99 (*s*, 3H, NH^a), δ 2.13 (*s*, *omethyl*-18H of CH$_3^b$ on Mes), δ 2.16 (*s*, *para*-9H of CH$_3^c$ on Mes) and δ 6.76 (*s*, *m*- 6H^d of Mes).

^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -44.85 (*s*).

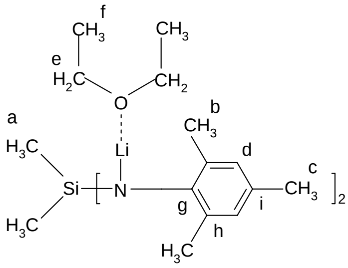
Elemental analysis: Found: C 77.46 %, H 8.15 %, N 7.97 % and calc.: C 78.06 %, H 8.14 %, N 8.27 %

Mass Spectra: 507 m/z (M^+ of $C_{33}H_{41}N_3Si$), 372 m/z (M^+ - $C_9H_{12}N$), 238 m/z (M^+ - $C_{18}H_{24}N_2$ and 134 m/z (M^+ - $C_{24}H_{29}N_2Si$).

5.2.13 Synthesis of [{$Me_2Si(NLiMes)_2(OEt_2)$}$_2$] (13)

$$Me_2Si(NHMes)_2 + 2\ n\text{-}BuLi \longrightarrow [\{Me_2Si(NLiOEt_2Mes)_2\}] + 2\ n\text{-}BuH$$

To a stirred suspension of dimethylbis-(mesitylamino)-silane $Me_2Si(NHMes)_2$ (1.88 g, 5.75 mmol) in hexane (25 mL) at -78 °C was added n-BuLi (4.60 mL, 11.5 mmol from a 2.5 M solution in hexane) over a period of one hour. After completion of addition the reaction mixture was allowed to come to room temperature and heated at 70 °C for 2 hrs. A yellow solution of lithiated compound was obtained. After the solution was cooled to room temperature, 20 mL of Et_2O was added. The colorless solution was stored at -10 °C and after two days crystals were formed.



Yield: 1.82 g (94 % with respect to $Me_2Si(NHMes)_2$)

Analysis: Molecular Formula: $C_{48}H_{78}N_4Si_2O_2Li_4$ Formula weight: 825.07 g/mol

IR (cm^{-1}): 3010 (w), 1605 (w), 1472 (m), 1418 (m), 1373 (w), 1297 (s), 1265 (vw), 1228 (s), 1158 (s), 1096 (w), 1068 (w), 962 (s), 910 (br), 868 (vw), 850 (w), 801 (br), 740 (w), 680 (br), 625 (w), 560 (m), 526 (br), 435 (br), 395 (vw), 365 (w), 280 (w), 227 (w).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 0.33 (*s*, 12H, CH_3^a), δ 0.88 (*t*, 12H, CH_3^f), δ 2.31 (*s*, 6H, CH_3^c), δ 2.33 (*s*, 12H^b), δ 3.03 (*m*, 8H, CH_2^e) and aromatic protons at δ 6.68 (*s*, 4H^d of Mes).

^{13}C-NMR (125 MHz, C_6D_6): δ 2.30(s, C^a), δ 13.55 (s, C^f), δ 19.34 (s, C^b), δ 21.15 (s, C^c), δ 65.45 (s, C^e), δ 128.44 (s, C^d), δ 122.32 (s, C^h), δ 127.05 (s, C^i) and δ 141.11 (s, C^g).

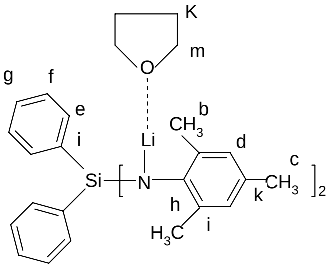
^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -23.06 (*s*).

^{7}Li-NMR (100 MHz, C_6D_6 ppm): 1.47 (*s*) and 1.917 (*s*).

5.2.14 Synthesis of $[(Li(OC_4H_8)_4][Li_3\{Ph_2Si(NMes)_2\}_2]\cdot 2THF$ (14)

$$Ph_2Si(NHMes)_2 + 2\ n\text{-}BuLi + 6\ THF \longrightarrow [(Li(OC_4H_8)_4][Li_3\{Ph_2Si(NMes)_2\}_2]\cdot 2THF + 2\ n\text{-}BuH$$

$[(Li(OC_4H_8)_4][Li_3\{Ph_2Si(NMes)_2\}_2]\cdot 2THF$ (**14**) was prepared as described for the compound **13** from $Ph_2Si(NHMes)_2$ (1.75 g, 3.88 mmol) and n-BuLi (3.11 mL, 7.77 mmol from a 2.5 M solution in hexane). This compound was recrystallized from the suspension of Et_2O and THF at 10 °C over a period of 4 days.



Yield: 1.71 g (92 % with respect to $Ph_2Si(NHMes)_2$)

Analysis: Molecular Formula: $C_{84}H_{91}N_4Si_2O_6Li_4$ Formula weight: 1336.55 g/mol

IR (cm^{-1}): 3073 (w), 3010 (w), 1606 (w), 1475 (br), 1418 (s), 1374 (w), 1298 (s), 1242 (sh), 1184 (vw), 1158 (m), 1103 (br), 1066 (w), 1039 (m), 1004 (vw), 966 (m), 909 (br), 855 (m), 762 (m), 740 (w), 702 (br), 688 (w), 644 (m), 591 (m), 561 (m), 513 (w), 493 (m), 443 (w), 396 (br), 370 (w), 292 (w), 260 (m), 248 (vw), 229 (w).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 1.81 (*m*, $8H^k$), δ 2.20 (*s*, *o*-24H, of CH_3 on Mes), δ 2.30 (*s*, *p*-12H, of CH_3 on Mes), δ 3.69 (*t*, $8H^m$), δ 6.67 (*s*, *m*- $4H^d$ of Mes) and δ 7.05-7.66 (br, $10H^{e,f,g}$ Ph).

^{13}C-NMR (125 MHz, C_6D_6 ppm): δ 25.15(s, C^k), δ 66.85(s, C^m), δ19.34 (s, C^b), δ 21.15 (s, C^c), δ 65.45 (s, C^e), δ 122.07 (s, C^i), δ 128.44 (s, C^d), δ 125.34 (s, C^e), δ 126.85 (s, C^e), δ 127.05 (s, C^k) δ 129.15 (s, C^f), δ 127.54 (s, C^g), δ 138.25 (s, C^i) and δ 140.71 (s, C^h).

^{29}Si-NMR (500 MHz C_6D_6 ppm): δ -43.875 (*s*).

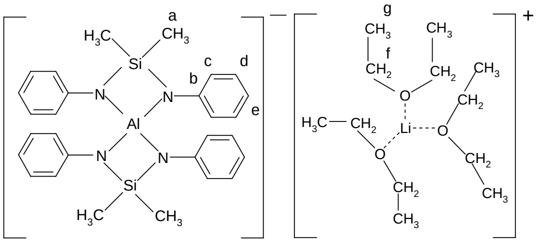
^{7}Li-NMR (500 MHz C_6D_6 ppm): δ 0.46(*s*), δ 1.71(*s*) and δ 1.89 (*s*).

5.2.15 Synthesis of $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Al]\cdot Tol$ (15)

$$Me_2Si(NHPh)_2 + 2\ n\text{-}BuLi \xrightarrow{+1\ \cdot Tol} Me_2Si(NLiPh)_2 + 2\ n\text{-}BuH \qquad \textbf{(I)}$$

$$2\ Me_2Si(NLiPh)_2 + AlCl_3 + 3\ Et_2O \longrightarrow [Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Al]\cdot Tol + 3\ LiCl \qquad \textbf{(II)}$$

Complex $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Al]\cdot Tol$ (**15**) was prepared by following the experimental procedure described in [84]. To a stirred suspension solution of $Me_2Si(NHPh)_2$ (2.00 g, 8.26 mmol) in hexane (40 mL) at -78 ^{o}C was added a solution of n-BuLi (6.61 mL, 16 mmol from a 2.5 M solution in hexane) over a period of 2 hrs. After completion of addition the reaction mixture was allowed to come to room temperature and heated at 70 ^{o}C for 2 hrs and yellow solution of lithiated compound was obtained. After the solution was cooled to room temperature it was added to a solution of $AlCl_3$ (0.550 g, 4.13 mmol) in molar ratio 2:1 in 20 mL Et_2O at -20 ^{o}C drop by drop. It was allowed to come to room temperature and a white precipitate formed during the warming process. The reaction slurry was stirred for 20 hrs and filtration was carried out to seperate the precipitated LiCl and a colorless filtrate. Precipitated LiCl and product remained on the filter was washed with 25 mL of dry toluene. Then the colorless filtrate in toluene was concentrated to ca. 15 mL and stored at -25 ^{o}C. After two days colorless crystals were formed.



Yield: 1.25 g (70 % with respect to $Me_2Si(NHPh)_2$)

Analysis: Molecular Formula: $C_{47}H_{70}N_4Si_2Li_1O_3Al$ Formula weight: 829.17 g/mol

IR (cm^{-1}): 3056 (w), 1586 (br), 1478 (br), 1387 (m), 1331 (w), 1303 (sh), 1253 (w), 1231 (w), 1212 (m), 1180 (m), 1149 (w), 1076 (br), 1029 (m), 995 (s), 958 (w), 935 (s), 898 (w), 828 (br), 791 (m), 749 (s), 691 (s), 637 (w), 611 (w), 559 (w), 520 (w), 485 (w), 459 (w), 389 (br), 362 (w), 336 (w), 288 (w), 256 (m).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 0.67 (*s*, 6H, CH_3^a), δ 0.86 (*t*, 18H, CH_3 *of sol.Et_2O*), δ 2.92 (*m*, 12H, CH_2 *of sol. Et_2O),* δ 6.62 (*d*, 6H, CH_3^c), δ 7.08 (*t*, 6H, CH_3^d) and δ 6.76 (*t,* 6H, CH_3^e).

^{13}C-NMR (125 MHz, C_6D_6 ppm): δ 1.51 (s, C^a), δ 14.72 (s, C, CH_3 *sol.Et_2O*), δ 65.35 (s, C, CH_2 *Sol.E_2tO*), δ 150.07 (s, C^b), δ 146.34 (s, C^c), δ 146.20 (s, C^d) and δ 129.95 (s, C^d).

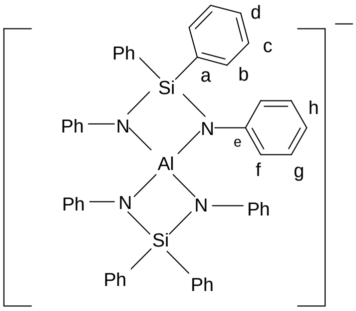
^{29}Si-NMR (500 MHz, C_6D_6 ppm): δ -4.14 (*s*).

5.2.16 Synthesis of $[Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2Al]\cdot 3THF$ (16)

$$\mathrm{Ph_2Si(NHPh)_2 \quad + \quad 2\ n\text{-}BuLi \longrightarrow Ph_2Si(NLiPh)_2 \quad + \quad 2\ n\text{-}BuH} \qquad \textbf{(I)}$$

$$\mathrm{2\ Ph_2Si(NLiPh)_2 + AlCl_3 + 7\ C_4H_8O \longrightarrow [Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2Al]\cdot 3THF + 3\ LiCl} \ \textbf{(II)}$$

The synthesis procedure of $[Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2Al]\cdot 3THF$ (**16**) is the same as that of complex $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Al]\cdot 1Tol$ (**15**) from $Ph_2Si(NHPh)_2$ (1.76 g, 4.80 mmol), n-BuLi (3.84 mL, 9.61 mmol from a 2.5 M solution in hexane) and $AlCl_3$ (0.320 g, 2.40 mmol) in 15 mL Et_2O giving a colorless white crystalline product. Crystals were obtained at -20 °C after one week from a THF solution.



Yield: 1.18 g (62 % with respect to $Ph_2Si(NHPh)_2$)

Analysis: Molecular Formula: $C_{76}H_{82}N_4Si_2LiO_7Al$ Formula weight: 1253.56 g/mol

IR (cm^{-1}): 3068 (w), 3045 (w), 3008 (w), 1588 (sh), 1482 (sh), 1448 (vw), 1429 (m), 1381 (w), 1326 (vw), 1299 (br), 1175 (m), 1150 (vw), 1108 (s), 1065 (w), 1041 (br), 994 (s), 955 (vw), 933 (s), 886 (w), 823 (sh), 765 (w), 738 (br), 702 (w), 690 (br), 664 (s), 615 (m), 584 (w), 570 (m), 520 (w), 488 (br), 465 (w), 406 (br), 378 (w), 295 (w).

^{1}H-NMR (500 MHz, C_4D_8O ppm): δ 1.82 (*m,* 16H of CH_2 *Sol.THF*), δ 3.72 (*t,* 16H of CH_2 *Sol. THF*), δ 6.20 (*br, p-* 4H of Ph), δ 6.61 (*d, o-* 8H of Ph), δ 7.34 (*br, toluene sol.*) and δ 8.03 (*t, m- 8*H of Ph).

^{13}C-NMR (125 MHz, C_4D_8O ppm): δ 24.41(s, second C from O *Sol. THF*), δ 66.48 (s, first C from O *Sol. THF*), δ 114.27 (s, C^f), δ 117.36 (s, C^h), δ 129.62 (s, C^g), δ 128.49 (s, C^c), δ 134.71 (s, C^a), δ 136.37 (s, C^b), δ 137.69 (s, C^d) and δ 152.70 (s, C^e).

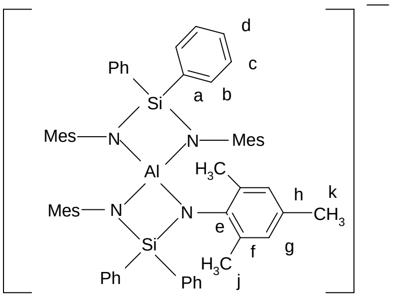
^{29}Si-NMR (100 MHz, C_4D_8O ppm): δ -28.25 (*s*).

5.2.17 Synthesis of [Li(OC_4H_8)$_4$][{$Ph_2Si(NMes)_2$}$_2$Al] (17)

$Ph_2Si(NHMes)_2$ + 2 n-BuLi $\longrightarrow$ $Ph_2Si(NLiMes)_2$ + 2 BuH **(I)**

2 $Ph_2Si(NLiMes)_2$ + $AlCl_3$ + 4 C_4H_8O $\longrightarrow$ [Li(OC_4H_8)$_4$][{$Ph_2Si(NMes)_2$}$_2$Al] + 3 LiCl **(II)**

The complex (**17**) was synthesized from $Ph_2Si(NHMes)_2$ (1.74 g, 3.86 mmol), n-BuLi (3.09 mL, 7.73 mmol from a 2.5 M solution in hexane) and $AlCl_3$ (0.257 g, 1.93 mmol) in 15 mL Et_2O as described for [Li(OEt_2)$_3$][{$Me_2Si(NPh)_2$}$_2$Al]·Tol (**15**) giving a white crystalline product. Crystals were obtained at -20 °C after one week in THF.



Yield: 1.10 g (64 % with respect to $Ph_2Si(NHMes)_2$)

Analysis: Molecular Formula: $C_{64}H_{80}N_4Si_2LiO_4Al$ Formula weight: 1058.11 g/mol

IR (cm^{-1}): 3357 (vw), 3073 (w), 3010 (w), 1606 (w), 1591 (vw), 1472 (br), 1426 (m), 1382 (w), 1336 (vw), 1304 (s), 1283 (vw), 1247 (br), 1183 (w), 1157 (m), 1107 (br), 1062 (s), 963 (s), 921 (br), 875 (w), 852 (s), 791 (sh), 769 (w), 742 (m), 722 (w), 704 (br), 668 (w), 643 (w), 601 (m), 569 (m), 538 (w), 5110 (m), 4788 (w), 477(vw), 443 (s), 407 (br), 381 (w), 355 (w), 330 (w), 284 (w), 248 (vw), 229 (w).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 1.82 (*m*, 16H of CH_2 *Sol.THF*), δ 3.72 (*t*, 16H of CH_2 *Sol.THF*), δ 2.15 (*s*, *o and p* -36H of CH_3 on Mes), δ 2.09 (*s*, *p*-6H of CH_3^c on Mes), δ 6.83 (*s*, *m*- 8H of Mes) and δ 7.04 -7.17 (*br*, 20H of Ph).

^{13}C-NMR (125 MHz, C_4D_8O ppm): δ 28.42(s, second C from O *Sol. THF*), δ 65.45 (s, first C from O *Sol. THF*), δ 19.89 (s, C^j), δ 22.05 (s, C^k), δ 125.27 (s, C^f), δ 133.15 (s, C^g), δ

130.21 (s, C^h), δ 129.49 (s, C^a), 130.21 (s, C^c), δ 133.15 (s, C^b), δ 133.95 (s, C^d) and δ 144.36 (s, C^e).

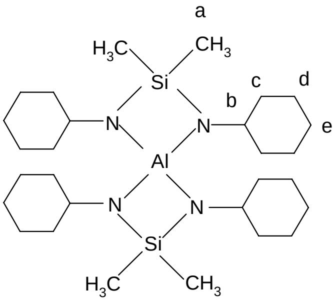
^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -33.84 (*s*).

5.2.18 Synthesis of $[Li(OEt_2)_3][\{Me_2Si(NCy)_2\}_2Al]$ (18)

$$Me_2Si(NHCy)_2 + 2\ n\text{-}BuLi \longrightarrow Me_2Si(NLiCy)_2 + 2\ n\text{-}BuH \qquad \textbf{(I)}$$

$$2\ Me_2Si(NLiCy)_2 + AlCl_3 + 3\ Et_2O \longrightarrow [Li(OEt_2)_3][\{Me_2Si(NCy)_2\}_2Al] + 3\ LiCl \qquad \textbf{(II)}$$

The method of synthesis of $[Li(OEt_2)_3][\{Me_2Si(NCy)_2\}_2Al]$ **(18)** is the same as that of $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Al]\cdot Tol$ **(15)** from $Me_2Si(NHCy)_2$ (1.90 g, 7.47 mmol), n-BuLi (5.98 mL, 14 mmol from a 2.5 M solution in hexane) and $AlCl_3$ (0.498 g, 3.73 mmol) in 15 mL Et_2O forming a white amorphous product.



Yield: 1.40 g (70 % with respect to $Me_2Si(NHCy)_2$)

Analysis: Molecular Formula: $C_{40}H_{86}N_4Si_2Li_1O_3Al$ Formula weight: 761.00 g/mol

IR (cm^{-1}): 1448 (m), 1402 (w), 1358 (w), 1336 (w), 1242 (m), 1209 (m), 1185 (w), 1109 (s), 1067 (w), 987 (m), 923 (w), 891 (m), 855 (s), 828 (br), 808 (w), 781 (w), 757 (s), 730 (w), 660 (w), 625 (w), 537 (vw), 513 (w), 488 (w), 463 (w), 419 (m), 339 (w), 303 (w), 287 (w), 255 (w), 227 (br).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 0.44 (*s*, 12H, CH_3^a), δ 1.20- 1.30 (*br*, $20H^{c,d,e}$ Cy), δ 1.44 - 1.48 (*br*, $20H^{c,d,e}$ Cy*)* and δ 3.17 (*m*, $4H^b$, Cy protons near to N).

^{13}C-NMR (125 MHz, C_6D_6 ppm): δ 3.33(s, C^a), δ 25.86 (s, C^d), δ 26.45 (s, CH_2 from ether), δ 26.61 (s, C^e), δ 40.18 (s, C^c), δ 54.10 (s, C^b) and δ 65.40 (s, CH_3 from ether)

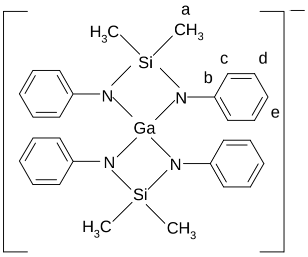
^{29}Si-NMR (500 MHz, C_6D_6 ppm): δ -6.56 (*s*).

5.2.19 Synthesis of $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Ga]$ (19)

$Me_2Si(NHPh)_2$ + 2 n-BuLi $\longrightarrow$ $Me_2Si(NLiPh)_2$ + 2 n-BuH **(I)**

2 $Me_2Si(NLiPh)_2$ + $GaCl_3$ + 3 Et_2O $\longrightarrow$ $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Ga]$ + 3 LiCl **(II)**

Ionic complex $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Ga]$ **(19)** was synthesized as described for $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Al]\cdot Tol$ **(15)** from $Me_2Si(NHPh)_2$ (2.00 g, 8.26 mmol), n-BuLi (6.61 mL, 16 mmol from a 2.5 M solution in hexane) and $GaCl_3$ (0.485 g, 2.75 mmol) in Et_2O giving a white crystalline product. Crystals were obtained at room temperature in Et_2O solvent after 24 hours.



Yield: 1.20 g (68 % with respect to $Me_2Si(NHPh)_2$)

Analysis: Molecular Formula: $C_{47}H_{69}N_4Si_2O_3LiGa$ Formula weight: 870.90 g/m

IR (cm^{-1}): 3056 (w), 1586 (br), 1482 (br), 1389 (w), 1331 (w), 1297 (br), 1244 (m), 1175 (s), 1149 (w), 1060 (br), 1025 (w), 989 (s), 954 (w), 927 (s), 868 (w), 835 (m), 786 (w), 752 (br), 689 (s), 624 (w), 605 (w), 514 (w), 467 (w), 402 (m), 356 (m), 330 (m), 288 (w), 256 (m).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 0.51 (*m*, 30H^a and *Sol. Et$_2$O*), δ 2.63 (m, 12H, CH_2 of Sol. *Et$_2$O*) and δ 6.88 - 7.18 (*br*, 20H of Ph).

^{13}C-NMR (125 MHz, C_6D_6 ppm): δ 2.05 (s, C^a), δ 13.72 (s, C, CH_3 *sol.Et$_2$O*), δ 63.26 (s, C, CH_2 *Sol.E$_2$tO*), δ 153.37 (s, C^b), δ 127.04 (s, C^c), δ 146.19 (s, C^d) and δ 129.30 (s, C^d).

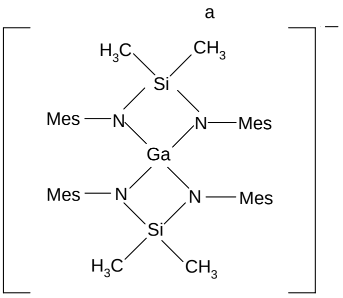
^{29}Si-NMR (500 MHz, C_6D_6 ppm): δ -11.16 (*s*).

5.2.20 Synthesis of $[Li(OEt_2)_4][\{Me_2Si(NMes)_2\}_2Ga]$ (20)

$Me_2Si(NHMes)_2$ + 2 n-BuLi $\longrightarrow$ $[Me_2Si(NLiMes)_2]$ + 2 n-BuH **(I)**

2 $Me_2Si(NLiMes)_2$ + $GaCl_3$ + 4 Et_2O $\longrightarrow$ $[Li(OEt_2)_4][\{Me_2Si(NMes)_2\}_2Ga]$ + 3 LiCl **(II)**

The synthesis procedure of $[Li(OEt_2)_4][\{Me_2Si(NMes)_2\}_2Ga]$ **(20)** is the same as that of $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Al]\cdot Tol$ **(15)** from $Me_2Si(NHMes)_2$ (1.75 g, 5.42 mmol), n-BuLi (4.33 mL, 10 mmol from a 2.5 M solution in hexane) and $GaCl_3$ (0.480 g, 2.71 mmol) in 15 mL Et_2O giving a white crystalline product. Crystals were obtained at 10 ^oC in Et_2O solvent after 24 hours.



Yield: 1.40 g (70 % with respect to $Me_2Si(NHMes)_2$)

Analysis: Molecular Formula: $C_{56}H_{87}N_4Si_2O_4LiGa$ Formula weight: 1013.14 g/mol

IR (cm^{-1}): 3010 (w), 1606 (vw), 1473 (br), 1430 (w), 1381 (w), 1303 (s), 1247 (br), 1184 (w), 1156 (s), 1061 (m), 962 (s), 851 (m), 829 (m), 791 (s), 755 (m), 738 (w), 716 (w), 696 (w), 653 (w), 561 (w), 547 (m), 516 (w), 468 (w), 405 (s), 357 (w), 336 (vw), 284 (vw), 227 (w).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 0.031 (*t*, 36H, CH_3^a and *Et₂O Sol.*), δ 0.031 (*s*, 36H, CH_3^a and *Et₂O Sol.*), δ 2.95 (*m*, 16H of CH_2 *Et₂O Sol*), δ 2.10 (*s*, 36H, CH_3 of Mes) and δ 6.99 (*br*, 8H of Mes).

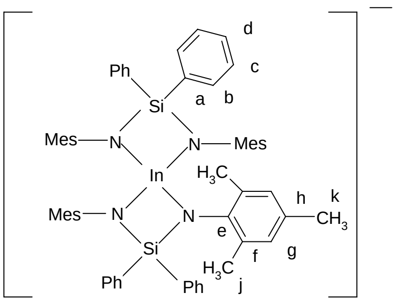
^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -1.10 (*s*).

5.2.21 Synthesis of $[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2Ga]$ (21)

$$Ph_2Si(NHMes)_2 + 2\ n\text{-}BuLi \longrightarrow [Ph_2Si(NLiMes)_2] + 2\ n\text{-}BuH \qquad \textbf{(I)}$$

$$2\ Ph_2Si(NLiMes)_2 + GaCl_3 + 4\ C_4H_8O \longrightarrow [Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2Ga] + 3\ LiCl \qquad \textbf{(II)}$$

Complex $[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2Ga]$ **(21)** was synthesized from $Ph_2Si(NHMes)_2$ (1.83 g, 4.06 mmol), n-BuLi (3.25 mL, 8.1 mmol from a 2.5 M solution in hexane) and $GaCl_3$ (0.358 g, 2.03 mmol) in 15 mL Et_2O as described for **(15)** giving a white crystalline product. Crystals were obtained at -20 ^oC after one week from THF solution.



Yield: 1.35 g (67 % with respect to $Ph_2Si(NHMes)_2$)

Analysis: Molecular Formula: $C_{76}H_{92}N_4Si_2O_4LiGa$ Formula weight: 1259.00 g/mol

IR (cm^{-1}): 3063 (w), 3010 (w), 1606 (vw), 1566 (vw), 1471 (s), 1425 (s), 1374 (vw), 1305 (br), 1280 (w), 1245 (sh), 1189 (vw), 1159 (m), 1117 (br), 1066 (vw), 1038 (s), 965 (m), 916 (br), 883 (m), 849 (s), 780 (sh), 743 (s), 715 (br), 657 (s), 621 (w), 596 (s), 574 (w), 545 (m), 527 (m), 505 (br), 483 (w), 467 (w), 435 (w), 423 (w), 405 (vw), 377 (vw), 356 (m), 334 (w), 283 (vw), 257 (m), 226 (w).

^{1}H-NMR (500 MHz, C_4D_8O ppm): δ 1.83 (*s*, 36H of CH_3 on Mes), δ 6.65 (*s*, *m*- 8H of Mes), δ 6.77 and δ 6.94 (*br*, 20H of Ph and toluene solvent).

^{13}C-NMR (125 MHz, C_4D_8O ppm): δ 24.67(s, second C from O *Sol. THF*), δ 64.54 (s, first C from O *Sol. THF*), δ 13.97 (s, C^j), δ 21.09 (s, C^k), δ 123.35 (s, C^f), δ 137.45 (s, C^g), δ 130.03(s, C^h), δ 129.36 (s, C^a), δ 129.67 (s, C^c), δ 133.15 (s, C^b), δ 133.95 (s, C^d) and δ 146.19 (s, C^e).

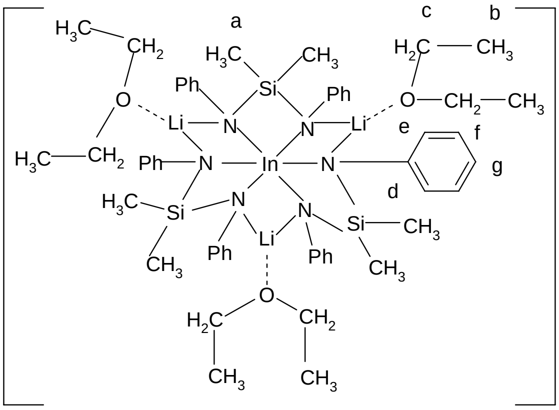
^{29}Si-NMR (100 MHz, C_4D_8O ppm): δ -40.78 (*s*).

5.2.22 Synthesis of [{$Me_2Si(NPh)_2Li(OEt_2)$}$_3$In] (22)

$Me_2Si(NHPh)_2$ + 2 n-BuLi $\longrightarrow$ $Me_2Si(NLiPh)_2$ + 2 n-BuH **(I)**

3 $Me_2Si(NLiPh)_2$ + $InCl_3$ + 3 Et_2O $\longrightarrow$ [{$Me_2Si(NPh)_2Li(OEt_2)$}$_3$In] + 3 LiCl **(II)**

The method of synthesis of [{$Me_2Si(NPh)_2Li(OEt_2)$}$_3$In] (**22**) is analogous to [$Li(OEt_2)_3$][{$Me_2Si(NPh)_2$}$_2$Al]·Tol **(15)** from $Me_2Si(NHPh)_2$ (2.75 g, 11 mmol) in hexane (40 mL), n-BuLi (9.09 mL, 22 mmol from a 2.5 M solution in hexane) and $InCl_3$ (0.837 g, 3.6 mmol) in 25 mL of Et_2O giving a white crystalline product. After two days colorless crystals were obtained in Et_2O.



Yield: 1.55 g (65 % with respect to $Me_2Si(NHPh)_2$)

Analysis: Molecular Formula: $C_{54}H_{78}N_6Si_3Li_3O_3In$ Formula weight: 1079.13 g/mol

IR (cm^{-1}): 3376 (m), 3056 (w), 1605 (sh), 1496 (br), 1385 (m), 1326 (w), 1282 (br), 1256 (w), 1178 (s), 1146 (w), 1090 (w), 1076 (w), 1048 (w), 1024 (w), 993 (s), 909 (br), 882 (w), 822 (w), 787 (w), 747 (sh), 692 (s), 614 (w), 599 (m), 569 (m), 522 (m), 488 (w), 425 (br), 303 (w), 233 (m), 245 (w).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 0.58 (m, 36H, $CH_3^{a,b}$), δ 2.64 (m, 12H, CH_2^{c}) and δ 6.88 - 7.29 (*br*, 30H of Ph).

^{13}C-NMR (125 MHz, C_6D_6 ppm): δ 2.15 (s, C^a), δ 14.12 (s, C, CH_3 *sol.Et₂O*), δ 65.26 (s, C, CH_2 *Sol.E₂tO*), δ 117.04 (s, C^e), δ 119.39 (s, C^g), δ 131.30 (s, C^f) and δ 153.27 (s, C^d).

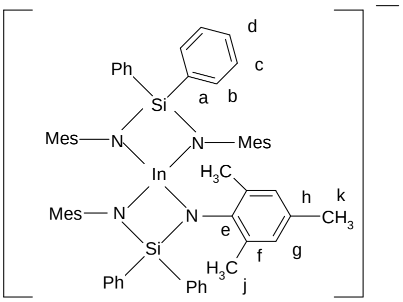
^{29}Si-NMR (500 MHz, C_6D_6 ppm): δ -11.16 (*s*).

5.2.23 Synthesis of $[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2In]$ (23)

$Ph_2Si(NHMes)_2$ + 2 n-BuLi $\longrightarrow$ $Ph_2Si(NLiMes)_2$ + 2 n-BuH **(I)**

2 $Ph_2Si(NLiMes)_2$ + $InCl_3$ + 4 C_4H_8O $\longrightarrow$ $[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2In]$ + 3 LiCl **(II)**

The ionic complex $[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2In]$ **(23)** was synthesized from $Ph_2Si(NHMes)_2$ (1.74 g, 3.86 mmol), n-BuLi (3.09 mL, 7.73 mmol from a 2.5 M solution in hexane) and $InCl_3$ (0.427g, 1.93 mmol) in 15 mL Et_2O as described for $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Al]\cdot 1Tol$ **(15)** giving a white crystalline product. Crystals were obtained at -20 °C after 48 hrs from THF solution.



Yield: 1.18 g (64 % with respect to $Ph_2Si(NHMes)_2$)

Analysis: Molecular Formula: $C_{76}H_{92}N_4Si_2O_4LiIn$ Formula weight: 1303.51 g/mol

IR (cm^{-1}): 3357 (vw), 3073 (w), 3010 (w), 1606 (w), 1470 (sh), 1423 (s), 1374 (w), 1304 (s), 1241 (br), 1184 (vw), 1156 (s), 1107 (s), 1066 (vw), 1038 (s), 962 (m), 896 (br), 851 (sh), 770 (m), 740(m), 701 (sh), 647 (w), 594 (w), 570 (w), 536 (w), 510 (br), 478 (w), 407 (br), 373 (w), 330 (br), 280 (w), 248 (vw), 229 (w).

^{1}H-NMR (500 MHz, C_4D_8O ppm): δ 1.834 (*s*, 36H, of CH_3 on Mes), δ 6.66 (*s*, *m*- 8H of Mes) and δ 7.05-7.66 (br, 20H of Ph).

^{13}C-NMR (125 MHz, C_4D_8O ppm): δ 22.41(*s*, second C from O *Sol.THF*), δ 65.54 (*s*, first C from O *Sol.THF*), δ 19.89 (s, C^j), δ 21.07 (s, C^k), δ 125.27 (s, C^h), δ 127.26 (s, C^g), δ 144.82 (s, C^e), δ 125.27 (s, C^c), δ 131.45 (s, C^a), δ 132.27 (s, C^b) and δ 133.10 (s, C^d),

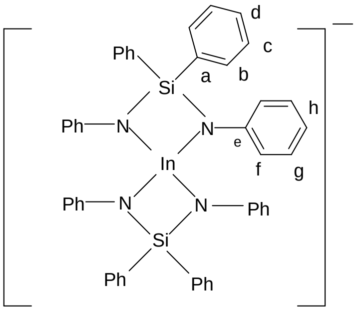
^{29}Si-NMR (100 MHz, C_4D_8O ppm): δ -43.43 (*s*).

5.2.24 Synthesis of $[Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2In]\cdot 2THF$ (24)

$Ph_2Si(NHPh)_2 + 2\ n\text{-}BuLi \longrightarrow Ph_2Si(NLiPh)_2 + 2\ n\text{-}BuH$ **(I)**

$2\ Ph_2Si(NLiPh)_2 + InCl_3 + 4\ C_4H_8O \longrightarrow [Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2In]\cdot 2THF + 3LiCl$ **(II)**

$[Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2In]\cdot 2THF$ (**24**) was synthesized as described for (**15**) from $Ph_2Si(NHPh)_2$ (1.75 g, 4.78 mmol), n-BuLi (3.82 mL, 9.56 mmol from a 2.5 M solution in hexane) and $InCl_3$ (0.530 g, 2.39 mmol) in 15 mL Et_2O giving a white crystalline product. Crystals were obtained at -20 °C after one week in THF.



Yield: 1.10 g (58 % with respect to $Ph_2Si(NHPh)_2$)

Analysis: Molecular Formula: $C_{79}H_{40}N_4Si_2O_6LiIn$ Formula weight: 1319.09 g/mol

IR (cm^{-1}): 3068 (w), 3045 (w), 3008 (w), 1591 (sh), 1480 (sh), 1448 (vw), 1429 (m), 1326 (vw), 1299 (br), 1175 (m), 1149 (vw), 1109 (s), 1067 (w), 1037 (m), 994 (sh), 959 (vw), 932 (s), 878 (w), 823 (sh), 765 (w), 739 (br), 691 (br), 664 (s), 615 (m), 571 (m), 523 (m), 487 (br), 467 (w), 406 (br), 380 (w), 294 (w), 240 (w), 207 (m).

^{1}H-NMR (500 MHz, C_4D_8O ppm): δ 1.77 (*m*, 16H of CH_2 *Sol.THF*), δ 3.68 (*t*, 16H of CH_2 *Sol. THF*), δ 6.230 (*br, p-* 8H of Ph), δ 6.71 (*d, o-* 16H of Ph), δ 7.34 (*br, toluene solvent*) and δ 8.05 (*t, m-* 16H of Ph).

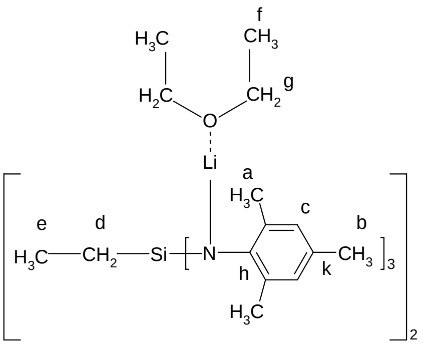
^{13}C-NMR (125 MHz, C_4D_8O ppm): δ 24.64(s, second C from O *Sol. THF*), δ 66.32 (s, first C from O *Sol. THF*), δ 113.68 (s, C^f), δ 117.38 (s, C^h), δ 120.21 (s, C^g), δ 128.46 (s, C^c), δ 134.73 (s, C^a), δ 138.04 (s, C^b), δ 146.86 (s, C^d) and δ 154.70 (s, C^e).

^{29}Si-NMR (100 MHz, C_4D_8O ppm): δ -26.23 (*s*).

5.2.25 Synthesis of $[Li(OEt_2)_3][Li_5\{EtSi(NMes)_3\}_2]$ (25)

$EtSi(NHMes)_3 + 3\ n\text{-}BuLi \longrightarrow [Li(OEt_2)_3][Li_5\{EtSi(NMes)_3\}_2] + 3\ n\text{-}BuH$

Lithiated complex $[Li(OEt_2)_3][Li_5\{EtSi(NMes)_3\}_2]$ (**25**) was synthesized according to the synthesis procedure of (**13**) from $EtSi(NHMes)_3$ (1.75 g, 3.81 mmol) and n-BuLi (4.57 mL, 11 mmol from a 2.5 M solution in hexane). After a period of 4 days colorless needle like crystals were obtained from Et_2O at -20 °C.



Yield: 1.65 g (94.28 % with respect to EtSi(NHMes)$_3$)

Analysis: Molecular Formula: $C_{70}H_{104}N_6Si_2O_3Li_6$ Formula weight: 1175.41 g/mol

IR (cm^{-1}): 3366 (vw), 3009 (w), 2956 (w), 1609 (w), 1481 (br), 1444 (w), 1420 (br), 1385 (w), 1292 (s), 1270 (w), 1225 (br), 1156 (s), 1118 (w), 1087 (w), 1059 (m), 1012 (w), 960 (s), 895 (br), 853 (sh), 768 (s), 692 (w), 665 (w), 621 (w), 594 (w), 553 (w), 517 (br), 476 (vw), 409 (w), 370 (vw), 301 (w), 281 (w), 276 (w).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 0.784 (*q*, 4H^d of CH$_2$), δ 1.06 (*t*, 6H^e, CH$_3$), δ 2.14 (*s*, *o*-36H^a, of CH$_3$ on Mes), δ 2.16 (*s*, *p*-18H^b, of CH$_3$ on Mes) and δ 6.71(*s*, *m*- 12H^c of Mes).

^{13}C-NMR (125 MHz, C_6D_6 ppm): δ 6.12 (s, C^e), δ 16.05 (s, C^d), δ 15.74 (s, C^f), δ 17.24 (s, C^a), δ 20.11 (s, C^b), δ 65.15 (s, C^g), δ 128.64 (s, C^c), δ 127.11 (s, C^k) and δ 141.12 (s, C^k).

^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -21.72 (*s*).

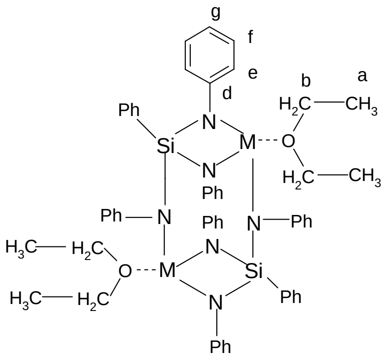
^{7}Li-NMR (200 MHz, C_6D_6 ppm): δ 1.39(*s*), 1.75 (*s*), 3.001(*s*) and 3.528 (*s*).

5.2.26 Synthesis of [{PhSi(NPh)$_3$(AlOEt$_2$)}$_2$]·2Tol (26)

$$\mathrm{PhSi(NHPh)_3} + 3\ \text{n-BuLi} \xrightarrow{\qquad} \mathrm{PhSi(NLiPh)_3} + 3\ \text{n-BuH} \qquad \textbf{(I)}$$

$$2\ \mathrm{PhSi(NLiPh)_3} + 2\ \mathrm{AlCl_3} + 2\ \mathrm{Et_2O} \xrightarrow{\qquad} \mathrm{[PhSi(NPh)_3AlOEt_2]_2{\cdot}2Tol} + 6\ \mathrm{LiCl} \qquad \textbf{(II)}$$

[PhSi(NPh)$_3$AlOEt$_2$]$_2$·2Tol (**26**) was synthesized as described for (**15**) from PhSi(NHPh)$_3$ (1.025 g, 2.68 mmol) in hexane (25 mL), n-BuLi (3.22 mL, 8.06 mmol from a 2.5 M solution in hexane) and AlCl$_3$ (0.358 g, 2.68 mmol) in 20 mL of Et$_2$O leading to a white crystalline product. After 6 days colorless square like crystals were formed at -20 ^{o}C.



Yield: 0.80 g (68 % with respect to $PhSi(NHPh)_3$)

Analysis: Molecular Formula: $C_{70}H_{60}N_6Si_2O_2Al_2$ Formula weight: 1127.38 g/mol.

IR (cm^{-1}): 3367 (vw), 3050 (w), 3013 (w), 1599 (sh), 1496 (sh), 1478 (sh), 1432 (w), 1380 (m), 1290 (br), 1236 (w), 1177 (w), 1151 (w), 1111 (m), 1077 (m), 1028 (m), 998 (s), 932 (br), 913 (sh), 896 (br), 825 (m), 749 (br), 732 (w), 686 (w), 666 (w), 615 (w), 582 (w), 523 (w), 513 (w), 488 (br), 387 (w), 366 (w), 341 (w), 274 (w), 232 (w).

^{1}H-NMR (400 MHz, C_6D_6 ppm): δ 0.737 (*t*, 12H, CH_3^a), δ 3.77 (*q*, 8H, of CH_2^b*)* and δ 6.57-7.72 (*br*, 40H of Ph).

^{13}C-NMR (125 MHz, C_6D_6 ppm): δ 15.49 (s, C^a), δ 65.85 (s, C^b), δ 117.02 (s, C^e), δ 118.65 (s, C^g), δ 128.75 (s, C^f) and δ 146.15 (s, C^d).

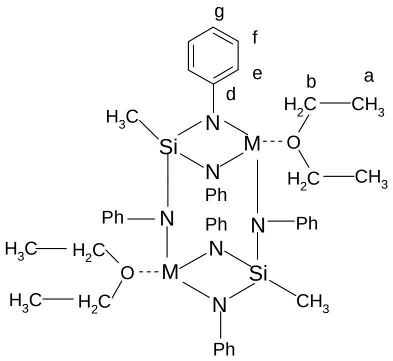
^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -41.67 (*s*).

5.2.27 Synthesis of [{MeSi(NPh)₃(AlOEt₂)}₂]·2Tol (27)

$$MeSi(NHPh)_3 + 3\ n\text{-}BuLi \longrightarrow MeSi(NLiPh)_3 + 3\ n\text{-}BuH \qquad \textbf{(I)}$$

$$2\ MeSi(NLiPh)_3 + 2\ AlCl_3 + 2\ Et_2O \longrightarrow [MeSi(NPh)_3AlOEt_2]_2{\cdot}2Tol + 6\ LiCl \qquad \textbf{(II)}$$

$[MeSi(NPh)_3AlOEt_2]_2{\cdot}2Tol$ (**27**) was synthesized as described in [85] from $MeSi(NHPh)_3$ (1.76 g, 5.51 mmol) in hexane (40 mL), n-BuLi (6.62 mL, 16 mmol from a 2.5 M solution in hexane) and $AlCl_3$ (0.735 g, 5.51 mmol) in 25 mL of Et_2O leading to a white crystalline product. After one week colorless crystals were obtained in Et_2O at -20 °C.



Yield: 1.45 g (70 % with respect to $MeSi(NHPh)_3$)

Analysis: Molecular Formula: $C_{60}H_{72}N_6Si_2O_2Al_2$ Formula weight: 1019.38 g/mol

IR (cm^{-1}): 3375 (vw), 3040 (w), 1660 (m), 1588 (s), 1480 (br), 1430 (w), 1382 (m), 1295 (br), 1235 (m), 1177 (w), 1151 (w), 1094 (w), 1074 (m), 1026 (m), 996 (m), 959 (w), 905 (w), 827 (w), 747 (w), 728 (w), 688 (m), 655 (w), 620 (w), 553 (w), 529 (m), 454 (m), 372 (w), 358 (w), 319 (w), 270 (m).

^{1}H-NMR (500 MHz, C_6D_6 ppm): δ 0.33 (*s*, 6H, $CH_3{}^c$), δ 0.87 (*t*, 12H, $CH_3{}^a$), δ 3.52 (*m*, 8H, of $CH_2{}^b$*)* and δ 6.88 -7.32 (*br,* 30H of Ph).

^{13}C-NMR (125 MHz, C_6D_6 ppm): δ 9.53 (s, C^c), δ 15.53(s, C^a), δ 65.45 (s, C^b), δ 116.54 (s, C^e), δ 119.05 (s, C^g), δ 129.45 (s, C^f) and δ 146.51 (s, C^d).

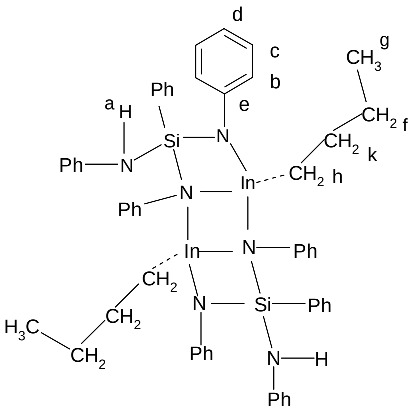
^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -29.77 (*s*).

5.2.28 Synthesis of $[\{PhSi(NPh)_2(NHPh)(n\text{-}BuIn)\}]_2\cdot Tol$ (28)

$$PhSi(NHPh)_3 + 3\ n\text{-}BuLi \longrightarrow PhSi(NLiPh)_2(NHPh) + 2\ n\text{-}BuH \quad \textbf{(I)}$$

$$2\ PhSi(NLiPh)_2(NHPh) + 2\ InCl_3 + 2\ n\text{-}BuLi \longrightarrow [\{PhSi(NPh)_2(NHPh)(n\text{-}BuIn)\}]_2\cdot Tol + 6\ LiCl \quad \textbf{(II)}$$

$[\{PhSi(NPh)_2(NHPh)(n\text{-}BuIn)\}]_2\cdot Tol$ (**28**) was synthesized from $PhSi(NHPh)_3$ (1.71 g, 4.48 mmol) in hexane and n-BuLi (5.37 mL, 13.44 mmol from a 2.5 M solution in hexane) and $InCl_3$ (0.991 g, 4.48 mmol) in 20 mL of Et_2O leading to a white crystalline product. Colorless crystals were obtained after 3 days from a toluene solution at -20 ^{o}C.



Yield: 1.34 g (65 % with respect to $PhSi(NHPh)_3$)

Analysis: Molecular Formula: $C_{66}H_{60}N_6Si_2In_2$ Formula weight: 1222.02 g/mol

IR (cm^{-1}): 3378 (m), 3050 (w), 3013 (w), 1599 (sh), 1478 (sh), 1427 (w), 1377 (s), 1299 (br), 1212 (s), 1173 (w), 1153 (w), 1112 (m), 1079 (m), 1028 (w), 994 (s), 957 (s), 931 (w), 894 (br), 798 (m), 765 (w), 746 (s), 685 (sh), 634 (m), 616 (w), 600 (w), 580 (m), 541 (m), 489 (br), 398 (w), 319 (w), 274 (w), 251 (w).

^{1}H-NMR (400 MHz, C_6D_6 ppm): δ 3.76 (*s*, 2H, NH^a), δ 0.628 (*t*, 6H of CH^g,), δ 1.03-1.10 (*m*, 8H, $CH_2^{f,k}$), δ 1.46 (*t*, 4H, of CH_2^h), δ 7.57 (*m*, 6H of CH^d), δ 7.702 (*m*, 12H of CH^c), δ 6.67 (*m*, 12H CH^b) and δ 7.04-7.70 (*br*, 10H of Ph on Si).

^{13}C-NMR (125 MHz, C_6D_6 ppm): δ 15.53(s, C^g), δ 28.19 (s, C^f), δ 29.53 (s, C^k), δ 65.85 (s, C^h), δ 117.65 (s, C^b), δ 119.68 (s, C^d), δ 129.37 (s, C^c) and δ 145.50 (s, C^e).

^{29}Si-NMR (100 MHz, C_6D_6 ppm): δ -41.45 (*s*).

5.3 Crystallography

Within this work single-crystal X-ray structure analyses have been done using the following instrument:

- Image plate detector STOE-IPDS:
- Mo-K_{α} radiation (λ = 71.069 pm), graphite monochromator
- Determination of the lattice constants with the help of orientation matrix of up to 8000 reflections from multiple images
- Determination of the reflections intensity by the definition of reflection profile of the corresponding integration box

The structures were solved with SHELXS-97 and refined using program X-STEP 32 [85].

a) **Structure Solution** proceeded with the help of Patterson- or direct methods followed by difference fourier synthesis.

b) **Structure Refinement** proceeded with the full-matrix least-squares against F^2 method. The following weighting functions have been used:

$$w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP) \qquad \text{with} \qquad P = 1/3 \max(0, F_o^2) + 2/3\, F_c^2$$

Coefficient parameters a and b values proposed by SHELXL-97 have been taken. Therefore, for acquired reliability factor values applied,

$$R_1 = \frac{\sum \left\| F_o \right| - \left| F_c \right\|}{\sum \left| F_c \right|} \qquad wR_2 = \sqrt{\frac{\sum \left[w \left(F_o^2 - F_c^2 \right)^2 \right]}{\sum \left[w \left(F_o^2 \right)^2 \right]}}$$

The program DIAMOND has been used for the drawing illustration of the structures [86].

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7 Appendix

7.1 Abbreviations and symbols used in the text

THF	tetrahydrofuran	Cy	cyclohexane
Et	ethyl	Tol	toluene
Hex	n-hexane	R and R’	alkyl or aryl
Mes	mesityl	Ph	phenyl
Bu	n-butyl	*t*-Bu/^{t}Bu	tertiary butyl
n-BuLi	n-butyllithium	*i*-Pr/^{i}Pr	isopropyl
Me	methyl	Mp.	melting point
(no.)	compound number	sol.	solvent
[no.]	literature reference number	RT	room temperature
c. n.	coordination number	ave.	average
appox.	approximately	Fig.	figure

Abbreviations used in Nuclear Magnetic Resonance spectroscopy

δ	chemical shift	*s*	singlet
d	doublet	*dd*	doublet of doublet
t	triplet	*m*	multiplet
br	broad		

Abbreviations used in IR spectra

br	broad	m	medium
s	strong	sh	sharp
w	weak	vw	very weak

7.2 List of compounds

1) $Me_2Si(NHPh)_2$ (**1**)
2) $Me_2Si(NHCy)_2$ (**2**)
3) $Ph_2Si(NHPh)_2$ (**3**)
4) $Me_2Si(NHMes)_2$ (**4**)
5) $Ph_2Si(NHMes)_2$ (**5**)
6) $PhSiCl(NHMes)_2$ (**6**)
7) $Ph_2SiCl(NHMes)$ (**7**)
8) $MeSi(NHPh)_3$ (**8**)
9) $MeSi(NHMes)_3$ (**9**)
10) $EtSi(NHMes)_3$ (**10**)
11) $PhSi(NHPh)_3$ (**11**)
12) $PhSi(NHMes)_3$ (**12**)
13) $[\{Me_2Si(NLiMes)_2(OEt_2)\}_2]$ (**13**)
14) $[(Li(OC_4H_8)_4][Li_3\{Ph_2Si(NMes)_2\}_2]\cdot 2THF$ (**14**)
15) $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Al]\cdot Tol$ (**15**)
16) $[Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2Al]\cdot 3THF$ (**16**)
17) $[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2Al]$ (**17**)
18) $[Li(OEt_2)_3][\{Me_2Si(NCy)_2\}_2Al]$ (**18**)
19) $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Ga]$ (**19**)
20) $[Li(OEt_2)_4][\{Me_2Si(NMes)_2\}_2Ga]$ (**20**)
21) $[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2Ga]$ (**21**)
22) $[\{Me_2Si(NPh)_2Li(OEt_2)\}_3In]$ (**22**)
23) $[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2In]$ (**23**)
24) $[Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2In]\cdot 2THF$ (**24**)
25) $[Li(OEt_2)_3][Li_5\{EtSi(NMes)_3\}_2]$ (**25**)
26) $[\{PhSi(NPh)_3(AlOEt_2)\}_2]\cdot 2Tol$ (**26**)
27) $[\{MeSi(NPh)_3(AlOEt_2)\}_2]\cdot 2Tol$ (**27**)
28) $[\{PhSi(NPh)_2(NHPh)(n\text{-}BuIn)\}_2]\cdot Tol$ (**28**)

7.3 Crystallographic appendix

Table 7.3.1: Crystal data and structure refinement for $Ph_2Si(NHPh)_2$ **(3)**

Identification code	ipds3179
Empirical formula	$C_{24}H_{22}N_2Si$
Formula weight (g/mol)	366.53
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\,\bar{1}$
Unit cell dimensions	
a; b; c; (Å)	10.276(1); 10.396(2); 10.465(1)
α; β; γ; (°)	80.16 (2); 66.01 (1); 80.15(2)
Volume V ($Å^{3)}$	999.9(2)
No. of formulas per unit cell Z	2
Calculated density (g/cm^{-1})	1.217
Absorption coefficient μ(MoKα) /mm^{-1}	0.128
F(000)	388
Crystal size (mm)	0.11 x 0.19 x 0.48
Theta range for data collection (°)	2.00 - 25.86
Absorption correction	numerical
Total reflections collected	7051
Unique reflections observed	3602
Reflections independent with ($I>2\sigma(I)$); R_{int}	2301; 0.0439
Data / restraints / parameters	3602/0/244
R1; wR2 ($I>2\sigma(I)$)	0.0433; 0.0870
R1; wR2 (all data)	0.0800; 0.0971
Goodness of fit on F^2	0.909
Largest diff. peak and hole (e /$Å^3$)	0.211; -0.191

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [Å^{2}x10^3] for **3**

Atom	x	y	z	Ueq
Si(1)	9341(1)	1348(1)	8050(1)	41(1)
N(1)	8493(2)	1342(2)	9854(2)	46(1)
N(2)	9398(2)	-214(2)	7686(2)	49(1)
C(1)	11281(2)	1570(2)	7422(2)	41(1)
C(2)	12243(2)	1423(2)	6046(2)	53(1)
C(3)	13695(3)	1498(2)	5629(3)	63(1)
C(4)	14216(3)	1719(2)	6584(3)	64(1)
C(5)	13298(3)	1870(2)	7943(3)	56(1)
C(6)	11850(2)	1801(2)	8358(2)	45(1)
C(7)	8341(2)	2668(2)	7233(2)	43(1)
C(8)	8997(3)	3301(2)	5906(3)	60(1)
C(9)	8255(3)	4318(2)	5335(3)	69(1)
C(10)	6837(3)	4702(2)	6087(3)	68(1)
C(11)	6159(3)	4093(2)	7408(3)	59(1)
C(12)	6904(2)	3087(2)	7980(3)	50(1)
C(13)	8123(2)	2366(2)	10696(2)	40(1)
C(14)	8507(2)	3620(2)	10119(2)	48(1)
C(15)	8138(3)	4618(2)	10957(3)	52(1)
C(16)	7403(3)	4400(2)	12382(3)	57(1)
C(17)	7033(3)	3162(2)	12965(2)	58(1)
C(18)	7373(2)	2154(2)	12141(2)	47(1)
C(19)	8326(2)	-993(2)	7888(2)	43(1)
C(20)	8670(2)	-2329(2)	7766(2)	51(1)
C(21)	7630(3)	-3104(2)	7956(3)	59(1)
C(22)	6232(3)	-2578(2)	8273(3)	61(1)
C(23)	5882(3)	-1265(2)	8404(3)	62(1)
C(24)	6909(2)	-476(2)	8215(3)	56(1)

Bond lengths [Å] for **3**

Si(1)–N(1)	1.7271(19)
Si(1)-N(2)	1.7164(16)
N(1)-H(1)	0.86(2)
N(2)-H(2)	0.86(2)
C(1)-Si(1)	1.871(2)
C(7)-Si(1)	1.871(2)
C(1)-C(2)	1.393(3)
C(1)-C(6)	1.398(3)
C(3)-C(2)	1.386(3)
C(4)-C(3)	1.377(3)
C(5)-C(4)	1.367(3)
C(6)-C(5)	1.381(3)
C(7)-C(8)	1.376(3)
C(7)-C(12)	1.393(3)
C(9)-C(8)	1.391(3)
C(10)-C(9)	1.370(4)
C(11)-C(10)	1.366(4)
C(12)-C(11)	1.387(3)
C(13)-C(14)	1.390(3)
C(13)-N(1)	1.401(2)
C(13)-C(18)	1.388(3)
C(14)-C(15)	1.377(3)
C(15)-C(16)	1.368(3)
C(16)-C(17)	1.373(3)
C(17)-C(18)	1.379(3)
C(19)-C(24)	1.384(3)
C(19)-C(20)	1.387(3)
C(19)-N(2)	1.404(3)
C(21)-C(20)	1.377(3)
C(22)-C(21)	1.370(3)
C(24)-C(23)	1.378(3)
C(23)-C(22)	1.366(3)

Bond angles [deg] for **3**

N(1)-Si(1)-C(7)	107.55(9)
N(1)-Si(1)-C(1)	111.33(9)
N(2)-Si(1)-C(1)	102.90(9)
N(2)-Si(1)-N(1)	106.88(9)
N(2)-Si(1)-C(7)	115.39(8)
C(7)-Si(1)-C(1)	112.68(9)
C(13)-N(1)-Si(1)	130.40(14)
C(19)-N(2)-Si(1)	132.83(14)
C(24)-C(19)-N(2)	122.15(18)
C(20)-C(19)-N(2)	120.09(18)

Table 7.3.2: Crystal data and structure refinement for $Ph_2Si(NHMes)_2$ **(5)**

Identification code	ipds3291
Empirical formula	$C_{30}H_{34}N_2Si$
Formula weight (g/mol)	450.68
Temperature (K)	220
Wavelength (Å)	0.7107
Crystal system	monoclinic
Space group	$P\ 2_1/c$
Unit cell dimensions	
a; b; c; (Å)	9.721 (1); 11.874(1); 22.146(2)
β; (°)	95.30(1)
Volume V ($Å^{3)}$	2544.9(3)
No. of formulas per unit cell Z	4
Calculated density (g/cm^{-1})	1.176
Absorption coefficient μ(MoKα) /mm^{-1}	0.112
F(000)	968
Crystal size (mm)	0.22 x 0.30 x 0.30
Theta range for data collection (°)	2.20 - 25.91
Absorption correction	numerical
Total reflections collected	19431
Unique reflections observed	4705
Reflections independent with ($I>2\sigma(I)$); R_{int}	3376; 0.0501
Data / restraints / parameters	4705/0/434
R1; wR2 ($I>2\sigma(I)$)	0.0378, 0.0902
R1; wR2 (all data)	0.0598, 0.1006
Goodness of fit on F^2	1.024
Largest diff. peak and hole (e /$Å^3$)	0.244; -0.256

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [Å^{2}x10^3] for **5**

Atom	x	y	z	Ueq
N(1)	3804(2)	1072(1)	1247(1)	35(1)
N(2)	3345(2)	3408(1)	1243(1)	32(1)
Si(1)	2960(1)	2169(1)	856(1)	29(1)
C(1)	3649(2)	673(1)	1847(1)	31(1)
C(2)	4558(2)	1061(1)	2336(1)	34(1)
C(3)	4366(2)	705(2)	2920(1)	38(1)
C(4)	3311(2)	-34(1)	3039(1)	40(1)
C(5)	2467(2)	-443(1)	2548(1)	40(1)
C(6)	2616(2)	-120(1)	1953(1)	37(1)
C(7)	5750(2)	1835(2)	2244(1)	51(1)
C(8)	3091(3)	-368(2)	3678(1)	59(1)
C(9)	1700(3)	-641(2)	1439(1)	54(1)
C(10)	2406(2)	4294(1)	1364(1)	30(1)
C(11)	1799(2)	4964(1)	886(1)	34(1)
C(12)	850(2)	5798(2)	1020(1)	41(1)
C(13)	492(2)	5986(1)	1602(1)	42(1)
C(14)	1122(2)	5324(2)	2063(1)	41(1)
C(15)	2078(2)	4490(1)	1960(1)	34(1)
C(16)	2167(2)	4825(2)	248(1)	47(1)
C(17)	-546(3)	6885(2)	1734(2)	62(1)
C(18)	2753(2)	3817(2)	2482(1)	44(1)
C(19)	1020(2)	2050(1)	788(1)	32(1)
C(20)	187(2)	1922(2)	243(1)	42(1)
C(21)	-1244(2)	1808(2)	231(1)	51(1)
C(22)	-1876(2)	1810(2)	761(1)	48(1)
C(23)	-1073(2)	1938(2)	1309(1)	46(1)
C(24)	348(2)	2062(2)	1320(1)	39(1)
C(25)	3672(2)	2044(1)	99(1)	33(1)
C(26)	4711(2)	2763(2)	-77(1)	36(1)
C(27)	5287(2)	2616(2)	-619(1)	43(1)
C(28)	4835(2)	1747(2)	-1006(1)	46(1)
C(29)	3823(2)	1021(2)	-845(1)	45(1)
C(30)	3257(2)	1157(2)	-298(1)	40(1)

Bond lengths [Å] for **5**

N(1)-Si(1)	1.7277(15)	C(13)-C(17)	1.516(3)
N(2)-Si(1)	1.7266(15)	C(14)-C(15)	1.392(3)
C(1)-C(2)	1.410(2)	C(15)-C(18)	1.506(3)
C(1)-C(6)	1.412(2)	C(19)-C(20)	1.397(3)
C(1)-N(1)	1.432(2)	C(19)-C(24)	1.399(2)
C(2)-C(3)	1.391(3)	C(19)-Si(1)	1.8830(17)
C(2)-C(7)	1.508(3)	C(20)-C(21)	1.395(3)
C(3)-C(4)	1.393(3)	C(21)-C(22)	1.374(3)
C(4)-C(5)	1.389(3)	C(22)-C(23)	1.389(3)
C(4)-C(8)	1.504(3)	C(23)-C(24)	1.388(3)
C(5)-C(6)	1.392(3)	C(25)-C(26)	1.405(2)
C(6)-C(9)	1.511(3)	C(25)-C(30)	1.407(3)
C(10)-C(15)	1.406(2)	C(25)-Si(1)	1.8771(18)
C(10)-C(11)	1.408(2)	C(26)-C(27)	1.381(3)
C(10)-N(2)	1.435(2)	C(27)-C(28)	1.387(3)
C(11)-C(12)	1.404(3)	C(28)-C(29)	1.379(3)
C(11)-C(16)	1.500(3)	C(29)-C(30)	1.385(3)
C(12)-C(13)	1.384(3)	N(1)-H(1)	0.8376(1)
C(13)-C(14)	1.385(3)	N(2)-H(2)	0.8558(1)

Bond angles [deg] for **5**

N(2)-Si(1)-N(1)	108.79(8)	C(26)-C(25)-Si(1)	122.28(13)
N(2)-Si(1)-C(25)	115.46(7)	C(30)-C(25)-Si(1)	120.60(13)
N(1)-Si(1)-C(25)	100.99(7)	C(27)-C(26)-C(25)	121.62(17)
N(2)-Si(1)-C(19)	105.87(7)	C(1)-N(1)-Si(1)	128.96(12)
N(1)-Si(1)-C(19)	114.14(7)	C(10)-N(2)-Si(1)	127.22(11)
C(25)-Si(1)-C(19)	111.81(8)		

Table 7.3.3: Crystal data and structure refinement for PhSiCl(NHMes)$_2$ **(6)**

Identification code	ipds3277
Empirical formula	$C_{24}H_{29}N_2SiCl$
Formula weight (g/mol)	409.03
Temperature (K)	220
Wavelength (Å)	0.7107
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a; b; c; (Å)	8.920(1); 11.094(1); 11.929(1)
α; β; γ; (°)	95.27(2); 92.66(1); 102.405(1)
Volume V (Å$^{3)}$	1145.1(2)
No. of formulas per unit cell Z	2
Calculated density (g/cm^{-1})	1.186
Absorption coefficient μ(MoKα) /mm^{-1}	0.231
F(000)	436
Crystal size (mm)	0.20 x 0.28 x 0.28
Theta range for data collection (°)	2.42 - 25.86
Absorption correction	numerical
Total reflections collected	9841
Unique reflections observed	4105
Reflections independent with (I>2σ(I)); R_{int}	2605; 0.0516
Data / restraints / parameters	4105 /0/261
R1; wR2 (I>2σ(I))	0.0626, 0.1657
R1; wR2 (all data)	0.1031, 0.1891
Goodness of fit on F^2	1.038
Largest diff. peak and hole (e /Å^3)	0.676; -0.396

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [$Å^2$x10^3] for **6**

Atom	**x**	**y**	**Z**	**Ueq**
N(1)	461(4)	3784(3)	1530(3)	43(1)
N(2)	1275(4)	1624(3)	1916(3)	41(1)
Si(1)	952(1)	2970(1)	2577(1)	39(1)
Cl(1)	3003(1)	3752(1)	3538(1)	55(1)
C(1)	1026(4)	3864(3)	422(3)	38(1)
C(2)	288(4)	3022(3)	-486(3)	47(1)
C(3)	887(5)	3115(3)	-1541(3)	54(1)
C(4)	2157(5)	4011(4)	-1744(3)	48(1)
C(5)	2850(4)	4848(3)	-825(3)	45(1)
C(6)	2324(4)	4794(3)	250(3)	39(1)
C(7)	-1139(6)	2044(4)	-330(4)	71(1)
C(8)	2766(6)	4093(5)	-2901(4)	72(1)
C(9)	3125(5)	5720(3)	1219(3)	54(1)
C(10)	2483(4)	987(3)	2161(3)	35(1)
C(11)	2453(4)	325(3)	3111(3)	45(1)
C(12)	3616(5)	-300(3)	3308(3)	48(1)
C(13)	4815(5)	-292(3)	2595(3)	46(1)
C(14)	4810(4)	358(3)	1656(3)	40(1)
C(15)	3672(4)	1018(3)	1431(3)	35(1)
C(16)	1172(6)	267(5)	3901(4)	68(1)
C(17)	6082(6)	-964(5)	2848(4)	68(1)
C(18)	3750(5)	1763(4)	429(3)	50(1)
C(19)	-604(4)	2918(3)	3578(3)	40(1)
C(20)	-2137(5)	2555(4)	3175(4)	52(1)
C(21)	-3332(5)	2615(4)	3872(4)	58(1)
C(22)	-3003(5)	3043(4)	4991(4)	56(1)
C(23)	-1528(6)	3392(5)	5412(4)	72(1)
C(24)	-323(5)	3343(4)	4712(4)	63(1)

Bond lengths [Å] for **6**

Si(1)- N(1)	1.701(3)	C(11)-C(12)	1.389(5)
Si(1)- N(2)	1.709(3)	C(11)-C(16)	1.509(5)
Si(1)-Cl(1)	2.0865(14)	C(12)-C(13)	1.395(5)
C(1)-C(2)	1.402(5)	C(13)-C(14)	1.387(5)
C(1)-C(6)	1.412(5)	C(13)-C(17)	1.515(5)
C(1)-N(1)	1.440(5)	C(14)-C(15)	1.403(5)
C(2)-C(3)	1.393(6)	C(15)-C(18)	1.510(5)
C(2)-C(7)	1.516(6)	C(19)-C(24)	1.384(5)
C(3)-C(4)	1.384(6)	C(19)-C(20)	1.389(6)
C(4)-C(5)	1.396(5)	C(19)-Si(1)	1.868(4)
C(4)-C(8)	1.510(6)	C(20)-C(21)	1.391(5)
C(5)-C(6)	1.389(5)	C(21)-C(22)	1.371(6)
C(6)-C(9)	1.513(5)	C(22)-C(23)	1.348(7)
C(10)-C(15)	1.400(4)	C(23)-C(24)	1.398(6)
C(10)-N(2)	1.442(4)	N(1)-H(1)	0.8372(1)
		N(2)-H(2)	0.7068(1)

Bond angles [deg] for **6**

C(1)-N(1)-Si(1)	129.0(2)	C(10)-N(2)-Si(1)	128.9(3)
N(1)-Si(1)-N(2)	105.85(17)	C(15)-C(10)-N(2)	119.4(3)
N(1)-Si(1)-C(19)	105.19(15)	C(15)-C(10)-C(11)	120.3(3)
N(2)-Si(1)-C(19)	120.16(16)	C(19)-C(20)-C(21)	121.9(4)
N(1)-Si(1)-Cl(1)	116.57(12)	C(20)-C(19)-Si(1)	119.9(3)
N(2)-Si(1)-Cl(1)	104.07(12)	C(24)-C(19)-Si(1)	123.2(3)

Table 7.3.4: Crystal data and structure refinement for $Ph_2SiCl(NHMes)$ **(7)**

Identification code	ipds3283
Empirical formula	$C_{21}H_{22}NSiCl$
Formula weight (g/mol)	351.94
Temperature (K)	220
Wavelength (Å)	0.710
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a; b; c; (Å)	9.876(1); 10.402(2); 11.443(2)
α; β; γ; (°)	63.561(2); 81.854(2); 64.427(2)
Volume V ($Å^{3)}$	947.51(2)
No. of formulas per unit cell Z	2
Calculated density (g/cm^{-1})	1.234
Absorption coefficient μ(MoKα) /mm^{-1}	0.267
F(000)	372
Crystal size (mm)	0.38 x 0.38 x 0.76
Theta range for data collection (°)	2.29 - 25.92
Absorption correction	numerical
Total reflections collected	7316
Unique reflections observed	3381
Reflections independent with (I>2σ(I)); R_{int}	2797; 0.0267
Data / restraints / parameters	3381/0/221
R1; wR2 (I>2σ(I))	0.0407; 0.108
R1; wR2 (all data)	0.0510; 0.124
Goodness of fit on F^2	1.105
Largest diff. peak and hole (e /$Å^3$)	0.299; -0.378

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [Å^{2}x10^3] for **7**

Atom	**x**	**y**	**z**	**Ueq**
Si(1)	1874(1)	1697(1)	559(1)	35(1)
Cl(1)	3518(1)	2216(1)	962(1)	57(1)
N(1)	108(2)	2931(2)	746(2)	43(1)
C(1)	1997(2)	2161(2)	-1214(2)	36(1)
C(2)	1671(3)	3712(3)	-2154(2)	45(1)
C(3)	1725(3)	4088(3)	-3475(2)	48(1)
C(4)	2116(3)	2930(3)	-3895(2)	47(1)
C(5)	2463(3)	1380(3)	-2987(3)	48(1)
C(6)	2395(2)	1007(3)	-1667(2)	40(1)
C(7)	2347(2)	-421(2)	1636(2)	33(1)
C(8)	3846(3)	-1537(3)	1954(2)	43(1)
C(9)	4194(3)	-3128(3)	2710(3)	52(1)
C(10)	3062(3)	-3630(3)	3168(2)	49(1)
C(11)	1575(3)	-2558(3)	2860(2)	45(1)
C(12)	1223(2)	-967(3)	2096(2)	38(1)
C(13)	-953(2)	2703(2)	1717(2)	36(1)
C(14)	-2387(3)	2995(2)	1329(2)	39(1)
C(15)	-3422(3)	2768(3)	2267(2)	43(1)
C(16)	-3086(3)	2234(3)	3582(2)	44(1)
C(17)	-1671(3)	1979(3)	3938(2)	44(1)
C(18)	-598(3)	2210(2)	3035(2)	40(1)
C(19)	-2791(3)	3503(3)	-79(2)	49(1)
C(20)	-4222(3)	1934(4)	4586(3)	65(1)
C(21)	890(3)	1982(3)	3474(2)	52(1)

Bond lengths [Å] for **7**

Si(1)-N(1)	1.715(2)	C(8)-C(9)	1.386(3)
Si(1)-C(7)	1.857(2)	C(10)-C(9)	1.376(4)
Si(1)-C(1)	1.863(2)	C(11)-C(10)	1.381(4)
Si(1)-Cl(1)	2.0813(9)	C(12)-C(11)	1.388(3)
N(1)-C(13)	1.428(3)	C(14)-C(15)	1.388(3)
C(1)-C(6)	1.398(3)	C(14)-C(19)	1.508(3)
C(1)-C(2)	1.403(3)	C(15)-C(16)	1.386(3)
C(2)-C(3)	1.382(3)	C(16)-C(17)	1.391(4)
C(3)-C(4)	1.376(4)	C(16)-C(20)	1.514(4)
C(5)-C(4)	1.389(3)	C(18)-C(17)	1.392(3)
C(6)-C(5)	1.380(4)	C(18)-C(13)	1.403(3)
C(7)-C(12)	1.394(3)	C(18)-C(21)	1.506(3)
C(7)-C(8)	1.401(3)	N(1)-H(1)	0.7885(2)

Bond angles [deg] for **7**

N(1)-Si(1)-C(7)	113.28(10)	C(12)-C(7)-Si(1)	121.01(16)
N(1)-Si(1)-C(1)	106.95(10)	C(13)-N(1)-Si(1)	132.83(15)
C(7)-Si(1)-C(1)	113.57(10)	C(13)-C(18)-C(21)	121.3(2)
N(1)-Si(1)-Cl(1)	111.28(8)	C(2)-C(1)-Si(1)	120.44(18)
C(7)-Si(1)-Cl(1)	107.12(7)	C(6)-C(1)-Si(1)	122.26(16)
C(1)-Si(1)-Cl(1)	104.31(7)	C(8)-C(7)-Si(1)	121.14(16)

Table 7.3.5: Crystal data and structure refinement for MeSi(NHPh)$_3$ **(8)**

Identification code	ipds3318
Empirical formula	$C_{19}H_{21}N_3Si$
Formula weight (g/mol)	319.48
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	I 2/a
Unit cell dimensions	
a; b; c; (Å)	18.570(2); 9.919(1); 19.419(2)
β (°)	94.50(1)
Volume V (Å$^{3)}$	3562.4(6)
No. of formulas per unit cell Z	8
Calculated density (g/cm^{-1})	1.191
Absorption coefficient μ(MoKα) /mm^{-1}	0.135
F(000)	1360
Crystal size (mm)	0.13 x 0.15 x 0.52
Theta range for data collection (°)	3.16 - 25.88
Absorption correction	numerical
Total reflections collected	5033
Unique reflections observed	2594
Reflections independent with (I>2σ(I))); R_{int}	1756; 0.0413
Data / restraints / parameters	2594/0/208
R1; wR2 (I>2σ(I))	0.0447; 0.112
R1; wR2 (all data)	0.0752; 0.129
Goodness of fit on F^2	1.071
Largest diff. peak and hole (e /Å^3)	0.284; -0.275

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [Å^{2}x10^3] for **8**

Atom	x	y	z	Ueq
Si(1)	4253(1)	164(1)	3002(1)	32(1)
N(1)	4012(1)	122(3)	2123(1)	34(1)
N(2)	5033(1)	-787(3)	3115(1)	37(1)
N(3)	4484(1)	1807(3)	3213(1)	34(1)
C(1)	3506(1)	-446(4)	3515(2)	46(1)
C(2)	3776(1)	-972(3)	1706(2)	34(1)
C(3)	3661(1)	-2238(3)	1986(2)	42(1)
C(4)	3438(2)	-3319(4)	1566(2)	54(1)
C(5)	3326(2)	-3169(5)	865(2)	61(1)
C(6)	3443(2)	-1925(5)	577(2)	56(1)
C(7)	3666(1)	-818(4)	991(2)	43(1)
C(8)	5434(1)	-1268(3)	3715(2)	32(1)
C(9)	5153(2)	-1318(4)	4347(2)	45(1)
C(10)	5563(2)	-1804(4)	4925(2)	57(1)
C(11)	6265(2)	-2226(4)	4878(2)	54(1)
C(12)	6555(1)	-2175(4)	4249(2)	46(1)
C(13)	6147(1)	-1711(3)	3662(2)	37(1)
C(14)	4061(1)	2955(3)	3324(1)	30(1)
C(15)	3312(1)	2971(3)	3139(2)	34(1)
C(16)	2910(1)	4109(3)	3249(2)	40(1)
C(17)	3226(1)	5269(4)	3536(2)	47(1)
C(18)	3962(1)	5263(4)	3711(2)	49(1)
C(19)	4371(1)	4120(3)	3615(2)	38(1)

Bond lengths [Å] for **8**

Si(1)-N(1)	1.731(2)	C(8)-N(2)	1.415(3)
Si(2)-N(2)	1.728(2)	C(9)-C(10)	1.392(4)
Si(3)-N(3)	1.724(3)	C(10)-C(11)	1.380(5)
C(1)-Si(1)	1.870(3)	C(11)-C(12)	1.373(5)
C(2)-C(3)	1.391(4)	C(12)-C(13)	1.396(4)
c(2)-C(7)	1.395(4)	C(14)-C(19)	1.390(4)
C(2)-N(1)	1.403(4)	C(14)-C(15)	1.408(3)
C(3)-C(4)	1.390(5)	C(14)-N(3)	1.409(4)
C(4)-C(5)	1.368(6)	C(15)-C(16)	1.379(4)
C(5)-C(6)	1.378(6)	C(16)-C(17)	1.387(5)
C(6)-C(7)	1.403(5)	C(17)-C(18)	1.383(4)
C(8)-C(9)	1.373(4)	C(18)-C(19)	1.384(5)
C(8)-C(13)	1.405(4)	N(1)-H(1)	0.860(1)
		N(2)-H(2)	0.860(1)
		N(3)-H(3)	0.860(1)

Bond angles [deg] for **8**

N(3)-Si(1)-N(2)	107.12(11)	C(9)-C(8)-N(2)	122.4(2)
N(3)-Si(1)-N(1)	107.26(12)	C(13)-C(8)-N(2)	118.9(3)
N(2)-Si(1)-N(1)	105.18(11)	C(15)-C(14)-N(3)	121.4(2)
N(3)-Si(1)-C(1)	111.07(14)	C(19)-C(14)-N(3)	120.97(19)
N(2)-Si(1)-C(1)	113.93(14)	C(8)-N(2)-Si(1)	132.1(2)
N(1)-Si(1)-C(1)	111.87(12)	C(14)-N(3)-Si(1)	131.89(15)
		C(2)-N(1)-Si(1)	129.3(2)

Table 7.3.6: Crystal data and structure refinement for $MeSi(NHMes)_3$ **(9)**

Identification code	ipds3311
Empirical formula	$C_{28}H_{39}N_3Si$
Formula weight (g/mol)	445.71
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	P c a n
Unit cell dimensions	
a; b; c; (Å)	12.338(1); 15.677(1); 27.522(2)
α; β; γ; (°)	90.00; 90.00; 90.00
Volume V (Å$^{3)}$	5322.3(6)
No. of formulas per unit cell Z	8
Calculated density (g/cm^{-1})	1.112
Absorption coefficient μ(MoKα) /mm^{-1}	0.107
F(000)	1366
Crystal size (mm)	0.22 x 0.30 x 0.38
Theta range for data collection (°)	2.23 - 25.93
Absorption correction	numerical
Total reflections collected	24013
Unique reflections observed	5156
Reflections independent with ($I>2\sigma(I)$); R_{int}	3522; 0.0514
Data / restraints / parameters	5156 /0/289
R1; wR2 ($I>2\sigma(I)$)	0.0499; 0.1234
R1; wR2 (all data)	0.0806; 0.1367
Goodness of fit on F^2	0.909
Largest diff. peak and hole (e /Å^3)	0.296; -0.272

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [Å^{2}x10^3] for **9**

Atom	x	y	z	Ueq
Si(1)	4876(1)	1544(1)	1279(1)	32(1)
N(1)	5339(1)	823(1)	1703(1)	37(1)
N(2)	5763(1)	2391(1)	1336(1)	36(1)
N(3)	4837(1)	965(1)	749(1)	38(1)
C(1)	3492(2)	1988(2)	1347(1)	50(1)
C(2)	5637(2)	3288(1)	1287(1)	37(1)
C(3)	5356(2)	3659(1)	838(1)	44(1)
C(4)	5113(2)	3125(2)	400(1)	57(1)
C(5)	5321(2)	4546(2)	801(1)	57(1)
C(6)	5572(2)	5080(2)	1182(1)	61(1)
C(7)	5589(3)	6043(2)	1119(2)	93(1)
C(8)	5825(2)	4702(2)	1624(1)	57(1)
C(9)	5851(2)	3820(2)	1687(1)	43(1)
C(10)	6101(2)	3440(2)	2179(1)	56(1)
C(11)	5954(2)	1023(1)	2132(1)	38(1)
C(12)	5411(2)	1277(2)	2558(1)	47(1)
C(13)	4192(2)	1293(2)	2586(1)	65(1)
C(14)	6025(3)	1528(2)	2958(1)	59(1)
C(15)	7143(3)	1532(2)	2950(1)	61(1)
C(16)	7785(3)	1830(2)	3387(1)	95(1)
C(17)	7660(2)	1243(2)	2533(1)	57(1)
C(18)	7088(2)	982(2)	2120(1)	43(1)
C(19)	7678(2)	669(2)	1676(1)	53(1)
C(20)	5417(2)	200(1)	637(1)	34(1)
C(21)	6473(2)	242(1)	445(1)	38(1)
C(22)	6992(2)	1086(2)	336(1)	50(1)
C(23)	7018(2)	-512(2)	344(1)	45(1)
C(24)	6553(2)	-1308(2)	421(1)	47(1)
C(25)	7183(2)	-2109(2)	302(1)	65(1)
C(26)	5510(2)	-1335(1)	606(1)	46(1)
C(27)	3797(2)	-650(2)	924(1)	52(1)
C(28)	4931(2)	-597(1)	718(1)	39(1)

Bond lengths [Å] for **9**

Si(1)-N(1)	1.7207(18)	C(14)-C(15)	1.379(4)
Si(1)-N(2)	1.7276(17)	C(15)-C(17)	1.388(4)
Si(1)-N(3)	1.7206(17)	C(15)-C(16)	1.513(4)
C(1)-Si(1)	1.854(2)	C(17)-C(18)	1.401(3)
C(2)-C(9)	1.407(3)	C(18)-C(19)	1.505(3)
C(2)-C(3)	1.409(3)	C(20)-C(28)	1.403(3)
C(2)-N(2)	1.422(3)	C(20)-C(21)	1.406(3)
C(3)-C(5)	1.396(3)	C(20)-N(3)	1.430(3)
C(3)-C(4)	1.497(4)	C(21)-C(23)	1.388(3)
C(5)-C(6)	1.377(4)	C(21)-C(22)	1.502(3)
C(6)-C(8)	1.388(4)	C(23)-C(24)	1.390(3
C(6)-C(7)	1.519(4)	C(24)-C(26)	1.384(3)
C(8)-C(9)	1.394(3)	C(24)-C(25)	1.513(3)
C(9)-C(10)	1.510(3)	C(26)-C(28)	1.394(3)
C(11)-C(18)	1.401(3)	C(27)-C(28)	1.512(3)
c(11)-C(12)	1.409(3)	N(1)-H(1)	0.860(1)
C(11)-N(1)	1.437(3)	N(2)-H(2)	0.860(1)
C(12)-C(14)	1.393(3)	N(3)-H(3)	0.860(1)
C(12)-C(13)	1.506(4)		

Bond angles [deg] for **9**

N(1)-Si(1)-C(1)	118.97(10)	C(11)-N(1)-Si(1)	125.97(14)
N(1)-Si(1)-N(2)	103.50(9)	C(2)-N(2)-Si(1)	133.04(14)
N(2)-Si(1)-C(1)	106.63(10)	C(9)-C(2)-N(2)	119.44(19)
N(3)-Si(1)-N(1)	103.77(9)	C(20)-N(3)-Si(1)	127.66(13)
N(3)-Si(1)-N(2)	119.96(9)	C(18)-C(11)-N(1)	119.84(19)
N(3)-Si(1)-C(1)	104.92(10)	C(21)-C(20)-N(3)	120.36(18)
		C(28)-C(20)-N(3)	119.84(19)

Table 7.3.7: Crystal data and structure refinement for EtSi(NHMes)$_3$ **(10)**

Identification code	ipds3303
Empirical formula	$C_{29}H_{41}N_3Si$
Formula weight (g/mol)	459.74
Temperature (K)	220
Wavelength (Å)	0.7107
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a; b; c; (Å)	9.673(2); 10.026(3); 15.300(3)
α; β; γ; (°)	101.57(3); 100.815(2); 104.632(3)
Volume V (Å$^{3)}$	1361.18
No. of formulas per unit cell Z	2
Calculated density (g/cm^{-1})	1.122
Absorption coefficient μ(MoKα) /mm^{-1}	0.107
F(000)	500
Crystal size (mm)	0.15 x 0.22 x 0.38
Theta range for data collection (°)	2.17 - 26.00
Absorption correction	numerical
Total reflections collected	10613
Unique reflections observed	4913
Reflections independent with ($I>2\sigma(I)$); R_{int}	3510; 0.0330
Data / restraints / parameters	4913 /0/133
R1; wR2 ($I>2\sigma(I)$)	0.0433; 0.0870
R1; wR2 (all data)	0.0800; 0.0971
Goodness of fit on F^2	2.018
Largest diff. peak and hole (e /Å^3)	0.836; -0.671

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [$Å^2$x10^3] for **10**

Atom	x	y	z	Ueq
Si(1)	2021(1)	4543(1)	2575(1)	27(1)
N(1)	3917(4)	4885(4)	2795(2)	29(1)
N(2)	1190(4)	4958(4)	3458(2)	31(1)
N(3)	1355(4)	2696(4)	2214(2)	33(1)
C(1)	645(5)	4062(4)	4014(3)	27(1)
C(2)	4989(5)	6043(4)	2652(3)	28(1)
C(3)	1606(5)	3897(5)	4770(3)	31(1)
C(4)	-877(5)	3331(5)	3813(3)	31(1)
C(5)	1041(5)	2973(5)	5280(3)	36(1)
C(6)	2021(5)	1706(5)	1780(3)	31(1)
C(7)	5734(5)	5785(5)	1963(3)	32(1)
C(8)	5353(5)	7436(5)	3232(3)	32(1)
C(9)	2792(6)	991(5)	2311(3)	39(1)
C(10)	-1403(5)	2448(5)	4349(3)	36(1)
C(11)	3376(6)	-11(6)	1876(4)	46(1)
C(12)	1876(6)	1400(5)	828(3)	39(1)
C(13)	5335(6)	4304(6)	1308(4)	44(1)
C(14)	-451(5)	2241(5)	5079(3)	35(1)
C(15)	6833(5)	6906(5)	1856(3)	37(1)
C(16)	3214(6)	4735(5)	5047(3)	42(1)
C(17)	4623(6)	7788(6)	4004(4)	46(1)
C(18)	7197(6)	8294(5)	2419(3)	38(1)
C(19)	6431(5)	8532(5)	3094(3)	36(1)
C(20)	1569(6)	5653(5)	1775(3)	41(1)
C(21)	2997(7)	1326(6)	3346(4)	53(1)
C(22)	-1948(6)	3499(6)	3003(4)	45(1)
C(23)	2496(7)	386(6)	418(4)	50(1)
C(24)	-1032(7)	1226(6)	5633(4)	52(1)
C(25)	3236(7)	-345(6)	934(4)	49(1)
C(26)	1038(7)	2133(6)	235(4)	53(1)
C(27)	8383(7)	9504(6)	2294(4)	57(2)
C(28)	-76(8)	5445(7)	1392(5)	70(2)
C(29)	3851(9)	-1492(8)	469(5)	74(2)

Bond lengths [Å] for **10**

Si(1)-N(1)	1.733(4)	C(10)-C(16)	1.399(7)
Si(1)-N(2)	1.731(4)	C(10)-C(13)	1.416(6)
Si(1)-N(3)	1.732(4)	C(11)-C(16)	1.399(7)
Si(1)-C(29)	1.876(5)	C(11)-C(17)	1.525(7)
N(2)-C(10)	1.431(6)	C(12)-C(23)	1.392(7)
N(3)-C(19)	1.429(6)	C(12)-C(21)	1.513(7)
N(1)-C(1)	1.435(6)	C(13)-C(15)	1.390(7)
C(1)-C(4)	1.412(6)	C(13)-C(25)	1.515(7)
C(2)-C(5)	1.407(6)	C(15)-C(18)	1.386(8)
C(2)-C(7)	1.403(6)	C(16)-C(27)	1.407(8)
C(3)-C(8)	1.413(6)	C(16)-C(26)	1.520(7)
C(3)-C(5)	1.400(7)	C(18)-C(28)	1.518(7)
C(4)-C(8)	1.501(7)	C(19)-C(22)	1.400(7)
C(8)-C(14)	1.390(7)	C(22)-C(23)	1.397(7)
C(8)-C(26)	1.526(7)	C(22)-C(26)	1.515(8)
C(9)-C(18)	1.388(7)	C(24)-C(27)	1.533(9)
N(1)-H(1)	0.860(3)	C(28)-C(29)	1.400(8)
N(2)-H(2)	0.860(3)		
N(3)-H(3)	0.860(3)		

Bond angles [deg] for **10**

N(2)-Si(1)-N(3)	103.07(19)	N(2)-Si(1)-C(29)	105.2(2)
N(1)-Si(1)-N(2)	103.42(19)	C(10)-N(2)-Si(1)	128.6(3)
N(3)-Si(1)-N(1)	120.79(18)	C(19)-N(3)-Si(1)	127.5(3)
N(4)-Si(1)-C(29)	120.5(2)	C(1)-N(1)-Si(1)	128.8(3)
N(3)-Si(1)-C(29)	105.0(2)		

Table 7.3.8: Crystal data and structure refinement for PhSi(NHMes)$_3$ **(12)**

Identification code	ipds3289
Empirical formula	$C_{33}H_{41}N_3Si$
Formula weight (g/mol)	507.78
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\,\bar{1}$
Unit cell dimensions	
a; b; c; (Å)	10.813(1); 11.259(1); 12.632(1)
α; β; γ; (°)	82. 24(1); 74.52(1); 85.53(1)
Volume V (Å$^{3)}$	1466.7(2)
No. of formulas per unit cell Z	2
Calculated density (g/cm^{-1})	1.150
Absorption coefficient μ(MoKα) /mm^{-1}	0.106
F(000)	548
Crystal size (mm)	0.25 x 0.32 x 0.40
Theta range for data collection (°)	2.62 - 25.92
Absorption correction	numerical
Total reflections collected	9012
Unique reflections observed	5273
Reflections independent with (I>2σ(I)); R_{int}	4037; 0.0439
Data / restraints / parameters	5273/0/498
R1; wR2 (I>2σ(I))	0.0471; 0.123
R1; wR2 (all data)	0.0657; 0.148
Goodness of fit on F^2	1.083
Largest diff. peak and hole (e /Å^3)	0.338; -0.541

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [Å^{2}x10^3] for **12**

Atom	**x**	**y**	**z**	**Ueq**
Si(1)	7178(1)	2716(1)	2556(1)	34(1)
N(1)	5873(2)	3069(2)	1999(2)	39(1)
N(2)	8324(2)	3654(2)	1764(2)	38(1)
N(3)	7426(2)	1196(2)	2474(2)	38(1)
C(1)	4995(2)	2283(2)	1804(2)	36(1)
C(2)	4175(2)	1607(2)	2678(2)	41(1)
C(3)	3366(2)	818(2)	2445(2)	44(1)
C(4)	3340(2)	693(2)	1374(2)	44(1)
C(5)	4142(2)	1402(2)	523(2)	44(1)
C(6)	4958(2)	2210(2)	704(2)	40(1)
C(7)	4120(3)	1709(3)	3869(2)	57(1)
C(8)	2451(3)	-147(3)	1138(3)	60(1)
C(9)	5753(3)	2992(3)	-250(2)	56(1)
C(10)	8465(2)	4142(2)	621(2)	36(1)
C(11)	7953(2)	5301(2)	381(2)	40(1)
C(12)	8036(2)	5753(2)	-712(2)	44(1)
C(13)	8618(2)	5092(2)	-1576(2)	44(1)
C(14)	9145(2)	3961(2)	-1327(2)	44(1)
C(15)	9087(2)	3468(2)	-242(2)	40(1)
C(16)	7323(3)	6062(3)	1295(2)	51(1)
C(17)	8688(4)	5623(3)	-2761(2)	60(1)
C(18)	9693(3)	2230(3)	-21(2)	52(1)
C(19)	8042(2)	176(2)	2940(2)	35(1)
C(20)	9153(2)	260(2)	3307(2)	38(1)
C(21)	9681(2)	-786(2)	3779(2)	43(1)
C(22)	9197(2)	-1908(2)	3870(2)	44(1)
C(23)	8133(2)	-1968(2)	3457(2)	42(1)
C(24)	7545(2)	-958(2)	3004(2)	37(1)
C(25)	9806(2)	1423(2)	3177(3)	48(1)
C(26)	9784(4)	-3017(3)	4395(3)	66(1)
C(27)	6390(3)	-1080(3)	2585(3)	55(1)
C(28)	6931(2)	3059(2)	4018(2)	39(1)
C(29)	6793(2)	2185(3)	4925(2)	47(1)
C(30)	6573(3)	2481(3)	5999(2)	54(1)
C(31)	6468(3)	3666(3)	6184(2)	57(1)
C(32)	6604(3)	4552(3)	5308(2)	67(1)
C(33)	6836(3)	4254(3)	4233(2)	54(1)

Bond lengths [Å] for **12**

Si(1)-N(1)	1.7355(18)	C(13)-C(14)	1.386(3)
Si(1)-N(2)	1.706(2)	C(13)-C(17)	1.519(4)
Si(1)-N(3)	1.724(2)	C(14)-C(15)	1.394(3)
N(1)-H(1)	0.82(3)	C(15)-C(18)	1.516(3)
N(2)-H(2)	0.77(3)	C(19)-C(24)	1.407(3)
N(3)-H(3)	0.81(3)	C(19)-C(20)	1.413(3)
C(1)-C(2)	1.392(3)	C(19)-N(3)	1.420(3)
C(1)-C(6)	1.414(3)	C(20)-C(21)	1.398(3)
C(1)-N(1)	1.436(3)	C(20)-C(25)	1.504(3)
C(2)-C(3)	1.404(3)	C(21)-C(22)	1.384(4)
C(3)-C(4)	1.387(3)	C(22)-C(23)	1.393(3)
C(4)-C(5)	1.387(4)	C(22)-C(26)	1.510(4)
C(4)-C(8)	1.510(3)	C(23)-C(24)	1.388(3)
C(5)-C(6)	1.396(3)	C(24)-C(27)	1.503(3)
C(6)-C(9)	1.497(4)	C(28)-C(29)	1.390(3)
C(10)-C(15)	1.404(3)	C(28)-C(33)	1.398(3)
C(10)-C(11)	1.405(3)	C(28)-Si(1)	1.882(2)
C(10)-N(2)	1.446(3)	C(29)-C(30)	1.395(3)
C(11)-C(12)	1.386(3)	C(30)-C(31)	1.377(4)
C(11)-C(16)	1.512(3)	C(31)-C(32)	1.371(4)
C(12)-C(13)	1.386(3)	C(32)-C(33)	1.395(4)

Bond angles [deg] for **12**

N(2)-Si(1)-N(3)	118.55(9)	C(1)-N(1)-Si(1)	129.06(16)
N(2)-Si(1)-N(1)	103.92(10)	C(1)-N(1)-H(1)	111(2)
N(3)-Si(1)-N(1)	102.43(9)	Si(1)-N(1)-H(1)	113(2)
N(2)-Si(1)-C(28)	105.53(10)	C(10)-N(2)-Si(1)	126.88(15)
N(3)-Si(1)-C(28)	111.20(10)	C(10)-N(2)-H(2)	113(2)
N(1)-Si(1)-C(28)	115.42(10)	Si(1)-N(2)-H(2)	118(2)
C(29)-C(28)-Si(1)	123.68(17)	C(19)-N(3)-Si(1)	139.92(15)
C(33)-C(28)-Si(1)	119.56(19)	C(19)-N(3)-H(3)	109(2)
		Si(1)-N(3)-H(3)	110(2)

Table 7.3.9: Crystal data and structure refinement for
$[\{Me_2Si(NLiMes)_2(OEt_2)\}_2]$ (**13**)

Identification code	ipds3374
Empirical formula	$C_{48}H_{78}N_4Si_2O_2Li_4$
Formula weight (g/mol)	825.07
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a; b; c; (Å)	11.670(1); 15.002(1); 15.284(1)
α; β; γ; (°)	67.50(1); 84.55(1); 85.76 (1)
Volume V ($Å^{3)}$	2458.2(4)
No. of formulas per unit cell Z	2
Calculated density (g/cm^{-1})	1.115
Absorption coefficient μ(MoKα) /mm^{-1}	0.112
F(000)	896
Crystal size (mm)	0.22 x 0.34 x 0.60
Theta range for data collection (°)	2.19 - 25.99
Absorption correction	numerical
Total reflections collected	18987
Unique reflections observed	8975
Reflections independent with (I>2σ(I)); R_{int}	5510; 0.0392
Data / restraints / parameters	8975/0/547
R1; wR2 (I>2σ(I))	0.0779; 0.222
R1; wR2 (all data)	0.116; 0.249
Goodness of fit on F^2	0.909
Largest diff. peak and hole (e /$Å^3$)	1.103; -0.432

[*]Li atoms are coordinated to diethyl ether and could not lead to better *w*R2 value in the structure refinement.

Atomic coordinates [x10^{4}] and equivalent isotropic displacement parameters [Å^{2}x10^{3}] for **13**

Atom	x	y	z	Ueq
Si(1)	4308(1)	3698(1)	2707(1)	30(1)
Si(2)	743(1)	6448(1)	2233(1)	27(1)
Li(1)	2288(4)	4307(4)	3163(4)	31(1)
Li(2)	2746(4)	5799(4)	1830(4)	33(1)
Li(3)	1996(6)	2905(5)	2232(5)	50(2)
Li(4)	3070(6)	7258(5)	2684(4)	48(2)
N(1)	3056(2)	3068(2)	3082(2)	31(1)
N(2)	3895(2)	4842(2)	2646(2)	29(1)
N(3)	1141(2)	5282(2)	2347(2)	28(1)
N(4)	2005(2)	7069(2)	1851(2)	29(1)
O(1)	2128(3)	1989(2)	1617(2)	71(1)
O(2)	3282(3)	8410(3)	2980(3)	77(1)
C(1)	4876(3)	3675(3)	1507(3)	50(1)
C(2)	5473(3)	3189(3)	3568(3)	39(1)
C(3)	2940(3)	2168(2)	3852(2)	33(1)
C(4)	3618(3)	1322(3)	3922(3)	42(1)
C(5)	3450(4)	459(3)	4710(3)	56(1)
C(6)	2607(4)	369(3)	5439(3)	60(1)
C(7)	1910(3)	1181(3)	5354(3)	49(1)
C(8)	2061(3)	2063(2)	4588(2)	35(1)
C(9)	4481(3)	1307(3)	3126(3)	58(1)
C(10)	2443(5)	-584(3)	6278(4)	93(2)
C(11)	1251(3)	2907(2)	4553(2)	38(1)
C(12)	4532(2)	5438(2)	2913(2)	29(1)
C(13)	5605(3)	5838(2)	2429(2)	35(1)
C(14)	6163(3)	6456(2)	2723(3)	41(1)
C(15)	5766(3)	6705(2)	3475(2)	40(1)
C(16)	4742(3)	6299(2)	3965(2)	37(1)
C(17)	4130(3)	5684(2)	3703(2)	32(1)
C(18)	6158(3)	5577(3)	1623(3)	46(1)
C(19)	6421(4)	7353(3)	3782(3)	54(1)
C(20)	3086(3)	5203(3)	4315(2)	39(1)
C(21)	2597(5)	2317(4)	597(3)	73(1)
C(22)	3367(5)	1645(4)	374(5)	91(2)
C(23)	1429(5)	1239(4)	1879(5)	92(2)
C(24)	885(4)	1021(4)	2880(5)	90(2)
C(25)	-399(3)	6930(2)	1346(2)	37(1)
C(26)	129(3)	6541(3)	3396(2)	43(1)
C(27)	477(2)	4675(2)	2114(2)	27(1)
C(28)	830(3)	4420(2)	1324(2)	28(1)
C(29)	201(3)	3783(2)	1101(2)	36(1)
C(30)	-789(3)	3365(2)	1641(2)	37(1)
C(31)	-1138(3)	3615(2)	2405(2)	38(1)
C(32)	-563(3)	4268(2)	2647(2)	32(1)
C(33)	1851(3)	4896(3)	670(2)	36(1)
C(34)	-1452(3)	2681(3)	1379(3)	51(1)
C(35)	-1061(3)	4518(3)	3473(3)	44(1)
C(36)	2120(3)	7916(2)	1019(2)	29(1)

C(37)	1473(3)	8790(2)	898(2)	35(1)
C(38)	1617(3)	9599(3)	48(3)	45(1)
C(39)	2392(3)	9604(3)	-698(3)	46(1)
C(40)	3069(3)	8770(2)	-560(2)	39(1)
C(41)	2953(3)	7938(2)	276(2)	31(1)
C(42)	662(3)	8884(3)	1694(3)	45(1)
C(43)	2511(4)	10481(3)	-1613(3)	68(1)
C(44)	3749(3)	7076(2)	383(2)	37(1)
C(45)	3055(6)	8549(5)	3811(5)	103(2)
C(46)	2100(6)	7930(5)	4370(4)	112(3)
C(47)	4142(4)	9116(4)	2360(4)	75(2)
C(48)	4462(5)	8981(4)	1496(5)	92(2)

Bond lengths [Å] for **13**

Li(1)-N(3)	2.029(6)
Li(1)-N(1)	2.045(6)
Li(1)-N(2)	2.060(5)
Li(1)-Si(1)	2.595(5)
Li(2)-N(2)	2.019(6)
Li(2)-N(4)	2.043(6)
Li(2)-N(3)	2.048(6)
Li(2)-Si(2)	2.577(6)
Li(3)-O(1)	1.930(7)
Li(3)-N(1)	1.966(6)
Li(4)-N(4)	1.968(6)
Li(4)-O(2)	1.984(7)
N(1)-Si(1)	1.728(3)
N(2)-Si(1)	1.717(3)
N(3)-Si(2)	1.722(3)
N(4)-Si(2)	1.732(2)
C(1)-Si(1)	1.902(4)
C(2)-Si(1)	1.892(3)
C(3)-N(1)	1.417(4)
C(3)-C(8)	1.418(5)
C(3)-C(4)	1.418(5)
C(3)-Li(3)	2.608(7)
C(12)-N(2)	1.398(4)
C(17)-Li(4)	2.579(7)
C(21)-O(1)	1.504(6)
C(23)-O(1)	1.349(6)
C(23)-C(24)	1.521(9)
C(25)-Si(2)	1.894(3)
C(26)-Si(2)	1.903(3)
C(27)-N(3)	1.400(4)
C(27)-C(28)	1.419(4)
C(27)-C(32)	1.432(4)
C(27)-Li(1)	2.670(5)
C(28)-C(29)	1.402(4)
C(28)-C(33)	1.510(4)
C(28)-Li(3)	2.536(7)
C(29)-C(30)	1.392(5)
C(29)-Li(3)	2.765(7)
C(30)-C(31)	1.376(5)
C(30)-C(34)	1.518(4)
C(31)-C(32)	1.402(5)
C(36)-C(41)	1.414(4)
C(36)-N(4)	1.417(4)
C(36)-C(37)	1.420(4)
C(36)-Li(4)	2.670(7)
C(45)-O(2)	1.363(7)
C(45)-C(46)	1.483(9)
C(47)-C(48)	1.423(8)
C(47)-O(2)	1.495(6)

Bond angles [deg] for **13**

N(3)-Li(1)-N(1)	131.6(3)	N(3)-Si(2)-N(4)	104.60(12)
N(3)-Li(1)-N(2)	106.3(2)	N(3)-Si(2)-C(25)	108.72(14)
N (1)-Li(1)-N(2)	82.9(2)	N(4)-Si(2)-C(25)	112.79(14)
N(3)-Li(1)-C(11)	111.7(2)	N(3)-Si(2)-C(26)	113.08(15)
Li(2)-Li(1)-C(11)	165.1(3)	N(4)-Si(2)-C(26)	109.61(14)
Si(1)-Li(1)-C(11)	110.0(2)	C(25)-Si(2)-C(26)	108.09(17)
Li(2)-Li(1)-C(27)	76.05(19)	N(3)-Si(2)-Li(2)	52.43(14)
Si(1)-Li(1)-C(27)	124.6(2)	N(4)-Si(2)-Li(2)	52.26(15)
C(11)-Li(1)-C(27)	91.93(18)	C(25)-Si(2)-Li(2)	122.88(16)
N(2)-Li(2)-N(4)	132.4(3)	C(26)-Si(2)-Li(2)	129.03(17)
N(2)-Li(2)-N(3)	107.1(3)	N(4)-Li(2)-C(12)	104.6(2)
N(4)-Li(2)-N(3)	83.8(2)	N(3)-Li(2)-C(12)	123.3(2)
N(2)-Li(2)-C(44)	111.4(2)	N(1)-C(3)-Li(3)	48.01(19)
N(4)-Li(2)-C(44)	76.7(2)	C(8)-C(3)-Li(3)	108.1(3)
N(2)-Li(2)-C(12)	30.72(12)	C(4)-C(3)-Li(3)	111.0(3)
N(4)-C(36)-Li(4)	45.93(18)	C(8)-C(11)-Li(1)	100.3(2)
C(37)-C(36)-Li(4)	110.0(2)	N(2)-C(12)-C(17)	120.2(3)
C(36)-N(4)-Li(2)	118.8(2)	N(2)-C(12)-Li(2)	47.55(18)
Si(2)-N(4)-Li(2)	85.67(18)	C(17)-C(12)-Li(2)	105.9(2)
Li(4)-N(4)-Li(2)	97.0(3)	C(13)-C(12)-Li(2)	115.9(2)
C(23)-O(1)-C(21)	113.6(4)	C(16)-C(17)-Li(4)	84.1(2)
C(23)-O(1)-Li(3)	122.1(4)	C(12)-C(17)-Li(4)	94.0(2)
C(21)-O(1)-Li(3)	118.7(3)	C(20)-C(17)-Li(4)	96.7(3)
C(45)-O(2)-C(47)	109.2(4)	C(22)-C(21)-O(1)	115.1(5)
C(45)-O(2)-Li(4)	129.9(4)	O(1)-C(23)-C(24)	110.5(5)
C(47)-O(2)-Li(4)	117.6(4)	N(3)-C(27)-C(28)	120.3(3)
N(2)-Si(1)-N(1)	104.15(13)	N(3)-C(27)-C(32)	123.4(3)
N(2)-Si(1)-C(2)	109.20(14)	N(3)-C(27)-Li(1)	48.30(18)
N(1)-Si(1)-C(2)	112.97(14)	C(28)-C(27)-Li(1)	106.7(2)
N(2)-Si(1)-C(1)	112.43(16)	C(32)-C(27)-Li(1)	113.7(2)
N(1)-Si(1)-C(1)	109.24(15)	C(29)-C(28)-Li(3)	84.0(2)
C(2)-Si(1)-C(1)	108.85(17)	C(27)-C(28)-Li(3)	96.2(2)
N(2)-Si(1)-Li(1)	52.37(14)	C(33)-C(28)-Li(3)	93.6(3)
N(1)-Si(1)-Li(1)	51.86(14)	C(30)-C(29)-C(28)	122.3(3)
C(2)-Si(1)-Li(1)	123.47(16)	C(41)-C(36)-Li(4)	110.8(2)
C(1)-Si(1)-Li(1)	127.68(17)		

Table 7.3.10: Crystal data and structure refinement for $[(Li(OC_4H_8)_4][Li_3\{Ph_2Si(NMes)_2\}_2]\cdot2THF$ (**14**)

Identification code	ipds3408
Empirical formula	$C_{84}H_{91}N_4Si_2O_6Li_4$
Formula weight (g/mol)	1336.55
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	P 2_1/n
Unit cell dimensions	
a; b; c; (Å)	12.262(1); 28.047(2); 24.020(2)
β (°)	101.54(1)
Volume V ($Å^{3)}$	8093.09
No. of formulas per unit cell Z	4
Calculated density (g/cm^{-1})	1.097
Absorption coefficient μ(MoKα) $/mm^{-1}$	0.095
F(000)	2844
Crystal size (mm)	0.22 x 0.30 x 0.30
Theta range for data collection (°)	2.18 - 25.98
Absorption correction	numerical
Total reflections collected	62170
Unique reflections observed	15428
Reflections independent with (I>2σ(I)); R_{int}	9815; 0.0552
Data / restraints / parameters	15428/0/871
R1; wR2 (I>2σ(I))	0.0687; 0.1892
R1; wR2 (all data)	0.1052; 0.211
Goodness of fit on F^2	0.909
Largest diff. peak and hole ($e/Å^3$)	0.688; -0.305

*Solvated Li atom is coordinated to four THF molecules and could not lead to better *w*R2 value in refinement. And two non coordinating THF molecules are present in formula units per unit cell.

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [Å^{2}x10^3] for **14**

Atom	x	y	z	Ueq
Si(1)	1998(1)	1258(1)	3317(1)	30(1)
Si(2)	1352(1)	-263(1)	2220(1)	33(1)
N(1)	2128(2)	713(1)	3634(1)	33(1)
N(2)	1031(2)	1146(1)	2709(1)	32(1)
N(3)	931(2)	-162(1)	2843(1)	35(1)
N(4)	2395(2)	150(1)	2254(1)	34(1)
Li(1)	666(4)	519(1)	3101(2)	37(1)
Li(2)	2440(4)	161(2)	3130(2)	40(1)
Li(3)	1682(5)	778(2)	2163(2)	55(1)
Li(4)	1761(5)	2655(2)	378(3)	68(2)
O(1)	916(2)	3069(1)	792(1)	79(1)
O(2)	2264(2)	3035(1)	-194(1)	78(1)
O(3)	804(3)	2141(1)	8(1)	97(1)
O(4)	3063(2)	2379(1)	849(1)	69(1
O(5)	-2884(13)	3289(6)	3070(6)	384(7)
O(6)	900(20)	5991(11)	5499(11)	556(17)
C(1)	1571(2)	1757(1)	3766(1)	37(1)
C(2)	839(3)	2119(1)	3542(1)	48(1)
C(3)	584(3)	2490(1)	3877(2)	62(1)
C(4)	1058(3)	2509(1)	4450(2)	60(1)
C(5)	1777(3)	2155(1)	4685(1)	58(1)
C(6)	2035(3)	1785(1)	4349(1)	51(1)
C(7)	3391(2)	1471(1)	3161(1)	35(1)
C(8)	4009(2)	1165(1)	2878(1)	44(1)
C(9)	5001(3)	1297(1)	2736(1)	55(1)
C(10)	5430(3)	1748(1)	2883(2)	61(1)
C(11)	4856(3)	2058(1)	3166(2)	59(1)
C(12)	3856(2)	1924(1)	3302(1)	43(1)
C(13)	2349(2)	597(1)	4221(1)	32(1)
C(14)	1462(2)	490(1)	4500(1)	37(1)
C(15)	1683(3)	332(1)	5060(1)	43(1)
C(16)	2751(3)	271(1)	5373(1)	47(1)
C(17)	3624(3)	388(1)	5105(1)	43(1)
C(18)	3446(2)	552(1)	4544(1)	37(1)
C(19)	275(2)	540(1)	4189(1)	48(1)
C(20)	2959(3)	93(2)	5984(1)	66(1)
C(21)	4422(3)	673(1)	4281(1)	50(1)
C(22)	263(2)	1427(1)	2334(1)	32(1)
C(23)	575(2)	1747(1)	1934(1)	40(1)
C(24)	-245(3)	1974(1)	1529(1)	49(1)
C(25)	-1365(3)	1905(1)	1498(1)	54(1)
C(26)	-1679(3)	1605(1)	1906(1)	49(1)
C(27)	-898(2)	1373(1)	2317(1)	38(1)
C(28)	1779(3)	1856(1)	1942(1)	54(1)
C(29)	-2236(4)	2146(2)	1050(2)	82(1)
C(30)	-1290(3)	1057(1)	2744(1)	51(1)
C(31)	1810(2)	-904(1)	2135(1)	41(1)
C(32)	2704(3)	-1011(1)	1882(2)	64(1)
C(33)	3060(3)	-1482(1)	1834(2)	81(1)

C(34)	2540(4)	-1848(1)	2032(2)	80(1)
C(35)	1657(5)	-1756(1)	2281(2)	84(1)
C(36)	1291(4)	-1292(1)	2334(2)	65(1)
C(37)	253(2)	-137(1)	1555(1)	39(1)
C(38)	85(3)	-422(1)	1068(1)	64(1)
C(39)	-612(4)	-279(2)	565(2)	91(2)
C(40)	-1166(4)	149(2)	532(2)	81(1)
C(41)	-1035(3)	439(1)	1002(1)	56(1)
C(42)	-343(2)	294(1)	1503(1)	44(1)
C(43)	441(2)	-490(1)	3170(1)	37(1)
C(44)	1097(3)	-701(1)	3660(1)	43(1)
C(45)	611(3)	-1007(1)	4002(1)	56(1)
C(46)	-509(3)	-1113(1)	3888(2)	63(1)
C(47)	-1149(3)	-909(1)	3404(2)	60(1)
C(48)	-706(3)	-603(1)	3049(1)	47(1)
C(49)	2331(3)	-610(1)	3813(1)	50(1)
C(50)	-1008(4)	-1439(2)	4276(2)	88(1)
C(51)	-1461(3)	-403(1)	2525(2)	68(1)
C(52)	3319(2)	184(1)	1988(1)	35(1)
C(53)	4371(2)	14(1)	2272(1)	46(1)
C(54)	5321(3)	99(1)	2050(2)	63(1)
C(55)	5290(3)	349(1)	1550(2)	67(1)
C(56)	4259(3)	498(1)	1261(2)	60(1)
C(57)	3277(3)	420(1)	1463(1)	45(1)
C(58)	4483(3)	-246(1)	2830(1)	59(1)
C(59)	6342(4)	450(2)	1330(3)	107(2)
C(60)	2194(3)	599(1)	1111(1)	59(1)
C(61)	1208(4)	3215(1)	1370(2)	85(1)
C(62)	239(6)	3531(4)	1450(5)	208(6)
C(64)	-170(5)	3265(3)	543(3)	138(3)
C(63)	-607(8)	3484(4)	986(4)	191(5)
C(65)	1813(4)	3478(1)	-433(2)	71(1)
C(66)	2630(4)	3669(2)	-758(2)	92(1)
C(67)	3307(6)	3265(2)	-857(3)	138(3)
C(68)	3120(5)	2890(2)	-477(3)	113(2)
C(69)	53(9)	2217(3)	-510(3)	235(6)
C(70)	-826(7)	1853(2)	-575(3)	149(3)
C(71)	-554(5)	1540(2)	-78(3)	112(2)
C(72)	630(4)	1659(2)	176(2)	90(1)
C(73)	3554(4)	1919(2)	769(2)	95(1)
C(74)	4586(5)	1885(2)	1189(3)	139(2)
C(75)	4846(5)	2364(3)	1412(4)	154(3)
C(76)	3838(4)	2646(2)	1264(3)	105(2)
C(77)	-98(14)	6296(3)	5141(6)	229(7)
C(78)	-2695(11)	2851(3)	3084(7)	262(8)
C(79)	-1301(14)	6113(4)	5180(6)	252(7)
C(80)	-1519(13)	2974(4)	2469(4)	237(6)
C(81)	-2133(11)	2645(5)	2722(5)	211(4)
C(82)	130(20)	5794(9)	5730(10)	349(10)
C(83)	-907(15)	5701(6)	5507(7)	251(6)
C(84)	-1590(14)	3399(6)	2816(7)	278(6)

Bond lengths [Å] for **14**

Si(1)-N(1)	1.700(2)	C(22)-Li(3)	2.607(5)
Si(1)-N(2)	1.716(2)	C(52)-C(53)	1.415(4)
Si(1)-C(1)	1.904(3)	C(52)-C(57)	1.417(4)
Si(1)-C(7)	1.917(3)	C(43)-N(3)	1.418(3)
Si(1)-Li(1)	2.624(4)	C(13)-C(14)	1.418(4)
Si(1)-Li(3)	3.035(5)	C(42)-C(41)	1.387(4)
Si(1)-Li(2)	3.170(4)	C(19)-Li(1)	2.751(6)
Si(2)-N(3)	1.701(2)	O(4)-C(76)	1.442(5)
Si(2)-N(4)	1.714(2)	O(4)-C(73)	1.451(5)
Si(2)-C(37)	1.905(3)	O(4)-Li(4)	1.925(7)
Si(2)-C(31)	1.907(3)	C(49)-Li(2)	2.733(5)
Si(2)-Li(2)	2.610(5)	O(1)-C(61)	1.422(5)
Si(2)-Li(3)	2.952(5)	O(1)-C(64)	1.454(6)
N(3)-Li(2)	2.053(5)	O(1)-Li(4)	1.955(7)
N(3)-Li(1)	2.054(5)	C(41)-C(40)	1.374(5)
N(2)-Li(3)	1.960(5)	C(60)-Li(3)	2.771(6)
N(2)-Li(1)	2.085(5)	O(2)-C(68)	1.420(5)
N(1)-C(13)	1.420(3)	O(2)-C(65)	1.430(4)
N(1)-Li(2)	2.048(5)	O(2)-Li(4)	1.937(6)
N(1)-Li(1)	2.057(5)	O(3)-C(69)	1.407(6)
N(4)-C(52)	1.410(3)	O(3)-C(72)	1.439(5)
N(4)-Li(3)	1.958(5)	O(3)-Li(4)	1.955(8)
N(4)-Li(2)	2.095(5)	C(77)-O(6)	1.60(3)
C(22)-N(2)	1.406(3)	C(78)-O(5)	1.247(16)
C(22)-C(23)	1.420(4)	C(82)-O(6)	1.31(3)
C(22)-C(27)	1.424(4)	O(5)-C(85)	1.837(19)

Bond angles [deg] for **14**

N(1)-Si(1)-C(1)	114.68(11)	N(2)-C(22)-Li(3)	47.69(16)
N(2)-Si(1)-C(1)	113.28(12)	C(23)-C(22)-Li(3)	93.24(19)
N(1)-Si(1)-C(7)	111.15(11)	C(27)-C(22)-Li(3)	128.0(2)
N(2)-Si(1)-C(7)	112.42(11)	C(22)-N(2)-Li(3)	100.3(2)
C(1)-Si(1)-C(7)	103.80(11)	Li(3)-N(2)-Li(1)	90.5(2)
N(1)-Si(1)-Li(1)	51.58(12)	C(13)-N(1)-Si(1)	129.33(16)
N(2)-Si(1)-Li(1)	52.50(12)	C(13)-N(1)-Li(2)	113.11(19)
N(3)-Si(2)-N(4)	101.58(10)	Si(1)-N(1)-Li(2)	115.20(17)
N(3)-Si(2)-C(37)	114.73(12)	C(13)-N(1)-Li(1)	121.8(2)
N(4)-Si(2)-C(37)	108.14(11)	Si(1)-N(1)-Li(1)	88.06(14)
N(3)-Si(2)-C(31)	113.53(11)	Li(2)-N(1)-Li(1)	71.00(19)
N(4)-Si(2)-C(31)	114.06(12)	C(52)-N(4)-Si(2)	133.08(17)
C(37)-Si(2)-C(31)	104.98(12)	C(52)-N(4)-Li(3)	05.7(2)
N(3)-Si(2)-Li(2)	51.81(13)	Si(2)-N(4)-Li(3)	106.8(2)
N(1)-Si(1)-N(2)	101.83(10)	C(52)-N(4)-Li(2)	126.3(2)
C(61)-O(1)-C(64)	108.9(4)	C(38)-C(37)-Si(2)	123.9(2)
C(61)-O(1)-Li(4)	127.7(3)	C(42)-C(37)-Si(2)	120.1(2)
C(64)-O(1)-Li(4)	123.3(4)	C(12)-C(7)-Si(1)	124.7(2)
C(68)-O(2)-Li(4)	123.5(3)	C(8)-C(7)-Si(1)	119.47(19)
C(65)-O(2)-Li(4)	127.6(3)	N(4)-C(52)-C(53)	119.8(2)
C(69)-O(3)-C(72)	106.4(4)	N(4)-C(52)-C(57)	123.0(2)
C(72)-O(3)-Li(4)	132.3(3)	C(53)-C(52)-C(57)	116.9(2)
O(2)-C(65)-C(66)	106.0(3)	N(4)-C(52)-Li(3)	44.19(15)
O(1)-C(61)-C(62)	103.9(5)	C(53)-C(52)-Li(3)	139.9(2)
C(4)-C(3)-C(2)	120.5(3)	N(4)-Li(3)-N(2)	129.3(3)
O(4)-Li(4)-O(2)	107.1(3)	N(4)-Li(3)-Li(1)	86.57(19)
O(4)-Li(4)-O(1)	113.7(3)	N(4)-Li(3)-Si(1)	109.0(2)
O(2)-Li(4)-O(1)	108.0(3)	N(2)-Li(3)-Si(1)	31.83(11)
O(4)-Li(4)-O(3)	108.9(3)	C(22)-Li(3)-Si(1)	60.90(11)
O(2)-Li(4)-O(3)	109.3(3)	Li(2)-Li(3)-Si(1)	64.58(14)
O(1)-Li(4)-O(3)	109.8(3)	Si(2)-Li(3)-Si(1)	112.97(15)
Li(2)-N(3)-Li(1)	70.97(19	N(3)-Li(1)-N(1)	105.3(2)
N(1)-Li(2)-N(3)	105.7(2)	N(3)-Li(1)-N(2)	126.0(2)
N(1)-Li(2)-N(4)	129.4(2)	N(1)-Li(1)-N(2)	79.60(17)

Table 7.3.11: Crystal data and structure refinement for $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Al]\cdot Tol$ **(15)**

Identification code	ipds3198
Empirical formula	$C_{47}H_{70}N_4Si_2O_3AlLi$
Formula weight (g/mol)	829.17
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 2_1/n
Unit cell dimensions	
a; b; c; (Å)	11.364(6); 32.680(1); 13.604(1)
β (°)	94.32(1)
Volume V (Å$^{3)}$	5037.7(2)
No. of formulas per unit cell Z	4
Calculated density (g/cm^{-1})	1.093
Absorption coefficient μ(MoKα) /mm^{-1}	0.128
F(000)	1792
Crystal size (mm)	0.26 x 0.30 x 0.76
Theta range for data collection (°)	1.90 - 24.95
Absorption correction	numerical
Total reflections collected	33186
Unique reflections observed	8683
Reflections independent with (I>2σ(I)); R_{int}	5674; 0.0515
Data / restraints / parameters	8683/0/535
R1; wR2 (I>2σ(I))	0.0574; 0.1515
R1; wR2 (all data)	0.0880; 0.1682
Goodness of fit on F^2	1.048
Largest diff. peak and hole (e /Å^3)	0.630; -0.344

[*] It crystallizes with one toluene non coordinating molecule formula units per unit cell.

Atomic coordinates [x10^{4}] and equivalent isotropic displacement parameters [Å^{2}x10^{3}] for **15**

Atom	x	y	z	Ueq
Al(1)	10422(1)	3786(1)	6981(1)	41(1)
Si(1)	12491(1)	3690(1)	6256(1)	42(1)
Si(2)	8365(1)	3768(1)	7749(1)	53(1)
Li(1)	5447(4)	3551(2)	2079(3)	58(1)
N(1)	11939(2)	4009(1)	7135(1)	44(1)
N(2)	11097(2)	3484(1)	6004(1)	43(1)
N(3)	8951(2)	4039(1)	6802(2)	48(1)
N(4)	9715(2)	3534(1)	8018(2)	49(1)
O(1)	4389(2)	3895(1)	1273(1)	61(1)
O(2)	5239(2)	2971(1)	2102(2)	79(1)
O(3)	6640(2)	3807(1)	2925(1)	62(1)
C(1)	13090(3)	3949(1)	5178(2)	61(1)
C(2)	13626(2)	3320(1)	6786(2)	59(1)
C(3)	12525(2)	4293(1)	7749(2)	45(1)
C(4)	11944(2)	4495(1)	8471(2)	61(1)
C(5)	12515(3)	4783(1)	9086(3)	80(1)
C(6)	13694(3)	4878(1)	9000(3)	78(1)
C(7)	14284(3)	4680(1)	8301(3)	69(1)
C(8)	13724(2)	4393(1)	7683(2)	56(1)
C(9)	10703(2)	3191(1)	5317(2)	42(1)
C(10)	11468(2)	2944(1)	4812(2)	54(1)
C(11)	11043(3)	2652(1)	4136(2)	69(1)
C(12)	9845(3)	2597(1)	3938(3)	80(1)
C(13)	9078(3)	2836(1)	4420(3)	74(1)
C(14)	9490(2)	3129(1)	5100(2)	55(1)
C(15)	7864(3)	4081(1)	8788(2)	82(1)
C(16)	7137(2)	3415(1)	7315(3)	81(1)
C(17)	8396(2)	4319(1)	6146(2)	49(1)
C(18)	8998(2)	4487(1)	5380(2)	58(1)
C(19)	8450(3)	4766(1)	4719(3)	79(1)
C(20)	7300(4)	4888(1)	4804(3)	87(1)
C(21)	6694(3)	4725(1)	5555(3)	83(1)
C(22)	7219(2)	4448(1)	6212(2)	66(1)
C(23)	10079(2)	3256(1)	8751(2)	49(1)
C(24)	9293(3)	3032(1)	9288(2)	65(1)
C(25)	9703(4)	2747(1)	9994(2)	82(1)
C(26)	10887(4)	2683(1)	10203(3)	85(1)
C(27)	11674(3)	2906(1)	9699(2)	74(1)
C(28)	11289(2)	3186(1)	8986(2)	56(1)
C(29)	683(3)	4453(2)	2064(4)	97(1)
C(30)	508(3)	4202(2)	1210(4)	120(2)
C(31)	411(5)	3778(4)	1310(7)	200(5)
C(32)	470(5)	3659(3)	2317(9)	186(4)
C(33)	637(5)	3889(3)	3124(7)	181(4)
C(34)	749(3)	4288(3)	2921(4)	129(2)
C(35)	809(5)	4861(2)	1896(6)	183(3)
C(36)	4061(3)	4328(1)	2648(3)	94(1)
C(37)	3739(3)	4239(2)	1631(3)	94(1)
C(38)	4024(4)	3818(1)	251(3)	95(1)
C(39)	4785(4)	3509(1)	-161(2)	92(1)

C(40)	3232(5)	3048(2)	2367(4)	147(2)
C(41)	4137(6)	2763(2)	2222(5)	134(2)
C(42)	7263(5)	2880(2)	1823(4)	124(2)
C(43)	6192(6)	2683(2)	2099(4)	125(2)
C(44)	7374(3)	4093(1)	1463(3)	84(1)
C(45)	7398(3)	4121(1)	2541(3)	86(1)
C(46)	6012(4)	3454(1)	4329(2)	95(1)
C(47)	6768(5)	3780(1)	3973(3)	101(1)

Bond lengths [Å] for **15**

N(1)-Al(1)	1.8692(19)	C(17)-C(18)	1.402(4)
N(2)-Al(1)	1.865(2)	C(17)-C(22)	1.411(4)
N(3)-Al(1)	1.865(2)	C(18)-C(19)	1.394(4)
N(4)-Al(1)	1.866(2)	C(19)-C(20)	1.380(5)
N(2)-Si(1)	1.7311(19)	C(20)-C(21)	1.383(5)
N(4)-Si(2)	1.728(2)	C(21)-C(22)	1.377(5)
N(3)-Si(2)	1.737(2)	C(23)-N(4)	1.389(3)
N(1)-Si(1)	1.738(2))	C(23)-C(24)	1.403(4)
Li(1)-O(3)	1.903(5)	C(23)-C(28)	1.406(4)
Li(1)-O(2)	1.913(6)	C(24)-C(25)	1.392(5)
Li(1)-O(1)	1.926(5)	C(25)-C(26)	1.370(5)
C(1)-Si(1)	1.866(3)	C(26)-C(27)	1.377(5)
C(2)-Si(1)	1.874(3)	C(27)-C(28)	1.381(4)
C(3)-N(1)	1.385(3)	C(29)-C(34)	1.281(6)
C(3)-C(4)	1.392(4)	C(29)-C(35)	1.363(7)
C(3)-C(8)	1.411(3)	C(29)-C(30)	1.425(6)
C(4)-C(5)	1.386(4)	C(30)-C(31)	1.397(11)
C(5)-C(6)	1.388(5)	C(31)-C(32)	1.421(13)
C(6)-C(7)	1.367(5)	C(32)-C(33)	1.331(11)
C(7)-C(8)	1.383(4)	C(33)-C(34)	1.341(9)
C(9)-N(2)	1.389(3)	C(36)-C(37)	1.433(5)
C(9)-C(14)	1.403(3)	C(37)-O(1)	1.451(4)
C(9)-C(10)	1.404(4)	C(38)-O(1)	1.442(4)
C(10)-C(11)	1.387(4)	C(38)-C(39)	1.467(5)
C(11)-C(12)	1.379(5)	C(41)-O(2)	1.445(6)
C(13)-C(14)	1.388(4)	C(43)-O(2)	1.435(6)
C(15)-Si(2)	1.868(3)	C(44)-C(45)	1.468(5)
C(16)-Si(2)	1.871(3)	C(45)-O(3)	1.463(4)
C(17)-N(3)	1.395(3)	C(47)-O(3)	1.425(4)

Bond angles [deg] for **15**

N(3)-Al(1)-N(2)	123.69(9)	N(3)-Si(2)-C(16)	113.55(13)
N(3)-Al(1)-N(4)	82.05(9)	C(15)-Si(2)-C(16)	108.24(16)
N(2)-Al(1)-N(4)	121.94(10)	O(3)-Li(1)-O(2)	120.5(3)
N(3)-Al(1)-N(1)	130.63(10)	O(3)-Li(1)-O(1)	118.3(3)
N(2)-Al(1)-N(1)	81.98(9)	O(2)-Li(1)-O(1)	121.0(2)
N(4)-Al(1)-N(1)	122.23(9)	C(3)-N(1)-Si(1)	129.37(16)
N(2)-Si(1)-N(1)	89.84(9)	C(3)-N(1)-Al(1)	136.60(17)
N(2)-Si(1)-C(1)	113.83(12)	C(9)-N(2)-Si(1)	130.16(16)
N(1)-Si(1)-C(1)	116.16(12)	C(9)-N(2)-Al(1)	135.65(16)
N(2)-Si(1)-C(2)	114.71(12)	Si(1)-N(2)-Al(1)	94.18(10)
N(1)-Si(1)-C(2)	113.30(12)	C(17)-N(3)-Si(2)	128.95(17)
C(1)-Si(1)-C(2)	108.31(13)	C(17)-N(3)-Al(1)	137.09(17)
N(4)-Si(2)-N(3)	89.95(10)	Si(2)-N(3)-Al(1)	93.81(10)
N(4)-Si(2)-C(15)	113.43(13)	C(23)-N(4)-Si(2)	130.81(17)
N(3)-Si(2)-C(15)	115.95(15)	C(23)-N(4)-Al(1)	135.13(17)
N(4)-Si(2)-C(16)	115.06(15)	Si(2)-N(4)-Al(1)	94.06(10)

Table 7.3.12: Crystal data and structure refinement for
$[Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2Al]\cdot 3THF$ **(16)**

Identification code	ipds3342
Empirical formula	$C_{76}H_{82}N_4Si_2O_7AlLi$
Formula weight (g/mol)	1253.56
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\,\bar{1}$
Unit cell dimensions	
a; b; c; (Å)	14.255(1); 15.153(1); 17.201(1)
α; β; γ; (°)	89.53(1); 88.36(1); 85.22(1)
Volume V ($Å^{3)}$	3700.5(6)
No. of formulas per unit cell Z	2
Calculated density (g/cm^{-1})	1.125
Absorption coefficient $\mu(MoK\alpha)$ /mm^{-1}	0.113
F(000)	1332
Crystal size (mm)	0.38 x 0.44 x 0.52
Theta range for data collection (°)	2.20 - 25.97
Absorption correction	numerical
Total reflections collected	34996
Unique reflections observed	13419
Reflections independent with ($I>2\sigma(I)$); R_{int}	9407; 0.0371
Data / restraints / parameters	13419/0/824
R1; wR2 ($I>2\sigma(I)$)	0.0689; 0.1984
R1; wR2 (all data)	0.0944; 0.2235
Goodness of fit on F^2	1.057
Largest diff. peak and hole (e /$Å^3$)	0.425; -0.402

*Solvated Li atom is coordinated to four THF molecules and could not lead to better *w*R2 value in refinement. And three non coordinating THF molecules with disorder are present in formula units per unit cell.

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [$Å^2$x10^3] for **16**

Atom	x	y	z	Ueq
Al(1)	2304(1)	2539(1)	7243(1)	35(1)
Si(1)	4132(1)	2148(1)	7155(1)	37(1)
Si(2)	473(1)	2931(1)	7258(1)	38(1)
Li(1)	1152(4)	2315(4)	12375(3)	66(1)
N(1)	3372(2)	2755(2)	7788(1)	38(1)
N(2)	3193(2)	1882(2)	6617(1)	38(1)
N(3)	1217(2)	2112(2)	7683(1)	40(1)
N(4)	1436(1)	3409(2)	6853(1)	38(1)
O(1)	115(2)	3104(2)	11998(2)	73(1)
O(2)	1964(2)	1963(2)	11486(1)	70(1)
O(3)	1870(2)	2813(2)	13176(2)	83(1)
O(4)	522(2)	1327(2)	12793(2)	84(1)
O(5)	-5813(5)	3823(5)	11900(4)	185(3)
O(6)	-2859(4)	1955(8)	12985(8)	254(5)
O(7)	3070(14)	-2083(11)	9929(6)	390(9)
C(1)	3527(2)	3301(2)	8415(1)	42(1
C(2)	2823(2)	3933(2)	8677(2)	51(1)
C(3)	2953(3)	4469(2)	9314(2)	69(1)
C(4)	3791(3)	4388(3)	9698(2)	82(1)
C(5)	4499(3)	3779(3)	9447(2)	81(1)
C(6)	4381(2)	3237(3)	8810(2)	60(1)
C(7)	3125(2)	1338(2)	5972(1)	38(1)
C(8)	3908(2)	1064(2)	5483(2)	48(1)
C(9)	3806(2)	539(2)	4838(2)	57(1)
C(10)	2943(3)	257(2)	4661(2)	60(1)
C(11)	2164(2)	515(2)	5137(2)	58(1)
C(12)	2254(2)	1049(2)	5781(2)	47(1)
C(13)	4804(2)	1157(2)	7603(2)	47(1)
C(14)	4487(3)	811(3)	8312(2)	66(1)
C(15)	4922(4)	16(3)	8613(3)	92(1)
C(16)	5675(4)	-418(3)	8205(3)	100(2)
C(17)	6006(3)	-84(3)	7511(3)	89(1)
C(18)	5572(2)	695(2)	7219(2)	63(1)
C(19)	4977(2)	2835(2)	6614(2)	44(1)
C(20)	4702(2)	3261(2)	5918(2)	56(1)
C(21)	5264(3)	3835(3)	5533(2)	74(1)
C(22)	6118(3)	4002(3)	5839(3)	83(1)
C(23)	6415(3)	3591(3)	6510(3)	81(1)
C(24)	5853(2)	3010(2)	6898(2)	62(1)
C(25)	1059(2)	1367(2)	8126(1)	42(1)
C(26)	188(2)	1248(2)	8509(2)	57(1)
C(27)	68(3)	494(3)	8951(2)	74(1)
C(28)	779(3)	-167(3)	9024(2)	76(1)
C(29)	1647(3)	-71(2)	8652(2)	68(1)
C(30)	1780(2)	683(2)	8206(2)	52(1)
C(31)	1531(2)	4181(2)	6425(1)	38(1)
C(32)	2417(2)	4526(2)	6365(2)	48(1)

C(33)	2547(2)	5282(2)	5932(2)	60(1)
C(34)	1801(3)	5734(2)	5551(2)	62(1)
C(35)	930(2)	5410(2)	5611(2)	56(1)
C(36)	786(2)	4647(2)	6041(2)	45(1)
C(37)	-348(2)	2507(2)	6535(2)	49(1)
C(38)	-70(3)	2443(2)	5746(2)	60(1)
C(39)	-659(4)	2105(3)	5201(2)	86(1)
C(40)	-1514(4)	1829(3)	5434(3)	98(2)
C(41)	-1805(3)	1888(3)	6204(4)	98(2)
C(42)	-1230(2)	2225(3)	6752(3)	72(1)
C(43)	-269(2)	3669(2)	7952(2)	50(1)
C(44)	-1049(2)	4217(2)	7698(2)	67(1)
C(45)	-1561(4)	4803(3)	8200(3)	100(2)
C(46)	-1312(5)	4848(3)	8953(4)	115(2)
C(47)	-551(5)	4304(3)	9236(3)	109(2)
C(48)	-26(3)	3724(3)	8729(2)	70(1)
C(49)	-432(4)	3769(3)	12444(3)	97(1)
C(50)	-1342(5)	3954(6)	12068(5)	171(4)
C(51)	-1372(5)	3360(6)	11443(4)	158(3)
C(52)	2569(9)	2205(5)	10258(4)	215(6)
C(53)	1838(4)	1201(3)	11021(3)	90(1)
C(54)	2278(7)	1384(5)	10251(3)	174(4)
C(55)	2417(4)	2595(3)	11017(3)	96(1)
C(56)	1538(5)	3190(10)	13870(4)	262(8)
C(57)	2272(5)	3335(7)	14373(4)	176(4)
C(58)	3102(5)	3101(6)	13981(3)	139(3)
C(59)	2853(4)	2634(5)	13259(3)	123(2)
C(60)	-483(3)	1347(3)	12911(2)	76(1)
C(61)	-685(4)	532(3)	13358(3)	97(1)
C(62)	184(4)	169(4)	13630(4)	118(2)
C(63)	913(4)	478(4)	13079(4)	111(2)
C(64)	-5001(8)	3342(7)	11703(5)	171(4)
C(65)	-4201(6)	3851(9)	11952(8)	222(7)
C(66)	-4702(7)	4522(6)	12466(6)	180(4)
C(67)	-5651(6)	4595(6)	12198(6)	164(3)
C(68)	-3355(8)	1265(7)	12914(6)	187(4)
C(69)	-4119(7)	1294(7)	13416(5)	179(4)
C(70)	-3911(10)	1991(11)	13982(6)	240(7)
C(71)	-3038(14)	2208(10)	13692(7)	273(11)
C(72)	2676(15)	-2732(9)	10369(11)	302(11)
C(73)	2679(8)	-2616(10)	11106(9)	220(6)
C(74)	2808(8)	-1604(7)	11172(6)	173(3)
C(75)	3072(10)	-1347(7)	10431(7)	203(5)
C(76)	-365(4)	2949(4)	11294(2)	102(2)

Bond lengths [Å] for **16**

N(1)-Al(1)	1.864(2)
N(2)-Al(1)	1.866(2)
N(3)-Al(1)	1.866(2)
N(4)-Al(1)	1.866(2)
N(1)-Si(1)	1.729(2)
N(2)-Si(1)	1.725(2)
N(3)-Si(2)	1.734(2)
N(4)-Si(2)	1.731(2)
Li(1)-O(4)	1.931(7)
Li(1)-O(3)	1.934(6)
Li(1)-O(2)	1.943(6)
Li(1)-O(1)	1.945(7)
C(13)-Si(1)	1.884(3)
C(19)-Si(1)	1.879(3)
C(37)-Si(2)	1.885(3)
C(43)-Si(2)	1.883(3)
C(1)-C(2)	1.395(4)
C(1)-N(1)	1.399(3)
C(1)-C(6)	1.407(4)
C(2)-C(3)	1.394(4)
C(3)-C(4)	1.378(6)
C(7)-N(2)	1.399(3)
C(7)-C(12)	1.399(4)
C13)-C(14)	1.402(5)
C(25)-N(3)	1.387(3)
C(29)-C(30)	1.393(4)
C(31)-N(4)	1.390(3)
C(49)-O(1)	1.435(5)
C(53)-O(2)	1.437(5)
C(53)-C(54)	1.482(8)
C(56)-O(2)	1.430(5)
C(57)-O(3)	1.381(6)
C(57)-C(58)	1.409(8)
C(60)-O(3)	1.415(6)
C(61)-O(4)	1.439(5)
C(64)-O(4)	1.447(5)
C(65)-O(5)	1.353(10)
C(68)-O(5)	1.321(9)
C(69)-O(6)	1.318(13)
C(72)-O(6)	1.290(16)
C(73)-O(7)	1.383(18)
C(76)-O(7)	1.416(14)
C(77)-O(1)	1.438(5)

Bond angles [deg] for **16**

N(1)-Al(1)-N(4)	125.10(10)
N(1)-Al(1)-N(2)	82.10(9)
N(4)-Al(1)-N(2)	123.27(9)
N(1)-Al(1)-N(3)	125.01(9)
N(4)-Al(1)-N(3)	82.26(10)
N(2)-Al(1)-N(3)	125.05(11)
N(2)-Si(1)-N(1)	90.31(10)
N(2)-Si(1)-C(19)	114.16(11)
N(1)-Si(1)-C(19)	113.48(12)
N(2)-Si(1)-C(13)	113.58(12)
N(1)-Si(1)-C(13)	114.95(12)
C(19)-Si(1)-C(13)	109.42(13)
N(4)-Si(2)-N(3)	90.23(10)
N(4)-Si(2)-C(43)	114.25(12)
N(3)-Si(2)-C(43)	115.79(12)
N(4)-Si(2)-C(37)	115.01(12)
N(3)-Si(2)-C(37)	114.26(12)
C(43)-Si(2)-C(37)	106.97(13)
C(1)-N(1)-Al(1)	133.46(18)
Si(1)-N(1)-Al(1)	93.77(10)
C(7)-N(2)-Si(1)	132.77(18)
C(7)-N(2)-Al(1)	133.36(18)
Si(1)-N(2)-Al(1)	93.80(10)
C(25)-N(3)-Si(2)	133.19(19)
C(25)-N(3)-Al(1)	132.91(19)
Si(2)-N(3)-Al(1)	93.66(10)
C(31)-N(4)-Si(2)	133.14(18)
C(31)-N(4)-Al(1)	133.04(17)
Si(2)-N(4)-Al(1)	93.76(10)
O(4)-Li(1)-O(3)	109.9(3)
O(4)-Li(1)-O(2)	111.3(3)
O(3)-Li(1)-O(2)	110.4(3)
O(4)-Li(1)-O(1)	102.8(3)
O(3)-Li(1)-O(1)	114.6(3)
O(2)-Li(1)-O(1)	107.6(3)
C(2)-C(1)-N(1)	120.4(2)
N(1)-C(1)-C(6)	122.2(3)
N(2)-C(7)-C(12)	120.1(2)
N(2)-C(7)-C(8)	122.8(2)
C(18)-C(13)-Si(1)	122.2(2)
C(14)-C(13)-Si(1)	119.8(2)
C(24)-C(19)-Si(1)	123.3(2)
C(20)-C(19)-Si(1)	119.4(2)

Table 7.3.13: Crystal data and structure refinement for $[Li(OEt_2)_3][\{Me_2Si(NPh)_2\}_2Ga]$ **(19)**

Identification code	ipds3207
Empirical formula	$C_{47}H_{69}N_4Si_2O_3GaLi$
Formula weight (g/mol)	870.90
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P\ 2_1/n$
Unit cell dimensions	
a; b; c; (Å)	11.408(6); 32.618(2); 13.603(1)
β (°)	94.64(7)
Volume V (Å$^{3)}$	5045.0(5)
No. of formulas per unit cell Z	4
Calculated density (g/cm^{-1})	1.147
Absorption coefficient μ(MoKα) /mm^{-1}	0.633
F(000)	1860
Crystal size (mm)	0.38 x 0.40 x 0.44
Theta range for data collection (°)	2.18 - 25.00
Absorption correction	numerical
Total reflections collected	28294
Unique reflections observed	8296
Reflections independent with (I>2σ(I)); R_{int}	6050; 0.0456
Data / restraints / parameters	8296/0/523
R1; wR2 (I>2σ(I))	0.0480; 0.1209
R1; wR2 (all data)	0.0689; 0.1335
Goodness of fit on F^2	1.035
Largest diff. peak and hole (e /Å^3)	0.611; -0.332

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [$Å^2$x10^3] for **19**

Atom	x	y	z	Ueq
Ga(1)	5431(1)	1202(1)	6965(1)	44(1)
Si(1)	7537(1)	1310(1)	6243(1)	45(1)
Si(2)	3338(1)	1224(1)	7738(1)	58(1)
Li(1)	10453(5)	1447(2)	12069(4)	60(1)
N(1)	6156(2)	1514(1)	5973(2)	47(1)
N(2)	7003(2)	984(1)	7108(2)	47(1)
N(3)	4669(2)	1456(1)	8026(2)	54(1)
N(4)	3908(2)	947(1)	6796(2)	53(1)
O(1)	10223(3)	2028(1)	12092(2)	81(1)
O(2)	11664(2)	1200(1)	12909(2)	66(1)
O(3)	9392(2)	1100(1)	11269(2)	63(1)
C(1)	8163(3)	1054(1)	5176(2)	64(1)
C(2)	8642(3)	1685(1)	6795(3)	62(1)
C(3)	5728(3)	1808(1)	5299(2)	45(1)
C(4)	6478(3)	2056(1)	4786(2)	57(1)
C(5)	6018(4)	2350(1)	4116(3)	72(1)
C(6)	4835(4)	2405(1)	3936(3)	83(1)
C(7)	4084(4)	2160(1)	4433(3)	78(1)
C(8)	4522(3)	1868(1)	5104(2)	58(1)
C(9)	7568(3)	699(1)	7734(2)	46(1)
C(10)	6961(3)	491(1)	8432(2)	64(1)
C(11)	7521(4)	202(1)	9057(3)	82(1)
C(12)	8694(4)	111(1)	9009(3)	82(1)
C(13)	9313(3)	315(1)	8334(3)	70(1)
C(14)	8760(3)	602(1)	7707(2)	58(1)
C(15)	2128(4)	1583(2)	7290(3)	89(1)
C(16)	2816(4)	913(2)	8770(3)	91(1)
C(17)	3375(3)	671(1)	6124(2)	53(1)
C(18)	2215(3)	538(1)	6172(3)	71(1)
C(19)	1699(4)	262(1)	5498(3)	87(1)
C(20)	2313(5)	107(1)	4755(4)	91(2)
C(21)	3457(4)	230(1)	4686(3)	81(1)
C(22)	3992(3)	509(1)	5361(2)	61(1)
C(23)	5065(3)	1736(1)	8749(2)	53(1)
C(24)	4295(4)	1961(1)	9297(2)	68(1)
C(25)	4712(5)	2245(1)	10000(3)	87(1)
C(26)	5897(5)	2312(1)	10194(3)	90(1)
C(27)	6673(4)	2088(1)	9675(3)	77(1)
C(28)	6263(3)	1808(1)	8969(2)	58(1)
C(29)	5722(5)	539(2)	12061(6)	117(2)
C(30)	5789(5)	698(3)	12916(5)	144(3)
C(31)	5690(6)	1090(4)	13157(7)	176(4)
C(32)	5502(7)	1327(4)	12365(10)	190(5)
C(33)	5428(6)	1224(4)	11342(9)	209(6)
C(34)	5525(5)	799(3)	11194(5)	140(3)
C(35)	5847(6)	140(3)	11867(8)	206(4)
C(36)	12396(4)	922(2)	11437(3)	92(1)
C(37)	12426(4)	889(2)	12519(3)	92(1)
C(38)	11039(5)	1551(2)	14315(3)	103(2)

C(40)	12238(6)	2128(2)	11805(4)	127(2)
C(41)	11159(8)	2322(2)	12080(4)	131(3)
C(42)	8237(7)	1937(3)	12388(6)	161(3)
C(43)	9099(8)	2223(2)	12239(5)	148(3)
C(44)	9755(5)	1489(2)	9835(3)	96(2)
C(45)	9004(5)	1180(1)	10257(3)	96(2)
C(46)	9112(4)	665(2)	12655(3)	94(1)
C(47)	8750(4)	759(1)	11640(4)	92(1)

Bond lengths [Å] for **19**

N(1)-Ga(1)	1.929(2)	C(15)-Si(2)	1.874(4)
N(2)-Ga(1)	1.923(2)	C(16)-Si(2)	1.868(4)
N(3)-Ga(1)	1.931(2)	C(17)-N(4)	1.387(4)
N(4)-Ga(1)	1.924(3)	C(37)-O(2)	1.463(5)
N(1)-Si(1)	1.722(3)	C(38)-C(39)	1.487(7)
N(2)-Si(1)	1.732(2)	C(39)-O(2)	1.429(5)
N(3)-Si(2)	1.714(3)	C(40)-C(41)	1.460(9)
N(4)-Si(2)	1.738(3)	C(41)-O(1)	1.436(7)
Li(1)-O(2)	1.899(6)	C(42)-C(43)	1.382(10)
Li(1)-O(1)	1.914(6)	C(43)-O(1)	1.460(8)
Li(1)-O(3)	1.930(6)	C(44)-C(45)	1.468(7)
C(1)-Si(1)	1.866(3)	C(45)-O(3)	1.437(4)
C(2)-Si(1)	1.870(3)	C(46)-C(47)	1.441(6)
C(3)-N(1)	1.388(4)	C(47)-O(3)	1.445(5)
C(9)-N(2)	1.385(4)		

Bond angles [deg] for **19**

N(2)-Ga(1)-N(4)	132.70(11)	N(4)-C(17)-C(22)	120.8(3)
N(2)-Ga(1)-N(1)	79.42(10)	N(3)-C(23)-C(28)	121.3(3)
N(4)-Ga(1)-N(1)	125.35(10)	N(3)-C(23)-C(24)	122.5(3)
N(2)-Ga(1)-N(3)	123.76(10)	O(2)-Li(1)-O(1)	120.3(3)
N(4)-Ga(1)-N(3)	79.55(11)	O(2)-Li(1)-O(3)	118.8(3)
N(1)-Ga(1)-N(3)	122.67(11)	O(1)-Li(1)-O(3)	120.7(3)
N(1)-Si(1)-N(2)	90.90(12)	C(3)-N(1)-Si(1)	132.5(2)
N(1)-Si(1)-C(1)	114.11(15)	C(3)-N(1)-Ga(1)	132.7(2)
N(2)-Si(1)-C(1)	115.58(14)	Si(1)-N(1)-Ga(1)	94.79(11)
N(1)-Si(1)-C(2)	114.11(14)	C(9)-N(2)-Si(1)	131.1(2)
N(2)-Si(1)-C(2)	113.03(14)	C(9)-N(2)-Ga(1)	133.9(2)
C(1)-Si(1)-C(2)	108.47(16)	Si(1)-N(2)-Ga(1)	94.69(11)
N(3)-Si(2)-N(4)	91.19(12)	C(23)-N(3)-Si(2)	133.1(2)
N(3)-Si(2)-C(16)	113.47(17)	C(23)-N(3)-Ga(1)	132.1(2)
N(4)-Si(2)-C(16)	115.60(19)	Si(2)-N(3)-Ga(1)	94.79(12)
N(3)-Si(2)-C(15)	114.42(19)	C(17)-N(4)-Si(2)	130.8(2)
N(4)-Si(2)-C(15)	113.32(16)	C(17)-N(4)-Ga(1)	134.7(2)
C(16)-Si(2)-C(15)	108.3(2)	Si(2)-N(4)-Ga(1)	94.30(12)
N(1)-C(3)-C(8)	120.8(3)	C(28)-C(23)-C(24)	116.2(3)
N(1)-C(3)-C(4)	122.1(3)	C(25)-C(24)-C(23)	121.4(4)
N(2)-C(9)-C(10)	120.8(3)	C(26)-C(25)-C(24)	121.1(4)
N(2)-C(9)-C(14)	122.8(3)	C(25)-C(26)-C(27)	118.6(4)
N(4)-C(17)-C(18)	122.3(3)	C(28)-C(27)-C(26)	120.6(4)

Table 7.3.14: Crystal data and structure refinement for $[Li(OEt_2)_4][\{Me_2Si(NMes)_2\}_2Ga]$ **(20)**

Identification code	ipds3372
Empirical formula	$C_{56}H_{87}N_4Si_2O_4GaLi$
Formula weight (g/mol)	1013.14
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	$P\ 2_1\ 2_1\ 2_1$
Unit cell dimensions	
a; b; c; (Å)	17.842(4); 18.629(2); 18.687(2)
α; β; γ; (°)	90.00; 90.00; 90.00
Volume V (Å$^{3)}$	6210.92
No. of formulas per unit cell Z	4
Calculated density (g/cm^{-1})	1.083
Absorption coefficient μ(MoKα) /mm^{-1}	0.524
F(000)	2180
Crystal size (mm)	0.10 x 0.22 x 0.68
Theta range for data collection (°)	2.28 - 25.98
Absorption correction	numerical
Total reflections collected	22889
Unique reflections observed	11949
Reflections independent with (I>2σ(I)); R_{int}	7742; 0.0588
Data / restraints / parameters	11949/0/613
R1; wR2 (I>2σ(I))	0.0630; 0.1482
R1; R2 (all data)	0.1083; 0.1716
Goodness of fit on F^2	1.010
Largest diff. peak and hole (e /Å^3)	0.486; -0.688
Flack- Parameter	-0.066(2)

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [Å^{2}x10^3] for **20**

Atom	x	y	z	Ueq
Ga(1)	-6921(1)	-572(1)	-7383(1)	34(1)
Si(1)	-5875(1)	209(1)	-8050(1)	49(1)
Si(2)	-7965(1)	-1297(1)	-6646(1)	41(1)
Li(1)	-12016(6)	-370(7)	-6261(8)	79(4)
N(1)	-6187(2)	-657(3)	-8140(2)	39(1)
N(2)	-6486(2)	383(2)	-7364(3)	42(1)
N(3)	-7992(2)	-775(2)	-7401(2)	40(1)
N(4)	-7008(2)	-1198(2)	-6555(2)	40(1)
O(1)	-11488(3)	-851(3)	-7086(3)	85(2)
O(2)	-12808(4)	-1072(4)	-5991(5)	139(3)
O(3)	-12341(6)	647(5)	-6486(5)	170(4)
O(4)	-11420(5)	-296(5)	-5356(5)	137(3)
C(1)	-5976(5)	779(4)	-8872(4)	74(2)
C(2)	-4862(4)	337(5)	-7784(4)	80(3)
C(3)	-6060(3)	-1146(3)	-8711(3)	38(1)
C(4)	-5421(3)	-1616(4)	-8713(4)	53(2)
C(5)	-5325(4)	-2085(4)	-9279(5)	74(2)
C(6)	-5805(4)	-2131(4)	-9846(5)	73(2)
C(7)	-6403(4)	-1656(4)	-9864(4)	60(2)
C(8)	-6551(3)	-1176(3)	-9306(3)	43(1)
C(9)	-4844(4)	-1578(5)	-8123(5)	79(2)
C(10)	-5686(7)	-2644(7)	-10474(7)	128(5)
C(11)	-7213(3)	-667(4)	-9363(4)	59(2)
C(12)	-6572(3)	984(3)	-6910(3)	43(1)
C(13)	-7016(5)	1574(4)	-7118(4)	67(2)
C(14)	-7105(4)	2139(4)	-6629(5)	76(2)
C(15)	-6791(5)	2155(4)	-5975(5)	73(2)
C(16)	-6343(4)	1581(4)	-5782(4)	64(2)
C(17)	-6210(3)	1003(4)	-6233(4)	50(2)
C(18)	-7379(6)	1586(5)	-7846(5)	97(3)
C(19)	-6906(7)	2796(5)	-5471(6)	117(4)
C(20)	-5690(4)	412(4)	-6005(4)	66(2)
C(21)	-8577(3)	-948(4)	-5905(4)	60(2)
C(22)	-8246(4)	-2264(4)	-6744(4)	66(2)
C(23)	-8618(3)	-510(3)	-7791(3)	43(1)
C(24)	-8932(3)	-914(4)	-8363(4)	54(2)
C(25)	-9512(3)	-631(5)	-8771(4)	67(2)
C(26)	-9806(4)	34(5)	-8653(4)	71(2)
C(27)	-9518(3)	445(4)	-8079(4)	68(2)
C(28)	-8935(3)	172(3)	-7636(4)	52(2)
C(29)	-8650(4)	-1663(4)	-8520(4)	71(2)
C(30)	-10434(4)	355(7)	-9123(5)	111(4)
C(31)	-8681(4)	591(4)	-7003(4)	71(2)
C(32)	-6495(3)	-1570(3)	-6113(3)	39(1)
C(33)	-6083(4)	-2155(3)	-6390(3)	50(2)
C(34)	-5557(4)	-2496(4)	-5950(4)	66(2)
C(35)	-5429(4)	-2296(4)	-5251(4)	69(2)
C(36)	-5851(4)	-1726(4)	-4986(4)	60(2)
C(37)	-6372(3)	-1359(3)	-5395(3)	47(2)

C(38)	-6231(4)	-2444(4)	-7127(4)	64(2)
C(39)	-4835(5)	-2665(5)	-4793(6)	101(3)
C(40)	-6840(4)	-766(3)	-5062(4)	61(2)
C(41)	-12481(11)	-619(12)	-7913(10)	273(13)
C(42)	-11702(7)	-871(9)	-7839(7)	154(6)
C(43)	-10563(6)	-1826(7)	-7191(7)	136(4)
C(44)	-10708(4)	-1061(6)	-7017(6)	95(3)
C(45)	-12670(11)	-2327(9)	-5409(9)	198(8)
C(46)	-12661(13)	-1860(7)	-6079(10)	207(9)
C(47)	-14115(8)	-1161(12)	-6197(10)	227(11)
C(48)	-13576(7)	-859(9)	-5759(11)	192(8)
C(49)	-11132(17)	1180(12)	-6973(17)	320(20)
C(50)	-11560(40)	1090(20)	-6730(20)	660(30)
C(51)	-13180(20)	1169(15)	-5976(14)	370(20)
C(52)	-13196(18)	952(16)	-6572(16)	360(20)
C(53)	-11899(13)	-926(11)	-4271(10)	219(8)
C(54)	-11466(17)	-1014(12)	-5000(14)	390(30)
C(55)	-10321(9)	349(10)	-5292(9)	189(7)
C(56)	-11043(10)	355(9)	-5230(20)	410(30)

Bond lengths [Å] for **20**

N(1)-Ga(1)	1.935(4)	C(23)-C(28)	1.421(9)
N(2)-Ga(1)	1.940(4)	C(23)-N(3)	1.423(6)
N(3)-Ga(1)	1.947(4)	C(32)-N(4)	1.415(7)
N(4)-Ga(1)	1.943(4)	C(32)-C(37)	1.415(9)
N(1)-Si(1)	1.715(5)	C(41)-C(42)	1.475(18)
N(2)-Si(1)	1.714(5)	C(42)-O(1)	1.458(13)
N(3)-Si(2)	1.714(5)	C(43)-C(44)	1.484(14)
N(4)-Si(2)	1.725(5)	C(44)-O(1)	1.452(10)
Li(1)-O(2)	1.990(14)	C(45)-C(46)	1.52(2)
Li(1)-O(4)	2.004(16)	C(46)-O(2)	1.500(15)
Li(1)-O(1)	2.017(16)	C(47)-C(48)	1.38(2)
Li(1)-O(3)	2.026(16)	C(48)-O(2)	1.492(13)
C(1)-Si(1)	1.876(7)	C(49)-C(50)	0.91(5)
C(2)-Si(1)	1.889(7)	C(50)-O(3)	1.68(5)
C(3)-C(8)	1.416(8)	C(51)-C(52)	1.18(3)
C(3)-N(1)	1.421(7)	C(52)-O(3)	1.64(3)
C(12)-N(2)	1.413(7)	C(53)-C(54)	1.57(2)
C(12)-C(17)	1.421(9)	C(54)-O(4)	1.497(19)
C(21)-Si(2)	1.881(7)	C(55)-C(56)	1.294(19)
C(22)-Si(2)	1.878(7)	C(56)-O(4)	1.407(18)

Bond angles [deg] for **20**

N(1)-Ga(1)-N(2)	79.5(2)	C(28)-C(23)-N(3)	121.2(5)
N(1)-Ga(1)-N(4)	125.96(19)	N(3)-C(23)-C(24)	120.7(5)
N(2)-Ga(1)-N(4)	124.6(2)	C(33)-C(32)-N(4)	120.0(5)
N(1)-Ga(1)-N(3)	129.44(19)	N(4)-C(32)-C(37)	121.2(5)
N(2)-Ga(1)-N(3)	124.78(17)	O(2)-Li(1)-O(4)	102.0(8)
N(4)-Ga(1)-N(3)	79.58(18)	O(2)-Li(1)-O(1)	103.5(7)
N(2)-Si(1)-N(1)	92.5(2)	O(4)-Li(1)-O(1)	115.3(6)
N(2)-Si(1)-C(1)	116.4(3)	O(2)-Li(1)-O(3)	117.7(7)
N(1)-Si(1)-C(1)	114.8(3)	O(4)-Li(1)-O(3)	105.2(7)
N(2)-Si(1)-C(2)	112.8(3)	O(1)-Li(1)-O(3)	113.0(8)
N(1)-Si(1)-C(2)	117.1(3)	C(3)-N(1)-Si(1)	128.7(4)
C(1)-Si(1)-C(2)	103.7(4)	C(3)-N(1)-Ga(1)	135.2(4)
N(3)-Si(2)-N(4)	92.8(2)	Si(1)-N(1)-Ga(1)	94.1(2)
N(3)-Si(2)-C(22)	117.2(3)	C(12)-N(2)-Si(1)	131.8(4)
N(4)-Si(2)-C(22)	112.1(3)	C(23)-N(3)-Si(2)	129.8(3)
N(3)-Si(2)-C(21)	113.2(3)	Si(2)-N(3)-Ga(1)	93.9(2)
N(4)-Si(2)-C(21)	117.7(3)	C(32)-N(4)-Si(2)	130.2(4)
C(22)-Si(2)-C(21)	104.3(3)	C(32)-N(4)-Ga(1)	135.0(4)
N(1)-C(3)-C(4)	121.2(5)	Si(2)-N(4)-Ga(1)	93.7(2)
N(2)-C(12)-C(17)	120.4(5)		

Table 7.3.15: Crystal data and structure refinement for $[\{Me_2Si(NPh)_2Li(OEt_2)\}_3In]$ (**22**)

Identification code	ipds3230
Empirical formula	$C_{54}H_{78}N_6Si_3O_3Li_3In$
Formula weight (g/mol)	1079.13
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	trigonal
Space group	$R\bar{3}c$
Unit cell dimensions	
a; b; c; (Å)	18.526(1); 18.516(1); 32.844(2)
γ (°)	120.00
Volume V ($Å^{3)}$	9750.5(1)
No. of formulas per unit cell Z	6
Calculated density (g/cm^{-1})	1.103
Absorption coefficient μ(MoKα) /mm^{-1}	0.459
F(000)	3408
Crystal size (mm)	0.30 x 0.30 x 0.30
Theta range for data collection (°)	2.88 - 25.95
Absorption correction	numerical
Total reflections collected	24130
Unique reflections observed	2112
Reflections independent with $(I>2\sigma(I))$; R_{int}	1853; 0.0350
Data / restraints / parameters	2112/0/244
R1; wR2 $(I>2\sigma(I))$	0.0333; 0.1322
R1; wR2 (all data)	0.0397; 0.1377
Goodness of fit on F^2	1.213
Largest diff. peak and hole ($e/Å^3$)	0.951; -0.392

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [Å^{2}x10^3] for **22**

Atom	**x**	**y**	**z**	**Ueq**
C(1)	6688(3)	6419(2)	465(1)	51(1)
C(2)	7477(3)	7239(3)	416(2)	70(1)
C(3)	9295(2)	5226(2)	541(1)	40(1)
C(4)	7375(2)	4942(2)	162(1)	22(1)
C(5)	7990(2)	5721(2)	10(1)	32(1)
C(6)	7879(2)	6024(2)	-359(1)	43(1)
C(7)	7174(2)	5585(2)	-583(1)	49(1)
C(8)	6564(2)	4813(2)	-442(1)	48(1)
C(9)	6664(2)	4496(2)	-79(1)	32(1)
N(1)	7441(2)	4629(2)	537(1)	20(1)
Si(1)	8325(1)	4992(1)	833	22(1)
In(1)	6667	3333	833	15(1)
O(1)	6667	5989(2)	833	42(1)
Li(1)	6667	4959(4)	833	35(2)

Bond lengths [Å] for **22**

In(1)-N(1)	2.305(2)	C(4)-N(1)	1.393(4)
N(1)-Si(1)	1.726(3)	C(4)-C(9)	1.397(4)
N(1)-Li(1)	2.062(5)	C(4)-C(5)	1.409(4)
O(1)-Li(1)	1.906(8)	C(5)-C(6)	1.394(5)
C(3)-Si(1)	1.886(3)	C(6)-C(7)	1.359(5)
C(1)-O(1)	1.438(4)	C(7)-C(8)	1.385(5)
C(1)-C(2)	1.500(6)	C(8)-C(9)	1.383(4)

Bond angles [deg] for **22**

N(1)-In(1)-N(1)^{III}	67.59(12)	C(4)-N(1)-Si(1)	126.8(2)
N(1)-In(1)-N(1)^{IV}	67.59(12)	C(4)-N(1)-Li(1)	94.27(19)
N(1)-In(1)-N(1)^{I}	103.48(7)	Si(1)-N(1)-Li(1)	106.47(12)
N(1)-In(1)-N(1)^{IV}	168.34(11)	C(4)-N(1)-In(1)	131.9(2)
N(1)^{IV}-In(1)-N(1)^{III}	103.48(12)	Si(1)-N(1)-In(1)	98.23(11)
N(1)-In(1)-N(1)^{II}	103.48(7)	Li(1)-N(1)-In(1)	86.97(18)
N(1)-Si(1)-N(1^{III})	95.94(17)	O(1)-C(1)-C(2)	113.2(3)
N(1)-Si(1)-C(3)	112.28(13)	N(1)-C(4)-C(5)	123.1(3)
N(1^{III})-Si(1)-C(3^{I})	114.37(13)	N(1)-C(4)-Li(1)	53.05(18)
N(1)-Si(1)-C(3)	114.36)13)	N(1)-Li(1)-C(4)^{III}	119.9(3)
N(1^{III})-Si(1)-C(3^{I})	112.27(13)	C(9)-C(4)-Li(1)	99.07(18)
C(3^{I})-Si(1)-C(3)	107.5(2)	C(5)-C(4)-Li(1)	116.6(3)

Symmetry transformations used to generate equivalent atoms:

I) y+1/3, x-1/3,-z+1/6 II) -x+4/3, -x+y+2/3,-z+1/6 III) -x+y+1,-x+1, z

IV) -y+1,x-y,z V) x-y+1/3, -y+2/3, -z+1/6

Table 7.3.16: Crystal data and structure refinement for $[Li(OC_4H_8)_4][\{Ph_2Si(NMes)_2\}_2In]$ **(23)**

Identification code	ipds3315
Empirical formula	$C_{76}H_{92}N_4Si_2O_4LiIn$
Formula weight (g/mol)	1303.51
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	$P\ 2_1\ c\ n$
Unit cell dimensions	
a; b; c; (Å)	13.912(1); 19.448(1); 27.432(2)
α; β; γ; (°)	90.00; 90.00; 90.00
Volume V ($Å^{3)}$	7421.63(1)
No. of formulas per unit cell Z	4
Calculated density (g/cm^{-1})	1.170
Absorption coefficient μ(MoKα) /mm^{-1}	0.399
F(000)	2768
Crystal size (mm)	0.38 x 0.52 x 0.60
Theta range for data collection (°)	2.22 - 25.95
Absorption correction	numerical
Total reflections collected	31691
Unique reflections observed	13483
Reflections independent with (I>2σ(I)); R_{int}	11382; 0.0284
Data / restraints / parameters	13483/0/802
R1; wR2 (I>2σ(I))	0.0331; 0.0807
R1; R2 (all data)	0.0462; 0.0945
Goodness of fit on F^2	1.068
Largest diff. peak and hole (e /$Å^3$)	0.559; -0.372
Flack- Parameter	-0.0124(2)

*Solvated Li atom is coordinated to four THF molecules having a disorder in C atoms therfore could not lead to better *w*R2 value in refinement.

Atomic coordinates [x10^{4}] and equivalent isotropic displacement parameters [Å^{2}x10^{3}] for **23**

Atom	**x**	**y**	**z**	**Ueq**
In(1)	-190(1)	2577(1)	1209(1)	35(1)
Si(1)	1621(1)	3227(1)	1139(1)	40(1)
Si(2)	-1662(1)	1568(1)	1168(1)	39(1)
Li(1)	-4937(9)	2740(6)	3708(4)	100(4)
N(1)	855(2)	3130(1)	1622(1)	40(1)
N(2)	865(2)	2916(2)	701(1)	39(1)
N(3)	-1685(2)	2438(2)	1071(1)	42(1)
N(4)	-482(2)	1503(1)	1335(1)	40(1)
O(1)	-5482(3)	3208(2)	3145(2)	104(1)
O(2)	-3570(4)	2658(2)	3581(2)	115(1)
O(3)	-5500(4)	1843(3)	3801(2)	144(2)
O(4)	-5058(5)	3263(3)	4275(2)	160(2)
C(1)	2733(3)	2672(2)	1197(1)	49(1)
C(2)	3667(3)	2899(2)	1117(2)	59(1)
C(3)	4455(4)	2453(3)	1140(2)	80(2)
C(4)	4317(4)	1771(3)	1244(2)	78(1)
C(5)	3394(4)	1529(3)	1329(2)	70(1)
C(6)	2627(3)	1971(2)	1305(1)	58(1)
C(7)	2069(3)	4130(2)	1028(1)	50(1)
C(8)	2309(4)	4566(2)	1412(2)	67(1)
C(9)	2664(4)	5215(3)	1330(2)	84(2)
C(10)	2774(4)	5453(3)	863(2)	85(2)
C(11)	2546(4)	5042(3)	480(2)	80(1)
C(12)	2199(3)	4387(2)	558(2)	66(1)
C(13)	795(3)	2986(2)	192(1)	40(1)
C(14)	1271(3)	2530(2)	-127(1)	55(1)
C(15)	1894(4)	1961(3)	74(2)	91(2)
C(16)	1187(4)	2625(3)	-627(1)	71(1)
C(17)	638(3)	3137(3)	-830(1)	68(1)
C(18)	578(5)	3251(4)	-1379(2)	110(2)
C(19)	164(3)	3573(2)	-515(1)	60(1)
C(20)	224(3)	3504(2)	-11(1)	45(1)
C(21)	-321(4)	4000(2)	312(1)	61(1)
C(22)	765(3)	3441(2)	2091(1)	47(1)
C(23)	1282(3)	3190(2)	2493(1)	63(1)
C(24)	1967(4)	2600(3)	2437(2)	87(2)
C(25)	1137(4)	3493(3)	2951(2)	87(2)
C(26)	502(5)	4025(3)	3025(2)	91(2)
C(27)	377(6)	4355(4)	3525(2)	152(4)
C(28)	11(4)	4265(3)	2627(2)	81(2)
C(29)	134(3)	4000(2)	2160(1)	57(1)
C(30)	-360(4)	4323(2)	1739(2)	74(1)
C(31)	-1912(3)	1042(2)	601(1)	56(1)
C(32)	-1364(4)	1152(3)	182(1)	77(1)
C(33)	-1468(5)	733(4)	-229(2)	102(2)
C(34)	-2123(6)	205(4)	-222(2)	110(3)
C(35)	-2663(5)	93(3)	172(3)	101(2)
C(36)	-2565(4)	509(2)	584(2)	70(1)
C(37)	-2518(3)	1234(2)	1646(1)	46(1)

C(38)	-2291(4)	642(2)	1906(2)	70(1)
C(39)	-2861(5)	391(3)	2275(2)	85(2)
C(40)	-3685(4)	741(3)	2404(2)	83(2)
C(41)	-3939(4)	1317(3)	2154(2)	75(1)
C(42)	-3355(3)	1561(2)	1771(2)	62(1)
C(43)	-2409(3)	2946(2)	1017(1)	48(1)
C(44)	-2740(3)	3309(2)	1423(2)	65(1)
C(45)	-2384(4)	3160(2)	1926(2)	79(1)
C(46)	-3430(4)	3834(3)	1353(3)	98(2)
C(47)	-3780(4)	4004(3)	899(4)	121(3)
C(48)	-4530(5)	4573(4)	841(5)	197(5)
C(49)	-3437(4)	3652(3)	508(3)	107(2)
C(50)	-2741(3)	3117(2)	549(2)	71(1)
C(51)	-2350(5)	2767(3)	99(2)	102(2)
C(52)	114(2)	1070(2)	1595(1)	39(1)
C(53)	682(3)	567(2)	1363(2)	57(1)
C(54)	553(4)	445(3)	827(2)	92(2)
C(55)	1362(4)	207(2)	1623(2)	79(1)
C(56)	1522(4)	312(3)	2115(2)	89(2)
C(57)	2351(6)	-40(4)	2384(3)	153(4)
C(58)	922(4)	775(3)	2345(2)	84(2)
C(59)	232(3)	1147(2)	2106(1)	56(1)
C(60)	-369(4)	1671(2)	2375(1)	68(1)
C(61)	-5168(14)	1325(9)	4110(8)	398(16)
C(62)	-5921(15)	959(8)	4308(6)	263(8)
C(63)	-6705(11)	1099(8)	4025(8)	260(8)
C(64)	-6380(11)	1618(7)	3655(5)	249(8)
C(65)	-2929(10)	3216(5)	3537(7)	260(8)
C(66)	-1982(8)	2974(7)	3448(6)	207(6)
C(67)	-2091(9)	2275(7)	3427(6)	221(7)
C(68)	-3058(7)	2060(5)	3491(4)	155(4)
C(69)	-5302(7)	2986(4)	2641(3)	138(3)
C(70)	-5368(10)	3624(5)	2354(3)	171(4)
C(71)	-5827(10)	4100(4)	2610(3)	193(5)
C(72)	-5830(6)	3901(3)	3120(2)	111(2)
C(73)	-4131(9)	3432(9)	4564(5)	110(4)
C(73A)	-4777(15)	2844(9)	4768(7)	165(9)
C(74)	-4526(6)	3431(5)	5055(3)	141(3)
C(75)	-5379(9)	3845(5)	4982(2)	183(5)
C(76)	-5726(7)	3698(5)	4464(3)	145(3)

Bond lengths [Å] for **23**

In(1)-N(1)	2.133(3)	C(31)-Si(2)	1.894(4)
In(1)-N(2)	2.128(3)	C(37)-Si(2)	1.888(4)
In(1)-N(3)	2.132(3)	C(1)-C(2)	1.389(6)
In(1)-N(4)	2.156(3)	C(1)-C(6)	1.404(6)
N(1)-Si(1)	1.710(3)	C(13)-N(2)	1.408(4)
N(2)-Si(1)	1.708(3)	C(22)-N(1)	1.427(4)
N(3)-Si(2)	1.712(3)	C(43)-N(3)	1.420(5)
N(4)-Si(2)	1.708(3)	C(52)-N(4)	1.382(4)
Li(1)-O(4)	1.864(11)	C(61)-O(3)	1.394(11)
Li(1)-O(3)	1.929(13)	C(62)-C(63)	1.366(17)
Li(1)-O(2)	1.941(13)	C(63)-C(64)	1.501(17)
Li(1)-O(1)	1.948(11)	C(64)-O(3)	1.361(13)
C(1)-Si(1)	1.893(4)	C(65)-O(2)	1.409(11)
C(7)-Si(1)	1.887(4)		

Bond angles [deg] for **23**

N(2)-In(1)-N(3)	126.56(10)	C(52)-N(4)-Si(2)	139.6(2)
N(2)-In(1)-N(1)	73.86(10)	C(52)-N(4)-In(1)	124.1(2)
N(3)-In(1)-N(1)	145.46(11)	Si(2)-N(4)-In(1)	93.80(12
N(2)-In(1)-N(4)	122.32(10)	O(4)-Li(1)-O(3)	110.3(6)
N(3)-In(1)-N(4)	73.79(11)	O(4)-Li(1)-O(2)	106.4(6)
N(1)-In(1)-N(4)	122.11(10)	O(3)-Li(1)-O(2)	110.3(6)
N(2)-Si(1)-N(1)	96.99(13)	O(4)-Li(1)-O(1)	111.8(6)
N(2)-Si(1)-C(7)	114.75(15)	O(3)-Li(1)-O(1)	111.7(6)
N(1)-Si(1)-C(7)	115.76(15)	O(2)-Li(1)-O(1)	106.1(5)
N(2)-Si(1)-C(1)	111.13(16)	C(2)-C(1)-C(6)	116.1(4)
N(1)-Si(1)-C(1)	112.40(15)	C(2)-C(1)-Si(1)	124.8(3)
C(7)-Si(1)-C(1)	105.89(17)	C(6)-C(1)-Si(1)	119.1(3)
N(4)-Si(2)-N(3)	97.66(14)	C(12)-C(7)-Si(1)	121.8(3)
N(4)-Si(2)-C(37)	113.13(15)	C(8)-C(7)-Si(1)	121.5(3)
N(3)-Si(2)-C(37)	115.81(16)	C(20)-C(13)-N(2)	120.2(3)
N(4)-Si(2)-C(31)	110.95(16)	N(2)-C(13)-C(14)	121.4(3)
N(3)-Si(2)-C(31)	113.77(16)	C(23)-C(22)-N(1)	121.0(4)
C(37)-Si(2)-C(31)	105.63(17)	C(29)-C(22)-N(1)	120.2(3)
C(22)-N(1)-Si(1)	134.9(2)	C(36)-C(31)-Si(2)	123.7(3)
C(22)-N(1)-In(1)	129.2(2)	C(32)-C(31)-Si(2)	119.5(3)
Si(1)-N(1)-In(1)	93.98(11)	C(42)-C(37)-Si(2)	123.4(3)
C(13)-N(2)-Si(1)	134.9(2)	C(38)-C(37)-Si(2)	119.9(3)
C(13)-N(2)-In(1)	129.3(2)	C(44)-C(43)-N(3)	120.2(3)
Si(1)-N(2)-In(1)	94.21(11)	C(50)-C(43)-N(3)	119.5(4)
C(43)-N(3)-Si(2)	135.9(2)	N(4)-C(52)-C(53)	121.8(3)
C(43)-N(3)-In(1)	128.5(2)	N(4)-C(52)-C(59)	121.0(3)
Si(2)-N(3)-In(1)	94.57(13)		

Table 7.3.17: Crystal data and structure refinement for $[Li(OC_4H_8)_4][\{Ph_2Si(NPh)_2\}_2In]\cdot 2THF$ **(24)**

Identification code	ipds3324
Empirical formula	$C_{79}H_{40}N_4Si_2O_6LiIn$
Formula weight (g/mol)	1319.09
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P\ 2_1/c$
Unit cell dimensions	
a; b; c; (Å)	17.901(1); 19.554(1); 21.454(1)
β (°)	98.02(1)
Volume V ($Å^{3)}$	7436.46
No. of formulas per unit cell Z	4
Calculated density (g/cm^{-1})	1.178
Absorption coefficient μ(MoKα) /mm^{-1}	0.401
F(000)	2680
Crystal size (mm)	0.14 x 0.49 x 0.68
Theta range for data collection (°)	2.18 - 25.90
Absorption correction	numerical
Total reflections collected	39996
Unique reflections observed	14244
Reflections independent with (I>2σ(I)); R_{int}	10595; 0.0507
Data / restraints / parameters	14244/0/838
R1; wR2 (I>2σ(I))	0.0486; 0.1331
R1; wR2 (all data)	0.0698; 0.1483
Goodness of fit on F^2	1.028
Largest diff. peak and hole (e /$Å^3$)	0.798; -0.536

*It recrystallizes with two non coordinating THF molecules having a disorder in C and O atoms are present in formula units per unit cell.

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [$Å^2$x10^3] for **24**

Atom	**x**	**y**	**z**	**Ueq**
In(1)	2395(1)	670(1)	2583(1)	32(1)
Si(1)	1640(1)	667(1)	1305(1)	33(1)
Si(2)	3312(1)	709(1)	3797(1)	32(1)
Li(1)	-2475(4)	5(4)	2271(4)	63(2)
N(1)	1506(1)	200(1)	1970(1)	35(1)
N(2)	2369(2)	1146(1)	1689(1)	35(1)
N(3)	2456(1)	1081(1)	3506(1)	34(1)
N(4)	3380(2)	258(2)	3116(1)	38(1)
O(1)	-2667(2)	-781(2)	1723(2)	77(1)
O(2)	-2268(2)	-375(2)	3110(2)	72(1)
O(3)	-1639(2)	567(2)	2122(2)	62(1)
O(4)	-3365(2)	571(2)	2143(2)	89(1)
O(5)	-2742(3)	2667(4)	-1224(4)	200(4)
O(6)	-2898(5)	3349(5)	1461(3)	216(4)
C(1)	816(2)	1215(2)	980(2)	43(1)
C(2)	770(2)	1883(2)	1186(2)	59(1)
C(3)	146(3)	2293(3)	976(3)	85(2)
C(4)	-437(3)	2027(3)	552(3)	83(2)
C(5)	-402(2)	1372(3)	334(2)	74(1)
C(6)	221(2)	968(2)	539(2)	58(1)
C(7)	1896(2)	103(2)	655(2)	43(1)
C(8)	2219(2)	-538(2)	796(2)	50(1)
C(9)	2438(3)	-965(3)	337(2)	69(1)
C(10)	2337(3)	-757(3)	-280(3)	81(2)
C(11)	2030(3)	-133(3)	-443(2)	74(2)
C(12)	1801(3)	302(2)	18(2)	59(1)
C(13)	1026(2)	-325(2)	2074(2)	36(1)
C(14)	532(2)	-635(2)	1586(2)	42(1)
C(15)	51(2)	-1160(2)	1707(2)	54(1)
C(16)	44(3)	-1399(2)	2314(2)	65(1)
C(17)	527(3)	-1108(2)	2799(2)	69(1)
C(18)	1007(2)	-584(2)	2682(2)	53(1)
C(19)	2870(2)	1604(2)	1481(2)	34(1)
C(20)	3441(2)	1903(2)	1908(2)	48(1)
C(21)	3966(2)	2343(2)	1716(2)	59(1)
C(22)	3947(2)	2507(2)	1088(2)	57(1)
C(23)	3384(2)	2227(2)	656(2)	54(1)
C(24)	2854(2)	1784(2)	850(2)	45(1)
C(25)	4124(2)	1331(2)	3975(2)	37(1)
C(26)	4554(2)	1498(2)	3501(2)	49(1)
C(27)	5135(2)	1967(2)	3599(2)	61(1)
C(28)	5311(2)	2284(2)	4170(2)	66(1)
C(29)	4898(2)	2128(2)	4652(2)	59(1)
C(30)	4312(2)	1657(2)	4555(2)	46(1)
C(31)	3260(2)	174(2)	4520(2)	38(1)
C(32)	3894(2)	2(2)	4947(2)	45(1)
C(33)	3850(2)	-442(2)	5443(2)	55(1)
C(34)	3167(3)	-721(2)	5531(2)	61(1)
C(35)	2524(2)	-549(2)	5125(2)	64(1)
C(36)	2572(2)	-108(2)	4623(2)	49(1)

C(37)	1964(2)	1500(2)	3776(1)	33(1)
C(38)	2105(2)	1719(2)	4404(2)	43(1)
C(39)	1606(2)	2146(2)	4655(2)	52(1)
C(40)	952(2)	2372(2)	4297(2)	57(1)
C(41)	797(2)	2157(2)	3680(2)	58(1)
C(42)	1290(2)	1727(2)	3423(2)	45(1)
C(43)	3912(2)	-190(2)	2938(2)	39(1)
C(44)	3854(3)	-428(2)	2318(2)	61(1)
C(45)	4369(3)	-884(3)	2128(3)	81(2)
C(46)	4963(3)	-1115(3)	2544(3)	82(2)
C(47)	5037(2)	-889(2)	3163(3)	69(1)
C(48)	4526(2)	-431(2)	3359(2)	49(1)
C(49)	-2215(4)	-1391(4)	1777(4)	123(3)
C(50)	-3435(6)	-1634(6)	1236(6)	169(4)
C(51)	-3396(4)	-882(4)	1334(4)	120(3)
C(52)	-1588(4)	-969(5)	3950(4)	142(4)
C(53)	-2358(5)	-1248(5)	3827(4)	173(5)
C(54)	-2794(3)	-829(3)	3356(3)	91(2)
C(55)	-1618(3)	1297(3)	2217(4)	120(3)
C(56)	-821(4)	1509(4)	2379(5)	131(3)
C(57)	-359(3)	870(3)	2381(3)	86(2)
C(58)	-881(2)	349(3)	2043(3)	71(1)
C(59)	-3959(4)	609(4)	2505(3)	107(2)
C(60)	-4614(5)	874(6)	2026(5)	180(5)
C(61)	-4291(4)	1315(5)	1622(4)	128(3)
C(62)	-3570(4)	991(6)	1569(4)	159(4)
C(63)	-2766(4)	2354(4)	-1787(3)	112(2)
C(64)	-1969(3)	2106(3)	-1852(3)	81(2)
C(65)	-1500(3)	2322(3)	-1242(3)	83(2)
C(66)	-3551(4)	3136(4)	976(3)	109(2)
C(67)	-3208(4)	2607(3)	590(3)	107(2)
C(68)	-2207(4)	3023(4)	1219(4)	117(2)
C(69)	-2868(7)	-1954(4)	1676(7)	181(5)
C(70)	-2480(3)	2464(3)	877(3)	94(2)
C(71)	-1978(4)	2844(4)	-954(4)	119(3)
C(72)	-1574(3)	-355(4)	3537(3)	94(2)
C(73)	4871(6)	-590(5)	112(4)	122(3)
C(74)	4155(12)	-90(20)	417(8)	622(15)
C(75)	349(6)	-40(12)	4529(5)	153(5)
C(76)	4559(6)	208(11)	223(5)	184(6)
C(77)	-317(7)	942(8)	5014(11)	300(13)
C(78)	4230(20)	576(16)	358(16)	710(50)
C(79)	14(13)	504(8)	4744(18)	370(30)

Bond lengths [Å] for **24**

In(1)- N(1)	2.127(2)	Li(1)-O(4)	1.928(8)
In(1)- N(2)	2.127(3)	C(1)-C(2)	1.385(6)
In(1)- N(3)	2.124(3)	C(1)-C(6)	1.407(5)
In(4)- N(4)	2.122(3)	C(1)-Si(1)	1.877(4)
N(1)-Si(1)	1.738(3)	C(7)-Si(1)	1.885(4)
N(2)-Si(1)	1.720(3)	C(13)-N(1)	1.378(4)
N(3)-Si(2)	1.734(2)	C(19)-N(2)	1.385(4)
N(4)-Si(2)	1.727(3)	C(25)-Si(2)	1.892(3)
Li(1)-O(1)	1.937(9)	C(31)-Si(2)	1.882(3)
Li(1)-O(2)	1.934(8)	C(37)-N(3)	1.386(4)
Li(1)-O(3)	1.918(8)	C(43)-N(4)	1.386(4)

Bond angles [deg] for **24**

N(4)-In(1)-N(3)	73.26(10)	N(2)-C(19)-C(20)	120.4(3)
N(4)-In(1)-N(1)	131.47(11)	C(30)-C(25)-Si(2)	123.7(3)
N(3)-In(1)-N(1)	132.57(10)	C(26)-C(25)-Si(2)	119.3(3)
N(4)-In(1)-N(2)	124.30(11)	C(36)-C(31)-Si(2)	119.7(2)
N(3)-In(1)-N(2)	131.85(11)	C(32)-C(31)-Si(2)	123.1(3)
N(1)-In(1)-N(2)	73.15(10)	N(3)-C(37)-C(38)	122.8(3)
N(2)-Si(1)-N(1)	94.26(12)	N(3)-C(37)-C(42)	120.6(3)
N(2)-Si(1)-C(1)	111.81(15)	N(4)-C(43)-C(44)	120.6(3)
N(1)-Si(1)-C(1)	114.49(15)	N(4)-C(43)-C(48)	122.8(3)
N(2)-Si(1)-C(7)	115.20(15)	O(3)-Li(1)-O(4)	107.2(4)
N(1)-Si(1)-C(7)	112.07(15)	O(3)-Li(1)-O(2)	108.8(4)
C(1)-Si(1)-C(7)	108.63(16)	O(4)-Li(1)-O(2)	113.6(4)
N(4)-Si(2)-N(3)	94.13(13)	O(3)-Li(1)-O(1)	115.4(4)
N(4)-Si(2)-C(31)	115.52(15)	O(4)-Li(1)-O(1)	107.2(4)
N(3)-Si(2)-C(31)	112.81(14)	O(2)-Li(1)-O(1)	104.8(4)
N(4)-Si(2)-C(25)	110.84(15)	C(13)-N(1)-Si(1)	133.2(2)
N(3)-Si(2)-C(25)	114.77(14)	C(13)-N(1)-In(1)	130.7(2)
C(31)-Si(2)-C(25)	108.40(14)	Si(1)-N(1)-In(1)	96.01(12)
C(2)-C(1)-C(6)	117.8(4)	C(19)-N(2)-Si(1)	132.9(2)
C(2)-C(1)-Si(1)	119.9(3)	C(19)-N(2)-In(1)	129.7(2)
C(6)-C(1)-Si(1)	122.3(3)	Si(1)-N(2)-In(1)	96.55(12)
C(8)-C(7)-Si(1)	120.1(3)	C(37)-N(3)-Si(2)	132.7(2)
C(12)-C(7)-Si(1)	123.2(3)	C(37)-N(3)-In(1)	131.28(19)
N(1)-C(13)-C(18)	121.0(3)	Si(2)-N(3)-In(1)	96.04(12)
N(1)-C(13)-C(14)	122.7(3)	C(43)-N(4)-Si(2)	133.5(2)
N(2)-C(19)-C(24)	123.3(3)	C(43)-N(4)-In(1)	130.0(2)
		Si(2)-N(4)-In(1)	96.31(12)

Table 7.3.18: Crystal data and structure refinement for $[Li(OEt_2)_3][Li_5\{EtSi(NMes)_3\}_2]$ **(25)**

Identification code	ipds3339
Empirical formula	$C_{70}H_{104}N_6Si_2O_3Li_6$
Formula weight (g/mol)	1175.41
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P\ 2_1/c$
Unit cell dimensions	
a; b; c; (Å)	19.039(1); 15.808(1); 23.360(2)
β (°)	90.723(1)
Volume V ($Å^{3)}$	7029.21
No. of formulas per unit cell Z	4
Calculated density (g/cm^{-1})	1.111
Absorption coefficient μ(MoKα) /mm^{-1}	0.098
F(000)	2544
Crystal size (mm)	0.10 x 0.10 x 0.80
Theta range for data collection (°)	2.06 - 25.95
Absorption correction	numerical
Total reflections collected	36858
Unique reflections observed	13507
Reflections independent with ($I>2\sigma(I)$); R_{int}	7631; 0.0740
Data / restraints / parameters	13507/0/798
R1; wR2 ($I>2\sigma(I)$)	0.0607; 0.1452
R1; wR2 (all data)	0.1185; 0.1680
Goodness of fit on F^2	0.931
Largest diff. peak and hole (e /$Å^3$)	0.448; -0.391

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [Å^{2}x10^3] for **25**

Atom	**x**	**y**	**z**	**Ueq**
Si(1)	1786(1)	2991(1)	-1213(1)	23(1)
Si(2)	2392(1)	1870(1)	461(1)	23(1)
Li(1)	2448(2)	1598(3)	-926(2)	33(1)
Li(2)	2835(2)	3144(3)	-479(2)	32(1)
Li(3)	1954(2)	3374(3)	252(2)	29(1)
Li(4)	1054(2)	2741(3)	-331(2)	28(1)
Li(5)	1480(2)	1318(3)	-273(2)	28(1)
Li(6)	2986(4)	-2996(4)	1719(3)	63(2)
N(1)	2657(1)	2726(2)	-1286(1)	26(1)
N(2)	2473(1)	1143(1)	-95(1)	26(1)
N(3)	1733(1)	3629(1)	-597(1)	24(1)
N(4)	2865(1)	2798(2)	359(1)	26(1)
N(5)	1365(1)	2050(1)	-998(1)	25(1)
N(6)	1508(1)	2210(1)	366(1)	24(1)
O(97)	2641(2)	-3879(2)	1238(1)	68(1)
O(98)	2980(2)	-3072(2)	2535(1)	77(1)
O(99)	3369(1)	-2034(2)	1370(1)	63(1)
C(1)	1293(1)	3458(2)	-1846(1)	32(1)
C(2)	1501(2)	3152(2)	-2445(1)	41(1)
C(3)	3186(1)	2866(2)	-1682(1)	26(1)
C(4)	3692(1)	2209(2)	-1773(1)	31(1)
C(5)	4218(1)	2306(2)	-2177(1)	41(1)
C(6)	4287(2)	3029(3)	-2506(2)	47(1)
C(7)	3823(2)	3677(2)	-2403(1)	44(1)
C(8)	3282(1)	3624(2)	-2002(1)	33(1)
C(9)	2826(2)	4402(2)	-1945(2)	41(1)
C(10)	3655(2)	1395(2)	-1439(1)	37(1)
C(11)	4835(2)	3099(3)	-2976(2)	77(1)
C(12)	1664(1)	4517(2)	-606(1)	25(1)
C(13)	2256(1)	5073(2)	-559(1)	28(1)
C(14)	2990(1)	4720(2)	-495(1)	36(1)
C(15)	2164(2)	5945(2)	-562(1)	35(1)
C(16)	1507(2)	6331(2)	-602(1)	35(1)
C(17)	1420(2)	7281(2)	-611(2)	51(1)
C(18)	933(1)	5793(2)	-638(1)	35(1)
C(19)	994(1)	4918(2)	-637(1)	29(1)
C(20)	338(1)	4388(2)	-664(2)	40(1)
C(21)	3475(1)	3123(2)	629(1)	26(1)
C(22)	4104(1)	3247(2)	312(1)	29(1)
C(23)	4165(1)	2980(2)	-301(1)	41(1)
C(24)	4693(1)	3639(2)	568(2)	40(1)
C(25)	4706(2)	3911(2)	1126(2)	43(1)
C(26)	5350(2)	4326(3)	1394(2)	77(1)
C(27)	4100(2)	3782(2)	1439(1)	40(1)
C(28)	2877(2)	3332(2)	1607(1)	41(1)
C(29)	2531(2)	1389(2)	1195(1)	36(1)
C(30)	2413(2)	440(2)	1272(2)	48(1)
C(31)	980(1)	2118(2)	787(1)	25(1)

C(32)	755(1)	2827(2)	1112(1)	29(1)
C(33)	1059(1)	3696(2)	1010(1)	36(1)
C(34)	246(1)	2732(2)	1532(1)	38(1)
C(35)	-70(2)	1965(2)	1645(1)	42(1)
C(36)	-587(2)	1871(3)	2128(2)	69(1)
C(37)	115(1)	1284(2)	1305(1)	39(1)
C(38)	621(1)	1343(2)	879(1)	30(1)
C(39)	764(2)	581(2)	513(1)	39(1)
C(40)	879(1)	1625(2)	-1362(1)	26(1)
C(41)	3496(1)	3400(2)	1209(1)	30(1)
C(42)	1843(2)	1069(2)	-2015(1)	43(1)
C(43)	574(2)	769(2)	-2197(1)	40(1)
C(44)	-139(2)	786(2)	-2079(2)	41(1)
C(45)	-668(2)	351(3)	-2470(2)	65(1)
C(46)	-332(2)	1210(2)	-1586(1)	38(1)
C(47)	147(1)	1618(2)	-1230(1)	31(1)
C(48)	-123(1)	2056(2)	-702(2)	40(1)
C(49)	2877(1)	423(2)	-183(1)	27(1)
C(50)	3590(1)	310(2)	10(1)	32(1)
C(51)	3960(2)	954(2)	378(2)	50(1)
C(52)	3957(2)	-420(2)	-142(2)	39(1)
C(53)	3679(2)	-1072(2)	-461(1)	38(1)
C(54)	4090(2)	-1867(2)	-602(2)	57(1)
C(55)	2979(2)	-977(2)	-635(1)	36(1)
C(56)	2581(1)	-261(2)	-504(1)	29(1)
C(57)	1813(2)	-264(2)	-686(1)	37(1)
C(58)	3087(3)	-1703(3)	824(2)	85(2)
C(59)	2311(3)	-1777(3)	822(2)	92(2)
C(60)	4093(2)	-1797(3)	1481(4)	114(2)
C(61)	4161(3)	-916(3)	1682(4)	128(3)
C(62)	3082(3)	-4360(4)	862(2)	96(2)
C(63)	3806(3)	-4015(4)	856(3)	100(2)
C(64)	2719(4)	-2456(5)	2930(3)	113(2)
C(65)	2386(3)	-1755(4)	2643(3)	123(2)
C(66)	3188(3)	-3838(4)	2854(2)	93(2)
C(67)	3517(4)	-4442(4)	2477(3)	124(2)
C(68)	1920(3)	-4186(4)	1203(3)	103(2)
C(69)	1487(3)	-3766(4)	1606(3)	120(2)
C(70)	1080(2)	1162(2)	-1852(1)	32(1)

Bond lengths [Å] for **25**

Li(1)-N(1)	2.013(5)
Li(1)-N(2)	2.070(6)
Li(1)-N(5)	2.188(5)
Li(2)-N(1)	2.022(5)
Li(2)-N(4)	2.030(5)
Li(2)-N(3)	2.247(5)
Li(3)-N(4)	1.971(5)
Li(3)-N(6)	2.045(5)
Li(3)-N(3)	2.061(5)
Li(4)-N(5)	1.997(5)
Li(4)-N(3)	2.012(5)
Li(4)-N(6)	2.017(5)
Li(5)-N(2)	1.950(5)
Li(5)-N(6)	2.053(5)
Li(5)-N(5)	2.059(5)
Li(6)-O(99)	1.877(7)
Li(6)-O(97)	1.903(7)
Li(6)-O(98)	1.911(7)
N(1)-Si(1)	1.721(2)
N(2)-Si(2)	1.742(2)
N(3)-Si(1)	1.762(2)
N(4)-Si(2)	1.739(2)
N(5)-Si(1)	1.765(2)
N(6)-Si(2)	1.777(2)
C(1)-C(2)	1.537(4)
C(1)-Si(1)	1.890(3)
C(3)-N(1)	1.394(3)
C(3)-C(8)	1.427(4)
C(10)-Li(1)	2.624(5)
C(12)-N(3)	1.410(3)
C(12)-Li(3)	2.749(5)
C(14)-Li(2)	2.510(6)
C(21)-N(4)	1.411(3)
C(23)-Li(2)	2.574(5)
C(29)-Si(2)	1.892(3)
C(31)-N(6)	1.423(3)
C(33)-Li(3)	2.527(5)
C(39)-Li(5)	2.580(5)
C(40)-N(5)	1.419(3)
C(48)-Li(4)	2.624(5)
C(49)-N(2)	1.391(3)
C(49)-Li(1)	2.663(6)
C(57)-Li(5)	2.758(6)
C(58)-O(99)	1.474(6)
C(58)-C(59)	1.482(7)
C(60)-O(99)	1.449(5)
C(60)-C(61)	1.474(7)
C(62)-O(97)	1.441(6)
C(62)-C(63)	1.483(7)
C(64)-O(98)	1.435(6)
C(64)-C(65)	1.438(9)
C(66)-C(67)	1.446(8)
C(66)-O(98)	1.473(6)
C(68)-C(101)	1.425(8)
C(68)-O(97)	1.457(6)

Bond angles [deg] for **25**

N(1)-Li(1)-N(2)	134.2(3)
N(1)-Li(1)-N(5)	82.48(19)
N(2)-Li(1)-N(5)	101.2(2)
N(1)-Li(2)-N(4)	144.3(3)
N(1)-Li(2)-N(3)	81.49(18)
N(4)-Li(2)-N(3)	103.0(2)
N(4)-Li(3)-N(6)	86.2(2)
N(4)-Li(3)-N(3)	112.4(2)
N(6)-Li(3)-N(3)	102.8(2)
N(5)-Li(4)-N(3)	86.73(19)
N(5)-Li(4)-N(6)	105.9(2)
N(3)-Li(4)-N(6)	105.6(2)
N(2)-Li(5)-N(6)	85.7(2)
N(2)-Li(5)-N(5)	110.4(2)
N(6)-Li(5)-N(5)	102.3(2)
O(99)-Li(6)-O(97)	118.1(4)
O(99)-Li(6)-O(98)	119.4(4)
O(97)-Li(6)-O(98)	122.4(4)
N(1)-Si(1)-N(3)	106.55(11)
N(1)-Si(1)-N(5)	105.35(11)
N(3)-Si(1)-N(5)	102.59(11)
N(1)-Si(1)-C(1)	119.15(12)
N(3)-Si(1)-C(1)	112.50(12)
N(5)-Si(1)-C(1)	109.23(12)
N(4)-Si(2)-N(2)	113.76(11)
N(4)-Si(2)-N(6)	102.68(11)
N(2)-Si(2)-N(6)	101.45(10)
N(4)-Si(2)-C(29)	113.38(13)
N(2)-Si(2)-C(29)	113.42(13)
N(6)-Si(2)-C(29)	110.87(12)
Li(2)-Li(3)-C(12)	73.82(18)
C(33)-Li(3)-C(12)	104.30(18)
Si(2)-Li(3)-C(12)	144.1(2)
N(5)-Li(4)-C(48)	77.15(17)
N(3)-Li(4)-C(48)	137.3(2)
N(6)-Li(4)-C(48)	116.8(2)
N(2)-Li(5)-C(39)	107.7(2)
N(6)-Li(5)-C(39)	78.55(18)
N(5)-Li(5)-C(39)	141.9(2)
N(2)-Li(5)-C(57)	73.72(16)
N(6)-Li(5)-C(57)	150.8(2)
N(5)-Li(5)-C(57)	104.2(2)
C(3)-N(1)-Si(1)	137.1(2)
C(3)-N(1)-Li(1)	124.4(2)
Si(1)-N(1)-Li(1)	88.80(16)
C(3)-N(1)-Li(2)	116.9(2)
Si(1)-N(1)-Li(2)	88.79(16)
Li(1)-N(1)-Li(2)	86.1(2)
C(2)-C(1)-Si(1)	117.3(2)
N(1)-C(3)-C(8)	125.4(3)
N(1)-C(3)-C(4)	118.4(3)
C(4)-C(10)-Li(1)	100.3(2)
N(3)-C(12)-C(19)	121.7(2)
N(3)-C(12)-C(13)	122.5(2)
C(19)-C(12)-C(13)	115.7(2)
N(3)-C(12)-Li(3)	46.90(16)
C(19)-C(12)-Li(3)	120.1(2)
C(13)-C(12)-Li(3)	101.43(19)
C(13)-C(14)-Li(2)	105.0(2)
C(13)-C(15)-C(16)	123.1(3)
C(12)-C(19)-C(20)	119.8(3)
N(4)-C(21)-C(41)	123.5(2)
N(4)-C(21)-C(22)	120.5(2)
C(22)-C(23)-Li(2)	92.19(19)
C(30)-C(29)-Si(2)	118.9(2)
C(38)-C(31)-N(6)	122.6(2)
C(32)-C(31)-N(6)	120.5(2)
C(32)-C(33)-Li(3)	100.9(2)
C(38)-C(39)-Li(5)	98.2(2)
C(141)-C(40)-N(5)	123.4(2)
N(5)-C(40)-C(47)	120.3(2)
C(47)-C(48)-Li(4)	99.29(19)
N(2)-C(49)-C(56)	118.8(2)
N(2)-C(49)-C(50)	125.3(3)
N(2)-C(49)-Li(1)	50.22(16)
C(56)-C(49)-Li(1)	94.0(2)
C(50)-C(49)-Li(1)	125.0(2)

Table 7.3.19: Crystal data and structure refinement for [{PhSi(NPh)$_3$(AlOEt$_2$)}$_2$]·2Tol (**26**)

Identification code	ipds3250
Empirical formula	$C_{70}H_{60}N_6Si_2Al_2O_2$
Formula weight (g/mol)	1127.38
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a; b; c; (Å)	10.535(1); 12.479(1); 12.889(1)
α; β; γ; (°)	83.803(1); 68.359(1); 83.127(1)
Volume V (Å$^{3)}$	1559.77
No. of formulas per unit cell Z	1
Calculated density (g/cm^{-1})	1.200
Absorption coefficient μ(MoKα) /mm^{-1}	0.135
F(000)	592
Crystal size (mm)	0.22 x 0.38 x 0.44
Theta range for data collection (°)	2.09 - 25.91
Absorption correction	numerical
Total reflections collected	11165
Unique reflections observed	5665
Reflections independent with (I>2σ(I); R$_{int}$	2967; 0.0683
Data / restraints / parameters	5665/0/362
R1; wR2 (I>2σ(I))	0.0683; 0.1656
R1; wR2 (all data)	0.1409; 0.2026
Goodness of fit on F^2	0.999
Largest diff. peak and hole (e /Å^3)	0.620; -0.549

*It recrystallizes with two non coordinating toluene molecules having a disorder in C atoms are present in formula units per unit cell.

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [Å^{2}x10^3] for **26**

Atom	**x**	**y**	**z**	**Ueq**
Al(1)	6000(1)	958(1)	283(1)	31(1)
Si(1)	3214(1)	165(1)	1473(1)	29(1)
N(1)	4413(3)	978(3)	1530(3)	31(1)
N(2)	3798(3)	-1186(3)	1214(3)	30(1)
N(3)	6881(3)	-378(3)	-149(3)	30(1)
O(1)	7123(3)	1883(2)	532(2)	39(1)
C(1)	1508(4)	316(3)	2640(3)	34(1)
C(2)	638(5)	-512(4)	2834(4)	48(1)
C(3)	-688(5)	-439(5)	3601(4)	58(1)
C(4)	-1186(5)	468(5)	4207(4)	60(2)
C(5)	-366(5)	1282(4)	4055(4)	53(1)
C(6)	977(4)	1213(4)	3276(4)	42(1)
C(7)	4302(4)	1475(3)	2520(3)	31(1)
C(8)	4200(5)	2596(4)	2516(4)	42(1)
C(9)	4133(5)	3101(4)	3444(4)	56(1)
C(10)	4189(5)	2496(5)	4376(4)	57(2)
C(11)	4288(5)	1392(4)	4402(4)	50(1)
C(12)	4350(5)	876(4)	3477(4)	42(1)
C(13)	4063(4)	-2024(3)	1929(3)	33(1)
C(14)	4771(4)	-3005(4)	1528(4)	42(1)
C(15)	5021(5)	-3844(4)	2246(4)	51(1)
C(16)	4570(6)	-3741(4)	3376(5)	61(2)
C(17)	3869(5)	-2774(4)	3793(4)	50(1)
C(18)	3600(4)	-1940(4)	3090(4)	39(1)
C(19)	7338(4)	-1326(3)	334(3)	32(1)
C(20)	7939(4)	-2244(4)	-264(4)	40(1)
C(21)	8460(5)	-3148(4)	215(4)	50(1)
C(22)	8404(5)	-3183(4)	1306(4)	56(1)
C(23)	7798(5)	-2303(4)	1917(4)	53(1)
C(24)	7267(4)	-1390(4)	1453(4)	41(1)
C(25)	7360(9)	3832(5)	166(7)	113(3)
C(26)	7765(5)	2757(4)	-285(4)	55(1)
C(27)	9035(7)	994(7)	961(8)	126(3)
C(28)	7717(7)	1582(5)	1406(6)	73(2)
C(29)	8587(7)	-4527(7)	3981(5)	114(3)
C(30)	9545(11)	-3883(6)	4038(6)	209(7)
C(31)	10930(10)	-4113(9)	3427(9)	327(16)
C(32)	11357(7)	-4987(11)	2760(7)	470(30)
C(33)	10398(12)	-5631(7)	2703(5)	217(10)
C(34)	9013(11)	-5401(6)	3313(6)	166(5)
C(35)	8130(20)	-5919(13)	3203(16)	252(10)

Bond lengths [Å] for **26**

N(1)-Al(1)	1.842(3)	C(1)-C(6)	1.395(6)
N(2)-Al(1^{I})	1.855(3)	C(1)-C(2)	1.405(6)
N(3)-Al(1)	1.845(3)	C(1)-Si(1)	1.874(4)
Al(1)-N(2^{I})	1.855(3)	C(7)-N(1)	1.439(5)
N(1)-Si(1)	1.739(3)	C(13)-N(2)	1.390(5)
N(2)-Si(1)	1.747(3)	C(19)-N(3)	1.394(5)
N(3)-Si(1^{I})	1.736(3)	C(26)-O(1)	1.470(6)
O(1)-Al(1)	1.876(3)	C(27)-C(28)	1.434(10)
Si(1)-N(3^{I})	1.736(3)	C(28)-O(1)	1.475(6)

Bond angles [deg] for **26**

N(3)-Al(1)-N(2^{I})	83.06(14)	N(1)-Si(1)-N(2)	115.86(16)
N(1)-Al(1)-N(3)	117.11(16)	N(3^{I})-Si(1)-C(1)	113.78(17)
N(1)-Al(1)-N(2)	128.91(15)	N(1)-Si(1)-C(1)	114.28(16)
N(1)-Al(1)-O(1)	106.05(14)	N(2)-Si(1)-C(1)	112.78(18)
N(3)-Al(1)-O(1)	113.35(14)	C(7)-N(1)-Si(1)	123.8(3)
N(2^{I})-Al(1)-O(1)	107.00(15)	C(7)-N(1)-Al(1)	121.7(3)
N(3^{I})-Si(1)-N(1)	108.04(17)	Si(1)-N(1)-Al(1)	113.72(16)
N(3^{I})-Si(1)-N(2)	89.56(15)		

Symmetry transformations used to generate equivalent atoms:

I) -x+1,-y,-z

Table 7.3.20: Crystal data and structure refinement for
$[\{MeSi(NPh)_3(AlOEt_2)\}_2]\cdot 2Tol$ (**27**)

Identification code	ipds3366
Empirical formula	$C_{60}H_{72}N_6Si_2Al_2O_2$
Formula weight (g/mol)	1019.38
Temperature (K)	220
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a; b; c; (Å)	10.902(1); 11.913(1); 12.703(1)
α; β; γ; (°)	62.29(1); 77.33(1); 86.720(1)
Volume V ($Å^{3)}$	1423.18
No. of formulas per unit cell Z	1
Calculated density (g/cm^{-1})	1.189
Absorption coefficient μ(MoKα) /mm^{-1}	0.140
F(000)	544
Crystal size (mm)	0.10 x 0.30 x 0.44
Theta range for data collection (°)	2.36 - 26.02
Absorption correction	numerical
Total reflections collected	10241
Unique reflections observed	5162
Reflections independent with ($I>2\sigma(I)$); R_{int}	3178; 0.044
Data / restraints / parameters	5162/0/325
R1; wR2 ($I>2\sigma(I)$)	0.0511; 0.115
R1; wR2 (all data)	0.0961; 0.1343
Goodness of fit on F^2	0.971
Largest diff. peak and hole (e /$Å^3$)	0.515; -0.281

[*]It crystallizes with two toluene non coordinating molecules formula units per unit cell.

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [Å^{2}x10^3] for **27**

Atom	**x**	**y**	**z**	**Ueq**
Al(1)	3455(1)	4564(1)	6061(1)	26(1)
Si(1)	4165(1)	4070(1)	4227(1)	26(1)
N(1)	5698(2)	4604(2)	3397(2)	27(1)
N(2)	3353(2)	5272(2)	4453(2)	27(1)
N(3)	4047(2)	3213(2)	5796(2)	27(1)
O(1)	1844(2)	4110(2)	7085(2)	37(1)
C(1)	3365(3)	3278(3)	3571(3)	42(1)
C(2)	6115(2)	4632(3)	2227(2)	29(1)
C(3)	6570(3)	3563(3)	2130(3)	43(1)
C(4)	6998(3)	3597(3)	1008(3)	52(1)
C(5)	6974(3)	4702(4)	-44(3)	52(1)
C(6)	6520(3)	5767(3)	27(3)	49(1)
C(7)	6101(3)	5741(3)	1148(2)	38(1)
C(8)	3022(2)	6419(2)	3571(2)	28(1)
C(9)	3055(3)	6630(3)	2388(2)	37(1)
C(10)	2716(3)	7764(3)	1521(3)	46(1)
C(11)	2325(3)	8731(3)	1800(3)	48(1)
C(12)	2284(3)	8550(3)	2970(3)	42(1)
C(13)	2626(3)	7420(3)	3837(2)	34(1)
C(14)	4359(3)	1964(2)	6482(2)	31(1)
C(15)	4173(3)	1425(3)	7753(2)	39(1)
C(16)	4457(3)	180(3)	8446(3)	53(1)
C(17)	4930(4)	-563(3)	7902(4)	64(1)
C(18)	5137(4)	-58(3)	6654(3)	56(1)
C(19)	4863(3)	1191(3)	5951(3)	42(1)
C(20)	537(4)	3276(5)	6212(4)	90(2)
C(21)	1153(3)	2996(3)	7247(3)	59(1)
C(22)	422(4)	4666(4)	8555(3)	76(1)
C(23)	1047(3)	5079(3)	7251(3)	50(1)
C(24)	9367(5)	947(4)	2066(4)	74(1)
C(25)	10484(4)	1613(4)	1950(5)	75(1)
C(26)	10548(6)	1839(5)	2891(6)	104(2)
C(27)	9653(7)	1505(6)	3916(6)	109(2)
C(28)	8537(7)	838(6)	4035(5)	111(2)
C(29)	8481(4)	607(4)	3106(5)	89(2)
C(30)	9259(5)	696(5)	1105(5)	104(2)

Bond lengths [Å] for **27**

Al(1)-N(1^{I})	1.824(2)	C(2)-C(3)	1.389(4)
N(1)-Al(1^{I})	1.824(2)	C(2)-C(7)	1.396(4)
N(2)-Al(1)	1.840(2)	C(2)-N(1)	1.441(3)
N(3)-Al(1)	1.847(2)	C(3)-C(4)	1.381(4)
N(1)-Si(1)	1.742(2)	C(8)-N(2)	1.396(3)
N(2)-Si(1)	1.744(2)	C(14)-N(3)	1.398(3)
N(3)-Si(1)	1.744(2)	C(21)-O(1)	1.470(4)
O(1)-Al(1)	1.8771(19)	C(22)-C(23)	1.494(4)
C(1)-Si(1)	1.867(3)	C(23)-O(1)	1.471(3)

Bond angles [deg] for **27**

N(3)-Al-N(2)	82.97(10)	Si(1)-N(1)-Al(1’)	114.81(11)
N(1’)-Al-N(3)	124.78(10)	N(3)-Si(1)-N(2)	88.88(10)
N(1’)-Al-N(2)	121.14(10)	N(2)-Si(1)-C(1)	115.80(13)
N(1’)-Al-O	106.41(10)	N(3)-Si(1)-C(1)	114.73(12)
N(2)-Al-O	110.69(10)	N(1)-Si(1)-N(3)	113.62(11)
N(3)-Al-O	109.11(10)	N(1)-Si(1)-N(2)	110.68(11)
C(2)-N(1)-Si(1)	120.19(19)	N(1)-Si(1)-C(1)	111.41(12)
C(2)-N(1)-Al(1’)	123.46(18)		

Symmetry transformations used to generate equivalent atoms:

I) -x+1,-y+1,-z+1

Table 7.3.21: Crystal data and structure refinement for [{PhSi(NPh)$_2$(NHPh)(n-BuIn)}$_2$]·Tol **(28)**

Identification code	ipds3175
Empirical formula	$C_{66}H_{60}N_6Si_2In_2$
Formula weight (g/mol)	1222.00
Temperature (K)	220
Wavelength(Å)	0.71073
Crystal system	monoclinic
Space group	P 2_1/c
Unit cell dimensions	
a; b; c; (Å)	10.443(1); 15.888(2); 18.505(2)
β (°)	90.30(1)
Volume V (Å$^{3)}$	3069.78
No. of formulas per unit cell Z	4
Calculated density (g/cm^{-1})	1.359
Absorption coefficient μ(MoKα) /mm^{-1}	0.838
F(000)	1276
Crystal size (mm)	0.22 x 0.22 x 0.52
Theta range for data collection (°)	2.55 - 25.89
Absorption correction	numerical
Total reflections collected	4960
Unique reflections observed	4461
Reflections independent with (I>2σ(I)); R_{int}	4504; 0.0200
Data / restraints / parameters	4461/0/298
R1;wR2 (I>2σ(I))	0.0627; 0.1926
R1; wR2 (all data)	0.0862; 0.217
Goodness of fit on F^2	0.962
Largest diff. peak and hole (e /Å^3)	1.079; -1.117

*It recrystallizes with one non coordinating toluene molecule having a disorder in C atoms, is present in formula units per unit cell.

Atomic coordinates [x10^4] and equivalent isotropic displacement parameters [Å^{2}x10^3] for **28**

Atom	**x**	**y**	**z**	**Ueq**
In(1)	516(1)	-883(1)	5333(1)	34(1)
Si(1)	196(2)	466(1)	6410(1)	37(1)
N(1)	886(6)	505(4)	5525(3)	32(1)
N(2)	-422(7)	-521(4)	6308(3)	38(2)
N(3)	1364(8)	620(5)	7049(4)	45(2)
C(1)	1760(11)	-1963(6)	5240(5)	52(2)
C(2)	-1276(10)	-807(5)	7503(4)	42(2)
C(3)	2695(12)	-614(7)	6847(6)	62(3)
C(4)	4940(14)	-597(8)	7082(8)	78(4)
C(5)	2021(8)	983(5)	5381(4)	34(2)
C(6)	-1075(9)	1307(6)	6599(4)	42(2)
C(7)	-742(11)	2122(6)	6814(6)	58(3)
C(8)	-2451(10)	-2252(6)	6984(5)	51(2)
C(9)	4198(11)	1926(7)	5046(6)	60(3)
C(10)	-1120(8)	-1017(5)	6772(4)	34(2)
C(11)	3868(13)	-1023(7)	6850(7)	69(3)
C(12)	-1672(15)	2732(8)	6880(7)	76(3)
C(13)	-2985(15)	2532(8)	6741(7)	82(4)
C(14)	-1992(10)	-1331(6)	7968(5)	51(2)
C(15)	-1738(9)	-1743(5)	6517(5)	43(2)
C(16)	3660(12)	633(7)	7313(7)	66(3)
C(17)	-2326(9)	1100(6)	6472(5)	47(2)
C(18)	3043(9)	600(6)	5076(5)	46(2)
C(19)	3173(11)	2322(7)	5367(5)	57(3)
C(20)	-2595(10)	-2041(6)	7706(5)	48(2)
C(21)	2080(9)	1844(6)	5536(5)	47(2)
C(22)	4140(11)	1078(7)	4905(6)	60(3)
C(23)	-3316(12)	1710(8)	6525(6)	69(3)
C(24)	4863(13)	209(9)	7338(8)	79(4)
C(25)	2541(9)	201(5)	7069(4)	39(2)
C(26)	1511(11)	-2616(5)	5850(5)	56(3)
C(27)	2523(13)	-3321(7)	5812(6)	70(3)
C(28)	2243(17)	-3990(8)	6398(8)	86(4)

Bond lengths [Å] for **28**

In(1)-N(1)	2.136(7)	C(2)-C(3)	1.355(13)
In(1)-N(2)	2.266(6)	C(5)-C(6)	1.403(12)
In(1)-N(2’)	2.237(6)	C(4)-C(5)	1.386(16)
In(1)-C(25)	2.159(10)	C(3)-C(4)	1.367(19)
Si(1)-N(3)	1.793(7)	C(25)-C(26)	1.514(14)
N(3)-H(1)	0.86(2)	C(26)-C(27)	1.513(9)
Si(2)-C(1)	1.916(9)	C(27)-C(28)	1.5008(1)
C(1)-C(2)	1.37(2)		
C(1)-C(6)	1.399(12)		

Bond angles [deg] for **28**

N(25)-In-N(2’)	103.1(3)	N(1)-Si-N(2)	109.7(4)
N(1)-In-C(25)	124.1(3)	N(3)-Si-C(1)	113.5(4)
N(25)-In-N(2)	71.6(2)	N(2)-Si-C(1)	105.5(4)
C(25)-In-N(2’)	123.3(3)	N(1)-Si-C(1)	115.1(3)
N(2’)-In-N(2)	87.7(2)	C(7)-N(1)-Si(1)	131.1(6)
C(9)-In-N(2)	133.1(3)	C(7)-N(1)-In(1)	128.53(3)
N(1)-Si-N(3)	118.4(4)	Si(1)-N(1)-In(1)	99.976(4)
N(3)-Si-N(2)	94.8(3)		

Symmetry transformations used to generate equivalent atoms:

I) -x,-y,-z+1

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EIDESSTATTLICHE ERKLÄRUNG

Ich erkläre hiermit, die vorliegende Dissertationsschrift selbständig und nur unter Verwendung der angegebenen Quellen und Hilfsmittel angefertigt zu haben.

Die Arbeit wurde bisher an keiner anderen Hochschule oder Universität zur Promotion eingereicht.

DECLARATION

I declare that all work presented herein was completed by myself, the undersigned, unless explicitly stated and referenced otherwise. No part of this work has been previously presented in any other university or high school.

……………………….

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