

## THE REACTION OF $TiCl_4$ AND $CpTiCl_3$ WITH TRIDENTATE TRIAMINOSILYL LIGANDS. CRYSTAL AND MOLECULAR STRUCTURE OF A TITANABICYCLOHEPTANE WITH AN UNUSUAL Si-N-Li-Cl-Ti CHAIN

D.J. BRAUER, H. BÜRGER and G.R. LIEWALD

*Anorganische Chemie, Fachbereich 9, Universität-Gesamthochschule, D-5600 Wuppertal (F.R.G.)*

(Received December 16th, 1985)

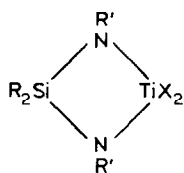
### Summary

The reaction of lithiated triaminosilanes  $RSi(NLiR')_3$  ( $R = Me, t-Bu, Ph$ ;  $R' = t-Bu, SiMe_3$ ) with  $TiCl_4$  and  $CpTiCl_3$  gives, in poor yields, the novel spiro- and monocyclic sila-titana-diazacyclobutane derivatives  $Ti[(NR')_2Si(Me)(NHR')]_2$  ( $R' = SiMe_3$  (VII)),  $R'NH(Ph)SiNR'TiX^1X^2NR'$  ( $R' = SiMe_3, X^1 = X^2 = Cl$  (VIII),  $R' = t-Bu, X^1 = X^2 = Cl$  (X) and  $R' = SiMe_3, X^1 = Cl, X^2 = Cp$  (XIII)). Cleavage of VII with  $TiCl_4$  yields  $R'NH(Me)SiNR'TiCl_2NR'$  ( $R' = SiMe_3$ ), while  $Me_2SiNR'-TiCl_2NR'$  ( $R' = SiMe_3$  (XI) and  $t-Bu$  (XII)) were obtained with  $Me_2Si(NHSiMe_3)_2$  and  $Me_2Si(NH-t-Bu)_2$ . If the synthesis of XIII is performed at  $-30^\circ C$ , the monolithiated cyclic titanium amide  $R'(Li)N(Ph)SiNR'Ti(Cl)(Cp)NR'$  ( $R' = SiMe_3$  (XIV)) is isolated as diethyletherate. It crystallizes in the monoclinic space group  $P2_1/n$  with  $a$  11.033(1),  $b$  17.504(2),  $c$  18.001(2) Å,  $\beta$  98.21(2)°,  $Z = 4$ ,  $D_x$  1.151 g  $cm^{-3}$  and  $R = 0.045$  for 4277 observed reflections. The structure contains an unusual heteronuclear bicyclo[3.1.1]heptane system with CpTi and PhSi groups at the bridge-heads. The main bridge contains the Ti-bonded Cl atom, a  $Li \cdot O(C_2H_5)_2$  moiety and an  $NSiMe_3$  fragment whereas  $NSiMe_3$  groups are found in the other two bridges. Important bond distances are Li-Cl (2.455(7) Å), Ti-Cl (2.364(1) Å) and Ti-N (1.859(6) Å).

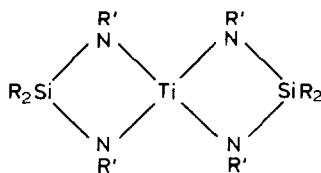
### Introduction

Monocyclic (A) and spirocyclic titanium amides (B) with siladiazatitanacyclobutane structure have been described previously [1-3]. These derivatives are readily formed, and they show both high volatility and thermal stability. Structural investigations reveal that although the Ti-N bond lengths in two spiranes (B:  $R = Me, R' = t-Bu$  [2] and B:  $R = Ph, R' = SiMe_3$  [3]) are longer than those in a monocyclic derivative A:  $R' = t-Bu$  [4], they are still shorter than in  $CiTi[N(SiMe_3)_2]_3$

[5a]. These observations suggest that the coordination sites of a tetravalent Ti atom are more easily saturated by bidentate diaminosilyl ligands than by monodentate bis(trimethylsilyl)amino groups. In fact, it has not been possible to place more than three of the latter ligands about a Ti atom (e.g.,  $\text{Ti}[\text{N}(\text{SiMe}_3)_2]_3$  or  $\text{CITi}[\text{N}(\text{SiMe}_3)_2]_3$  [5]).



(A)



(B)

(R = Me;

(R = Me, Ph;

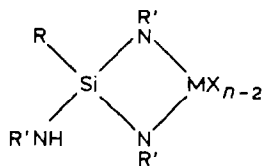
R' = *i*-Pr, *t*-Bu,  $\text{SiMe}_3$ ;

R' = *i*-Pr, *t*-Bu,  $\text{SiMe}_3$ )

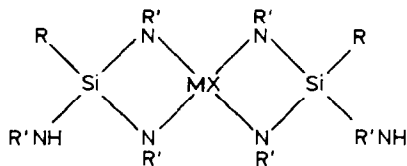
X = F, Cl, Br,  $\text{NMe}_2$ ,  $\text{NEt}_2$ )

Compounds **A** and **B** may be conveniently synthesized from dimetallated diaminosilanes  $\text{R}_2\text{Si}[\text{N}(\text{M})\text{R}']_2$ . Some of these compounds have been characterized, e.g. M = Li, (I), Na, K, Rb, or Cs for R = Me and R' =  $\text{Me}_3\text{Si}$  [6] and  $\text{Me}_2\text{Si}[\text{N}(\text{Li})\text{t-Bu}]_2$  (II) [7], but usually the metallated (preferentially lithiated) amine ligands are not isolated but used for reactions in situ.

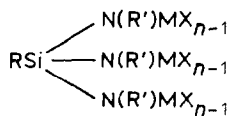
The ability of triaminosilanes to function as tridentate ligands in transition metal complexes does not appear to have been tested previously. Acting as bidentate (**C**, **D**) or tridentate ligands (**E**, **F**) they may form different kinds of complexes with transition metal halides  $\text{MX}_n$ .



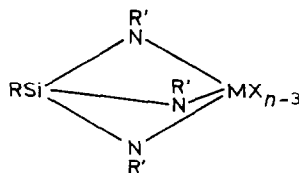
(C)



(D)



(E)



(F)

In previous investigations we have studied the syntheses and molecular structures of several trisubstituted triaminosilanes  $\text{RSi}[\text{NR}'(\text{Li})]_3$  with R = Me, R' =  $\text{SiMe}_3$  (III), R = *t*-Bu, R' =  $\text{SiMe}_3$  (IV), R = Ph, R' =  $\text{SiMe}_3$  (V) [8] and R = Ph, R' = *t*-Bu (VI) [7]. These are suitable starting materials for the preparation of type **C** to **F** complexes, and have been shown to form cluster-shaped dimers with  $\text{Li}_6$  cores.

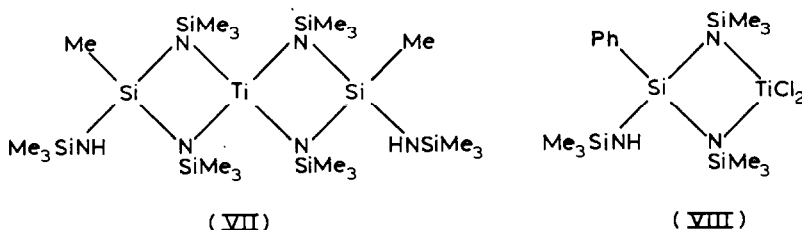
The present study was directed towards the synthesis of bicyclo[1.1.1]pentane-type transition metal complexes **F** with titanium as one of the ring atoms. Although this goal was not achieved, we made some interesting observations which are reported below.

### The reaction of lithiated triaminosilanes with $\text{TiCl}_4$

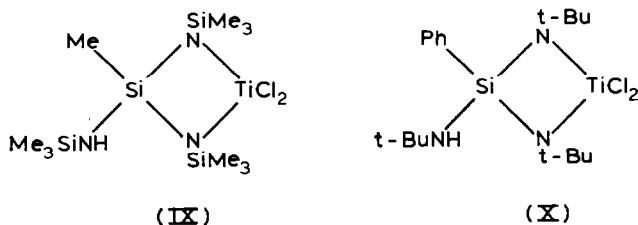
Previous investigations [1,2] have shown that  $\text{TiCl}_4$  and dilithiated bis-(amino)silanes (I,II) form monocyclic (**A**) or spirobicyclic titanium amides (**B**) depending on the experimental conditions. Accordingly we have treated  $\text{TiCl}_4$  in a 1/1 molar ratio with the trilitiated triaminosilanes III, IV, V and VI. The intended reaction (eq. 1) however did not proceed, unexpected compounds being formed instead.



Thus the reaction of III with  $\text{TiCl}_4$  in a 1/1 molar ratio gave a 9% yield of the novel spirocyclic titanium tetraamide VII, while no reaction product could be isolated from the analogous reaction with IV.



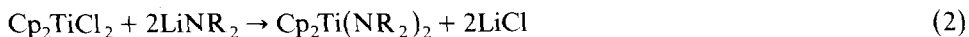
In contrast, the related phenyl compound V yielded 14% of the monocyclic dichlorotitanium diamide VIII. The surprising appearance of NH groups in VII and VIII is certainly not due to accidental partial hydrolysis of III and V or incomplete lithiation of the triaminosilanes. Nevertheless reaction of partially lithiated triaminosilanes, metallated by addition of only two equivalents of *n*-BuLi, gave substantially higher yields of VII and VIII, (28 and 30%, respectively). We believe that the hydrogen atom was abstracted from diethyl ether which was used as a solvent. The analogous methyl substituted monocyclic amide IX was obtained by cleavage of VIII with  $\text{TiCl}_4$  in a yield of 68%. Finally, attempts to synthesize *t*-butylamino derivatives employing VI as a starting material failed. However, the monocyclic dichlorotitanium diamide X was obtained in poor yield, 16%, from the reaction of  $\text{PhSi}(\text{NH-}t\text{-Bu})_3$ , which had been partially lithiated as described above, with  $\text{TiCl}_4$ .



Presumably higher yields would have been obtained if only dilithiated triaminosilanes had been employed; however, the partially metallated materials are mixtures in which the trilitiated species dominate [7,8].

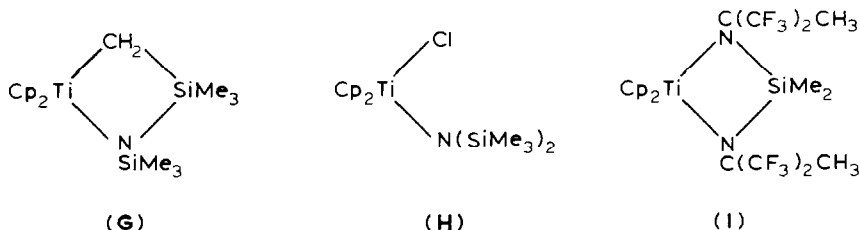
### Lithiated triaminosilanes and cyclopentadienyltitanium chlorides

Cyclopentadienyltitanium chlorides  $\text{CpTiCl}_3$  and  $\text{Cp}_2\text{TiCl}_2$  are particularly stable tri- and bifunctional titanium derivatives, and their chemistry is well developed. Cyclopentadienyltitanium amides were first obtained by Chandra and Lappert [9] according to eqs. 2 and 3:

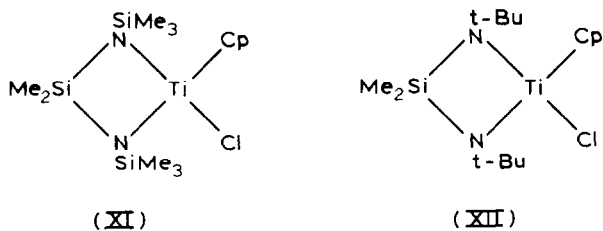


Attempts to synthesize bis(trimethylsilyl)amino analogues according to eq. 2 ( $\text{R} = \text{SiMe}_3$ ) failed. Thus reduction to  $(\text{Cp}_2\text{TiCl})_2$  was observed in refluxing THF when  $\text{Cp}_2\text{TiCl}_2$  was treated with  $\text{NaN}(\text{SiMe}_3)_2$  or  $\text{KN}(\text{SiMe}_3)_2 \cdot 2$  dioxane [10], whereas **G** was isolated from the reaction of  $\text{Cp}_2\text{TiCl}_2$  with  $\text{LiN}(\text{SiMe}_3)_2$  in pentane [11]. Subsequently formation of **G** via HCl elimination from the intermediate **H** was observed [12].

On the other hand, a cyclic diaminosilyl dicyclopentadienyltitanium diamide (**I**) has been obtained with the  $\text{Me}_2\text{Si}[\text{NC}(\text{CF}_3)_2\text{CH}_3]_2$  ligand [13].



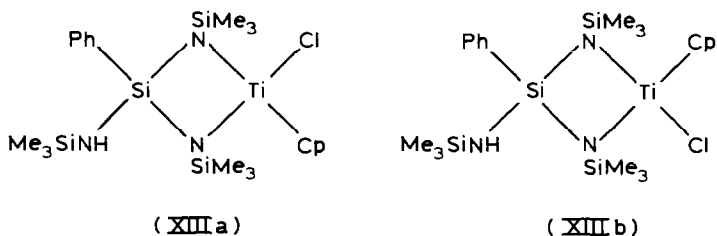
In order to examine the reactivity of  $\text{Cp}_2\text{TiCl}_2$  and  $\text{CpTiCl}_3$  towards polyolithiated polyaminosilanes, these halides were first treated with the dilithiated bidentate ligands  $\text{Me}_2\text{Si}[\text{N}(\text{Li})\text{SiMe}_3]_2$  (**I**) and  $\text{Me}_2\text{Si}[\text{N}(\text{Li})\text{t-Bu}]_2$  (**II**). While reactions with  $\text{Cp}_2\text{TiCl}_2$  lead to tar-like products from which individual molecules could not be isolated, the others produced the cyclic CpTi derivatives **XI** and **XII** in yields of 53 and 18%, respectively.



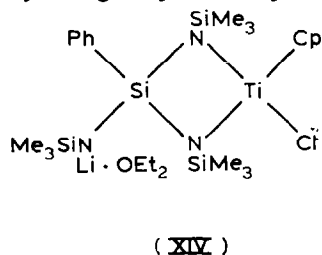
The ready formation of **XI** prompted us to investigate the reaction of  $\text{CpTiCl}_3$  with **III** to **VI** according to eq. 1. However, no products could be isolated from reactions of **III**, **IV** and **VI** under a variety of conditions. However, the reaction of **V** with  $\text{CpTiCl}_3$  at room temperature in ether/petroleum ether gave a very small amount of an orange crystalline product (**XIII**), which was isolated from the tar by sublimation in vacuo and analyzed by spectroscopic methods. In contrast to the observations made in the course of the synthesis of **IX** and **X**, even the use of "dilithiated" amine did not lead to any isolable material. The IR spectrum of **XIII**

suggests that NH ( $3370\text{ cm}^{-1}$ ), SiNHSi ( $955\text{ cm}^{-1}$ ), PhSi ( $1113\text{ cm}^{-1}$ ) and CpTi groups ( $1020\text{ cm}^{-1}$ ) are present. The  $^1\text{H}$  NMR spectrum reveals two doublets ( $\delta$  0.01/0.07 and 0.23/0.29 ppm), in a 2/1 intensity ratio, attributed to NSiMe<sub>3</sub> and NHSiMe<sub>3</sub> groups, respectively. Furthermore, a signal at 6.44 ppm is attributed to the Cp ligand while signals at 7.32 and 7.77 ppm are typical of *m*-, *p*-, and *o*-C<sub>6</sub>H<sub>5</sub> protons respectively. The mass spectrum shows diagnostic peaks at 515 ( $M^+$ ), 15%, and 500 ( $M - \text{CH}_3$ )<sup>+</sup>, 88%, both associated with the isotopic pattern expected for one Ti and Cl atom per ion.

From all this evidence we conclude that the orange product is most likely to be a 1/1 mixture of the two stereoisomers (a) and (b) of XIII.



The modest success in synthesizing XIII prompted us to investigate the reaction of CpTiCl<sub>3</sub> with V in diethyl ether at  $-30^\circ\text{C}$ . After filtration of the LiCl and partial removal of the solvent yellow crystals separated out, and after recrystallization from petroleum ether/toluene afforded 31% of XIV. The surprising formulation follows from analyses, infrared, Raman and  $^1\text{H}$ ,  $^{29}\text{Si}$  and  $^7\text{Li}$  NMR spectra. It is confirmed by a single crystal X-ray structural investigation reported below.



The fact that only one stereoisomer was isolated, rather than two as in the case of XIII, suggests that this isomer formed preferentially, and the LiCl contacts revealed by the X-ray analysis for the solid state may also be important in solution.

The fact that XIV could be isolated proves that the NH group in NHSiMe<sub>3</sub>-substituted sila-titana-diazacyclobutanes does not arise from incompletely lithiated triaminosilanes. Though Li and Cl atoms may come sufficiently close to be eliminated as LiCl, this elimination does not occur, attack on the ether molecule taking place instead. Obviously the substantial deviation from planarity of the four-membered ring required for the formation of the strained bicyclopentane molecule (F) is not acceptable for siladiazacyclobutane derivatives, which are generally found to be essentially planar.

Crystalline XIV is stable at room temperature for weeks. In solution, slow precipitation of LiCl is observed even at  $-25^\circ\text{C}$ , but apparently intermolecular rather than intramolecular elimination of LiCl is favoured.

## Properties

The physical properties of the compounds VII to XIV are set out in Table 1. The monocyclic compounds VIII to XIV are coloured, but the spirocyclic derivative VII is colourless. A similar blue-shift of the CT absorption into the UV has also been observed for the spirane **B** ( $R = \text{Me}$ ,  $R' = \text{SiMe}_3$ ) [1]. All the compounds except XIV are sufficiently stable to be sublimed in vacuo. While a freshly recrystallized specimen of VIII has a m.p. 106–107°C, a sample kept at room temperature for 24 h melts at 83–85°C. All compounds are readily soluble in aromatic hydrocarbons; the solubility in petroleum ether of VII, VIII and XI is good, while the other compounds are only moderately soluble in aliphatic hydrocarbons. All compounds are rapidly hydrolyzed by moisture.

### NMR spectra

The  $^1\text{H}$  and, in some cases the  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and  $^7\text{Li}$  spectra of VII to XIV were recorded, and the data are listed in Table 2. The spectra convincingly confirm the suggested formulations. The occurrence of two  $^{29}\text{Si}$  resonances for the  $\text{SiMe}_3$  groups in VII is consistent with the presence of two chemically non-equivalent pairs of exocyclic  $\text{SiMe}_3$  groups. The large high field shift of the endocyclic  $^{29}\text{Si}$  resonances in VII, VIII, XI, XII and XIV should be noted [14].

### Infrared and Raman spectra

Infrared and Raman spectra of compounds VII to XIV were recorded, and the observed frequencies are given in the experimental section. Though no complete assignments can be given here, some typical vibrations may be assigned by comparison with related molecules and by analogy with the spectra of disiladiazacyclobutane derivatives [1,15]. Thus, the following diagnostic assignments ( $\text{cm}^{-1}$ ) can be made:  $\nu(\text{NH})$  3365 (VII), 3358 (VIII), 3360 (IX), 3360 (X), 3370 (XIII).  $\delta(\text{HN}(\text{Si}_2))$  1189 (VII), 1186 (VIII), 1194 (IX).  $\omega_1$  [15] 1071 (VII), 952 (VIII), 965 (IX), 973 (XI), 955 (XIII), 958 (XIV).  $\omega'_1$  [15] 986 (VII),  $\omega_5$  [15] 916 (VII).

The group vibrations of the substituents were observed in the expected places. It should be noted that  $\omega_1$ , the pseudo-asymmetric exocyclic SiN stretching vibration,

TABLE 1  
PHYSICAL PROPERTIES OF COMPOUNDS VII TO XIV

	M.p. (°C)	Subl. temp. (°C/Torr)	Colour
VII	98–99	100/10 <sup>-3</sup>	colourless
VIII	106–107 <sup>a</sup> 83–85	80/10 <sup>-3</sup>	yellow
IX	40–42	65/10 <sup>-3</sup>	yellow
X	> 165(dec.)	105/10 <sup>-3</sup>	orange
XI	83–85	60/10 <sup>-3</sup>	yellow
XII	116–118	80/10 <sup>-3</sup>	yellow
XIII	–	120/10 <sup>-3</sup>	yellow
XIV	> 70(dec.)	–	

<sup>a</sup> See text.

TABLE 2  
NMR PARAMETERS FOR COMPOUNDS VII TO XIV

	VII	VIII	IX	X	XI	XII	XIII	XIV
$\delta(^1H)$ (ppm)	<i>a</i>	<i>a</i>	<i>a</i>	<i>b</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
NSiMe <sub>3</sub>	0.12	0.26	0.48		0.17		0.01 0.07	0.04
N(H, Li)SiMe <sub>3</sub>	0.09	0.17	0.23				0.23 0.29	-0.01
SiMe <sub>2</sub> , SiMe	0.42		1.03		0.22 0.42	0.40 0.60		
NCMe <sub>3</sub>				1.30		1.32		
NHNCMe <sub>3</sub>				1.32				
(OCH <sub>2</sub> )CH <sub>3</sub>								1.29
OCH <sub>2</sub>								3.65
C <sub>5</sub> H <sub>5</sub>					6.36	6.33	6.44	6.38
<i>m, p</i> -C <sub>6</sub> H <sub>5</sub>		7.34		7.17			7.32	7.20
<i>o</i> -C <sub>6</sub> H <sub>5</sub>		7.59		7.67			7.77	7.45
$\delta(^{13}C)$ (ppm) <sup>c</sup>								
NSiMe <sub>3</sub>	3.58	1.97			2.89			
NHSiMe <sub>3</sub>	2.58	2.67						
SiMe <sub>2</sub> , SiMe	2.96				3.50	5.02 5.55		
(C)Me <sub>3</sub>						34.08		
C(Me <sub>3</sub> )						63.13		
C <sub>5</sub> H <sub>5</sub>					114.12	112.80		
C <sub>6</sub> H <sub>5</sub>		128.53 131.07 134.16 135.04						
$\delta(^{29}Si)$ (ppm) <sup>d</sup>								
SiMe <sub>3</sub>	-14.31 -14.73	-0.66			-7.6			-9.5
N(H, Li)SiMe <sub>3</sub>	-6.49	0.63						-25.3
SiMe <sub>2</sub> , SiMe	-62.79				-56.5	-52.8		-87.7
SiPh		-75.80						
$\delta(^7Li)$ (ppm) <sup>e</sup>								0.46

<sup>a</sup> In CCl<sub>4</sub> against internal TMS. <sup>b</sup> In C<sub>6</sub>D<sub>6</sub> against internal TMS. <sup>c</sup> In C<sub>6</sub>D<sub>6</sub> = 127.96 ppm. <sup>d</sup> In C<sub>6</sub>D<sub>6</sub> against external TMS. <sup>e</sup> In C<sub>6</sub>D<sub>6</sub> against external LiI/H<sub>2</sub>O.

appears near 970 cm<sup>-1</sup> as an infrared absorption coinciding with a Raman line for monocyclic compounds, but splits into a Raman component near 1070 cm<sup>-1</sup> and an infrared absorption near 985 cm<sup>-1</sup> for spirocyclic derivatives [15].

#### Mass spectra

Electron impact mass spectra of VII to XIII were recorded. Molecular ions *M*<sup>+</sup> were observed in all cases with medium abundance (3–15%), but [*M* - CH<sub>3</sub>]<sup>+</sup> ions appear with typically high abundance and are the basis peaks for VIII, IX, X and XI. Observed mass peaks and their relative abundances are given in the Experimental section.

## Molecular and crystal structure of XIV

### *X-Ray data collection and reduction*

A crystal of XIV having the principal dimensions  $0.38 \times 0.38 \times 0.67$  mm was sealed in a thin-walled glass capillary under argon. The space group was determined from the symmetry and systematic absences revealed by Weissenberg photographs. Lattice constants at  $23^\circ\text{C}$  were obtained by a least-squares method from the Bragg angles of 40 reflections which were centered by a Siemens AED 1 diffractometer employing Zr-filtered Mo- $K_\alpha$  radiation,  $\lambda(\text{Mo-}K_\alpha)$   $0.71073 \text{ \AA}$ . Thus XIV crystallizes in the space group  $P2_1/n$  with  $a$   $11.033(1)$ ,  $b$   $17.504(2)$ ,  $c$   $18.001(2) \text{ \AA}$ ,  $\beta$   $98.21(1)^\circ$ ,  $Z = 4$  and  $D_x$   $1.151 \text{ g cm}^{-3}$ .

Intensity data ( $hkl$ ,  $hkl$ ,  $4 \leq 2\theta \leq 50^\circ$ ) were collected by the  $\omega$ - $2\theta$  step scan technique. The number (54–62,  $\Delta\omega$   $0.02^\circ$ ,  $0.61\text{s/step}$ ) of steps was so chosen that the peak fell in the middle two-thirds of the scan range. If the initial scan yielded an intensity between 2 and  $25\sigma(I)$ , then the measurement was repeated, and the results were combined. Crystal and diffractometer stability were monitored by hourly checking of three standard reflections. The data were corrected for the 4.7% decay in the standards, and for absorption ( $\mu(\text{Mo-}K_\alpha)$   $4.8 \text{ cm}^{-1}$ , transmission 0.809–0.863), and converted into structure factor amplitudes. Of the 6039 unique reflections, only the 4277 with  $|F_0| \geq 4\sigma(F_0)$  were deemed observed and used in the refinement of the structure.

### *Structure solution and refinement*

The structure was solved by a combination of multiresolution direct methods and

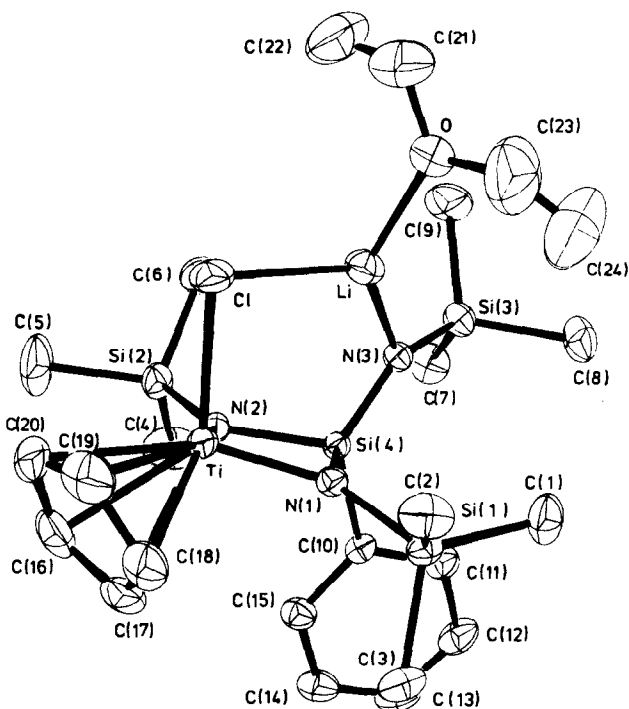


Fig. 1. A perspective drawing of the non-hydrogen atoms of XIV with 20% probability thermal ellipsoids.



standard Fourier techniques. The low electron density found near the ethyl C atoms indicates that the ether molecule is disordered. Since the electron density in this region was consistent with an ordered-atom model, the irregular values derived for the C–C and C–O bond lengths should not be regarded as significant.

The structure was refined by large-block, least-squares methods using the program SHELX-76 [16]. Dispersion corrected, relativistic Hartree-Fock scattering factors were used for all atoms except H, SDS [17]. The latter were introduced in idealized positions (C–H 0.95 Å), assigned group isotropic thermal parameters, and allowed to ride on the appropriate C atom. Only the H atoms of C(23) and C(24), where the disorder is most severe, were not included. With all non-hydrogen atoms anisotropic, refinement of the 329 parameters converged ( $|\Delta/\sigma|_{\max} = 0.71$ ) with

TABLE 3

POSITIONAL AND EQUIVALENT <sup>a</sup> ISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS OF XIV

Atom	x	y	z	U
Ti	0.12591(5)	0.31324(3)	0.64393(3)	0.0496(2)
Cl	0.06910(9)	0.19202(5)	0.59245(6)	0.0816(4)
Si(1)	0.27010(9)	0.40065(5)	0.51236(5)	0.0551(3)
Si(2)	0.2694(1)	0.23348(6)	0.80224(5)	0.0695(4)
Si(3)	0.55827(9)	0.17907(6)	0.63749(6)	0.0672(4)
Si(4)	0.36221(7)	0.30176(4)	0.65689(4)	0.0424(3)
N(1)	0.2469(2)	0.3432(1)	0.5885(1)	0.0456(8)
N(2)	0.2523(2)	0.2849(1)	0.7189(1)	0.0480(8)
N(3)	0.4225(2)	0.2242(1)	0.6261(1)	0.0525(9)
O	0.2613(3)	0.0945(2)	0.4926(2)	0.110(1)
C(1)	0.4148(4)	0.3756(3)	0.4778(2)	0.095(2)
C(2)	0.1414(4)	0.3868(2)	0.4350(2)	0.088(2)
C(3)	0.2777(4)	0.5032(2)	0.5404(2)	0.081(2)
C(4)	0.3882(6)	0.2801(3)	0.8713(3)	0.143(3)
C(5)	0.1200(6)	0.2244(4)	0.8383(3)	0.154(3)
C(6)	0.3203(4)	0.1353(2)	0.7862(2)	0.099(2)
C(7)	0.6570(4)	0.1998(3)	0.7282(2)	0.095(2)
C(8)	0.6513(4)	0.2014(3)	0.5604(3)	0.101(2)
C(9)	0.5383(4)	0.0733(2)	0.6352(3)	0.117(2)
C(10)	0.4640(3)	0.3829(2)	0.6956(2)	0.050(1)
C(11)	0.5805(3)	0.3935(2)	0.6744(2)	0.066(1)
C(12)	0.6507(4)	0.4569(2)	0.6982(3)	0.087(2)
C(13)	0.6072(4)	0.5104(2)	0.7427(3)	0.092(2)
C(14)	0.4934(4)	0.5014(2)	0.7644(2)	0.083(2)
C(15)	0.4233(3)	0.4384(2)	0.7411(2)	0.066(1)
C(16)	0.0130(5)	0.3832(3)	0.7226(3)	0.102(2)
C(17)	0.0479(4)	0.4332(2)	0.6720(4)	0.092(2)
C(18)	–0.0105(5)	0.4160(3)	0.6032(3)	0.099(2)
C(19)	–0.0823(4)	0.3532(4)	0.6086(4)	0.111(3)
C(20)	–0.0698(5)	0.3323(3)	0.6815(5)	0.115(3)
C(21)	0.200(1)	0.0300(6)	0.4842(6)	0.226(6)
C(22)	0.203(1)	–0.0088(5)	0.5506(8)	0.247(8)
C(23)	0.252(1)	0.1282(7)	0.4133(5)	0.235(7)
C(24)	0.327(1)	0.1638(8)	0.3981(7)	0.250(7)
Li	0.2824(6)	0.1681(4)	0.5747(4)	0.083(3)

<sup>a</sup>  $U = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$ .

TABLE 4  
SELECTED DISTANCES (Å) IN XIV

Ti–Cl	2.364(1)	Ti–C(20)	2.376(6)	Li–Cl	2.455(7)
Ti–N(1)	1.853(3)	Si(1)–N(1)	1.747(3)	Li–N(3)	1.950(7)
Ti–N(2)	1.864(2)	Si(2)–N(2)	1.737(3)	Li–O	1.949(8)
Ti–C(16)	2.358(6)	Si(3)–N(3)	1.681(3)	Si(1,2)–C <sup>a</sup>	1.856(8)
Ti–C(17)	2.352(4)	Si(4)–N(1)	1.793(2)	Si(3)–C <sup>b</sup>	1.870(9)
Ti–C(18)	2.393(6)	Si(4)–N(2)	1.786(3)	Si(4)–C(10)	1.881(3)
Ti–C(19)	2.399(5)	Si(4)–N(3)	1.642(3)	Ti–Ct <sup>c</sup>	2.072(5)

<sup>a</sup> Mean Si–C bond length of Si(1) and Si(2). <sup>b</sup> Mean Si–C bond length for Si(3). <sup>c</sup> Distance to the center of mass of the Cp ring.

TABLE 5  
SELECTED ANGLES (°) IN XIV

N(1)–Ti–N(2)	86.8(1)	Ti–Cl–Li	89.9(2)
N(1)–Si(4)–N(2)	91.0(1)	O–Li–Cl	101.5(3)
Ti–N(1)–Si(4)	90.6(1)	O–Li–N(3)	133.9(4)
Ti–N(2)–Si(4)	90.5(1)	Cl–Li–N(3)	124.2(3)
Cl–Ti–N(1)	102.35(8)	Si(3)–N(3)–Si(4)	138.1(2)
Cl–Ti–N(2)	100.04(8)	Si(3)–N(3)–Li	116.9(2)
Ti–N(1)–Si(1)	141.5(1)	Si(4)–N(3)–Li	104.2(2)
Ti–N(2)–Si(2)	137.8(2)	N–Si(1,2)–C <sup>a</sup>	110.1(7)
Si(1)–N(1)–Si(4)	127.0(1)	N(3)–Si(3)–C <sup>b</sup>	113(2)
Si(2)–N(2)–Si(4)	128.7(1)	C–Si(1,2)–C <sup>a</sup>	109(2)
N(1)–Si(4)–N(3)	112.6(1)	C–Si(3)–C <sup>b</sup>	105.9(9)
N(2)–Si(4)–N(3)	114.7(1)	Cl–Ti–Ct <sup>c</sup>	114.4(1)
N(1)–Si(4)–C(10)	106.1(1)	N(1)–Ti–Ct <sup>c</sup>	121.9(1)
N(2)–Si(4)–C(10)	108.4(1)	N(2)–Ti–Ct <sup>c</sup>	126.0(1)
N(3)–Si(4)–C(10)	120.0(1)		

<sup>a</sup> Mean bond angle at Si(1) and Si(2). <sup>b</sup> Mean bond angle at Si(3). <sup>c</sup> Ct is the center of mass of the Cp ring.

$R = \Sigma \| F_0 \| - | F_c \| / \Sigma \| F_0 \| = 0.045$  and  $R_w = [\Sigma_w (| F_0 \| - | F_c \|)^2 / \Sigma_w | F_0 |^2]^{1/2} = 0.057$  where the summations are made over the observed reflections and  $w^{-1} = \sigma^2(F_0) + 0.0004 | F_0 |^2$ . Corresponding residuals for all reflections are 0.071 and 0.061 respectively. The final difference Fourier synthesis (0.54 to  $-0.16e/\text{Å}^3$ ) confirms the structure, only peaks near O, C(23) and C(24) exceeding  $0.25 e/\text{Å}^3$ . Atomic coordinates are listed in Table 3, and the numbering scheme is defined in Fig. 1 [18] \*.

#### Description and discussion of the structure

Crystals of XIV consist of discrete, monomeric molecules separated by normal Van der Waals distances. Bond distances and angles are listed in Tables 4 and 5 respectively. The structural study reveals the presence of a heteronuclear bicyclo[3.1.1]heptane entity which contains the bridgeheads Ti and Si(4) and includes an unusual Cl–Li–N(3) bridge.

\*  $F_0$ ,  $F_c$  lists, tables of hydrogen coordinates and anisotropic thermal parameters may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen, by quoting the deposit number CSD 51771, the names of the authors, and literature reference.

The Li coordination is completed by the ether molecule, the Li,Cl,N(3),O fragment being roughly planar (r.m.s. deviation 0.03 Å). Comparison with other Li structures requires due consideration of the coordination numbers (cn) involved. Thus the Li(cn3)–Cl(cn2) bond in XIV is 0.15(2) Å shorter than the Li(cn4)–Cl(cn2) bond in  $[(C_4H_8O)_2LiCpCrCl_3]_2 \cdot C_4H_8O_2$  (2.61(2) Å) [19], 0.122(7) Å shorter than the Li(cn6)–Cl(cn6) bond in LiCl (2.577 Å), but somewhat longer than the Li(cn4)–Cl(cn3) distances in  $[ClLiOP(NMe_2)_3]_4$ , 2.36(1)–2.44(1) Å [20]. The Li(cn3)–N(cn3) distance in XIV is 0.06(1) Å longer than that of (TMEDA)LiNH-(C<sub>6</sub>H<sub>2</sub>-t-Bu<sub>3</sub>), 1.895(8) Å, [21], somewhat smaller than the Li(cn2)–N(cn4) distances in  $[LiN(SiMe_3)_2]_n$  (1.99(3) Å for  $n=2$  [21] and 2.00(2) Å for  $n=3$  [22]) and 0.105(9) Å shorter than the Li(cn3)–N(cn4) bonds in  $[Et_2OLiN(SiMe_3)_2]_2$ , 2.055(5) Å [23]. On the other hand, the Li(cn3)–O(cn3) distances in the latter compound, 1.943(6) Å, agree well with that found in XIV. Compared to ether, a titanium-bonded Cl atom is a weak Lewis base, and this view is supported by the fact that the Li–Cl distance is 0.51(1) Å longer than the Li–O valence even though the Cl covalent radius is only 0.33 Å larger than that of O [24].

The Ti–Cl bond in XIV is more than 0.1 Å longer than those in CpTiCl<sub>3</sub> [25], (CpTiCl<sub>2</sub>)<sub>2</sub>O [26] and Cl<sub>2</sub>Ti(t-BuN)<sub>2</sub>SiMe<sub>2</sub> [4], 2.223(14), 2.239(2) and 2.250(2) Å respectively. This lengthening may not be solely caused by the Li–Cl interaction since the mean Ti–C distance in XIV, 2.38(2) Å, is also longer than the values found in CpTiCl<sub>3</sub> and (CpTiCl<sub>2</sub>)<sub>2</sub>O, 2.31(4) and 2.31(2) Å, respectively. The average Ti–N linkage in XIV, 1.859(6) Å, may be compared with those reported for other TiN<sub>2</sub>Si four-membered ring systems. In fact it lies between that in Cl<sub>2</sub>Ti(t-BuN)<sub>2</sub>SiMe<sub>2</sub>, 1.829(5) Å [4], and those in the spirocyclic compounds Ti[(t-BuN)<sub>2</sub>SiMe<sub>2</sub>]<sub>2</sub> [2] and Ti[(Me<sub>3</sub>SiN)<sub>2</sub>SiPh<sub>2</sub>]<sub>2</sub> [3], 1.890(4) and 1.918(2) Å respectively.

The averages of the endocyclic N–Si bond lengths in each of the last three compounds (1.766(5), 1.742(10) and 1.750(2) Å respectively) are all significantly shorter than the corresponding value in XIV, 1.790(4) Å. While the latter is relatively long, the third N–Si bond formed by the ring atom Si(4) is remarkably short, 1.642(3) Å. Perhaps the N–Si valencies in the four-membered ring are weakened in order to relieve transannular Si(4)–Ti repulsions, while the bond strength thus lost is recovered by shortening of the third N–Si(4) interaction. Thus the mean N–Si(4) bond length, 1.741 Å, compares well with that of the corresponding bonds in  $[(Me_3SiNLi)_3SiPh]_2$ , 1.733(6) Å [7]. While the average N–SiMe<sub>3</sub> bond length in the trithio derivative (1.690(3) Å) is similar to that formed by the lithium-bonded N atom in XIV (i.e., N(3) 1.681(3) Å), the mean of such distances involving titanium-bonded N atoms is significantly longer, 1.742(7) Å. These differences in N–SiMe<sub>3</sub> bonding probably reflect the greater relative covalence of Ti–N compared to Li–N bonds.

In contrast to the near planarity found for previously investigated TiN<sub>2</sub>Si four-membered rings [2–4], the ring in XIV is folded by 11.5° along the N(1)–N(2) line. This bend shortens the Cl–N(3) distance and thus probably results from bonding of Li to these atoms. Bond distances and angles in the SiMe<sub>3</sub>, Cp and Ph groups are not unusual, the rings being planar to within experimental error.

## Experimental

### Syntheses

Lithiated aminosilanes were prepared by published procedures [6–8].

TABLE 6  
 ELEMENTAL ANALYSES

Compound	Formula	Analyses (Found (calcd.) (%))				
		C	H	Cl	N	Ti
VII	$C_{20}H_{62}N_6Si_8Ti$				12.4 (12.75)	7.4 (7.26)
VIII	$C_{15}H_{33}Cl_3N_3Si_4Ti$	36.8 (37.03)	7.0 (6.84)	14.1 (14.57)	8.6 (8.64)	9.5 (9.84)
IX	$C_{10}H_{30}Cl_2N_3Si_4Ti$			16.8 (16.70)	9.6 (9.90)	11.2 (11.28)
X	$C_{18}H_{35}Cl_2N_3SiTi$			16.0 (16.17)	9.4 (9.59)	11.1 (10.93)
XI	$C_{13}H_{29}ClN_2Si_3Ti$			9.3 (9.30)	7.5 (7.37)	12.6 (12.57)
XII	$C_{15}H_{29}ClN_2SiTi$			10.2 (10.16)	7.9 (8.03)	13.6 (13.73)
XIV	$C_{24}H_{47}ClLiN_3OSi_4Ti$			5.7 (5.95)	7.0 (7.05)	

*2,5-Bis(trimethylsilylamino)-2,6-dimethyl-1,3,5,7-tetrakis(trimethylsilyl)-1,3,5,7-tetraza-2,6-disila-4-titana-spiro[3.3]heptane (VII)*. (a) To 28.7 mmol III in 400 ml  $Et_2O$  and 170 ml petroleum ether prepared from 8.8 g  $MeSi(NHSiMe_3)_3$  5.44 g (28.7 mmol)  $TiCl_4$  in 250 ml petroleum ether was added at  $0^\circ C$ . The mixture was stirred for 24 h, the  $LiCl$  filtered off, and the residue sublimed in vacuo. Yield 1.8 g (9.5%). (b) 6.75 g (21.9 mmol)  $MeSi(NHSiMe_3)_3$  in 100 ml  $Et_2O$  and 500 ml petroleum ether were lithiated with 43.8 mmol  $BuLi$  in *n*-hexane and, as in (a), the reagent obtained was treated with 2.08 g (11 mmol)  $TiCl_4$  in 250 ml petroleum ether; 1.5 g of VII separated as crystals; sublimation in vacuo of the residue yielded an additional 2.6 g; total yield 28%. Elemental analyses are given in Table 6. Raman: 126m, 154m, 182vs, 219vw, 227vw, 243vw, 343s, 416vs, 471m, 479w, 589s, 632vs, 687s, 741w, 775w, 783w, 804w, 845w, 985w, 1071m, 1259w, 1414m. IR: 393m, 474w, 513w, 595s, 628s, 658vs, 681w, 700m, 730w, 752sh, 771vs, 788vw, 842vs, 943s, 986vs, 1019sh, 1075sh, 1189vs, 1249vs, 3365m. MS:  $m/e = 658 (M)^+$ , 3%; 643 ( $M - Me$ )<sup>+</sup>, 13%; 570, 1%; 554, 7%; 421, 10%; 292, 100%; 275, 100%; 233, 8%; 219, 9%; 203, 100%; 187, 21%; 130, 59%; 100, 10%; 73, 45%. Peaks at  $m/e = 292, 275$  and 203 are probably due to hydrolysis in the inlet system.

*1,3-Bis(trimethylsilyl)-4,4-dichloro-2-phenyl-2-trimethylsilylamino-1,3-diaza-2-sila-4-titana-cyclobutane (VIII)*. (a) A solution of 3.33 g (17.5 mmol)  $TiCl_4$  in 200 ml  $Et_2O$  was added to a solution of 6.8 g (17.5 mmol) V in 500 ml  $Et_2O$  at  $0^\circ C$ . After filtration the tar-like residue was sublimed in vacuo, to yield 14% of VIII. (b) 10.1 g (27 mmol)  $PhSi(NHSiMe_3)_3$  were lithiated with 54 mmol  $BuLi$  in *n*-hexane, and 5.2 g (27 mmol)  $TiCl_4$  in 200 ml  $Et_2O$  were slowly added at  $0^\circ C$ . Work-up as above yielded 30% of VIII. Raman: 113vw, 144m, 161vw, 178m, 199w, 239s, 260m, 290w, 349s, 477w, 522s, 620vw, 638vs, 701m, 742m, 761w, 797m, 847m, 945m, 1000vs, 1020s, 1031m, 1118w, 1260m, 1441w, 1586s. IR: 440w, 481s, 525m, 605m, 670vw, 698w, 722vw, 797w, 795m, 840vs, 849w, 952vs, 1018sh, 1118s, 1186s, 1202m, 1252vs, 3358m. MS:  $m/e = 485 (M)^+$ , 10%; 470 ( $M - Me$ )<sup>+</sup>, 100%; 301, 31%; 265, 16%; 192, 40%; 135, 31%; 131, 42%; 130, 31%; 93, 79%; 73, 68%.

*1,3-Bis(trimethylsilyl)-4,4-dichloro-2-methyl-2-trimethylsilylamino-1,3-diaza-2-sila-4-titana-cyclobutane (IX)*. To a solution of 1.6 g (2.4 mmol) of VII in 20 ml petroleum ether was added 0.46 g (2.4 mmol)  $\text{TiCl}_4$ . The mixture was stirred for 3 h, then the residue was sublimed in vacuo to give a yield of 68%. Raman: 152w, 174s, 256m, 281m, 345w, 470m, 505s, 634vs, 694m, 748m, 805m, 850vw, 966w, 1022s. IR: 374m, 434w, 469s, 503m, 598s, 632vw, 659m, 688m, 722m, 756vw, 771w, 806m, 845vs, 880sh, 921sh, 965vs, 1025m, 1194vs, 3360m. MS:  $m/e = 423 (M)^+$ , 5%; 408 ( $M - \text{Me}$ )<sup>+</sup>, 100%; 392, 11%; 320, 6%; 292, 15%; 275, 13%; 203, 33%; 187, 12%; 146, 58%; 130, 98%; 100, 31%; 93, 98%; 73, 100%.

*1,3-Di-*t*-butyl-2-*t*-butylamino-4,4-dichloro-2-phenyl-1,3-diaza-2-sila-4-titana-cyclobutane (X)*. 11.3 g (35 mmol)  $\text{PhSi}(\text{NH-}t\text{-Bu})_3$  were lithiated in 50 ml  $\text{Et}_2\text{O}$  with 70 mmol BuLi in *n*-hexane, and 6.64 g (35 mmol)  $\text{TiCl}_4$  in 200 ml  $\text{Et}_2\text{O}$  were added at 0°C. After 20 h stirring LiCl was filtered off and the residue sublimed in vacuo; yield 16%. Raman: 180s, 200vw, 214m, 257s, 289vs, 320w, 351vw, 372vw, 426m, 465m, 542sh, 561vs, 620m, 655vw, 703w, 778vs, 802m, 846m, 918m, 998vs, 1030s, 1075s, 1112m, 1159m, 1191w, 1218s, 1442s, 1462s. IR: 348vw, 388w, 430s, 464w, 488w, 503sh, 542vs, 559sh, 656w, 673w, 697s, 721vw, 749vs, 778vs, 806s, 840s, 890vw, 920m, 971vw, 1022vs, 1110s, 1182vs, 1223vs, 3360m. MS:  $m/e = 437 (M)^+$ , 3%; 422 ( $M - \text{Me}$ )<sup>+</sup>, 100%; 365, 40%; 350, 8%; 310, 58%; 293, 14%; 233, 8%; 217, 19%; 196, 6%; 136, 20%; 135, 15%; 58, 57%; 57, 69%.

*1,3-Bis(trimethylsilyl)-4-chloro-4- $\eta^5$ -cyclopentadienyl-2,2-dimethyl-1,3-diaza-2-sila-4-titana-cyclobutane (XI)*. This was made as described for VII, from 29 mmol I and 29 mmol  $\text{CpTiCl}_3$ ; yield 53%. Raman: 115s, 139s, 167s, 183m, 212vs, 237w, 254s, 284m, 304vs, 331m, 371vw, 381vw, 434m, 456sh, 468s, 612vw, 628s, 658m, 688s, 735m, 754vw, 787m, 816vw, 848w, 968m, 1068m, 1130s, 1251vw, 1265vw. IR: 440m, 465w, 578m, 609w, 653m, 684w, 722s, 729sh, 751vw, 777s, 804vs, 843vs, 866s, 973vs, 1021m, 1155vw, 1171vw, 1254vs. MS:  $m/e = 380 (M)^+$ , 7%; 365 ( $M - \text{Me}$ )<sup>+</sup>, 100%; 349, 9%; 329, 21%; 315, 9%; 130, 27%; 100, 11%; 73, 29%.

*1,3-Di-*t*-butyl-4-chloro-4- $\eta^5$ -cyclopentadienyl-2,2-dimethyl-1,3-diaza-2-sila-4-titana-cyclobutane (XII)*. Analogous to IX, from 22 mmol II and 22 mmol  $\text{CpTiCl}_3$ , yield 18%. Raman: 129s, 208s, 279vs, 328w, 411vw, 440w, 549m, 619vw, 661w, 784m, 816vw, 922w, 1033m, 1075m, 1132m, 1204 vw, 1234w, 1374w, 1451w, 1471vw. IR: 371w, 402s, 431s, 516s, 543w, 564w, 621w, 657w, 675s, 721m, 776vs, 802vs, 819vw, 849vs, 891w, 918vw, 974w, 1034vs, 1068sh, 1192vs, 1216vw, 1228vw, 1249s. MS:  $m/e = 348 (M)^+$ , 5%; 333 ( $M - \text{Me}$ )<sup>+</sup>, 88%; 318, 5%; 313, 4%; 277, 66%; 241, 12%, 220, 24%; 211, 14%; 200, 8%; 185, 11%; 155, 14%; 73, 31%; 58, 100%; 57, 12%.

*1,3-Bis(trimethylsilyl)-4-chloro-4- $\eta^5$ -cyclopentadienyl-2-phenyl-2-trimethylsilylamino-1,3-diaza-2-sila-4-titana-cyclobutane (XIII)*. Analogous to X, yield a few mg. IR: 411w, 463w, 515m, 589m, 606m, 700w, 724sh, 738w, 753vw, 787m, 805m, 839vs, 848w, 955vs, 1020s, 1113m, 1179m, 1203s, 1250s, 3370w. MS:  $m/e = 515 (M)^+$ , 15%; 500 ( $M - \text{Me}$ )<sup>+</sup>, 88%; 465, 20%; 450, 10%; 369, 20%; 354, 27%; 337, 51%; 292, 59%; 265, 68%; 249, 27%; 203, 34%; 130, 63%; 73, 100%.

*1,3-Bis(trimethylsilyl)-4-chloro-4- $\eta^5$ -cyclopentadienyl-2-(*N*-lithiotrimethylsilylamino)-2-phenyl-1,3-diaza-2-sila-4-titana-cyclobutane-diethyl ether (XIV)*. To a solution of 6.4 mmol IV in 300 ml  $\text{Et}_2\text{O}$  and 300 ml petroleum ether at  $-30^\circ\text{C}$  was added a solution of 4.7 g (21 mmol)  $\text{CpTiCl}_3$  in 200 ml  $\text{Et}_2\text{O}$ . The mixture was stirred for 1 h at  $-30^\circ\text{C}$  then for 2 h at  $0^\circ\text{C}$ . The LiCl was filtered off and the volume of the solution reduced to 25 ml. Yellow crystals separated at  $-25^\circ\text{C}$ , and were recrystal-

lized from petroleum ether/toluene. Yield 31%. Raman: 154m, 223vs, 255w, 422w, 540m, 637m, 660w, 715s, 865vw, 943w, 1006vs, 1129s. IR: 422w, 468w, 519m, 593s, 634s, 658w, 676vs, 702vw, 712vw, 739w, 751w, 789vw, 805m, 840vs, 859vw, 958vs, 1021m, 1112m, 1155m, 1171vw, 1180vw, 1199vw, 1249vs.

*Spectra* were obtained as described in ref. 15b.

### Acknowledgement

Support by the Fonds der Chemie and by Bayer AG through a gift of chemicals is gratefully acknowledged.

### References

- 1 H. Bürger and D. Beiersdorf, *Z. Anorg. Allgem. Chem.*, 459 (1979) 111.
- 2 D.J. Brauer, H. Bürger, E. Essig and W. Geschwandter, *J. Organomet. Chem.*, 190 (1980) 343.
- 3 W.D. Beiersdorf, D.J. Brauer and H. Bürger, *Z. Anorg. Allgem. Chem.*, 475 (1981) 56.
- 4 R.A. Jones, M.H. Seeberger, J.L. Atwood and W.E. Hunter, *J. Organomet. Chem.*, 247 (1983) 1.
- 5 (a) C. Airoidi, D.C. Bradley, H. Chudzynska, M.B. Hursthouse, K.M.A. Malik and P.R. Raithby, *J. Chem. Soc., Dalton Trans.*, (1980) 2010; (b) M.F. Lappert, P.P. Power, A.R. Sanger and R.C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood Ltd, Chichester (1980).
- 6 D.J. Brauer, H. Bürger, W. Geschwandter, G.R. Liewald and C. Krüger, *J. Organomet. Chem.*, 248 (1983) 1.
- 7 D.J. Brauer, H. Bürger and G.R. Liewald, *J. Organomet. Chem.*, 308 (1986) 119.
- 8 D.J. Brauer, H. Bürger, G.R. Liewald and J. Wilke, *J. Organomet. Chem.*, 287 (1985) 305.
- 9 G. Chandra and M.F. Lappert, *Inorg. Nucl. Chem. Lett.*, 1 (1965) 83.
- 10 K. Issleib and G. Bätz, *Z. Anorg. Allgem. Chem.*, 369 (1969) 83.
- 11 C.R. Bennett and D.C. Bradley, *J. Chem. Soc., Chem. Commun.*, (1974) 29.
- 12 S.J. Simpson and R.A. Andersen, *Inorg. Chem.*, 20 (1981) 3627.
- 13 T. Kitazume and J.M. Shreeve, *Inorg. Chem.*, 16 (1977) 2040.
- 14 H.C. Marsmann, *Chem.-Ztg.*, 97 (1973) 128.
- 15 (a) H. Bürger, E. Bogusch and F. Geymayer, *Z. Anorg. Allgem. Chem.*, 475 (1967) 124; (b) H. Bürger, W. Geschwandtner and G.R. Liewald, *J. Organomet. Chem.*, 259 (1983) 145.
- 16 G.M. Sheldrick, *SHELX-76: Program for crystal structure determination*, University of Cambridge, England (1976).
- 17 *International Tables for X-ray Crystallography*, Vol. IV, Birmingham, Kynoch Press (1974).
- 18 C.K. Johnson, *ORTEP: Report ORNL-3794*, Oak Ridge National Laboratory, Tennessee (1965).
- 19 B. Müller and J. Krausse, *J. Organomet. Chem.*, 44 (1972) 141.
- 20 D. Barr, W. Clegg, R.E. Mulvey and R. Snaith, *J. Chem. Soc., Chem. Commun.*, (1984) 79.
- 21 T. Fjeldberg, P.B. Hitchcock, M.F. Lappert and A.J. Thorne, *J. Chem. Soc., Chem. Commun.*, (1984) 822.
- 22 D. Mootz, A. Zinnius and B. Böttcher, *Angew. Chem., Int. Ed. Engl.*, 8 (1969) 378. R.D. Rogers, J.L. Atwood and R. Grüning, *J. Organomet. Chem.*, 157 (1978) 229.
- 23 L.M. Engelhardt, A.S. May, C.L. Raston and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1983) 1671.
- 24 L. Pauling, *The Nature of the Chemical Bond*, 3rd. Ed., Ithaca: Cornell University Press (1960).
- 25 L.M. Engelhardt, R.I. Papasergio, C.L. Raston and A.H. White, *Organometallics*, 3 (1984) 18.
- 26 U. Thewalt, and D. Schomburg, *J. Organomet. Chem.*, 127 (1977) 169.