

Dimethyl-, diphenyl- and cyclotetramethylene silylchloride derivatives of guanidine, their synthesis and structure. Formation of pentacoordinated silicon compounds and an unexpected diionic disila-diguanidinium dichloride

Janne Maaranen^{a,b}, Ove S. Andell^{b,*}, Tiina Vanne^b, Ilpo Mutikainen^c

^a Department of Organic Chemistry, University of Helsinki, P.O. Box 55, FIN-00014, Finland

^b Borealis Polymers Oy, R&D, P.O. Box 330, FIN-06101 Porvoo, Finland

^c Department of Inorganic Chemistry, University of Helsinki, P.O. Box 55, FIN-00014, Finland

Received 2 June 2004; received in revised form 2 September 2005; accepted 6 September 2005

Available online 13 October 2005

Abstract

The reaction of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2*a*]pyrimidinyl potassium, [hpp][−]K⁺ (**1**), with dimethyldichlorosilane, diphenyldichlorosilane or cyclotetramethylenedichlorosilane (1,1-dichloro silolane) in THF resulted in the formation of the in solid-state unexpected diionic dimer $\lambda^4\text{Si}[\text{Me}_2\text{SiCl}(\text{hpp})]_2$ (**2**) (76%), as well as $\lambda^5\text{Si}-\text{Ph}_2\text{SiCl}(\text{hpp})$ (**3**) (87%) and $\lambda^5\text{Si}-(\text{CH}_2)_4\text{SiCl}(\text{hpp})$ (**4**) (28%). Compounds **3** and **4** are the first synthesised examples of four ring ($-\lambda^5\text{Si}-\text{N}-\text{C}=\text{N}-$) guanidine structures. ¹H and ¹³C NMR show the compounds to have a symmetric guanidine unit in solution. ²⁹Si NMR analysis shows the structures, in selected solvents, to be of $\lambda^5\text{Si}$ -type for **3** and to the major part for **2**. Compound **4**, on the other hand, is of ionic $\lambda^4\text{Si}$ -type. The syntheses and molecular structures of the compounds are discussed.

© 2005 Elsevier B.V. All rights reserved.

Keywords: $\lambda^5\text{Si}$ -Guanidine structures; Crystal structure; Diionic dimer

1. Introduction

The chemistry of pentacoordinated silicon compounds has been studied extensively by previous authors [1–7]. Compounds with cyclic frameworks, strained silacarbon rings, spirobisilaflorenes, silaphenanthrolines, silanaphthyls and amidinates with $\lambda^5\text{Si}$ -coordination can readily be assembled [8–16]. Additionally structures with zwitterionic frameworks and $\lambda^5\text{Si}$ atoms have been made [17,18]. Pentacoordinated silicon compounds can be utilised in various organic syntheses [19–22] as well as when studying reaction pathways and transition stages in organic reactions [23–26].

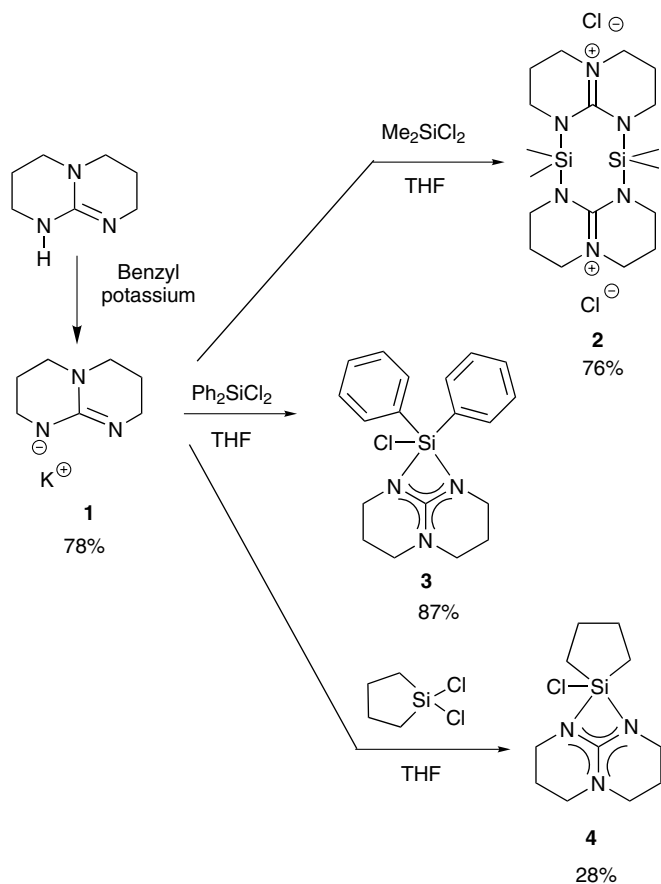
In this report, we discuss a unique silane diionic guanidinium dimer and two $\lambda^5\text{Si}$ -coordinated four membered ring species synthesised via the reaction between guanidinate and R_2SiCl_2 (R = Me, Ph, silolane) compounds (Scheme 1). These new compounds came out of our work when synthesising new ligand structures for olefin polymerisation catalysts and other organometal-based catalytic processes.

2. Results and discussion

Our previous efforts in working with guanidates have led us to prefer the potassium salt which has given cleaner reactions compared to the lithium equivalent. Deprotonation of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido-[1,2*a*]pyrimidine (hpp-H) with benzyl potassium in toluene afforded after isolation the potassium guanidinate [hpp][−]K⁺ (**1**) in 78% yield. Subsequent reaction of **1** with Me_2SiCl_2 in

* Corresponding author. Present address: Åbo Akademi University, Laboratory of Polymer Technology, Biskopsgatan 8, FIN-20500 Turku, Finland. Tel.: +358 2 215 4921; fax: +358 2 215 4866.

E-mail address: ove.andell@abo.fi (O.S. Andell).



Scheme 1. Synthesis of $[\text{hpp}]^-\text{K}^+$ (**1**), $[\text{Me}_2\text{SiCl}(\text{hpp})]_2$ (**2**), $\lambda^4\text{Si}-\text{Ph}_2\text{SiCl}(\text{hpp})$ (**3**) and $\lambda^5\text{Si}-(\text{CH}_2)_4\text{SiCl}(\text{hpp})$ (**4**).

THF gave the diionic $[\text{Me}_2\text{SiCl}(\text{hpp})]_2$ (**2**) in 76% yield. The reaction of **1** with Ph_2SiCl_2 in THF gave $\text{Ph}_2\text{SiCl}(\text{hpp})$ (**3**) in 87% yield and the reaction with 1,1-dichloro silolane gave $(\text{CH}_2)_4\text{SiCl}(\text{hpp})$ (**4**) in 28% yield, respectively.

The solution ^1H and ^{13}C NMR analysis (Section 4) showed that the $[\text{hpp}]^-$ unit in the compounds **2–4** were always symmetric about its axis in the solvents selected. Both sides of the bicyclic $[\text{hpp}]^-$ unit in each compound were always seen chemically and magnetically equivalent in the spectra. This indicated that the Si atom in each of the compound was either coordinated via $\lambda^4\text{Si}$ - or $\lambda^5\text{Si}$ -atoms to two equivalent $[\text{hpp}]^-$ nitrogen's, or that the system had adopted a dimeric structure with 4 equivalent $[\text{hpp}]^-$ nitrogen's linked by two equivalent silicon atoms. In solution, the ^1H NMR spectra of $[\text{hpp}]^-$ substrates normally indicate the non-symmetry of the two rings in the guanidine, giving multiplets or doublets-of-doublets and with the axial-equatorial protons identifiable. Contrary to this are the ^1H NMR spectra of **2–4** at room temperature giving just three signals for the six CH_2 s in each $[\text{hpp}]^-$ unit. Also and slightly unexpectedly, all CH_2 s next to a nitrogen in the $[\text{hpp}]^-$ appeared as triplets and the in between lying CH_2 occur as a narrow multiplet in the spectra due to a relatively fast exchange between the boat and skew-boat (twist-form) conformations, giving indistinguishable

axial-equatorial protons. This can also be seen in the COSY H–C spectra for compounds **3** and **4**. A fully dynamic variable temperature experiment that would have revealed behaviour also at lower temperatures was not in the scope of this study.

To investigate the $\lambda^n\text{Si}$ -coordination patterns and the possibility of dimeric structures, single crystal X-ray analysis (XRD) (Table 1) and ^{29}Si NMR analyses of the compounds were carried out. Analytically pure crystals of **2** and **3** for XRD analysis were obtained from cold pentane and of **4** from cold toluene. The solid-state structure of **2** was found to be a diionic dimer with $\lambda^4\text{Si}$ -coordinated silicon atoms shown in Fig. 1 and schematically in Scheme 2. Compounds **3** and **4** were shown to have $\lambda^5\text{Si}$ -hpp coordinated structures as shown in Figs. 2 and 3, respectively. Selected bond lengths and angles for **2–4** are shown in Table 2.

In **2**, the Si(1) and Si(1A) atoms are tetrahedral and the dimer structure is symmetric (Fig. 1). The bond length Si(1)–N(1) is 1.772 Å and Si(1)–N(9A) is 1.771 Å (Table 2), which is a typical covalent bonded Si–N value [10]. The Si atoms together with the N–C–N atoms of the guanidinium framework form an eight membered ring system which adopts a 'boat' like puckered configuration. The Cl atoms are situated at 4.574 Å from the Si atoms and at 6.339 Å from the N(5) and N(5A) nitrogen's giving a diionic molecule. One chlorine is situated below and one above the plane formed by the two parallel $[\text{hpp}]^-$ units. The angles N(5)–C(10)–N(9) and N(5)–C(10)–N(1) are equal and the sum of the N–C–N angles around C(10) is 360.0° , indicating the planar configuration. The C(10)–N(5) and the C(10A)–N(5A) bond lengths are 1.315 Å. Häfelinger and Kuske [27] quote the average length for a C–N primary amine bond to 1.470 Å and for an unconjugated C=N bond 1.273 Å.

Published similar structures consist of one Sn compound $(\text{hpp})_2\text{Sn}_2\text{Cl}_2$ by Foley [28] and structures of the type $(\text{hpp})_2\text{M}_2$ (M = Au–Cl [29], Cu [30], AlMe₂ [31]) all containing chelating N → M bonds. The C(10)–N(5) is shorter in **2** and N(1)–C(10) and N(9)–C(10) are longer than the comparative bonds in the cited Sn, Al, Au and Cu structures.

Regarding compounds **3** and **4**, no examples of 4-ring ($-\lambda^5\text{Si}-\text{N}-\text{C}=\text{N}-$) guanidine systems could be found in the literature. We therefore looked at 4-ring $\lambda^5\text{Si}$ -amidines as well as 5-ring $\lambda^5\text{Si}$ and 4-ring $\lambda^6\text{Si}$ -guanidine systems. The examples we found were a guanidine (**5**) by Kummer [32] together with a $\lambda^6\text{Si}$ -bis-amidine (**6**) and $\lambda^5\text{Si}$ -amidine (**7**) by Karsch [33–35] (Scheme 3).

In **3**, the Si atom has adopted a distorted trigonal bipyramidal geometry (Fig. 2), where the N(9) and the Cl(1) occupy apical positions and the C(17), C(11) and N(1) equatorial positions. The distortion from trigonal bipyramidal geometry described as the distance of Si(1) from the plane of the equatorial substituents is 0.131 Å. Karsch et al. [33] have reported Si–Cl bond lengths from 2.185 to 2.197 Å in $\lambda^6\text{Si}$ -bis-amidine (**6**) and 2.007 to

Table 1
Crystal structure and refinement data for 2–4

	2	3	4
Empirical formula	C ₁₈ H ₃₆ Cl ₂ N ₆ Si ₂	C ₁₉ H ₂₂ ClN ₃ Si	C ₁₁ H ₂₀ ClN ₃ Si
Formula weight	463.60	355.94	257.84
Temperature (K)	193(2)	193(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Colour	Colourless transparent	Colourless transparent	Colourless transparent
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	7.7430(15)	8.5760(17)	13.341
<i>b</i> (Å)	13.525(3)	9.875(2)	9.758
<i>c</i> (Å)	13.888(3)	21.140(4)	9.809
<i>V</i> (Å ³)	1398.9(5)	1790.3(6)	1269.0
<i>Z</i>	4	4	4
<i>D</i> _{calc.} (Mg/m ³)	1.296	1.321	1.350
Absolute coefficients (mm ⁻¹)	0.345	0.286	0.374
<i>F</i> (000)	584	752	552
Crystal size (mm ³)	0.50 × 0.20 × 0.20	50 × 0.50 × 0.40	0.20 × 0.20 × 0.10
θ range for data collection (°)	2.73 to 25.26	2.56 to 24.25	5.06 to 27.48
Index ranges	0 ≤ <i>h</i> ≤ 9, 0 ≤ <i>k</i> ≤ 16, 16 ≤ <i>l</i> ≤ 16	−9 ≤ <i>h</i> ≤ 9, 11 ≤ <i>k</i> ≤ 0, 0 ≤ <i>l</i> ≤ 24	−17 ≤ <i>h</i> ≤ 17, 10 ≤ <i>k</i> ≤ 12, −12 ≤ <i>l</i> ≤ 11
Reflections collected	2675	3130	8439
Independent reflections	2488 [<i>R</i> _{int} = 0.0389]	2875 [<i>R</i> _{int} = 0.0664]	2881 [<i>R</i> _{int} = 0.0860]
Completeness to theta	25.26° 97.6%	24.25° 99.8%	27.48° 98.9%
Maximum and minimum transmission	0.9342 and 0.8465	0.8943 and 0.8703	0.9636 and 0.9290
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2488/0/168	2875/0/217	2881/0/145
Goodness-of-fit on <i>F</i> ²	1.030	1.090	0.967
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] <i>R</i> ₁	0.0767, <i>wR</i> ₂ = 0.1953	0.0651, <i>wR</i> ₂ = 0.1723	0.0539, <i>wR</i> ₂ = 0.0911
<i>R</i> indices (all data) <i>R</i> ₁	0.1071, <i>wR</i> ₂ = 0.2086	0.0807, <i>wR</i> ₂ = 0.1840	0.1241, <i>wR</i> ₂ = 0.1080
Largest difference peak and hole (e Å ⁻³)	0.514 and −0.493	0.545 and −0.290	0.319 and −0.305

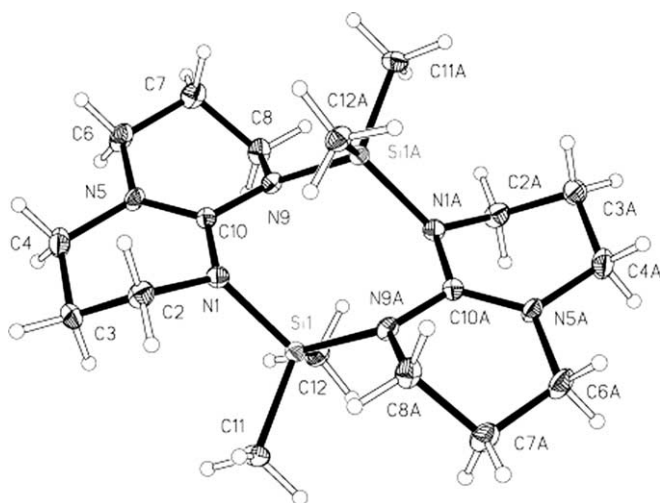
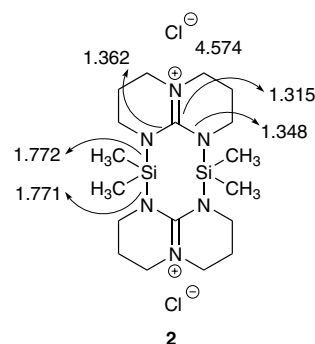


Fig. 1. Solid-state structure of 2. Chlorines in the lattice are omitted (thermal ellipsoids at the 30% probability level).

2.032 Å in λ⁵Si-amidine (7). In 3, the apical Si(1)–Cl(1) bond is lengthened to a value of 2.240 Å (Scheme 3). The apical Si(1)–N(9) bond length in 3 is extended to a value of 1.978 Å and with the equatorial Si(1)–N(1) bond to 1.777 Å. Similar lengths were reported by Karsch in the λ⁶Si-bis-amidine structure (6), where the Si–N bonds were 1.841–1.837 Å when the chelating nitrogen's were



Scheme 2. Bond lengths in (Å).

trans to each other, and Si–N bonds of 1.915–1.914 Å when *trans* to a Si–Cl bond [33]. The N(5)–C(10) bond length is 1.311(7) Å in 3 which is the shortest C–N bond length among compounds 2–4.

In 4, the Si atom also has a distorted trigonal bipyramidal geometry (Fig. 2), where the Cl(1) and N(9) occupy the apical positions, and the C(11), C(14) and N(1) the equatorial positions. The distortion from the trigonal bipyramidal geometry is 0.145 Å, which is 0.013 Å longer than in 3. The Si(1)–Cl(1) bond in 4 is similar to that in 3 lengthened [33] to 2.254 Å (Table 2). The Si(1)–N(9) bond in 4 is 2.006 Å and Si(1)–N(1) = 1.785 Å. The apical Si(1)–N(9) is also *trans* to

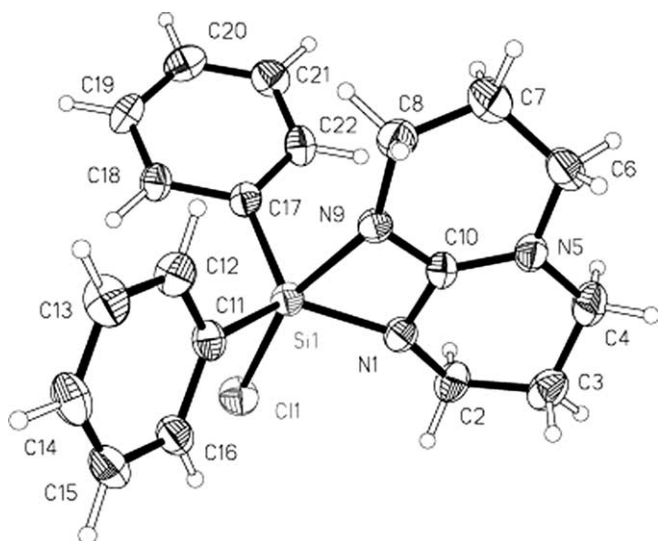


Fig. 2. Solid-state structure of **3** (thermal ellipsoids at the 30% probability level).

a Si–Cl bond which leads to a longer bond length [35]. The N(5)–C(10) = 1.325(3) Å distance in **4** is the longest N(5)–C(10) bond length of the complexes **2–4** (Scheme 3).

Compounds **2–4** were also analysed in solution with ^{29}Si NMR over the range 60 to –190 ppm. The in solid-state pentacoordinate compound **3** shows one signal in $\text{C}_2\text{D}_2\text{-Cl}_4$ at –77.3 ppm and in CDCl_3 at –77.2 ppm. Compound **3** thus keeps its $\lambda^5\text{Si}$ -coordination from solid state in both solvents [32]. The ^{13}C NMR spectra of **3** in CDCl_3 reveal only 4 signals originating from the $[\text{hpp}]^-$ unit, indicating a symmetric structure, where the two rings are equal on the timescale of the NMR experiment. The suggestion is

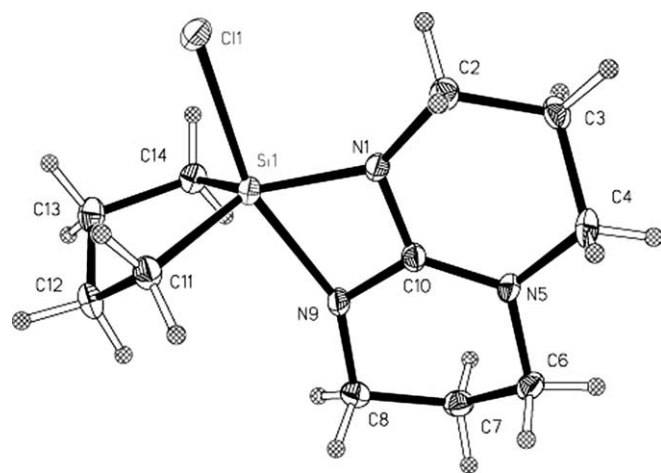


Fig. 3. Solid-state structure of **4** (thermal ellipsoids at the 30% probability level).

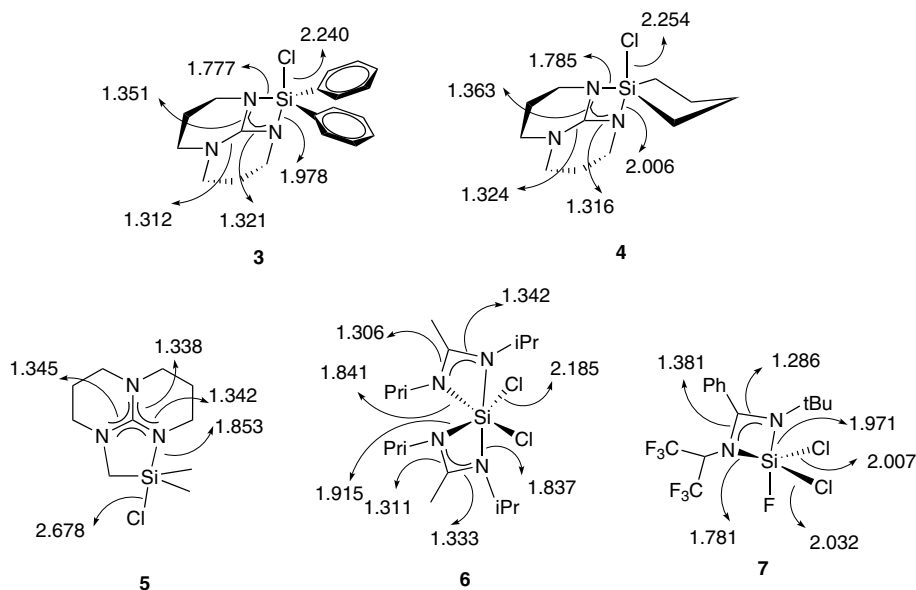
therefore that **3** is a monomeric compound with symmetric guanidine unit, having a formally anionic silicon atom in a $\lambda^5\text{Si}$ -coordination state.

The in solid-state pentacoordinate compound **4**, on the other hand, showed one peak at 26.1 ppm in tetrachloroethane (decomposed in CDCl_3), which should be explained as an ionic $\lambda^4\text{Si}$ -compound [32]. The ^{13}C NMR of **4** in $\text{THF-}d_8$ also showed only 4 signals from the guanidine unit, leading to the conclusion of a symmetric molecule with respect to the two rings in the structure.

The in solid-state tetracoordinate dimeric compound **2** has in benzene solution one peak at –52.2 ppm in the ^{29}Si NMR spectrum. This shift value is in the area between the border values for an ionic $\lambda^4\text{Si}$ - and a $\lambda^5\text{Si}$ -coordination

Table 2
Selected bond lengths (Å) and angles (°) for compounds **2**, **3** and **4**

2		3		4	
<i>Bond lengths (Å)</i>					
N(1)–C(10)	1.362(5)	N(1)–C(10)	1.351(7)	N(1)–C(10)	1.363(3)
N(5)–C(10)	1.315(5)	N(5)–C(10)	1.311(7)	N(5)–C(10)	1.325(3)
N(9)–C(10)	1.348(5)	N(9)–C(10)	1.321(6)	N(9)–C(10)	1.316(3)
Si(1)–C(1)	4.574	Si(1)–C(1)	2.240(19)	Si(1)–C(1)	2.2539(10)
Si(1)–N(1)	1.772(4)	Si(1)–N(1)	1.777(4)	Si(1)–N(1)	1.785(2)
Si(1)–N(9A)	1.771(4)	Si(1)–N(9)	1.978(4)	Si(1)–N(9)	2.006(2)
Si(1)–C(12)	1.835(5)	Si(1)–C(17)	1.870(5)	Si(1)–C(14)	1.875(3)
Si(1)–C(11)	1.846(5)	Si(1)–C(11)	1.874(5)	Si(1)–C(11)	1.871(2)
		Si(1)–C(10)	2.333(5)	Si(1)–C(10)	2.368(3)
<i>Bond angles (°)</i>					
C(10)–N(1)–Si(1)	120.4(3)				
C(10)–N(9)–Si(1A)	123.3(3)				
N(5)–C(10)–N(9)	121.6(4)	N(5)–C(10)–N(9)	126.8(5)	N(9)–C(10)–N(5)	128.6(3)
N(5)–C(10)–N(1)	121.2(4)	N(5)–C(10)–N(1)	126.4(5)	N(5)–C(10)–N(1)	125.2(2)
N(9)–C(10)–N(1)	117.2(4)	N(9)–C(10)–N(1)	106.8(4)	N(9)–C(10)–N(1)	106.2(2)
C(12)–Si(1)–C(11)	110.0(2)	C(11)–Si(1)–C(17)	114.1(2)	C(11)–Si(1)–C(14)	98.49(12)
N(1)–Si(1)–N(9)#1	109.39(18)	N(1)–Si(1)–N(9)	69.44(19)	N(1)–Si(1)–N(9)	68.57(9)
		N(9)–Si(1)–C(1)	160.61(14)	N(9)–Si(1)–C(1)	159.72
		N(1)–Si(1)–C(11)	125.3(2)	N(1)–Si(1)–C(11)	127.95(11)
		N(1)–Si(1)–C(17)	119.0(2)	N(1)–Si(1)–C(14)	131.59(11)
		N(5)–C(10)–Si(1)	173.0(4)	N(5)–C(10)–Si(1)	173.0(2)



Scheme 3. Selected bond lengths (Å) of **3** and **4** in comparison to λ^5 Si-chloro-dimethyl-(3,4,7,8-tetrahydro-2*H*,6*H*-pyrimido[1,2-*a*]pyrimidin-1-yl-methyl-*C'*1',*N'*9')-silicon (**5**) [32], *cis*-dichlorosilicon (bis)methyl-isopropyl amidinate (**6**) and λ^5 Si-1,3-diaza-1-tert-butyl-4-phenyl-3-(bistrifluoromethylmethyl-ene)-2,2-dichloro-2-fluoro-2-silacyclobute-3-ene (**7**).

state [32]. If we assume a similar level for the border value for a λ^5 Si-coordinated **2** as for very similar structures in C_6D_6 (−57 ppm, referred by Kummer et al. [32]), the shift value of −52.2 ppm for compound **2** will indicate that the major part is in a λ^5 Si-coordination state and a minor part in an ionic λ^4 Si-coordination state. In the ^{13}C NMR (C_6D_6), only 5 types of carbons are shown in the molecule. The spectra indicate that **2** is a compound with symmetric guanidine unit (both ionic λ^4 Si- and λ^5 Si-forms having identical and symmetric guanidine spectra) over the time-scale of the NMR measurement at room temperature. If the minor part in the ionic λ^4 Si- or the major part in the λ^5 Si-form of **2** are of a dimeric or monomeric form can not be concluded from these measurements, since the guanidine unit for all the compounds **2–4** regardless of Si-coordination form is shown to be highly symmetric in the 1H and ^{13}C NMR spectra.

The preference in solid state for **3** and **4** to form λ^5 Si-structures and for **2** to form a dimeric ionic λ^4 Si-structure most likely originates from steric reasons. The two bulky phenyls in **3** and the strained cyclic ring in **4** prevent the formation of a dimeric structure. In the λ^5 Si-forms of **3** and **4**, one nitrogen from the [hpp][−] takes up an apical position and the other an equatorial, leading to the fact that the apical Si–N bond is longer than the equatorial giving a potentially strained structure. The Si–N bond lengths in **2** and the equatorial Si–N bond lengths of **3** and **4** are very similar (1.772, 1.777 and 1.785 Å, respectively), while the apical Si–N bond lengths of **3** and **4** are not only longer but also very similar (1.978 and 2.006 Å, respectively).

A further aspect of interest in the background to the solid state structures is the C–Si–C and N–Si–N angles. In **2**, the dimeric ionic λ^4 Si-structure has C(12)–Si(1)–C(11) = 110.0(2)° and N(1)–Si(1)–N(9)#1 = 109.39(18)°,

both very close to the expected angle in a tetrahedron, being a very low strain ideal situation. In **3** and **4**, on the other hand, we have a more strained situation, where N(1)–Si(1)–N(9) = 69.44(19)° and 68.57(9)°, respectively, both much smaller than the ideal 90° for an apical–equatorial position. The C–Si–C angle in **3** and **4** is also smaller than the ideal 120° for an equatorial–equatorial position (C(11)–Si(1)–C(17) = 114.1(2)° and C(11)–Si(1)–C(14) = 98.49(12)°). The silacarbyclic ring in **4** is here restricting the angle C(11)–Si(1)–C(14) which is close to the expected angle for a silolane.

The differences in solution structures of compounds **2–4**, indicated by their ^{29}Si NMR spectra (vide supra), are to some extent explained by the differences in steric strain. Compound **3** keeps the λ^5 Si-form in solution, while **4** by forming the ionic λ^4 Si-structure releases strain in the system. Compound **2** on the other hand forms an equilibrium with one minor ionic λ^4 Si- and one major λ^5 Si-form.

It appears from this that if the substituents on the Si-atom are small enough, the system releases strain by forming a dimeric structure such as in **2**. A similar explanation is valid for compound **4** in solution, where the release of the chlorine atom from the silicon atom is forming an ionic λ^4 Si-structure.

3. Summary

Reacting [hpp][−] K⁺ with Me₂SiCl₂ gave the in solid state dimeric diionic species λ^4 Si-[Me₂SiCl(hpp)]₂ (**2**) which in C_6D_6 solution exists mainly as a λ^5 Si-type structure. The same reaction with Ph₂SiCl₂ gave λ^5 Si-Ph₂SiCl(hpp) (**3**) having a distorted trigonal bipyramidal silicon structure both in solid state and in CDCl₃ and CD₂Cl₄ solution. The product formed from 1,1-dichlorosilolane led to

$\lambda^5\text{Si}(\text{CH}_2)_4\text{SiCl}(\text{hpp})$ (**4**) which in solid state has a penta-coordinated structure but in CD_2Cl_4 solution is forming an ionic $\lambda^4\text{Si}$ -species. The preference for **2–4** in solid-state and solution for the formation of $\lambda^5\text{Si}$ -structures vs. ionic $\lambda^4\text{Si}$ -structures originate most probably from steric reasons where bulky groups prevent the formation of dimeric forms and the formation of ionic $\lambda^4\text{Si}$ -forms releases strain in the molecule.

4. Experimental

4.1. General procedures

The operations were carried out in argon or nitrogen atmosphere using standard Schlenk, vacuum and dry box techniques. Solvents were dried with potassium benzophenone ketyl and distilled under argon prior to use. 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2*a*]pyrimidine hpp-H (Fluka) was used as purchased. The $[\text{hpp}]^-\text{K}^+$ was prepared according to the literature [36]. ^1H and ^{13}C NMR and the COSY H–C spectra were recorded using JEOL JNM-EX 270 MHz FT NMR spectrometer at 25 °C. ^1H NMR was referenced to residual hydrogen in the deuterated solvents. ^{29}Si NMR spectra were recorded at 25 °C from +60 to –190 ppm using external reference with a Bruker Avance 600 operated at 119.23 MHz. Direct inlet MS spectra were produced by VG TRIO 2 quadrupole mass spectrometer in an electron impact ionisation mode (EIMS) (70 eV). The ^1H and ^{13}C NMR and MS spectra were recorded at Fortum Oil and Gas Oy, Analytical Research department, Finland. The elemental analyses were carried out by Analytische Laboratorien GmbH in Lindlar, Germany.

4.2. Crystallography

Crystal data of **2** and **3** were collected with a Rigaku AFC-7S diffractometer at 133(2) K, using graphite monochromatised Mo $\text{K}\alpha$ radiation, 0.71073 Å. Data were reduced by the TEXSAN package. Crystal data of **4** were collected with a Nonius KappaCCD area-detector diffractometer at 173(2) K, using graphite monochromatised Mo $\text{K}\alpha$ radiation, 0.71073 Å: COLLECT (Nonius, 2002). The crystals were fixed at fibres using the oil-drop technique.

4.3. Preparation of compounds

4.3.1. Synthesis of $[\text{Me}_2\text{SiCl}(\text{hpp})]_2$; 7,7,14,14-tetramethyl-2,3,5,6,9,10,12,13-octahydro-1*H*,4*H*,8*H*,11*H*-6*a*,7*a*,13*a*,14*a*-tetraaza-3*a*,10*a*-diazonia-7,14-disilanaphtho[1',8':5,6,7]cycloocta [1,2,3-*de*]naphthalene dichloride (**2**)

$[\text{hpp}]^-\text{K}^+$ (**1**) (13.0 g, 73.1 mmol) in 200 ml of THF was added as a slurry to a solution of 55 ml (438.6 mmol) of Me_2SiCl_2 in 50 ml THF over 3 h at ambient temperature and stirred for 2 h. The colour changed from yellow to dark yellow. The gelly KCl was filtrated off and washed with 2×30 ml of THF. The solvent was removed under

vacuum and the residue extracted into 3×30 ml of pentane and filtered again to remove trace insolubles. The analytically pure product was obtained by recrystallisation from refluxing in pentane and then cooling to –30 °C yielding colourless, needle-like crystals that were filtered and washed with a small amount of cold pentane and dried under vacuum. Yield 12.9 g (76%, calculated as monomer). (Found: C, 46.52; H, 7.80; N, 18.24; Cl, 15.15; Si 12.05%); $\text{C}_{18}\text{H}_{36}\text{Cl}_2\text{N}_6\text{Si}_2$ requires C, 46.63; H, 7.83; Cl, 15.29; N, 18.13; Si, 12.12%; m/z 231 (monomeric M^+ , 9%), 216 ($\text{M} - \text{CH}_3$, 13%), 196 ($\text{M} - \text{Cl}$, 14%), 138 ($\text{M} - \text{SiClMe}_2$, 100%); ^1H NMR (C_6D_6 , δ): 3.09 (t, 4H, CH_2), 2.21 (t, 4H, CH_2), 1.16 (m, 4H, CH_2), 0.96 (s, 6H, CH_3). ^{13}C NMR (C_6D_6 , δ): 154.2 (CN_3), 45.1 (CH_2), 39.1 (CH_2), 23.3 (CH_2), 8.8 (CH_3). ^{29}Si NMR (C_6D_6 , δ): –52.2.

4.3.2. Synthesis of $\lambda^5\text{Si}-\text{Ph}_2\text{SiCl}(\text{hpp})$; 1,1-diphenyl-3,4,6,7-tetrahydro-2*H*,5*H*-1*a*,7*a*-diazia-4*a*-azonia-1-silacyclobuta[*de*]naphthalene chloride (**3**)

$[\text{hpp}]^-\text{K}^+$ (**1**) (3.0 g, 16.9 mmol) in 50 ml of THF was added as a slurry to a solution of 21 ml (101.5 mmol) of Ph_2SiCl_2 in 50 ml THF over 3 h at ambient temperature and stirred for 2 h. The colour changed from whitish to light yellow. The gelly KCl was filtrated off and washed with 2×30 ml of THF. The solvent was removed under vacuum and the product washed with 3×30 ml pentane and dried under vacuum. The analytically pure product was obtained by recrystallisation from refluxing pentane and then gradually cooling to –30 °C. Yield 5.2 g (87%) of white, needle-like crystals. (Found: C, 63.89; H, 6.20; N, 11.97; Cl, 9.90; Si, 7.74%); $\text{C}_{19}\text{H}_{22}\text{ClN}_3\text{Si}$ requires C, 64.11; H, 6.23; N, 11.81; Cl, 9.96; Si, 7.89%; m/z 355 (M^+ , 40%), 320 ($\text{M} - \text{Cl}$, 45%), 278 ($\text{M} - \text{Ph}$, 52%), 138 ($\text{M} - \text{SiClPh}_2$, 75%), 40 (100%); ^1H NMR (CDCl_3 , δ): 7.74 (dd, 4H, CH), 7.34 (d, 2H, CH), 7.32 (d, 4H, CH), 3.25 (t, 4H, CH_2), 3.15 (t, 4H, CH_2), 1.96 (m, 4H, CH_2). ^{13}C NMR (CDCl_3 , δ): 155.1 (CN_3), 141.0 (C_q), 134.0 (CH), 128.3 (CH), 127.2 (CH), 46.6 (CH_2), 38.8 (CH_2), 23.2 (CH_2). ^{29}Si NMR (CDCl_3 , δ): –77.4. ^{29}Si NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, δ): –77.3.

4.3.3. Synthesis of $\lambda^5\text{Si}-(\text{CH}_2)_4\text{SiCl}(\text{hpp})$; 3,4,6,7-tetrahydro-2*H*,5*H*-spiro[1*a*,7*a*-diazia-4*a*-azonia-1-silacyclobuta[*de*]naphthalene-1,1'-silolane] chloride (**4**)

$[\text{hpp}]^-\text{K}^+$ (**1**) (2.6 g, 14.7 mmol) dissolved in 200 ml of THF was added into a solution of 55 ml (88.0 mmol) of 1,1-dichloro silolane in 50 ml THF over 3 h 30 min at ambient temperature. The colour changed from whitish to grey. The solution was stirred for 72 h at ambient temperature after which the mixture containing a gelly precipitate of KCl was evaporated under vacuum. The solid was washed with 3×30 ml pentane and then extracted into 3×300 ml of toluene and filtrated. Pure product was isolated by recrystallisation from heated at 65 °C toluene, and then cooled at –30 °C. Yield 1.05 g (28%) of colourless, needle-like solid. The product decomposes in CH_2Cl_2 and CHCl_3 . (Found: C, 51.07; H, 7.70; Cl, 13.95; N, 16.39;

Si, 10.70%); $C_{11}H_{20}ClN_3Si$ requires C, 51.24; H, 7.82; Cl, 13.75; N, 16.30; Si, 10.89%; m/z 257 (M^+ , 11%), 228 ($M - C_2H_5$, 37%), 201 ($M - C_4H_9$, 38%), 138 ($M - SiClC_4H_8$, 100%); 1H NMR (THF- d_8 , δ): 3.20 (t, overlapping, 4H, CH_2), 3.10 (t, overlapping, 4H, CH_2), 1.90 (m, 4H, CH_2), 1.78 (q, 2H, equatorial), 1.68 (q, 2H, axial), 0.90 (q, 2H, equatorial), 0.8 (q, 2H, axial). ^{13}C NMR (THF- d_8 , δ): 154.0 (CN_3), 45.4 (CH_2), 39.5 (CH_2), 25.0 (CH_2), 23.4 (CH_2), 18.8 (CH_2). ^{29}Si NMR ($C_2D_2Cl_4$, δ): 26.1 (decomposed in $CDCl_3$).

Acknowledgements

Discussions with Professors Markku Leskelä and Tapio Hase at the Helsinki University are gratefully acknowledged. The authors thank Mrs. Päivi Pennanen, Åbo Akademi University, for her assistance in running the ^{29}Si NMR spectra.

Appendix A. Supplementary data

Crystallographic data for the structural analysis of **2–4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 239595, 239596 and 239597. Copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax.(int. code) +44(1223)336 033 or E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.09.002.

References

- [1] R.J.P. Corriu, A. Kpoton, M. Poirier, G. Royo, A. De Saxe, J.C. Young, *Journal of Organometallic Chemistry* 395 (1990) 1.
- [2] C. Chuit, R.J.P. Corriu, C. Reye, J.C. Young, *Chemical Reviews* (Washington, DC, United States) 93 (1993) 1371.
- [3] A.R. Bassindale, S.G. Glynn, J. Jiang, D.J. Parker, R. Turtle, P.G. Taylor, S.S.D. Brown, *Organosilicon Chemistry II: From Molecules to Materials*, [Münchener Silicontage], 2nd ed., Munich, 1994, 1996, p. 411.
- [4] R.R. Holmes, *Chemical Reviews* (Washington, DC, United States) 90 (1990) 17.
- [5] K. Tamao, T. Hayashi, Y. Ito, *Bulletin de la Societe Chimique de France* 132 (1995) 556.
- [6] H.H. Karsch, R. Richter, E. Witt, *Journal of Organometallic Chemistry* 521 (1996) 185.
- [7] H.H. Karsch, *Organosilicon Chemistry I* (1994) 95.
- [8] D. Ballweg, Y. Liu, I.A. Guzei, R. West, *Silicon Chemistry I* (2002) 57.
- [9] M. Spiniello, J.M. White, *Organometallics* 19 (2000) 1350.
- [10] G. Klebe, K. Hensen, H. Fuess, *Chemische Berichte* 116 (1983) 3125.
- [11] J. Belzner, D. Schaer, *Organosilicon Chemistry II: From Molecules to Materials*, [Münchener Silicontage], 2nd ed., Munich, 1994, 1996, p. 459.
- [12] I. Kalikhman, B. Gostevskii, V. Kingston, S. Krivonos, D. Stalke, B. Walfort, T. Kottke, N. Kocher, D. Kost, *Organometallics* 23 (2004) 4828.
- [13] P. Kumar, R. Shankar, *Journal of Organometallic Chemistry* 687 (2003) 190.
- [14] K. Tamao, Y. Tarao, Y. Nakagawa, K. Nagata, Y. Ito, *Organometallics* 12 (1993) 1113.
- [15] H.H. Karsch, T. Segmüller, in: N. Auner, J. Weis (Eds.), *Silicon and Germanium Compounds with Amidate Ligands in Organosilicon Chemistry V: From Molecules to Materials*, European Silicon Days, 1st. September, 2001 (2003), Meeting Date 2001, Munich, Germany, 2003, Wiley-VCH, pp. 270–276.
- [16] G. Klebe, *Journal of Organometallic Chemistry* 293 (1985) 147.
- [17] R. Tacke, M. Pülm, B. Wagner, *Advances in Organometallic Chemistry* 44 (1999) 221.
- [18] D. Kost, I. Kalikhman, S. Krivonos, R. Bertermann, C. Burschka, R.E. Neugebauer, M. Pülm, R. Willeke, R. Tacke, *Organometallics* 19 (2000) 1083.
- [19] D. Schinzer, in: H. Waldmann (Ed.), *Organic Synthesis Highlights II*, VCH, Weinheim, Germany, 1995, pp. 123–127.
- [20] A. Hosomi, *Reviews on Heteroatom Chemistry* 7 (1992) 214.
- [21] R. Corriu, *Organosilicon Chem.* (1994) 157.
- [22] M. Weinmann, O. Walter, G. Huttner, H. Lang, *Journal of Organometallic Chemistry* 561 (1998) 131.
- [23] A.R. Bassindale, S.J. Glynn, P.G. Taylor, N. Auner, B. Herrschaft, *Journal of Organometallic Chemistry* 619 (2001) 132.
- [24] J.M. Anglada, C. Bo, J.M. Bofill, R. Crehuet, J.M. Poblet, *Organometallics* 18 (1999) 5584.
- [25] H.M. Cho, M.E. Lee, C.H. Kim, *Organometallics* 21 (2002) 2017.
- [26] Y.I. Baukov, Y.E. Ovchinnikov, A.G. Shipov, E.P. Kramarova, V.V. Negrebetsky, Y.T. Struchkov, *Journal of Organometallic Chemistry* 536/537 (1997) 399.
- [27] G. Häfelfinger, F.K.H. Kuske, in: S. Patai, Z. Rappoport (Eds.), *The Chemistry of Amidines and Imidates*, Vol. 2, John Wiley & Sons Ltd., 1991, pp. 3–100.
- [28] S.R. Foley, G.P.A. Yap, S. Richeson, *Polyhedron* 21 (2002) 619.
- [29] M.D. Irwin, H.E. Abdou, A.A. Mohamed, J.P. Fackler Jr., *Chemical Communications* (Cambridge, United Kingdom) (2003) 2882.
- [30] F.A. Cotton, X. Feng, D.J. Timmons, *Inorganic Chemistry* 37 (1998) 4066.
- [31] S.L. Aeilts, M.P. Coles, D.C. Swenson, R.F. Jordan, V.G. Young Jr., *Organometallics* 17 (1998) 3265.
- [32] D. Kummer, S.H.A. Halim, W. Kuhs, G. Mattern, *Journal of Organometallic Chemistry* 446 (1993) 51.
- [33] H.H. Karsch, P.A. Schlüter, M. Reisky, *European Journal of Inorganic Chemistry* (1998) 433.
- [34] H.H. Karsch, P.A. Schlüter, F. Bienlein, M. Herker, E. Witt, A. Sladek, M. Heckel, *Z. Anorg. Allg. Chem.* 624 (1998) 295.
- [35] H.H. Karsch, F. Bienlein, A. Sladek, M. Heckel, K. Burger, *Journal of the American Chemical Society* 117 (1995) 5160.
- [36] O. Andell, J. Maaranen, J. Hoikka, T. Vanne, S. Rautio. WO 2002016374, 2002, Borealis Technology Oy, Finland, Campbell, Neil.