Chapter 6

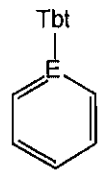
Synthesis and Structure of the First Heavy Cyclobutadiene Dianion Consisting of Silicon Atoms

Summary

Dark-green crystals of trisilagermacyclobutadiene dianion dipotassium salt **21a** was obtained by the reaction of 2,3-dichloro-1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]trisila-germacyclobutene **9**, which has a endocyclic Si=Ge double bond, with 4.4 molar amount of potassium graphite (KC_8) in THF. Tetasilacyclobutadiene dianion dipotassium salt **21b** was also obtained by the reduction of the corresponding 1,2,3,4-tetrabromocyclotetrasilane derivative **23** with KC_8. Molecular structure of the silicon analogue of cyclobutadiene dianion **21b** was determined by NMR spectroscopy and X-ray crystallography. X-ray crystallographic analysis shows that tetasilacyclobutadiene dianion **20b** does not have a characteristic planar geometry, as found in the aromatic compound, indicating that tetasilacyclobutadiene dianion can be classified as non-aromatic.

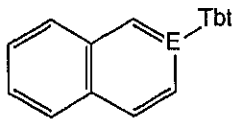
Introduction

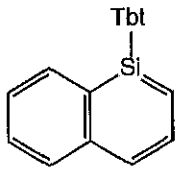
Aromaticity is one of the most fundamental concepts in organic chemistry, and studies on the chemistry of aromatic and anitaromatic compounds in carbon system have been well-established for more than 100 years.[1] As compared with the history of the research for aromaticity in carbon system, the chemistry of aromatic compounds containing heavier Group 14 elements (Si, Ge, and Sn) is relatively a new field of research, which has explosively developed in recent years.[2] Since the isolation of the first stable 2-silanaphthalene derivative by Okazaki, Tokitoh, and co-workers in 1997,[3] the heavy analogue of neutral aromatic compounds such as benzene, naphthalene, and anthracene containing silicon or germanium atom were synthesized.[4-8] The evidence for aromaticity of these compounds were confirmed by NMR spectra as well as by X-ray structural analyses. The heavy analogue of cyclopentadienide ion and cyclopentadiene dianion, e.g. silole and germole anion and its dianion derivatives, were also prepared as alkali metal salts,[9,10] and aromaticity in some of those compounds were demonstrated by X-ray analyses.



Heavy benzene

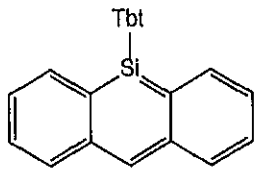
E = Si; N. Tokitoh (2000)
E = Ge; N. Tokitoh (2002)





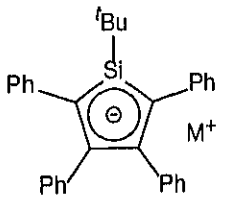
Heavy naphthalene

E = Si; R. Okazaki (1997)
E = Ge; N. TTokitoh (2001)
N. Tokitoh (2002)



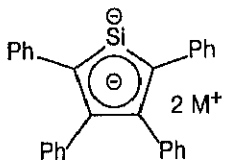
Heavy anthracene

N. Tokitoh (2002)



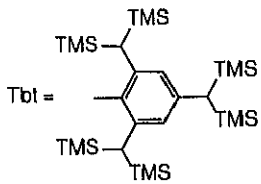
Heavy cyclopentadienide ion

P. Boudjouk (1993)



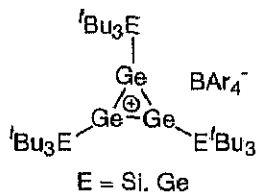
Heavy cyclopentadiene dianion

E = Si; P. Boudjouk (1994)
E = Ge; P. Boudjouk (1995)

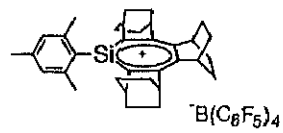


In contrast to neutral and anionic heavy aromatic compounds, only two examples of cationic species which show aromatic character are known at the present. In 1997, Sekiguchi

et al. successfully synthesized germanium analogue of cyclopropenylium ion ($R_3Ge_3^+$) by the reaction of the corresponding cyclotrigermene with trityl tetraarylborates (trityl = triphenylmethyl).[11] In 2000, Komatsu et al. succeeded in the observation of the silatropilyium ion with rigid bicyclo[2.2.2]octane units by NMR spectra at low temperature.[12] The aromaticity and free state of the silatropilyium ion were supported by theoretical calculations.



Heavy cyclopropenylium ion
A. Sekiguchi (1997)



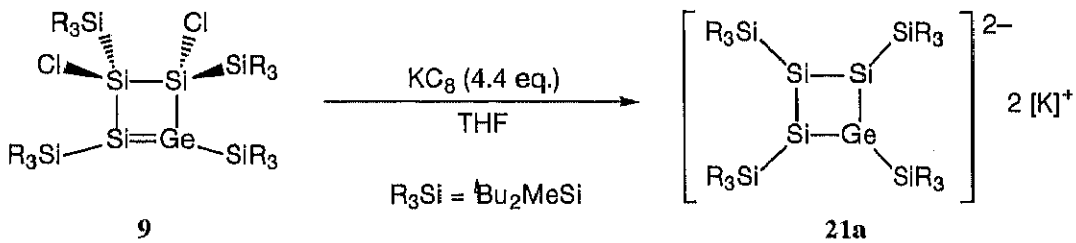
Heavy tropinylium ion
K. Komatsu (2000)

The fundamental Hükel's rule predicts the cyclobutadiene dianion ($R_4C_4^{2-}$) to be aromatic, and many experimental and theoretical investigations for its aromaticity are reported.[13-18] Quite recently, Sekiguchi et al. reported the synthesis and characterization of the silyl-substituted cyclobutadiene dianion dilithium salt which has a planar four-membered ring geometry in the solid state.[19] The evidence for aromaticity of the cyclobutadiene dianion derivatives was confirmed by not only X-ray analyses but also MCD spectrum in solution.[19] Although the explosive development of the chemistry of heavy aromatic compounds containing of silicon or germanium atom in recent years as mentioned above, heavy analogue of cyclobutadiene dianion is completely unknown up to date. As described in chapter 1, the author successfully synthesized the dichlorotrisilagermacyclobutene derivative **9**, which may be a good precursor of heavy cyclobutadiene dianion, by the reaction of the cyclotrisilene **3** with $GeCl_2$ dioxane in THF. In this chapter, synthesis and characterization of the dipotassium salt of trisilagermacyclobutadiene dianion are described. The author also reports synthesis and structure of the first silicon analogue of cyclobutadiene dianion as well as some reactivity of the heavy cyclobutadiene dianions.

Results and Discussion

Synthesis and Characterization of Trisilagermacyclobutadiene Dianion

The crystals of **9** and 4.4 molar amount of potassium graphite (KC_8) were placed in a reaction vessel, and oxygen-free, dry THF was introduced by vacuum transfer. The reaction mixture became a dark-green solution within 10 minutes with stirring at room temperature. The resulting KCl and graphite were removed by filtration after exchange of the solvent to hexane. The reaction mixture was recrystallized from a mixture of hexane and THF to afford dark-green crystals of 1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]trisilagermacyclobutadiene dianion dipotassium salt **21a** in 90% yield (Scheme 6-1).



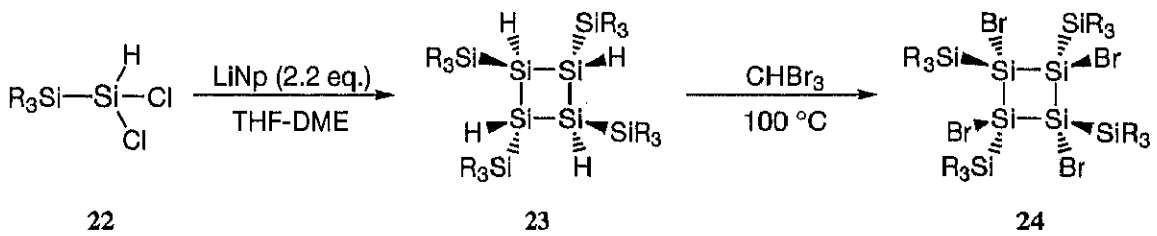
Scheme 6–1

The structure of **21a** was determined by ^1H, ^{13}C and ^{29}Si NMR spectroscopy. In the ^1H and ^{13}C NMR spectra of **21a** in toluene-d_8, three kinds of signals arising from $^tBu_2MeSi$ groups were observed. The ^{29}Si NMR spectrum showed signals at δ = 9.1, 11.0, 23.5, 36.1, and 91.7. The signal at the lowest field (δ = 91.7) is assigned to diagonal silicon atom relative to skeletal germanium atom, and the signal at δ = 36.1 can be assigned to skeletal silicon atoms bounded to the germanium atom. This difference of ^{29}Si resonances in the four-membered ring indicates that compound **21a** has a distorted structure in which one potassium cation located mainly on the germanium atom and another counter cation was coordinated with trisilaallylic anion moiety. The structural feature of **21a** in solution was probably due to the difference of relative electronegativities between silicon and germanium

atoms, and to a considerable Coulombic repulsion between the skeletal atoms. Although the X-ray single-crystal analysis of **21a** was also succeeded, the exact structure of **21a** could not be confirmed because of the disorder problem in the four-membered ring skeleton.

Synthesis and Characterization of Tetrasilacyclobutadiene Dianions

In the case of the synthesis of tetrasilacyclobutadiene dianion derivative, dihalo-cyclotetrasilene[20] which may be a good precursor of tetrasilacyclobutadiene dianion could not be prepared from the cyclotrisilene **3**, because the experimentally available dihalo-silylenes were unknown up to date. Therefore, the author has synthesized the four-membered ring compounds consisting of silicon atoms by the stepwise method as shown Scheme 6-2. First, $^{t}Bu_2MeSi$-substituted tetrasilacyclotetrasilane derivative **23** was prepared by the reductive condensation of $^{t}Bu_2MeSiSiHCl_2$ **22** with lithium naphthalenide (LiNp) in DME-THF solution in 39% yield (Scheme 6-2). Next, 1,2,3,4-tetrabromocyclotetrasilane derivative **24** was prepared by the bromination of **23** with $CHBr_3$ (Scheme 6-2). The structures of **23** and **24** were confirmed by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, as well as X-ray crystallography. As shown Figure 6-1 and 6-2, cyclotetrasilane derivatives **23** and **24** have highly symmetrical structures in which four $^{t}Bu_2MeSi$ groups are arranged in *all-trans* configuration relative each others. Thus, for compounds **23** and **24**, ^{1}H and ^{13}C NMR spectra showed the existence of only one kind of signal due to $^{t}Bu_2MeSi$ group, respectively . ^{29}Si NMR spectra for **23** and **24** revealed two resonances which are assigned to skeletal silicon atoms and silyl substituents, respectively.



Scheme 6–2

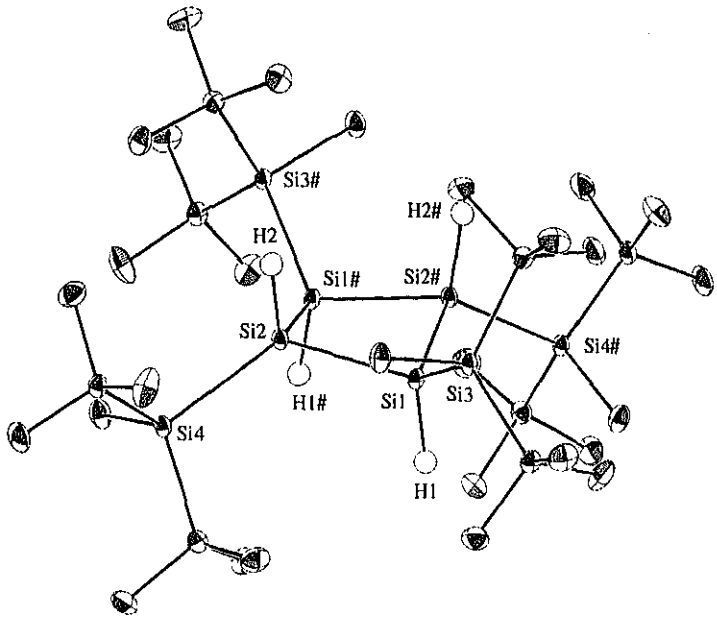


Figure 6–1. ORTEP drawing of **23** (Hydrogen atoms are omitted for clarity).

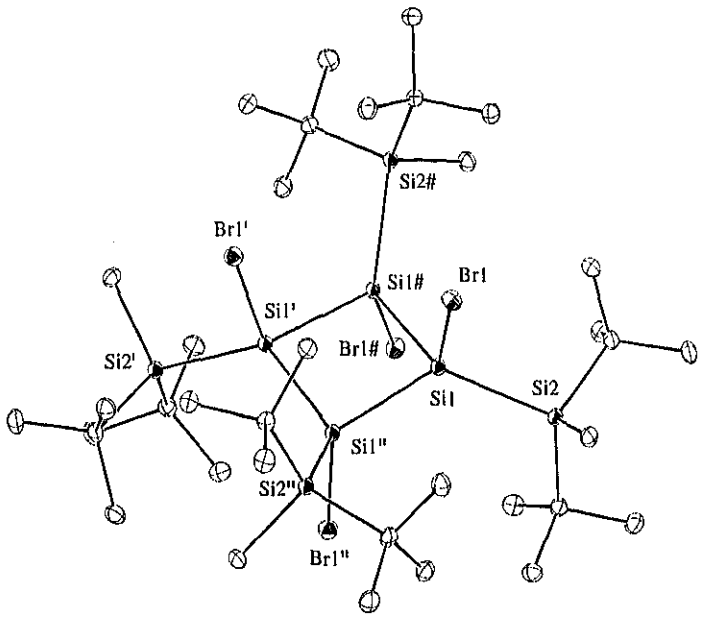
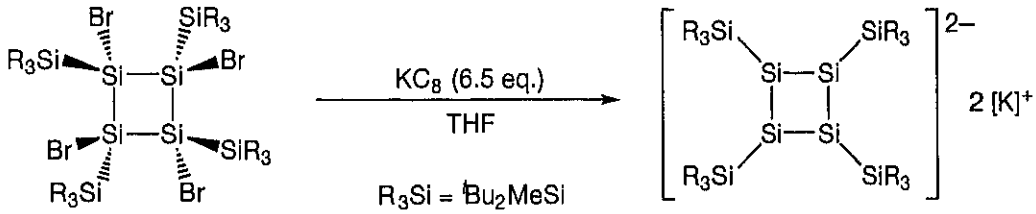


Figure 6–2. ORTEP drawing of **24** (Hydrogen atoms are omitted for clarity).

Treatment of **24** with 6 molar amount of KC_8 in oxygen-free, dry THF at room temperature afforded dark-green solution within 10 minutes. The resulting KBr salt and graphite were removed by filtration after exchange of the solvent to hexane. The reaction mixture was recrystallized from a mixture of hexane and THF to afford dark-green crystals of 1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]tetrasilacyclobutadiene dianion dipotassium salt **21b** in 73% yield (Scheme 6-3).



24 **20b**

Scheme 6–3

The structure of **21b** was determined by ^1H, ^{13}C and ^{29}Si NMR spectroscopy. The NMR data on the structure of **21b** in toluene-d_8 indicate a highly symmetrical structure. Thus, in the ^1H and ^{13}C NMR spectra of **21b** in toluene-d_8, only one kind of signal arising from $^tBu_2MeSi$ group was observed. The ^{29}Si NMR spectrum showed signals at δ = 11.8 and 18.4. The signal at δ = 18.4 is assigned to skeletal silicon atom, and the signal at δ = 11.8 can be assigned to silyl-substituent.

X-ray Structure of Tetrasilacyclobutadiene Dianion

A single crystal of **21b** containing THF suitable for X-ray diffraction analysis was obtained by recrystallization from a mixture of hexane and THF, and the molecular structure of **21b** was determined by X-ray crystallography (Figure 6-3). The dipotassium salt **21b** contains four molecules of THF. The two potassium atoms (K1 and K2) are located above and below, both being 1,3-coordinated to silicon atoms in the four-membered ring skeleton, as well as coordinated by the oxygen atoms of the THF molecules.

The four-membered ring deviates from planarity, as demonstrated by the dihedral angle of 34.16(2)° between Si1S2iSi3/Si1Si3Si4 planes. The bond length of Si1-Si2 is 2.2989(8) Å which slightly shorter than the normal Si-Si single bond but significantly longer than the Si=Si double bond lengths of cyclic disilenes (2.138 – 2.257 Å).[20,21] The bond length of Si1-Si4 (2.3301(8) Å), Si2-Si3 (2.3300(8) Å), and Si3-Si4 (2.3576(8) Å) lie in the normal region for Si-Si single bond (2.33 - 2.37 Å). The structural features suggest that **21b** has a cyclotetrasilene structure that the potassium cations were bonded to the Si3 and Si4 atoms and also interact with the diagonal silicon atoms, respectively. This experimental observation by X-ray crystallographic analysis for **21b** did not satisfy the inherent definitions of aromaticity for the geometry criteria, such as the planarity of the four-membered ring and the lack of bond alternation, indicating that the heavy cyclobutadiene dianion **21b** can be classified as non-aromatic.

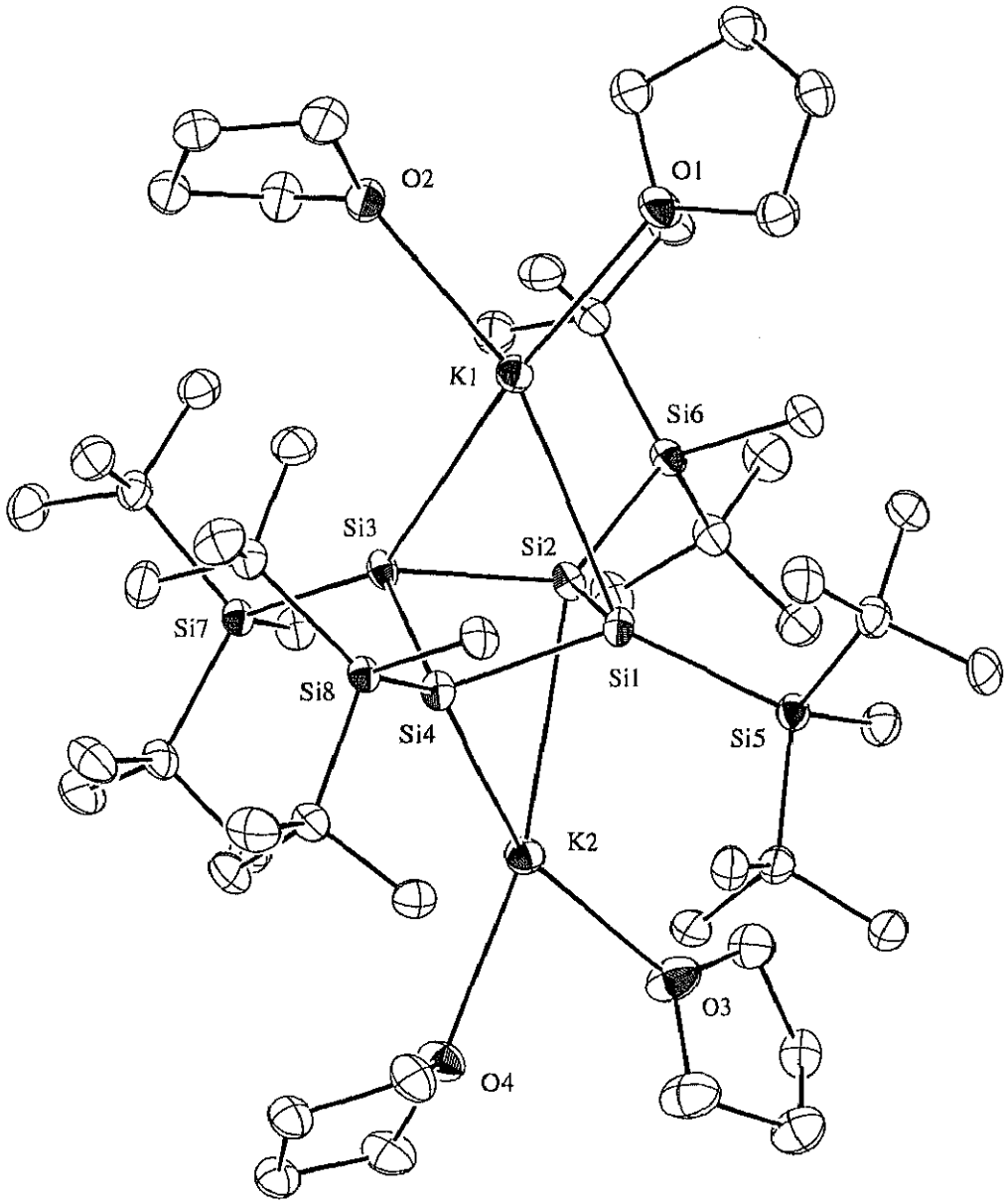


Figure 6–3. ORTEP drawing of **21b** (Hydrogen atoms are omitted for clarity).

Conclusion

Heavy cyclobutadiene dianion **21b** was obtained as dark-green crystals by the reduction of dichlorotrisilagermacyclobutene **9**, which has a endocyclic Ge=Si double bond, with KC_8. Silicon analogue of cyclobutadiene dianion **21b** was also synthesized by the reaction of the corresponding tetrabtromocyclotetrasilane **24** with KC_8. X-ray crystallographic analysis of **21b** showed that the four-membered ring skeleton of **21b** deviates from planarity and the existence of bond alternation, indicating that the silicon analogue of cyclobutadiene dianion **21b** can be classified as non-aromatic.

Experimental Section

General procedure

All reactions involving air-sensitive compounds were carried out under argon atmosphere using high-vacuum line and standard Schlenk techniques and dry, oxygen-free solvents. Dichlorodimethylsilane was presented by Shin-Etsu Co. $^{t}Bu_2MeSiNa$ was prepared was synthesized by the reaction of $^{t}Bu_2MeSiBr$ with Na in heptane according to the literature procedure in chapter 1. NMR spectra were recorded on a Brüker AC-300FT NMR spectrometer (^{1}H NMR at 300.13 MHz; ^{13}C NMR at 75.47 MHz; ^{29}Si NMR at 59.63 MHz). Mass spectra were obtained on a JEOL JMS SX-102 instrument (EI, 70 eV). UV spectra were recorded on a Shimadzu UV-3150 UV-visible spectrophotometer in hexane. Elemental analyses were performed at the Analytical Centers of Tsukuba University (Tsukuba, Japan) and Tohoku University (Sendai, Japan).

Synthesis of 1,2,3,4-Tetrakis[di-*tert*-butyl(methyl)silyl]trisilagermacyclobutadiene Dianion Dipotassium salt 21a

The crystals of **9** (prepared by the reaction of the cyclotrisilene **3** (70 mg. 0.098 mmol) and $GeCl_2$ dioxane (24 mg, 0.10mmol)) and KC_8 (58 mg, 0.43 mmol) were placed in a reaction vessel with a magnetic stirrer bar. After degassing the tube, oxygen-free, dry THF (2.0 mL) was introduced by vacuum transfer and stirred at room temperature to give a dark-green solution of **21a** within 30 munites. After the solvent was removed in vacuo, degassed hexane was introduced by vacuum transfer. After the graphite and resulting potassium salt had been removed from the tube, the solution was cooled to afford dark-green crystals of **21a**(thf)$_2$ (82 mg, 90%). ^{1}H NMR (toluene-d_8, δ) 0.53 (s, 6 H), 0.55 (s, 3 H), 0.56 (s, 3 H), 1.35 (s, 18 H), 1.38 (s, 36 H), 1.41 (s, 18 H), 1.45 (t, J = 3.6 Hz, 8 H), 3.41 (t, J = 3.6 Hz, 8 H); ^{13}C NMR (toluene-d_8, δ) −1.7, −0.6, 0.8, 22.0, 22.4, 23.1, 25.7

(THF), 31.4, 31.5 (3C), 68.0 (THF); ^{29}Si NMR (toluene-d_8, δ) 9.1, 11.0, 23.5, 36.1, 91.7.

Preparation of ^{t}Bu$_2$MeSiSiH$_2$Cl (22)

A solution of freshly prepared ^{t}Bu$_2$MeSiNa [from ^{t}Bu$_2$MeSiBr (47 mmol) and Na (390 mmol)] in heptane (150 mL) was added at –40 °C to a solution of $HSiCl_3$ (51 g, 370 mmol) in hexane (100 mL). The mixture was allowed to warm to room temperature and stirred for 2 h. Sodium chloride was filtered off, and the mixture was concentrated in vacuo. ^{t}Bu$_2$MeSiSiH$_2$Cl was isolated by Kugelrohr distillation under reduced pressure as a colorless solid (7.0 g, 27 mmol, 58%). bp 90–100°C / 10 mmHg; ^{1}H NMR (C_6D_6, δ) 0.04 (s, 3 H), 0.97 (s, 18 H), 5.86 (s, 1 H), ^{13}C NMR (C6D6, δ) -9.2, 20.9, 28.9; ^{29}Si NMR (C_6D_6, δ) 3.8 (^{t}Bu$_2$Me*Si*), 12.6 (*Si*HCl$_2$).

Preparation of *trans,trans,trans*-1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]-cyclotetrasilane (23)

A 1,2-dimethoxyethane (DME) solution of lithium naphthalenide [from naphthalene 48 mmol and lithium metal 200 mmol] was added at –78 °C to a solution of ^{t}Bu$_2$MeSiSiHCl$_2$ (5.7 g, 22 mmol) in THF (30 mL). The mixture was allowed to warm to room temperature and stirred for 15 h. After removal solvents in vacuo, haxane was introduced and resulting lithium chloride was filtered off. Naphthalene was separated by Kugelrohr distillation under reduced pressure (50°C, 0.1 mmHg), and then residue was recrystallization from hexane gave pure **23** as colorless crystals (1.6 g, 39% yield), mp 213-215 °C; ^{1}H NMR (C_6D_6, δ) 0.33 (S, 12 H), 1.19 (s, 72 H), 4.03 (s, 4 H), ^{13}C NMR (C_6D_6, δ) –5.5, 21.7, 29.9; ^{29}Si

NMR (C_6D_6, δ) −86.4 ($^1J_{29Si-1H}$ = 162.6 Hz), 13.8 ($^tBu_2MeSi$); UV-Vis (hexane) λ_{max}/nm (ε) 223 (sh, 29000), 282 (6800), 300 (sh, 4600), Anal. Calc for $C_{36}H_{88}Si_8$: C, 57.98; H, 11.89%. Found: C, 57.68; H, 11.84%.

Preparation of *trans,trans,trans*-1,2,3,4-tetrabromo-1,2,3,4-tetrakis[di-*tert*-butyl(methyl)silyl]cyclotetrasilane (24).

The $CHBr_3$ solution of **23** (200 mg, 268 mmol) was stirred at 110 °C for 2h. After the solvent was removed in vacuo, residue was recystallized from hexane gave colorless crysytals of **2** (262 mg, 92%). mp xx-xx °C; ^{1}H NMR (C_6D_6, δ) 0.62 (s, 12 H), 1.29 (s, 72 H); ^{13}C NMR (C_6D_6, δ) −3.1, 23.3, 31.0; ^{29}Si NMR (C_6D_6, δ) 0.1 (*Si*Br), 21.3 ($^tBu_2MeSi$).

Synthesis of 1,2,3,4-Tetrakis[di-*tert*-butyl(methyl)silyl]tetrasilacyclobutadiene Dianion Dipotassium salt (21b)

The crystals of tetrabromocyclotetrasilane **24** (48 mg, 0.045 mmol) and KC_8 (42 mg, 0.31 mmol) were placed in a reaction vessel with a magnetic stirrer bar. After degassing the tube, oxygen-free, dry THF (1.5 mL) was introduced by vacuum transfer and stirred at room temperature to give a dark-green solution of **21b** within 30 munites. After the solvent was removed in vacuo, degassed hexane was introduced by vacuum transfer. After the graphite and resulting potassium salt had been removed from the tube, the solution was cooled to afford dark-green crystals of **21b**(thf)$_2$ (29 mg, 73%); ^{1}H NMR (toluene-d_8, δ) 0.55 (s, 12 H), 1.40 (s, 72 H), 1.44 (t, J = 6.5 Hz, 8 H), 3.42 (t, J = 6.5 Hz, 8 H); ^{13}C NMR (toluene-d_8, δ) −0.5, 22.4, 25.8 (THF), 31.4, 68.0 (THF); ^{29}Si NMR (toluene-d_8, δ)

11.8 (^{t}Bu$_2$Me*Si*), 18.4.

X-ray Crystal Structure Determination of 23

A single crystal of **23** for X-ray diffraction was grown from a hexane solution. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo–Ka radiation (λ= 0.71070 Å). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Details of crystal data and structure refinement of are summarized in Table 6-1a. The final atomic parameters, the bond length, and the bond angles of **23** are listed in Table 6-1b, and Table 6-1c, respectively.

X-ray Crystal Structure Determination of 24

A single crystal of **24** for X-ray diffraction was grown from a hexane-toluene solution. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo–Ka radiation (λ= 0.71070 Å). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Details of crystal data and structure refinement of are summarized in Table 6-2a. The final atomic parameters, the bond length, and the bond angles of **24** are listed in Table 6-2b, and Table 6-2c, respectively.

Table 6-1a. Crystal data and structure refinement for **23**

Empirical formula	$C_{36}H_{88}Si_8$	
Formula weight	745.78	
Temperature	120 K	
Wavelength	0.71070 Å	
Crystal system, space group	Monoclinic, *C2*	
Unit cell dimensions	a = 23.9370(8) Å b = 8.4010(2) Å c = 16.9270(6) Å	alpha = 90 deg. beta = 135.000(1) deg. gamma = 90 deg.
Volume	2406.94(13) Å^3	
Z, Calculated density	2, 1.029 Mg/m^3	
Absorption coefficient	0.245 mm^-1	
F(000)	832	
Crystal size	0.3 x 0.2 x 0.2 mm	
Theta range for data collection	2.41 to 27.91 deg.	
Limiting indices	0<=h<=31, 0<=k<=10, -22<=l<=15	
Reflections collected / unique	2971 / 11603 [R(int) = 0.0130]	
Completeness to theta = 27.94	96.8%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2971 / 0 / 208	
Goodness-of-fit on F^2	1.072	
Final R indices [I>2sigma(I)]	R1 = 0.0254, wR2 = 0.0699	
R indices (all data)	R1 = 0.0255, wR2 = 0.0701	
Absolute structure parameter	0.11(9)	
Extinction coefficient	0.0244(14)	
Largest diff. peak and hole	0.266 and -0.255 e.Å^-3	

Table 6-1b. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **23**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Si(1)	5118(1)	3738(1)	1091(1)	16(1)
Si(2)	5973(1)	4181(1)	855(1)	16(1)
Si(3)	5107(1)	5164(1)	2298(1)	16(1)
Si(4)	7190(1)	2756(1)	2083(1)	16(1)
C(1)	4052(1)	5801(3)	1411(1)	28(1)
C(2)	5717(1)	7083(2)	2796(1)	21(1)
C(3)	5347(1)	8049(3)	1749(2)	31(1)
C(4)	5691(1)	8119(3)	3519(2)	36(1)
C(5)	6585(1)	6751(3)	3453(2)	34(1)
C(6)	5406(1)	3760(2)	3443(1)	21(1)
C(7)	5370(1)	4591(3)	4220(2)	35(1)
C(8)	4816(1)	2375(3)	2877(2)	35(1)
C(9)	6239(1)	3087(3)	4158(2)	40(1)
C(10)	7359(1)	2127(3)	3307(1)	28(1)
C(11)	8037(1)	4164(2)	2631(1)	20(1)
C(12)	8850(1)	3334(3)	3481(2)	35(1)
C(13)	7919(1)	4838(3)	1680(2)	40(1)
C(14)	8061(1)	5551(3)	3245(2)	36(1)
C(15)	7079(1)	844(2)	1362(1)	21(1)
C(16)	6402(1)	-128(3)	1055(2)	31(1)
C(17)	7828(1)	-194(3)	2137(2)	37(1)
C(18)	6868(1)	1177(3)	282(2)	34(1)

Table 6-1c. Bond lengths [Å] and angles [deg] for **23**

Si(1)-Si(2)	2.3754(6)	Si(1)-Si(2)#1	2.3754(6)	Si(1)-Si(3)	2.3834(6)
Si(1)-H(1)	1.41(3)	Si(2)-Si(1)#1	2.3755(6)	Si(2)-Si(4)	2.3834(6)
Si(2)-H(2)	1.43(3)	Si(3)-C(1)	1.8861(17)	Si(3)-C(2)	1.9234(19)
Si(3)-C(6)	1.9234(17)	Si(4)-C(10)	1.8854(17)	Si(4)-C(15)	1.9182(19)
Si(4)-C(11)	1.9263(17)	C(2)-C(4)	1.538(2)	C(2)-C(3)	1.537(2)
C(2)-C(5)	1.538(2)	C(6)-C(9)	1.532(2)	C(6)-C(8)	1.534(3)
C(6)-C(7)	1.545(2)	C(11)-C(13)	1.532(2)	C(11)-C(14)	1.536(3)
C(11)-C(12)	1.544(2)	C(15)-C(16)	1.541(2)	C(15)-C(18)	1.539(2)
C(15)-C(17)	1.539(2)				
Si(2)-Si(1)-Si(2)#1	88.595(19)	Si(2)-Si(1)-Si(3)	126.72(2)	Si(2)#1-Si(1)-Si(3)	116.26(2)
Si(2)-Si(1)-H(1)	102.9(9)	Si(2)#1-Si(1)-H(1)	107.8(9)	Si(3)-Si(1)-H(1)	111.5(9)
Si(1)-Si(2)-Si(1)#1	88.590(19)	Si(1)-Si(2)-Si(4)	116.25(2)	Si(1)#1-Si(2)-Si(4)	126.72(2)
Si(1)-Si(2)-H(2)	107.9(9)	Si(1)#1-Si(2)-H(2)	103.9(9)	Si(4)-Si(2)-H(2)	110.7(9)
C(1)-Si(3)-C(2)	106.56(9)	C(1)-Si(3)-C(6)	108.04(8)	C(2)-Si(3)-C(6)	116.50(7)
C(1)-Si(3)-Si(1)	106.29(6)	C(2)-Si(3)-Si(1)	109.39(5)	C(6)-Si(3)-Si(1)	109.54(6)
C(10)-Si(4)-C(15)	106.86(9)	C(10)-Si(4)-C(11)	107.99(8)	C(15)-Si(4)-C(11)	116.48(7)
C(10)-Si(4)-Si(2)	106.17(6)	C(15)-Si(4)-Si(2)	109.38(5)	C(11)-Si(4)-Si(2)	109.44(6)
C(4)-C(2)-C(3)	107.64(16)	C(4)-C(2)-C(5)	108.69(15)	C(3)-C(2)-C(5)	108.21(15)
C(4)-C(2)-Si(3)	112.24(12)	C(3)-C(2)-Si(3)	107.30(12)	C(5)-C(2)-Si(3)	112.56(13)
C(9)-C(6)-C(8)	108.81(18)	C(9)-C(6)-C(7)	108.58(16)	C(8)-C(6)-C(7)	107.08(15)
C(9)-C(6)-Si(3)	111.77(11)	C(8)-C(6)-Si(3)	108.31(11)	C(7)-C(6)-Si(3)	112.14(14)
C(13)-C(11)-C(14)	108.78(18)	C(13)-C(11)-C(12)	108.70(16)	C(14)-C(11)-C(12)	107.05(15)
C(13)-C(11)-Si(4)	111.80(11)	C(14)-C(11)-Si(4)	108.31(11)	C(12)-C(11)-Si(4)	112.04(14)
C(16)-C(15)-C(18)	108.21(15)	C(16)-C(15)-C(17)	107.50(16)	C(18)-C(15)-C(17)	108.76(15)
C(16)-C(15)-Si(4)	107.33(12)	C(18)-C(15)-Si(4)	112.62(14)	C(17)-C(15)-Si(4)	112.21(12)

Table 6-2a. Crystal data and structure refinement for **24**

Empirical formula	$C_{36}H_{84}Br_4Si_8$	
Formula weight	1061.39	
Temperature	120 K	
Wavelength	0.71070 Å	
Crystal system, space group	Tetragonal, $I4_1/a$	
Unit cell dimensions	a = 12.8810(4) Å b = 12.881 Å c = 30.5170(6) Å	alpha = 90 deg. beta = 90 deg. gamma = 90 deg.
Volume	5063.39(19) Å^3	
Z, Calculated density	4, 1.392 Mg/m^3	
Absorption coefficient	3.393 mm^-1	
F(000)	2208	
Crystal size	0.3 x 0.3 x 0.1 mm	
Theta range for data collection	2.55 to 27.88 deg.	
Limiting indices	0<=h<=16, -11<=k<=11, 0<=l<=39	
Reflections collected / unique	3013 / 3013 [R(int) = 0.0510]	
Completeness to theta = 27.94	99.5%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3013 / 0 / 110	
Goodness-of-fit on F^2	1.097	
Final R indices [I>2sigma(I)]	R1 = 0.0272, wR2 = 0.0714	
R indices (all data)	R1 = 0.0309, wR2 = 0.0730	
Extinction coefficient	0.0189(14)	
Largest diff. peak and hole	0.492 and -0.496 e.Å^-3	

Table 6-2b. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **24**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	4399(1)	-918(1)	494(1)	23(1)
Si(1)	4441(1)	-1310(1)	1224(1)	15(1)
Si(2)	3672(1)	202(1)	1584(1)	16(1)
C(1)	4153(2)	1316(2)	1238(1)	22(1)
C(2)	4084(2)	451(2)	2183(1)	20(1)
C(3)	4012(2)	-518(2)	2474(1)	25(1)
C(4)	3395(2)	1312(2)	2382(1)	27(1)
C(5)	5213(2)	847(2)	2202(1)	24(1)
C(6)	2190(2)	127(2)	1508(1)	21(1)
C(7)	1697(2)	1222(2)	1518(1)	29(1)
C(8)	1663(2)	-566(2)	1855(1)	25(1)
C(9)	1959(2)	-340(2)	1056(1)	24(1)

Table 6-2c. Bond lengths [Å] and angles [deg] for **24**

Br(1)-Si(1)	2.2847(5)	Si(1)-Si(1)#1	2.3998(7)	Si(1)-Si(1)#2	2.3999(7)
Si(1)-Si(2)	2.4465(7)	Si(2)-C(1)	1.887(2)	Si(2)-C(6)	1.926(2)
Si(2)-C(2)	1.930(2)	C(2)-C(3)	1.536(3)	C(2)-C(5)	1.541(3)
C(2)-C(4)	1.545(3)	C(6)-C(9)	1.537(3)	C(6)-C(8)	1.541(3)
C(6)-C(7)	1.547(3)				
Br(1)-Si(1)-Si(1)#1	105.34(3)	Br(1)-Si(1)-Si(1)#2	99.29(3)	Si(1)#1-Si(1)-Si(1)#2	89.748(3)
Br(1)-Si(1)-Si(2)	104.60(2)	Si(1)#1-Si(1)-Si(2)	125.52(3)	Si(1)#2-Si(1)-Si(2)	128.29(3)
C(1)-Si(2)-C(6)	107.27(9)	C(1)-Si(2)-C(2)	108.29(9)	C(6)-Si(2)-C(2)	113.24(9)
C(1)-Si(2)-Si(1)	102.79(7)	C(6)-Si(2)-Si(1)	107.89(6)	C(2)-Si(2)-Si(1)	116.51(6)
C(3)-C(2)-C(5)	107.76(16)	C(3)-C(2)-C(4)	108.71(17)	C(5)-C(2)-C(4)	106.92(16)
C(3)-C(2)-Si(2)	113.35(13)	C(5)-C(2)-Si(2)	110.42(13)	C(4)-C(2)-Si(2)	109.46(13)
C(9)-C(6)-C(8)	107.78(17)	C(9)-C(6)-C(7)	107.18(17)	C(8)-C(6)-C(7)	109.52(16)
C(9)-C(6)-Si(2)	108.63(13)	C(8)-C(6)-Si(2)	112.54(14)	C(7)-C(6)-Si(2)	110.99(14)

Symmetry transformations used to generate equivalent atoms: #1 -y+1/4,x-3/4,-z+1/4 #2 y+3/4,-x+1/4,-z+1/4

X-ray Crystal Structure Determination of 21b(thf)$_4$

A single crystal of **21b**(thf)$_4$ for X-ray diffraction was grown from a hexane-THF solution. Diffraction data were collected at 120 K on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) employing graphite-monochromatized Mo–Ka radiation (λ= 0.71070 Å). The structure was solved by the direct method and refined by the full-matrix least-squares method using SHELXL-97 program. Details of crystal data and structure refinement of are summarized in Table 6-3a. The final atomic parameters, the bond length, and the bond angles of **21b**(thf)$_4$ are listed in Table 6-3b, and Table 6-3c, respectively.

Table 6-3a. Crystal data and structure refinement for **21b**(thf)$_4$

Empirical formula	$C_{52}H_{116}K_2O_4Si_8$	
Formula weight	1108.37	
Temperature	120 K	
Wavelength	0.71070 Å	
Crystal system, space group	Triclinic, *P* -1	
Unit cell dimensions	a = 13.0830(7) Å b = 13.3180(4) Å c = 22.2070(10) Å	alpha = 89.659(3) deg. beta = 88.870(2) deg. gamma = 61.283(3) deg.
Volume	3392.7(3) Å^3	
Z, Calculated density	2, 1.085 Mg/m^3	
Absorption coefficient	0.317 mm^-1	
F(000)	1220	
Crystal size	0.3 x 0.3 x 0.25 mm	
Theta range for data collection	2.53 to 28.01 deg.	
Limiting indices	0<=h<=17, -14<=k<=16, -29<=l<=29	
Reflections collected / unique	14318 / 31807 [R(int) = 0.0280]	
Completeness to theta = 27.94	87.2%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14318 / 0 / 596	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0532, wR2 = 0.1472	
R indices (all data)	R1 = 0.0607, wR2 = 0.1535	
Extinction coefficient	0.0190(12)	
Largest diff. peak and hole	0.841 and -0.446 e.Å^-3	

Table 6-3b. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **21b**(thf)$_4$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
K(1)	3814(1)	3785(1)	3505(1)	38(1)
K(2)	7359(1)	3795(1)	1505(1)	38(1)
Si(1)	5669(1)	4579(1)	2939(1)	33(1)
Si(2)	4730(1)	4586(1)	2073(1)	33(1)
Si(3)	5395(1)	2637(1)	2216(1)	31(1)
Si(4)	6904(1)	2630(1)	2781(1)	31(1)
Si(5)	6133(1)	6030(1)	3191(1)	30(1)
Si(6)	2853(1)	6052(1)	1829(1)	31(1)
Si(7)	5772(1)	1482(1)	1343(1)	28(1)
Si(8)	7654(1)	1462(1)	3644(1)	28(1)
O(1)	1994(2)	5354(2)	4135(1)	54(1)
O(2)	2670(2)	2564(2)	3678(1)	46(1)
O(3)	7652(2)	5371(2)	890(1)	55(1)
O(4)	9698(2)	2574(2)	1322(1)	47(1)
C(1)	5494(2)	7218(2)	2620(1)	41(1)
C(2)	5396(2)	6706(2)	3958(1)	39(1)
C(3)	4070(2)	7347(2)	3859(1)	48(1)
C(4)	5644(3)	5794(2)	4446(1)	50(1)
C(5)	5752(2)	7577(2)	4198(1)	49(1)
C(6)	7792(2)	5521(2)	3169(1)	35(1)
C(7)	8056(2)	6533(2)	3145(1)	43(1)
C(8)	8401(2)	4769(2)	3712(1)	44(1)
C(9)	8338(2)	4800(2)	2593(1)	44(1)
C(10)	2353(2)	7240(2)	2401(1)	42(1)
C(11)	1675(2)	5559(2)	1857(1)	37(1)
C(12)	436(2)	6580(2)	1889(1)	46(1)
C(13)	1790(2)	4802(2)	1315(1)	45(1)
C(14)	1833(2)	4849(2)	2432(1)	44(1)
C(15)	2924(2)	6718(2)	1060(1)	39(1)
C(16)	3625(2)	7354(2)	1154(1)	49(1)
C(17)	1713(2)	7586(2)	821(1)	52(1)
C(18)	3568(3)	5792(2)	571(1)	51(1)
C(19)	5155(2)	2407(2)	651(1)	38(1)
C(20)	4893(2)	664(2)	1445(1)	35(1)
C(21)	3598(2)	1566(2)	1468(1)	41(1)
C(22)	5070(3)	-188(3)	939(1)	56(1)
C(23)	5163(2)	14(2)	2049(1)	47(1)
C(24)	7396(2)	474(2)	1137(1)	35(1)
C(25)	7553(2)	-73(3)	508(1)	53(1)
C(26)	8004(2)	-454(2)	1604(1)	53(1)
C(27)	8042(2)	1186(2)	1108(1)	43(1)
C(28)	7374(2)	2373(2)	4344(1)	38(1)
C(29)	7006(2)	459(2)	3836(1)	34(1)
C(30)	7402(3)	-122(3)	4454(1)	53(1)
C(31)	7302(3)	-453(2)	3350(1)	51(1)
C(32)	5674(2)	1168(2)	3876(1)	44(1)
C(33)	9331(2)	642(2)	3538(1)	36(1)
C(34)	9749(2)	1543(2)	3526(1)	42(1)
C(35)	9993(2)	-224(3)	4037(1)	58(1)
C(36)	9696(2)	7(2)	2926(1)	49(1)
C(37)	1832(2)	6404(2)	4403(1)	47(1)
C(38)	710(2)	6864(2)	4768(1)	43(1)
C(39)	3(2)	6469(3)	4399(1)	55(1)
C(40)	929(3)	5291(3)	4197(2)	63(1)
C(41)	2562(3)	1978(2)	3162(1)	49(1)
C(42)	3076(2)	734(2)	3349(1)	44(1)
C(43)	2850(2)	804(2)	4033(1)	44(1)
C(44)	2383(3)	2061(3)	4182(1)	54(1)
C(45)	6799(2)	6397(2)	607(1)	48(1)
C(46)	7486(2)	6825(2)	233(1)	46(1)
C(47)	8578(3)	6438(3)	600(1)	58(1)
C(48)	8777(3)	5303(3)	832(2)	72(1)
C(49)	10368(2)	1983(2)	1836(1)	50(1)
C(50)	11073(2)	744(2)	1638(1)	45(1)
C(51)	11239(2)	817(2)	956(1)	46(1)
C(52)	10471(3)	2082(3)	818(1)	56(1)

Table 6-2b. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **21b**(thf)$_4$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

K(1)-O(1)	2.6673(17)	K(1)-O(2)	2.7092(18)	K(1)-Si(1)	3.3038(8)
K(1)-Si(3)	3.4044(7)	K(1)-Si(2)	3.7034(8)	K(1)-Si(4)	3.8848(8)
K(2)-O(3)	2.6709(18)	K(2)-O(4)	2.7104(18)	K(2)-Si(2)	3.3011(8)
K(2)-Si(4)	3.4000(7)	K(2)-Si(1)	3.6958(7)	K(2)-Si(3)	3.8854(8)
Si(1)-Si(2)	2.2989(8)	Si(1)-Si(4)	2.3301(8)	Si(1)-Si(5)	2.3602(8)
Si(2)-Si(3)	2.3300(8)	Si(2)-Si(6)	2.3597(8)	Si(3)-Si(4)	2.3576(8)
Si(3)-Si(7)	2.3728(7)	Si(4)-Si(8)	2.3719(7)	Si(5)-C(1)	1.886(2)
Si(5)-C(6)	1.939(2)	Si(5)-C(2)	1.939(2)	Si(6)-C(10)	1.882(2)
Si(6)-C(15)	1.942(2)	Si(6)-C(11)	1.942(2)	Si(7)-C(19)	1.897(2)
Si(7)-C(24)	1.938(2)	Si(7)-C(20)	1.938(2)	Si(8)-C(28)	1.895(2)
Si(8)-C(33)	1.935(2)	Si(8)-C(29)	1.937(2)	O(1)-C(40)	1.439(3)
O(1)-C(37)	1.440(3)	O(2)-C(44)	1.434(3)	O(2)-C(41)	1.438(3)
O(3)-C(45)	1.435(3)	O(3)-C(48)	1.434(4)	O(4)-C(52)	1.426(3)
O(4)-C(49)	1.434(3)	C(2)-C(4)	1.540(3)	C(2)-C(3)	1.542(4)
C(2)-C(5)	1.544(3)	C(6)-C(8)	1.532(3)	C(6)-C(7)	1.544(3)
C(6)-C(9)	1.546(3)	C(11)-C(13)	1.532(3)	C(11)-C(12)	1.537(3)
C(15)-C(16)	1.535(4)	C(15)-C(17)	1.547(3)	C(15)-C(18)	1.546(3)
C(20)-C(21)	1.535(3)	C(20)-C(22)	1.536(3)	C(20)-C(23)	1.543(3)
C(24)-C(26)	1.520(3)	C(24)-C(27)	1.543(3)	C(24)-C(25)	1.543(3)
C(29)-C(31)	1.527(3)	C(29)-C(32)	1.533(3)	C(29)-C(30)	1.542(3)
C(33)-C(34)	1.540(3)	C(33)-C(35)	1.540(3)	C(33)-C(36)	1.546(3)
C(37)-C(38)	1.510(3)	C(38)-C(39)	1.518(4)	C(39)-C(40)	1.513(4)
C(41)-C(42)	1.518(4)	C(42)-C(43)	1.536(3)	C(43)-C(44)	1.518(4)
C(45)-C(46)	1.510(4)	C(46)-C(47)	1.519(4)	C(47)-C(48)	1.496(4)
C(49)-C(50)	1.516(3)	C(50)-C(51)	1.535(3)	C(51)-C(52)	1.523(4)
O(1)-K(1)-O(2)	82.07(6)	O(1)-K(1)-Si(1)	116.89(5)	O(2)-K(1)-Si(1)	160.17(4)
O(1)-K(1)-Si(3)	153.92(5)	O(2)-K(1)-Si(3)	103.16(4)	Si(1)-K(1)-Si(3)	57.329(16)
O(1)-K(1)-Si(2)	120.00(5	)O(2)-K(1)-Si(2)	129.03(4)	Si(1)-K(1)-Si(2)	37.763(14)
Si(3)-K(1)-Si(2)	37.978(14	)O(1)-K(1)-Si(4)	151.65(4)	O(2)-K(1)-Si(4)	125.61(4)
Si(1)-K(1)-Si(4)	36.714(14)	Si(3)-K(1)-Si(4)	37.004(13)	Si(2)-K(1)-Si(4)	50.121(13)
O(3)-K(2)-O(4)	81.87(6)	O(3)-K(2)-Si(2)	116.94(5)	O(4)-K(2)-Si(2)	160.31(4)
O(3)-K(2)-Si(4)	153.87(5)	O(4)-K(2)-Si(4)	103.25(4)	Si(2)-K(2)-Si(4)	57.383(16)
O(3)-K(2)-Si(1)	119.92(5)	O(4)-K(2)-Si(1)	129.08(4)	Si(2)-K(2)-Si(1)	37.835(14)
Si(4)-K(2)-Si(1)	38.054(14)	O(3)-K(2)-Si(3)	151.73(4)	O(4)-K(2)-Si(3)	125.75(4)
Si(2)-K(2)-Si(3)	36.710(14)	Si(4)-K(2)-Si(3)	37.008(13)	Si(1)-K(2)-Si(3)	50.176(13)
Si(2)-Si(1)-Si(4)	88.09(3)	Si(2)-Si(1)-Si(5)	123.58(3)	Si(4)-Si(1)-Si(5)	129.37(3)
Si(2)-Si(1)-K(1)	80.58(2)	Si(4)-Si(1)-K(1)	85.33(2)	Si(5)-Si(1)-K(1)	133.53(3)
Si(2)-Si(1)-K(2)	61.74(2)	Si(4)-Si(1)-K(2)	64.08(2)	Si(5)-Si(1)-K(2)	95.05(2)
K(1)-Si(1)-K(2)	130.63(2)	Si(1)-Si(2)-Si(3)	88.12(3)	Si(1)-Si(2)-Si(6)	123.57(3)
Si(3)-Si(2)-Si(6)	129.65(3)	Si(1)-Si(2)-K(2)	80.43(2)	Si(3)-Si(2)-K(2)	85.41(2)
Si(6)-Si(2)-K(2)	133.25(3)	Si(1)-Si(2)-K(1)	61.65(2)	Si(3)-Si(2)-K(1)	64.04(2)
Si(6)-Si(2)-K(1)	95.45(2)	K(2)-Si(2)-K(1)	130.45(2)	Si(2)-Si(3)-Si(4)	86.72(3)
Si(2)-Si(3)-Si(7)	117.42(3)	Si(4)-Si(3)-Si(7)	122.18(3)	Si(2)-Si(3)-K(1)	77.98(2)
Si(4)-Si(3)-K(1)	82.64(2)	Si(7)-Si(3)-K(1)	149.59(3)	Si(2)-Si(3)-K(2)	57.88(2)
Si(4)-Si(3)-K(2)	60.24(2)	Si(7)-Si(3)-K(2)	88.09(2)	K(1)-Si(3)-K(2)	121.415(19)
Si(1)-Si(4)-Si(3)	86.74(3)	Si(1)-Si(4)-Si(8)	117.45(3)	Si(3)-Si(4)-Si(8)	122.01(3)
Si(1)-Si(4)-K(2)	77.86(2)	Si(3)-Si(4)-K(2)	82.75(2)	Si(8)-Si(4)-K(2)	149.70(3)
Si(1)-Si(4)-K(1)	57.96(2)	Si(3)-Si(4)-K(1)	60.36(2)	Si(8)-Si(4)-K(1)	87.82(2)
K(2)-Si(4)-K(1)	121.554(19)	C(1)-Si(5)-C(6)	105.07(10)	C(1)-Si(5)-C(2)	106.18(10)
C(6)-Si(5)-C(2)	112.96(10)	C(1)-Si(5)-Si(1)	109.59(8)	C(6)-Si(5)-Si(1)	113.41(7)
C(2)-Si(5)-Si(1)	109.27(7)	C(10)-Si(6)-C(15)	106.16(11)	C(10)-Si(6)-C(11)	105.27(10)
C(15)-Si(6)-C(11)	112.76(10)	C(10)-Si(6)-Si(2)	109.46(8)	C(15)-Si(6)-Si(2)	109.49(7)
C(11)-Si(6)-Si(2)	113.33(7)	C(19)-Si(7)-C(24)	104.75(10)	C(19)-Si(7)-C(20)	105.40(10)
C(24)-Si(7)-C(20)	112.48(10)	C(19)-Si(7)-Si(3)	110.69(7)	C(24)-Si(7)-Si(3)	116.42(7)
C(20)-Si(7)-Si(3)	106.61(6)	C(28)-Si(8)-C(33)	105.26(10)	C(28)-Si(8)-C(29)	104.94(10)
C(33)-Si(8)-C(29)	112.63(10)	C(28)-Si(8)-Si(4)	110.76(8)	C(33)-Si(8)-Si(4)	106.62(7)
C(29)-Si(8)-Si(4)	116.15(7)	C(40)-O(1)-C(37)	109.21(19)	C(40)-O(1)-K(1)	121.23(14)
C(37)-O(1)-K(1)	129.27(15)	C(44)-O(2)-C(41)	104.44(19)	C(44)-O(2)-K(1)	136.33(16)
C(41)-O(2)-K(1)	116.75(14)	C(45)-O(3)-C(48)	109.5(2)	C(45)-O(3)-K(2)	129.35(15)
C(48)-O(3)-K(2)	121.09(16)	C(52)-O(4)-C(49)	105.00(19)	C(52)-O(4)-K(2)	136.39(16)
C(49)-O(4)-K(2)	116.09(14)	C(4)-C(2)-C(3)	107.8(2)	C(4)-C(2)-C(5)	108.4(2)
C(3)-C(2)-C(5)	107.9(2)	C(4)-C(2)-Si(5)	112.15(15)	C(3)-C(2)-Si(5)	106.99(16)

Table 6-2b (continued). Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **21b**(thf)$_4$. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

C(5)-C(2)-Si(5)	113.37(16)	C(8)-C(6)-C(7)	109.09(19)	C(8)-C(6)-C(9)	107.83(19)
C(7)-C(6)-C(9)	106.90(18)	C(8)-C(6)-Si(5)	111.57(16)	C(7)-C(6)-Si(5)	112.16(16)
C(9)-C(6)-Si(5)	109.09(15)	C(13)-C(11)-C(12)	109.53(19)	C(13)-C(11)-C(14)	107.7(2)
C(12)-C(11)-C(14)	106.85(19)	C(13)-C(11)-Si(6)	111.67(16)	C(12)-C(11)-Si(6)	111.90(17)
C(14)-C(11)-Si(6)	108.97(15)	C(16)-C(15)-C(17)	108.1(2)	C(16)-C(15)-C(18)	107.7(2)
C(17)-C(15)-C(18)	108.4(2)	C(16)-C(15)-Si(6)	107.04(16)	C(17)-C(15)-Si(6)	113.50(17)
C(18)-C(15)-Si(6)	111.86(16)	C(21)-C(20)-C(22)	108.0(2)	C(21)-C(20)-C(23)	107.14(18)
C(22)-C(20)-C(23)	108.2(2)	C(21)-C(20)-Si(7)	106.91(15)	C(22)-C(20)-Si(7)	114.87(16)
C(23)-C(20)-Si(7)	111.47(16)	C(26)-C(24)-C(27)	107.0(2)	C(26)-C(24)-C(25)	109.8(2)
C(27)-C(24)-C(25)	106.13(19)	C(26)-C(24)-Si(7)	112.57(15)	C(27)-C(24)-Si(7)	108.78(15)
C(25)-C(24)-Si(7)	112.20(17)	C(31)-C(29)-C(32)	107.2(2)	C(31)-C(29)-C(30)	109.6(2)
C(32)-C(29)-C(30)	106.39(19)	C(31)-C(29)-Si(8)	112.00(15)	C(32)-C(29)-Si(8)	109.10(15)
C(30)-C(29)-Si(8)	112.24(16)	C(34)-C(33)-C(35)	107.8(2)	C(34)-C(33)-C(36)	106.82(19)
C(35)-C(33)-C(36)	108.2(2)	C(34)-C(33)-Si(8)	106.93(15)	C(35)-C(33)-Si(8)	115.18(16)
C(36)-C(33)-Si(8)	111.52(16)	O(1)-C(37)-C(38)	105.8(2)	C(37)-C(38)-C(39)	101.88(19)
C(40)-C(39)-C(38)	101.6(2)	O(1)-C(40)-C(39)	106.0(2)	O(2)-C(41)-C(42)	105.26(19)
C(41)-C(42)-C(43)	103.60(19)	C(44)-C(43)-C(42)	104.1(2)	O(2)-C(44)-C(43)	106.97(19)
O(3)-C(45)-C(46)	105.6(2)	C(45)-C(46)-C(47)	102.0(2)	C(48)-C(47)-C(46)	102.1(2)
O(3)-C(48)-C(47)	106.6(3)	O(4)-C(49)-C(50)	105.1(2)	C(49)-C(50)-C(51)	104.0(2)
C(52)-C(51)-C(50)	103.65(19)	O(4)-C(52)-C(51)	107.0(2)		

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