



A reactive Si₄ cage: K(SitBu₃)₃Si₄

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ABSTRACT

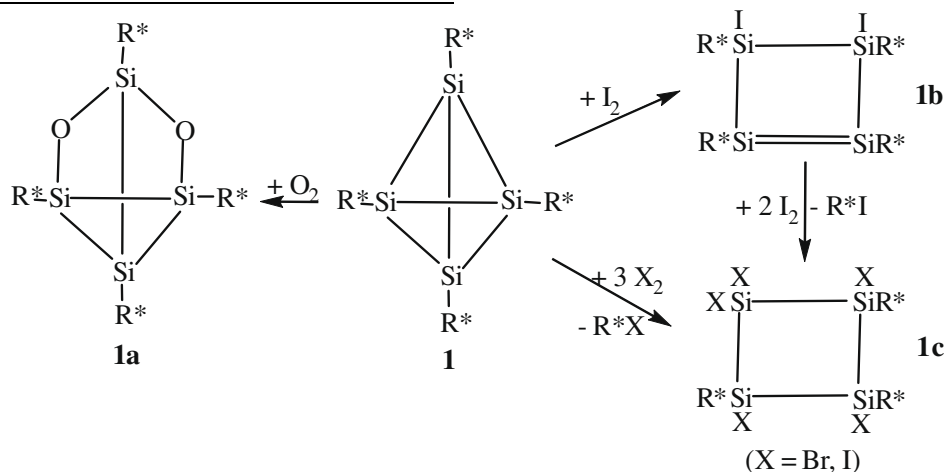
KR^{*}₃Si₄, **2**, (R^{*} = SitBu₃), formed by the reaction of R^{*}₄Si₄ with **2** KC₈, is an orange red solid stable at r.t. but decomposes in solution into R^{*}₄Si₄ and a compound that reacts with excess Me₃SiCl to form (Me₃Si)₄R^{*}₃ClSi₈. Compound **2** is very sensitive to air and moisture. Its alcoholysis does not stabilize the protonated species HR^{*}₃Si₄ and ends up in R^{*}₃Si₃H₃. Compound **2** reacts with 1/2 equivalent ICl to form a violet solid R^{*}₆Si₈. A 1:1 reaction of **2** with SiBr₄ runs differently to form ditetrahydranyl, R^{*}₃Si₄–Si₄R^{*}₃ which is stable at r.t. but transforms into its violet isomer R^{*}₆Si₈ at higher temperatures. Compound **2** crystallizes as R^{*}₃Si₄K(18-crown-6) and its crystal structure shows a Si₄-cage with a short Si–K linkage. It opens up at higher temperatures to acquire a unique structure in which a –CH₂–CH₂– group detaches itself from an ether to insert into Si–Si linkage of Si₄-unit to form a bicyclic ring. The residual chain (CH₂)₁₀O₆ closes itself on to a Si atom to form R^{*}₃Si₃(CH₂–CH₂)Si(C₁₀H₂₀O₆)K(18-C-6).

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1. Introduction

Tetrasupersilyl-*tetrahydro*-tetrasilane R^{*}₄Si₄, **1** (R^{*} = SitBu₃ = supersilyl) was isolated in 1993 as the first molecular silatetrahedrane [1]. This highly strained cage compound with symmetrical structure, formed by the reaction of NaR^{*} with R^{*}–SiBr₂–SiBr₂–R^{*},

has high thermal stability (m. p. > 350 °C) and shows no sign of dissociation into R^{*}Si≡SiR^{*}. It does not undergo cleavage of the bulky R^{*} (without structural transformations) in its reactions with water, alcohols (MeOH, EtOH), acids (HBr, CF₃COOH, CF₃SO₃H), quaternary ammonium halides (Bu₄NBr, Me₄NF), Me₄PF, CsF, KF, ICl, CCl₄, methyl lithium, etc. It is oxidized in solution by oxygen into



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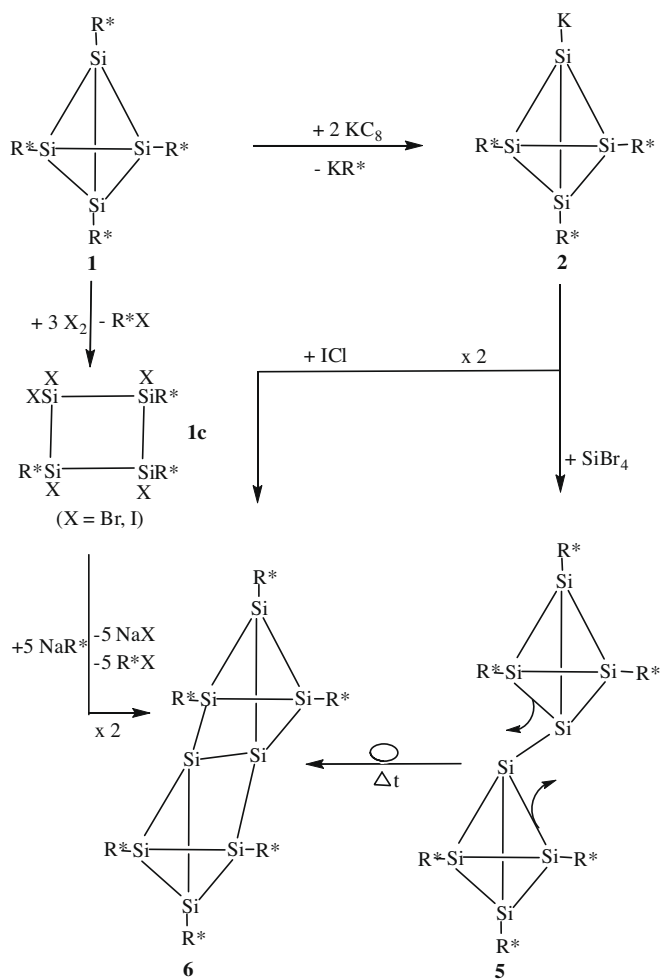
$R^*_4Si_4O_2$, **1a** [2] and by iodine into $R^*_4Si_4I_2$, **1b** [3a,3b]. Compound **1** undergoes addition cum substitution reaction with I_2 or Br_2 to form $R^*_3Si_4I_5$ [3c] or $R^*_3Si_4Br_5$ [3d], **1c**. It is reduced by sodium naphthalenide $NaC_{10}H_8$ into $Na_2Si_4R^*_4$ [4]. Another tetrasilatetrahedrane R_4Si_4 along with its anion $R_3Si_4^-$, where $R = SiMe[CH(SiMe_3)_2]_2$, were reported a decade later but their chemistry is still awaited [5].

2. Results and discussion

Compound **1** reacts with two equivalents of KC_8 with selective cleavage of an exo-cyclic Si–Si linkage to form a 1:1 mixture of $KR^*_3Si_4$ and KR^* . Solvated $KR^*_3Si_4 \cdot 2THF$ was isolated as red crystals by repeated crystallization from THF solutions. It turns into orange red solid on loss of THF in vacuum to form $KR^*_3Si_4$, **2**. Compound **2** is highly sensitive to air and turns green in it. It reacts with methanol or ethanol (ROH) at r.t. to form *cis-trans*-trisupersilylcyclotrisilane, $R^*_3Si_3H_3$, **3** [6] instead of the expected trisupersilyl-tetrahydro-tetrasilane, $R^*_3Si_4H$, (Scheme 1). Destabilization of the tetrahedron due to steric accessibility caused by the tiny proton facilitates further reaction towards **3** [6].

Compound **2** is stable as a solid at r.t. but undergoes slow disproportionation in solution in benzene, toluene or THF (slower) to form a mixture of $R^*_4Si_4$ and a light yellowish brown solid (say **A**), inflammable in air and insoluble in common organic solvents except THF which forms dark red solution. Compound **A** could not be crystallized as such or as its complex with 18-crown-6. Its ^{29}Si NMR spectrum shows one signal at 13.39 ppm attributable to R^* groups. The exocyclic R^* groups in Si_4 -tetrahedra, such as **1**, **2**, **7** and $(i-Pr)_3SiR^*_3Si_4$ absorb around 53–50 ppm in their ^{29}Si NMR spectra. The signal shifts to higher fields between 50–40 ppm in other non-tetrahedral Si_4 -species like cyclotetrasilene, $R^*_4Si_4I_2$ [3a,3b] or cyclotetrasilanes $R^*_3Si_4X_5$ ($X = Br$ or I) [3c,3d], $R^*_2Si_4I_6$ [3c]. A larger shift to higher field at 13.39 ppm is, therefore, indicative of absence of Si_4 -ring structure in **A**. Its reaction with excess Me_3SiCl provides $(Me_3Si)_4R^*_3ClSi_8$, **4** which did not form single crystals for X-ray analysis. Compound **4** does not explain path of its formation or possible composition of **A**. Both 1H and ^{29}Si NMR spectra (Experimental) show that each of the positions occupied by R^* or Me_3Si groups is nonequivalent in **4** which may have a distorted octasilabucane structure.

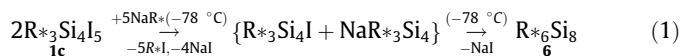
The high stability of $R^*_4Si_4$, **1** led us to postulate the possibility of existence of a ditetrahedranyl $R^*_3Si_4-Si_4R^*_3$, **5**, which may be accessible by metathesis of $MR^*_3Si_4$ ($M = \text{alkali metal}$) with $R^*_3Si_4X$ ($X = \text{halogen}$). The latter is unstable at r.t. and reaction of $R^*_4Si_4$ or $R^*_6Si_8$ [3d] with halogens or halogenating agents does not provide isolable $R^*_3Si_4X$. A 2:1 reaction of $R^*_3Si_4K$ with iodine mono chloride (ICl) was, therefore, done to generate a possible intermediate $R^*_3Si_4I$ at low temperatures (which decomposes otherwise into $R^*_4Si_4$ and others), so that, it may react with **2**, in situ, to form $R^*_3Si_4-Si_4R^*_3$, **5**. However, the reaction did not yield $R^*_3Si_4-Si_4R^*_3$, **5** but resulted in the violet isomer $R^*_6Si_8$, **6** [7] (Scheme 2). Compound **6** is very stable to irradiation and could not be transformed into $R^*_3Si_4-Si_4R^*_3$, **5**. However, a 1:1 reaction



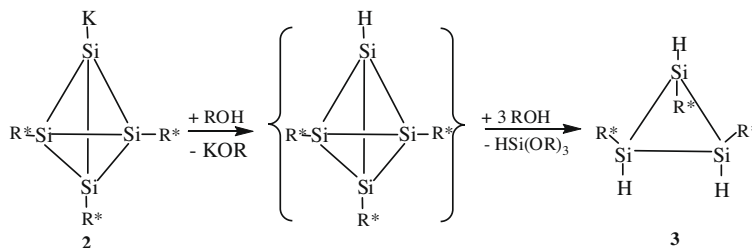
Scheme 2. Formation of $(R^*_3Si_4)_2$.

of $R^*_3Si_4K$ with $SiBr_4$ provides an orange yellow solid, $R^*_3Si_4-Si_4R^*_3$, **5**. Like **6**, it is also insoluble in common organic solvents at r.t. It was purified by slow extraction with THF at its reflux temperature or in partial vacuum with benzene at about 60 °C. Extraction with benzene at its reflux temperature led to slow conversion of orange yellow $R^*_3Si_4-Si_4R^*_3$, **5** into its violet isomer $R^*_6Si_8$, **6** (Scheme 2).

In the reaction of $R^*_3Si_4I_5$, **1c** with NaR^* in THF, compound **6** is formed in almost quantitative amounts even at -78 °C (Scheme 2) [7]. The reaction occurs as shown in Eq. (1).



Similarly reaction of $R^*_3Si_4I$ (generated from $KR^*_3Si_4 + ICl$ at -78 °C) with $KR^*_3Si_4$ results in $R^*_6Si_8$ and not $R^*_3Si_4-Si_4R^*_3$. A metathetical reaction between two tetrahedral Si_4 -clusters destabilizes the



Scheme 1. Protolysis of $KR^*_3Si_4$, **2**.

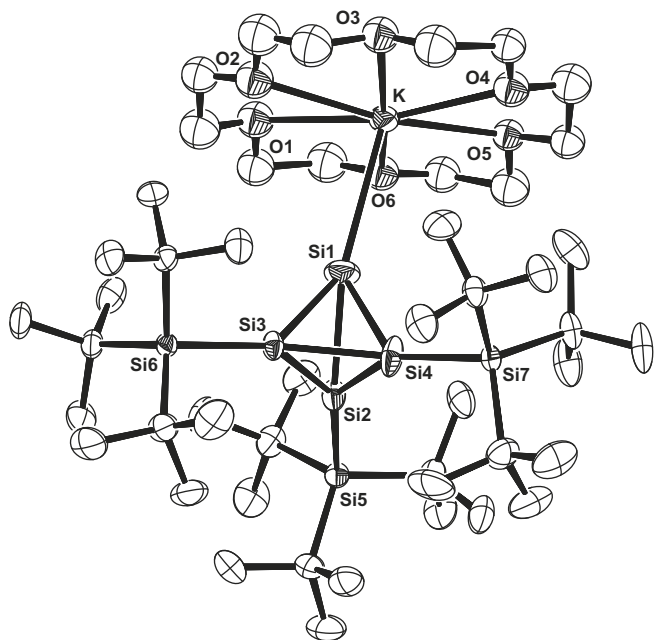


Fig. 1. Molecular structure of **7**. The part of disordered 18-crown-6 having slightly higher occupation factor is depicted. The ellipsoids are drawn at the 25% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Si1–K 3.2911(16), Si1–Si2 2.3493(19), Si1–Si3 2.3467(18), Si1–Si4 2.3581(2), Si2–Si4 2.2450(16), Si2–Si3 2.2691(15), Si3–Si4 2.2678(16), Si2–Si5 2.3141(14), Si4–Si7 2.3120(15), Si3–Si6 2.3213(14), Si1–Si3–Si4 61.43(7), Si1–Si4–Si3 60.93(6), Si3–Si1–Si4 57.63(5), Si1–Si3–Si2 61.16(6), Si1–Si2–Si3 61.05(5), Si2–Si1–Si3 57.79(5), Si1–Si2–Si4 61.71(7), Si1–Si4–Si2 61.32(6), Si4–Si1–Si2 56.97(5), Si2–Si3–Si4 59.32(5), Si2–Si4–Si3 60.37(5), Si3–Si2–Si4 60.31(5), K–Si1–Si2 146.79(7), K–Si1–Si3 152.31(7), K–Si1–Si4 138.00(8).

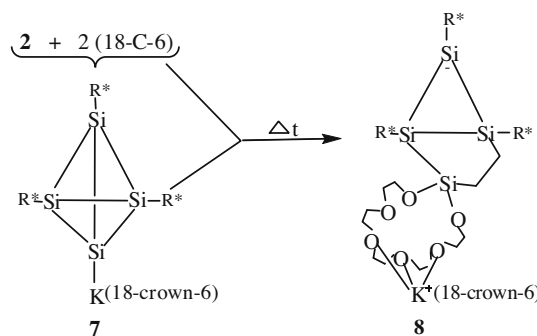
strained species with the result that a Si–Si linkage in each participating tetrahedron opens up to form less strained tricyclopentasilane rings bridged together as shown in **6** [7] or as observed in $R^*Cl_2Si_9$ [8]. Thus, it is not possible to bring together two heavily loaded tetrahedra to generate a ditetrahdanyl $R^*_3Si_4-Si_4R^*_3$, metathetically. The latter may possibly arise by radical dimerization. A reaction between KR^* with R^*Br does not occur due to steric effects of large R^* groups but radical oxidation of KR^* at low temperatures provides good yields of R^*-R^* [9]. Similarly, $KR^*_3Si_4$ is likely to undergo oxidation into $R^*_3Si_4$ radicals which dimerize at low temperatures to form ditetrahdanyl, $R^*_3Si_4-Si_4R^*_3$, **5**.

Compound **2** complexes with 18-crown-6 to form a red solid, $R^*_3Si_4K(18\text{-crown-6})$, **7** which, unlike **2**, is stable to disproportionation at r.t. perhaps because of bulk and bond strength of 18-crown-6 compared to THF or benzene. X-ray structure of **7** is shown in Fig. 1 (Table 1). The Si–K bond distances in silyl–potassium derivatives are reported in the range 3.30–3.58 Å (sum of covalent radii of Si and K atoms is 3.38 Å) [10]. The observed distance of 3.291(16) Å in **7** is the shortest among potassium–silyl derivatives. The reported Si_4 -cluster $R_3Si_4K(18\text{-crown-6})$ where $R = SiMe[CH(SiMe_3)_2]_2$ exists as ion pair with Si–K distance of 8.852 Å [5]. All Si–Si bond distances emanating from Si1 bound to K (that is, Si1 bonded to Si2, Si3 or Si4) are slightly elongated (due to lowered ligand cover) with bond distances between 2.347(18) and 2.358(18) Å compared to other Si–Si bond distances in Si_4 skeletal with range 2.245(16)–2.269(15) Å. The latter distances are significantly shorter than the single bond distance (2.34 Å) and those reported in the precursor $R^*_4Si_4$ (2.315–2.330 Å or 2.326–2.341 Å) [1]. The exocyclic Si–Si bonds in **7**, 2.312(15)–2.321(14) Å, are also shorter than those in precursor $R^*_4Si_4$ (2.355–2.365 Å or 2.356–2.371 Å) [1].

Cluster $R^*_3Si_4K(18\text{-C-6})$ has low solubility in common organic solvents at r.t. Attempts to dissolve it in refluxing benzene or hot

Table 1
Crystallographic data for compounds **7** and **8**.

	7	8
Formula	$C_{54}H_{111}KO_6Si_7$	$C_{63}H_{132}KO_{12}Si_7$
Molecular weight (g mol ⁻¹)	1092.152	1317.412
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
<i>a</i> (Å)	12.8575(3)	13.7254(1)
<i>b</i> (Å)	27.3905(4)	17.5932(2)
<i>c</i> (Å)	19.2001(4)	32.5660(3)
β (°)	91.8783(10)	96.3284(7)
<i>V</i> (Å ³)	7658.1(2)	7815.91(13)
<i>Z</i>	4	4
ρ (g cm ⁻³)	1.07343(3)	1.11959(2)
μ (mm ⁻¹)	0.243	0.226
Crystal size (mm)	0.21 × 0.19 × 0.09	0.18 × 0.13 × 0.09
θ -Range (°)	3.16–24.12	3.20–24.11
Reflections measured	20654	24214
Number of independent reflections	10722	12404
Reflections with $I \geq 2\sigma(I)$	6747	8886
R_{int}	0.0435	0.0277
Mean value $\sigma(I)/I$	0.0643	0.0386
Parameter/restraints	623/2	741/0
$R(F_{obs})$	0.0650	0.0681
$R_w(F^2)$	0.1732	0.1945
<i>S</i>	1.040	1.035
Maximum electron density e Å ⁻³	0.764	0.589
Minimum electron density e Å ⁻³	–0.685	–0.427



Scheme 3. Formation of **8**.

toluene at 80 °C, destabilizes the tetrahedral structure with the result that one of the Si–Si linkages opens up to release inherent strain and in the process accommodates a $-CH_2-CH_2-$ group. In this way, the strained tetrahedron transform into a more stable bicyclic arrangement with reduction in the number of three membered strained rings from four to one as shown in Scheme 3. The residual chain $(CH_2)_{10}O_6$ of ether closes onto one of the Si atoms of the bicycle and offers three additional coordination sites to K to make it nine in compound, **8** (Scheme 3). Compound **8** is also obtained from 1:2 reaction of **2** with 18-crown-6. A similar reaction of cryptofix-222 with **2** was done to lend support to the above observation [11] (Table 1).

The X-ray structure of $R^*_3Si_3(CH_2-CH_2)Si(C_{10}H_{20}O_6)K(18\text{-crown-6})$, **8**, is shown in Fig. 2 (Table 1). Besides high coordination number 9, there is an unsymmetrical coordination of K to three of the outer oxygen atoms, K–O7 = 2.821(4), K–O8 = 3.058(4), K–O12 = 2.952(3) Å, in the chain $(CH_2)_{10}O_6$ created due to opening up of an 18-crown-6 ring. The two Si–O linkages in **8**, thus formed, are almost of the same bond length, ca. 1.65 Å which is significantly shorter than the single bond distance of 1.77 Å. The Si–C bonds in the pentagon ring are 1.874(9) Å (Si7–C36) and 1.946(6) Å (Si3–C35) (Si–C single bond distance = 1.88 Å). The negatively charged silicon Si4 is pyramidal with angle sum = 309.65°. The tetrahedral structure comprising initially of 4 triangles

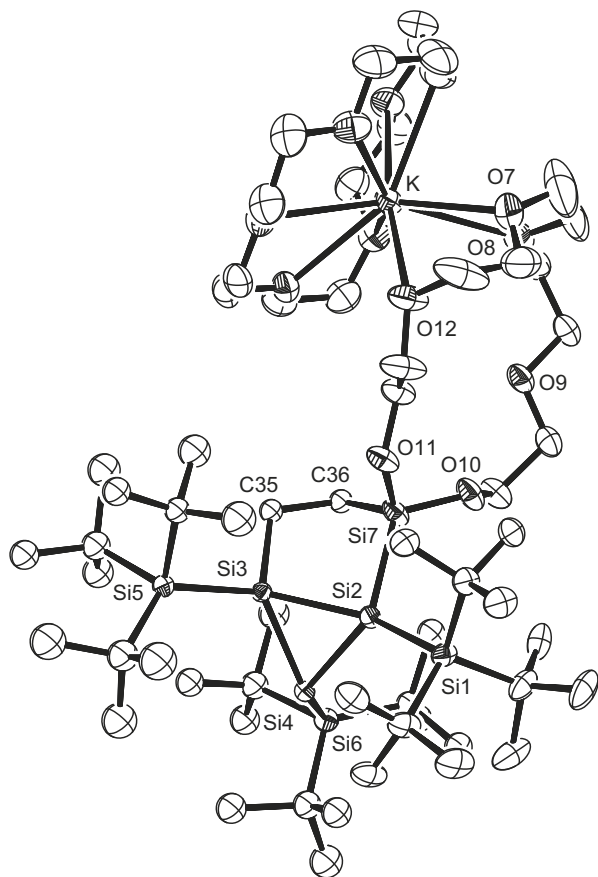


Fig. 2. Molecular structure of **8**. Of the disordered atoms only those having slightly higher occupation factor are depicted. The ellipsoids are drawn at the 25% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): K–O7 2.821(4), K–O8 3.058(4), K–O12 2.952(3), K–O(1–6) 2.837–2.984 Å, Si7–O11 1.651(3), Si7–O10 1.648(3), Si7–C36 1.874(9), Si3–C35 1.946(6), Si2–Si3 2.3631(19), Si2–Si4 2.4285(18), Si3–Si4 2.324(2), C35–C36 1.572(11), Si2–Si3–Si4 62.41(6), Si3–Si4–Si2 59.59(6), Si4–Si2–Si3 58.00(6), Si1–Si2–Si4 122.60(6), Si1–Si2–Si7 112.84(5), Si1–Si2–Si3 148.27(6), Si2–Si4–Si6 125.28(7), Si3–Si4–Si6 124.72(8), Si2–Si7–C36 104.3(3), C36–Si7–O11 114.0(3), O11–Si7–O10 101.90(16), Si2–Si7–O10 120.83(13).

changes into a bicycle with a triangle Si2–Si3–Si4 and a pentagon Si2–Si3–C35–C36–Si7 joined at the bridgehead Si2–Si3 with bond length 2.3631(19) Å. The structure of **8** is a separated ion pair with K–Si bond distance of 9.54 Å.

3. Conclusions

A highly strained Si₄-tetrahedron R^{*}₄Si₄, **1** acquires extreme stability when overloaded with very bulky groups like Si^t-Bu₃ = R^{*}. As expected, this highly symmetrical molecule shows reduced reactivity in exocyclic cleavage. It maintains Si₄-cage in solid state in KR^{*}₃Si₄, **2** or its complexes R^{*}₃SiK(THF)₂ and R^{*}₃Si₄K(18-C-6). Solutions of **2** in weakly coordinating solvents undergo decomposition into R^{*}₄Si₄ and a compound that reacts with Me₃SiCl to form (Me₃Si)₄R^{*}₃ClSi₈, **4**. Protolysed species and halo derivatives like R^{*}₃Si₄X (X = H, Br or I) are not isolable and decompose at low temperatures with the former ending up as R^{*}₃Si₃H₃ and the latter into R^{*}₄Si₄ plus others. A reaction between KR^{*}₃Si₄ and ICl at low temperatures does not provide a ditetrahydronyl R^{*}₃Si₄-Si₄R^{*}₃ and ends up in the cleavage of a Si–Si linkage in each of the participating tetrahedron to form tricyclopentasilane rings fused together at a Si–Si edge as reported in R^{*}₆Si₈ [7]. A probable ditetrahydronyl R^{*}₃Si₄–

Si₄R^{*}₃ formed in the reaction of **2** with SiBr₄ may arise by low temperature dimerization of R^{*}₃Si₄ radicals.

4. Materials and methods

All experiments were carried out in flame dried glass ware using standard schlenk techniques under dry nitrogen atmosphere. Air and moisture were carefully excluded. The solvent THF was freshly distilled over benzophenone-sodium before use. Solvents *n*-heptane and benzene were distilled over sodium metal and kept in schlenks over molecular sieves. The following compounds were synthesized by literature procedures: R^{*}-SiBr₂-SiBr₂-R^{*} [12], NaR^{*} [13], R^{*}₄Si₄ [1]. NMR spectra: Jeol GX-270 (¹H/¹³C/²⁹Si: 270.17/67.94/53.67 MHz) and a Jeol EX-400 (¹H/¹³C/²⁹Si: 399.78/100.54/79.43 MHz). NMR spectra were recorded conventionally or with INEPT and DEPT pulse sequences using empirically optimized parameters for the mentioned groups. Mass spectral measurements were done on Jeol MStation JMS 700.

4.1. Synthesis of **2**

Potassium graphite KC₈ (0.420 g, 3.11 mmol) was added as such to a suspension of R^{*}₄Si₄, **1** (1.335 g, 1.47 mmol) in THF (80 mL) at –78 °C. The reaction mixture was stirred and allowed to warm slowly up to –10 °C over 12 h. The cold mixture was filtered to remove graphite and the concentrated filtrate (15–20 mL) was kept at –78 °C to get a red solid which was recrystallized to obtain pure, R^{*}₃Si₄K·2THF. It was washed with *n*-pentane and dried at r.t. in low vacuum (200 torr). ¹H NMR (C₆D₆) integration of *t*-Bu₃Si protons (δ = 1.28) versus THF multiplets at δ = 3.46 and 1.58 indicated two molecules of THF per KR^{*}₃Si₄. Red crystals of R^{*}₃Si₄K(THF)₂ got desolvated easily *in vacuo* (10^{–2} torr/r.t.) to give an orange red solid, KR^{*}₃Si₄, **2** (0.660 g, 0.88 mmol, 60% yield). It changes colour at ~90 °C. ¹H NMR (THF-d₈, 399.78 MHz, 25 °C) δ 1.22 (s, 81H, 3R^{*}). ¹³C NMR (THF-d₈, 100.54 MHz, 25 °C) δ 31.99 (s, 9Me₃C), 24.42 (s, 9CMe₃). ²⁹Si NMR (THF-d₈, 79.43 MHz, 25 °C) δ 51.86 (s, 3R^{*}), –106.42 (s, skeletal Si₄ showing equivalence) [5].

4.2. Synthesis of **3**

Compound **2** (0.329 g, 0.44 mmol) in THF (10 mL) was reacted with ethanol (0.1 mL, 1.76 mmol) at r.t. The dark reddish brown reaction mixture was stirred for about 2 h at r.t. till its colour changed to pale yellow. THF was removed *in vacuo*. The sticky residual suspension was evacuated at r.t./0.1 torr to trap (EtO)₃SiH which was characterized by comparison with reported NMR data [14]. The residual white solid was treated with benzene (3 mL) and filtered. The insoluble white solid KOEt was characterized by hydrolysis to EtOH. The benzene solution was evacuated to obtain a white solid, R^{*}₃Si₃H₃, **3**. ¹H NMR (C₆D₆, 399.78 MHz, 25 °C) δ 1.32 (s, 81H, 3R^{*}), 2.58 (AB₂: ³J_{HH} = 9.9 Hz, 1H, SiH), 2.77 (AB₂: ³J_{HH} = 9.9 Hz, 2H, 2SiH). ²⁹Si{H} NMR (C₆D₆, 79.43 MHz, 25 °C) δ 29.08 (s, 2R^{*}), 23.73 (s, R^{*}), –153.30 (2 Si-skeletal), –161.20 (1 Si-skeletal) [6].

MS (FAB⁺, Xe, NBA) *m/z* (%): 684.8(50) [M⁺], 681.8(40) [R^{*}₃Si₃]⁺, 484.7(100) [M–R^{*}H]⁺, 427.7(60) [M⁺–R^{*}H–Bu]⁺, 284.7(70) [M–2R^{*}H]⁺, 227.7(20) [M⁺–2R^{*}H–Bu]⁺.

4.3. Synthesis of **4**

Compound **2** (0.750 g, 1.00 mmol) was taken in benzene (5 mL) and stirred for 72 h at r.t. The suspension was filtered and washed with benzene. The residue was extracted with boiling benzene till it was free of products soluble in it. The insoluble residue was evacuated to get yellowish brown solid **A**, (0.212 g). The orange

coloured benzene solution was concentrated and cooled to crystallize out $R^*_4Si_4$, **1** (0.270 g, 0.30 mmol). Decomposition of **2** could not be monitored by 1H NMR measurements in C_6D_6 due to low solubility of **2**, **1** and insolubility of **A**. Compound **A** is very sensitive to exposure and catches fire in air. It is insoluble in common non-polar organic solvents. It is highly soluble in THF and forms dark red solutions.

1H NMR (THF- d_8 , 270.17 MHz, 25 °C) δ 1.36 (s, R*). ^{29}Si NMR (THF- d_8 , 53.67 MHz, 25 °C) δ 13.39 (s, R*), –15.62 (s, Si-skeletal).

MS of **A** did not give any assignable spectrum. Different modes of measurements were tried. Compound **A**, (0.706 g,) was dissolved in THF (10 mL) and treated with Me_3SiCl (0.5 mL, 4 mmol) at r.t. The reaction mixture was stirred for 24 h and evacuated to remove THF, Me_3SiCl , $(Me_3Si)_2O$ or Me_6Si_2 . The residue was taken in benzene (5 mL) and filtered to remove KCl (0.164 g, 2.20 mmol). The filtrate was evacuated to get reddish brown residue which was purified by crystallisation from *n*-heptane solution at –78 °C to isolate **4** (0.470 g, 0.41 mmol). It decomposes at ~ 160 °C without melting. 1H and ^{29}Si NMR of the mother liquor indicated besides **4**, presence of R^*H [13], R^*-R^* [13] and some other minor products.

1H NMR of **4** (C_6D_6 , 270.17 MHz, 25 °C) δ = 1.43 (bs, 27H, R*), 1.33 (bs, 27H, R*), 1.31 (bs, 27H, R*), 0.26 (s, 9H, Me_3Si), 0.32 (s, 9H, Me_3Si), 0.467 (s, 9H, Me_3Si), 0.475 (s, 9H, Me_3Si). ^{29}Si NMR (C_6D_6 , 53.67 MHz, 25 °C) δ 32.71 (s, R*), 31.6 (s, R*), 31.24 (s, R*), –5.7 (s, Me_3Si), –6.52 (s, Me_3Si), –6.83 (s, Me_3Si), –8.95 (s, Me_3Si). Singlet signals at –29.32, –35.35, –38.88, –45.74, –49.02, –53.49 and –60.00 ppm are attributed to skeletal-silicons.

MS (DEI⁺, 70 eV): *m/z* (%), 1150.3(60) [M^+], 1115.3(70) [$M-Cl$]⁺, 1042.4(55) [$M-Me_3SiCl$]⁺, 968.4(34) [$M-Me_3SiCl-Me_3Si$]⁺, 951.3(100) [$M-R^*$]⁺, 915.3(74) [$M-R^*Cl$]⁺, 842.4(78) [$M-R^*Cl-Me_3Si$]⁺, 715.3(61) [$M-R^*-R^*Cl$]⁺. MS-HR $C_{48}H_{117}ClSi_{15}$ (M^+), Calc. 1150.5380. Found 1150.5394.

4.4. Synthesis of **6**

Compound **2** (0.492 g, 0.66 mmol) in THF (20 mL) was cooled to –78 °C. Iodine mono chloride (0.33 mmol, 4.0 mL of 0.083 molar solution in *n*-heptane) was taken in THF (5 mL) and added to it over a period of 1 h. Addition caused darkening of reaction mixture to violet brown suspension. It was allowed to come to r.t. over 12 h, concentrated to half the volume and filtered. The residue was washed with THF and then purified by extraction with boiling benzene. The violet solid, **6** (0.165 g, 0.116 mmol) was characterized as reported $R^*_6Si_8$ [7].

4.5. Synthesis of **5**

Compound **2** (0.910 g, 1.21 mmol) in THF (20 mL) was cooled to –78 °C and $SiBr_4$ (1.2 mmol, 3.0 mL of 0.4 molar solution in THF) in THF (5 mL) was added to it over a period of 2 h. The purple red suspension was slowly allowed to come to r.t. over 12 h. The suspension was filtered to get light orange yellow solid, **5b**. It was purified and separated from KBr by slow extraction with THF (20 mL) at its boiling point or with benzene (20 mL) boiling at 60 °C under partial pressure 220 torr. Extraction with benzene at its normal boiling temperature was avoided because of change of **5** into its dark violet isomer, **6**. The orange yellow **5** (0.560 g, 0.39 mmol) is almost insoluble in benzene, *n*-heptane, THF and toluene at room temperature.

1H NMR (toluene- d_8 , 270.17 MHz, 60 °C) δ 1.50 (bs, 162H, R*). ^{29}Si NMR (toluene- d_8 , 53.67 MHz, 60 °C) δ 52.21 (s, 6R*). ^{29}Si NMR shows a weak signal due to low solubility and skeletal-Si could not be observed.

MS (FAB⁺, Xe, NBA) *m/z* (%): 1452.5(0.5) [$M+O_2$]⁺, 1420.6(1) [M^+], 1253.5(1) [$M+O_2$]⁺, 1221.4(6) [$M-R^*$]⁺, 1164.4(2) [$M-R^*-Bu$]⁺, 1022.2(6) [$M-2R^*$]⁺, 820.1(5) [$M-3R^*H$]⁺, 737.8(10)

[$R^*_3Si_5^+$], 709.7(90) [$R^*_3Si_4^+$], 681.8(100) [$R^*_3Si_3^+$]. MS-HR for $C_{60}H_{135}Si_{13}$: [$M-R^*$]⁺ Calc. 1220.7580. Found 1220.7598.

4.6. Synthesis of **7**

Compound **2** (0.375 g, 0.50 mmol) and 18-crown-6 (0.264 g, 1.00 mmol) were reacted in *n*-heptane (20 mL) at r.t. for 2 h and the brick red solid, thus obtained, was isolated. NMR of the filtrate indicated presence of 18-c-6, $R^*_4Si_4$ and $KR^*_3Si_4$. The brick red solid, with low solubility in benzene or toluene, was extracted at r.t. using 10 mL benzene to get orange red crystals of $R^*_3Si_4K$ (18-crown-6), **7** (0.280 g, 0.28 mmol, 56% yield). It turns brown at 110 °C without melting. 1H NMR (THF- d_8 , 399.78 MHz, 25 °C) δ 3.66 (s, 24H, 12CH₂), 1.23 (s, 81H, 3R*). ^{13}C NMR (THF- d_8 , 100.54 MHz, 25 °C) 32.16 (s, 9 Me_3C), 24.49 (s, 9 CMe_3), 70.35 (s, 12CH₂). ^{29}Si NMR (THF- d_8 , 79.43 MHz, 25 °C) δ 50.67 (s, 3R*). Both INEPT and conventional ^{29}Si NMR did not show resonance for Si_4 -skeletal.

Compound **7** decomposes in refluxing benzene or hot toluene at 80 °C to form a dark red sticky mass (unidentified) in red solution. The red solution deposited shining orange crystals of **8** which has been synthesized as stated below.

4.7. Synthesis of **8**

Compound **2** (0.300 g, 0.40 mmol) and 18-crown-6 (0.211 g, 0.80 mmol) were reacted for 2 h at r.t. in THF (20 mL). The dark red solution was evacuated to get a red solid. The crude solid has low solubility in benzene, toluene or *n*-heptane. It was dissolved in hot toluene at 80 °C or refluxing benzene to obtain shining orange single crystals of $R^*_3Si_3(CH_2-CH_2)Si(C_{10}H_{20}O_6)K(C_{12}H_{24}O_6)$, **8** (0.230 g, 0.18 mmol, 45% yield). It decomposes at about 180 °C. 1H NMR (THF- d_8 , 399.78 MHz, 25 °C) δ 1.283 (s, 27H, R*), 1.278 (s, 27H, R*), 1.24 (s, 27H, R*), 3.620 (s, 24H, 18-C-6 ring), 3.615 (s, 12H, 3 C_2H_4), 3.572 (bs, 8H, 2 C_2H_4), 3.568 (bs, 4H, 2 C_2H_4). ^{13}C NMR (THF- d_8 , 100.54 MHz, 25 °C) δ 32.94 (s, 3 Me_3C), 32.52 (s, 3 Me_3C), 32.45 (s, 3 Me_3C), 24.99 (s, 3 CMe_3), 24.58 (s, 3 CMe_3), 24.57 (s, 3 CMe_3), 70.33 (s, 12CH₂ 18-C-6 ring), 13.01 (s, CH₂-Si), 9.17 (s, CH₂-Si). The 10CH₂ groups in the newly formed Si(CH₂)₁₀O₆ ring are observed at δ 72.86, 72.71, 70.81, 70.73 70.61, 70.546, 70.546, 70.51, 62.12 and 62.02. ^{29}Si NMR (THF- d_8 , 79.43 MHz, 25 °C) δ 27.84 (s, R*), 24.49 (s, R*), 18.48 (s, R*). Two (out of possible four) skeletal silicon signals have been observed at –57.01 and –180.46 ppm.

MS (FAB⁺, Xe, NBA) *m/z* (%): 1262.7(5) [$M-CH_2$]⁺, 1246.7(3) [$M-CH_2O$]⁺, 1230.7(3) [$M-CH_2O_2$]⁺, 1214.7(7) [$M-CH_2O_3$]⁺, 1198.7(8) [$M-CH_2O_4$]⁺, 1127.8(13) [$M-KO_6CH_2$]⁺, 1093.8(16) [$M-KO_9$]⁺, 1077.7(65) [$M-R^*$]⁺, 1013.8(20) [$M-R^*O_4$]⁺, 973.7(25) [$M-KO_6C_{12}H_{24}$]⁺, 830.7(8) [$M-R^*_2O_3$]⁺, 681.7(3) [$R^*_3Si_3$]⁺, 303.4(100) [$K(18-C-6)$]⁺. MS-HR for $C_{48}H_{102}O_{12}Si_6K$: Calc. ($M-R^*$)⁺ 1077.5624. Found 1077.5542.

4.8. Crystal structure determination

Crystals of **7** and **8** were investigated at 200 K on a Nonius KapkaCCD diffractometer using Mo $K\alpha$ radiation. The structures were solved by direct methods with SIR97 [15] and refined by full-matrix least-square calculations on F^2 with SHELXL-97 [16]. The final shift/error_{max} was 0.001. The disorder of the complete 18-crown-6 in **7** was handled in a split model leading to a final site occupation factor (sof) 0.48:0.52. A split model was also applied in **8** to describe the disorder of Si3, Si4, ethylene bridge and the *tert*-butyl group bonded to Si5 and Si6 (final sof: 0.46:0.54). In either structures the disordered non-hydrogen atoms were refined with isotropic displacement parameters with the exception of Si3 and Si4

in **8**. The hydrogen atoms in **7** and **8** were calculated in idealized geometry and are riding on their parent atoms.

Supplementary material

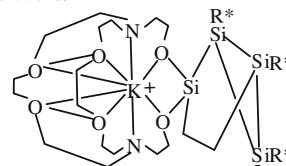
CCDC 755857 (**7**) and 755858 (**8**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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