Preparation of a Diethynyl Hypervalent Silicon Monomer by Coordination-selective Cleavage: Structure and Polymerization to give Novel Polycarbosilanes containing Main-chain Hexacoordinate Silicon

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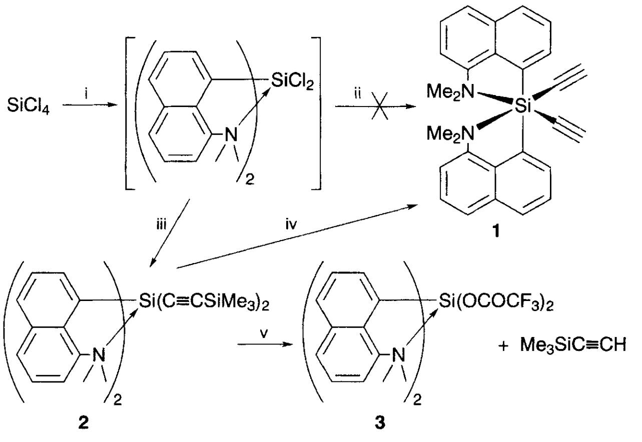
The hexacoordinate monomer $R_2Si(C{\equiv}CH)_2$ [R = 8-(dimethylamino)naphthyl; the X-ray crystal structure showing both nitrogens *trans* to the ethynyl groups], formed from $R_2Si(C{\equiv}CSiMe_3)_2$ by coordination-selective cleavage of the trimethylsilyl–acetylene bonds in the presence of $Bu^n{}_4NF$, undergoes palladium-catalysed cross-coupling polymerization with dihaloarenes to afford novel polycarbosilanes $[R_2SiC{\equiv}CArC{\equiv}C]_n$ (Ar = 1,4-phenylene, 4,4′-biphenylene, 9,10-anthrylene) containing hexacoordinate silicon.

The chemistry of silicon is very dependent on coordination number and valency state.[1] For instance, in spite of the negative charge, anionic hypercoordinate Si complexes are reactive towards nucleophiles such as Grignard reagents or hydride ion.[2] The Si atom in hypercoordinated compounds usually bears a partial positive charge as shown by *ab initio* calculations[3] for silanes. Three types of polymeric materials containing hypercoordinate Si have been reported: (*a*) hexacoordinate poly(phthalocyaninatosiloxane)s possessing interesting electrical and optical properties,[4a] (*b*) insoluble low-dimensional phthalocyaninatosilicon polymers containing main chain acetylene and phenylene groups,[4b] and (*c*) various penta- and hexa-coordinate poly(organosiliconate) ionomeric materials,[5,6] which have proved difficult to characterize. The preparation of polycarbosilanes containing hypercoordinate Si is of interest in order to study the effect of coordination number on polymer properties (*e.g.* electroconductivity, nonlinear optical). Previously, hypercoordination has been introduced into a functional polycarbosilane containing tetracoordinated Si,[7] whereas here the preparation of polymers starting from a hypervalent monomer is reported. The new hexacoordinate Si compounds described here contain the 8-(dimethylamino)naphthyl ligand which was introduced previously in order to obtain stable hypercoordinate species.[8]

Initial attempts to prepare the diethynyl hexacoordinate monomer $R_2Si(C{\equiv}CH)_2$ [R = 8-(dimethylamino)naphthyl] **1** from $SiCl_4$ by reaction of the intermediate R_2SiCl_2 with ethynyl Grignard or sodium derivatives were unsuccessful. However $R_2Si(C{\equiv}CSiMe_3)_2$ **2** can be prepared in 42% overall yield by treating $SiCl_4$ with [8-(dimethylamino)naphthyl]lithium followed by lithium trimethylsilylacetylide (Scheme 1). The previously characterized[9] intermediate dichlorosilane R_2SiCl_2 was not isolated. The ^{29}Si NMR spectrum of **2** shows the resonance for the $SiMe_3$ groups at δ −19.7 and that for hexacoordinate Si at δ −63.1. The IR spectrum exhibits a ν(C≡C) absorbance at 2093 cm^{-1}.

The fluoride ion-promoted activation of Si–C bonds can be explained in terms of mechanisms involving hypercoordinate Si species.[1] In particular, cleavage of silicon–acetylene bonds in the presence of F^- has been postulated to occur *via* hypercoordinate intermediates,[10] in which case silicon–acetylene bonds where the Si is already hexacoordinated should be less susceptible to attack. Indeed, under these conditions coordination-selective cleavage of the trimethylsilyl–acetylene bonds in **2**, which contains bonds between acetylene and both tetracoordinated and hexacoordinated Si, was observed. In this way, **1** was obtained in 50% yield on treatment of **2** with tetra-*n*-butylammonium fluoride followed by hydrolysis (Scheme 1). The ^1H NMR spectrum exhibits two signals for the diastereotopic Me groups at δ 1.2 and 2.6. The ^{29}Si NMR spectrum of **1** shows a signal at δ −63.8 whereas that for the tetracoordinate compound $Ph_2Si(C{\equiv}CH)_2$ lies at δ −48.2.[11] The IR spectrum exhibits a ν(C≡C) absorbance at 2026 cm^{-1}, close to that for $Ph_2Si(C{\equiv}CH)_2$ (2044 cm^{-1}).[12] Compound **1** can be recrystallized pure (mp 157.8–158.3 °C) from cyclohexane but the resulting crystals are unsuitable for X-ray crystal structure determination.

Crystallization of **1** from methanol gave methanol-containing crystals (mp 138–140 °C) which were used for the structure determination (Fig. 1).[†] As observed previously for such hexacoordinated compounds,[1] both N atoms are directed towards Si, giving a formally hexacoordinate complex of structure approximating to a bicapped tetrahedron, with the C(1)–Si–C(11) angle enlarged to 134° and the other C–Si–C angles diminished somewhat from 109°. In terms of the



Scheme 1 *Reagents and conditions*: i, [8-(dimethylamino)naphthyl]lithium, Et_2O, 15 h, room temp.; ii, HC≡CM (M = Na, MgBr); iii, $Me_3SiC{\equiv}CLi$, THF, 2 d, reflux; iv, $Bu^n{}_4NF$, THF, 10 min, room temp.; v, CF_3CO_2H, $CHCl_3$, 4 h, reflux

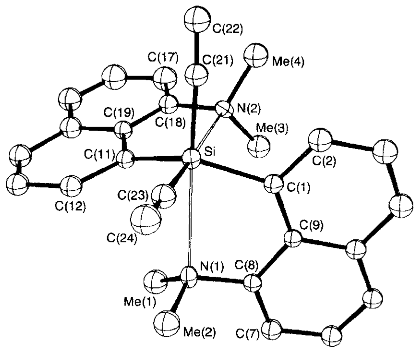
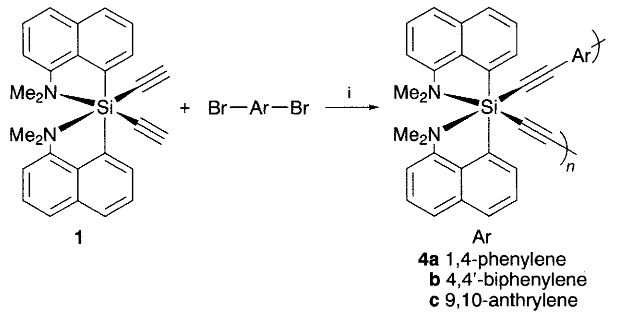


Fig. 1 Molecular structure of **1**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Si–C(1) 1.877(9), Si–C(11) 1.848(9), Si–C(21) 1.851(11), Si–C(23) 1.840(11), Si···N(1) 2.836(8), Si···N(2) 2.789(8), C(1)–Si–C(11) 134.0(4), C(21)–Si–C(23) 98.0(4), C(1)–Si–C(21) 105.7(4), C(1)–Si–C(23) 104.5(4), C(11)–Si–C(21) 103.0(4), C(11)–Si–C(23) 106.2(4), N(1)–Si–C(1) 72.0(3), N(1)–Si–C(11) 77.8(3), N(1)–Si–C(21) 177.0(4), N(1)–Si–C(23) 84.5(3), N(2)–Si–C(1) 76.9(3), N(2)–Si–C(11) 72.2(3), N(2)–Si–C(21) 82.3(3), N(2)–Si–C(23) 178.4(4), N(1)–Si–N(2) 95.3(2).

terminology previously introduced,[13] **1** is a (4 + 2)-coordinate complex. Both N atoms lie *trans* to the ethynyl groups, whereas in the compound R_2SiH_2 [R = 8-(dimethylamino)naphthyl] one N is *trans* to one H ligand and *cis* to the other whilst the second N is *cis* to both H ligands.[14] The Si centre is chiral. The Si···N distances of *ca.* 2.8 Å, which lie towards the upper end of the range observed for (4 + 2)-coordinate complexes, are shorter than the sum of the van der Waals radii (3.5 Å), indicating an interaction.[1] The mean Si–C≡ bond length of 1.845 Å is at the upper limit of the range observed for alkynylsilanes containing tetracoordinate Si (1.82–1.84 Å).[15–21]

In the protiodesilylation of disilylacetylenes, the protonation of the triple bond is the rate determining step.[22] The reaction proceeds *via* the most stable β-carbocation (stronger β-effect) and gives rise to a monosilylated acetylene after loss of the better stabilizing group.[22,23] Although β-effects in hypercoordinate Si compounds have not been studied systematically, it has been pointed out that in the case of vinyl cations the β-effect should be higher for hypercoordinate than for tetracoordinate Si.[22] On treatment of **2** with CF_3CO_2H (2 equiv.) for 4 h in refluxing $CHCl_3$, coordination-selective cleavage of the two bonds between the hexacoordinate Si and the acetylene groups took place affording the bis(trifluoroacetate) derivative **3** (identified by elemental analysis and MS) in 41% yield after recrystallization from *n*-heptane. No formation of **1** was detected, confirming the higher β-effect for hexa- than for tetracoordinate Si. GC analysis of the reaction mixture showed the formation of trimethylsilylacetylene, reaching a maximum yield of *ca.* 85% after about 10 h at room temp. Solutions of **3** in CH_2Cl_2 were found to be electrically non-conducting. The ^{29}Si NMR spectrum of **3** exhibits a signal at δ −76.3.

Monomer **1** undergoes palladium-catalysed cross-coupling polymerization with dihaloarenes affording soluble polymers **4a–c** containing hexacoordinate Si in the backbone together with acetylene and arylene groups (Scheme 2). The ^1H NMR spectra show two signals for the diastereotopic Me groups in similar positions to those for **1**. A principal ^{29}Si NMR resonance is observed for each polymer around δ −60, close to that for **1**. Two additional minor resonances with very similar chemical shifts can be distinguished for **4a** and **4c**, perhaps reflecting the existence of triads owing to the chiral nature of the Si centre. The IR ν(C≡C) stretch for **4a** occurs at 2154 cm^{-1} and that for **4b** at 2148 cm^{-1}, the corresponding polymers containing tetracoordinate Si showing a band at 2145 cm^{-1}.[24] In the case of the anthrylene-containing polymer **4c**, the ν(C≡C) absorbance lies at 2134 cm^{-1} as compared with 2110 cm^{-1} for the corresponding polymer containing tetracoordinate Si.[24] In order to obtain polymers of appreciable molecular mass, it is necessary to carry out the reaction in the presence of triphenylphosphane and to use dibromo- rather than diiodo-arenes. The polydispersities (M_w/M_n), but excepting **4a** not the molecular masses, of the polymers (Table 1) are similar to those for the analogous polymers containing tetracoordinate Ph_2Si groups.[2,4]



Scheme 2 *Reagents and conditions*: i, $(PPh_3)_2PdCl_2$, CuI, PPh_3, Et_3N, PhMe, 16 h, 89 °C

Table 1 Molecular mass data[a] for polymers **4a–c**

Polymer	M_w	M_n	M_w/M_n	n^b
4a	53 000	11 800	4.5	114
4b	67 400	18 000	3.7	125
4c	7 800	3 400	2.3	14

[a] Determined by SEC with reference to polystyrene standards. [b] Number of units calculated from value of M_w.

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Footnote

† *Crystal data* for **1**: $C_{28}H_{26}N_2Si\cdot0.38MeOH$, M = 430.8, rhombohedral, space group $R\bar{3}$, a = 15.258(4) Å, γ = 91.40(2)°, V = 3549(2) Å^3, D_c = 1.209, D_m = 1.18(2) g cm^{-3}, μ = 1.14 cm^{-1}, Z = 6. 1597 Unique reflections up to (sin θ)/λ = 0.435, 1114 with $F_o \geqslant 3.0\sigma(F_o)$, Enraf-Nonius CAD-4 diffractometer, Mo-Kα radiation, λ = 0.71069, T = 22 °C. Solution by direct methods (SHELXS-86). $R(R_w)$ = 0.069(0.075), $w = 1/[\sigma^2(F_o) + 0.0030\ F^2]$ for 161 refined parameters (anisotropic temperature factors for the Si and N atoms; the H atoms were taken into account in the refinement with isotropic temperature factors and Me_3 as rigid groups, SHELX-76). Residual electron density: 0.62 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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