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2-[(8-Dimethylaminonaphthalen-1-yl)dimethylsilyl]-*N*,*N*,4,4-tetramethyl-1,2,3,3*a*,4,5-hexahydro-4-sila-5,9*b*-ethenobenz[*e*]inde-9-amine. An unexpected by-product from the reaction of 1-lithio-8-dimethylaminonaphthalene with chlorodimethylvinylsilane

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Abstract

Reaction of 1-lithio-8-dimethylaminonaphthalene with chlorodimethylvinylsilane gives the expected vinylsilane **4** in very poor yield in addition to a large quantity of polymeric material. In addition, the polycyclic silane **6** was obtained in 9% yield; complex **6** arises via an intramolecular cycloaddition of the silene intermediate **7**. © 2002 Published by Elsevier Science B.V.

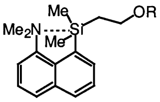
Keywords: Silaalkene; Pentavalent silicon; Silicon β effect; Cycloaddition

1. Introduction

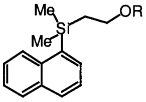
The stabilisation of positive charge by β-silicon is well established [1–3], and has been exploited in synthetic organic chemistry [3]. It is generally accepted that the mechanism of stabilisation by β-silicon is by σ–π conjugation between the polarisable C–Si bond and the carbocation p-orbital (Fig. 1) [1–3].

The σ–π stabilisation of the β-silylcarbenium ion results in significant positive charge build-up on the silicon, rendering it more Lewis acidic and hence more susceptible to attack by nucleophiles to form a pentavalent–silyl stabilised carbenium ion (Fig. 2); this is often followed by elimination of the silicon substituent resulting in an unsaturated product [4].

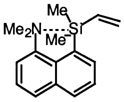
The C–Si bond of the pentavalent silicon is of higher energy and more polarisable and thus should be even more effective at stabilising positive charge by hyperconjugation. To investigate the β-effect of pentavalent silicon we chose to prepare the model dimethylaminonaphthylsilylethanol **1**. The peri-interaction between the dimethylamino and silicon substituents causes the silicon to distort towards a trigonal bipyramidal geometry [5]. X-ray structural studies [2,3,6–9] and solvolysis rate studies [1] of derived esters **2** and comparison with **3** were expected to provide us with an estimate of the effectiveness of C–Si hyperconjugation involving the pentavalent silicon in **1** compared to the tetravalent silicon in **3**.



1; R = H
2; R = COR’



3; R = COR’



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The vinyl silane **4** appeared to be a sensible precursor to **1** and was anticipated to be readily prepared by reaction of 1-lithio-8-dimethylaminonaphthalene (**5**) [10] with chlorodimethylvinylsilane.

2. Results and discussion

A slurry of **5** in diethyl ether was treated with a solution of chlorodimethylvinylsilane. The resulting complex mixture was separated by exhaustive chromatography giving the expected vinylsilane in only a very poor yield (20%), in addition to a large amount of

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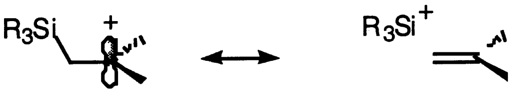


Fig. 1.

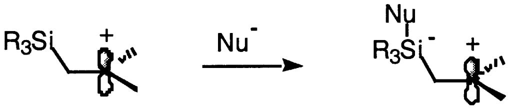
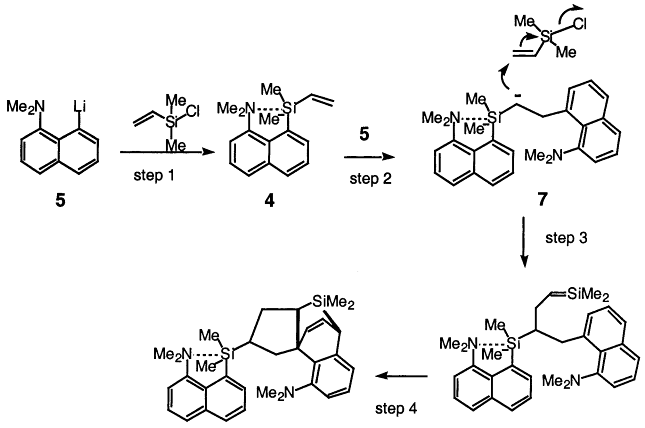


Fig. 2.



Scheme 1.

polymeric material (ca. 70%). An additional compound crystallised from several of the chromatography fractions in 9% yield, and was shown by X-ray crystallography to have the polycyclic structure **6**. Compound **6** incorporates two dimethylaminonaphthalene and two vinylsilane moieties in its structure. A mechanism to account for the formation of **6** is outlined in Scheme 1.

The first step involves reaction of the lithio naphthalene **5** in the expected fashion with vinyldimethylchlorosilane to give the vinylsilane **4**. The vinylsilane **4** appears to then undergo an addition reaction with a second molecule of the lithionaphthalene **5** giving the α-silyl anion intermediate **7**, a species whose formation presumably reflects the stabilising effect of silicon on carbanions at the α position [11]. The anion **7** then undergoes an allylic displacement of chloride from chlorodimethylvinylsilane to give the reactive silaalkene **8**. Generation of silaalkenes by allylic displacement of halide from substituted vinylhalosilanes has been demonstrated previously [12–15], and is expected to be efficient when the nucleophile is sterically congested. The silaalkene **8** is then captured by the naphthalene ring in an intramolecular [4+2] cycloaddition reaction, a reaction which is typical of these reactive dienophiles [16].

It is likely that the polymeric material which makes up the remainder of the product arises from further reaction of the anion **7** with the allylsilane **4** in an anion polymerisation mechanism.

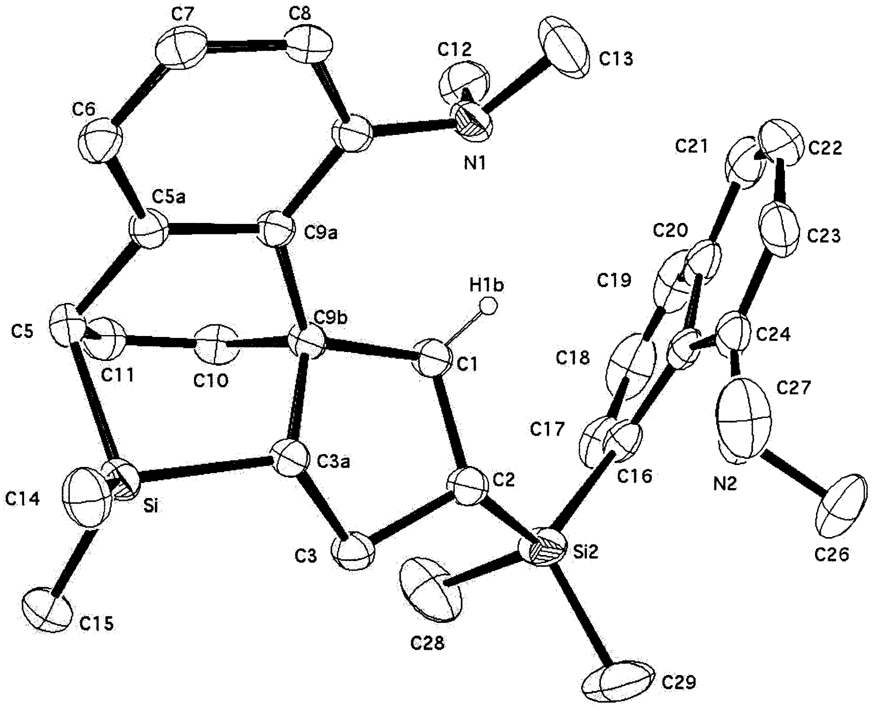


Fig. 3. Thermal ellipsoid plot of compound **6**. Ellipsoids are at the 20% probability level.

3. Molecular structure

The structure of **6** which depicts 20% ellipsoids is presented in Fig. 3 and was drawn using the program ORTEP 3 [17]. Hydrogen atoms with the exception of H(1B) are omitted for clarity. Selected bond distances, angles, and dihedral angles are presented in Table 1. The N2···Si2 distance which is 3.046(3) Å is well within the sum of the van der Waals radii (3.65 Å) [18]. The geometry at Si2 shows distortions towards a trigonal bipyramidal geometry with the carbons C2, C16, and C29 defining the basal plane (mean C–Si2–C angle 113.4°) and the peri nitrogen N2 occupying one apical site and C28 occupying the second apical site (mean C–Si2–C28 angle 105.1°). Steric repulsion between the dimethylamino substituent (N2) and the silicon substituent (Si2) causes the naphthalene ring system to twist from planarity with Si2 lying below the plane defined by C16–C25 by 0.74 Å and N2 lying 0.48 Å above the plane. Strain is also apparent in the spiro-ring system, for example, the C9a–C9b–C1 bond angle is 121°. This presumably relieves some of the strain arising from the close contact between N1 and the C1 methylene group (N1···C1 2.991(4) Å, N1···H1B 2.25 Å).

There are some interesting features also evident in the cycloadduct; the Si–C5 bond distance which is 1.904(3) Å is significantly longer than the Si–C3a bond distance which is 1.879(3) Å, even though both bonds are between silicon and 2° carbon atoms. The C3a–C9a distance which is 1.583(4) Å is longer than a typical C–C bond distance. It is worth noting that these are the bonds which are broken in the *retro* Diels alder reaction (Scheme 1, reverse step 4). Similar structural distortions have been noted previously in cyclopentadiene cycloadducts [19].

Table 1
Bond distances (Å) and angles (°) for compound **6**

Bond lengths			
Si–C(15)	1.855(3)	Si–C(14)	1.856(3)
Si–C(3A)	1.879(3)	Si–C(5)	1.904(3)
Si(2)–C(29)	1.860(5)	Si(2)–C(2)	1.874(3)
Si(2)–C(16)	1.883(3)	Si(2)–C(28)	1.895(5)
N(1)–C(9)	1.426(4)	N(1)–C(12)	1.453(4)
N(1)–C(13)	1.455(5)	N(2)–C(24)	1.427(4)
N(2)–C(27)	1.466(5)	N(2)–C(26)	1.471(5)
C(1)–C(2)	1.538(4)	C(1)–C(9B)	1.552(4)
C(2)–C(3)	1.548(4)	C(3)–C(3A)	1.530(4)
C(3A)–C(9B)	1.583(4)	C(5)–C(11)	1.490(4)
C(5)–C(5A)	1.503(4)	C(5A)–C(6)	1.388(4)
C(5A)–C(9A)	1.409(4)	C(6)–C(7)	1.363(4)
C(7)–C(8)	1.366(4)	C(8)–C(9)	1.396(4)
C(9)–C(9A)	1.397(4)	C(9A)–C(9B)	1.547(4)
C(9B)–C(10)	1.513(4)	C(10)–C(11)	1.323(4)
C(16)–C(17)	1.395(5)	C(16)–C(25)	1.428(5)
C(17)–C(18)	1.377(7)	C(18)–C(19)	1.321(7)
C(19)–C(20)	1.405(7)	C(20)–C(21)	1.401(7)
C(20)–C(25)	1.423(5)	C(21)–C(22)	1.326(7)
C(22)–C(23)	1.388(7)	C(23)–C(24)	1.365(5)
C(24)–C(25)	1.423(5)		
Bond angles			
C(15)–Si–C(14)	109.10(17)	C(15)–Si–C(3A)	114.09(15)
C(14)–Si–C(3A)	112.59(15)	C(15)–Si–C(5)	112.37(16)
C(14)–Si–C(5)	111.79(16)	C(3A)–Si–C(5)	96.51(13)
C(29)–Si(2)–C(2)	110.3(2)	C(29)–Si(2)–C(16)	116.79(19)
C(2)–Si(2)–C(16)	113.29(14)	C(29)–Si(2)–C(28)	104.4(3)
C(2)–Si(2)–C(28)	105.99(19)	C(16)–Si(2)–C(28)	104.9(2)
C(9)–N(1)–C(12)	113.0(3)	C(9)–N(1)–C(13)	116.3(3)
C(12)–N(1)–C(13)	110.7(3)	C(24)–N(2)–C(27)	115.2(3)
C(24)–N(2)–C(26)	110.2(3)	C(27)–N(2)–C(26)	110.0(3)
C(2)–C(1)–C(9B)	107.9(2)	C(1)–C(2)–C(3)	104.4(2)
C(1)–C(2)–Si(2)	115.3(2)	C(3)–C(2)–Si(2)	117.1(2)
C(3A)–C(3)–C(2)	102.8(2)	C(3)–C(3A)–C(9B)	102.0(2)
C(3)–C(3A)–Si	120.7(2)	C(9B)–C(3A)–Si	111.19(19)
C(11)–C(5)–C(5A)	110.3(2)	C(11)–C(5)–Si	102.5(2)
C(5A)–C(5)–Si	104.26(19)	C(6)–C(5A)–C(9A)	121.0(3)
C(6)–C(5A)–C(5)	121.4(3)	C(9A)–C(5A)–C(5)	117.6(2)
C(7)–C(6)–C(5A)	119.9(3)	C(6)–C(7)–C(8)	119.9(3)
C(7)–C(8)–C(9)	121.9(3)	C(8)–C(9)–C(9A)	118.8(3)
C(8)–C(9)–N(1)	120.5(3)	C(9A)–C(9)–N(1)	120.7(2)
C(9)–C(9A)–C(5A)	118.0(2)	C(9)–C(9A)–C(9B)	129.3(2)
C(5A)–C(9A)–C(9B)	112.5(2)	C(10)–C(9B)–C(9A)	106.4(2)
C(10)–C(9B)–C(1)	111.5(2)	C(9A)–C(9B)–C(1)	121.6(2)
C(10)–C(9B)–C(3A)	107.9(2)	C(9A)–C(9B)–C(3A)	106.0(2)
C(1)–C(9B)–C(3A)	102.6(2)	C(11)–C(10)–C(9B)	118.3(3)
C(10)–C(11)–C(5)	116.6(3)	Si–C(14)–H(14A)	109.5
C(17)–C(16)–C(25)	115.6(3)	C(17)–C(16)–Si(2)	115.4(3)
C(25)–C(16)–Si(2)	127.8(2)	C(18)–C(17)–C(16)	123.8(5)
C(19)–C(18)–C(17)	120.1(5)	C(18)–C(19)–C(20)	120.8(5)
C(21)–C(20)–C(19)	121.0(5)	C(21)–C(20)–C(25)	119.6(4)
C(19)–C(20)–C(25)	119.3(5)	C(22)–C(21)–C(20)	121.3(5)
C(21)–C(22)–C(23)	120.6(5)	C(24)–C(23)–C(22)	120.5(5)
C(23)–C(24)–C(25)	120.7(4)	C(23)–C(24)–N(2)	122.7(4)
C(25)–C(24)–N(2)	116.5(3)	C(20)–C(25)–C(24)	116.4(4)
C(20)–C(25)–C(16)	119.2(3)	C(24)–C(25)–C(16)	124.4(3)

4. Experimental

4.1. Crystallography

Diffraction data were recorded on an Enraf Nonius CAD4f diffractometer operating in the $\theta/2\theta$ scan. Crystal data and structure refinement details for **6** are presented in Table 2. Unit cell dimensions were corrected for any θ zero errors by centring reflections at both positive and negative θ angles. The data were corrected for Lorentz and polarisation effects (Process_data) [20]. Structures were solved by direct methods (SHELXS-86) [21] and were refined on F^2 (SHELXL-97) [22].

4.2. Synthesis

General experimental details are reported elsewhere [7]. 1-Dimethylaminonaphthalene and chlorodimethylvinylsilane were purchased from Aldrich and used without further purification.

Table 2
Crystal data and structure refinement for compound **6**

Empirical formula	$C_{32}H_{42}N_2Si_2$
Formula weight	510.86
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system, space group	Triclinic, $P\bar{1}$,
Unit cell dimensions	
a (Å)	10.495(4)
b (Å)	12.575(4)
c (Å)	12.664(3)
α (°)	78.41(3)
β (°)	85.01(2)
γ (°)	65.92(2)
V ($Å^{-3}$)	1494.7(8)
Z, D_{calc} (Mg m^{-3})	2, 1.135
Absorption coefficient (mm^{-1})	0.141
$F(000)$	552
Crystal size (mm)	0.5 × 0.4 × 0.3
Theta range for data collection (°)	2.13–24.97
Limiting indices	$0 \leq h \leq 12$, $-13 \leq k \leq 14$, $-14 \leq l \leq 15$
Reflections collected/unique	5549/5236 [$R_{int} = 0.0171$]
Completeness to theta = 24.97	100.0%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5236/0/325
Weighting scheme	$w = 1\sigma^2(F_o^2)+(0.06980P)^2+0.8730P]$ Where $P = (F_o^2+2F_c^2)/3$
Goodness-of-fit on F^2	1.015
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0589$, $wR_2 = 0.1409$
R indices (all data)	$R_1 = 0.0910$, $wR_2 = 0.1603$
Largest difference peak and hole (e $Å^{-3}$)	0.551 and −0.440

4.2.1. *Reaction of 1-lithio 8- dimethylaminonaphthalene* **5** *with chlorodimethylvinylsilane*

To a cooled (−78 °C) solution of 1-dimethylaminonaphthalene (2.50 g, 0.0146 mol) in anhydrous Et_2O (20 ml) under nitrogen, was added a solution of *n*-butyllithium in hexane (2.4 M, 8.1 ml, one equivalent). This mixture was then allowed to reach room temperature (r.t.) and stirred for 24 h, during which time a yellow precipitate of 8-(dimethylamino)-1-naphthyllithium etherate formed. This suspension was then chilled on ice then chlorodimethylvinylsilane (2.12 ml, 0.0146 mol, one equivalent) was added and then stirred at r.t. for a further 24 h. The resulting LiCl solid was filtered off and the solvent removed by rotary evaporation to give viscous yellow oil. This was taken up into CH_2Cl_2 then washed with HCl (0.25 M) several times, washed with 10% aqueous $NaHCO_3$ solution (3 × 50 ml), and H_2O (3 × 30 ml), dried ($MgSO_4$), filtered, and concentrated by rotary evaporation to give 4.92 g of viscous yellow oil. This was then separated by column chromatography (ether–petroleum). Compound **4** was the first fraction eluted and was obtained as a pale yellow viscous oil (1.85 g, 19.06%); ^{1}H-NMR ($CDCl_3$) δ 7.80 (2H, m), 7.59 (1H, d, $J = 8.1$ Hz), 741 (2H, m), 7.27 (1H, d, $J = 7.2$ Hz), 6.42 (1H, dd, $J = 20.55$ Hz, $J = 14.55$ Hz), 5.90 (1H, dd, $J = 14.70$ Hz, $J = 3.60$ Hz), 5.64 (1H, dd, $J = 20.40$ Hz, $J = 3.90$ Hz), 2.54 (6H, s), 0.34 (6H, s); ^{13}C-NMR ($CDCl_3$) δ 152.22, 142.61, 136.35, 134.82, 134.55, 134.42, 129.50, 128.33, 125.52, 125.19, 125.14, 116.33, 47.44, 0.32; ^{29}Si-NMR ($CDCl_3$) δ −15.62. The second fraction eluted from the column gave colourless crystals of compound **6** (1.35 g) m.p. 127–130 °C upon standing, ^{1}H-NMR ($CDCl_3$) 7.95 (1H, m), 7.76 (1H, d, $J = 8.1$ Hz), 7.57 (1H, d, $J = 8.1$ Hz), 7.48–7.38 (2H, m), 7.28 (1H, d, $J = 8.1$ Hz), 7.0–6.8 (3H, m), 6.29 (1H, dd, $J = 7.2$, 7.2 Hz), 5.6 (1H, d, $J = 7.2$ Hz), 3.49 (1H, d, $J = 6$ Hz), 2.65 (6H, s), 2.5 (6H, s), 1.75 (1H, m), 1.7–1.5 (2H, m), 1.5–0.9 (2H, m), 0.58 (1H, m), 0.39 (3H, s), 0.36 (3H, s), 0.0 (3H, s), −2.66 (3H, s). ^{29}Si-NMR ($CDCl_3$) δ −2.99, −4.16.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 176953 for compound **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc,cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] J.B. Lambert, Tetrahedron 46 (1990) 2677.
[2] J.M. White, Aust. J. Chem. 48 (1995) 1227.
[3] J.M. White, C.I. Clark, Topics in Stereochemistry (chapter 3), 1999, p. 22.
[4] M.A. Brook, C. Henry, R. Jueschke, P. Modi, Synlett (1993) 97.
[5] F. Carre, R.J.P. Corriu, A. Kpotan, M. Poirier, G. Royo, J.C. Young, J. Organomet. Chem. 470 (1994) 43.
[6] J.M. White, G.B. Robertson, J. Org. Chem. 57 (1992) 4638.
[7] A.J. Green, Y.L. Kuan, J.M. White, J. Org. Chem. 60 (1995) 2734.
[8] V.Y. Chan, C.I. Clark, J. Giordano, A.J. Green, A. Karalis, J.M. White, J. Org. Chem. 61 (1996) 5227.
[9] A.J. Green, J. Giordano, J.M. White, Aust. J. Chem. 53 (2000) 285.

[10] J.T.B.H. Jastrzebski, C.T. Knaap, G. van Koten, J. Organomet. Chem. 255 (1983) 287.

[11] E.W. Colvin, Silicon Reagents in Organic Synthesis, Academic Press, London, 1988.

[12] G. Delpon-Lacaze, C. de Battisti, C. Couret, J. Organomet. Chem. 514 (1996) 59.

[13] P.R. Jones, M.E. Lee, J. Organomet. Chem. 232 (1982) 33.

[14] P.R. Jones, T.F.O. Lim, R.A. Pierce, J. Am. Chem. Soc. 102 (1980) 4970.

[15] P.R. Jones, T.F.O. Lim, J. Am. Chem. Soc. 99 (1977) 2013.

[16] A.S. Andrei, I.M. Clarkson, J.A.K. Howard, J.P.G. Steel, Tetrahedron Lett. 37 (1996) 2491.

[17] L.J. Farrugia, J. Appl. Crystallogr. 20 (1997) 565.

[18] A Bondi, J. Phys. Chem. 68 (1964) 441.

[19] B.R. Pool, J.M. White, Org. Lett. 22 (2000) 3505.

[20] R.W. Gable, B.F. Hoskins, A. Linden, I.A.S. McDonald, R.J. Steen, Process_data Program for Processing of CAD-4 Diffractometer Data, University of Melbourne, Australia, 1994.

[21] G.M. Sheldrick, in: G.M. Sheldrick, C. Kruger, R. Goddard (Eds.), SHELXS-86: Crystallographic Computing 3, Oxford University Press, Oxford, England, 1985, pp. 175–189.

[22] G.M. Sheldrick, SHELXL-97 Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.