

[4 + 2]Cycloadditions of organometallic-substituted siloles with dimethyl acetylenedicarboxylate and tetracyanoethylene

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Abstract

1-Sila-2,4-cyclopentadienes (siloles) bearing five organyl groups and a diethylboryl group in 3-position (**3**), four organyl groups, a trimethylstannyl and a diethylboryl group in 2,4-positions (**4**), four organyl groups, a diethylboryl group in 3-position and a hydrido function at the silicon atom (**5**) react by [4 + 2]cycloaddition with dimethyl acetylenedicarboxylate, MeOC(O)–C≡C–C(O)OMe (**1**), and tetracyanoethylene, (NC)₂C=C(CN)₂ (**2**), to give 7-silanorbornadienes (**6–8**) and 7-silanorbornenes (**10–12**), respectively. The silole **5** is converted into isomers **8** and **8'**, and **12** and **12'**, in which the SiMe group in each major isomer (**8** and **12**) occupies the *syn*-position with respect to the C(2)=C(3) bond. The molecular structure of **10a** was determined by X-ray analysis. The 7-silanorbornadiene (**7**) rearranges into a benzene derivative by formation of an Si–O bond and 1,3-migration of the trimethylstannyl group. All products were characterised in solution by multinuclear magnetic resonance (¹H-, ¹¹B-, ¹³C-, ²⁹Si-, ¹¹⁹Sn-NMR spectroscopy). The geometries of 1,4,7,7-tetramethyl-7-silanorbornadiene, -7-silanorbornene, and -7-silanorbornane were optimised by ab initio MO calculations (RHF/6-311+G(d,p)) and chemical shifts δ²⁹Si were calculated (GIAO-RHF/6-311+G(d,p)).

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1. Introduction

1-Sila-2,4-cyclopentadienes (siloles) are reactive dienes [**1**] which readily undergo [4 + 2]cycloadditions with activated alkynes or alkenes to give 7-silanorbornadiene or 7-silanorbornene derivatives, respectively. Since 1,1-organoboration of bis(1-alkynyl)silanes has opened a convenient access to organometallic-substituted siloles [**2–4**], we have now explored the reactivity of such siloles towards the dienophiles dimethyl acetylenedicarboxylate, MeOC(O)–C≡C–C(O)OMe (**1**), and tetracyanoethylene, (NC)₂C=C(CN)₂ (**2**). The siloles **3–5** (Scheme 1) were used. In comparison with **3**, where the Et₂B group is the sole organometallic substituent, the silole **4** bears an additional trimethylstannyl group in 2-position, and this may have an influence on the stability of its [4 + 2]cycloaddition

products. In the case of the siloles **5**, the silicon atom bears a methyl group and a hydrido function, and therefore, two different isomers can be formed by [4 + 2]cycloaddition.

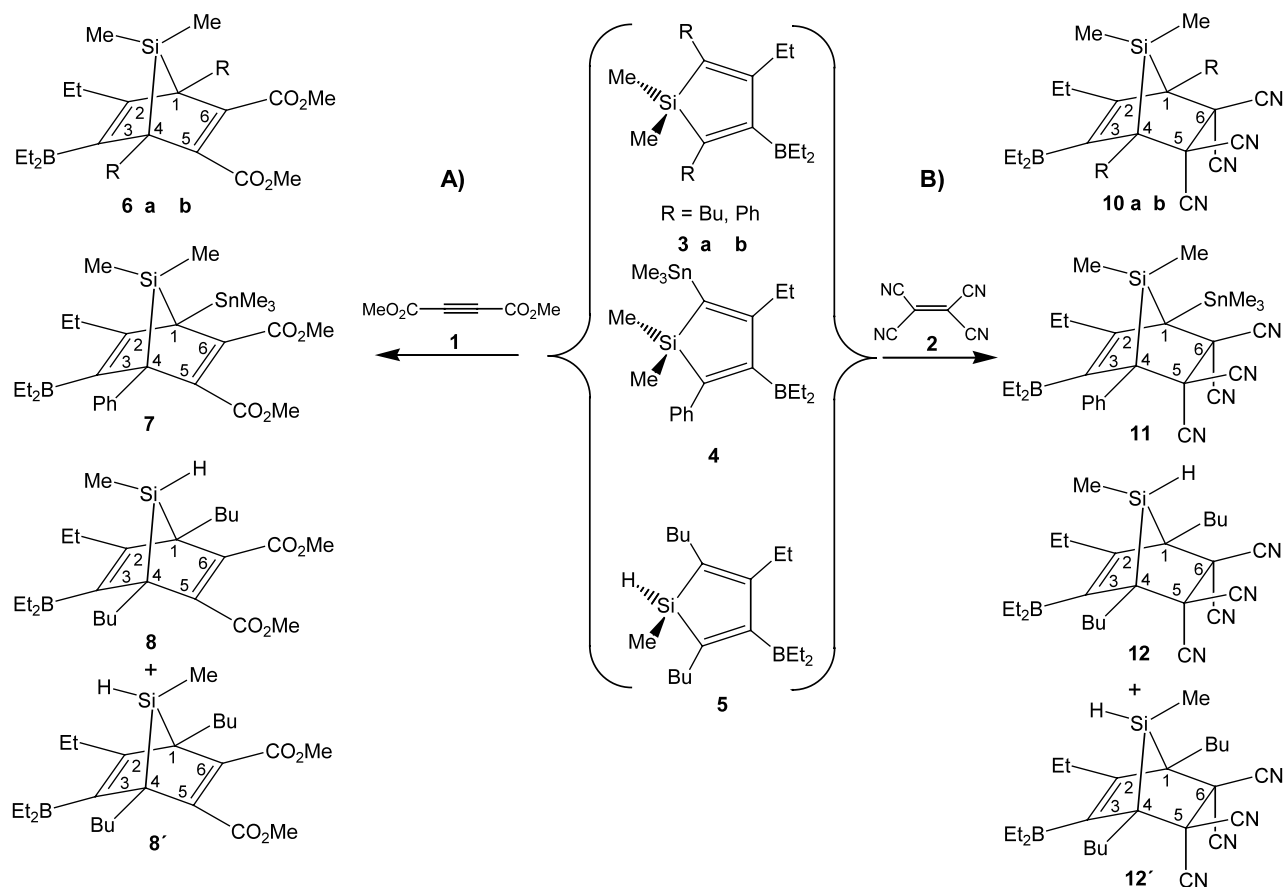
2. Results and discussion

2.1. Reactions of the siloles **3–5** with MeO(O)C–C≡C–C(O)OMe (**1**)

All siloles **3–5** react with MeO(O)C–C≡C–C(O)OMe (**1**) at room temperature in benzene solution within minutes to give [4 + 2]cycloaddition products, the 7-silanorbornadiene derivatives **6–8**, in quantitative yield (Scheme 1A). These compounds are colourless, air- and moisture-sensitive oils which become waxy solids after some time of storage. The proposed structures are based on the ¹H (experimental), ¹¹B-, ¹³C-, ²⁹Si- and ¹¹⁹Sn-NMR data (Table 1). In the case of **5**, a mixture containing the two isomers **8** and **8'** in an ca. 8:1 molar

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Scheme 1.

ratio was obtained (see Fig. 1), the major isomer with the SiMe group in *syn*-position with respect to the C(2)=

C(3) bond, in agreement with an approach of the dienophile to the less hindered side of the silole 5 [5].

Table 1
 ^{11}B -, ^{13}C - and ^{29}Si -NMR data ^{a,b} of the 7-silanorbornadienes (5–8)

	6a	6b	7 ^c	8	8'
$\delta^{13}\text{C}(1)$	57.0 (50.2)	62.7 (46.9)	49.2 (39.1) [402.2]	55.9 (51.0)	56.0
$\delta^{13}\text{C}(2)$	150.2 (4.5)	149.4	151.8 [2.5]	150.5 (4.9)	149.7
$\delta^{13}\text{C}(3)$	148.9 (br)	146.8 (br)	150.2 (br)	149.2 (br)	148.6 (br)
$\delta^{13}\text{C}(4)$	56.9 (49.7)	65.4 (46.9)	69.3 (43.4) [39.1]	56.4 (51.3)	56.5
$\delta^{13}\text{C}(5)$	145.3 (3.4)	140.4	140.2 [2.3]	144.9	145.0
$\delta^{13}\text{C}(6)$	145.6 (3.4)	147.9	155.3 [36.2]	145.7 (3.7)	145.6
$\delta^{13}\text{C}(\text{SiMe})$	−2.4 (43.1), −1.7 (45.6)	−4.2 (45.5), −2.5 (47.9)	−2.4 (43.5), −1.3 (48.1)	−3.6 (39.7)	−3.4
$\delta^{13}\text{C}(\text{Et}_2\text{B})$	21.8 (br) 9.3	21.2 (br), 9.7	21.4 (br), 9.7	22.0 (br), 9.4	21.8 (br) 9.3
$\delta^{13}\text{C}(\text{Et})$	23.6, 15.5	24.0, 15.0	28.8 [22.1], 15.3	23.4, 15.6	23.5, 15.3
$\delta^{13}\text{C}(\text{CO}_2\text{Me})$	166.4, 166.8, 51.15, 51.18	165.9, 167.7, 51.3, 51.5	166.9 [9.5], 168.1 [6.3], 51.3, 51.9	166.3, 166.6, 51.23, 51.25	166.2, 166.4, 51.18, 51.21
$\delta^{13}\text{C}(1\text{-R}, 4\text{-R})$	33.4, 33.5, 26.7, 29.2, 23.9, 24.0, 14.2, 14.2	139.0, 140.1, 130.3, 132.3, 127.2, 128.7, 125.6, 126.7	−5.5 [353.9] 138.4, 128.8, 127.9, 126.2	33.6, 33.3, 28.6, 26.5, 23.8, 23.7, 14.1, 14.1	33.5, 33.4, 29.2, 26.2, 23.9, 23.8, 13.9, 13.9
$\delta^{29}\text{Si}$	77.1	81.3	85.1 [14.7]	52.8	50.6
$\delta^{11}\text{B}$	88.0	85.0	89.0	83.0	83.0

^a See Scheme 1 for numbering; for better comparison, numbering in Tables, Figures and Schemes does not follow nomenclature in all cases.

^b Coupling constants $J(^{29}\text{Si}, ^{13}\text{C})$ are given in parentheses, and $J(^{119}\text{Sn}, ^{13}\text{C})$ and $^2J(^{119}\text{Sn}, ^{29}\text{Si})$ in brackets (± 0.2 Hz); the broad ^{13}C -NMR signals for carbon atoms linked to boron are indicated by (br).

^c $\delta^{119}\text{Sn}$ −33.5.

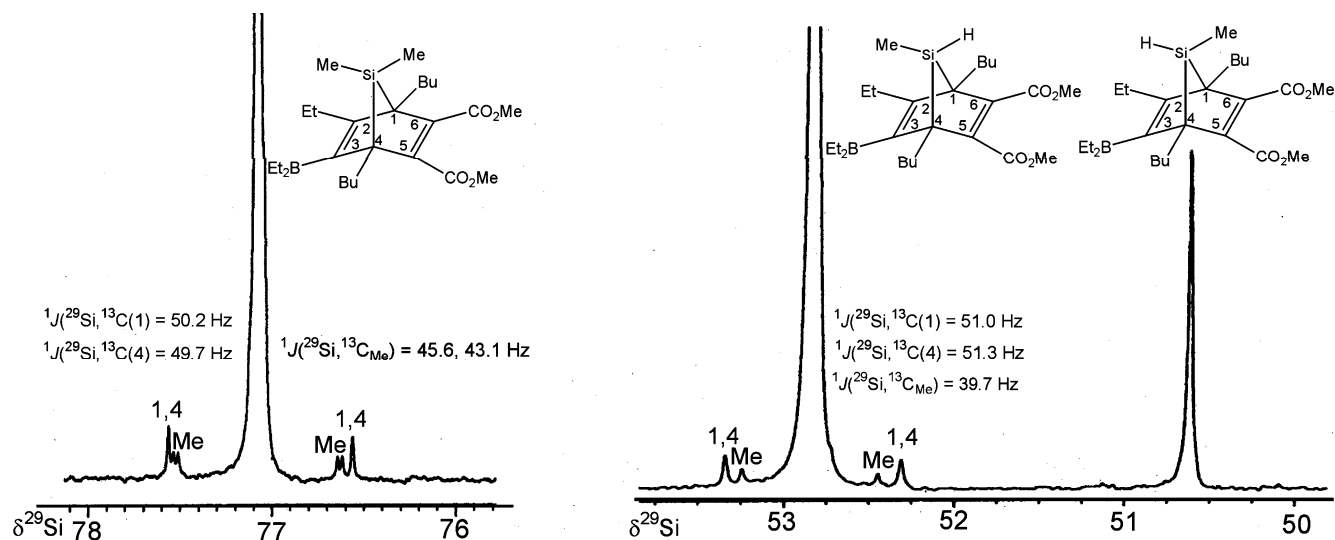


Fig. 1. $^{29}\text{Si}\{^1\text{H}\}$ -NMR (49.7 MHz) spectrum of the mixture of isomers **8** and **8'** (C_6D_6 , $23 \pm 1^\circ\text{C}$), showing the ^{13}C satellite signals for the major isomer **8**, corresponding to ^{29}Si satellites in ^{13}C -NMR spectra (see Table 1).

The assignment of the ^{13}C -NMR spectra is greatly aided by the observation of ^{29}Si satellites for $^1J(^{29}\text{Si}, ^{13}\text{C})$, and in turn the ^{29}Si -NMR spectra can be recorded to show the corresponding ^{13}C satellites (see Figs. 1 and 2). In the case of **7**, $^{117/119}\text{Sn}$ satellites in the ^{13}C -NMR spectra and ^{13}C satellites in the ^{119}Sn -NMR

spectra (Fig. 3) provide additional information. The unique electronic structure of 7-silanorbornadienes [6] is reflected by typical ^{29}Si nuclear deshielding [7,8] when compared with other tetraorganosilanes [9]. The diagnostic value of ^{11}B -NMR spectra is low in monitoring the reactions of the siloles with the dienophiles. All

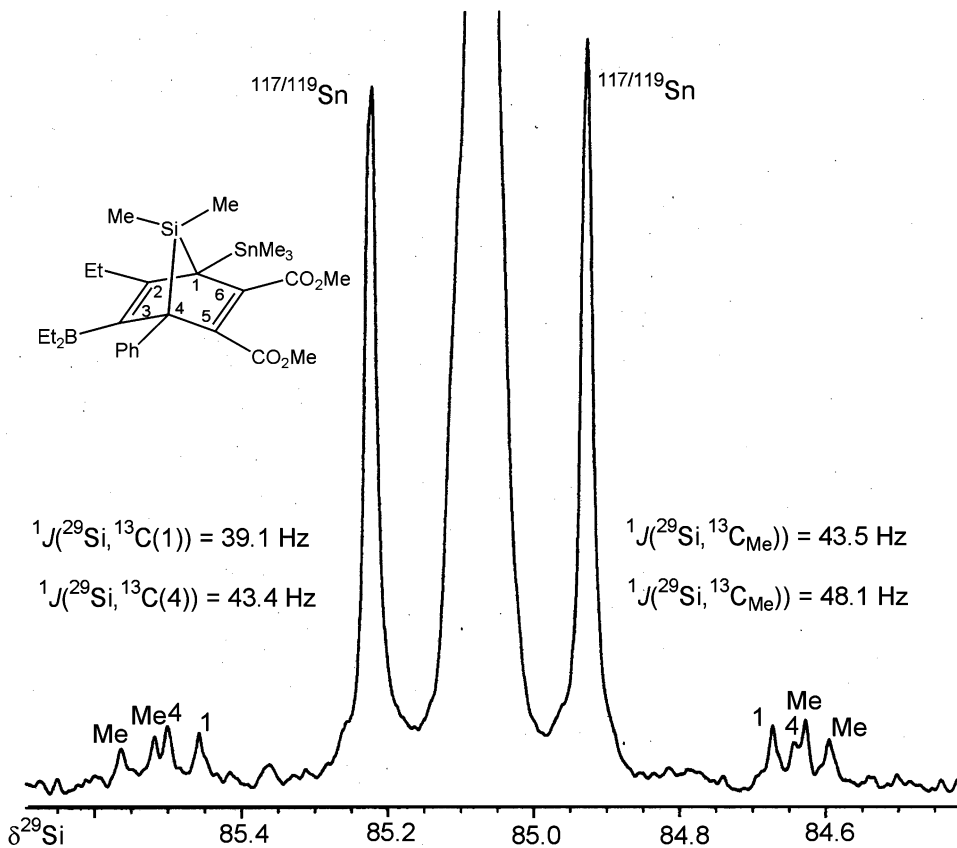


Fig. 2. $^{29}\text{Si}\{^1\text{H}\}$ -NMR (49.7 MHz) spectrum (recorded by using the refocused INEPT pulse sequence) of the 7-silanorbornadiene **7**, showing ^{13}C and $^{117/119}\text{Sn}$ satellites (see Table 1 for ^{13}C -NMR data).

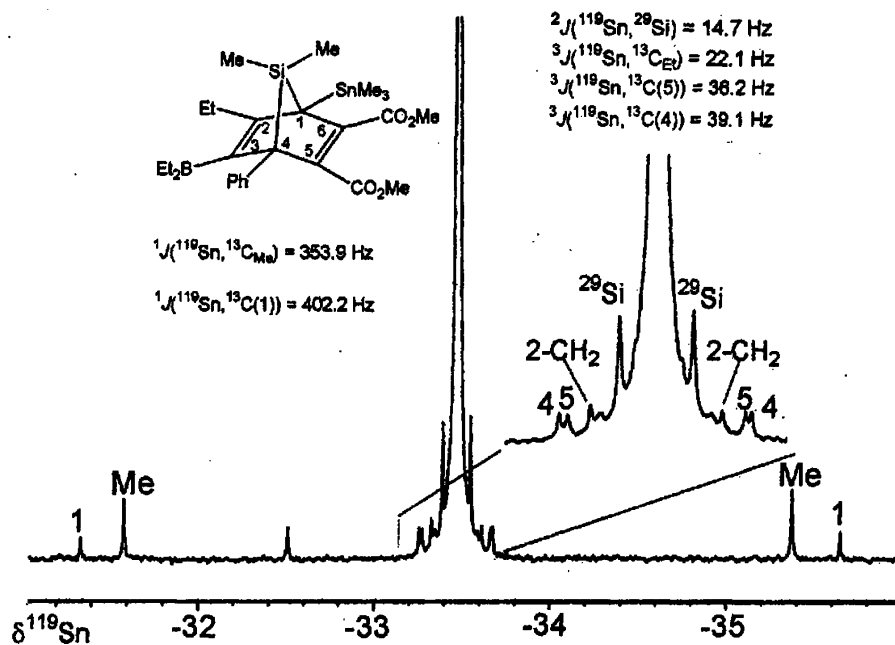


Fig. 3. $^{119}\text{Sn}\{^1\text{H}\}$ -NMR (93.3 MHz) spectrum (recorded by using the refocused INEPT pulse sequence) of the 7-silanorbornadiene **7** (C_6D_6 , $23 \pm 1^\circ\text{C}$), showing ^{13}C and ^{29}Si satellites (see Table 1 for ^{13}C -NMR data).

products give rise to a broad ^{11}B -NMR signal at $\delta^{11}\text{B}$ 86 ± 3 , in the same region as the siloles, typical of triorganoboranes with insignificant $\text{CB}(\text{pp})\pi$ interactions [10], since the CCB plane of the Et_2B group is, on average, oriented perpendicular to the plane $\text{B}-\text{C}(2)=\text{C}(3)$.

2.2. Isomerisation of the 7-silanorbornadiene derivative **7** into a benzene derivative **9**

When the compound **7** was stored either in solution or in pure state, rearrangements took place within several days, and the new set of NMR data (Table 2) indicates that a benzene derivative **9** was formed (Scheme 2). We propose that the labile $\text{Sn}-\text{C}$ bond is responsible, and the migration of the SnMe_3 group is accompanied by formation of the $\text{Si}-\text{O}$ bond leading selectively to **9**. This is related to the isomerisation process proposed for other 7-silanorbornadienes [11] which finally ends by oxidation to give benzene derivatives and $(\text{Me}_2\text{SiO})_n$. This type of isomerisation was not observed in the case of the other products **6** or **8**.

2.3. Reactions of the siloles **3–5** with $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$ (**2**)

Similar to the behaviour of **1**, there is also a smooth reaction of **3–5** with **2**, and the 7-silanorbornene derivatives **10–12** (Scheme 1B) are formed without side products. The compounds **10–12** are waxy or crystalline (**10a**), colourless, air- and moisture-sensitive solids which can be stored in the dark under argon for

several months. Their NMR spectra (^1H -NMR in experimental part; ^{13}C -, ^{11}B -, ^{29}Si -, ^{119}Sn -NMR in Table 3) are conclusive with respect to the 7-silanorbornene structure in solution (see Figs. 4 and 5 for typical ^{13}C -NMR spectra), and the molecular structure of **10a** in the solid state could be determined by X-ray analysis (vide infra). Again, in the case of **5**, isomers **12** and **12'** (molar ratio ca. 4:1) are obtained (see Fig. 5), in which the SiMe group in **12** is in *syn*-position with respect to the $\text{C}(2)=\text{C}(3)$ bond, as confirmed by $^1\text{H}/^1\text{H}$ NOE difference experiments [irradiation of $^1\text{H}(\text{SiMe})$ transition and observation of NOE effects on $^1\text{H}(\text{Et})$ and $^1\text{H}(\text{BEt}_2)$ resonances]. The nuclear magnetic shielding of ^{29}Si in the 7-silanorbornenes is still reduced when compared with other tetraorganosilanes [9]; however, the missing $\text{C}=\text{C}$ bond in the framework leads to increased ^{29}Si nuclear shielding in comparison with the 7-silanorbornadienes.

2.4. Ab initio MO calculations of 1,4,7,7-tetramethyl-7-silanorbornadiene, -7-silanorbornene, and -7-silanorbornane

The calculated geometries [12] of the 7-sila-norbornadiene (**13**), 7-silanorbornene (**14**), and 7-silanorbornane (**15**) (Table 4) are in agreement with expectations and experimental parameters if available. The calculated [12–14] ^{29}Si chemical shifts (Table 4) follow closely the trend of experimental data, the ^{29}Si nucleus in the 7-silanorbornadiene being most deshielded. The calculated nuclear shielding tensors show that deshielding contributions in **13** arise mainly from the magnetic shielding

Table 2
 ^{13}C -, ^{29}Si - and ^{119}Sn -NMR data ^{a,b} of the benzene derivative **9**

$\delta^{13}\text{C}(1)$	$\delta^{13}\text{C}(2)$	$\delta^{13}\text{C}(3)$	$\delta^{13}\text{C}(4)$	$\delta^{13}\text{C}(5)$	$\delta^{13}\text{C}(6)$	$\delta^{29}\text{Si}$	$\delta^{119}\text{Sn}$
133.4 (68.2) [10.6]	141.5 [7.2]	147.0 (br)	147.1 [5.8]	151.2 [38.6]	126.1 [7.5]	21.8 [11.2]	−6.1 [11.2]
1-SiMe ₂ , 1.3 (59.3), 1.5 (59.6)	2-Et, 31.2, 17.1	3-Bet ₂ , 22.0 (br), 23.6 (br), 9.7, 9.3	4-Ph, 141.8, 129.1, 128.2, 127.8	5-CO ₂ Me, 170.5 [2.1], 51.4	6-C-SnMe ₃ , 115.6 [655.7], 50.6 (OMe), [39.1], −7.0 (SnMe ₃), [320.3]		

^a See formula **9** in Scheme 2 for numbering.

^b Coupling constants $J(^{29}\text{Si}, ^{13}\text{C})$ are given in parentheses, and $J(^{119}\text{Sn}, ^{13}\text{C})$ and $^3J(^{119}\text{Sn}, ^{29}\text{Si})$ in brackets (± 0.2 Hz); the broad ^{13}C -NMR signals for carbon atoms linked to boron are indicated by (br).

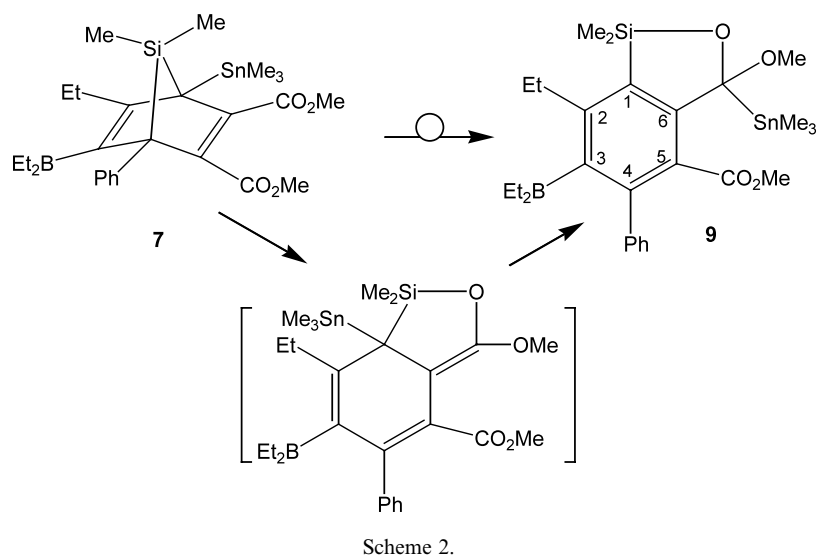


Table 3
 ^{11}B -, ^{13}C - and ^{29}Si -NMR data ^{a,b} of the 7-silanorbornenes **10–12**

	10a	10b	11 ^c	12	12'
$\delta^{13}\text{C}(1)$	54.9 (49.2)	59.0 (48.9)	44.3 (36.5) [245.4]	55.57 (51.2)	55.1
$\delta^{13}\text{C}(2)$	147.6	147.2	150.0 [5.4]	147.6	148.6
$\delta^{13}\text{C}(3)$	152.1 (br)	150.4 (br)	154.2 (br)	150.4 (br)	152.1 (br)
$\delta^{13}\text{C}(4)$	55.3 (49.7)	59.1 (48.1)	62.0 (45.9) [28.6]	55.63 (50.1)	55.3
$\delta^{13}\text{C}(5)$	52.8	52.0	53.6	53.2 (9.4)	53.7
$\delta^{13}\text{C}(6)$	53.9	55.6	56.5 (11.6) [30.2]	54.1 (9.1)	53.8
$\delta^{13}\text{C}(\text{SiMe})$	−4.2 (62.1), 2.1 (40.8)	−3.1 (62.6), 4.5 (41.4)	−4.7 (62.0), 5.3 (40.8)	−8.7 (61.1)	0.6 (38.4)
$\delta^{13}\text{C}(\text{Et}_2\text{B})$	21.5 (br) 9.0	22.0 (br), 8.8	212.0 (br), 9.1	21.9 (br), 9.1	22.4 (br) 9.5
$\delta^{13}\text{C}(\text{Et})$	23.6, 15.5	25.9, 13.1	30.4 [18.0], 14.4	23.9, 15.6	23.6, 15.7
$\delta^{13}\text{C}(\text{CN})$	113.8, 113.0, 112.9, 112.7	113.6, 113.1, 111.41, 111.37	114.8 [6.5], 114.5, 113.7 [6.3], 112.4	113.5, 113.2, 113.1, 112.8	113.5, 112.8, 112.52, 112.50
$\delta^{13}\text{C}$ (1-R, 4-R)	31.9, 31.7, 29.6, 27.9, 23.39, 23.35, 13.77, 13.71	134.2, 133.2, 131.8, 129.8, 129.7, 129.5, 129.2, 129.1	−6.3 [349.4], 135.3, 129.8, 129.7, 129.4	31.94, 31.88, 29.8, 27.9, 23.4, 23.3, 13.72, 13.70	32.8, 32.2, 29.2, 27.3, 23.2, 23.0, 13.82, 13.75
$\delta^{29}\text{Si}$	33.6	38.4	41.6 [3.0]	14.7	11.5
$\delta^{11}\text{B}$	85.0	89.0	89.0	84.0	84.0

^a See Scheme 3 for numbering; for better comparison, numbering in Tables, Figures and Schemes does not follow nomenclature in all cases.

^b Coupling constants $J(^{29}\text{Si}, ^{13}\text{C})$ are given in parentheses, and $J(^{119}\text{Sn}, ^{13}\text{C})$ and $^2J(^{119}\text{Sn}, ^{29}\text{Si})$ in brackets (± 0.2 Hz); the broad ^{13}C -NMR signals for carbon atoms linked to boron are indicated by (br).

^c $\delta^{119}\text{Sn}$ 1.1.

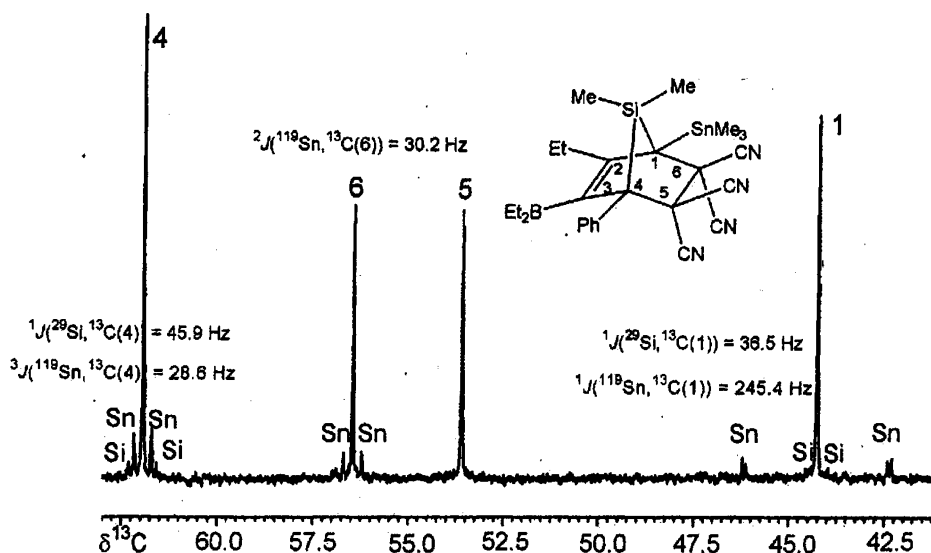


Fig. 4. $^{13}\text{C}\{^1\text{H}\}$ -NMR (62.9 MHz) spectrum of **11** (C_6D_6 , $23 \pm 1^\circ\text{C}$), showing the ^{13}C signals in the range for the saturated ring carbon atoms 1, 4, 5, and 6 with $^{117/119}\text{Sn}$ and ^{29}Si satellites.

tensor in the z -axis which should pass through the silicon atom and the middle of the plane of the four olefinic carbon atoms. This indicates that the C=C and Si–C bonds are involved in the deshielding.

2.5. X-ray structural analysis of the 7-silanorbornene derivative (**10a**)

The molecular structure of **10a** is shown in Fig. 6, and selected bond lengths and angles are given in the legend. The structural parameters are comparable with other 7-silanorbornadiene and 7-silanorbornene derivatives [15]

or 7-germanorbornenes [16a]. Typical are the elongated Si–C(bridgehead) bonds (191.7(2), 191.8(3) pm), when compared with the Si–C(Me) distances (184.5(3), 185.9(3) pm), and the small (c.f. the angle C(1)–C(7)–C(4) = 94° in norbornadiene [16b]) endocyclic bond angle at the silicon atom ($82.32(11)^\circ$). The six-membered ring is folded at the line connecting the bridgehead carbon atoms (114.8°), and the CCB plane of the BEt_2 group is twisted by 60.7° against the B–C=C plane. The angles CCB in the BEt_2 group are markedly wider, by almost 10° , than the expected tetrahedral angle, apparently a common feature of ethylboron compounds [17].

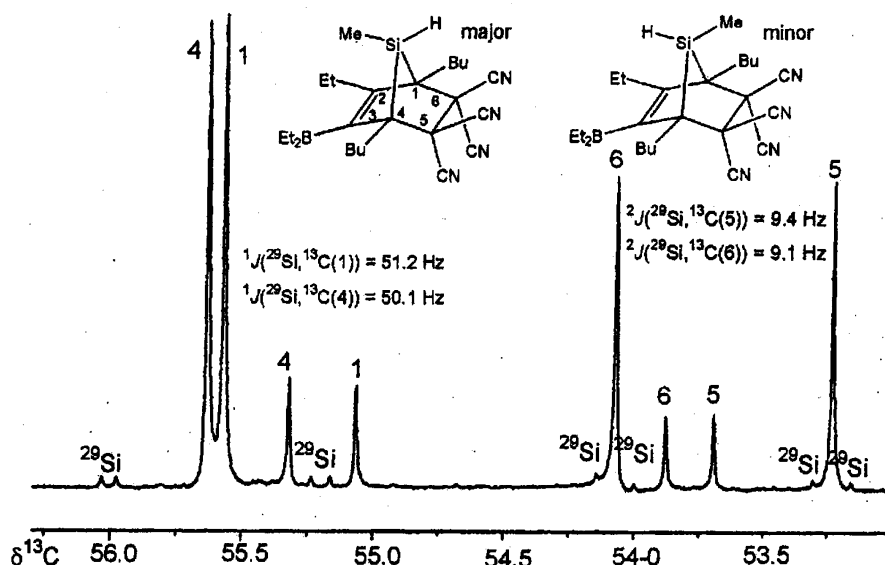


Fig. 5. $^{13}\text{C}\{^1\text{H}\}$ -NMR (62.9 MHz) spectrum of the mixture of isomers **12** and **12'** (C_6D_6 , $23 \pm 1^\circ\text{C}$), showing the ^{13}C signals in the range for the saturated ring carbon atoms 1, 4, 5, and 6 with ^{29}Si satellites for the major isomer **12**.

Table 4

Calculated optimised ^a geometries [pm, °] ^b and chemical shifts $\delta^{29}\text{Si}$ ^{c,d} of 1,4,7,7-tetramethyl-7-silanorbornadiene (**13**), -7-silanorbornene (**14**) and -7-silanorbornane (**15**)

	Si–C(1,4)	Si–C(Me)	C–C	C–C	C(1)SiC(4)	C(Me)SiC(Me)	$\delta^{29}\text{Si}$
13	194.1	188.7	132.5 (2–3)	152.7 (1–2)	80.5	106.6	77.8
14	191.9	188.4, 189.0	132.8 (C=C), 155.6 (5–6)	152.1 (1–2), 156.2 (3–4)	82.1	107.6	34.9
15	190.9	188.7	155.9 (2–3)	154.9 (1–2)	83.3	108.3	12.0

^a Computation of vibrational frequencies indicates that the structures represent potential energy minima.

^b RHF/6-311+G** [12–14].

^c GIAO-RHF/6-311+G** [13,14]; calculated isotropic shielding $\sigma(^{29}\text{Si}) = 1/3[\sigma(\text{xx}) + \sigma(\text{yy}) + \sigma(\text{zz})]$ with $\sigma(\text{xx}) = \sigma(\text{yy}) = \sigma(\text{zz}) = 396.7$ in SiMe_4 ; set to $\delta^{29}\text{Si} = 0$.

^d Magnetic shielding tensors (note that σ and δ have opposite signs): **13**: $\sigma(\text{xx}) = 388.7$, $\sigma(\text{yy}) = 366.9$, $\sigma(\text{zz}) = 200.6$; **14**: $\sigma(\text{xx}) = 385.9$, $\sigma(\text{yy}) = 366.2$, $\sigma(\text{zz}) = 333.5$; **15**: $\sigma(\text{xx}) = 399.4$, $\sigma(\text{yy}) = 380.4$, $\sigma(\text{zz}) = 374.3$.

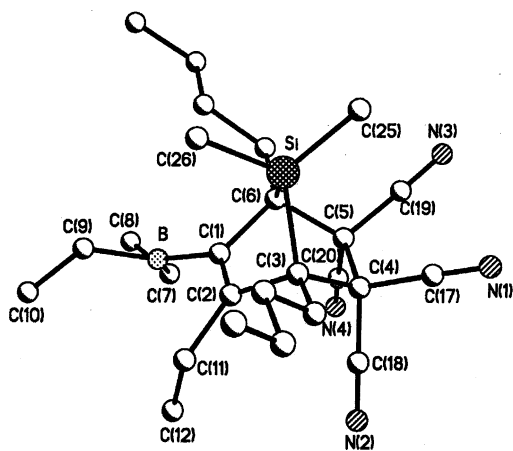


Fig. 6. Molecular structure of the 7-silanorbornene **10a** (hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and angles [°]: Si–C(3) 191.8(3), Si–C(6) 191.7(2), Si–C(25) 185.9(3), Si–C(26) 184.5(3), C(1)–C(2) 135.1(3), C(1)–C(6) 154.2(3), C(4)–C(5) 160.3(4), C(2)–C(3) 153.0(4), C(3)–C(4) 159.3(4), C(5)–C(6) 158.3(4), C(1)–B 158.8(4), B–C(7) 155.9(4), B–C(9) 157.6(5), C(2)–C(11) 150.8(4), C(3)–C(13) 153.2(4), C(4)–C(17) 148.0(4), C(4)–C(18) 147.7(4), C(5)–C(19) 148.8(4), C(5)–C(20) 148.2(3), C(6)–C(21) 153.2(4), C–N 113.5(3) (mean value); C(3)–Si–C(6) 82.32(11), C(25)–Si–C(26) 108.9(2), C(3)–Si–C(25) 117.6 (2), C(3)–Si–C(26) 113.9(1), C(6)–Si–C(25) 117.6(1), C(8)–C(7)–B 119.0(3), C(10)–C(9)–B 119.6(3), C(13)–C(3)–Si 122.8(2), C(21)–C(6)–Si 121.8(2).

3. Conclusions

It appears that all types of siloles, accessible by 1,1-organoboration of bis(1-alkynyl)silanes, undergo smoothly [4+2]cycloadditions with suitable dienophiles, usually activated alkynes and alkenes. Acetylene itself does not react, and also reactions with propyne, 1-hexyne, 3-hexyne, and ethynyl(trimethyl)silane (all between 20 and 80 °C) could not be induced. The stability of the 7-silanorbornadienes **5–8** is remarkable, although in the case of **7** slow rearrangement to a new benzene derivative **9** occurred. The molar ratios 8:1 and 4:1 of the isomers **8/8'** and **12/12'**, respectively, indicate that the approach of $\text{MeO}_2\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{Me}$ to the silole ring is more stereoselective than that of $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$. The molecular structure of **10a** shows the expected features,

of which the small endocyclic bond angle C(1)SiC(4) (82.32(11)°) is particularly noteworthy.

4. Experimental

4.1. General

The preparation and handling of all compounds were carried out in an atmosphere of dry argon, and carefully dried solvents and oven-dried glassware were used throughout. Starting materials were commercially available (**1** and **2**) or were prepared as described (siloles **3** [2a], **4** [3a] and **5** [4]). NMR measurements in C_6D_6 with samples in 5 mm tubes at 23 ± 1 °C: Bruker ARX 250 and Bruker DRX 500: ^1H -, ^{11}B -, ^{13}C -NMR and ^{29}Si -, ^{119}Sn -NMR (refocused INEPT [18] based on $^1J(^{29}\text{Si}, ^1\text{H})$ ca. 185 Hz, $^2J(^{29}\text{Si}, ^1\text{H}_{\text{Me}})$ ca. 7 Hz, and $^2J(^{119}\text{Sn}, ^1\text{H}_{\text{Me}})$ ca. 52 Hz); chemical shifts are given with respect to Me_4Si [$\delta^1\text{H}$ ($\text{C}_6\text{D}_5\text{H}$) = 7.15; $\delta^{13}\text{C}$ (C_6D_6) = 128.0; $\delta^{29}\text{Si} = 0$ for $\Xi(^{29}\text{Si}) = 19.867184$ MHz]; external Me_4Sn [$\delta^{119}\text{Sn} = 0$ for $\Xi(^{119}\text{Sn}) = 37.290665$ MHz]; external $\text{BF}_3\text{-OEt}_2$ [$\delta^{11}\text{B} = 0$ for $\Xi(^{11}\text{B}) = 32.083971$ MHz].

4.2. Reaction of the siloles **3–5** with dimethyl acetylenedicarboxylate **1** and tetracycanoethylene **2** (general procedure)

The siloles (3 mmol) were dissolved in C_6H_6 (5 ml), and equimolar amounts of **1** or **2** as solutions in C_6H_6 (10 ml) were added at room temperature (r.t.). The mixtures were kept stirring for 12–24 h; then volatile materials were removed in vacuo. The residues were dissolved in hexane and kept at low temperature (–70 to –90 °C) in order to obtain crystalline material. This was successful in the case of **10a**. In all other cases, colourless, or yellowish (**7**), air-sensitive oils were isolated after hexane had been removed in vacuo; these oils turned into waxy solids after several days of storage. **6a**: ^1H -NMR (250 MHz): $\delta^1\text{H} = 0.18, 0.23$ (s, s, 3H, 3H,

SiMe₂), 3.43, 3.43 (s, s, 3H, 3H, OMe), overlapping multiplets for 1-Bu, 4-Bu, 2-Et and 3-Et₂B groups. **6b**: ¹H-NMR (250 MHz): $\delta^1\text{H} = 0.26, 0.39$ (s, s, 3H, 3H, SiMe₂), 1.45, 1.30, 1.04 (m, m, t, 2H, 2H, 6H, BEt₂), 2.16, 2.03, 0.66 (m, m, t, 1H, 1H, 3H, 2-Et), 3.31, 3.33 (s, s, 3H, 3H, OMe), 6.88–7.10, 7.20–7.30 (m, m, 10H, 1-Ph, 4-Ph). **7**: ¹H-NMR (250 MHz): $\delta^1\text{H} = 0.36, 0.43$ (s, s, 3H, 3H, SiMe₂), 0.46 (s, ²*J*(¹¹⁹Sn, ¹H_{Me}) = 53.0 Hz, 9H, SnMe₃), 1.44, 1.27, 1.10 (m, m, t, 2H, 2H, 6H, BEt₂), 2.49, 2.42, 1.00 (m, m, t, 1H, 1H, 3H, 2-Et), 3.41, 3.45 (s, s, 3H, 3H, OMe), 7.00–7.10 (m, 5H, 4-Ph). **8**: ¹H-NMR (250 MHz): $\delta^1\text{H} = 0.24$ (d, ³*J*(H,H) = 2.5 Hz, 3H, SiMe), 3.42, 3.43 (s, s, 3H, 3H, OMe), 4.72 (q, ³*J*(H,H) = 2.5 Hz, ¹*J*(²⁹Si, ¹H_i) = 197.1 Hz, 1H, SiH), overlapping multiplets for 1-Bu, 4-Bu, 2-Et, and 3-BEt₂ groups. **8'**: ¹H-NMR (250 MHz): $\delta^1\text{H} = 0.27$ (d, ³*J*(H,H) = 2.6 Hz, 3H, SiMe), 3.30, 3.30(s, 6H, OMe), 4.76(q, ³*J*(H,H) = 2.6 Hz, 1H, SiH), and overlapping multiplets for 1-Bu, 4-Bu, 2-Et, and 3-BEt₂ groups. **10a** (m.p. 95–97 °C): ¹H-NMR (250 MHz): $\delta^1\text{H} = -0.12, 0.48$ (s, s, 3H, 3H, SiMe₂), overlapping multiplets for 1-Bu, 4-Bu, 2-Et, and 3-BEt₂ groups. **10b**: ¹H-NMR (250 MHz): $\delta^1\text{H} = 0.63, 1.02$ (s, s, 3H, 3H, SiMe₂), 1.16, 0.93 (m, t, 4H, 6H, BEt₂), 2.18, 2.04, 0.49 (m, m, t, 1H, 1H, 3H, 2-Et), 7.30–7.60 (m, 10H, 1-Ph, 4-Ph). **11**: ¹H-NMR (250 MHz): $\delta^1\text{H} = 0.07, 0.76$ (s, s, 3H, 3H, SiMe₂), 0.38 (s, ²*J*(¹¹⁹Sn, ¹H_{Me}) = 54.7 Hz, 9H, 1-SnMe₃), 1.06, 0.83 (m, t, 4H, 6H, BEt₂), 2.16, 1.81, 0.88 (m, m, t, 1H, 1H, 3H, 2-Et), 7.00–7.30 (m, 5H, 4-Ph). **12**: ¹H-NMR (250 MHz): $\delta^1\text{H} = 0.08$ (d, ³*J*(H,H) = 2.7 Hz, 3H, SiMe), 4.98 (q, ³*J*(H,H) = 2.7 Hz, ¹*J*(²⁹Si, ¹H) = 189.6 Hz, 1H, SiH), overlapping multiplets for 1-Bu, 4-Bu, 2-Et and 3-BEt₂ groups. **12'**: ¹H-NMR (250 MHz): $\delta^1\text{H} = 0-41$ (d, ³*J*(H,H) = 3.7 Hz, 3H, SiMe), 3.67 (q, ³*J*(H,H) = 3.7 Hz, 1H, SiH), overlapping multiplets for 1-Bu, 4-Bu, 2-Et, and 3-BEt₂ groups.

4.3. Rearrangement of **7** to **9**

A solution of **7** (0.1 g, 0.17 mmol) in C₆H₆ (1 ml) was kept for 5 days at r.t., and then NMR spectra indicated complete rearrangement. After removing of the solvent in vacuo, a yellowish oil was left which turned into a waxy solid after several days of storage. **9**: ¹H-NMR (250 MHz): $\delta^1\text{H} = 0.38, 0.45$ (s, s, 3H, 3H, SiMe₂), 0.29 (s, ²*J*(¹¹⁹Sn, ¹H_{Me}) = 52.5 Hz, 9H, SnMe₃), 1.35, 1.10 (m, t, 4H, 6H, BEt₂), 2.40, 0.95 (m, t, 2H, 3H, 2-Et), 3.37, 3.45 (s, s, 3H, 3H, OMe), 7.10–7.30 (m, 5H, 4-Ph).

4.4. Crystal structure determination of the norbornene **10a**

A single crystal of **10a**, recrystallised from pentane at –20 °C, was sealed under argon in a Lindemann capillary. Intensity data collection was carried out on a Siemens P4 diffractometer with Mo–K_α-radiation

($\lambda = 71.073$ pm, graphite monochromator) at r.t. The hydrogen atoms are in calculated positions. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

10a: C₂₆H₃₉BN₄Si, colourless prism: 0.25 × 0.20 × 0.16 mm³; it crystallises in the monoclinic space group *P*2(1)/*c*; *a* = 9.3308(7), *b* = 13.4994(12), *c* = 21.9530(18) Å, $\beta = 96.316(5)^\circ$, *Z* = 4, $\mu = 0.105$ mm^{–1}; 6250 reflections collected in the range 2–25° in θ , 4795: reflections independent (*I* > 2σ(*I*)); full-matrix least-squares refinement with 290 parameters, *R*₁/*wR*₂-values 0.0604/0.1645, no absorption correction; max./min. residual electron density 0.415/–0.202 × 10^{–6} e pm^{–3}.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-183250 (**10a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; www: <http://www.ccdc.cam.ac.uk>].

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