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Synthesis and molecular structures of 1-chloro-1-silacyclopent-2-enes. Combination of 1,2-hydroboration, 1,1-organoboration and protodeborylation

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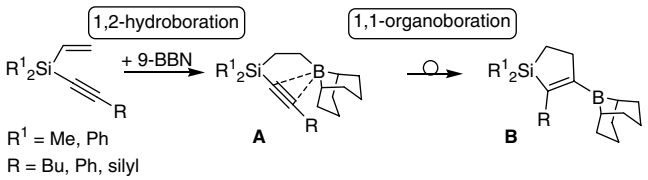
The reaction of alkyn-1-yl(chloro)(methyl)vinyl- and alkyn-1-yl(chloro)(phenyl)-vinylsilane with 9-borabicyclo[3.3.1]nonane (9-BBN) afforded selectively 1-silacyclopent-2-ene derivatives containing a Si–Cl function, as a result of consecutive 1,2-hydroboration and 1,1-organoboration. Protodeborylation with acetic acid left the Si–Cl functions in various 1-silacyclopent-2-enes untouched, whereas acetic acid in the presence of dipropylamine led to conversion of the Si–Cl into the Si–OAc function. New starting materials and all products were characterized in solution by multinuclear NMR spectroscopy (^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR), and the molecular structures of two 1-silacyclopent-2-ene derivatives were determined by X-ray analysis. The gas phase geometries of 1-silacyclopent-2-enes were optimized by DFT calculations [B3LYP/6-311+G(d,p) level of theory], found to be in reasonable agreement with the results of the crystal structure determination, and NMR parameters were calculated at the same level of theory.

Keywords: silanes; heterocycles; hydroboration; organoboration; NMR; X-ray analysis; DFT calculations

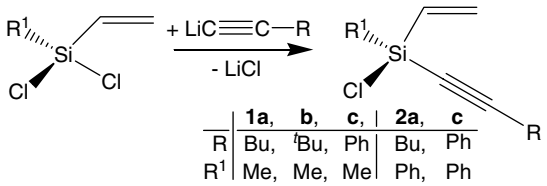
Introduction

In contrast with 1-silacyclopent-3-ene derivatives,[1–4] the corresponding isomers, 1-silacyclopent-2-enes[5,6] are less readily accessible,[7] and therefore the latter have received less attention. We have shown (Scheme 1) that the combination of 1,2-hydroboration, leading to the intermediate **A**, followed by 1,1-organoboration, opens up a straightforward route to such compounds of type **B**.[8–10]

In the present work, we report that heterocycles related to **B** can be readily prepared with Si–Cl functions, which greatly extend the scope of further applications. Moreover, the dialkylboryl group can be removed by protodeborylation without affecting the Si–Cl functions. We have aimed for characterization of the new 1-silacyclopent-2-enes in solution by multinuclear NMR spectroscopy and in the solid state by X-ray structural analysis.



Scheme 1. Reaction of alkyn-1-yl(vinyl)diorganosilanes using 9-BBN at ambient temperature: consecutive 1,2-hydroboration and 1,1-organoboration.



Scheme 2. Syntheses of alkyn-1-ylsilanes.

Results and Discussion

Synthesis of alkyn-1-yl(chloro)(methyl)vinyl-, 1, and alkyn-1-yl(chloro)(phenyl)vinyl-silane 2

The alkyn-1-ylvinylsilanes **1** and **2**, both bearing four different substituents at silicon, were prepared (Scheme 2) from the reactions of the respective dichlorosilanes in excess with alkynyl lithium reagents LiC≡C-R [R = Bu (**a**), ^{t}Bu (**b**), Ph (**c**)]. They had to be purified by fractional distillation and turned out to be stable towards redistribution reactions. Their ^{13}C and ^{29}Si NMR data are given in Table 1, and a representative ^{13}C NMR spectrum is shown in Fig. 1.

Reaction of alkyn-1-ylvinylsilanes 1 and 2 with 9-borabicyclo[3.3.1]nonane

It is well known that 9-BBN as a hydroborating reagent prefers vinyl over alkynyl groups[8–11] (Scheme 1). This was also found to be the case for **1** and **2**. Intermediates of type **A** could not be detected, and the reactions of the alkyn-1-ylsilanes with

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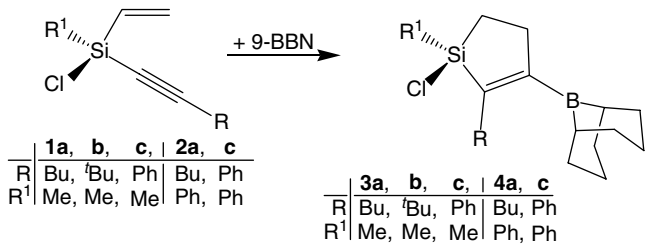
Table 1. ^{13}C and ^{29}Si NMR data[a] for starting silanes **1** and **2**

	$\delta^{13}C(Si-C\equiv)$	$\delta^{13}C(\equiv C)$	$\delta^{13}C(=C)$	$\delta^{13}C(SiC=)$	$\delta^{29}Si$
1a[b]	79.6 [112.5]	111.8 [21.3]	135.5	134.6 [84.4]	−12.8
1b[c]	77.6 [110.1]	119.5 [21.1]	135.4	134.6 [84.4]	−12.6
1c[d]	88.6 [107.2]	108.6 [21.8]	136.1	133.8 [84.8]	−11.8
2a[e]	78.3 [114.8]	113.6 [22.3]	137.1	133.1 [86.8]	−21.9
2c[f]	87.3 [112.3]	110.2 [21.7]	137.8	134.5 [85.2]	−20.9

[a] Measured in C_6D_6 at 23 °C; coupling constants $J(^{29}Si,^{13}C)$ [±0.4 Hz] are given in brackets; [b] other ^{13}C data: $\delta[J(^{29}Si,^{13}C)] = 2.6$ [67.2, Si–Me], 13.6, 19.7, 22.1, 30.4 (Bu); [c] other ^{13}C data: $\delta[J(^{29}Si,^{13}C)] = 2.7$ [67.2, Si–Me], 30.5, 28.4 (^{t}Bu); [d] other ^{13}C data: $\delta[J(^{29}Si,^{13}C)] = 2.3$ [67.5, Si–Me], 122.1, 132.4, 129.6, 128.6 (*i*, *o*, *p*, *m*, Ph); [e] other ^{13}C data: $\delta[J(^{29}Si,^{13}C)] = 133.2$ [89.1], 134.4, 128.4, 131.2 (*i*, *o*, *m*, *p*, Si–Ph), 13.7, 19.8, 22.1, 30.3 (Bu); [f] other ^{13}C data: $\delta[J(^{29}Si,^{13}C)] = 132.6$ [88.7], 121.8, 131.3, 129.8, 132.53, 132.45, 128.6, 128.6 (Si–Ph, Ph).



Scheme 3. Reaction of alkyn-1-yl(chloro)(vinyl)organosilanes with 9-BBN at ambient temperature: consecutive 1,2-hydroboration and 1,1-organoboration.

9-BBN proceeded smoothly to give the 1-chloro-1-silacyclopent-2-ene derivatives **3** and **4** in essentially quantitative yield (Scheme 3) as colorless oils or crystalline solids. Recently, we have found that the reaction of dichloro(hexyn-1-yl)vinylsilane affords the 1,1-dichloro-1-silacyclopent-2-ene **5a**[12] analogous to **3a** and **4a**.

The molecular structures of the heterocycles **3, 4** and **5a** can be deduced from the consistent set of NMR data (Table 2; see Filleux-Blanchard *et al*.[13] for ^{29}Si NMR data of related heterocycles), and a typical ^{13}C NMR spectrum is shown in Fig. 2 for compound **3a**.

Table 2. ^{11}B, ^{13}C and ^{29}Si NMR data[a] of 1-silacyclopent-2-ene derivatives **3**–**5**

	$\delta^{13}C$ (C-2)	$\delta^{13}C$ (C-3)	$\delta^{13}C$ (C-4)	$\delta^{13}C$ (C-5)	$\delta^{11}B$	$\delta^{29}Si$
3a[b]	144.9 [70.0]	170.5 (br)	34.0	12.7 [61.1]	85.8	38.2
3b[c]	148.3 [71.7]	170.1 (br)	33.0	13.1 [60.3]	85.1	37.0
3c[d]	146.4 [69.8]	174.6 (br)	33.1	13.3 [60.7]	85.2	37.4
4a[e]	143.5 [71.6]	172.7 (br)	32.3	12.9 [61.9]	86.0	27.3
4c[f]	144.7 [71.8]	176.7 (br)	33.3	13.5 [61.9]	86.2	25.8
5a[g]	144.9 [70.0]	170.5 (br)	32.0	12.7 [61.1]	85.8	38.2

[a] Measured in C_6D_6 at 23 °C, (br) indicates the ^{13}C NMR signal broadened by partially relaxed $^{11}B-^{13}C$ spin–spin coupling,[41] coupling constants belonging to $^1J(^{13}C,^{29}Si)$ and $^2J(^{13}C,^{29}Si)$ are given in square brackets; [b] other ^{13}C data: $\delta[J(^{13}C,^{29}Si)] = 2.6$ [55.2, Si–Me], 32.0 [7.1], 31.9, 23.4, 14.3 (Bu), 33.8, 33.8, 32.3 (br), 23.4 (9-BBN); [c] other ^{13}C data: $\delta[J(^{13}C,^{29}Si)] = 4.8$ [54.9, Si–Me], 33.6, 32.6 (br), 23.7 (9-BBN), 35.5, 33.9 (^{t}Bu); [d] other ^{13}C data: $\delta[J(^{13}C,^{29}Si)] = 1.9$ [56.7, Si–Me], 34.5, 34.3, 32.5 (br), 23.5 (9-BBN), 141.5, 128.6, 128.2, 126.8 (*i*, *o*, *m*, *p*, Ph); [e] other ^{13}C data: $\delta[J(^{13}C,^{29}Si)] = 33.8$, 32.5 (br), 23.5 (9-BBN), 33.9, 32.1, 23.3, 14.1 (Bu), 135.2 [74.6], 134.3, 130.5, 128.4 (*i*, *o*, *p*, *m*, Si–Ph); [f] other ^{13}C data: $\delta[J(^{13}C,^{29}Si)] = 34.5$, 34.6, 32.7 (br), 23.5 (9-BBN), 141.2 [6.6], 134.7 [64.5], 134.3, 130.7, 128.49, 128.46, 128.40, 126.9 (Ph, Si–Ph); [g] data already described.[12]

Protodeborylation of 1-chloro-3-[9-(9-borabicyclo[3.3.1]nonyl]-1-silacylopent-2-enes

Although B–C bonds invite for numerous attractive transformations,[14–16] further use of the 1-chloro-1-silacyclopent-2-enes may be hindered by the presence of the boryl group. Therefore, we have attempted to remove the boryl group by protodeborylation reactions. Treatment of the compounds **3, 4** and **5a** with an excess of acetic acid turned out to be the most useful approach (Scheme 4). The bicyclic boron-oxygen compound **11** formed in the course of these reactions has been isolated previously and characterized by X-ray structural analysis.[17]

Interestingly, the Si–Cl functions are not affected, in spite of the presence of acetic acid in excess, not even in the case of **5a** containing the $SiCl_2$ group. The retention of the 1-silacyclopent-2-ene structure follows conclusively from the NMR data sets (Table 3). Representative ^{13}C and ^{29}Si NMR spectra are shown in Fig. 3 for **7a** and **6a**, respectively. Again the 1-silacyclopent-2-ene derivatives

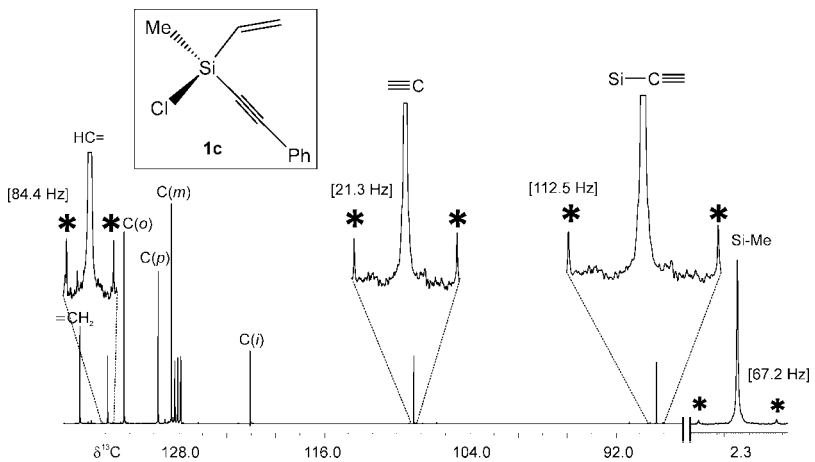


Figure 1. The 100.5 MHz proton decoupled ^{13}C NMR spectrum of starting silane **1c**. ^{29}Si satellites are marked by asterisks, corresponding to $^1J(^{29}Si,^{13}C)$ and $^2J(^{29}Si,^{13}C)$ spin–spin coupling constants.

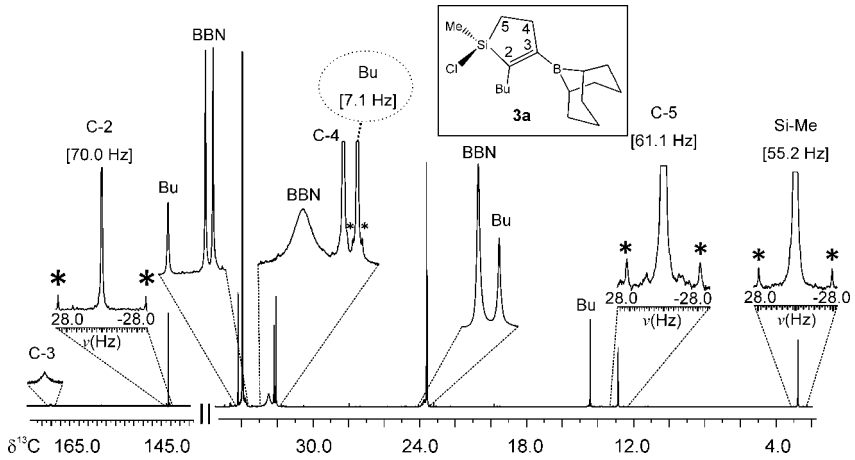
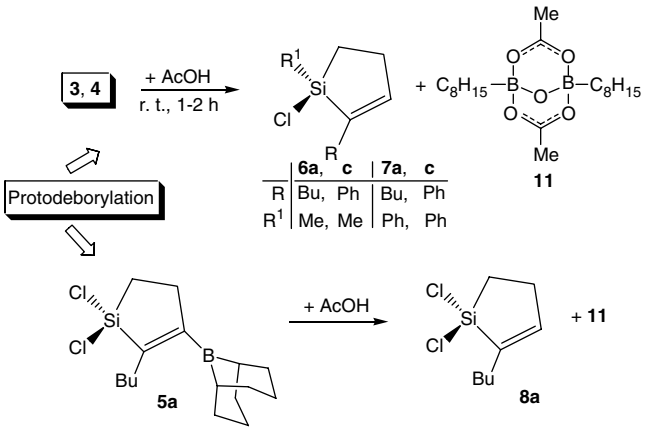


Figure 2. The 100.5 MHz ^{13}C NMR spectrum of 1-chloro-1-methyl-2-butyl-3-(9-borabicyclo[3.3.1]nonyl)-1-silacyclopent-2-ene (**3a**). ^{29}Si satellites, marked by asterisks, correspond to $^{1}J(^{29}Si,^{13}C)$ and $^{2}J(^{29}Si,^{13}C)$. Note the broad ^{13}C-3 signal, owing to partially relaxed one-bond $^{11}B-^{13}C$ coupling.[41] The $^{13}C(CH_2)$ signals of BBN in β-position relative to boron are broad as a result of restricted rotation of the BBN-group about the (C-3)-B bond.



Scheme 4. Protodeborylation of 1-silacyclopent-2-ene derivatives using an excess of acetic acid.

are colorless oils or crystalline solids, which are now stable towards dry air.

The Si–Cl functions allow for numerous reactions, as usual in the chemistry of chlorosilanes. The substitution of the Si–Cl function, not observed with acetic acid, can be readily induced by addition of dipropylamine (Scheme 5). This indicates a preferred nucleophilic substitution of the Si–Cl function by an acetate anion which is formed by acetic acid in the presence of the amine.

Table 3. ^{13}C and ^{29}Si NMR data[a] of protodeborylated 1-silacyclopent-2-ene derivatives **6–10**

	$\delta^{13}C$ (C-2)	$\delta^{13}C$ (C-3)	$\delta^{13}C$ (C-4)	$\delta^{13}C$ (C-5)	$\delta^{29}Si$
6a[b]	142.7 [70.6]	149.0 [15.5]	32.1	12.2 [59.3]	36.6
6c[c]	141.6 [70.9]	149.8 [14.7]	29.5	12.2 [60.1]	36.4
7a[d]	141.9 [71.9]	150.6 [15.7]	31.8	12.3 [60.7]	26.0
7c[e]	140.2 [73.1]	151.4 [15.2]	29.8	12.6 [60.9]	25.6
8a[f]	141.0 [85.0]	150.6 [22.4]	31.5	13.9 [69.6]	29.6
9c[g]	140.0 [73.4]	151.0 [14.1]	32.6	9.3 [62.3]	28.7
10a[h]	140.9 [74.2]	151.9 [15.2]	32.1	8.9 [62.9]	16.9

[a] Measured in C_6D_6 at 23 °C, coupling constants corresponding to $^{1}J(^{29}Si,^{13}C)$ and $^{2}J(^{29}Si,^{13}C)$ are given in square brackets; [b] other ^{13}C data: $\delta[J(^{13}C,^{29}Si)] = 2.2$ [56.4, Si–Me], 31.5 [6.1], 29.1, 22.9, 14.1 (Bu); [c] other ^{13}C data: $\delta[J(^{13}C,^{29}Si)] = 2.2$ [56.8, Si–Me], 138.5 [5.5], 129.0, 127.3, 126.8 (*i*, *o*, *p*, *m*, Ph); [d] other ^{13}C data: $\delta[J(^{13}C,^{29}Si)] = 31.5$ [5.9], 29.4, 22.8, 14.1 (Bu), 134.6 [75.1], 134.1, 130.7, 128.4 (*i*, *o*, *p*, *m*, Si–Ph); [e] other ^{13}C data: $\delta[J(^{13}C,^{29}Si)] = 137.9$ [5.6, *i*], 134.3 [77.7, *i*], 134.2, 130.9, 128.9, 128.5, 127.4, 127.1 (Si–Ph, Ph); [f] other ^{13}C data: $\delta[J(^{13}C,^{29}Si)] = 30.4$ [5.8], 27.6, 22.8, 14.1 (Bu); [g] other ^{13}C data: $\delta[J(^{13}C,^{29}Si)] = -1.6$ [60.5, Si–Me], 129.3, 128.9, 126.9, 127.0 (*i*, *o*, *m*, *p*, Ph), 22.2, 171.1 (CH_3COO); [h] other ^{13}C data: $\delta[J(^{13}C,^{29}Si)] = 32.2$ [5.5], 29.1, 22.8, 14.1 (Bu), 134.7 [79.3], 134.3, 130.4, 128.3 (*i*, *o*, *m*, *p*, Si–Ph), 22.2, 170.7 (CH_3COO).

X-ray structural analyses of the 1-silacyclopent-2-ene derivatives 3c and 7c

The molecular structures of the 1-silacyclopent-2-ene derivatives **3c** and **7c** are shown in Figs 4 and 5, respectively. Relevant bond lengths and angles are given in Table 4 together with data for the previously studied compound **B** (R^1 = Ph, R = ^{t}Bu).[8] Intermolecular interactions appear to be negligible for both **3c** and **7c**. The five-membered ring (Si1-C1-4) of **3c** shows considerable mean deviation of 83.0 pm from the mean plane. The phenyl group (C5–C10) is twisted by 30° and the CBC plane of 9-BBN is oriented by 122.2° against the mean plane of the five-membered ring. The geometry around the boron atom is trigonal planar within the experimental error, and additional interactions involving the boron atom were not observed. The geometry around the silicon atom is distorted tetrahedral with an expectedly small endocyclic angle ∠ C1–Si1–C4 = 94.9°. The slight elongations (when compared with **7c**) of the C1–C2 bond (135.7 pm) and C2–C3 bond (153.1 pm) may be due to hyperconjugation where the empty boron p_z orbital and C–Cσ bonds are involved.[18–20] All other bond lengths and angles are within expected range.[8–10]

In contrast to compound **3c**, all atoms of the five-membered ring (Si2–C1–4) of **7c** are almost in the same plane with slight mean deviation of 9.8 pm. Similar to **3c**, the molecule of **7c** has an expectedly small endocyclic C–Si–C angle (94.6°), and the other endocyclic angles are within the expected range if compared with the molecular structure of **3c** and two other analogous boryl-substituted compounds.[8,9]

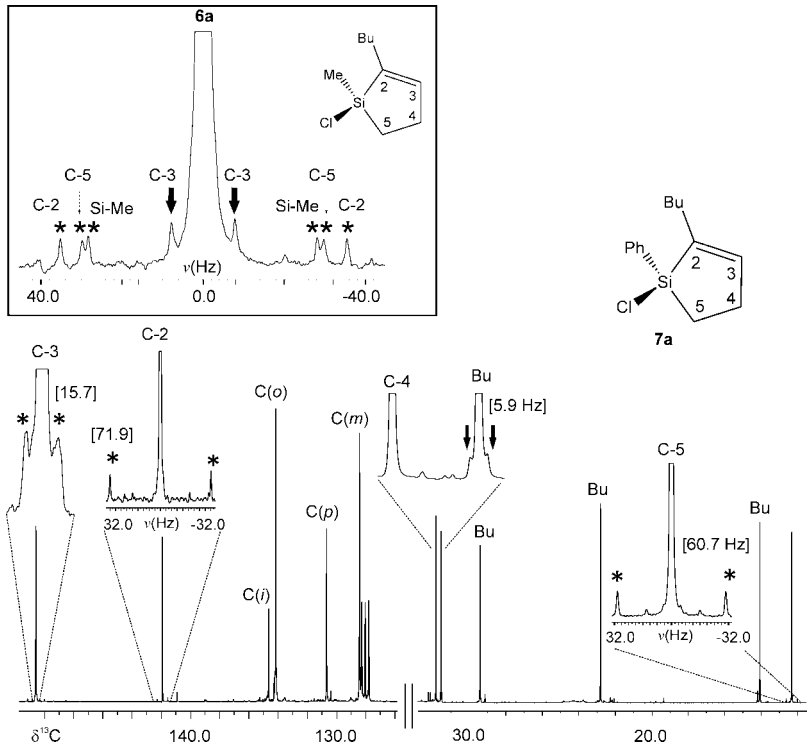
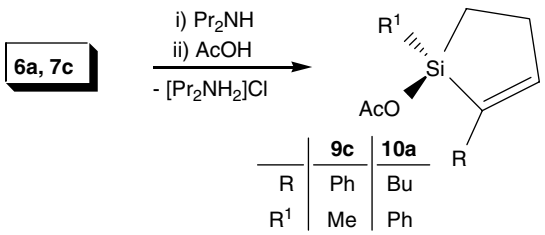


Figure 3. The 100.5 MHz ^{13}C NMR spectrum (measured as C_6D_6 solution) of the protodeborylated compound **7a**. In expansions ^{29}Si satellite signals are marked by asterisks, corresponding to $^{n}J(^{29}Si,^{13}C)$, $n = 1$ or 2 spin–spin coupling. Upper insert shows 59.6 MHz ^{29}Si NMR spectrum of **6a**; respective $J(^{29}Si,^{13}C)$ coupling satellites are marked in the same way as for **7a** except that $^{2}J(^{29}Si,^{13}C)$ are marked by arrows.



Scheme 5. Syntheses of 1-acetoxy-1-silacyclopent-2-ene derivatives.

DFT calculations

The geometries of **6c, 7c** and **8a** were optimized by DFT calculations (B3LYP[21–23]) at the 6-311+G(d,p)[24,25] level of theory. The calculated molecular gas-phase structure of **7c** corresponds closely to the experimental one of **7c** in the solid state. The optimized geometries were used to calculate the NMR parameters such as chemical shifts[26] and coupling constants.[27,28] In this context, the coupling constants $^{1}J(^{29}Si,^{13}C)$ and $^{2}J(^{29}Si,^{13}C)$[29,30] were of particular interest. The data for **6c, 7c** and **8a** are compared in Table 5. Typically for this level of theory, the calculated one-bond coupling constants are smaller[29] (10–15%) than the experimental values. This is also true for the $^{2}J[^{29}Si,^{13}C(R)]$ (R = Bu, Ph), which possesses a negative sign (reduced coupling constants $^{2}K > 0$), as expected,[29] for an intervening sp^2-hybridized carbon atom. However, the calculated values for $^{2}J[^{29}Si,^{13}C(3)]$ are somewhat greater than the experimental values. In the five-membered ring, this coupling constant represents the sum of contribution across two and three bonds, which may be of opposite signs, and both are expected to be sensitive to small structural changes. Given these problems, the agreement is reasonably satisfying.

Conclusions

The consecutive 1,2-hydroboration and intramolecular 1,1-organoboration of alkyn-1-yl(vinyl)silanes work successfully independent of other substituents on silicon to give 1-silacyclopent-2-ene derivatives in high yield. The protodeborylation with acetic acid is of particular interest here, since it leaves the Si–Cl functions untouched. The latter invite numerous further transformations. The calculation of coupling constants $^{n}J(^{29}Si,^{13}C)$ reproduces the experimental data reasonably well, and can become a valuable tool in organosilicon chemistry.

Experimental

Starting materials, measurements and calculations

The preparations and all handling of samples were carried out under an inert atmosphere (Ar), and carefully oven-dried glassware and dry solvents were used throughout. BuLi in hexane (1.6 M), 9-borabicyclo[3.3.1]nonane, 9-BBN, methyldi(chloro)(vinyl)silane, phenyldi(chloro)(vinyl)silane, 1-hexyne, 3,3-dimethyl-1-butyne,

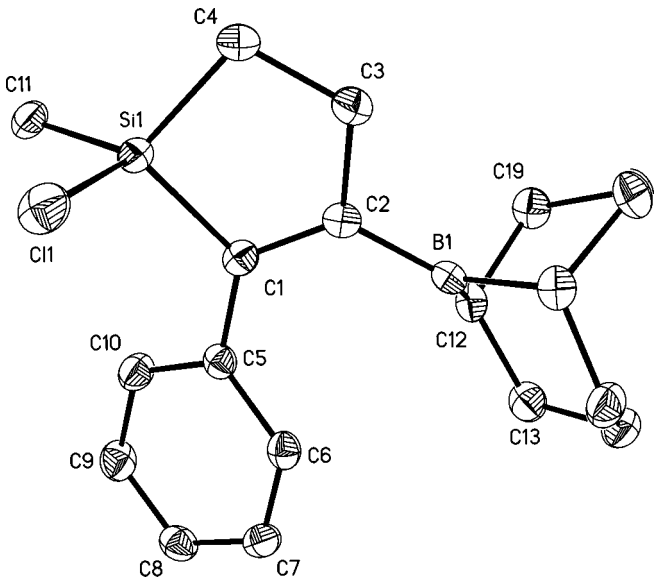


Figure 4. Molecular structure of 1-chloro-1-methyl-2-phenyl-3-(9-borabicyclo[3.3.1]-nonyl)-1-silacyclopent-2-ene, **3c**, ORTEP plot (drawn on 50% probability, hydrogen atoms are omitted for clarity).

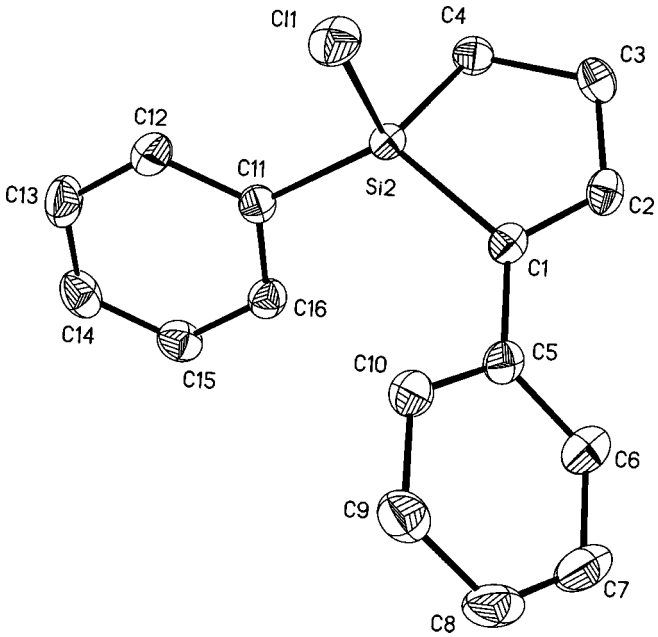


Figure 5. Molecular structure of 1-chloro-1,2-diphenyl-1-silacyclopent-2-ene, **7c** (ORTEP plot, 50% probability level; hydrogen atoms are omitted for clarity).

phenylethynyl, dipropylamine and glacial acetic acid were commercial products and were used without further purification. The alkyn-1-yl(chloro)(vinyl)silanes **1** and **2** were prepared by adapting literature procedures.[31–33] NMR measurements in C_6D_6 (concentration *ca* 10–15%, v/v) with samples in 5 mm tubes at 23 ± 1 °C: Varian Inova 300 and 400 MHz spectrometer for ^{1}H, ^{11}B, ^{13}C, and ^{29}Si NMR; chemical shifts are given with respect to Me_4Si [$\delta^{1}H$ (C_6D_5H) = 7.15; $\delta^{13}C$ (C_6D_6) = 128.0; $\delta^{29}Si$ = 0 for $\Xi(^{29}Si)$ = 19.867184 MHz]; external BF_3-OEt_2 [$\delta^{11}B$ = 0 for $\Xi(^{11}B)$ = 32.083971 MHz]. Chemical shifts $\delta^{1}H$ are given to ±0.04 ppm, $\delta^{13}C$ and $\delta^{29}Si$ to ±0.1 ppm, and $\delta^{11}B$ to ±0.5 ppm. ^{29}Si NMR spectra were measured by using the refocused INEPT pulse sequence,[34,35] based on $^{2}J[^{29}Si,^{1}H(=CH/CH_2)$ *ca* 12–15 Hz] and $^{3}J(^{29}Si, =C^{3}\text{-}^{1}H$, *ca* 20–25 Hz) after optimizing the refocusing delays. Mass spectra (EI, 70 eV): Finnigan MAT 8500 with direct inlet (data for ^{1}H, ^{11}B, ^{12}C, ^{35}Cl, ^{28}Si) and the melting points (uncorrected) were determined using a Büchi 510 melting point apparatus. MO calculations were carried out using the Gaussian 03 (Revision B02) program package[36] by optimizing geometries at the B3LYP/6-311+G(d,p) level of theory,[21–25] and the calculations of NMR parameters such as chemical shifts and coupling constants were performed at the same level.

Synthesis of the alkyn-1-yl(chloro)vinylsilanes 1a–c and 2a,c

A suspension of LiC≡C–Bu (19.5 mmol) was prepared in hexane (60 ml) and cooled to −78 °C. Then methyldi(chloro)(vinyl)silane (24 ml, 59 mmol, in three fold excess) was added slowly with constant stirring. The reaction mixture was warmed to room temperature and kept stirring for 3–4 h. Insoluble materials were filtered off and all volatiles were removed in a vacuum. The colorless oily residue was identified as a mixture of $Me(Cl)Si(HC{=}CH_2)C{\equiv}C{-}Bu$, **1a** and $MeSi(HC{=}CH_2)(C{\equiv}C{-}R)_2$. Pure **1a** yield 74%, was obtained by fractional distillation. Other silanes (**1b,c** and **2a,c**) were obtained following the identical procedure. **1a**. B.p. = 38–39 °C/0.1 Torr; ^{1}H NMR (400 MHz): δ = 0.5 [s, 3H, $^{2}J(^{29}Si,^{1}H)$ = 7.5 Hz, Si–Me], 0.7, 1.2, 1.9 (t, m, t, 9H, Bu), 5.8 [dd, 1H, $J(^{1}H,^{1}H)$ = 13.5, 4.1 Hz, $H_2C{=}$], 5.9 [dd, 1H, $J(^{1}H,^{1}H)$ = 20.2, 4.1 Hz, $H_2C{=}$], 6.1 [dd, 1H, $J(^{1}H,^{1}H)$ = 13.5, 20.2 Hz, =CH]; **1b**. B.p. = 39–41 °C/1.5 × 10^{-2} Torr; ^{1}H NMR (400 MHz): δ = 0.4 [s, 3H, $^{2}J(^{29}Si,^{1}H)$ = 7.4 Hz, Si–Me], 1.1 (s, 9H, ^{t}Bu), 5.4 [dd, 1H, $J(^{1}H,^{1}H)$ = 13.4, 4.3 Hz, $=CH_2$], 5.5 [dd, 1H, $J(^{1}H,^{1}H)$ = 20.0, 4.1 Hz, $=CH_2$], 5.6 [dd, 1H, $J(^{1}H,^{1}H)$ = 13.5, 20.1 Hz, Si–CH]; **1c**. B.p. = 55–58 °C/9 × 10^{-2} Torr; ^{1}H NMR (400 MHz): δ = 0.5 [s, 3H, $^{2}J(^{29}Si,^{1}H)$ = 7.6 Hz, Si–Me], 5.9 [dd, 1H, $J(^{1}H,^{1}H)$ = 13.4, 3.9 Hz, $=CH_2$], 6.0 [dd, 1H, $J(^{1}H,^{1}H)$ = 20.3, 4.1 Hz, $=CH_2$], 6.1[dd, 1H, $J(^{1}H,^{1}H)$ = 13.4, 20.3 Hz, HC=], 6.9, 7.3 (m, m, 5H, Ph); **2a**. B.p. = 115–120 °C/2.4 × 10^{-2} Torr; ^{1}H NMR (400 MHz): δ = 0.6, 1.2, 1.9 (t, m, t, 9H, Bu), 5.9 [dd, 1H, $J(^{1}H,^{1}H)$ = 13.7, 4.0 Hz, $=CH_2$], 6.0 [dd, 1H, $J(^{1}H,^{1}H)$ = 19.9, 4.0 Hz, $=CH_2$], 6.2 [dd, 1H, $J(^{1}H,^{1}H)$ = 13.4, 19.9 Hz, =CH], 7.1, 7.7 (m, m, 5H, Si–Ph); **2c**. B.p. = 122–125 °C/2.8 × 10^{-2} Torr; ^{1}H NMR (400 MHz): δ = 6.0 [dd, 1H, $J(^{1}H,^{1}H)$ = 13.5, 4.0 Hz, $=CH_2$], 6.2 [dd, 1H, $J(^{1}H,^{1}H)$ = 20.1, 4.1 Hz, $=CH_2$], 6.3 [dd, 1H, $J(^{1}H,^{1}H)$ = 13.4, 20.1 Hz, HC=], 6.9, 7.2, 7.3, 7.8 (m, m, m, m, 10H, Si–Ph, Ph).

Reactions of silanes 1a–c and 2a, c with 9-borabicyclo[3.3.1] nonane, 9-BBN

To a solution of silane **1a** (0.92 g; 4.96 mmol) in THF (10 ml) an equimolar amount of 9-BBN (0.62 g) was added in one portion. The reaction mixture was stirred at room temperature. After 2 h all readily volatile materials were removed under reduced pressure. The oily liquid left was identified as pure 1-silacyclopent-2-ene **3a** (NMR data in Table 2; see also Fig. 2). The same experimental procedure was followed for the synthesis of 1-silacyclopent-2-ene derivatives **3b, c** and **4a, c**. The yield was >95% (^{1}H NMR spectra) in all cases, and they were used in further reactions without purification. Compound **3c** was dissolved in pentane and kept undisturbed at room temperature. After several days, colorless crystals were growing. They were separated from the mother liquor and a single crystal of suitable dimensions was studied by

Table 4. Selected bond lengths (pm) and bond angles (deg) of 1-silacyclopent-2-ene derivatives **3c, 7c** and **B** for comparison

7c [$C_{16}H_{15}ClSi$]		**3c** [$C_{19}H_{26}BClSi$]		**B** [$C_{28}H_{37}BSi$][8]	
C1–C2	133.8(2)	C1–C2	135.7(2)	C3–C4	135.0(2)
C1–Si2	185.1(14)	C1–Si1	185.53(15)	C4–Si1	187.8(2)
C2–C3	150.3(2)	C2–C3	153.1(2)	C2–C3	153.1(2)
–	–	C2–B1	156.2(2)	C3–B1	157.0(2)
C3–C4	154.2(2)	C3–C4	154.0(2)	C1–C2	152.9(2)
C4–Si2	185.7(15)	C4–Si1	185.2(17)	C1–Si1	186.8(2)
C11–Si2	185.4(15)	C11–Si1	186.4(17)	C9–Si1	188.0(2)
Si2–Cl1	207.6(6)	Si1–Cl1	208.4(6)	–	–
C1–C5	147.3(19)	C1–C5	147.5(2)	C4–C5	152.7(2)
C2–C1–Si2	107.0(10)	C2–C1–Si1	109.3(11)	C3–C4–Si1	110.4(11)
C1–C2–C3	120.3(13)	C1–C2–C3	116.8(13)	C2–C3–C4	116.9(13)
C2–C3–C4	109.6(12)	C2–C3–C4	111.2(13)	C1–C2–C3	112.2(14)
C3–C4–Si2	103.7(10)	C3–C4–Si1	104.4(11)	C2–C1–Si	106.2(12)
C1–Si2–C4	94.6(7)	C1–Si1–C4	94.9(7)	C1–Si1–C4	93.7(8)
C11–Si2–Cl1	105.9(5)	C11–Si1–Cl1	105.7(6)	C9–Si1–C15	108.5(8)
C2–C1–C5	124.7(13)	C2–C1–C5	123.9(14)	C3–C4–C5	123.4(13)
–	–	C1–C2–B1	126.6(14)	C4–C3–B1	128.9(14)
–	–	C3–C2–B1	116.7(13)	C2–C3–B1	114.2(13)

Table 5. Comparison of calculated[a] and experimental [in brackets] coupling constants in Hz $^1J(^{29}Si,^{13}C)$ and $^2J(^{29}Si,^{13}C)$ for the 1-silacyclopent-2-enes **6c, 7c** and **8a**

Compound	**6c**	**7c**	**8a**
$^1J(^{29}Si,^{13}C(R^1))$	−51.2 [56.8] (Me)	−66.4 [77.7] (Ph)	–
$^1J(^{29}Si,^{13}C\text{-}2)$	−63.5 [70.9]	−65.3 [73.1]	−77.5 [85.0]
$^1J(^{29}Si,^{13}C\text{-}5)$	−52.9 [59.3]	−53.4 [60.9]	−61.9 [69.6]
$^2J(^{29}Si,^{13}C\text{-}3)$	−17.3 [15.5]	−17.2 [15.2]	−26.5 [22.4]
$^2J(^{29}Si,^{13}C\text{-}4)$	−4.1 [<5]]	−4.3 [<5]	−10.2 [n.d.]
$^2J(^{29}Si,^{13}C(R))$	−6.3 [5.5] (Ph)	−6.3 [5.6] (Ph)	−6.3 [5.8] (Bu)

[a] B3LYP/6-311+G(d,p) level of theory; n.d., not determined.

X-ray diffraction. In the same way compound **4c** was crystallized. However, precise diffraction data could not be collected. **3a**: ^{1}H NMR (400 MHz): δ = 0.5 [s, 3H, $^2J(^1H,^{29}Si)$ = 7.1 Hz, Si–Me], 0.9, 1.3, 1.5, 2.4 (t, m, m, m, 9H, Bu), 1.3, 1.9 (m, 14H, 9-BBN), 0.8 [ddd, 1H, $^2J(^1H,^1H)$ = 15.6 Hz, $^3J(^1H,^1H)$ = 5.0, 9.2 Hz, C^5H_2], 1.1 [ddd, 1H, $^2J(^1H,^1H)$ = 15.6 Hz, $^3J(^1H,^1H)$ = 3.5, 9.0 Hz, C^5H_2], 2.5, 2.6 (m, m, 2H, C^4H_2); MS: *m/z* (%) = 308 (85) [M^+], 273 (5) [$M^+ - Cl$], 265 (17) [$M^+ - C_3H_7$], 251 (36) [$M^+ - Bu$], 188 (17) [$M^+ - C_8H_{13}$], 187 (12) [$M^+ - BBN$], 153 (100), 152 (63); **3b**: ^{1}H NMR (400 MHz): δ = 0.6 [s, 3H, $^2J(^1H,^{29}Si)$ = 6.7 Hz, Si–Me], 1.1 (s, 9H, ^{t}Bu), 1.6–2.0 (m, 14H, 9-BBN), 0.8 [ddd, 1H, $^2J(^1H,^1H)$ = 15.3 Hz, $^3J(^1H,^1H)$ = 5.6, 8.8 Hz, C^5H_2[, 1.0 [ddd, 1H, $^2J(^1H,^1H)$ = 15.3 Hz, $^3J(^1H,^1H)$ = 4.1, 8.4 Hz, C^5H_2], 2.4 (m, 2H, C^4H_2); **3c**: yield after crystallization 74%; M.p. = 51–52 °C; ^{1}H NMR (400 MHz): δ = −0.3 [s, 3H, $^2J(^1H,^{29}Si)$ = 7.4 Hz, Si–Me], 0.9–1.9 (m, 14H, 9-BBN), 0.8 (m, 2H, C^5H_2), 2.0 (m, 2H, C^4H_2), 6.4–7.0 (m, 5H, Ph); MS: *m/z* (%) = 328 (53) [M^+], 293 (2) [$M^+ - Cl$], 207 (10) [$M^+ - BBN$], 172 (100); **4a**: ^{1}H NMR (400 MHz): δ = 0.7, 1.4, 2.6 (t, m, m, 9H, Bu), 1.2, 1.8 (m, m, 14H, 9-BBN), 1.2 (m, 2H, C^5H_2), 2.4 (m, 2H, C^4H_2), 7.2, 7.7 (m, m, 5H, Si–Ph); **4c**: m.p. = 43–45 °C; ^{1}H NMR (400 MHz): δ = 1.3–1.8 (m, 14H, 9-BBN), 0.8, 1.3 (m, m, 2H, C^5H_2), 2.8 (m, 2H, C^4H_2), 6.9–7.1, 7.6 (m, m, 10H, Si–Ph, Ph).

Reaction of 1-silacyclopent-2-ene derivatives 3 and 4 with acetic acid

To a solution of 1-silacyclopent-2-ene, **3a** (1 g, in 10 ml of pentane) glacial acetic acid (1.5 ml, in excess) was added. The reaction mixture was stirred at room temperature for 30–40 min, and all volatile materials were removed *in vacuo*. The oily compound left was identified as the mixture of boron–oxygen bicyclic compound **11** and the desired protodeborylated 1-silacyclopent-2-ene, **6a**. Pure samples of **6a** were obtained in two different ways: (i) all volatile materials were removed under reduced pressure, the mixture of the desired silane and boron-oxygen bicyclic compound **11**, was dissolved in pentane (*ca* 5 ml), and the solution was kept overnight at −35 °C. The precipitated compound **11** was separated from **6a** (soluble in pentane). This method is limited since other protodeborylated products also precipitated under these conditions. (ii) The mixture was heated (80–100 °C for 1–2 h) under reduced pressure (*ca* 10^{-2} Torr). All of the boron–oxygen bicyclic compound sublimed and was collected along the walls of the Schlenk tube. The desired compounds (>95%) remained as oils in pure state (>98%, ^{1}H NMR spectra). The compound **7c** was dissolved in pentane (2 ml) and was kept at room temperature. After few hours crystals suitable for X-ray diffraction were growing. They were separated from the solution and single crystal of appropriate dimensions was studied. **6a**: b.p. = 68–70 °C/1.7 × 10^{-1} Torr; ^{1}H NMR (400 MHz): δ = 0.4 (s, 3H, Si–Me), 0.8, 1.3, 1.9 (t, m, m, 9H, Bu), 0.9 (m, 2H, C^5H_2), 2.1 (m, 2H, C^4H_2), 6.2 (m, 1H, C^3H); **6c**. ^{1}H NMR (400 MHz): δ = 0.4 [s, 3H, $^2J(^{29}Si,^1H)$ = 7.1 Hz, Si–Me], 0.7 [ddd, 1H, $^3J(^1H,^1H)$ = 4.9, 9.5 Hz, $^2J(^1H,^1H)$ = 15.8 Hz, C^5H_2], 1.0 [ddd, 1H, $^2J(^1H,^1H)$ = 3.1, 9.2 Hz, $^2J(^1H,^1H)$ = 15.8 Hz, C^5H_2], 2.3 [ddd, 1H,$^3J(^1H,^1H)$ = 3.0, 5.1 Hz, $^2J(^1H,^1H)$ = 9.2 Hz, C^4H_2], 2.3 [ddd, 1H, $^3J(^1H,^1H)$ = 2.9, 4.9 Hz, $^2J(^1H,^1H)$ = 9.2 Hz, C^4H_2], 6.7 [t, 1H, $^3J(^1H,^1H)$ = 3.1 Hz, $^3J(^{29}Si,^1H)$ = 17.2 Hz, C^3H], 7.0, 7.1, 7.4, 7.4 (m, m, m, m, 10H, Si–Ph, Ph); **7a**. B.p. = 84–89 °C/2.4 × 10^{-2} Torr; yield = 79%; ^{1}H NMR (400 MHz): δ = 0.7, 1.1, 1.3, 2.2 (t, m, m, t, 9H, Bu), 1.0 (m, 2H, C^5H_2), 2.3 (m, 2H, C^4H_2), 6.4 (m, 1H, C^3H), 7.1, 7.6 (m, m, 5H, Ph); **7c**. Yield after recrystallization = 52%; m.p. = 42 °C; b.p. = 130–135 °C/2.7 × 10^{-2} Torr;^{1}H NMR (400 MHz): δ = 1.1

Table 6. Crystal data and structure refinement for **3c** and **7c**

Empirical formula	$C_{19}H_{26}BClSi$ (**3c**)	$C_{16}H_{15}ClSi$ (**7c**)
Formula weight	328.75	270.82
Temperature	133(2) K	133(2)
Wavelength	0.71073 Å	0.71069 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions	$a = 9.2670\ (6)$ Å	$a = 12.9920(13)$ Å
	$b = 16.3911\ (10)$ Å	$b = 6.3007(6)$ Å
	$c = 11.7822(7)$ Å	$c = 18.0750(18)$ Å
	$\beta = 100.622\ (5)^\circ$	$\beta = 110.529(8)^\circ$
Volume	1759.01 (19) Å^3	1385.6(2) Å^3
Z	4	4
Density (calculated)	1.241 mg/m^3	1.298 mg/m^3
Absorption coefficient	0.280 mm^{-1}	0.341
$F(000)$	704	568
Crystal size	0.73 × 0.64 × 0.60 mm	1.10 × 1.01 × 0.79 mm
Theta range for data collection	2.15–25.68°	1.68–25.64°
Index ranges	$-11 \le h \le 11, -19 \le k \le 19, -14 \le l \le 14$	$-15 \le h \le 15, -7 \le k \le 7, -21 \le l \le 21$
Reflections collected	23567	17848
Independent reflections	3321 [R(int) = 0.1053]	2615 [R(int) = 0.0827]
Completeness to theta	25.68°, 99.5%	25.64°, 99.8%
Data/restraints/parameters	3321/0/199	2615/0/223
Goodness-of-fit on F^2	1.067	1.139
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0390, wR_2 = 0.1048$	$R_1 = 0.0335, wR_2 = 0.0894$
R indices (all data)	$R_1 = 0.0428, wR_2 = 0.1026$	$R_1 = 0.0362, wR_2 = 0.0909$
Largest difference peak and hole	0.505 and −0.337 e.Å^{-3}	0.379 and −0.346 e.Å^{-3}

[ddd, 1H, $^3J(^1H,^1H) = 4.7, 9.1$ Hz, $^2J(^1H,^1H) = 15.7$ Hz, C^5H_2], 1.3 [ddd, 1H, $^3J(^1H,^1H) = 3.9, 9.1$ Hz, $^2J(^1H,^1H) = 16.1$ Hz, C^5H_2], 2.4–2.5 (m, 2H, C^4H_2), 6.9–7.1, 7.4, 7.6 (m, m, m, 11H, Si–Ph, Ph, C^3H); **8a**: ^{1}H NMR (400 MHz): $\delta = 0.8, 1.2, 2.2$ (t, m, t, 9H, Bu), 1.0 (m, 2H, C^5H_2), 2.4 (m, 2H, C^4H), 6.3 (m, 1H, C^3H); **9c**: ^{1}H NMR data (400 MHz): $\delta = 0.4$ [s, 3H, $^2J(^{29}Si,^1H) = 7.0$, Si–Me], 0.8 [ddd, 1H, $^2J(^1H,^1H) = 15.9$ Hz, $^3J(^1H,^1H) = 4.4, 9.5$ Hz, C^5H_2], 1.2 [ddd, 1H, $^2J(^1H,^1H) = 15.9$ Hz, $^3J(^1H,^1H) = 3.3, 9.4$ Hz, C^5H_2], 1.7 (s, 3H, CH_3COO), 2.5–2.6 (m, 2H, C^4H_2), 6.9 [t, 1H, $^3J(^1H,^1H) = 3.1$ Hz, C^3H], 7.2, 7.5 (m, m, 5H, Ph); **10a**: ^{1}H NMR data (400 MHz): $\delta = 0.8, 1.2, 2.3$ (t, m, m, 9H, Bu), 1.0 (m, 2H, C^5H_2), 2.5 (m, 2H, C^4H_2), 1.8 (s, 3H, CH_3COO), 6.6 (m, 1H, C^3H), 7.2, 7.6 (m, m, 5H, Si– Ph).

X-ray structural analyses of 3c and 7c

The X-ray crystal structural analyses (Table 6) of **3c** and **7c** were carried out for single crystals (selected in perfluorinated oil[37] at room temperature) at 133 (2) K using a STOE IPDS II system (Mo-K_α, 71.069 pm), equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97,[38] SHELXL-97[39] and WinGX.[40] The data have been deposited at the Cambridge Crystallographic Data Centre as supplementary publications nos CCDC 707599 (**3c**) and 707600 (**7c**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, www.ccdc.cam.ac.uk/data_request/cif.

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