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Synthesis of 1-silacyclopent-2-ene derivatives using 1,2-hydroboration, 1,1-organoboration and protodeborylation

Ezzat Khan[a]*, Oleg L. Tok[b] and Bernd Wrackmeyer[b]

The reaction of di(alkyn-1-yl)vinylsilanes $R^1(H_2C{=}CH)Si(C{\equiv}C{-}R)_2$ (R^1 = Me (1), Ph (2); R = Bu (a), Ph (b), Me_2HSi (c)) at 25°C with 1 equiv. of 9-borabicyclo[3.3.1]nonane (9-BBN) affords 1-silacyclopent-2-ene derivatives (3a–c, 4a,b), bearing one Si—C≡C—R function readily available for further transformations. These compounds are formed by consecutive 1,2-hydroboration followed by intramolecular 1,1-carboboration. Treated with a further equivalent of 9-BBN in benzene they are converted at relatively high temperature (80–100°C) into 1-alkenyl-1-silacyclopent-2-ene derivatives (5a,b, 6a,b) as a result of 1,2-hydroboration of the Si—C≡C—R function. Protodeborylation of the 9-BBN-substituted 1-silacyclopent-2-ene derivatives 3–6, using acetic acid in excess, proceeds smoothly to give the novel 1-silacyclopent-2-ene (7–10). The solution-state structural assignment of all new compounds, i.e. di(alkyn-1-yl)vinylsilanes and 1-silacyclopent-2-ene derivatives, was carried out using multinuclear magnetic resonance techniques (^1H, ^{13}C, ^{11}B, ^{29}Si NMR). The gas phase structures of some examples were calculated and optimized by density functional theory methods (B3LYP/6-311+G/(d,p) level of theory), and ^{29}Si NMR parameters were calculated (chemical shifts $\delta^{29}Si$ and coupling constants $^nJ(^{29}Si,^{13}C)$).

Keywords: vinylsilanes; hydroboration; carboboration; silacyclopentenes; protodeborylation

Introduction

Alkynylsilanes and alkyn-1-yl(vinyl)silanes are readily available[1] and have widespread applications in chemistry.[2] These silanes are attractive starting materials for application of hydroboration,[3] hydroalumination,[4] hydrogalation[5] and carboboration reactions,[6] leading to numerous novel cyclic and non-cyclic silicon compounds.[7,8] Among cyclic compounds, 1-silacyclopent-2-ene derivatives are of particular importance as the selective synthesis of these compounds in high yield has been a challenging goal. Very few derivatives of 1-silacyclopentene have been reported following a number of synthetic routes.[9–12] Attempted synthesis either afforded a mixture of isomers or led to compounds other than silacyclopentene derivatives, such as siloles, silacyclobutenes, silacyclohexenes and open chain silanes.[13–16] 1,2-Hydroboration of alkynyl(vinyl)silanes followed by intramolecular rearrangement, typical of a 1,1-carboboration reaction,[6d,e] provides an easy access to 1-silacyclopent-2-ene derivatives. Using this synthetic approach, it proved possible to obtain organo-substituted (**A**) as well as chloro-substituted derivatives (**B** and **C**) with a variety of substituents in the 2-position (Scheme 1).[3a,17]

In continuation of our previous work,[8e,17a] here we report 1-silacyclopent-2-ene derivatives bearing Si-alkynyl or Si-alkenyl functions. The protodeborylation of all novel heterocycles was successfully carried out without affecting other functionalities within the molecules. Considering the presence of ^1H, ^{11}B, ^{13}C and ^{29}Si nuclei, application of multinuclear magnetic resonance techniques was indicated, collecting numerous complementary NMR data, to confirm the solution-state structural assignments.

Experimental

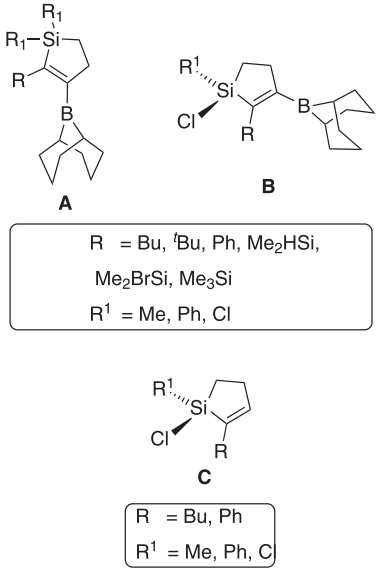
All preparative work and handling of air- and moisture-sensitive materials was carried out in an inert atmosphere (dry argon). Dichloro(methyl)vinylsilane, dichloro(phenyl)vinylsilane, 1-hexyne, ethynylbenzene, 3,3-dimethylbutyne, ^{n}BuLi in hexane (1.6 M) and 9-borabicyclo[3.3.1]nonane (9-BBN) were used as commercial products (Aldrich) without further purification. NMR spectra were recorded at 23°C using Varian Inova 300 MHz and 400 MHz spectrometers, both equipped with multinuclear units, using C_6D_6 solutions (~5–10% v/v) in 5 mm o.d. tubes. Chemical shifts are given with respect to Me_4Si [δ^1H (C_6D_5H) = 7.15, $\delta^{13}C$ (C_6D_6) = 128.0), $\delta^{29}Si$ = 0 for Me_4Si with (^{29}Si) = 19.867187 MHz], and $\delta^{11}B$ = 0 for BF_3-OEt_2 with (^{11}B) = 32.083971 MHz. ^{29}Si NMR spectra were recorded using the refocused INEPT pulse sequence with ^1H decoupling,[18] optimizing the delays based on $^{2,3}J(^{29}Si,^1H)_{vinyl}$ = 12–15 Hz and $^3J(^{29}Si{-}C\,C\,^1H)$ = 20–25 Hz.

All quantum chemical calculations were carried out using the Gaussian 09 program package.[19] Optimized geometries at the B3LYP/6-311+G(d,p) level of theory[20] were found to be minima by the absence of imaginary frequencies. NMR parameters were calculated at the same level of theory. Calculated nuclear

* *Correspondence to: Ezzat Khan, Department of Chemistry, University of Malakand, Chakdara 18550, Dir (Lower), Khyber Pakhtunkhwa, Pakistan. E-mail: ekhan@uom.edu.pk*

a *Department of Chemistry, University of Malakand, Chakdara 18550, Dir (Lower), Khyber Pakhtunkhwa, Pakistan*

b *Anorganische Chemie II, Universität Bayreuth, D-95440, Bayreuth, Germany*



Scheme 1. Heterocycles obtained via consecutive 1,2-hydroboration and 1,1-carboboration of alkynyl(vinyl)silanes (**A** and **B**). Compound **C** was obtained as a result of subsequent protodeborylation of **B** type compounds.

magnetic shielding constants $\sigma(^{29}Si)$ were converted to chemical shifts $\delta^{29}Si$ by $\delta^{29}Si$ (calcd) = $\sigma(^{29}Si, TMS) - \sigma(^{29}Si)$, with $\sigma(^{29}Si, TMS) = +340.1$ and [$\delta^{29}Si$ (TMS) = 0].

Synthesis of Alkyn-1-ylvinylsilanes 1 and 2 Used as Starting Materials

A suspension of Li—C≡C—Bu (19.5 mmol) was freshly prepared in hexane (~80 ml) and the solution was cooled to −78°C.[21] Dichloro(methyl)vinylsilane was slowly added with constant stirring (the molar ratio was kept at 2:1 with respect to lithiumalkynyl and corresponding silane). The reaction mixture was slowly warmed to room temperature and stirred for 3–4 h. After separating insoluble materials, all readily volatile materials were removed under reduced pressure (~10^{-2} torr). The colorless oily residue left was identified as Me(vinyl)Si(C≡C-Bu)$_2$, **1a**. The silane was obtained in reasonably pure form (>95% from NMR data), and Me(vinyl)(Cl)Si(C≡C—Bu) was obtained as a side product in the reaction mixture. A pure sample (>99%) of **1a** was obtained by fractional distillation.[17a] An identical work-up procedure was followed for the syntheses of **1b**,**c** and **2a**,**b**, and the same purity in case of all derivatives was achieved.

1a:, ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, $^2J(^{29}Si,^1H)$ = 7.5 Hz, Si—Me), 2.0, 1.2, 0.7 (t, m, t, 18H, $J(^1H,^1H)$ = 7.3, 6.9, 2 × Bu), 6.0 (dd, 1H, $J(^1H,^1H)$ = 4.5, 13.4 Hz, CH_2), 6.1 (dd, 1H, $J(^1H,^1H)$ = 4.5, 20.0 Hz, CH_2), 6.2 (dd, 1H, $J(^1H,^1H)$ = 13.4, 20.0 Hz, Si—CH); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 109.4 [20.0, R—C≡], 80.4 [103.4, Si—C≡], 134.0 (C), 135.4 [79.4, Si—C], 0.03 [63.3, Si—Me], 30.7, 22.1, 19.8, 13.7 (Bu); ^{29}Si NMR data: δ = −48.4.;

1b:, ^{1}H NMR (400 MHz): δ = 0.5 (s, 3H, $^2J(^{29}Si,^1H)$ = 7.6 Hz, Si—Me), 6.0 (dd, $J(^1H,^1H)$ = 4.6, 13.2 Hz, CH_2), 6.2 (dd, 1H, $J(^1H,^1H)$ = 4.6, 20.1 Hz, CH_2), 6.3 (dd, 1H, $J(^1H,^1H)$ = 13.2, 20.1 Hz, Si—CH), 6.9–7.4 (m, 10H, 2 × Ph); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 107.7 [19.6, R—C≡], 89.4 [101.2, Si—C≡], 135.4 (C), 134.0 [80.4, Si—C], 0.5 [63.9, Si—Me], 123.0 [2.1], 132.4, 128.5, 129.2 (i, o, m, p, Ph); ^{29}Si NMR: δ = −46.2.;

1c:, ^{1}H NMR (400 MHz): δ = 0.01 (d, 12H, $^2J(^{29}Si,^1H)$ = 7.6 Hz, $^2J(^1H,^1H)$ = 3.9 Hz, 2 × Me_2Si), 0.30 (s, 3H, $^2J(^{29}Si,^1H)$ = 7.6 Hz, Si—Me), 4.2 (sep., 2H, $^1J(^{29}Si,^1H)$ = 203.5 Hz, $^3J(^1H,^1H)$ = 3.9 Hz, 2 × SiH), 5.9 (m, 1H, CH), 6.1 (m, 2H, CH_2); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 114.3 [77.7, 15.1, R—C≡],110.2 [92.8, 12.6, Si—C≡],136.1 (C), 133.6 [79.9, Si—C]; −2.9 [56.1, Si—Me_2], −0.4 [63.4, Si—Me], ^{29}Si NMR: δ = −49.3, -38.3 ($^2J(^{29}Si,^{29}Si)$ = 1.5 Hz, Me_2HSi).;

2a:, ^{1}H NMR (400 MHz): δ = 0.6, 1.2, 1.9 (t, m, t, 18H, $J(^1H,^1H)$ = 7.2, 6.8, 2 × Bu), 6.0 (dd, 1H, $J(^1H,^1H)$ = 4.6, 13.2 Hz, CH_2), 6.1 (dd, 1H, $J(^1H,^1H)$ = 4.6, 20.1 Hz, CH_2), 6.2 (dd, 1H, $J(^1H,^1H)$ = 13.2, 20.1 Hz, HC), 7.1, 7.9 (m, m, 5H, Si—Ph); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 111.3 [20.2, R—C≡], 79.1 [107.2, Si—C≡], 135.5 (C), 134.3 [80.4, Si—C], 30.6, 22.1, 19.9, 13.7 (Bu), 137.1, 134.9, 128.3, 130.2 (i, o, m, p, Si—Ph); ^{29}Si NMR: δ = −51.8.;

2b:, ^{1}H NMR (400 MHz): δ = 6.2 (m, 2H, $J(^1H,^1H)$ = 8.8 Hz, CH_2), 6.0 (m, 1H, $J(^1H,^1H)$ = 8.8 Hz, HC), 6.8–6.9, 7.3 (m, m, 15H, Si—Ph, 2 × Ph); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 109.1 [20.1, R—C≡], 88.0 [105.3, Si—C≡], 136.9 (C), 135.1 [81.0, Si—C], 132.9 [84.1, *i*], 122.6 (*i*, ≡C—Ph), 132.7, 132.4, 130.7, 129.4, 128.6, 128.6 (aromatic carbons without assignment); ^{29}Si NMR: δ = −50.0.

Hydroboration of 1a–c and 2a,b Using 1 and 2 Equiv. of 9-BBN as Hydroborating Reagent. Syntheses of 1-Silacyclopent-2-ene Derivatives 3–6

Pure silane **2a** (0.57 g; 2.47 mmol) was dissolved in THF (10 ml) and 9-BBN (0.32 g; 2.47 mmol) was added as a solid in one portion. The reaction mixture was stirred at 25°C; after 30 min all volatile materials were removed under reduced pressure, and the colorless oily liquid left was identified as **3a**. The same experimental procedure was followed for the preparation of **3b**,**c** and **4a**,**b**. The products obtained were reasonably pure (>95 %,) and were studied by NMR spectroscopy. The oily compound **3a** was dissolved in C_6D_6 and one further equivalent of 9-BBN (2.47 mmol) was added. The reaction mixture was heated (80–100°C) for 40 min. The progress of the reaction was constantly monitored by ^{11}B NMR, and heating was stopped when all 9-BBN was consumed. The reaction solution showed quantitative formation of the 1-silacyclopent-2-ene derivative **5a** (NMR data). Other 1-silacyclopent-2-ene derivatives **5b** and **6a**,**b** were prepared in the same way as described for **5a**. When the corresponding silane was mixed with 2 equiv. of 9-BBN the same products were obtained. All derivatives obtained were colorless, oxygen- and moisture-sensitive oily liquids.

3a:, ^{1}H NMR (400 MHz): δ = 0.4 (s, 3H, $^2J(^{29}Si,^1H)$ = 7.0 Hz, Si—Me), 0.8, 0.9, 1.3, 2.1 (t, t, m, t, 18H, $J(^1H,^1H)$ = 7.2, 7.1, 6.9, 2 × Bu), 1.2–2.0 (m, 14H, 9-BBN), 0.8 (ddd, 1H, $J(^1H,^1H)$ = 14.9, 4.6, 9.0 Hz, C^5H_2), 1.2 (ddd, 1H, $J(^1H,^1H)$ = 14.9, 4.6, 9.0 Hz, C^5H_2), 2.5, 2.7 (m, m, 2H, C^4H_2); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 148.0 [67.5, C-2], 167.7^{br} (C-3), 34.2 (C-4), 11.1 [58.6, C-5], −0.4 [54.3, Si—Me], 32.8 [6.4], 33.6, 31.0, 22.2, 20.0, 14.4, 13.7 (2 × Bu), 33.8, 32.3^{br}, 23.6 (BBN), 109.5 [15.9, ≡C], 83.4 [84.7, Si—C≡]; ^{11}B NMR: δ = 85.6; ^{29}Si NMR: δ = −6.0.;

3b:, ^{1}H NMR (400 MHz): δ = 0.3 (s, 3H, $^2J(^{29}Si,^1H)$ = 7.1 Hz, Si—Me), 1.2–1.6 (m, 14H, 9-BBN), 0.9 (ddd, 1H, $J(^1H,^1H)$ = 15.0, 5.4, 8.9, C^5H_2), 1.3 (m, 1H, C^5H_2), 2.7 (m, 2H, C^4H_2), 6.7–7.2 (m, 10H, 2 × Ph); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 147.7 [67.9, C-2], 172.9^{br} (C-3), 34.8 [8.1, C-4], 11.5 [58.9, C-5], −1.0 [55.8, Si—Me], 34.6, 34.3, 32.5^{br}, 23.6 (BBN), 108.1 [16.0, ≡C], 92.8 [83.1, Si—C≡], 142.9 [6.0, *i*, C^2—Ph), 123.6 (*i*, ≡C—Ph), 132.3, 128.8, 128.5, 128.5, 128.4, 126.6 (aromatic carbons without assignment); ^{11}B NMR: δ = 86.1; ^{29}Si NMR: δ = −4.1.;

3c:, ^{1}H NMR (400 MHz): δ = 0.08 (d, 3H, $J(^1H,^1H)$ = 3.9 Hz, $^2J(^{29}Si,^1H)$ = 7.5 Hz, Me_2Si), 0.1 (d, 3H, $J(^1H,^1H)$ = 3.9 Hz, $^2J(^{29}Si,^1H)$ = 7.5 Hz, Me_2Si), 0.3 (d, 3H, $J(^1H,^1H)$ = 3.6 Hz, $^2J(^{29}Si,^1H)$ = 7.0 Hz, Me_2Si); 0.4 (s, 3H, $^2J(^{29}Si,^1H)$ = 7.0 Hz, MeSi), 0.5 (d, 3H, $J(^1H,^1H)$ = 3.6 Hz, $^2J(^{29}Si,^1H)$ = 7.0

Hz, Me_2Si), 0.7 (ddd, 1H, $J(^1H,^1H) = 5.0, 8.9, 14.9$ Hz, Si—C^5H_2), 1.1 (ddd, 1H, $J(^1H,^1H) = 5.0, 9.4, 14.9$ Hz, Si—C^5H_2), 1.4–2.0 (m, 14H, BBN); 2.7 (m, 2H, C^4H_2). 4.3 (sep., 1H, $^1J(^{29}Si,^1H) = 201.3$ Hz, Si—H), 4.6 (sep., 1H, $^1J(^{29}Si,^1H) = 178.8$ Hz, Si—H···B); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 137.5 [62.2, 53.1, C-2], 192.8^{br} (C-3), 39.2 [11.3, 7.7, C-4], 10.7 [57.3, C-5], −2.6 [55.5, Me_2Si], −2.6 [55.3, Me_2Si], −1.0 [50.8, Me_2Si], −0.9 [51.5, Me_2Si], 0.7 [54.8, Me_2Si], 34.4, 34.4, 33.2^{br}, 24.1 (BBN), 115.8 [73.8, 12.7, ≡C], 113.8 [79.2, 11.5, Si—C≡]; ^{11}B NMR was not measured; ^{29}Si NMR: δ [$J(^{29}Si,^{29}Si)$] = 2.9 [10.9,1.6], −39.1 [1.6, Me_2HSi—C≡], −22.3 [10.9, Me_2HSi—C].;

4a:, ^1H NMR (400 MHz): δ = 0.7, 1.2, 2.0 (t, m, t, 9H, $J(^1H,^1H) = 7.3, 6.9$, ≡-Bu), 0.7, 1.5, 2.7 (t, m, m, $J(^1H,^1H) = 7.0$, 9H, C^2—Bu), 1.2–1.8 (m, 14H, 9-BBN), 1.0, 1.3 (m, m, 2H, C^5H_2), 2.4, 2.5 (m, m, 2H, C^4H_2), 7.2, 7.8 (m, m, 5H, Si—Ph); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 146.3 [68.9, C-2], 170.1^{br} (C-3) 34.0 (C-4), 11.5 [59.7, C-5], 34.0, 32.9, 23.4, 14.3 (C—Bu), 30.9, 22.3, 20.1, 13.7 (≡C—Bu), 33.8, 32.4^{br}, 23.6 (BBN), 81.2 [89.6, Si—C≡], 111.7 [16.7, ≡C], 136.8 [71.9], 134.9, 128.2, 129.8 (i, o, m, p, Si—Ph); ^{11}B NMR: δ = 85.1 ; ^{29}Si NMR: δ = −9.1.;

4b., ^1H NMR (400 MHz): δ = 1.2 (m, 2H, CH_2), 2.8 (m, 2H, CH_2), 1.2–1.9 (m, 14H, BBN), 6.8–7.8 (m, 15H, Si—Ph, C^5—Ph, ≡C—Ph); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 145.9 [69.6, C-2], 175.3^{br} (C-3), 35.2 (C-4), 12.1 [60.0, C-5], 34.6, 34.5, 32.6^{br}, 23.6 (BBN), 90.6 [88.6, Si—C≡], 109.8 [16.4, ≡C], 142.5 [6.1, i], 135.6 [73.7, i], 123.2 (i), 135.0, 132.4, 130.2, 129.1, 128.6, 128.5, 128.4, 128.4, 126.6 (Si—Ph, 2 × Ph); ^{11}B NMR: δ = 84.5; ^{29}Si NMR: δ = −8.3.;

5a:, ^1H NMR (400 MHz): δ = 0.5 (s, 3H, $^2J(^{29}Si,^1H) = 6.5$ Hz, Si—Me), 0.9, 0.9, 1.4, 2.5 (t, t, m, m, 18H, $J(^1H,^1H) = 7.1, 7.3$, 2 × Bu), 1.6–2.0 (m, 28H, 2 × 9-BBN), 0.9 (m, 1H, C^5H_2), 1.1 (ddd, 1H, $J(^1H,^1H) = 15.0, 5.5, 8.0$ Hz, C^5H_2), 2.3, 2.8 (m, m, 2H, C^4H_2), 6.9 (t, 1H, $J(^1H,^1H) = 7.1$ Hz, C^3H); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 151.1 [60.6, C-2], 166.5^{br} (C-3), 32.2 (C-4), 12.4 [53.9, C-5], 1.5 [49.3, Si—Me], 33.81, 33.80, 33.79, 33.78, 32.3 (br), 23.6, 23.7 (2 × 9-BBN), 35.2, 34.9, 33.7, 33.4, 24.3, 23.8, 14.4, 14.3 (2 × Bu), 148.9^{br} [53.9, (B)C], 157.4 (C); ^{11}B NMR: δ = 84.4; ^{29}Si NMR: δ = 7.3.;

5b:, ^1H NMR (400 MHz): δ = 0.4 (s, 3H, $^2J(^{29}Si,^1H) = 6.4$ Hz, Si-Me), 1.5–2.1 (m, 28H, 2 × 9-BBN), 0.6 (ddd, 1H, $J(^1H,^1H) = 14.2, 5.5, 8.0$ Hz, C^5H_2), 0.8 (ddd, 1H, $J(^1H,^1H) = 14.2, 5.5, 8.0$ Hz, C^5H_2), 3.1 (m, 2H, C^4H_2), 6.5–6.9 (m, 10H, 2 × Ph), 7.6 (s, 1H, $^3J(^{29}Si,^1H) = 16.1$ Hz, C^3H); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 151.6 [61.1, C-2], 171.1^{br} (C-3), 33.8 (C-4), 13.0 [53.0, C-5], 1.0 [51.7, Si—Me], 34.8, 34.5, 34.5, 34.4, 32.4^{br}, 23.7 (2 × 9-BBN), 152.5^{br} ((B)C), 152.9 (C), 143.6 (i), 141.3 (i), 128.6, 128.3, 128.2, 128.16, 129.3 (p), 126.2 (p) (2 × Ph); ^{11}B NMR: δ = 85.3, ^{29}Si NMR: δ = 9.0.;

6a:, ^1H NMR (400 MHz): δ = 0.7, 0.8, 1.3–1.4, 2.1, 2.5 (t, t, m, m, m, 18H, $J(^1H,^1H) = 7.2, 7.3$, 2 × Bu), 1.3–1.9 (m, 28H, 2 × 9-BBN), 1.2 (m, 2H, C^5H_2), 2.8 (m, 2H, C^4H_2), 7.1–7.6 (m, 6H, Si—Ph, C^3H); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 148.6 [61.8, C-2], 169.1^{br} (C-3), 32.0 (C-4), 12.2 [53.4, C-5], 34.6, 34.4, 34.0, 33.9, 32.3^{br}, 31.5^{br}, 23.7, 23.6 (2 × 9-BBN), 36.0, 35.0, 34.1, 33.7, 23.6, 23.0, 14.2, 14.2 (2 × Bu), 146.5^{br} ((B)C), 159.9 (C), 140.5 [64.1], 134.6, 128.1, 129.0 (i, o, m, p, Si—Ph); ^{11}B NMR: δ = 85.6, ^{29}Si NMR: δ = 3.1.;

6b:, ^1H NMR (400 MHz): δ = 1.4–1.9 (m, 28H, 2 × 9-BBN), 1.3 (m, 2H, C^5H_2), 2.9 (m, 2H, C^4H_2), 7.0–7.2, 7.6, 7.6 (m, m, m, 15H, Si—Ph, 2 × Ph), 8.3 (s, 1H, $^3J(^{29}Si,^1H) = 16.9$ Hz, CH); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 149.1 [62.1, C-2], 174.6^{br} (C-3), 34.5 (C-4), 11.8 [53.9, C-5], 34.8, 34.7, 34.4, 34.3, 32.5^{br}, 32.1^{br}, 23.7, 23.7 (2 × 9-BBN), 149.4^{br} ((B)C), 155.6 (C), 144.1 [5.9. i], 140.7, 140.6, 134.8, 134.3, 129.8, 128.5, 128.5, 128.4, 128.4, 128.3, 128.1 (Si—Ph, 2 × Ph); ^{11}B NMR: δ = 85.4; ^{29}Si NMR: δ = 4.1.

Protodeborylation of 1-Silacyclopent-2-ene Derivatives 7–10

Compound **3a** (0.38 g, 1.07 mmol) was dissolved in pentane and acetic acid (approximately twofold excess) was slowly added at 25°C. The reaction afforded the desired protodeborylated silane **7a** and the oxygen–boron bicyclic compound **11**. The reaction mixture was heated at 100–120°C (oil bath temperature) under reduced pressure for 1–2 h; compound **11** sublimed and accumulated along the walls of the Schlenk tube as colorless crystals, leaving **7a** as an oily liquid in pure form (>95% from NMR data). All other reactions were performed in exactly the same way.

7a: ^1H NMR (300 MHz): δ = 0.3 (s, 3H, $^2J(^1H,^1H) = 7.3$ Hz, Si—Me), 0.7, 0.9, 1.3–1.5, 2.1, 2.3 (t, t, m, t, m, 18H, $J(^1H,^1H) = 7.2, 6.9, 6.8$, C^2Bu, ≡C—Bu), 1.0 (ddd, 1H, $J(^1H,^1H) = 15.1, 4.7, 9.0$ Hz, C^5H_2), 1.3 (m, 1H, C^5H), 2.3 (m, 2H, C^4H_2), 6.3 (m, 1H, $^3J(^{29}Si,^1H) = 14.6$ Hz, C^3H); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 143.3 [68.1, C-2], 146.7 [13.3, C-3], 32.7 [5.9, C-4], 10.4 [58.1, C-5], -0.7 [55.3, Si—Me], 32.4 [7.2], 30.3, 23.0, 14.3 (Bu), 31.0, 22.2, 20.0, 13.7 (≡C—Bu), 83.0 [86.4, Si—C≡], 109.3 [16.3, —C]; ^{29}Si NMR: δ = −8.6.

7b: ^1H NMR (400 MHz): δ = 0.6 (s, 3H, Si—Me), 0.8 (ddd, 1H, $J(^1H,^1H) = 15.3, 4.7, 9.4$, C^5H_2), 1.3 (ddd, 1H, $J(^1H,^1H) = 15.3, 4.7, 9.4$, C^5H_2), 2.4, 2.5 (m, m, 2H, C^4H_2), 6.8 (t, 1H, C^3H), 6.9, 7.2, 7.3, 7.7 (m, m, m, m, 10H, C^2Ph, ≡C—Ph); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 141.6 [69.1, C-2], 148.3 [12.7, C-3], 31.0 (C-4), 10.1 [59.1, C-6], −0.9 [56.4, Si—Me], 92.6 [84.4, Si—C≡], 108.1 [16.1, ≡C], 123.4, 132.3, 129.9, 128.5 (i, o, m, p, ≡C—Ph), 139.7 [5.6], 128.9, 127.2, 127.0 (i, o, m, p, Ph); ^{29}Si NMR: δ = −6.9.

8a: ^1H NMR (400 MHz): δ = 0.7, 0.8, 1.2, 2.1, 2.3 (t, t, m, t, m, 18H, $J(^1H,^1H) = 7.3, 7.0, 6.9$, C^2Bu, ≡C—Bu), 1.0 (m, 1H, C^5H), 1.2 (m, 1H, C^5H_2), 2.4 (m, 2H, C^4H_2), 6.4 (m, 1H, $^3J(^{29}Si,^1H) = 15.9$ Hz, C^3H), 7.2, 7.7 (m, m, 5H, Si—Ph); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 142.5 [69.4, C-2], 148.6 [13.4, C-3], 32.6 (C-4), 10.8 [58.4, C-5], 32.1 [8.7], 30.9, 30.7, 22.9, 22.2, 20.0, 14.2, 13.7 (2 × Bu), 80.8 [90.Si—C≡], 111.7 [16.2, ≡C], 136.3 [73.1], 134.9, 128.2, 129.8 (i, o, m, p, Si—Ph); ^{29}Si NMR: δ = −11.5.

8b: ^1H NMR (400 MHz): δ = 1.1, 1.3 (m, m, 2H, C^5H_2), 2.5 (m, 2H, C^4H_2), 7.0 (t, 1H, $^3J(^1H,^1H) = 3.0$ Hz, C^3H), 6.9, 7.1, 7.2, 7.4, 7.6, 7.9 (m, m, m, m, m, 15H, Si—Ph, 2 × Ph); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 140.4 [70.5, C-2], 150.0 [12.9, C-3], 31.3 (C-4), 10.8 [59.7, C-5], 90.3 [89.6, Si—C≡], 109.9 [16.7, ≡C], 139.2 [5.7, i], 135.2 [74.5, i], 123.1 (i), 134.9, 132.4, 130.0, 129.1, 128.8, 128.5, 128.5, 127.4, 127.1 (Si—Ph, 2 × Ph); ^{29}Si NMR: δ = −10.5.

9a: ^1H NMR (400 MHz): δ = 0.3 (s, 3H, Si—Me), 0.8, 0.9, 1.3, 2.1 (t, t, m, m, 18H, $J(^1H,^1H) = 7.1, 7.3$, 2 × Bu), 1.0 (m, 2H, C^5H_2), 2.4 (m, 2H, C^4H_2), 5.6 (d, 1H, $J(^1H,^1H) = 13.9$ Hz, CH), 6.3 (m, 1H, C^3H), 6.3 (dt, 1H, $J(^1H,^1H) = 7.3$ Hz, 13.8 Hz, C(Bu)H); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 144.7 [62.4, C-2], 145.6 [11.3, C-3], 32.2 (C-4), 10.8 [53.7, C-5], −0.6 [50.3, Si—Me], 33.8, 32.9, 32.5, 30.6, 23.1, 22.8, 14.2 (2 × Bu), 127.1 [64.8, Si—C], 150.8 (C); ^{29}Si NMR: δ = 2.7.

9b: ^1H NMR (300 MHz): δ = 0.3 (s, 3H, $^2J(^{29}Si,^1H) = 6.5$ Hz, Si—Me), 0.8–0.9 (m, 2H, C^5H_2), 2.4 (m, 2H, C^4H_2), 6.8 (t, 1H, $J(^1H,^1H) = 3.1$ Hz, $^3J(^{29}Si,^1H) = 13.7$ Hz, C^3H), 6.1 (d, 1H, $J(^1H,^1H) = 15.1$ Hz, CH), 7.4 (d, 1H, $J(^1H,^1H) = 15.1$ Hz, CH), 7.0–7.3, 7.4 (m, m, 10H, 2 × Ph); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 144.3 [63.1, C-2], 147.0 [11.2, C-3], 31.2 (C-4), 10.1 [54.2, C-5], −0.6 [54.0, Si—Me], 130.1 [63.6, Si—C], 148.5 (C), 140.4, 140.1, 128.8, 128.4, 128.2, 127.9, 127.0, 126.7 (2 × Ph); ^{29}Si NMR: δ = 5.1.

10a: ^1H NMR (300 MHz): δ = 0.7, 0.7, 1.0-1.3, 2.0, 2.2 (t, t, m, m, t, 18H, $J(^1H,^1H) = 7.3, 7.1, 6.8$, 2 × Bu), 0.9 (m, 2H, C^5H_2), 2.5 (m, 2H, C^4H_2), 5.9 (d, 1H, $J(^1H,^1H) = 14.0$ Hz, CH), 6.4 (m, 1H, C^3H), 6.5 (dt, 1H, $J(^1H,^1H) = 7.3, 14.0$ Hz, C(Bu)H), 7.1, 7.2, 7.5 (m, m, 5H, Si—Ph); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 143.7 [63.8, C-2], 147.1 [11.7, C-3], 30.9 (C-4), 11.1 [53.1, C-5], 34.5, 32.8, 32.2, 32.0, 23.0, 22.8, 21.7, 14.2, 14.2 (2 × Bu), 124.1 [67.5, Si—C], 152.5 (C=), 138.2 [65.5], 134.7,

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128.2, 129.4 (i, o, m, p, Si—Ph); ^{29}Si NMR: $\delta = -1.6$.

10b: ^{1}H NMR (300 MHz): δ = 1.0 (m, 2H, C^5H_2), 2.4 (m, 2H, C^4H_2), 6.3 (d, 1H, $J(^1H,^1H) = 15.4$ Hz, CH), 6.9 (t, 1H, $J(^1H,^1H) = 3.2$ Hz, C^3H), 7.5 (d, 1H, $J(^1H,^1H) = 15.4$ Hz, CH), 7.0–7.2, 7.3, 7.4, 7.7 (m, m, m, m, 15H, Si—Ph, 2 × Ph); ^{13}C NMR: δ [$J(^{29}Si,^{13}C)$] = 142.9 [64.8, C-2], 148.5 [11.3, C-3], 31.4 (C-4), 10.2 [56.8, C-5], 126.1 [66.4, Si—C], 149.8 (C), 140.0 [5.4, i], 139.5 (i), 137.8 [67.0, i], 134.9, 129.8, 128.8, 128.54, 128.52, 128.3, 128.1, 127.2, 126.8, (Si—Ph, 2 × Ph); ^{29}Si NMR: δ = 1.4.

Results and Discussion

The di(alkynyl)vinylsilane derivatives **1** and **2** were obtained by following the literature procedure.[22] These silanes are fairly stable at high temperature (up to 120°C under reduced pressure, 10^{-2} torr) and lighter fractions were removed at elevated temperature under reduced pressure.[22] The desired silanes were studied with the help of NMR spectroscopy (see Fig. 1 for a representative ^{29}Si NMR spectrum, and full set of data is summarized in the Experimental section).

Hydroboration of Silanes 1 and 2

Silanes **1** and **2** bear two functions; Si-vinyl and Si-alkynyl. These functions are readily available for hydroboration when treated with 9-BBN. It is well known that 9-BBN prefers the vinyl group over the alkynyl function.[23] Reactions between silanes **1**, **2** and 9-BBN were carried out in equimolar ratios at ambient temperature in THF (Scheme 2). The hydroborating reagent instantly gets attached to the terminal vinyl carbon (**D**), followed by intramolecular 1,1-carboboration via ultimate ring closure to afford 1-silacyclopent-2-ene derivatives **3** and **4**. No attempt has been made to isolate intermediates of type **D**. The activation of the Si—C bond, prior to final 1,1-carboboration, in **D** by the neighbored electron-deficient boron atom is indicated by a dashed line.

The proposed structure of the 1-silacyclopent-2-ene derivatives follows conclusively from NMR data. All ^{13}C nuclei in the five-membered ring show coupling with ^{29}Si, and the ^{13}C(3) NMR signals are typically broadened due to partially relaxed one-bond ^{13}C—^{11}B spin–spin coupling.[24] They could easily be identified and were found in the same range as reported for analogous heterocycles.[8e,17a] These compounds contain the Si—C≡C—R functionality, and both alkynyl ^{13}C nuclei are readily assigned. In addition to their ^{13}C chemicals shifts, these signals are

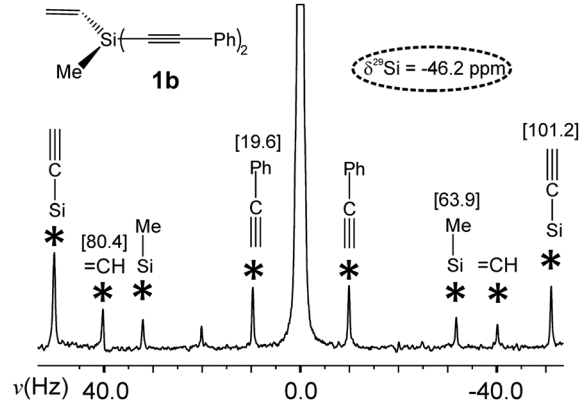
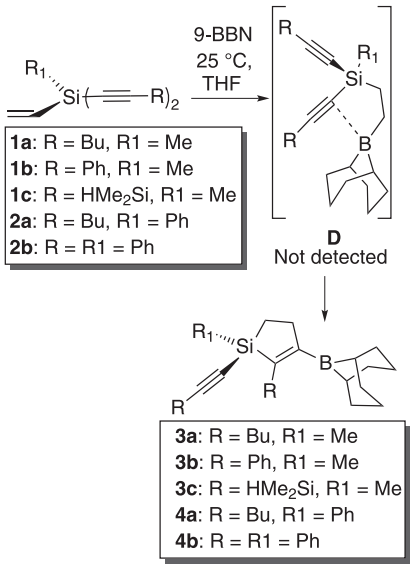


Figure 1. 59.57 MHz ^{29}Si{^{1}H} NMR spectrum of silane **1b**, showing ^{13}C satellites.

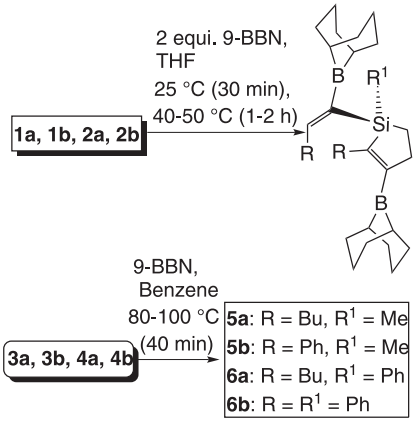


Scheme 2. Reaction of silanes **1** and **2** with one equivalent of 9-BBN resulting into the syntheses of 1-silacyclopent-2-ene derivatives.

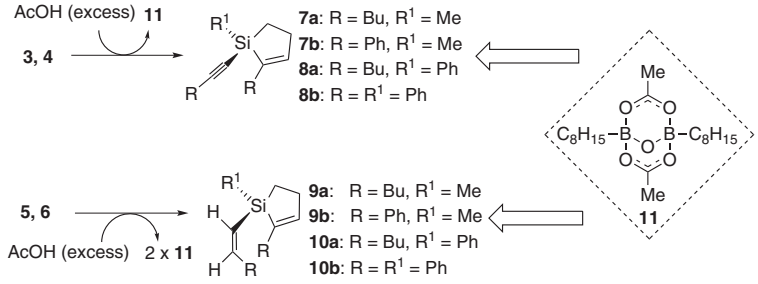
accompanied by ^{29}Si satellites for $^{1/2}J(^{29}Si,^{13}C)$. All the reactions in this series were highly selective and led to formation of the desired compounds in high purity (i.e. 90–95%). A consistent set of ^{1}H, ^{11}B, ^{13}C and ^{29}Si NMR data for 1-silacyclopent-2-ene derivatives **3** and **4** are summarized in the Experimental section.

Hydroboration of 1-Alkynyl-1-silacyclopent-2-ene Derivatives 3 and 4

Compounds obtained as a result of onefold 1,2-hydroboration of silanes **1** and **2** were characterized as 1-alkynyl-1-silacyclopent-2-ene derivatives. These compounds bear an Si-alkynyl function and invite further chemical study. They were treated with 1 equiv. of 9-BBN in benzene at a relatively high temperature (80–100°C) for 20 min and were completely converted into the 1-alkenyl-1-silacyclopent-2-ene derivatives **5** and **6** (Scheme 3). The same series of compounds were obtained as a result of twofold hydroboration of the starting precursors **1** and **2**. The first 1,2-hydroboration reaction selectively takes place at the vinyl group followed by intramolecular 1,1-vinylboration to afford 1-alkynyl-1-silacyclopent-2-ene derivatives **3** and **4**. The second hydroboration requires relatively harsh reaction conditions and



Scheme 3. Syntheses of silanes **5** and **6** by two possible routes.



Scheme 4. Protodeborylation of 1-silacyclopent-2-ene derivatives **3–6** (C_8H_{15} = cyclooctyl).

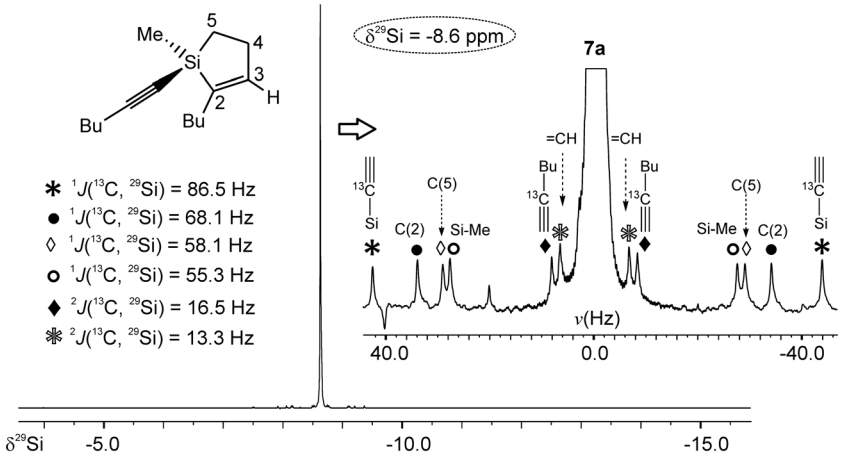


Figure 2. 59.57 MHz $^{29}Si\{^1H\}$ NMR spectrum of 1-methyl-1-(1-hexynyl)-2-butyl-1-silacyclopent-2-ene **7a** (in C_6D_6) ^{13}C satellites marked by different signs correspond to $^1J(^{29}Si,^{13}C)$ and $^2J(^{29}Si,^{13}C)$ spin–spin coupling.

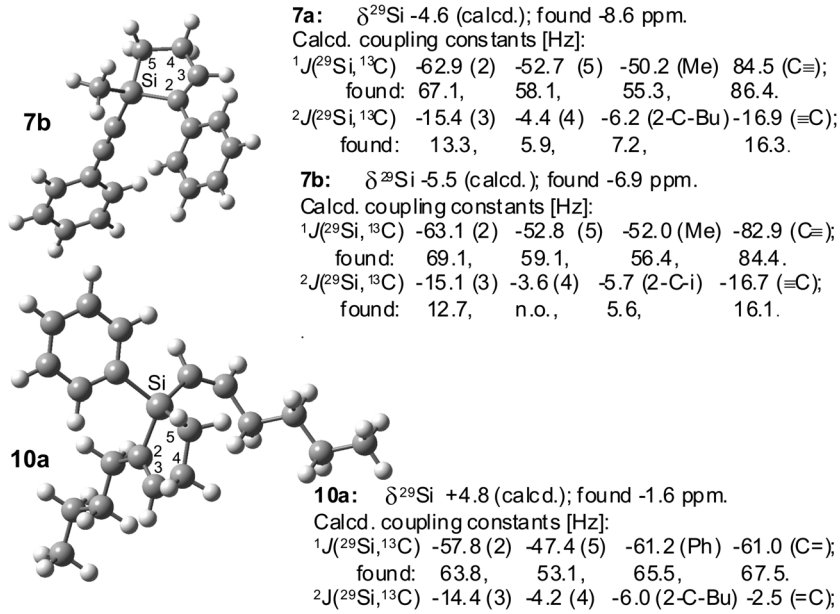


Figure 3. Calculated chemical shifts $\delta^{29}Si$ and optimized [B3LYP/6-311+G(d,p)] gas phase geometries of **7b** and **10a**; selected bond lengths (pm) and bond angles (°). **7b**: C2—Si 188.6, C5—Si 189.8, C(Me)—Si 188.1, ≡C—Si 184.1, C2—C3 134.7, C3—C4 151.1, C4—C5 155.4, C≡C 121.6, C2—Si—C5 94.0, ≡C—Si—C(Me) 107.9. **10a**: C2—Si 188.6, C5—Si 189.8, C(Ph) —Si 189.7, C—Si 188.5, C2—C3 134.3, C3—C4 151.4, C4—C5 155.6, CH CH 134.2; C2—Si—C5 93.90, CH—Si—C(Ph) 106.9.

the mixture was warmed to 40–50°C for 1-2 h. The products were obtained with the expected geometry with respect to =C-H and =C-BBN as reported for 1,2-hydroboration of other alkynylsilanes.[25] Again the proposed structures of these derivatives are supported by NMR spectroscopy, and all the important data are summarized in the Experimental section.

Protodeborylation Reactions

Typical of triorganoboranes, all 1-silycy clopent-2-enes **3–6** are sensitive to air. Clearly, the **B–C** functions invite numerous transformations.[26] Previously we have successfully substituted this function with hydrogen and have explored the boron–oxygen compound.[27] The same attempt for the removal of boryl groups by protodeborylation reaction was made for the 1-silacyclopent-2-ene derivatives **3–6**. Treatment of the compounds **3–6** with copious amounts of acetic acid turned out to be the successful approach (Scheme 4). The NMR data of bicyclic boron–oxygen compound **11** formed during the course of these reactions is in full agreement with the literature.[27] All other functions of the 1-silacyclopent-2-enes remained unaffected. The protodeborylation of all boron-containing 1-silacyclopent-2-ene derivatives afforded the desired products in essentially quantitative yield (>90%). The structural assignment of the 1-silacyclopent-2-ene derivatives **7–10** was confirmed by consistent NMR data sets (Experimental section). A representative ^{29}Si NMR for 1-silacyclopent-2-ene derivative **7a** is shown in Fig. 2.

The gas phase geometries of the 1-silacyclopent-2-ene derivatives **7a**,**b** and **10a** were optimized by calculations at the B3LYP/6-311+G(d,p) level of theory,[20] and ^{29}Si nuclear shielding[28] and coupling constants $^nJ(^{29}Si,^{13}C)$ ($n = 1$, 2)[29] were calculated at the same level (Fig. 3). The calculated data are close to those experimentally observed.[30] Apparently, the sign of $^2J(^{29}Si,^{13}C)$ is negative (reduced coupling constants $^2K(^{29}Si,^{13}C) > 0$), as expected for the sum of two coupling pathways in the five-membered rings. In **10a**, the small magnitude of $^2J(^{29}SiC\ ^{13}C)$ for the exocyclic alkenyl group is reproduced by the calculations. Frequently this coupling constant is too small for experimental observation, and it may be of either sign.[23]

Conclusions

The stereo- and regioselective 1,2-hydroboration of the vinyl group in di(alkynyl)vinylsilanes proceeds at ambient temperature, and is followed by intramolecular 1,1-vinylboration to afford selectively 1-alkynyl-1-silacyclopent-2-ene derivatives in high yield. Further 1,2-hydroboration of the alkynyl function gives 1-alkenyl-1-silacyclopent-2-ene derivatives. During the course of these reactions no side products or isomers were detected. The protodeborylation with an excess amount of acetic acid is of particular interest, since it cleaves solely the B—C bond(s), leaving all other bonds unaffected. The NMR data contain useful information on ^{29}Si—^{13}C coupling constants, confirmed by density functional theory calculations, and are diagnostic in the structural elucidation of such types of organosilicon compounds.

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References

[1] a) B. Wrackmeyer, E. Khan, A. Badshah, E. Molla, P. Thoma, O. L. Tok, W. Milius, R. Kempe, J. Senker, *Z. Naturforsch.* **2010**, *65b*, 119–127. b) B. Wrackmeyer, E. Khan, S. Bayer, O. L. Tok, E. V. Klimkina, W. Milius, R. Kempe, *Z. Naturforsch.* **2010**, *65b*, 725–744.

[2] a) H. Werner, M. Baum, D. Schneider, B. Windmuller, *Organometallics* **1994**, *13*, 1089–1097.b) D. Röttger, G. Erker, R. Fröhlich, S. Kotila, *Eur. J. Inorg. Chem.* **1996**, *129*, 5–9.c) H. Lang, U. Lay, M. Weinmann, *J. Organomet. Chem.* **1992**, *436*, 265–276.d) H. Lang, M. Weinmann, L. Zsolnai, *J. Organomet. Chem.* **1996**, *522*, 277–289.e) T. Kuhnen, M. Stradiotto, R. Ruffolo, D. Ulbrich, M. J. McGlinchey, M. A. Brook, *Organometallics* **1997**, *16*, 5048–5057. f) R. J. P. Corriu, W. E. Douglas, Z.-X. Yang, *J. Polym. Sci. Part C* **1990**, *28*, 431–437.

[3] a) B. Wrackmeyer, O. L. Tok, R. Kempe, *Inorg. Chim. Acta* **2005**, *358*, 4183–4190.b) B. Wrackmeyer, O. L. Tok, E. V. Klimkina, W. Milius, *Eur. J. Inorg. Chem.* **2010**, 2276–2282.

[4] a) W. Uhl, D. Heller, J. Kösters, E.-U. Würthwein, N. Ghavtadze, *Eur. J. Inorg. Chem.* **2012**, 1359–1368.b) W. Uhl, D. Heller, M. Rohling, J. Kösters, *Inorg. Chim. Acta* **2011**, *374*, 359–365.c)W. Uhl, D. Heller, *Z. Anorg. Allg. Chem.* **2010**, *636*, 581–588.

[5] a) W. Uhl, M. Claesener, S. Haddadpour, B. Jasper, I. Tiesmeyer, S. Zemke, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2889–2896.b) W. Uhl, H. R. Bock, F. Breher, M. Claesener, S. Haddadpour, B. Jasper, A. Hepp, *Organometallics* **2007**, *26*, 2363–2369.c) W. Uhl, J. Bohnemann, D. Heller, A. Hepp, M. Layh, *Z. Anorg. Allg. Chem.* **2012**, *638*, 68–75.

[6] a) B. Wrackmeyer, G. Kehr, J. Süβ, *Chem. Ber.* **1993**, *126*, 2221–2226.b) G. Dierker, J. Ugolotti, G. Kehr, R. Fröhlich, G. Erker, *Adv. Synth. Cat.* **2009**, *351*, 1080–1088.c) J. Ugolotti, G. Kehr, R. Fröhlich, G. Erker, *Chem. Commun.* **2010**, *46*, 3016–3018;d) B. Wrackmeyer, *Coord. Chem. Rev.* **2005**, *145*, 125–156.e) B. Wrackmeyer, *Heteroat. Chem.* **2006**, *17*, 188–206.

[7] a) B. Wrackmeyer, E. Khan, S. Bayer, K. Shahid, *Z. Naturforsch.* **2007**, *62b*, 1174–1182.b) B. Wrackmeyer, E. Khan, W. Milius, Z. Naturforsch. **2008**, *63b*, 1267–1275;c) B. Wrackmeyer, O. L. Tok, W. Milius, M. H. Bhatti, S. Ali, *Z. Naturforsch.* **2003**, *58b*, 133–138.d) B. Wrackmeyer, E. Khan, R. Kempe, *Z. Naturforsch.* **2007**, *62b*, 75–81.

[8] a) M. J. Ingleson, *Annu. Rep. Prog. Chem. Sect. A* **2013**, *109*, 28–52. b) B. Wrackmeyer, E. Khan, R. Kempe, *Appl. Organomet. Chem.* **2007**, *21*, 39–45.c) E. Khan, R. Kempe, B. Wrackmeyer, *Appl. Organomet. Chem.* **2009**, *23*, 204–211.d) E. Khan, S. Bayer, B. Wrackmeyer, *Z. Naturforsch.* **2009**, *64b*, 47–57.e) E. Khan, B. Wrackmeyer, R. Kempe, *Eur. J. Inorg. Chem.* **2008**, 5367–5372. f) B. Wrackmeyer, E. Khan, R. Kempe, *Appl. Organomet. Chem.* **2008**, *22*, 383–388.

[9] R. T. Conlin, D. L. Wood, *J. Am. Chem. Soc.* **1981**, *103*, 1843–1844.

[10] T. J. Barton, G. T. Burns, *Organometallics* **1983**, *2*, 1–4.

[11] H. Gilman, W. H. Atwell, *J. Am. Chem. Soc.* **1965**, *87*, 2678–2683.

[12] H. Gilman, O. L. Marrs, *J. Org. Chem.* **1964**, *29*, 3175–3179.

[13] B. Wrackmeyer, H. E. Maisel, W. Milius, M. H. Bhatti, S. Ali, *Z. Naturforsch.* **2003**, *58b*, 543–552.

[14] T. Sudo, N. Asao, Y. Yamamoto, *J. Org. Chem.* **2000**, *65*, 8919–8923.

[15] N. Asao, T. Shimada, Y. Yamamoto, *J. Am. Chem. Soc.* **2001**, *123*, 10899–10902.

[16] R. T. Conlin, M. Namavari, *J. Am. Chem. Soc.* **1988**, *110*, 3689–3690.

[17] a) E. Khan, B. Wrackmeyer, R. Kempe, *Appl. Organomet. Chem.* **2009**, *23*, 124–131.b) B. Wrackmeyer, O. L. Tok, W. Milius, A. Khan, A. Badshah, *Appl. Organomet. Chem.* **2006**, *20*, 99–105.

[18] a) G. A. Morris, R. Freeman, *J. Am. Chem. Soc.* **1979**, *101*, 760–762.b) G. A. Morris, *J. Am. Chem. Soc.* **1980**, *102*, 428–429.c) G. A. Morris, *J. Magn. Reson.* **1980**, *41*, 185–188.d) D. P. Burum, R. R. Ernst, *J. Magn. Reson.* **1980**, *39*, 163–168. e) J. Schraml, The Chemistry of Organic Silicon Compounds, Vol. *3* (Eds: Z. Rappaport, Y. Apeloig, Wiley: Chichester, **2001**, 223–339.

[19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, GAUSSIAN 09 (revision A.02), Gaussian, Inc, Wallingford, CT, **2010**.

[20] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *41*, 785–789.c) P. J. Stevens, F. J. Devlin, C. F. Chablowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623–11627. d) D. McLean, D. G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639–5648. e) R. Krishnan, J. S. Blinkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650–654.

[21] a) W. E. Davidsohn, M. C. Henry, *Chem. Rev.* **1967**, *67*, 73–106.b) L. Brandsma, Preparative Acetylenic Chemistry (2nd edn), Elsevier, Amsterdam, **1988**; c) L. Brandsma, Synthesis of Acetylenes, Allenes, Cumulenes: Methods and Techniques, Elsevier, Amsterdam, **2004**.

[22] E. Khan, B. Wrackmeyer, *Z. Naturforsch.* **2009**, *64b*, 1098–1106.

[23] a) C. A. Brown, R. A. Coleman, *J. Org. Chem.* **1979**, *44*, 2328–2329.b) H. C. Brown, A. W. Moerikofer, *J. Am. Chem. Soc.* **1963**, *85*, 2063–2065.

[24] B. Wrackmeyer, *Prog. NMR Spectrosc.* **1979**, *12*, 227–259.

[25] a) B. Wrackmeyer, H. E. Maisel, W. Milius, M. H. Bhatti, S. Ali, *J. Organomet. Chem.* **2003**, *669*, 72–78.b) B. Wrackmeyer, H. E. Maisel, E. Molla, A. Mottalib, A. Badshah, M. H. Bhatti, S. Ali, *Appl. Organomet. Chem.* **2003**, *17*, 465–472.

[26] a) A. Pelter, K. Smith, H. C. Brown, Borane Reagents, Academic Press, London, **1988**.b) H. C. Brown, Organic Syntheses via Boranes, Wiley, New York, **1975**.

[27] B. Wrackmeyer, E. Khan, R. Kempe, *Z. Naturforsch.* **2007**, *63b*, 275–279.

[28] K. Wollinski, J. F. Hinton, P. J. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251–8260.

[29] a) T. Helgaker, M. Jaszunski, M. Pecul, *Progr. NMR Spectrosc.* **2008**, *53*, 249–268.b) R. H. Contreras, V. Barone, J. C. Facelli, J. E. Peralta, *Annu. Rep. NMR Spectrosc.* **2003**, *51*, 167–260.c) R. H. Contreras, J. R. Cheeseman, M. J. Frisch, G. E. Scuseria, *Chem. Phys. Lett.* **2003**, *375*, 452–458.

[30] B. Wrackmeyer, *Annu. Rep. NMR Spectrosc.* **2006**, *57*, 1–49.

