Alkynylsilanes and Alkynyl(vinyl)silanes. Synthesis, Molecular Structures and Multinuclear Magnetic Resonance Study

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Alkynylsilanes bearing one to four alkynyl groups at silicon, with organyl groups (Me, Ph, Vin), H, Cl at silicon, and with substituents H, ^{n}Bu, ^{t}Bu, Ph, C_6H_4-4-Me, 3-thienyl, CH_2NMe_2 at the C≡C bond, were prepared, and their ^{13}C and ^{29}Si NMR data are reported. The results of X-ray structure analyses of three representative derivatives [di(phenylethynyl)dimethylsilane, di(phenylethynyl)methyl(phenyl)silane, and tri(phenylethynyl)methylsilane] are presented. The chemistry of mono- and dialkynylsilanes was further developed to prepare compounds with alternating Si atoms and C≡C bonds, affording new dialkynylsilanes as well as numerous new vinylsilanes which have also been characterized by ^{13}C and ^{29}Si NMR spectroscopy in solution. In the case of ethynyl(triphenylsilylethynyl)dimethylsilane, the molecular structure was determined by X-ray diffraction.

Key words: Alkynes, Silanes, NMR, X-Ray

Introduction

The reactivity of the C≡C bond in alkynylsilanes invites to a great number of useful transformations [1 – 3]. This synthetic potential can be tuned by selecting appropriate substituents at the C≡C bond as well as at the silicon atom. Since some chlorosilanes, and in particular numerous chloro(organo)silanes, are commercially available, a convenient entry into this kind of chemistry is provided. In the present work, we report some results on the synthesis, NMR spectroscopy and molecular structures of various alkynylsilanes, bearing up to four alkynyl groups, additional functions at silicon, *e. g.* vinyl group(s), an allyl group, chlorine or hydrogen. Numerous examples with different substituents at the C≡C bond, such as hydrogen, alkyl, phenyl or various silyl groups were also investigated. We have divided the alkynylsilanes into two classes, those accessible *via* conventional reactions of commercial chlorosilanes with alkynyllithium or ethynylmagnesium reagents (Scheme 1), and others obtained by more sophisticated stepwise procedures (Scheme 2 – 4). Many of these alkynylsilanes have already been used in reactions with dialkylboranes [4, 5] combining 1,2-hydroboration with 1,1-organoboration, or with triorganoboranes for 1,1-organoboration [6 – 8].

Results and Discussion

Synthesis

The alkynylsilanes shown in Scheme 1 were prepared *via* the reaction of the respective chlorosilanes with alkynyllithium or ethynyl-Grignard reagents (**1**, **13**), closely following reported procedures [9]. The alkynylsilanes **2a, d** were best obtained by treatment of the dichlorosilanes **9a, d** with $LiAlH_4$ [10]. In the case of **14**, the reaction of Me_2SiCl_2 with one equivalent of Li-C≡C-$SiMe_3$ afforded in the first step $Me_2Si(Cl)C≡C$-$SiMe_3$ which, upon treatment with HC≡C-MgBr/THF, gave the desired product [7b, 11]. Similarly, **20** was also prepared in two steps, from $SiCl_4$ *via* the reaction of $Cl_2Si(C≡C$-^{n}Bu$)_2$ (**9a**) with two equivalents of Li-C≡C-$SiMe_3$. It is important to note that these “mixed” species are kinetically sufficiently stable for many synthetic purposes. The most relevant NMR data of the alkynylsilanes **1 – 20** are listed in Table 1.

The access to alkynyl(vinyl)silanes or certain dialkynylsilanes containing two or more silicon atoms is more demanding. The most useful starting materials were the ethynylsilanes $Me_2(H)Si$-C≡C-H (**1**), $Me_2Si(C≡CH)_2$ (**13**) and $Me_2Si(C≡C$-$SiMe_3)$C≡C-H

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Table 1. ^{13}C and ^{29}Si NMR spectroscopic data[a] of silanes **1** – **20**.

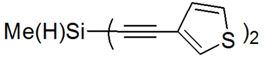
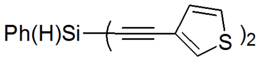
		$\delta^{29}Si$	$\delta^{13}C(Si\text{-}C\equiv)$	$\delta^{13}C(\equiv C)$	$\delta^{13}C(R/R^1)$
1	$Me_2(H)Si-C\equiv C-H$ in THF	−38.0	87.3 [84.3]	97.0 [16.0]	−2.7 [56.1] (Me)
2a	$H_2Si(C\equiv C{}^nBu)_2$	−87.0	74.5 [106.4]	111.5 [19.4]	13.6, 19.9, 22.1, 30.4 (^{n}Bu)
2d	$H_2Si(C\equiv C-SiMe_3)_2$	−88.6 −17.3 ($SiMe_3$)	101.7 [114.9] [11.9]	119.7 [17.9] [73.9]	−0.7 [56.5] ($SiMe_3$)
3a	$Me(H)Si(C\equiv C{}^nBu)_2$	−63.5	79.0 [102.3]	109.7 [20.4]	13.7, 19.9, 22.2, 30.7 (^{n}Bu) −1.9 [61.6] (Me)
3c	$Me(H)Si(C\equiv C-Ph)_2$	−61.0	87.9 [100.4]	107.9 [19.9]	122.8, 132.4, 128.5, 129.3 (Ph: *i*, *o*, *m*, *p*) −2.4 [62.3] (Me)
3e	$Me(H)Si(C\equiv C-C_6H_4\text{-}4\text{-}Me)_2$	−61.1	87.2 [100.9]	108.2 [20.1]	21.3 (Me), 119.9, 129.3, 132.3, 139.4 (Ph) −2.3 [62.1] (SiMe)
3f		−61.0	87.6 [100.3]	102.9 [20.2]	121.9, 125.7, 130.0, 131.0 (3-thienyl) −2.4 [62.3] (Me)
3g	$Me(H)Si(C\equiv C-CH_2NMe_2)_2$	−62.7	83.8 [102.5]	104.1 [19.4]	49.1, 44.6 (CH_2NMe_2) −1.9 [62.1] (SiMe)
4a[b]	$Ph(H)Si(C\equiv C{}^nBu)_2$	−65.5	76.8 [105.5]	111.4 [20.1]	13.6, 19.8, 21.9, 30.3 (^{n}Bu) 131.8 [81.6], 134.5, 128.0, 130.0 (SiPh: *i*, *o*, *m*, *p*)
4c[b]	$Ph(H)Si(C\equiv C-Ph)_2$	−63.6	85.6 [104.4]	108.5 [20.2]	122.5, 132.5, 128.5, 130.9 (Ph: *i*, *o*, *m*, *p*) 130.8 [83.8], 135.2, 128.7, 129.5 (SiPh: *i*, *o*, *m*, *p*)
4e	$Ph(H)Si(C\equiv C-C_6H_4\text{-}4\text{-}Me)_2$	−63.6	85.9 [104.3]	109.7 [20.4]	21.3 (Me), 119.7, 129.3, 132.5, 139.6 (Ph) 131.3, 135.3, 128.6, 130.7 (SiPh: *i*, *o*, *m*, *p*)
4f		−63.5	86.2 [104.4]	104.4 [20.6]	121.9, 125.5, 130.1, 131.4 (3-thienyl) 130.9 [83.9], 135.3, 128.6, 130.8 (SiPh: *i*, *o*, *m*, *p*)
5a	$Cl(H)Si(C\equiv C{}^nBu)_2$	−57.5	77.4 [125.8]	112.5 [25.9]	13.6, 19.7, 22.1, 30.1 (^{n}Bu)
5b	$Cl(H)Si(C\equiv C{}^tBu)_2$	−56.5	75.6 [125.4]	120.1 [25.1]	28.3, 30.1 (^{t}Bu)
5c	$Cl(H)Si(C\equiv C-Ph)_2$	−55.4	85.5 [124.3]	109.5 [25.5]	121.3, 128.5, 132.6, 130.1 (Ph: *i*, *o*, *m*, *p*)
5d	$Cl(H)Si(C\equiv C-SiMe_3)_2$	−60.1 {2.1}, −16.3 ($SiMe_3$)	103.3 [114.0] [11.5]	120.4 [20.0] [71.5]	−1.0 [56.6] ($SiMe_3$)
6a	$Me_2Si(C\equiv C{}^nBu)_2$	−41.9	82.1 [100.3]	107.8 [20.2]	13.8, 19.8, 22.2, 30.9 (^{n}Bu) 1.1 [61.0] ($SiMe_2$)
6b	$Me_2Si(C\equiv C{}^tBu)_2$	−41.4	80.0 [99.2]	115.8 [19.1]	28.2, 30.7 (^{t}Bu) 1.5 [62.1] ($SiMe_2$)
6c	$Me_2Si(C\equiv C-Ph)_2$	−39.3	90.9 [96.7]	105.9 [19.1]	122.6, 132.0, 128.2, 128.8 (Ph: *i*, *o*, *m*, *p*) 0.5 [62.5] ($SiMe_2$)
6d	$Me_2Si(C\equiv C-SiMe_3)_2$	−42.4, −18.4 ($SiMe_3$)	110.1 [90.0] [12.7]	115.2 [76.3] [15.2]	−0.2 [56.7] ($SiMe_3$) 0.6 [61.6] ($SiMe_2$)
6g	$Me_2Si(C\equiv C-CH_2NMe_2)_2$	−41.0	86.9 [98.3]	103.0 [19.5]	48.9, 43.9 (CH_2NMe_2) 0.9 [61.9] ($SiMe_2$)
7a	$Ph_2Si(C\equiv C{}^nBu)_2$	−49.2	79.6 [107.3]	111.8 [22.0]	13.6, 20.0, 22.2, 30.6 (^{n}Bu) 134.8 [82.7], 135.3, 128.3, 130.2 (SiPh: *i*, *o*, *m*, *p*)
8a	$(CH_2{=}CH)_2Si(C\equiv C{}^nBu)_2$	−54.6	78.6 [107.1]	110.4 [20.4]	30.8, 22.2, 19.9, 13.8 (^{n}Bu) 133.9 [81.2] (-CH=), 135.2 (=CH_2)
8c	$(CH_2{=}CH)_2Si(C\equiv C-Ph)_2$	−52.7	87.6 [105.1]	108.7 [20.0]	122.7, 132.4, 129.3, 128.5 (Ph: *i*, *o*, *m*, *p*) 132.4 [82.1] (-CH=), 136.7 (=CH_2)
9a	$Cl_2Si(C\equiv C{}^nBu)_2$	−48.8	78.7	112.6 [32.1]	13.5, 19.5, 22.1, 29.7 (^{n}Bu)
9b	$Cl_2Si(C\equiv C{}^tBu)_2$	−47.7	76.9 [153.7]	119.7 [30.8]	28.3, 29.8 (^{t}Bu)

Table 1 (continued).

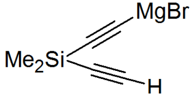
		δ^{29}Si	δ^{13}C(Si-C≡)	δ^{13}C(≡C)	δ^{13}C(R/R^1)
9c	$\mathrm{Cl_2Si{-}(\equiv{-}Ph)_2}$	−46.8	85.7 [157.7]	108.3 [31.9]	119.8, 128.3, 132.3, 130.4 (Ph: *i*, *o*, *m*, *p*)
9d	$\mathrm{Cl_2Si{-}(\equiv{-}SiMe_3)_2}$	−48.7, −18.0 (SiMe$_3$)	103.6 [145.3] [11.3]	119.8 [24.5] [71.4]	−0.8 [56.9] (SiMe$_3$)
10a	$\mathrm{Me(Ph)\ Si{-}(\equiv{-}{}^nBu)_2}$	−45.7	80.8 [103.5]	110.0 [19.9]	13.7, 19.9, 22.2, 30.7 (^{n}Bu) 0.9 [63.2] (SiMe) 135.9 [81.3], 134.4, 128.2, 130.0 (SiPh: *i*, *o*, *m*, *p*)
10c	$\mathrm{Me(Ph)\ Si{-}(\equiv{-}Ph)_2}$	−43.5	89.8 [101.2]	108.1 [19.8]	0.2 [63.8] (SiMe) 134.6 [82.5], 134.6, 128.5, 130.4 (SiPh: *i*, *o*, *m*, *p*) 122.5, 132.2, 128.2, 129.0 (Ph: *i*, *o*, *m*, *p*)
11a	$\mathrm{Me(Cl)\ Si{-}(\equiv{-}{}^nBu)_2}$	−34.9	80.1 [122.8]	110.8 [24.9]	13.6, 19.6, 22.1, 30.2 (^{n}Bu) 5.1 [73.7] (SiMe)
11c	$\mathrm{Me(Cl)\ Si{-}(\equiv{-}Ph)_2}$	−32.7	88.3 [121.3]	108.1 [24.5]	121.8, 132.6, 128.5, 129.8 (Ph: *i*, *o*, *m*, *p*) 4.6 [74.8] (SiMe)
12c	$\mathrm{Ph(Cl)\ Si{-}(\equiv{-}Ph)_2}$	−42.0	87.2 [126.1]	109.6 [25.2]	121.5, 132.7, 128.5, 130.0 (Ph: *i*, *o*, *m*, *p*) 132.6 [99.7], 134.4, 128.7, 131.8 (SiPh: *i*, *o*, *m*, *p*)
13	$\mathrm{Me_2Si{-}(\equiv{-}H)_2}$	−40.0	86.9 [95.7]	96.9 [18.7]	0.5 [62.8] (SiMe$_2$) 26.7, 68.5 (THF)
13(MgBr)	 in THF	−48.4	91.1, 108.5	93.2 (CH), 164.9 (CMgBr)	2.5 (SiMe$_2$) 26.7, 69.0 (THF)
15a	$\mathrm{HSi{-}(\equiv{-}{}^nBu)_3}$	−89.7	76.9 [116.3]	110.1 [23.5]	13.6, 19.8, 22.1, 30.4 (^{n}Bu)
15b	$\mathrm{HSi{-}(\equiv{-}{}^tBu)_3}$	−88.5	75.2 [116.1]	117.8 [22.5]	28.4, 30.0 (^{t}Bu)
15c	$\mathrm{HSi{-}(\equiv{-}Ph)_3}$	−86.4	85.1 [116.4]	108.4 [23.7]	122.3, 128.5, 130.1, 132.6 (Ph: *i*, *o*, *m*, *p*)
15d	$\mathrm{HSi{-}(\equiv{-}SiMe_3)_3}$	−92.7 {2.1}, −17.2 (SiMe$_3$)	102.9 [105.5], [12.0]	118.6 [18.2], [73.7]	−0.9 [56.6] (SiMe$_3$)
16a	$\mathrm{MeSi{-}(\equiv{-}{}^nBu)_3}$	−67.4	80.6 [112.8]	108.6 [22.7]	13.4, 19.5, 22.1, 30.1 (^{n}Bu) 2.4 [67.8] (SiMe)
16c	$\mathrm{MeSi{-}(\equiv{-}Ph)_3}$	−63.5	89.9 [112.7]	108.5 [22.5]	13.4, 19.4, 22.2, 30.0 (^{n}Bu) 3.1 [68.9] (SiMe)
17a	$\mathrm{PhSi{-}(\equiv{-}{}^nBu)_3}$	−71.9	78.4 [116.2]	110.0 [23.2]	30.2, 21.8, 19.7, 13.4 (^{n}Bu) 133.5 [90.3], 134.1, 127.7, 129.9 (SiPh: *i*, *o*, *m*, *p*)
17c	$\mathrm{PhSi{-}(\equiv{-}Ph)_3}$	−67.0	86.8	107.7	132.0, 134.5, 128.2, 130.6 (Ph: *i*, *o*, *m*, *p*) 133.2 [90.8], 134.0, 127.8, 129.8 (SiPh: *i*, *o*, *m*, *p*)
17e	$\mathrm{PhSi{-}(\equiv{-}C_6H_4\text{-}4\text{-}Me)_3}$	−69.1	87.3 [116.7]	108.7 [23.0]	21.3 (Me), 119.7, 132.6, 129.2, 139.5 (Ph) 135.1, 133.0, 128.6, 130.8 (SiPh: *i*, *o*, *m*, *p*)
18a	$\mathrm{ClSi{-}(\equiv{-}{}^nBu)_3}$	−68.2	79.4 [141.5]	110.8 [28.9]	13.5, 19.6, 22.0, 30.0 (^{n}Bu)
18b	$\mathrm{ClSi{-}(\equiv{-}{}^tBu)_3}$	−66.3	77.3 [134.6]	116.4 [29.4]	28.2, 30.2 (^{t}Bu)
18c	$\mathrm{ClSi{-}(\equiv{-}Ph)_3}$	−67.4	86.1 [142.0]	107.6 [28.7]	120.9, 128.3, 130.0, 132.2 (Ph: *i*, *o*, *m*, *p*)
18d	$\mathrm{ClSi{-}(\equiv{-}SiMe_3)_3}$	−68.0, −16.3 (SiMe$_3$)	104.4 [122.3] [11.8]	118.5 [22.2] [72.3]	−0.9 [56.7] (SiMe$_3$)
19a	$\mathrm{Si(\equiv{-}{}^nBu)_4}$	−95.1	79.4 [127.7]	108.7 [25.9]	13.5, 19.3, 22.1, 29.4 (^{n}Bu)
19b	$\mathrm{Si(\equiv{-}{}^tBu)_4}$	−93.8	80.4 [126.0]	114.8 [25.4]	28.2, 30.5 (^{t}Bu)

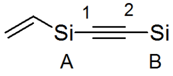
Table 1 (continued).

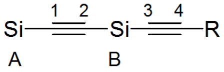
		δ^{29}Si	δ^{13}C(Si-C≡)	δ^{13}C(≡C)	δ^{13}C(R/R^1)
19c	$Si(-\equiv-Ph)_4$	−95.8	87.9 [130.3]	106.9 [26.6]	121.7, 128.6, 129.5, 132.8 (Ph: *i*, *o*, *m*, *p*)
19d	$Si(-\equiv-SiMe_3)_4$	−101.1 {2.2}, −16.6 ($SiMe_3$)	104.6 [118.4] [11.8]	117.7 [20.6] [75.3]	−0.9 [56.4] ($SiMe_3$)
19e	$Si(-\equiv-C_6H_4\text{-}4\text{-}Me)_4$	−92.7	86.5 [128.9]	107.5 [26.1]	21.8 (Me),120.2, 133.3, 130.1, 141.0 (Ph)
20	$(Me_3Si-\equiv-)_2Si(-\equiv-{}^nBu)_2$	−97.7, −16.4 ($SiMe_3$)	77.1$^\alpha$, 105.1$^\alpha$	109.8$^\beta$, 115.6$^\beta$	13.5, 19.6, 21.8, 30.0 (^{n}Bu) −0.5 [56.5] ($SiMe_3$)

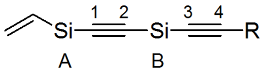
[a] In C_6D_6 or in CD_2Cl_2 at 296 K; $^nJ(^{29}Si,^{13}C)$ coupling constants [±0.5 Hz] are given in brackets; $^3J(^{29}Si,^{29}Si)$ coupling constants {±0.3 Hz} are given in braces;

[b] H. Q. Liu, J. F. Harrod, *Can. J. Chem.* **1990**, *68*, 1100.

Table 2. ^{13}C and ^{29}Si NMR spectroscopic data[a] of silanes **21** – **42**.







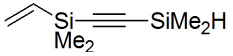
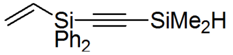
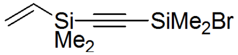
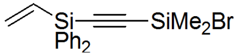
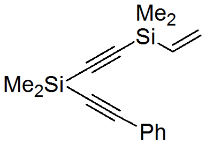
		δ^{29}Si (A)	δ^{29}Si (B)	δ^{29}Si (C)	δ^{13}C (Si-C(2) ≡)	δ^{13}C (Si-C(3) ≡)	δ^{13}C (C(1) ≡)	δ^{13}C (C(4) ≡)	δ^{13}C ($CH=CH_2$)	δ^{13}C (R)
21 [15]		−32.8	−38.5		111.8 [78.6] [12.9]		113.3 [79.0] [12.6]		133.2 ($=CH_2$), 136.0 [71.7] (=CH-)	−3.1 [56.1] [7.4] ($SiMe_2H$), −1.7 [57.5] ($SiMe_2$)
22 [15]		−32.3 {1.6} [13.3] [75.3] [77.0] [87.0]	−37.8 {1.6} [12.3] [56.1] [77.3]		116.5 [77.4] [13.2]		110.9 [87.2] [12.4]		133.1 [75.2] (=CH-), 137.1 ($=CH_2$)	−2.7 [56.1] ($SiMe_2$) 133.8 [77.1], 136.1, 128.9 130.8 (Ph: *i*, *o*, *m*, *p*)
23 [15]		−24.5 {1.8}	−8.7 {1.8}		115.9 [77.1] [16.1]		110.2 [92.4] [12.3]		134.5 [10.4] ($=CH_2$) 136.0 [72.1] (=CH-)	−1.3 [57.9] ($SiMe_2$) 4.8 [63.2] ($SiMe_2Br$)
24		−32.2 {1.7} [12.7] [75.6] [77.3] [84.5]	−7.4 {1.7} [15.4] [63.4] [90.4]		113.3 [90.3] [12.6]		111.7 [84.4] [15.5]		132.3 [75.8] (=CH-), 137.9 ($=CH_2$)	4.6 [63.5] ($SiMe_2$) 132.8 [77.3], 135.5, 128.5 130.7 (Ph: *i*, *o*, *m*, *p*)
25		−25.1 {1.8} [12.6] [57.7] [71.9] [79.6]	−40.6 {1.8} [14.9] [19.2] [62.3] [89.3] [97.7]		112.2 [89.3] [12.6]	91.2 [97.8]	113.8 [79.5] [14.8]	107.1 [19.3]	134.1 ($=CH_2$), 136.6 [72.0] (=CH-)	−1.1 [57.7] ($SiMe_2$(vin)) 1.0 [62.1] ($SiMe_2$) 123.6 (Ph), 128.9 (Ph) 129.5 (Ph), 132.8 (Ph)

Table 2 (continued).

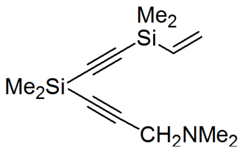
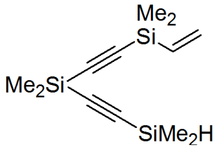
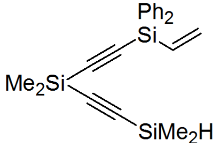
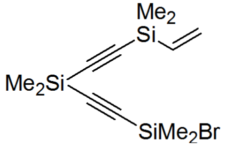
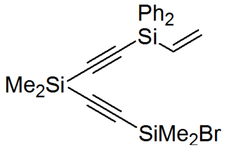
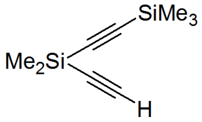
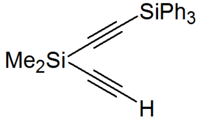
		δ^{29}Si (A)	δ^{29}Si (B)	δ^{29}Si (C)	δ^{13}C (Si-C(2) ≡)	δ^{13}C (Si-C(3) ≡)	δ^{13}C (C(1) ≡)	δ^{13}C (C(4) ≡)	δ^{13}C (CH=CH$_2$)	δ^{13}C (R)
26		−25.2 {1.7}	−41.6 {1.7} [14.9] [19.0] [62.2] [88.8] [98.3]		112.5 [88.8] [12.6]	86.8 [98.3]	113.2 [79.8] [14.7]	103.9 [19.0]	134.0 (=CH$_2$), 136.7 [71.6] (=CH-)	−1.1 [57.5] (SiMe$_2$(vin)) −1.1 [62.1] (SiMe$_2$) 44.4 (NMe$_2$), 49.3 (CH$_2$N)
27		−25.1 {1.8} [12.6] [57.6] [72.0] [79.3]	−42.0 {1.8} [15.0] [62.0] [89.3]	−38.0 {1.8} [12.6] [56.0] [78.2]	112.4 [89.3] [12.6]	111.7 [89.6] [12.6]	114.0 [79.4] [15.0]	112.9 [78.2] [15.2]	134.0 (=CH$_2$), 136.6 [72.1] (=CH-)	−2.8 [55.8] (SiMe$_2$(H)) −1.1 [57.7] (SiMe$_2$(vin)) 0.8 [62.0] (SiMe$_2$)
28		−32.6 {2.0} [13.1] [75.6] [77.1] [86.5]	−41.1 {2.0} [14.8] [62.2] [87.0] [89.2]	−37.6 [55.8]	115.3 [87.2] [13.3]	111.3 [89.2] [12.6]	109.6 [86.3] [14.8]	112.9 [77.2] [14.8]	132.7 [75.8] (=CH-), 137.6 (=CH$_2$)	−3.1 [56.1] (SiMe$_2$(H)) 0.3 [62.1] (SiMe$_2$) 133.3 [77.0], 135.5, 128.5 130.5 (Ph: *i*, *o*, *m*, *p*)
29		−24.9 {1.8} [12.4] [15.8] [57.7] [72.4] [78.7]	−41.0 {1.8} {1.9} [14.4] [15.0] [62.1] [86.4] [90.5]	−8.2 {1.9} [63.4] [91.4]	110.6 [90.5] [12.4]	113.5 [86.6] [15.5]	114.5 [78.7] [15.0]	109.8 [91.6] [14.6]	133.9 (=CH$_2$), 136.1 [72.4] (=CH-)	−1.6 [57.8] (SiMe$_2$(vin)) 0.1 [62.2] (SiMe$_2$) 4.2 [63.4] (SiMe$_2$(Br))
30		−32.6 {2.0} [12.6] [75.6] [77.1] [86.0]	−40.1 {2.0} [14.4] [62.4] [86.4] [88.2]	−7.4 {2.0} [16.3] [63.4] [91.1]	114.4 [88.5] [12.9]	113.0 [86.3] [15.7]	110.2 [86.1] [14.8]	109.7 [90.9] [14.4]	132.6 [75.6] (=CH-), 137.6 (=CH$_2$)	0.0 [62.3] (SiMe$_2$) 4.5 [63.3] (SiMe$_2$(Br)) 133.1 [77.0], 135.5, 128.5 130.5 (Ph: *i*, *o*, *m*, *p*)
14		−18.0 [12.3] [56.2] [75.6]	−40.4 [15.1] [18.6] [62.4] [90.5] [94.0]		109.7 [90.5] [12.3]	86.6 [94.1]	115.7 [75.7] [15.1]	95.0 [18.5]		−0.3 [56.2] (SiMe$_3$) 0.1 [62.3] (SiMe$_2$)
31		−29.7 [4.4] [5.8] [13.0] [77.0] [86.4]	−39.3 [14.7] [18.3] [62.6] [87.8] [94.0]		115.2 [87.7] [12.9]	86.4 [98.3]	110.1 [86.4] [14.6]	94.8 [18.4]		0.1 [62.6] (SiMe$_2$) 133.2 [77.1], 135.8, 128.4 130.2 (SiPh$_3$: *i*, *o*, *m*, *p*)

Table 2 (continued).

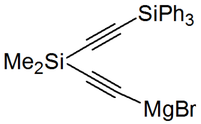
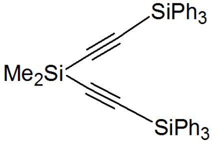
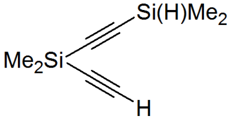
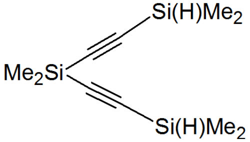
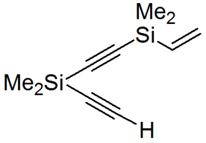
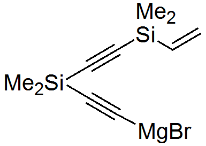
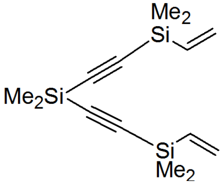
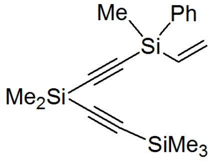
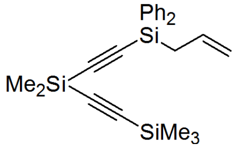
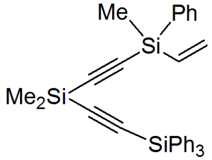
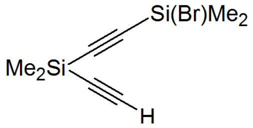
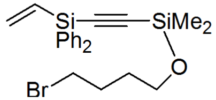
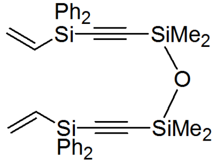
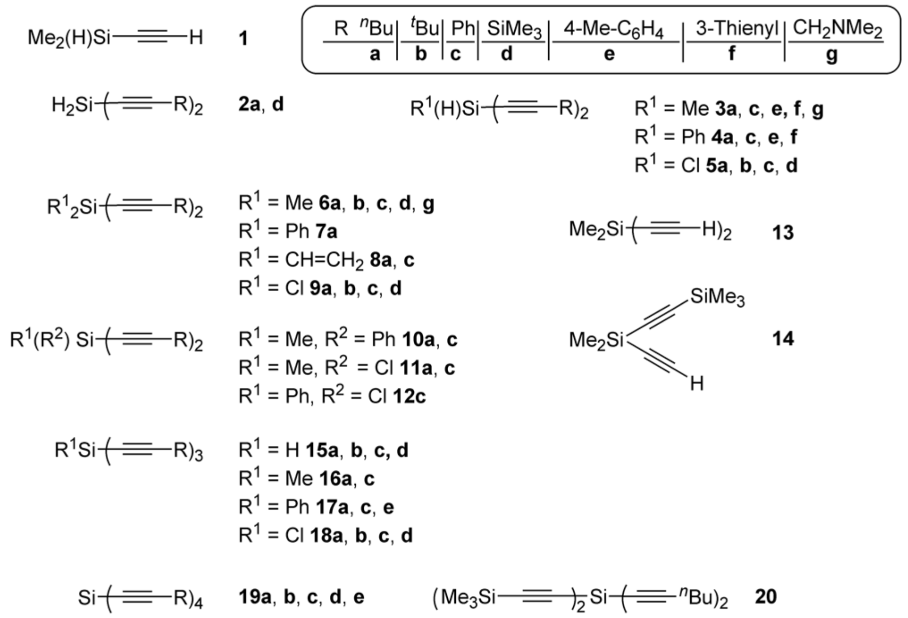
		δ^{29}Si (A)	δ^{29}Si (B)	δ^{29}Si (C)	δ^{13}C (Si-C(2) ≡)	δ^{13}C (Si-C(3) ≡)	δ^{13}C (C(1) ≡)	δ^{13}C (C(4) ≡)	δ^{13}C (CH=CH$_2$)	δ^{13}C (R)
31(MgBr)	 in THF	−20.3	−51.8		108.1	122.0	106.0	167.0		2.5 (Me) 26.7, 69.0 (THF) 135.1 [77.1], 136.6, 128.9 130.8 (SiPh$_3$: *i*, *o*, *m*, *p*)
32		−29.7	−40.2		115.4 [87.6] [13.0]		110.2 [86.5] [14.6]			0.2 [62.2] (SiMe$_2$) 133.3 [77.0], 135.9, 128.5 130.5 (SiPh$_3$: *i*, *o*, *m*, *p*)
33		−37.7 {2.0} [56.1]	−40.2 {2.0} [15.1] [18.5] [62.3] [89.8] [94.5]		111.9 [90.0] [12.5]	86.7 [94.5]	113.0 [77.8] [15.3]	95.5 [18.6]		−3.0 [56.0] (Si(H)Me$_2$) 0.3 [62.4] (SiMe$_2$)
34 [17]		−38.0 {1.8}	−41.4 {1.8}		111.7 [89.5] [12.4]		112.5 [77.9] [15.2]			−3.3 [56.2] (Si(H)Me$_2$) 0.2 [61.8] (SiMe$_2$)
35		−24.7 [12.6] [57.6] [71.9] [79.0]	−40.2 [15.0] [18.4] [62.2] [89.9] [94.2]		111.0 [89.9] [12.5]	86.4 [94.1]	113.6 [79.0] [14.9]	95.0 [18.5] (134.9)	133.6 (=CH$_2$), 136.0 [72.0] (=CH-)	−1.7 [57.6] (SiMe$_2$(vin)) 0.0 [62.2] (SiMe$_2$)
35(MgBr)	 in THF	−24.7	−50.0		108.5	117.5	108.9	165.7 (br)	133.5 (=CH$_2$), 138.0 (=CH-)	−0.9 (SiMe$_2$(vin)) 2.4 (SiMe$_2$)
36		−24.8	−41.7		111.5		113.6		133.6 (=CH$_2$) 136.2 (=CH-)	−1.7 [57.6] (SiMe$_2$(vin)) 0.1 [62.2] (SiMe$_2$)

Table 2 (continued).

		δ^{29}Si (A)	δ^{29}Si (B)	δ^{29}Si (C)	δ^{13}C (Si-C(2) ≡)	δ^{13}C (Si-C(3) ≡)	δ^{13}C (C(1) ≡)	δ^{13}C (C(4) ≡)	δ^{13}C (CH=CH$_2$)	δ^{13}C (R)
37		−28.7 {1.7} [4.4] [5.7] [12.8] [59.2] [73.6] [75.2] [82.9]	−41.6 {1.7} [14.7] [62.0] [87.4] [89.7]	−17.7 {1.6} [12.1] [56.2] [75.0]	113.7 [87.5] [12.8]	109.7 [89.7] [12.1]	111.3 [82.9] [14.6]	116.1 [75.0] [14.8]	134.7 [73.5] (=CH-), 135.6 (=CH$_2$)	−2.5 [59.2] (SiMe) −0.0 [56.2] (SiMe$_3$) 0.6 [62.0] (SiMe$_2$) ^{b} 135.0 [75.4], 134.7 [4.4] 128.5 [5.7], 130.3 (Ph: *i*, *o*, *m*, *p*)
38		−26.7 {2.0} [12.6] [56.2] [75.5]	−41.6 {1.8} {2.0} [14.8] [62.2] [88.0] [90.2]	−18.2 {1.8}	115.3 [88.1] [12.6]	110.1 [90.3] [12.5]	110.6 [84.9] [14.6]	116.1 [75.2] [14.8]	115.8 (=CH$_2$), 133.1 (=CH-)	−0.1 [56.1] (SiMe$_3$) 0.5 [62.1] (SiMe$_2$) 22.3 [54.9] (SiCH$_2$) 133.9 [75.9], 135.5, 128.5 130.4 (Ph: *i*, *o*, *m*, *p*)
39		−28.6 [12.7] [59.2] [73.6] [75.1] [82.5]	−40.6 {1.9} [14.6] [62.2] [87.1] [88.6]	−29.7 {1.9} [12.9] [76.9] [86.6]	113.0 [88.6] [12.8]	115.7 [87.2] [13.0]	111.8 [82.6] [14.8]	110.0 [86.6] [14.4]	134.6 [73.5] (=CH-), 135.5 (=CH$_2$)	−2.6 [59.2] (SiMe) 0.3 [62.3] (SiMe$_2$) ^{b} 134.9 [75.1], 134.6, 128.4 130.6 (SiPh: *i*, *o*, *m*, *p*) 133.3 [76.9], 135.9, 128.5 130.6 (SiPh$_3$: *i*, *o*, *m*, *p*)
40		−8.5 {2.0}	−39.6 {2.0} [62.4]		113.1 [87.2] [15.9]	85.9 [95.4]	109.9 [91.0] [15.0]	95.7 [18.6]		0.1 [62.5] (SiMe$_2$) 4.3 [63.6] (SiMe$_2$(Br))
41		−32.5	−9.0		116.8		108.2		132.8 (=CH-), 137.4 (=CH$_2$)	0.0 (SiMe$_2$) 29.8, 31.3 (CH$_2$) 34.4 (CH$_2$Br), 62.9 (CH$_2$O) 133.4, 135.4, 128.4 130.5 (Ph: *i*, *o*, *m*, *p*)
42		−32.1 {1.7} [13.2] [77.2] [84.4]	−17.0 {1.7} [15.1] [67.8] [88.6]		117.9 [88.5] [13.1]		108.0 [86.5] [15.0]		133.0 [75.2] (=CH-), 137.1 (=CH$_2$)	2.1 [67.6] (SiMe$_2$) 133.3 [75.2], 135.6, 128.4 130.2 (Ph: *i*, *o*, *m*, *p*)

[a] In C_6D_6 or in CD_2Cl_2 at 296 K; $^nJ(^{29}\text{Si},^{13}\text{C})$ coupling constants [±0.5 Hz] are given in brackets; $^3J(^{29}\text{Si},^{29}\text{Si})$ coupling constants {±0.3 Hz} are given in braces; $^nJ(^{13}\text{C},^{13}\text{C})$ coupling constants [±0.5 Hz] are given in parentheses; [b] prochiral methyl groups are not distinguished.



Scheme 1. Selection of alkynylsilanes prepared by conventional methods, using the reactions of chlorosilanes with alkynyllithium reagents or HC≡C-MgBr/THF (**1**, **13**) in one step or stepwise (**14**, **20**).

(**14**), all of which can be transformed into alkynyl-Grignard reagents upon reaction with EtMgBr. The Si-H function in **1** is useful, since it can be subsequently converted into the Si-Br function using allyl bromide and $PdCl_2$ [12]. This Si-Br function, *e. g.* in **23**, **24** or **29**, **30**, then invites to further transformations (Scheme 2). Repetitions of the sequence of the reactions shown in Scheme 2 offer a useful route to polyalkynyl-polysilanes containing several alternating silicon atoms and C≡C bonds. Another functional group at the terminal silicon atom, like a vinyl (Scheme 2) [13] or an allyl group (not shown), offers additional synthetic potential, in particular in cascade reactions, when intermolecular 1,2-hydroboration is combined with intramolecular 1,1-organoboration [14–16].

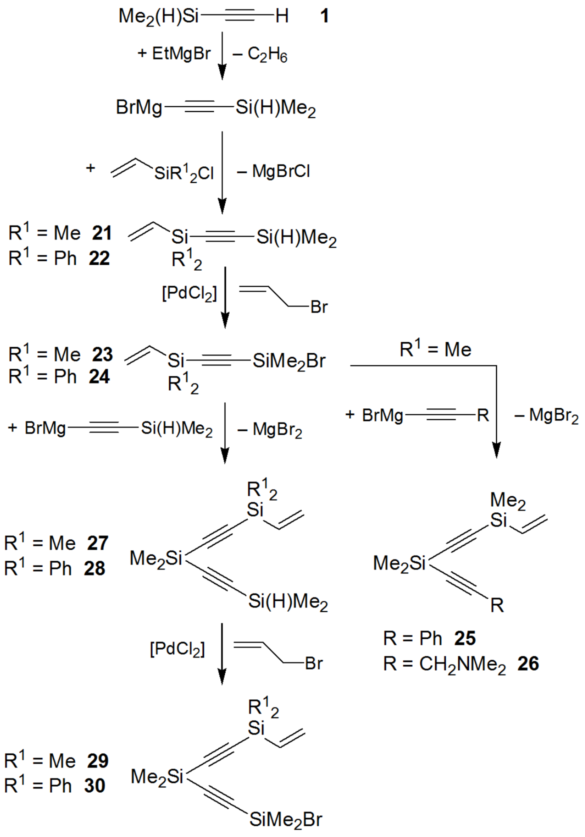
The alkynyl(vinyl)silanes shown in Scheme 2 are most conveniently characterized by their ^{13}C and ^{29}Si NMR spectra (Figs. 1 and 2). The most relevant NMR data are given in Table 2. The tentative assignment of the ^{13}C(alkyne) NMR signals (Fig. 1) on the basis of ^{29}Si satellites due to $^nJ(^{29}Si,^{13}C)$ (n = 1, 2) is unambiguously confirmed by observing the corresponding ^{13}C satellites in the ^{29}Si NMR spectra (Fig. 2).

Treatment of **13** with EtMgBr affords mixtures, in which one or both ethynyl groups bear MgBr. However, the products from reactions with chlorosilanes (Scheme 3) can be separated in favorable cases (*e.g.* **14**, **31**, **33**), and pure alkynylsilanes are obtained for further transformations.

Again, ^{13}C and ^{29}Si NMR spectra are most useful for structural assignments, in these cases for mixtures as well as for the purified compounds. Thus, Fig. 3 shows the typical ^{13}C NMR spectrum for the alkynyl carbon atoms of the mixture of **31** and **32**. The assignments are based on chemical shifts (Me_2Si-C≡C-H fragment in **31**) and ^{29}Si satellites corresponding to different values $^nJ(^{29}Si,^{13}C)$ (n = 1, 2). The latter assignment can be confirmed by ^{29}Si NMR spectra (Fig. 4), in which the $^{29}Si(SiMe_2)$ and $^{29}Si(SiPh_3)$ NMR signals are significantly different, showing the respective ^{13}C satellites. The performance of the INEPT pulse sequence is better for $SiMe_2$ than for $SiPh_3$ groups owing to the complex spin system of the ^1H nuclei in phenyl groups.

Protection of one C≡C group with $SiMe_3$ as in **14** enables to conduct further transformations into dialkynylsilanes with different alkynyl groups more selectively (Scheme 4), and the same strategy works for **31**, once it has been successfully separated from **32**.

The conversion of the Si-H into the Si-Br function (Scheme 2) works also if an ethynyl group is present, as shown for **33 / 40** in Scheme 5.



Scheme 2. Examples for the conversion of ethynyl(dimethyl)silane (**1**) into various other alkynylsilanes taking advantage of the ≡C-H and the Si-H functions.

Most reactions shown in Schemes 2 – 5 afford the products in high yield. Purification of the products contained in mixtures (Scheme 3), however, may be difficult. The Grignard route [11a] shown for **1**, **13**, **14** and **31** gives much better results than the lithiation of the ethynylsilanes with ^{n}BuLi. Apparently, numerous side reactions take place when ^{n}BuLi is used, and complex mixtures are obtained. Another point is of importance. It should be noted that silicon bromides may readily react with THF at room temperature with ether cleavage (Scheme 6). The bromide **24** is completely converted into **41** and **42** after 10 d, and this means that such side reactions can cause problems whenever slow reactions of silicon bromides are conducted in THF.

NMR parameters (Tables 1, 2)

Chemical shifts δ^{13}C of the alkynyl carbon atoms are found in the usual range [18, 19] with the exceptions of the ^{13}C(≡C-Mg) NMR signals for **13MgBr**, **31MgBr** and **35MgBr**. To the best of our knowledge, ^{13}C NMR signals of alkynyl Grignard reagents in THF have not been reported before. The ^{13}C(≡C-Mg) NMR signals are broadened, most likely due to exchange processes involving the coordinated THF molecules at the magnesium atom, and they are shifted significantly to higher frequencies (> 40 ppm) relative to the range typical of alkynes. This can be explained by the polar Mg-C(alkyne) bond which gives rise to magnetic field-induced $\sigma \rightarrow \pi$ electronic transitions leading to magnetic deshielding of the ^{13}C(≡C-Mg) nuclei. Calculations [20] of the ^{13}C(≡C-Mg) nuclear shielding were carried out for optimized gas phase geometries [B3LYP/6-311+G(d,p) level of theory] [21] of the model compounds $Me_2(H)Si\text{-}C{\equiv}C\text{-}MgCl$ (**M-Mg1**) [δ^{13}C(≡C-Mg) = 121.1], $Me_2(H)Si\text{-}C{\equiv}C\text{-}Mg(Cl)\text{-}OH_2$ (**M-Mg2**) [δ^{13}C(≡C-Mg) = 121.9], $Me_2(H)Si\text{-}C{\equiv}C\text{-}Mg(Cl)(OH_2)_2$ (**M-Mg3**) [δ^{13}C(≡C-Mg) = 140.2], and $Me_2(H)Si\text{-}C{\equiv}C\text{-}Mg(Cl)(OH_2)_3$ (**M-Mg4**) [δ^{13}C(≡C-Mg) = 148.2]. The calculated Mg–C bond lengths increase slightly in this sequence, and at the same time the ^{13}C(≡C-Mg) nuclear shielding decreases in the direction of the extreme value $\delta^{13}C(\equiv C^-) = 229.2$ calculated for the free anion $[Me_2(H)Si\text{-}C{\equiv}C]^-$. In the latter, the deshielding is clearly related to the presence of the lone pair of electrons, giving rise to $n \rightarrow \pi^*$ transitions, as indicated by the huge change in the calculated respective components to the ^{13}C chemical shift tensor.

Chemical shifts δ^{29}Si change with the number of alkynyl groups linked to silicon in the expected way [22]. Again, the data for the magnesium derivatives are somewhat different, since the ^{29}Si nuclei are better shielded (by up to 12.5 ppm) when compared with the respective unsubstituted alkynylsilane. This trend is well reproduced by the calculated ^{29}Si nuclear shielding for the model compounds **M-Mg1** ($\delta^{29}Si = -40.0$), **M-Mg2** ($\delta^{29}Si = -46.4$), **M-Mg3** ($\delta^{29}Si = -48.4$), and **M-Mg4** ($\delta^{29}Si = -49.0$), when compared with that for $Me_2(H)Si\text{-}C{\equiv}C\text{-}H$ (**1**) ($\delta^{29}Si = -40.8$) and the extreme value for the anion $[Me_2(H)Si\text{-}C{\equiv}C]^-$ ($\delta^{29}Si = -73.5$).

Coupling constants $J(^{29}Si,^{13}C)$ listed in Tables 1 and 2 follow the pattern known for alkynylsilanes [22], enlarging considerably the data set available so far. The presence of silyl groups at both alkynyl carbon atoms leads in general to somewhat smaller magni-

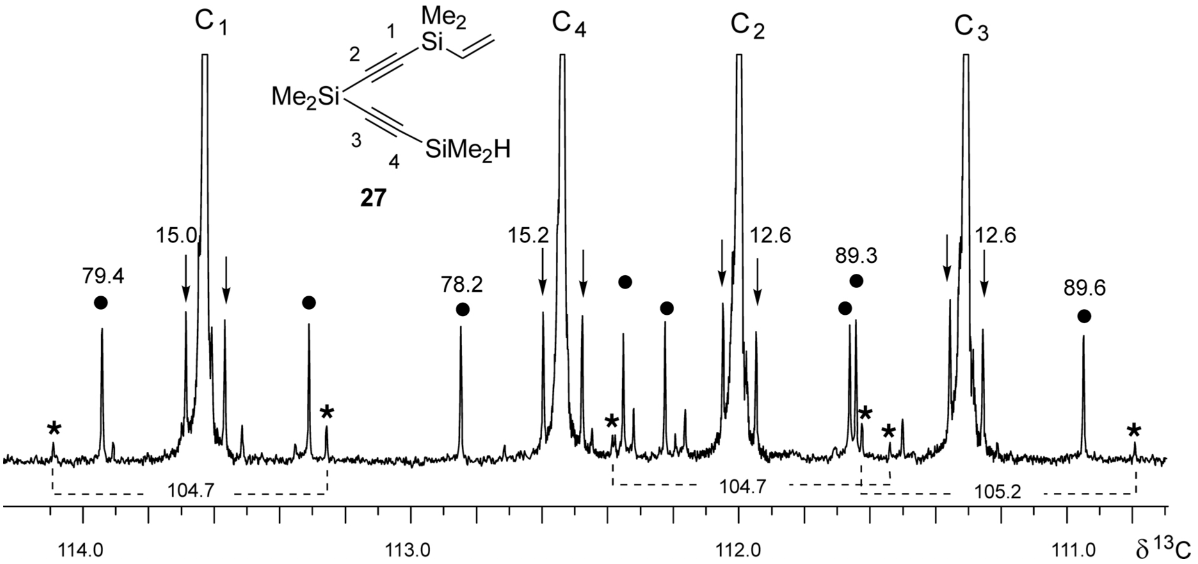


Fig. 1. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of **27** showing the regions of the ^{13}C(alkynyl) NMR signals (in C_6D_6, at 23 °C). The ^{29}Si satellites for $^1J(^{29}Si,^{13}C)$ are marked by filled circles and for $^2J(^{29}Si,^{13}C)$ by arrows, the ^{13}C satellites for $^1J(^{13}C,^{13}C)$ by asterisks (coupling constants are given in Hz).

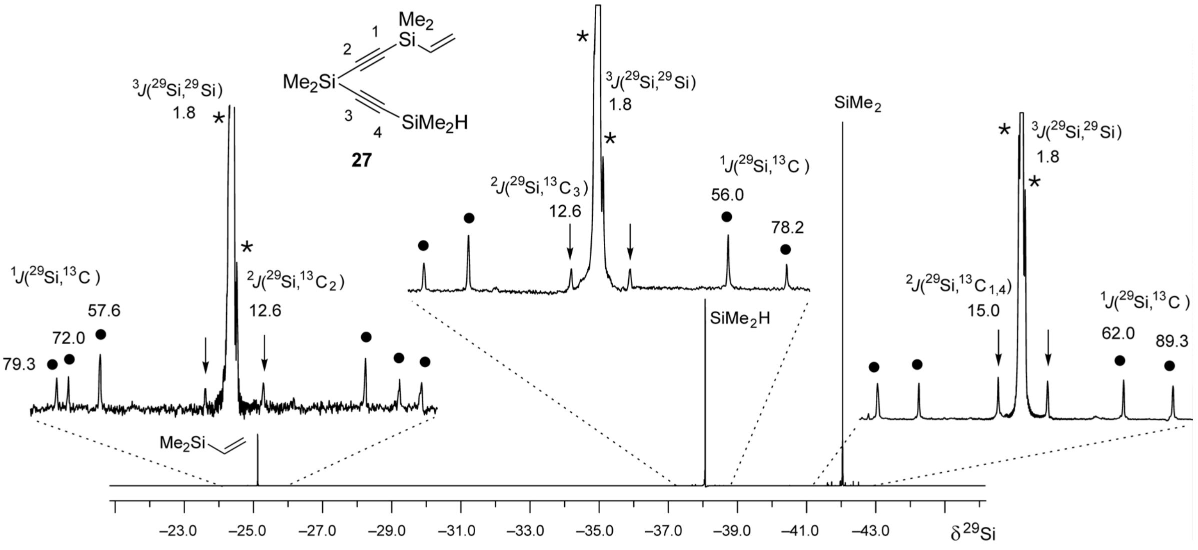
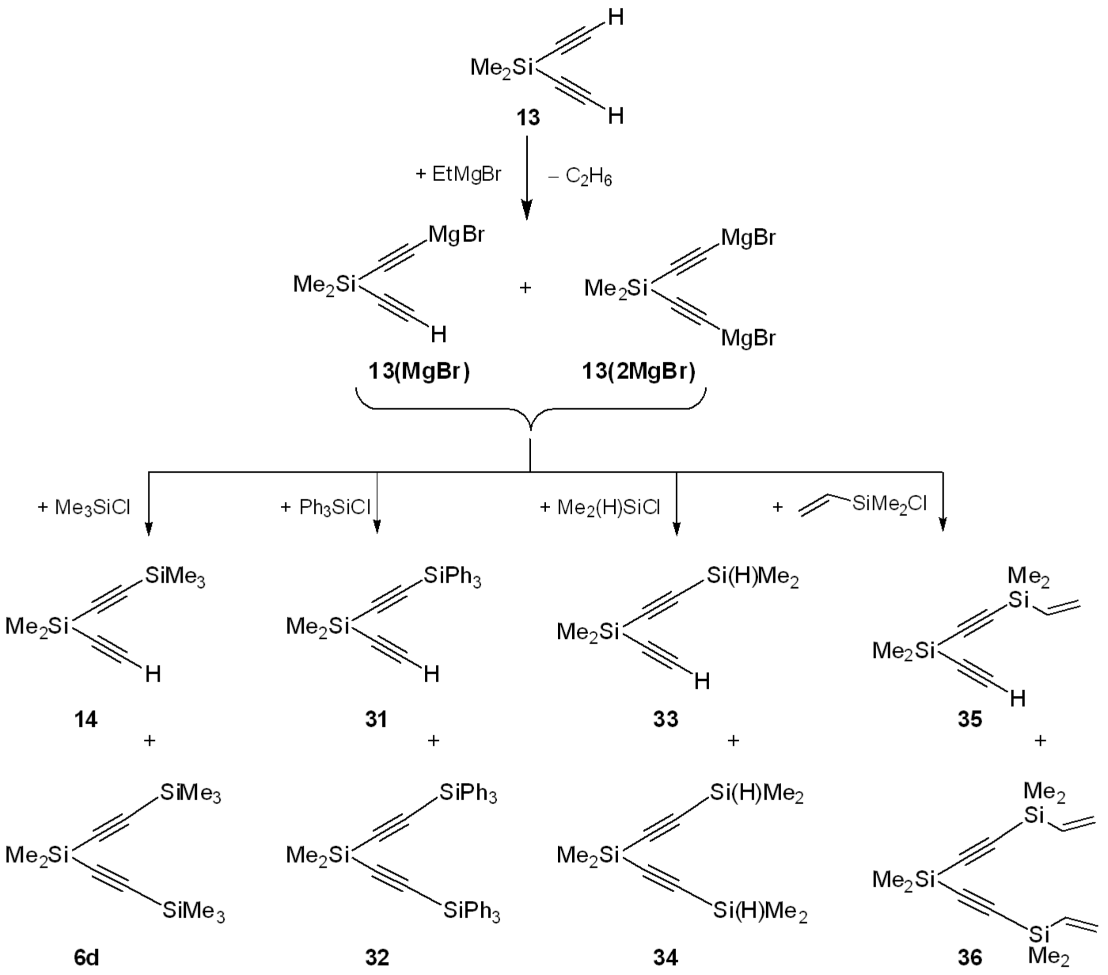


Fig. 2. 99.4 MHz $^{29}Si\{^1H\}$ NMR spectrum of **27** (refocused INEPT [22]; in C_6D_6, 23 °C). The ^{13}C satellites for $^1J(^{29}Si,^{13}C)$ are marked by filled circles and for $^2J(^{29}Si,^{13}C)$ by arrows, the ^{29}Si satellites for $^3J(^{29}Si,^{29}Si)$ by asterisks (coupling constants are given in Hz).

tudes of $|^nJ(^{29}Si,^{13}C)|$, and an increasing number of alkynyl groups at silicon causes larger magnitudes of $|^nJ(^{29}Si,^{13}C)|$. The comparison between alkynyl and chloro substituents at silicon shows that the chloro substituent leads to a larger increase in the magnitude of $|^nJ(^{29}Si,^{13}C)|$ ($n = 1, 2$).

*X-Ray structural studies of the alkynylsilanes **6c**, **10c**, **16c**, and **31***

The molecular structures of **6c**, **10c**, **16c**, and **31** are shown in Figs. 5, 6, 7, and 8, respectively. There are no appreciable intermolecular interactions. All



Scheme 3. Examples for the conversion of diethynyl(dimethyl)silane **13** into various other alkynylsilanes taking advantage of the ≡C-H function(s).

bond lengths and angles (Tables 3 and 4) are within the expected ranges [23], except for the bond length C23–C24 (106.0(2) pm) in **31**. This distance is too short for a C≡C bond, and the value determined here may be affected by C≡C and ≡C-H stretching vibrations, since similar "short" C≡C bonds were found for ethynyltin compounds [24], both at room temperature and 133 K. Other structural parameters of the Si-C≡C-Si unit in **31** are comparable to those of another disilylethyne (Table 4) [25]. The dialkynylsilane **31** is one of few structurally characterized examples of ethynylsilanes [23d, h]. There are no examples of structures of trialkynylsilanes in the literature, except for a distantly related hexaalkynyldisilane [26]. The structure of **6c** has recently been reported [27], parallel to our work (and in good agreement), whereas the structure **10c** represents the first example of a dialkynylsilane bearing two different additional substituents.

Conclusions

Direct structural information from X-ray diffraction is provided for alkynylsilanes, and the ^{13}C and ^{29}Si NMR data sets of alkynylsilanes available so far [19, 22] have been considerably enlarged, in particular with respect to coupling constants $^{n}J(^{29}\mathrm{Si},^{13}\mathrm{C})$ which frequently had been neglected. It has been demonstrated that the NMR data serve for unambiguous structural characterization of simple and more complex alkynylsilanes in solution. The first

6c		**10c**		**16c**	
Si1–C1	181.4(4)	Si1–C1	182.2(3)	C2–Si1	182.1(17)
Si1–C17	183.6(4)	Si1–C17	184.6(2)	Si1–C1	182.5(3)
Si1–C18	185.1(4)	Si1–C18	184.8(2)		
C1–C2	120.7(5)	C1–C2	121.1(3)	C2–C3	120.4(2)
C2–C3	142.9(5)	C2–C3	143.2(3)	C3–C4	143.4(2)
C1–Si1–C9	107.8(16)	C1–Si1–C9	106.2(10)	C2–Si1–C2A	106.0(6)
C1–Si1–C17	109.6(19)	C1–Si1–C17	109.3(12)	C2–Si1–C1	112.8(5)
C1–Si1–C18	107.7(18)	C1–Si1–C18	110.5(12)		
C17–Si1–C18	112.0(18)	C17–Si1–C18	112.4(13)		
C2–C1–Si1	175.6(3)	C2–C1–Si1	176.8(19)	C3–C2–Si1	169.8(15)
C1–C2–C3	176.8(4)	C1–C2–C3	177.4(2)	C2–C3–C4	175.5(19)

Table 3. Comparison of selected bond lengths (pm) and bond angles (deg) for compounds **6c**, **10c**, and **16c**.

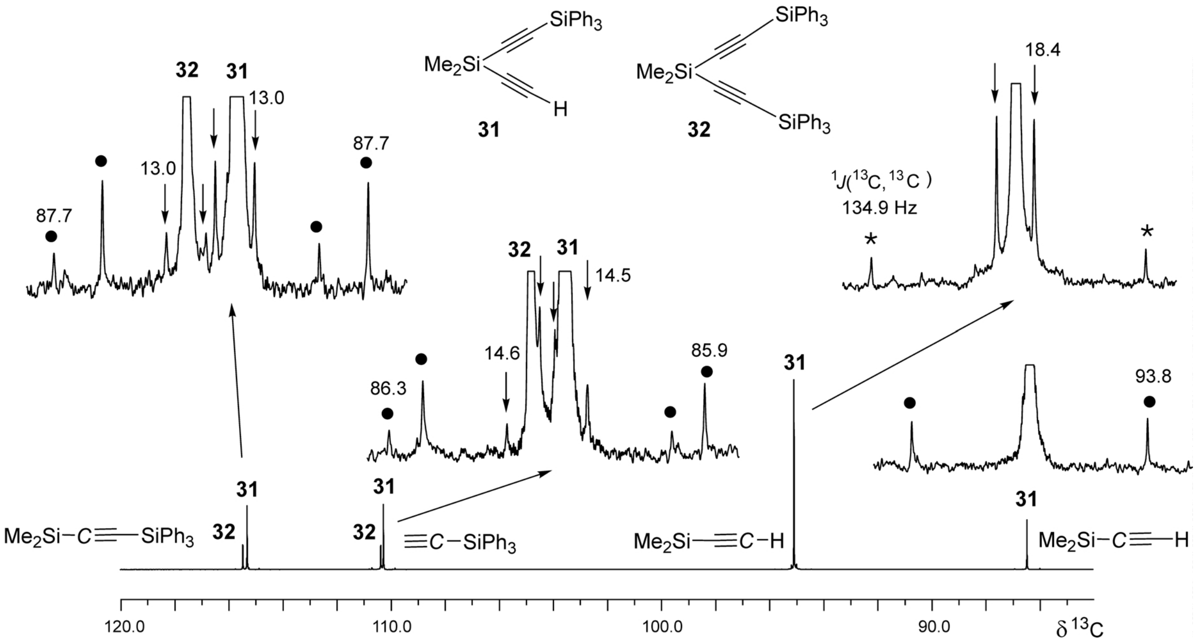


Fig. 3. 125.8 MHz ^{13}C{^{1}H} NMR spectrum of the reaction mixture of **31** and **32** showing the regions of the ^{13}C(alkynyl) NMR signals (CD$_2$Cl$_2$, at 23 °C). The ^{29}Si satellites for $^1J(^{29}\mathrm{Si},^{13}\mathrm{C})$ are marked by filled circles and for $^2J(^{29}\mathrm{Si},^{13}\mathrm{C})$ by arrows, the ^{13}C satellites for $^1J(^{13}\mathrm{C},^{13}\mathrm{C})$ in **31** by asterisks (coupling constants are given in Hz).

^{13}C(alkyne) chemical shifts of silylalkynyl Grignard reagents were measured and explained, supported by quantum chemical calculations. A successful strategy has been developed to prepare polyalkynylsilanes containing alternating silicon atoms and C≡C bonds.

Experimental Section

Starting materials and measurements

All syntheses and the handling of the samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. The deuterated solvent CD$_2$Cl$_2$ was distilled over CaH$_2$ in an atmosphere of argon. All other solvents were distilled from Na metal in an atmosphere of argon. Silicon halides, alkynes, ethynylmagnesium bromide in THF, and ^{n}BuLi (1.6 M in hexane) were commercial products and were used as received. NMR measurements: Bruker ARX 250, DRX 500: ^{1}H, ^{13}C, and ^{29}Si NMR [refocused INEPT [22, 28] based on $^1J(^{29}\mathrm{Si},^1\mathrm{H})$ = 200 Hz, $^{2,3}J(^{29}\mathrm{Si},^1\mathrm{H})$ = 25 Hz (Si-vinyl), 7 Hz (Si-Me) or 4–5 Hz (Si-Ph)]; Varian INOVA 400: ^{1}H, ^{13}C, ^{29}Si NMR; chemical shifts are given relative to Me$_4$Si [δ^1H(C$_6$D$_5$H) = 7.15, (CHDCl$_2$) = 5.31, (C$_6$D$_5$CD$_2$H) = 2.08 (± 0.01); δ^{13}C (C$_6$D$_6$) = 128.2, (CD$_2$Cl$_2$) = 53.8, (C$_6$D$_5$*C*D$_3$) = 20.4 (± 0.1); δ^{29}Si = 0 (± 0.1) for $\Xi(^{29}\mathrm{Si})$ = 19.867184 MHz]. EI-MS spectra: Finnigan MAT 8500 spectrometer (ionisation energy 70 eV) with direct inlet. The m/z data refer to the isotopes ^{1}H, ^{12}C, ^{16}O, and ^{28}Si. IR spectra: Perkin Elmer Spec-

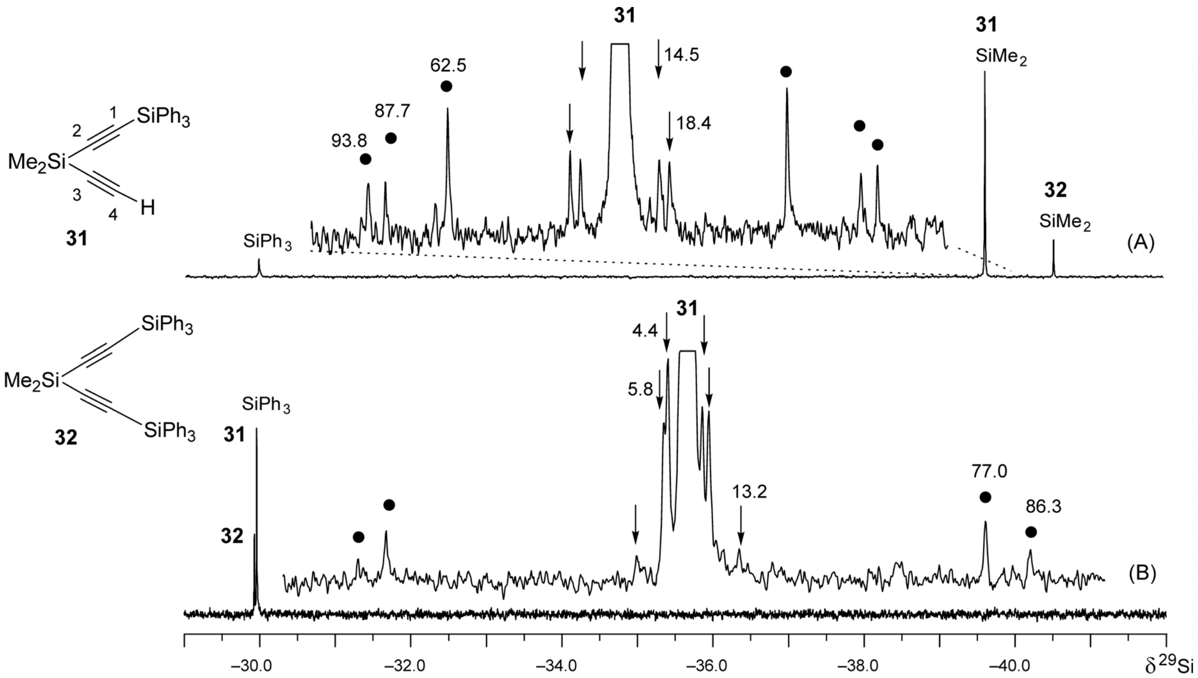
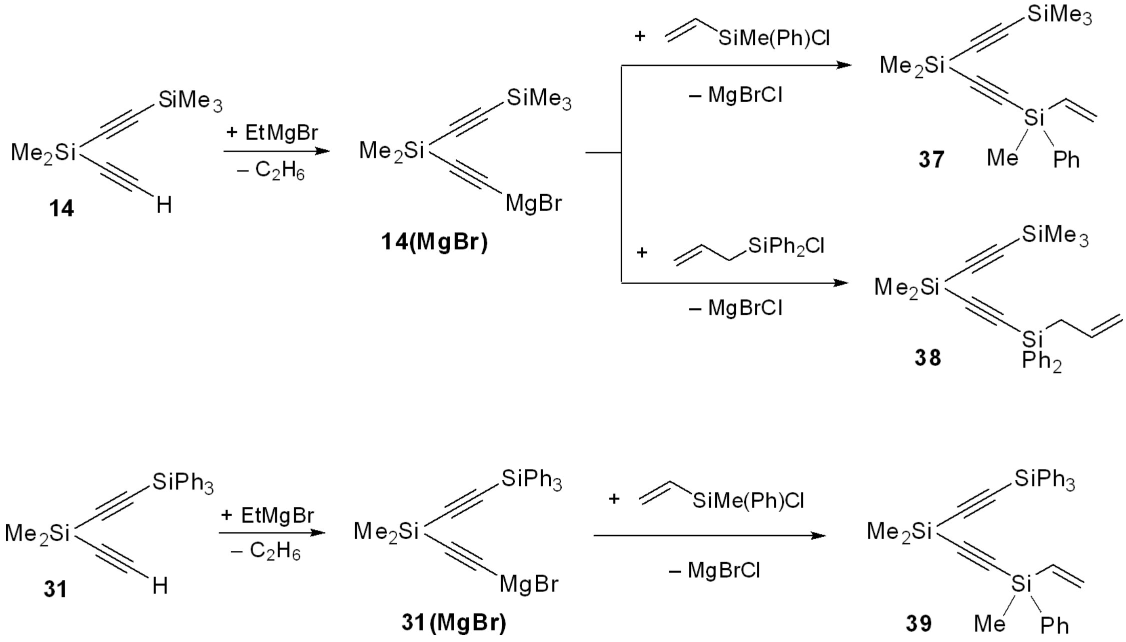


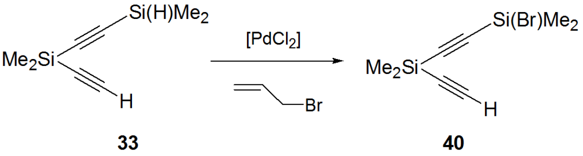
Fig. 4. 79.4 MHz ^{29}Si{^{1}H} NMR spectrum (refocused INEPT [22]) of the reaction mixture containing **31** and **32** (in CD_2Cl_2, at 23 °C). The ^{13}C satellites for $^{1}J(^{29}Si, ^{13}C)$ are marked by filled circles, for $^{2,3}J(^{29}Si, ^{13}C)$ by arrows (all coupling constants are given in Hz). (A) ^{29}Si{^{1}H} NMR spectrum for Me_2Si groups. (B) ^{29}Si{^{1}H} NMR spectrum for Ph_3Si groups.



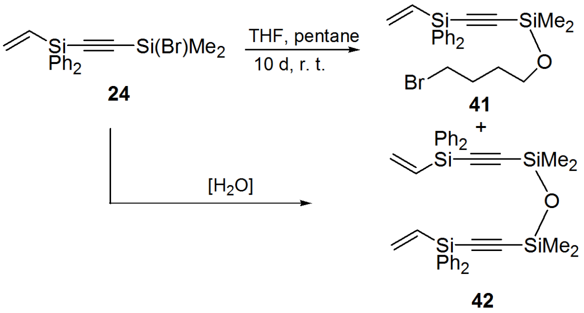
Scheme 4. Examples for the conversion of ethynyl(silylethynyl)silanes **14** and **31** into alkynyl(vinyl) (**37**, **39**) and allyl(alkynyl)silanes **38**.

Table 4. Comparison of selected bond lengths (pm) and bond angles (deg) for compounds **31** and $Ph_2(H)Si\text{-}C{\equiv}C\text{-}Si(H)Ph_2$ [25].

— **31** —		$Ph_2(H)Si\text{-}C{\equiv}C\text{-}Si(H)Ph_2$	
Si1–C1	183.9(12)		
Si1–C23	177.1(10)		
Si1–C21	185.1(11)		
Si1–C22	221.5(12)		
Si2–C2	184.2(11)	Si–C1	183.3(3)
Si2–C3	187.5(11)	Si–C2	186.2(2)
Si2–C9	188.2(10)	Si–C8	186.1(2)
Si2–C15	185.3(10)		
C1–C2	119.5(13)	C1–C1A	120.8(5)
C23–C24	106.0(2)		
C1–Si1–C23	110.1(6)		
C1–Si1–C21	109.6(5)		
C1–Si1–C22	106.9(4)		
C21–Si1–C23	109.9(5)		
C22–Si1–C23	107.6(4)		
C2–Si2–C3	108.7(5)	C1–Si–C2	112.84(9)
C2–Si2–C9	108.5(5)	C1–Si–C8	108.13(10)
C2–Si2–C15	108.8(5)		



Scheme 5. Example for the conversion of an Si-H into an Si-Br function in the presence of an ethynyl group.



Scheme 6. Example of the reaction of an alkynyl(bromo)-(vinyl)silane with THF. The product **42** is also obtained by hydrolysis.

trum 6 X (FT-IR-System). Melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

All quantum chemical calculations were carried out using the GAUSSIAN 03 program package [21]. Geometries were optimized at the B3LYP/6-311+G(d,p) level of theory, and nuclear shieldings were calculated [20] at the same level. The nuclear shielding constants were converted into chemical shifts $\delta^{13}C$ and $\delta^{29}Si$, using the calculated shielding constants for $SiMe_4$ with σ (^{13}C) = 184.0 and σ (^{29}Si) = 340.1, respectively.

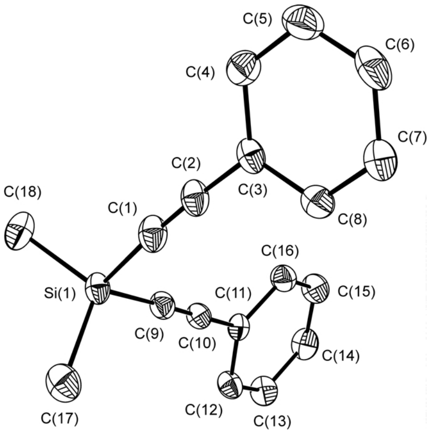


Fig. 5. Molecular structure of dimethyldi(phenylethynyl)-silane (**6c**) (ORTEP, 50 % probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths and angles are summarized in Table 3.

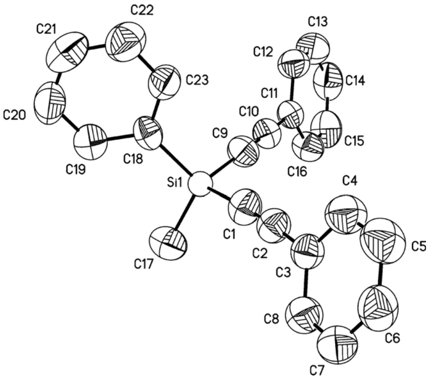


Fig. 6. Molecular structure of methyl(phenyl)di(phenylethynyl)silane (**10c**) (ORTEP, 40 % probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths and angles are summarized in Table 3.

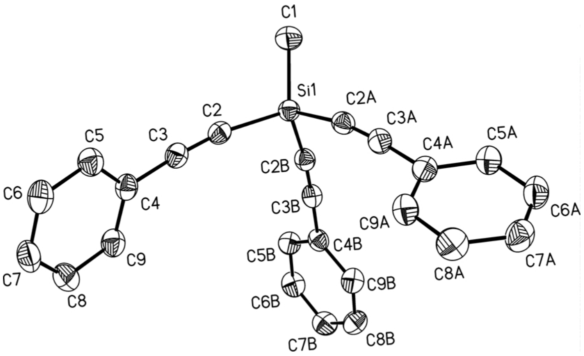


Fig. 7. Molecular structure of $MeSi(C{\equiv}C\text{-}Ph)_3$ (**16c**) (ORTEP, 40 % probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths and angles are summarized in Table 3.

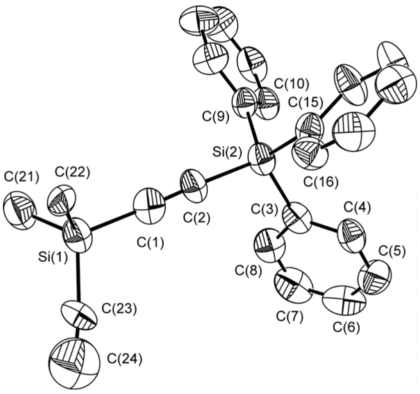


Fig. 8. Molecular structure of (HC≡C)$SiMe_2$(C≡C-$SiPh_3$) (**31**) (ORTEP, 30 % probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond lengths and angles are summarized in Table 4.

Most alkynyl silanes **1** – **20** (Scheme 1) and some others (Schemes 2 and 3) were prepared by well documented standard procedures [9] *via* the reaction of the silicon chlorides with freshly prepared alkynyllithium reagents in hexane. After filtering off the LiCl and removing the solvent *in vacuo*, the alkynylsilanes could be used, in most cases, for the NMR measurements (as well as for synthesis) without further purification. In the cases of alkynyl(chloro)silanes, mixtures were obtained which could be readily separated by fractional distillation (as described below for the example of the reaction of $HSiCl_3$ with Li-C≡C-^{n}Bu). The reaction of silicon chlorides with ethynylmagnesium bromide in THF was used to prepare **1** and **13**, and the products were removed from the reaction mixture together with the solvent (THF), and kept as solutions in THF. Compound **14** has been described [11a], and for convenience, we report our slightly modified procedure (*vide infra*).

*Dialkynylsilanes **2a, d***

Solid $LiAlH_4$ (0.57 g, 16.8 mmol) was added in one portion at r. t. to the solution of the respective dialkynyl(chloro)-silane **5** (3.5 mmol) in benzene (5 mL), and stirring of the mixture was continued for 72 h. All insoluble materials were filtered off, and the solvent was evaporated (20 Torr) to leave the alkynylsilanes **2a** as colorless liquids (93 % yield).

2a: ^{1}H NMR (250 MHz, C_6D_6, 23 °C): δ = 0.69 (t, 6H, CH_3), 1.10 – 1.30 (m, 8H, CH_2-CH_2), 1.92 (tt, 4H, ≡–CH_2), 4.47 (t, $^5J(^1H,^1H)$ = 1.2 Hz, 2H, Si-H, $^1J(^{29}Si,^1H)$ = 226.7 Hz).

2d: ^{1}H NMR (250 MHz, C_6D_6, 23 °C): δ = 0.01 (s, 18H, $SiMe_3$), 4.44 (s, 2H, Si-H, $^1J(^{29}Si,^1H)$ = 231.3 Hz).

*Chloro(dihexynyl)silane (**5a**) and trihexynylsilane (**15a**)*

A freshly prepared suspension of hexynyllithium (61 mmol) in hexane (40 mL) was cooled to −78 °C, and a solution of $HSiCl_3$ (1.94 mL, 60 mmol) in hexane (2 mL) was added dropwise. The mixture was warmed to r. t., and heated at reflux for 1 h. Insoluble materials were filtered off, and readily volatile materials were removed *in vacuo*. A yellowish liquid (4.48 g) was left which gave after fractional distillation dichloro(hexynyl)silane (11.2 %, 0.39 g; b. p. 30 °C/2 × 10^{-1} Torr), chloro(dihexynyl)silane (**5a**) (19.4 %, 0.85 g; b. p. 85 °C/2 × 10^{-1} Torr), and trihexynylsilane (**15a**) (35.2 %,1.85 g; b. p. 127 °C/2 × 10^{-1} Torr) as colorless liquids.

Dichloro(hexynyl)silane: ^{1}H NMR (250 MHz, C_6D_6): δ = 0.68 (t, 3H, CH_3), 1.11 (m, 4H, CH_2-CH_2), 1.81 (t, 2H, ≡C-CH_2), 5.38 (s, 1H, Si-H, $^1J(^{29}Si,^1H)$ = 314.7 Hz). – ^{13}C NMR (62.9 MHz; C_6D_6): $\delta[J(^{29}Si,^{13}C)]$ = 77.3 [136.8] (Si-C≡), 114.5 [28.6] (≡C-^{n}Bu), 13.5, 19.5, 22.0, 29.7 (^{n}Bu). – ^{29}Si NMR (49.7 MHz; C_6D_6): δ = −30.7. – IR (C_6D_6): ν (cm^{-1}) = 2183 (C≡C), 2145 (SiH).

5a: ^{1}H NMR (250 MHz, C_6D_6, 23 °C): δ = 0.65 (t, 6H, CH_3), 1.17 (m, 8H, CH_2-CH_2), 1.87 (t, 4H, ≡C-CH_2), 5.17 (s, 1H, Si-H,$^1J(^{29}Si, ^1H)$ = 276.1 Hz). – IR (C_6D_6): ν (cm^{-1}) = 2185 (C≡C), 2147 (SiH).

15a: ^{1}H NMR (250 MHz, C_6D_6, 23 °C): δ = 0.67 (t, 9H, CH_3), 1.20 (m, 12H, CH_2-CH_2), 1.90 (t, 6H, ≡C-CH_2), 4.83 (s, 1H, Si-H, $^1J(^{29}Si,^1H)$ = 237.9 Hz). – IR (C_6D_6): ν (cm^{-1}) = 2186 (C≡C), 2147 (SiH).

*Ethynyl(trimethylsilylethynyl)dimethylsilane (**14**)*

A solution of EtMgBr (6.8 mL, 6.8 mmol, 1 M in THF) in THF was added dropwise to a solution of **13** (9 mL, 7.0 mmol, 0.777 M in THF) in THF at 0 °C. The solution became yellow (**13(MgBr)**), was stirred for additional 1.5 h at r. t. and cooled to 0 °C. Then, Me_3SiCl (74 mg, 0.86 mL, 6.8 mmol) was added dropwise. The reaction mixture was stirred overnight, and then the solvent was removed (30 Torr), to leave an oily residue. The residue was extracted twice with portions of pentane (30 mL). Insoluble materials were filtered off, and pentane was removed *in vacuo* (20 Torr). The resulting mixture contained **14** together with **6d** (10 – 15 %). The residue was distilled twice *in vacuo* to give 0.669 g (55 %) of **14** as a colorless liquid (80 – 85 °C/10 Torr). – ^{1}H NMR (500 MHz, C_6D_6, 23 °C): δ = 0.09 (s, 9H, Me_3Si, $^2J(^{29}Si,^1H)$ = 6.6 Hz), 0.27 (s, 6H, Me_2Si, $^2J(^{29}Si,^1H)$ = 7.0 Hz), 2.00 (s, 1H, ≡CH, $^1J(^{13}C,^1H)$ = 238.4 Hz).

13(MgBr): ^{1}H NMR (500 MHz, THF, 23 °C): δ = 0.09 (s, 6H, CH_3), 1.80 (CH_2, THF), 2.58 (s, 2H, ≡CH), 3.6 (OCH_2, THF).

*Bromodimethylsilylethynyl(diphenyl)(vinyl)silane (**24**)*

The mixture of the silicon hydride **22** (1.41 g, 4.80 mmol) together with a 1.2-molar excess of allyl bromide (0.49 mL, 5.76 mmol) and $PdCl_2$ (3 mol %) was heated for 1 h at 70 °C. Insoluble materials were filtered off, unreacted allyl bromide was removed at reduced pressure, and the residue was distilled *in vacuo* to give 1.56 g (88 %) of the bromosilane **24** as a grey oil (130 – 135 °C/10^{-3} Torr). – ^{1}H NMR (250 MHz, C_6D_6, 23 °C): δ = 0.81 (s, 6H, $SiMe_2$), 6.05 (dd, 1H, =CH_2-*trans*, ^{3}J(H,H) = 19.4 Hz, ^{2}J(H,H) = 4.3 Hz), 6.34 (dd, 1H, =CH_2-*cis*, ^{3}J(H,H) = 14.4 Hz, ^{2}J(H,H) = 4.3 Hz), 6.49 (dd, 1H, =CH-, ^{3}J(H,H) = 19.4 Hz, ^{3}J(H,H) = 14.4 Hz), 7.44 (m, 6H, Ph), 7.67 (m, 4H, Ph).

NMR spectra in C_6D_6 (^{1}H, ^{13}C and ^{29}Si NMR) and EI-MS spectra indicated that the distillation residue consisted mainly of **42**. When the bromosilane **24** was dissolved in THF and pentane and left at r. t. for 10 d, the presence of **41** (*ca.* 80 %) and **42** (*ca.* 20 %) was evident from ^{1}H, ^{13}C and ^{29}Si NMR spectra.

*4-Bromobutoxydimethylsilylethynyl(diphenyl)(vinyl)silane (**41**)*: ^{1}H NMR (250 MHz, CD_2Cl_2, 23 °C): δ = 0.34 (s, 6H, $SiMe_2$), 1.72, 1.95 (m, m, 2H, 2H, CCH_2C), 3.43 (t, 2H, $BrCH_2$, ^{3}J(H,H) = 6.7 Hz), 3.79 (t, 2H, OCH_2, ^{3}J(H,H) = 6.2 Hz), 6.03 (dd, 1H, =CH_2-*trans*, ^{3}J(H,H) = 19.4 Hz, ^{2}J(H,H) = 4.1 Hz), 6.31 (dd, 1H, =CH_2-*cis*, ^{3}J(H,H) = 14.5 Hz, ^{2}J(H,H) = 4.1 Hz), 6.48 (dd, 1H, =CH-, ^{3}J(H,H) = 19.4 Hz, ^{3}J(H,H) = 14.5 Hz), 7.14 (m, 6H, Ph), 7.78 (m, 4H, Ph).

*1,1,3,3-Tetramethyl-1,3-bis[diphenyl(vinyl)silylethynyl]-disiloxane (**42**)*: ^{1}H NMR (250 MHz, C_6D_6, 23 °C): δ = 0.34 (s, 12H, $SiMe_2$), 6.07 (d, 2H, =CH_2-*trans*, ^{3}J(H,H) = 19.6 Hz), 6.07 (d, 2H, =CH_2-*cis*, ^{3}J(H,H) = 14.6 Hz), 6.40 (dd, 2H, =CH-, ^{3}J(H,H) = 19.6 Hz, ^{3}J(H,H) = 14.6 Hz), 7.14 (m, 12H, Ph), 7.78 (m, 8H, Ph). – EI-MS (70 eV) for $C_{36}H_{38}Si_4O$ (598.2): *m/z* (%) = 598 (26) $[M]^+$, 583 (15) $[M–CH_3]^+$, 571 (7) $[M–CH=CH_2]^+$, 520 (21) $[M–Ph]^+$, 494 (38) $[M–CH=CH_2–Ph]^+$, 463 (15), 401 (17), 386 (14), 259 (42), 233 (30), 209 (57), 197 (100), 159 (24), 135 (80), 105 (40).

*Synthesis of alkynyl(vinyl)silanes **25**, **26** and **27** (general procedure)*

To the solution of the alkynylmagnesium bromide (20 – 40 mmol, freshly prepared by treatment of the respective acetylene with EtMgBr) in 20 – 40 mL THF the equimolar amount of the bromide **23** was added at 0 °C within 0.5 – 1 h. The reaction mixture was allowed to reach ambient temperature and stirred for 1 h. The solvent was removed *in vacuo*, the residue was extracted with hexane, and insoluble materials were filtered off. After removing hexane *in vacuo* the residue was distilled at reduced pressure to give the alkynyl(vinyl)silanes **25**, **26** or **27**.

*Dimethyl(vinyl)silylethynyl(phenylethynyl)dimethylsilane (**25**)*: B. p. = 88 – 95 °C (8 × 10^{-3} Torr). – ^{1}H NMR (400 MHz, C_6D_6, 23 °C): δ = 0.35 (s, 6H, $SiMe_2$), 0.56 (s, 6H, $SiMe_2$), 6.04 (dd, 1H, =CH_2-*trans*, ^{3}J(H,H) = 20.0 Hz, ^{2}J(H,H) = 3.7 Hz), 6.10 (dd, 1H, =CH_2-*cis*, ^{3}J(H,H) = 14.5 Hz, ^{2}J(H,H) = 3.7 Hz), 6.27 (dd, 1H, =CH-, ^{3}J(H,H) = 20.0 Hz, ^{3}J(H,H) = 14.5 Hz, ^{2}J(^{29}Si, ^{1}H) = 7.5 Hz), 7.1 (m, 3H, Ph), 7.5 (m, 2H, Ph).

*1-(3-Dimethylamino)propynyl[dimethyl(vinyl)silylethynyl]dimethylsilane (**26**)*: B. p. = 91 – 96 °C (8 × 10^{-3} Torr). – ^{1}H NMR (400 MHz, C_6D_6, 23 °C): δ = 0.24 (s, 6H, Me_2Si), 0.39 (s, 6H, Me_2Si), 2.21 (s, 6H, NMe_2), 3.16 (s, 2H, CH_2N), 5.93 (dd, 1H, =CH_2-*trans*, ^{3}J(H,H) = 19.9 Hz, ^{2}J(H,H) = 3.9 Hz), 6.00 (dd, 1H, =CH_2-*cis*, ^{3}J(H,H) = 14.7 Hz, ^{2}J(H,H) = 3.9 Hz), 6.16 (dd, 1H, =CH-, ^{3}J(H,H) = 19.9 Hz, ^{3}J(H,H) = 14.7 Hz).

*Dimethylsilylethynyl[dimethyl(vinyl)silylethynyl]dimethylsilane (**27**)*: B. p. = 57 – 64 °C (5 × 10^{-3} Torr). – ^{1}H NMR (400 MHz, C_6D_6, 23 °C): δ = 0.16 (d, 6H, Me_2HSi, ^{3}J(H,H) = 3.8 Hz), 0.25 (s, 6H, Me_2Si), 0.39 (s, 6H, Me_2Si), 4.33 (sep, 1H, SiH, ^{3}J(H,H) = 3.8 Hz, ^{1}J(^{29}Si,^{1}H) = 203.4 Hz), 5.95 (dd, 1H, =CH_2-*trans*, ^{3}J(H,H) = 19.9 Hz, ^{2}J(H,H) = 3.8 Hz), 6.04 (dd, 1H, =CH_2-*cis*, ^{3}J(H,H) = 14.5 Hz, ^{2}J(H,H) = 3.8 Hz), 6.15 (dd, 1H, =CH-, ^{3}J(H,H) = 19.9 Hz, ^{3}J(H,H) = 14.5 Hz).

*Dimethylsilylethynyl[diphenyl(vinyl)silylethynyl]dimethylsilane (**28**)*

To the solution of **1MgBr** (5.69 mmol) in THF [freshly prepared by treatment of the solution of **1** (3.43 mL, 1.66 M in THF) in THF with EtMgBr (5.69 mL, 1 M in THF) at r. t., 1 h] the bromide **24** (2.11 g, 5.69 mmol) was added at 0 °C without any solvent. The rest of the bromide **24** was dissolved in pentane (1 mL) and added to the reaction mixture. The mixture was stirred for 1.5 h at r. t., readily volatile materials were removed *in vacuo*, and the oily residue was dissolved in pentane (40 mL). Insoluble materials were filtered off, and pentane was removed *in vacuo* to leave 0.20 g (94 %) of **28** as a colorless oil. – ^{1}H NMR (250 MHz, CD_2Cl_2, 23 °C): δ = 0.32 (d, 6H, *Me*$_2$HSi, ^{2}J(^{29}Si,^{1}H) = 7.8 Hz,^{3}J(H,H) = 3.8 Hz), 0.46 (s, 6H, Me_2Si, ^{2}J(^{29}Si,^{1}H) = 7.5 Hz), 4.19 (sep, 1H, SiH, ^{3}J(H,H) = 3.8 Hz, ^{1}J(^{29}Si,^{1}H) = 202.6 Hz), 6.06 (dd, 1H, =CH_2-*trans*, ^{3}J(H,H) = 19.4 Hz, ^{2}J(H,H) = 4.2 Hz), 6.34 (dd, 1H, =CH_2-*cis*, ^{3}J(H,H) = 14.5 Hz, ^{2}J(H,H) = 4.2 Hz), 6.51 (dd, 1H, =CH-, ^{3}J(H,H) = 19.4 Hz, ^{3}J(H,H) = 14.5 Hz), 7.45 (m, 6H, Ph), 7.70 (m, 4H, Ph).

*Bromodimethysilylethynyl[dimethyl(vinyl)silylethynyl]dimethylsilane (**29**)*

The synthesis was carried out as described for **24**, starting from the silicon hydride **27**, allyl bromide and $PdCl_2$ (3 mol %). The oily residue was distilled to give the bromide **29** (86 %). B. p. = 79 – 86 °C (8 × 10^{-3} Torr). – ^{1}H NMR (400 MHz, C_6D_6, 23 °C): δ = 0.24 (s, 6H, Me_2Si(vin)), 0.34 (s, 6H, Me_2Si), 0.52 (s, 6H, Me_2BrSi), 5.93 (dd, 1H, =CH_2-*trans*, ^{3}J(H,H) = 20.0 Hz, ^{2}J(H,H) = 3.7 Hz), 6.00 (dd, 1H, =CH_2-*cis*, ^{3}J(H,H) = 14.5 Hz, ^{2}J(H,H) = 3.7 Hz), 6.15 (dd, 1H, =CH-, ^{3}J(H,H) = 20.0 Hz, ^{3}J(H,H) = 14.5 Hz).

*Bromodimethylsilylethynyl[diphenyl(vinyl)silylethynyl]dimethylsilane (**30**)*

The synthesis was carried out as described for **24**, starting from 2.07 g (5.53 mmol) of **28**, 0.56 mL (6.64 mmol) allyl bromide and $PdCl_2$ (3 mol %). Readily volatile materials were removed *in vacuo*, and the oily residue was dissolved in pentane (30 mL). Insoluble materials were filtered off, and pentane was removed *in vacuo* to leave 2.23 g (89 %) of **30** as grey oil. – ^{1}H NMR (250 MHz, CD_2Cl_2, 23 °C): δ = 0.39 (s, 6H, Me_2Si), 0.71 (s, 6H, Me_2BrSi), 5.98 (dd, 1H, =CH_2-*trans*, ^3J(H,H) = 19.4 Hz, ^2J(H,H) = 4.2 Hz), 6.26 (dd, 1H, =CH_2-*cis*, ^3J(H,H) = 14.4 Hz, ^2J(H,H) = 4.2 Hz), 6.40 (dd, 1H, =CH-, ^3J(H,H) = 19.4 Hz, ^3J(H,H) = 14.4 Hz), 7.37 (m, 6H, Ph), 7.62 (m, 4H, Ph).

*Ethynyl(triphenylsilylethynyl)dimethylsilane (**31**)*

A solution of EtMgBr (12.96 mL, 12.96 mmol, 1 M in THF) in THF was added dropwise to a solution of **13** (40 mL, 12.96 mmol, 0.324 M in THF) in THF at 0 °C. The mixture was stirred for 1.5 h at r. t., cooled to 0 °C, and Ph_3SiCl, (3.82 g, 12.86 mmol) was added. The reaction mixture was stirred overnight, the solvent was removed *in vacuo*, and the resulting solid was extracted with portions of hexane (30 mL) and toluene (15 mL). After filtration the solvent was removed *in vacuo* to give a mixture containing **31** (70 – 80 %), **32** and Ph_3SiCl. The mixture was distilled *in vacuo* (150 – 170 °C/2 × 10^{-3} Torr) to give a mixture containig **31** and Ph_3SiCl. This mixture was dissolved in hexane (5 mL) and crystallized at −20 °C to give 2.16 g (46 %) of **31** as colorless crystals (m. p. 56 – 59 °C). The residue of the distillation contained **32**.

31: ^{1}H NMR (400 MHz, CD_2Cl_2, 23 °C): δ = 0.45 (s, 6H, Me_2Si), 2.58 (s, 1H, ≡CH, $^1J(^{13}C,^1H)$ = 240.0 Hz), 7.43 (m, 9H, Ph), 7.66 (m, 6H, Ph). **32**: ^{1}H NMR (CD_2Cl_2, 23 °C): δ = 0.60 (s, 6H, Me_2Si), 7.47 (m, 18H, Ph), 7.76 (m, 12H, Ph).

*Ethynyl(dimethylsilylethynyl)dimethylsilane (**33**)*

The synthesis was carried out as described for **14**, starting from **13** (35 mL, 8.05 mmol, 0.23 M in THF), EtMgBr (8.05 mL, 8.05 mmol, 1 M in THF) and $Me_2Si(H)Cl$, (760 mg, 0.89 mL, 8.05 mmol). The resulting mixture contained **33** together with **34** (15 %). The residue was distilled *in vacuo* to give 0.65 g (49 %) of **33** as a colorless liquid (58 – 62 °C/10 Torr). – ^{1}H NMR (250 MHz, C_6D_6, 23 °C): δ = 0.05 (d, 6H, Me_2HSi, ^3J(H,H) = 3.8 Hz), 0.24 (s, 6H, Me_2Si, $^2J(^{29}Si,^1H)$ = 7.6 Hz), 2.08 (s, 1H, ≡CH, $^1J(^{13}C,^1H)$ = 237.6 Hz), 4.24 (sep, 1H, SiH, ^3J(H,H) = 3.8 Hz, $^1J(^{29}Si,^1H)$ = 202.9 Hz).

*Ethynyl[dimethyl(vinyl)silylethynyl]dimethylsilane (**35**)*

The synthesis was carried out as described for **14**, starting from a solution of **13** (4 mL, 13.76 mmol, 3.44 M in THF) in THF (10 mL), EtMgBr (13.76 mmol, 1 M in THF) and $Me_2Si(vin)Cl$, (1.66 g, 1.89 mL, 13.76 mmol). The resulting mixture contained **35** together with **36** (10 – 15 %). The residue was distilled twice *in vacuo* to give 1.82 g (69 %) of **35** as a colorless liquid (90 – 100 °C/11 Torr). – ^{1}H NMR (400 MHz, C_6D_6, 23 °C): δ = 0.16 (s, 6H, $SiMe_2$(vin)), 0.25 (s, 6H, $SiMe_2$), 2.02 (s, 1H, ≡CH, $^1J(^{13}C,^1H)$ = 239.1 Hz), 5.85 (dd, 1H, =CH_2-*trans*, ^3J(H,H) = 19.8 Hz, ^2J(H,H) = 3.7 Hz), 5.89 (dd, 1H, =CH_2-*cis*, ^3J(H,H) = 14.5 Hz, ^2J(H,H) = 3.7 Hz), 6.08 (dd, 1H, =CH-, ^3J(H,H) = 19.8 Hz, ^3J(H,H) = 14.5 Hz).

*Trimethylsilylethynyl[methyl(phenyl)(vinyl)silylethynyl]dimethylsilane (**37**)*

A solution of **14** (235 mg, 1.3 mmol) in THF (2 mL) was cooled to 0 °C, and a solution of EtMgBr (1.3 mL, 1.3 mmol, 1 M in THF) in THF was added dropwise. The reaction mixture was allowed to reach ambient temperature, stirred for 1.5 h and cooled to 0 °C. A solution of Me(Ph)(vin)SiCl, (238 mg, 0.23 mL, 1.3 mmol) in THF (2 mL) was added dropwise. The reaction mixture was stirred overnight, and then the volatile materials were removed *in vacuo*. The oily residue was dissolved in hexane (15 mL), insoluble materials were filtered off, and hexane was removed *in vacuo* to give 343 mg (81 %) of the vinylbisacetylene **37** as a colorless oil. – ^{1}H NMR (500 MHz, CD_2Cl_2, 23 °C): δ = 0.29 (s, 9H, Me_3Si, $^2J(^{29}Si,^1H)$ = 7.0 Hz), 0.45 (s, 6H, Me_2Si, $^2J(^{29}Si,^1H)$ = 7.0 Hz), 0.60 (s, 3H, MeSi, $^2J(^{29}Si,^1H)$ = 7.0 Hz), 6.05 (dd, 1H, =CH_2-*trans*, ^3J(H,H) = 19.7 Hz, ^2J(H,H) = 4.0 Hz), 6.25 (dd, 1H, =CH_2-*cis*, ^3J(H,H) = 14.5 Hz, ^2J(H,H) = 4.0 Hz), 6.34 (dd, 1H, =CH-, ^3J(H,H) = 19.7 Hz, ^3J(H,H) = 14.5 Hz), 7.47 (m, 3H, Ph), 7.72 (m, 2H, Ph).

*Trimethylsilylethynyl[allyl(diphenyl)silylethynyl]dimethylsilane (**38**)*

The synthesis was carried out as described for **37**, starting from **14**, EtMgBr and allyl(chloro)diphenylsilane. The oily residue was distilled to give **38** (b. p. = 121 – 130 °C (5 × 10^{-3} Torr)). – ^{1}H NMR (400 MHz, C_6D_6, 23 °C): δ = 0.21 (s, 6H, $SiMe_2$), 0.31 (s, 9H, $SiMe_3$), 2.06 (dt, 2H, CH_2, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 1.1 Hz, $^2J(^{29}Si,^1H)$ = 9.0 Hz), 4.85 (m, 1H, =CH_2-*cis*), 4.91 (m, 1H, =CH_2-*trans*), 5.87 (ddt, 1H, =CH-, ^3J(H,H) = 16.9 Hz, ^3J(H,H) = 9.9 Hz, ^3J(H,H) = 7.9 Hz), 7.25 (m, 6H, Ph), 7.72 (m, 4H, Ph).

*Triphenylsilylethynyl[methyl(phenyl)(vinyl)silylethynyl]dimethylsilane (**39**)*

A solution of EtMgBr (0.80 mL, 0.80 mmol, 1 M in THF) in THF was added dropwise to a solution of **31** (237 mg, 0.65 mmol) in THF (4 mL). The reaction mixture was kept stirring for 2 h and cooled to 0 °C. A solution of Me(Ph)(vin)SiCl, (146 mg, 0.141 mL, 0.80 mmol) in THF (4 mL) was added dropwise. The reaction mixture was

Table 5. Crystallographic data of **6c**, **10c**, **16c**, and **31**.

	6c	**10c**	**16c**	**31**
Formula	$C_{18}H_{16}Si$	$C_{23}H_{18}Si$	$C_{25}H_{18}Si$	$C_{24}H_{22}Si_2$
Formula weight	260.40	322.46	346.48	366.60
Crystal	colorless prism	colorless plate	colorless prism	colorless prism
Dimensions, mm^3	$1.26 \times 0.89 \times 0.69$	$0.35 \times 0.18 \times 0.12$	$1.02 \times 0.37 \times 0.29$	$0.28 \times 0.19 \times 0.17$
Temperature, K	133(2)	293(2)	133(2)	293(2)
Crystal system	orthorhombic	monoclinic	trigonal	monoclinic
Space group	*Pbca*	$P2_1/c$	*R*3	$P2_1/c$
Lattice parameters				
a, pm	1461.16(15)	3678.0(7)	1725.1(2)	1510.4(3)
b, pm	1140.58(11)	597.79(12)		1165.1(2)
c, pm	1838.79(19)	1727.1(4)	565.50(10)	2530.3(5)
β, deg	90	99.0(3)	90	90.52(3)
γ, deg	90	90	120	90
Z	8	8	3	8
Absorption coefficient μ mm^{-1}	0.1	0.1	0.1	0.2
Radiation; λ, Å	MoK_α, 71.073 pm, graphite monochromator			
Measuring range ϑ, deg	2.2 – 25.7	2.4 – 26.1	2.4 – 25.6	1.9 – 26.1
Reflections collected	10753	20571	6315	32279
Independ. refl. $[I \geq 2\sigma(I)]/R_{\text{int.}}$	2127 / 0.092	2134 / 0.076	1146 / 0.089	1682 / 0.102
Absorption correction	none[a]	none[a]	none[a]	none[a]
Refined parameters	236	433	103	459
wR_2/R_1 $[I \geq 2\sigma(I)]$	0.132 / 0.052	0.086 / 0.046	0.074 / 0.029	0.133 / 0.055
Max./min. residual electron density, e pm$^{-3} \times 10^{-6}$	0.64 / −0.39	0.16 / −0.11	0.19 / −0.18	0.50 / −0.17

[a] Absorption corrections did not improve the parameter set.

stirred overnight, then the volatile materials were removed *in vacuo*, and the oily residue was dissolved in hexane (30 mL). Insoluble materials were filtered off, and hexane was removed *in vacuo*. The resulting mixture contained **39** (70 %) together with Me(Ph)(vin)SiCl and **31**. Volatile materials were removed by distillation (5×10^{-3} Torr). The distillation residue (147 mg, 28 %) was a colorless oil, containing **39** ($\geq$ 90 %) and several unidentified side products (5 – 10 %). – ^{1}H NMR (500 MHz, CD_2Cl_2, 23 °C): δ = 0.55 (s, 6H, Me_2Si, $^2J(^{29}Si,^1H)$ = 7.7 Hz), 0.62 (s, 3H, MeSi, $^2J(^{29}Si,^1H)$ = 7.3 Hz), 6.07 (dd, 1H, =CH_2-*trans*, ^3J(H,H) = 19.7 Hz, ^2J(H,H) = 4.0 Hz), 6.24 (dd, 1H, =CH_2-*cis*, ^3J(H,H) = 14.4 Hz, ^2J(H,H) = 4.0 Hz), 6.36 (dd, 1H, =CH-, ^3J(H,H) = 19.7 Hz, ^3J(H,H) = 14.4 Hz), 7.46 (m, 12H, Ph), 7.76 (m, 8H, Ph).

*Ethynyl(bromodimethylsilylethynyl)dimethylsilane (**40**)*

The synthesis was carried out as described for **24**, starting from **33**, allyl bromide and $PdCl_2$ (3 mol %). Readily volatile materials were removed *in vacuo*, and the oily residue was dissolved in pentane (30 mL). Insoluble materials were filtered off, and pentane was removed *in vacuo* to give **40** as a grey oil. – ^{1}H NMR (250 MHz, C_6D_6, 23 °C): δ = 0.18 (s, 6H, Me_2Si), 0.42 (s, 6H, Me_2BrSi), 2.04 (s, 1H, ≡CH, $^1J(^{13}C,^1H)$ = 238 Hz).

*X-Ray structure analyses of compounds **6c**, **10c**, **16c**, and **31***

The X-ray crystal structure analyses of **6c** (crystals from diethylether) and **16c** (crystals from hexane) were carried out at 133(2) K for single crystals (selected in perfluorinated oil [29] at r. t.) using a Stoe IPDS II (MoK_α, 71.069 pm) system equipped with an Oxford Cryostream low-temperature unit. Crystals of appropriate size of **10c** (crystals from hexane) and **31** (crystals after distillation) were sealed under argon in Lindemann capillaries, and the data collections were carried out at 20 °C (Stoe IPDS I). Structure solutions and refinements were accomplished using SIR97 [30], SHELXL97 [31] and WINGX [32]. Pertinent data are given in Table 5. CCDC 768291 (**6c**), 768293 (**10c**), 768292 (**16c**), and 768294 (**31**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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