

Selective Synthesis of Functional Alkynylmono- and -trisilanes

Florian Hoffmann,^[a] Jörg Wagler,^[a] and Gerhard Roewer*^[a]

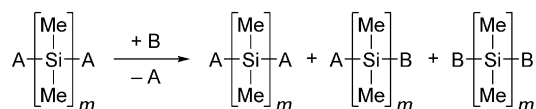
Keywords: Alkyne complexes / Alkynylsilanes / Cobalt / Molybdenum / Protecting groups

The selective synthesis of functional alkynylsilanes $\text{RC}\equiv\text{C}-(\text{SiMe}_2)_m\text{-X}$ ($m = 1, 3$) was investigated. Monofunctionalization with or without protecting groups gave moderate to good yields of alkynyldimethylmonosilanes $\text{RC}\equiv\text{CMe}_2\text{SiX}$ [$\text{R} = \text{Ph}$, $\text{X} = \text{Cl}$ (**1**), NEt_2 (**2**), OMe (**3**), H (**4**), Br (**5**), I (**6**), Cp (**8**), $\text{C}_5\text{H}_4\text{Li}$ (**10**), Ph (**11**); $\text{R} = \text{Pr}$, $\text{X} = \text{Ph}$ (**12**)]. Compounds **4** and **8** were converted into the (alkyne)transition-metal complexes $4\text{-Cp}_2\text{Mo}_2(\text{CO})_4$ (**13**) and $8\text{-Co}_2(\text{CO})_6$ (**14**), respectively, which

were characterized by X-ray diffraction. Stepwise extension and functionalization of the silane chain starting from 1-chloro-2-(diethylamino)tetramethyldisilane ($\text{Et}_2\text{NMe}_2\text{Si-SiMe}_2\text{Cl}$) yielded the trisilanes $\text{Ph}-(\text{SiMe}_2)_3\text{-X}$ [$\text{X} = \text{NEt}_2$ (**18**), OMe (**19**), Cl (**20**), H (**21**), $\text{C}\equiv\text{CPh}$ (**22**), $\text{C}\equiv\text{CPr}$ (**23**)]. The synthesized compounds were characterized by NMR and IR spectroscopy, **4**, **11**, **13**, and **14** also by UV/Vis spectroscopy.

Introduction

α,ω -Heterodifunctional methylsilanes $\text{A}-(\text{SiMe}_2)_m\text{-B}$ are key compounds in organosilicon chemistry. They are mostly prepared by monofunctionalization of the corresponding α,ω -homodifunctional silanes (Scheme 1).



Scheme 1. Preparation of α,ω -heterodifunctional methylsilanes by monofunctionalization.

This method works quite well for many monosilanes but loses selectivity toward the desired product with increasing chain length, finally approaching the statistical product distribution of 25:50:25. Eventually, this leads to separation difficulties and diminished yields. Thus, alternative and especially more selective routes are desirable.

Our group faced this problem when we started a study on the preparation of functional alkynylsilanes. They were required for the synthesis of (alkynylsilyl)transition-metal complexes,^[1,2] therefore their functionalities had to include halogen (for salt elimination), hydrogen (for oxidative addition), and cyclopentadienyl and phenyl groups (for cyclopentadienyl and arene complexation). In this article we report the selective synthesis of these functional alkynylmono- and -trisilanes by the use of protecting groups.

Results and Discussion

Monosilanes

The first synthetic target was chlorodimethyl(phenylethynyl)silane ($\text{PhC}\equiv\text{CMe}_2\text{SiCl}$, **1**).^[3] The preparation of this compound by monofunctionalization of dichlorodimethylsilane (Me_2SiCl_2) with phenylethynylmagnesium or -alkali compounds has a low selectivity; only moderate yields of 30–37% (Mg)^[3–5] and 44–55% (Li , Na)^[6,7] are reported. Our own experiments with phenylethynylmagnesium bromide ($\text{PhC}\equiv\text{CMgBr}$) gave 27–38% of **1** (as judged by ^{29}Si NMR spectroscopy; other products: dimethylbis(phenylethynyl)silane [$\text{Me}_2\text{Si}(\text{C}\equiv\text{CPh})_2$] and dichlorodimethylsilane (Me_2SiCl_2)) and thus confirmed the literature results. A catalyzed reaction between Me_2SiCl_2 and phenylacetylene ($\text{PhC}\equiv\text{CH}$) gives better yields (60–80%) but requires high-pressure equipment and is therefore not an easily accessible preparation method.^[8] In conclusion, the monofunctionalization of Me_2SiCl_2 appeared not to be the optimum synthetic route to **1**.

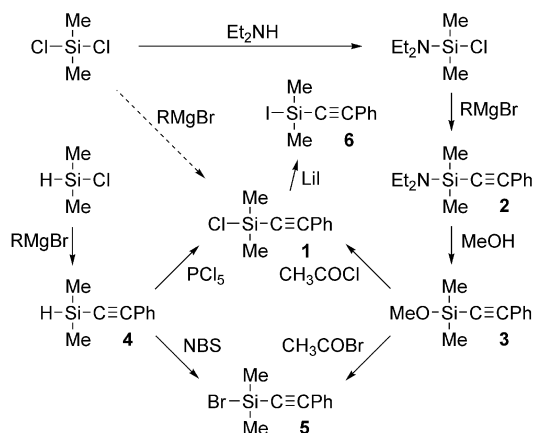
Hence, all further preparation attempts comprised the use of protecting groups. Two routes, starting from chloro-(diethylamino)dimethylsilane ($\text{Et}_2\text{NMe}_2\text{SiCl}$) and chlorodimethylsilane (HMe_2SiCl), respectively, were applied (Scheme 2).

Alkynylation of $\text{Et}_2\text{NMe}_2\text{SiCl}$, which is easily available from Me_2SiCl_2 and diethylamine (Et_2NH) in 81% yield,^[9,10] with $\text{PhC}\equiv\text{CMgBr}$ gave (diethylamino)dimethyl(phenylethynyl)silane ($\text{PhC}\equiv\text{CMe}_2\text{SiNEt}_2$, **2**)^[11,12] in 78% yield. Reaction of **2** with methanol^[13] yielded 91% of methoxydimethyl(phenylethynyl)silane ($\text{PhC}\equiv\text{CMe}_2\text{SiOMe}$, **3**),^[4,14] which reacted with acetyl chloride (CH_3COCl) to give a 90% yield of **1**. The total yield was 64% based on $\text{Et}_2\text{NMe}_2\text{SiCl}$ and 52% based on Me_2SiCl_2 , which is still moderate

[a] Institut für Anorganische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Str. 29, 09596 Freiberg, Germany
Fax: +49-3731-39-4058

E-mail: Gerhard.Roewer@chemie.tu-freiberg.de

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejic.200900769>.

Scheme 2. Syntheses of alkynylsilanes **1–6** ($R = \text{PhC}\equiv\text{C}$).

and comparable to the use of alkynylalkali salts but distinctly better than by the unprotected Grignard route.

The reaction of $\text{PhC}\equiv\text{CMgBr}$ with HMe_2SiCl gave dimethyl(phenylethynyl)silane ($\text{PhC}\equiv\text{CMe}_2\text{SiH}$, **4**)^[15] in 74% yield. Compound **4**, which is also commercially available (Fluka), is both an intermediate for the preparation of **1** and a target molecule itself (for oxidative addition). The chlorination of **4** to obtain **1** was examined with hydrogen chloride (HCl), tetrachloromethane [CCl_4 ; with and without aluminum chloride (AlCl_3)], ferric chloride (FeCl_3), sulfur chloride (SO_2Cl_2), and phosphorus pentachloride (PCl_5), with the lattermost giving the best results.^[16] The other reagents did not react or led to side products. The preparation of **1** was thus easily accomplished with PCl_5 in 85% yield. The total yield based on HMe_2SiCl was 63%.

In conclusion the most effective (but also most expensive) preparation method for **1** is the chlorination of commercially available **4** with PCl_5 . Nevertheless, functionalization with the use of a protecting group is a competitive route because of its lower cost (cf. Table 1).

Silyl bromides and iodides are better electrophiles than silyl chlorides and thus facilitate the preparation of silyl transition-metal complexes. Hence, feasible syntheses of bromodimethyl(phenylethynyl)silane ($\text{PhC}\equiv\text{CMe}_2\text{SiBr}$, **5**)^[17] and iododimethyl(phenylethynyl)silane ($\text{PhC}\equiv\text{CMe}_2\text{SiI}$, **6**)^[16] were desirable. As a result of the experiments on the preparation of **1**, synthesis routes starting from dibromo- and diiododimethylsilane were suspended from the beginning.

Instead, for **5** we applied the amino-protected and the halogenation route (Scheme 2). Reaction of **2** with methanol and subsequently excess acetyl bromide gave **5** in 71% yield based on $\text{Et}_2\text{NMe}_2\text{SiCl}$ and 58% based on Me_2SiCl_2 . The bromination of **4** was examined with elemental bromine (Br_2), hydrogen bromide (HBr), tetrabromomethane (CBr_4), and *N*-bromosuccinimide (NBS), with NBS giving the best results.^[16] The other reagents did not react or led to side products. Thus, **5** was obtained in 70% yield based on **4** and 52% based on HMe_2SiCl . In conclusion, both routes gave comparable results. The somewhat lower yield of the bromination route is balanced by the higher purity of the product (98% vs. 95% by NMR spectroscopy).

Because of the difficult handling of acetyl iodide the amino-protected route was not applicable to the synthesis of **6**. Additionally, the iodination of **4** with elemental iodine proved to be too slow to be of preparative usefulness. Finally, only halide exchange of **1** with lithium iodide (LiI) in dichloromethane was successful (Scheme 2). The hitherto unknown iodosilane **6** was thus synthesized in 79% yield with 90% purity (the balance is unreacted **1**).

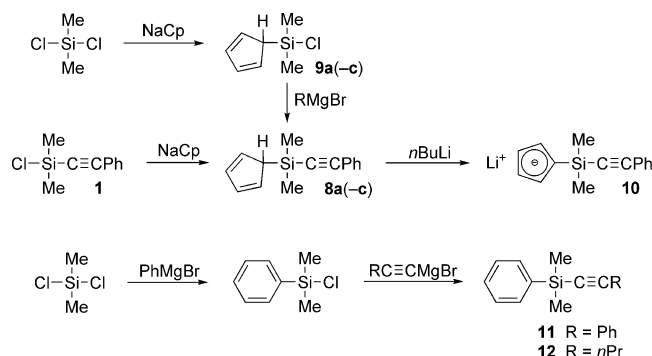
A problem in proving the identity of **5** and **6** was their extreme hydrolytic sensitivity and corrosivity. For this reason no satisfactory elemental analyses could be obtained. Furthermore, by GC-MS analysis only the corresponding disiloxane 1,3-bis(phenylethynyl)-1,1,3,3-tetramethyldisiloxane [$(\text{PhC}\equiv\text{CMe}_2\text{Si})_2\text{O}$, **7**]^[18,19] was observed. For comparison, a sample of **7** was prepared by hydrolysis of **5** in diethyl ether in 98% yield. Analysis of the ^{29}Si NMR and IR spectra of **5**, **6**, and **7** finally proved that the reaction products supposed to be **5** and **6** were not the disiloxane **7**. This was supported by their markedly higher densities (1.4–1.5 g/cm^3 vs. 1.0 g/cm^3) and their chemical behavior (on contact with air and humidity brown or pink color, respectively, and fuming, whereas **7** was inert to air and moisture). In addition, their ^{29}Si NMR signals showed an upfield shift of about 5 ppm or 25–30 ppm from that of **1**, which is characteristic for a replacement of Cl by Br or I, respectively.^[20,21] We therefore conclude that the obtained substances are the anticipated bromo- and iodosilanes **5** and **6**.

For the hitherto unknown cyclopentadienyl-functionalized alkynylsilane cyclopentadienyldimethyl(phenylethynyl)silane ($\text{CpSiMe}_2\text{C}\equiv\text{CPh}$, **8a–c**),^[22] two alternative synthetic pathways can be considered (Scheme 3). These are the reaction of **1** with sodium cyclopentadienide (NaCp)

Table 1. Comparison of preparation methods for **1**.

Starting silane	Reagent	Steps	Yield	Remark
Me_2SiCl_2	$\text{PhC}\equiv\text{CMgBr}$	1	30–37%	[3–5]
Me_2SiCl_2	$\text{PhC}\equiv\text{CMgBr}$	1	27–38%	yield by NMR, Cl/Br exchange
Me_2SiCl_2	$\text{PhC}\equiv\text{CLi}/\text{Na}$	1	44–55%	[6,7]
Me_2SiCl_2	$\text{PhC}\equiv\text{CH}$	1	60–80%	autoclave ^[8]
Me_2SiCl_2	$\text{PhC}\equiv\text{CMgBr}$	4	52%	amino route
Me_2SiHCl	(1) $\text{PhC}\equiv\text{CMgBr}$, (2) PCl_5	2	63%	costly silane
$\text{PhC}\equiv\text{CMe}_2\text{SiH}$	PCl_5	1	85%	costly silane

and the reaction of chloro(cyclopentadienyl)dimethylsilane (CpMe_2SiCl , **9a-c**),^[23] which is easily available from Me_2SiCl_2 and NaCp, with $\text{PhC}\equiv\text{CMgBr}$. Both routes were examined and gave comparable total yields of about 30% based on Me_2SiCl_2 . However, because of the above-described difficulties in the preparation of **1**, only the second route is recommended.



Scheme 3. Syntheses of alkynylsilanes **8–12**.

Cyclopentadienylsilane **8** was found to be unstable on prolonged storage giving a compound that is likely to be a Diels–Alder product. The reaction is slow (days–weeks) and can be reversed by heating to 150 °C for 1 h or distillation in vacuo. Thus, freshly prepared **8** should be immediately used or stored at –20 °C or below. It can also be converted to its stable lithium salt $\text{LiC}_5\text{H}_4\text{SiMe}_2\text{C}\equiv\text{CPh}$ (**10**) in 93% yield by action of *n*-butyllithium (*n*BuLi) (Scheme 3).

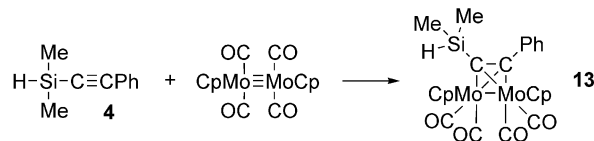
The target arylsilanes were chosen to be dimethyl(phenyl)(phenylethynyl)silane ($\text{PhMe}_2\text{SiC}\equiv\text{CPh}$, **11**)^[24] and the hitherto unknown dimethyl(pent-1-yn-1-yl)phenylsilane ($\text{PhMe}_2\text{SiC}\equiv\text{CPr}$, **12**). Analogously to **8**, there are two possible synthetic routes: via **1** or its propyl analogue, respectively, or via PhMe_2SiCl . Because of the easy availability of the latter reagent (also commercially), the second route was used throughout (Scheme 3). Compounds **11** and **12** were thus obtained in about 90% yield.

Alkyne Complexes

In order to synthesize solid derivatives for structural characterization, especially of the hitherto unknown silane **8**, complexation of the alkyne triple bonds of **1**, **4**, **8**, **11**, and **12** with transition-metal moieties was attempted.

Since complexes of functional alkynylsilanes with octacarbonyldicobalt [$\text{Co}_2(\text{CO})_8$] are already well known,^[16,25–33] we chose the tetracarbonyldicyclopentadienyldimolybdenum fragment $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ for **1** and **4**. However, after reaction of **1** with $\text{Cp}_2\text{Mo}_2(\text{CO})_4$ only its decomposition product hexacarbonyldicyclopentadienyldimolybdenum [$\text{Cp}_2\text{Mo}_2(\text{CO})_6$] was obtained. Nevertheless, with **4** the expected $\{\mu\text{-dimethyl}[(1,2\text{-}\eta^1:1,2\text{-}\eta^2)\text{-phenylethynyl}] \text{silane}\} \text{bis}[\text{dicarbonyl}(\eta^5\text{-cyclopentadienyl})\text{molybdenum-(I)}](\text{Mo–Mo})$ [$\text{PhC}\equiv\text{CSiMe}_2\text{H}\cdot\text{Cp}_2\text{Mo}_2(\text{CO})_4$, **13**] could be isolated in 42% yield as dark red crystals which were air-stable for at least several days (Scheme 4). The spectro-

scopic data of **13** were in agreement with the anticipated structure. It was also supported by comparison with the ^{95}Mo NMR, IR, and UV/Vis data of the analogous tolane complex $\text{PhC}\equiv\text{CPh}\cdot\text{Cp}_2\text{Mo}_2(\text{CO})_4$ ^[34] as well as literature data^[35–37] and finally confirmed by single-crystal X-ray diffraction analysis (Figure 1).



Scheme 4. Synthesis of complex **13**.

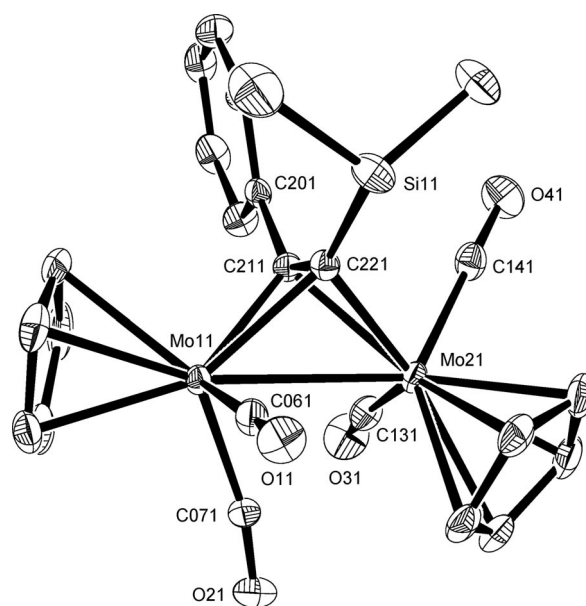
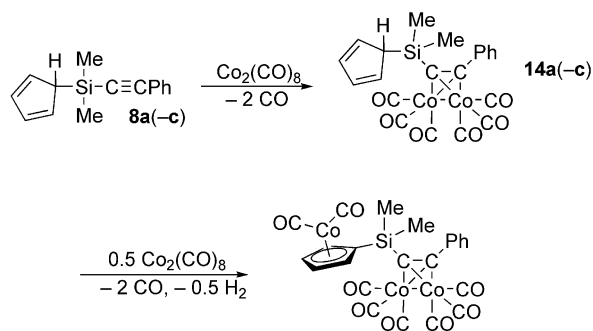


Figure 1. Molecular structure of **13** (ORTEP diagram with 20% ellipsoids, hydrogen atoms omitted for clarity, only the predominant part of the disordered structure is depicted). Selected bond lengths [pm]: Mo11–Mo21 293.38(4), Mo(11)–C(211) 211.1(3), Mo(11)–C(221) 218.0(3), Mo(21)–C(211) 220.5(3), Mo(21)–C(221) 217.6(3), C(211)–C(221) 134.7(4), Si(11)–C(221) 180.2(3), C(201)–C(211) 146.6(4).

Complex **13** crystallizes in the monoclinic space group $P2_1/c$ without solvent. The packing of the molecules in the crystal consists of head-to-tail chains of molecules, which are stacked in a parallel manner. Thirteen percent of the molecules exhibit a different orientation in statistical distribution. This fact handicaps the evaluation of the structural parameters. Notwithstanding the disorder, selected bond lengths are listed in the caption of Figure 1. The former alkyne triple bond exhibits a C–C distance of 135 pm, which corresponds to a double bond. The situation of the carbonyl ligands resembles the one already described in the literature for alkyne complexes of $\text{Cp}_2\text{Mo}_2(\text{CO})_4$: one CO group (C071–O21) is markedly bent with the C atom displaced toward the opposite Mo atom (Mo21), two ligands (C061–O11, C131–O31) are slightly bent, and only one

carbonyl ligand (C141–O41) is linear. This was interpreted as a transition situation between terminal and bridging carbonyl ligands.^[38,39]

In order to characterize compound **8** structurally, it was converted into $\{\mu\text{-cyclopentadienyldimethyl}[(1,2\text{-}\eta:1,2\text{-}\eta)\text{-phenylethynyl}] \text{silane}\} \text{bis}[\text{tricarbonylcobalt}(0)](Co\text{-}Co)$ (**14a-c**)^[22] by reaction with $\text{Co}_2(\text{CO})_8$ (Scheme 5). This complex was isolated as dark brown crystals (air-stable for at least some hours) in 39% yield. At first, the situation seemed to be troubled by the existence of three isomers each for the starting silane and the product, but spectral properties and single-crystal X-ray analysis showed the obtained solid to be solely the cyclopenta-2,4-dien-1-yl isomer **14a** (Figure 2). However, broadened ^1H and ^{13}C NMR signals for the cyclopentadienyl group and small additional peaks indicated that isomerization processes occurred in solution. The ^{59}Co NMR, IR, and UV/Vis data were typical for alkyne $\text{Co}_2(\text{CO})_6$ complexes.^[40–44]



Scheme 5. Synthesis of complex **14** and complexation with $\text{Co}_2(\text{CO})_8$.

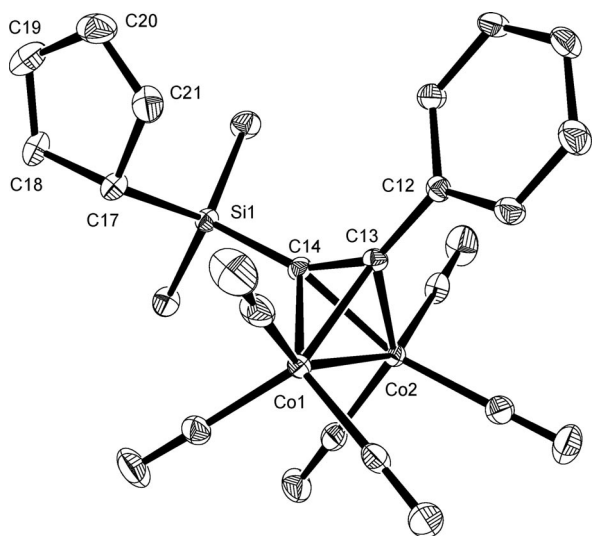


Figure 2. Molecular structure of **14a** (ORTEP diagram with 50% ellipsoids, hydrogen atoms omitted for clarity). Selected bond lengths [pm]: Co(1)–Co(2) 246.28(3), Co(1)–C(13) 197.26(18), Co(1)–C(14) 200.45(19), Co(2)–C(13) 197.37(17), Co(2)–C(14) 199.90(18), C(13)–C(14) 134.6(3), C(12)–C(13) 146.4(3), Si(1)–C(14) 185.1(2), Si(1)–C(17) 191.0(2), C(17)–C(18) 148.6(3), C(17)–C(21) 148.8(3), C(18)–C(19) 134.8(3), C(19)–C(20) 143.6(4), C(20)–C(21) 135.1(3).

Complex **14a** crystallizes solvent-free in the monoclinic space group Cc . The molecules form double layers with the carbonyl ligands inside and the organic groups outside the layers. Selected bond lengths are listed in the caption of Figure 2. The Co_2C_2 tetrahedron is somewhat distorted, probably because of the steric demand of the silyl group. For the same reason the two $\text{Co}(\text{CO})_3$ moieties, which are eclipsed in complexes of symmetrical alkynes, are twisted against each other. The length of the former triple bond is 135 pm and thus indicates a double-bond character in this complex. Interestingly, the phenyl and the silyl substituent are bent away from the axis of the former triple bond at different angles: $37.9(2)^\circ$ for the phenyl and $28.9(2)^\circ$ for the silyl group. The cyclopentadienyl ring is almost planar. The C–C single bond between the two double bonds is markedly shortened in comparison with the average value of cyclopentane (143.6 vs. 148 pm^[45]), whereas the lengths of the two other single bonds are not reduced. This points to conjugation and delocalization of the two double bonds.

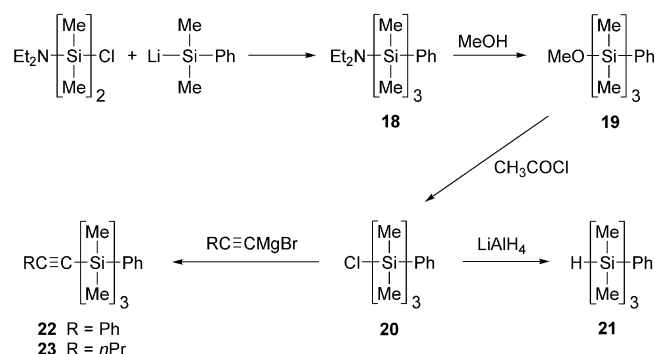
In order to obtain $(\text{OC})\text{Mo}(\text{alkyne})_3$ -type^[46–52] derivatives of **11** and **12**, these silanes were refluxed with tris(acetonitrile)tricarbonylmolybdenum $[\text{Mo}(\text{CO})_3(\text{MeCN})_3]$ in ethanol,^[46,47] but apart from decomposition of the starting molybdenum complex no reaction occurred.

Complexes **13** and **14a** contain reactive groups that allow for further complexation. Hence, **13** was mixed with $\text{Co}_2(\text{CO})_8$ in toluene to examine the reactivity of the Si–H bond, but it did not react, neither at room temperature (1 week) nor at 50°C (24 h). This is in contrast to hexacarbonyldicobalt complexes of alkynylhydrosilanes which react easily with $\text{Co}_2(\text{CO})_8$ to form trinuclear cobalt compounds.^[25–31] Complex **14a**, instead, was expected to react at the Cp ring (Scheme 5), and indeed on addition of $\text{Co}_2(\text{CO})_8$ a gas evolution occurred. Workup of the reaction mixture gave a dark brown oil in quantitative yield whose ^1H , ^{13}C , and ^{29}Si NMR spectra suggested it to be the anticipated trinuclear cobalt complex $\{^{13}\text{C NMR: } \delta = +204.5 [\text{C}_5\text{H}_4\text{Co}(\text{CO})_2], +199.7 [\text{Co}_2(\text{CO})_6\cdot\text{C}\equiv\text{C}] \text{ ppm; } ^{29}\text{Si NMR: } \delta = -8.3 \text{ ppm}\}$. Unfortunately, no crystals for further characterization could be obtained. The lithiation of the cyclopentadienyl ring in **14a** was attempted by addition of $n\text{BuLi}$ in hexane, yet the only identifiable product was $\text{LiCo}(\text{CO})_4$, thus hinting at decomposition.

Trisilanes

Functional alkynyl trisilanes were synthesized by extension of the silicon chain of a chlorosilane with a silyllithium compound. Thus, the product of the reaction of dimethyl(phenyl)silyllithium (PhMe_2SiLi) and $\text{Et}_2\text{NMe}_2\text{Si-SiMe}_2\text{Cl}$ was identified by ^{29}Si NMR spectroscopy as the anticipated 1-(diethylamino)-1,1,2,2,3,3-hexamethyl-3-phenyltrisilane ($\text{Et}_2\text{NMe}_2\text{Si-SiMe}_2\text{-SiMe}_2\text{Ph}$, **18**) (Scheme 6). Subsequent reaction with methanol afforded 1-methoxy-1,1,2,2,3,3-hexamethyl-3-phenyltrisilane ($\text{MeOMe}_2\text{Si-SiMe}_2\text{-SiMe}_2\text{Ph}$, **19**), which reacted with CH_3COCl to 1-chloro-1,1,2,2,3,3-hexamethyl-3-phenyltrisilane ($\text{ClMe}_2\text{Si-}$

SiMe₂-SiMe₂Ph, **20**)^[53,54] in 92 % crude yield. Hydrodehalogenation of **20** with lithium aluminum hydride (LiAlH₄) gave 1,1,2,2,3,3-hexamethyl-1-phenyltrisilane (HMe₂Si-SiMe₂-SiMe₂Ph, **21**) in 91 % crude yield, whereas alkynylation with PhC≡CMgBr or PrC≡CMgBr gave 1,1,2,2,3,3-hexamethyl-1-phenyl-3-(phenylethynyl)trisilane (PhC≡CMe₂Si-SiMe₂-SiMe₂Ph, **22**) and 1,1,2,2,3,3-hexamethyl-1-(pent-1-yn-1-yl)-3-phenyltrisilane (PrC≡CMe₂Si-SiMe₂-SiMe₂Ph, **23**) (**23**: 99 % crude yield), respectively.



Scheme 6. Syntheses of 1,3-heterodifunctional trisilanes **18–23**.

²⁹Si NMR, ¹³C NMR, and IR Spectroscopy

The ²⁹Si NMR spectroscopic data of the synthesized compounds are listed in Table 2. All signals appeared in the expected ranges. The ¹³C NMR shifts and IR data of the RC≡CSi moieties are listed in Table 3. Both depend on the substituents of the silicon atom and on the organic substituent R. As expected the carbon atom neighboring the silicon atom is more shielded than the other carbon atom (assignment proved by ²⁹Si satellites). Surprisingly, its chemical shift is also markedly influenced by the organic group R, whereas the shift of the second carbon signal does not change with R.

Furthermore, it is conspicuous that the ¹³C NMR shifts of the alkyne carbon atoms only slightly alter on complexation of the triple bond. This phenomenon has been observed several times in the literature.^[38,40,55–67] Considering the correlation between ¹³C NMR chemical shift and hybridization,^[68] it indicates an intermediate state between sp² and sp³ hybridization corresponding to a C–C bond order between 2 and 1. This is supported by the X-ray and IR data of **13** and **14a**, which, in contrast to the Lewis formulae (C–C single bond, Schemes 4 and 5), suggest a C=C double bond in these complexes.

Table 2. ²⁹Si NMR spectroscopic data of compounds **1–14** and **18–23**.

Compound	δ [ppm]	Compound	δ [ppm]
PhC≡CMe ₂ SiCl (1)	+0.4	PhC≡CMe ₂ SiC ₅ H ₄ Li (10)	–30.4
PhC≡CMe ₂ SiNEt ₂ (2)	–17.6	PhC≡CMe ₂ SiPh (11)	–21.7
PhC≡CMe ₂ SiOMe (3)	–6.2	PrC≡CMe ₂ SiPh (12)	–22.9
PhC≡CMe ₂ SiH (4)	–37.4	4-Cp ₂ Mo ₂ (CO) ₄ (13)	–9.5
PhC≡CMe ₂ SiBr (5)	–6.7	8a·Co ₂ (CO) ₆ (14a)	–0.6
PhC≡CMe ₂ SiI (6)	–29.5	14b	–10.6
(PhC≡CMe ₂ Si) ₂ O (7)	–16.5	14c	–10.8
PhC≡CMe ₂ SiCp (8a)	–18.6	Et ₂ N–(SiMe ₂) ₃ –Ph (18)	–0.6/–51.0/–19.5
8b	–28.3	MeO–(SiMe ₂) ₃ –Ph (19)	+19.3/–50.4/–18.8
8c	–28.7	Cl–(SiMe ₂) ₃ –Ph (20)	+26.3/–45.6/–19.2
CpMe ₂ SiCl (9a)	+25.4	H–(SiMe ₂) ₃ –Ph (21)	–36.3/–47.4/–18.3
9b	+14.7	PhC≡C–(SiMe ₂) ₃ –Ph (22)	–34.0/–47.2/–18.4
9c	+15.0	PrC≡C–(SiMe ₂) ₃ –Ph (23)	–35.2/–47.6/–18.4

Table 3. Selected ¹³C NMR and IR spectroscopic data of the herein reported alkynes.

Compound	δ(C≡C–Si) [ppm]	δ(C≡C–Si) [ppm]	ν(C≡C) [cm ^{–1}]
PhC≡CMe ₂ SiCl (1)	107.0	89.8	2161 ^[a]
PhC≡CMe ₂ SiNEt ₂ (2)	103.8	94.2	2155 ^[a]
PhC≡CMe ₂ SiOMe (3)	105.4	91.2	2157 ^[a]
PhC≡CMe ₂ SiH (4)	106.4	91.1	2158 ^[a]
PhC≡CMe ₂ SiBr (5)	107.5	89.2	2162 ^[a]
PhC≡CMe ₂ SiI (6)	108.2	89.0	2160 ^[a]
(PhC≡CMe ₂ Si) ₂ O (7)	104.2	93.3	2161 ^[a]
PhC≡CMe ₂ SiCp (8)	105.8	92.8	2156 ^[a]
PhC≡CMe ₂ SiC ₅ H ₄ Li (10)	105.7	98.1	2153 ^[b]
PhC≡CMe ₂ SiPh (11)	106.8	92.0	2156 ^[a]
PhC≡C–(SiMe ₂) ₃ –Ph (22)	107.6	93.4	2150 ^[a]
PrC≡CMe ₂ SiPh (12)	109.4	82.4	2173 ^[a]
PrC≡C–(SiMe ₂) ₃ –Ph (23)	109.9	83.2	2166 ^[a]
4-Cp ₂ Mo ₂ (CO) ₄ (13)	111.0	– ^[c]	1512 ^[d]
8a·Co ₂ (CO) ₆ (14a)	106.6	78.8	1579 ^[d]

[a] Neat liquid. [b] Solution in THF. [c] Signal hidden. [d] Solid in KBr.

Conclusions

Functional alkynyldimethylmonosilanes $\text{RC}\equiv\text{CMe}_2\text{SiX}$ are obtained in acceptable yields by monofunctionalization with the aid of protecting groups, whereas functional 1-phenyltrisilanes $\text{Ph}-(\text{SiMe}_2)_3-\text{X}$ can be synthesized by extension of a protected disilane chain with dimethylphenylsilyllithium (PhMe_2SiLi). Both methods should also be applicable to the synthesis of heterodifunctional disilanes.

Experimental Section

General Remarks:^[71] All operations were carried out under dry purified argon by using Schlenk or glovebox techniques. Solvents were dried by distillation from the following reagents and stored under argon until use: Na/benzophenone-ketyl [tetrahydrofuran (THF), diethyl ether (Et_2O), benzene, toluene, hexane], CaH_2 [CDCl_3 , dichloromethane (CH_2Cl_2)], LiAlH_4 (pentane), magnesium (methanol), Na/K alloy (C_6D_6). Chlorosilanes were distilled and stored under argon before use. Acetyl chloride and acetyl bromide were distilled from iron powder under argon and then stored under argon. The following chemicals were prepared according to known procedures: $\text{Et}_2\text{NMe}_2\text{SiCl}$,^[9,10] $\text{Et}_2\text{NMe}_2\text{Si}-\text{SiMe}_2\text{Cl}$,^[10,72] NaCp ,^[73] PhMe_2SiCl ,^[74a] $\text{Cp}_2\text{Mo}_2(\text{CO})_4$,^[75a] $\text{Cp}_2\text{Mo}_2(\text{CO})_4\cdot\text{PhC}\equiv\text{CPh}$,^[76] $\text{Co}_2(\text{CO})_8\cdot\text{PhC}\equiv\text{CPh}$,^[77] $\text{K}_3[\text{Co}(\text{CN})_6]$.^[75b] Powdered anhydrous lithium iodide (LiI) was prepared by drying the diethyl ether solvate $\text{LiI}\cdot\text{Et}_2\text{O}$ at 100 °C in vacuo for 2 h. All other chemicals were laboratory stock or purchased from the sources given below and used as received: Acros (2.5 M *n*BuLi in hexane, NBS), Aldrich (PCl_5), Fluka [$\text{Co}_2(\text{CO})_8$, Na_2SO_4 , NH_4Cl , $\text{PhC}\equiv\text{CH}$], Merck (acetyl bromide, acetyl chloride, lithium, Me_2SiHCl , Me_2SiCl_2 , $\text{PrC}\equiv\text{CH}$). Densities were determined by weighing a measured volume of liquid. Melting points were determined in sealed capillaries (under argon) and between thin glass plates (in air) with a Boëtius-type heating microscope. The heating rate was about 4 K/min. Elemental analyses were performed in duplicate with a CHN-O-Rapid (Heraeus) and the values averaged. The mass spectra were recorded with an HP 5890 Series II/HP 5989 A/HP 5971 Series (Hewlett–Packard). NMR spectra were measured with a DPX 400 Avance (Bruker) with tetramethylsilane Me_4Si (TMS) as internal standard for ^1H , ^{13}C , and ^{29}Si . The external standards for ^{14}N , ^{59}Co , and ^{95}Mo were nitromethane (CH_3NO_2), 0.1 M $\text{K}_3[\text{Co}(\text{CN})_6]$ solution in D_2O , and 1 M alkaline Na_2MoO_4 solution in H_2O , respectively.^[78] IR spectra were recorded with a Specord M 82 (VEB Carl Zeiss JENA) or a Nicolet 510 spectrometer. Liquid samples were prepared between NaCl plates, whereas solids were examined in KBr disks. UV/Vis spectra were recorded with a Specord S 100 (Analytik Jena AG) in the range 190–1000 nm. All reactions were monitored by NMR or IR spectroscopy. Assignments were made by comparison of the spectra with each other and with literature data.^[21,69,70,78–85] Missing NMR peaks are hidden by other peaks, mostly by those of the solvent. The crystal structures of **13** and **14a** were determined with a Bruker-Nonius X8 diffractometer with an APEX2-CCD detector using $\text{Mo-K}\alpha$ radiation. Suitable crystals were grown from [D_6]benzene/hexane at room temperature (**13**) or by slow warming of a hexane solution from –78 °C to –20 °C (**14a**). The structures were solved by direct methods (SHELXS-97)^[86a] and full-matrix least squares refined on F^2 (SHELXL-97).^[86b] Non-H atoms were refined anisotropically, whereas H atoms were considered in idealized positions (riding model). A population of 13% of the molecules of **13** were found disordered. Of these only the molybdenum and silicon atoms were refined anisotropically. Graphical representations were created with

ORTEP32.^[87] CCDC-642200 (**13**) and CCDC-642204 (**14a**) 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.

Alkynyldimethylmonosilanes

Chlorodimethyl(phenylethynyl)silane ($\text{PhC}\equiv\text{CMe}_2\text{SiCl}$, **1).** (a) **From Methoxydimethyl(phenylethynyl)silane (**3**):** A solution of silane **3** (13.40 g, 70.4 mmol) in hexane (20 mL) was cooled to 0 °C, and a solution of acetyl chloride (10.0 mL, 11.0 g, 140.8 mmol) in hexane (10 mL) was added dropwise. After warming up and stirring at room temperature for 16 d, the volatiles were evaporated in vacuo, and the residue was distilled under reduced pressure furnishing a colorless oil. Yield: 12.28 g (63.1 mmol, 90%). B.p. 70–71 °C (0.3 kPa). $\text{C}_{10}\text{H}_{11}\text{ClSi}$ (194.737 g/mol). Spectral data: see (b). (b) **From Dimethyl(phenylethynyl)silane (**4**):** Silane **4** (6.67 g, 7.2 mL, 41.6 mmol) was dissolved in THF (50 mL), and PCl_5 (95%) (9.12 g, 41.6 mmol) was added in small portions at room temperature with stirring. The mixture became warm, and the PCl_5 dissolved within a few hours. After cooling to room temperature, the solvent was removed in vacuo. The remaining oil was distilled under reduced pressure yielding a colorless oil. Yield: 6.87 g (35.3 mmol, 85%). B.p. 58–63 °C (0.2 kPa). Density: 1.06 g/mL. $\text{C}_{10}\text{H}_{11}\text{ClSi}$ (194.737 g/mol). ^1H NMR (400.1 MHz, CDCl_3 , 22 °C): δ = 7.49 (m, 2 H, Ph_{ortho}), 7.33 (m, 3 H, $\text{Ph}_{\text{meta} + \text{para}}$), 0.64 (s, $^1J_{\text{HC}} = 122.2$, $^2J_{\text{HSi}} = 7.5$ Hz, 6 H, SiMe_2) ppm. ^{13}C NMR (100.6 MHz, CDCl_3 , 22 °C): δ = 132.2 (s, 2 C, Ph_{ortho}), 129.4 (s, 1 C, Ph_{para}), 128.3 (s, 2 C, Ph_{meta}), 121.9 (s, 1 C, Ph_{ipso}), 107.0 (s, $^2J_{\text{CSi}} = 21$ Hz, 1 C, $\text{C}\equiv\text{C}-\text{Si}$), 89.8 (s, 1 C, $\text{C}\equiv\text{C}-\text{Si}$), 3.8 (s, $^1J_{\text{CSi}} = 66$ Hz, 2 C, SiMe_2) ppm. ^{29}Si NMR (79.5 MHz, CDCl_3 , 22 °C): δ = +0.4 [s (^1H -coupled: sept), $^2J_{\text{SiH}} = 7.5$, $^1J_{\text{SiC}(\text{Me})} = 65$ (2 C), $^1J_{\text{SiC}(\text{C}\equiv\text{C})} = 103$ (1 C), $^2J_{\text{SiC}(\text{C}\equiv\text{C})} = 21$ Hz (1 C)] ppm.

Bromodimethyl(phenylethynyl)silane ($\text{PhC}\equiv\text{CMe}_2\text{SiBr}$, **5).** (a) **From Chloro(diethylamino)dimethylsilane:** A solution of $\text{Et}_2\text{NMe}_2\text{SiCl}$ (5 mL, 4.59 g, 27.7 mmol) in Et_2O (5 mL) was added to a solution of $\text{PhC}\equiv\text{CMgBr}$ in Et_2O [prepared according to standard procedures^[88] from Mg (690 mg, 28.4 mmol), 1,2-dibromoethane (three drops), EtBr (3 mL, 4.38 g, 40.2 mmol), $\text{PhC}\equiv\text{CH}$ (3.2 mL, 2.98 g, 29.2 mmol), and Et_2O (60 mL)] at room temperature. The resulting mixture was refluxed for 2 h and then concentrated in vacuo. The residue was extracted with hexane in small portions. To the combined filtrates methanol (1.5 mL, 1.19 g, 37.0 mmol) was added dropwise at room temperature whereupon a white precipitate formed. After stirring at room temperature for 6 h, the solvent was evaporated in vacuo and the residue extracted with hexane (20 mL). The resulting hexane solution was cooled to 0 °C, and acetyl bromide (6 mL, 6.35 g, 80.9 mmol) was added dropwise whereupon again a white precipitate deposited. After warming up and stirring at room temperature for 2 d, the volatiles were evaporated in vacuo, and the liquid residue was distilled under reduced pressure furnishing a pale yellow oil. It turned brownish yellow after some time even under argon and fumed on contact with air. Yield: 4.71 g (19.7 mmol, 71%). B.p. 120–125 °C (1.5 kPa, ref.^[17] 124 °C/1.3 kPa). $\text{C}_{10}\text{H}_{11}\text{BrSi}$ (239.188 g/mol). Spectral data: see (b). (b) **From Dimethyl(phenylethynyl)silane (**4**):** A solution of **4** (4.6 mL, 4.28 g, 26.7 mmol) in CH_2Cl_2 (40 mL) was cooled to 0 °C in an ice bath. Then NBS (10.26 g, 57.6 mmol) was added slowly in small portions with stirring. At first it dissolved with effervescence, and the solution became yellow. Later on dissolution was incomplete, and the mixture gradually turned dark red brown. After stirring at 0 °C for 4 h and warming up to room temperature, the volatiles were removed in vacuo. The remaining black solid residue was extracted with hexane (70 mL) furnishing a red violet solution and a

dark brown solid, which was identified by NMR as succinimide. The extract was then concentrated in vacuo, and the remaining oil was distilled under reduced pressure to yield a colorless liquid containing a small amount of a white precipitate supposed to be co-sublimed succinimide. Yield: 4.46 g (18.6 mmol, 70%). B.p. 106–110 °C (0.7 kPa). Density: 1.4 g/mL (ref.^[17] 1.343 g/mL). $C_{10}H_{11}BrSi$ (239.188 g/mol). 1H NMR (400.1 MHz, $CDCl_3$, 22 °C): δ = 7.49 (m, 2 H, Ph_{ortho}), 7.31 (m, 3 H, $Ph_{meta+para}$), 0.79 (s, $^1J_{HC}$ = 122.6, $^2J_{HSi}$ = 7.5 Hz, 6 H, $SiMe_2$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 22 °C): δ = 132.1 (s, 2 C, Ph_{ortho}), 129.4 (s, 1 C, Ph_{para}), 128.3 (s, 2 C, Ph_{meta}), 121.7 (s, 1 C, Ph_{ipso}), 107.5 (s, $^2J_{CSi}$ = 20 Hz, 1 C, $C\equiv C-Si$), 89.2 (s, $^1J_{CSi}$ = 101 Hz, 1 C, $C\equiv C-Si$), 4.6 (s, $^1J_{CSi}$ = 64 Hz, 2 C, $SiMe_2$) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 22 °C): δ = -6.7 [s, $^1J_{SiC(Me)}$ = 64 (2 C), $^1J_{SiC(C\equiv C)}$ = 101 (1 C), $^2J_{SiC(C\equiv C)}$ = 20 Hz (1 C)] ppm.

Iododimethyl(phenylethynyl)silane (PhC $\equiv$ CMe $_2$ SiI, 6): Powdered anhydrous LiI (6.13 g, 45.8 mmol) was placed in a Schlenk tube, and silane **1** (6.5 mL, 6.70 g, 34.4 mmol) dissolved in CH_2Cl_2 (40 mL) was added at room temperature. A yellowish suspension formed, which gradually turned brownish and then violet. After stirring at room temperature for 2 d, the mixture was filtered and the residue washed with CH_2Cl_2 . From the combined filtrate and washings the volatiles were removed in vacuo. The remaining liquid was distilled under reduced pressure furnishing a colorless to pale pink oil. It fumed and turned bright pink on contact with air. Yield: 7.77 g (27.2 mmol, 79%). B.p. 110–115 °C (0.6 kPa). Density: 1.5 g/mL. $C_{10}H_{11}ISi$ (286.184 g/mol). 1H NMR (400.1 MHz, $CDCl_3$, 22 °C): δ = 7.47 (m, 2 H, Ph_{ortho}), 7.30 (m, 3 H, $Ph_{meta+para}$), 0.99 (s, $^1J_{HC}$ = 123.3, $^2J_{HSi}$ = 7.7 Hz, 6 H, $SiMe_2$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 22 °C): δ = 132.1 (s, 2 C, Ph_{ortho}), 129.4 (s, 1 C, Ph_{para}), 128.2 (s, 2 C, Ph_{meta}), 121.6 (s, 1 C, Ph_{ipso}), 108.2 (s, $^2J_{CSi}$ = 20 Hz, 1 C, $C\equiv C-Si$), 89.0 (s, $^1J_{CSi}$ = 99 Hz, 1 C, $C\equiv C-Si$), 5.8 (s, $^1J_{CSi}$ = 61 Hz, 2 C, $SiMe_2$) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 22 °C): δ = -29.5 [s, $^1J_{SiC(Me)}$ = 62 (2 C), $^1J_{SiC(C\equiv C)}$ = 99 (1 C), $^2J_{SiC(C\equiv C)}$ = 19 Hz (1 C)] ppm.

Cyclopentadienyldimethyl(phenylethynyl)silane (PhC $\equiv$ CMe $_2$ SiCp, 8a–c): A solution of PhC $\equiv$ CMgBr in Et $_2$ O [prepared according to standard procedures^[88] from Mg (1.455 g, 59.9 mmol), 1,2-dibromoethane (50 μ L), EtBr (4.7 mL, 6.87 g, 63.0 mmol), PhC $\equiv$ CH (6.5 mL, 6.05 g, 59.2 mmol), and Et $_2$ O (120 mL)] was added dropwise with stirring at room temperature to a solution of freshly distilled **9a–c** (7.56 g, 47.6 mmol) in Et $_2$ O (60 mL). After stirring overnight, the mixture was heated to reflux for 14 h. The solution was then cautiously hydrolyzed with 2 M NH_4Cl solution, washed with water, and dried with Na_2SO_4 . After evaporation of the Et $_2$ O in vacuo, the residual oil was distilled under reduced pressure. The small first fraction up to 110 °C was discarded. The main fraction contained the product, which was obtained as a light yellow oil. According to its NMR spectrum it consisted of the three isomers of **8** (ca. 75% **8a**, ca. 25% **8b**, traces **8c**).^[89] Yield: 6.82 g (30.4 mmol, 64%). B.p. 110–120 °C (0.2–0.3 kPa). $C_{15}H_{16}Si$ (224.379 g/mol): calcd. C 80.29, H 7.19; found C 81.21, H 7.41. 1H NMR (400.1 MHz, $CDCl_3$, 22 °C): δ = 7.48 (m, 2 H, Ph_{ortho}), 7.31 (m, 3 H, $Ph_{meta+para}$), 6.67 (br., $\Delta\nu_{1/2}$ = 11 Hz, 2 H, CH_{Cp}), 6.60 (br., $\Delta\nu_{1/2}$ = 15 Hz, 2 H, CH_{Cp}), 3.58 (br., $\Delta\nu_{1/2}$ = 13 Hz, 1 H, $SiCH_{Cp}$), 0.10 (s, $\Delta\nu_{1/2}$ = 2, $^1J_{HC}$ = 121.1, $^2J_{HSi}$ = 7.0 Hz, 6 H, $SiMe_2$) ppm (**8a**); δ = 7.00 (m, CH_{Cp}), 6.73 (dq, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1 Hz, CH_{Cp}), 6.62 (dq, $^3J_{HH}$ = 5, $^4J_{HH}$ = 1.5 Hz, CH_{Cp}), 3.15 (q, $^{3/4}J_{HH}$ = 1.5 Hz, CH_2), 0.40 (s, $SiMe_2$) ppm (**8b**); δ = 3.07 (q, $^{3/4}J_{HH}$ = 1.5 Hz, CH_2), 0.41 (s, $SiMe_2$) ppm (**8c**). ^{13}C NMR (100.6 MHz, $CDCl_3$, 22 °C): δ = 133.1 (br. s, $\Delta\nu_{1/2}$ = 15 Hz, 2 C, CH_{Cp}), 132.1 (s, $\Delta\nu_{1/2}$ = 4 Hz, 2 C, Ph_{ortho}), 131.1 (br. s, $\Delta\nu_{1/2}$ = 9 Hz, 2 C, CH_{Cp}), 128.7 (s, $\Delta\nu_{1/2}$ = 7 Hz, 1 C, Ph_{para}), 128.2 (s,

$\Delta\nu_{1/2}$ = 4 Hz, 2 C, Ph_{meta}), 122.9 (s, $\Delta\nu_{1/2}$ = 6 Hz, 1 C, Ph_{ipso}), 105.7 (s, $\Delta\nu_{1/2}$ = 4 Hz, 1 C, $C\equiv C-Si$), 92.4 (s, $\Delta\nu_{1/2}$ = 3 Hz, 1 C, $C\equiv C-Si$), 51.0 (br. s, $\Delta\nu_{1/2}$ = 13 Hz, 1 C, $SiCH_{Cp}$), -3.0 (s, $\Delta\nu_{1/2}$ = 4, $^1J_{CSi}$ = 59 Hz, 2 C, $SiMe_2$) ppm (**8a**); δ = 143.4 (s, 1 C, CH_{Cp}), 138.7 (s, 1 C, CH_{Cp}), 132.9 (s, 1 C, $SiCH_{Cp}$), 132.0 (s, 2 C, Ph_{ortho}), 128.5 (s, 1 C, CH_{Cp}), 128.2 (s, 2 C, Ph_{meta}), 123.2 (s, 1 C, Ph_{ipso}), 105.8 (s, 1 C, $C\equiv C-Si$), 92.8 (s, 1 C, $C\equiv C-Si$), 45.3 (s, 1 C, CH_2), -0.6 (s, 2 C, $SiMe_2$) ppm (**8b**); δ = 44.0 (s, 1 C, CH_2), -1.1 (s, 2 C, $SiMe_2$) ppm (**8c**). ^{29}Si NMR (79.5 MHz, $CDCl_3$, 22 °C): δ = -18.6 [s, $^1J_{SiC(sp^3)}$ = 59 (3 C), $^1J_{SiC(C\equiv C)}$ = 87 (1 C), $^2J_{SiC(C\equiv C)}$ = 16 Hz (1 C), **8a**], -28.3 [s, $^1J_{SiC(Me)}$ = 58 (2 C), $^1J_{SiC(Cp)}$ = 78 (1 C), $^1J_{SiC(C\equiv C)}$ = 87 (1 C), $^2J_{SiC(C\equiv C)}$ = 16 Hz (1 C), **8b**], -28.7 (s, **8c**) ppm.

Lithium [Dimethyl(phenylethynyl)silyl]cyclopentadienide (PhC $\equiv$ CMe $_2$ SiC $_5$ H $_4$ Li, 10): A solution of silane **8** (5.19 g, 23.1 mmol) in pentane (50 mL) was cooled to 0 °C. On adding 2.5 M *n*BuLi in hexane (10 mL, 25 mmol, diluted with 10 mL pentane) a white solid precipitated. After warming up to room temperature, stirring was continued for 3 h. The solid was then filtered off, washed with pentane, and dried in vacuo. Complex **10** is an air-sensitive white powder, which is well soluble in THF. Yield: 4.98 g (21.6 mmol, 93%). M.p. 150 °C (dec.). $C_{15}H_{15}LiSi$ (230.312 g/mol): calcd. C 78.23, H 6.57; found C 77.10, H 6.90. 1H NMR (400.1 MHz, 1.2 M in THF, 22 °C): δ = 7.33 (m, 2 H, Ph_{ortho}), 7.19 (m, 3 H, $Ph_{meta+para}$), 5.91 (m/br, 2 H, C_5H_4), 5.77 (br. m, 2 H, C_5H_4), 0.34 (s, $^1J_{HC}$ = 119.3 Hz, 6 H, $SiMe_2$) ppm. ^{13}C NMR (100.6 MHz, 1.2 M in THF, 22 °C): δ = 132.0 (s, 2 C, Ph_{ortho}), 128.7 (s, 2 C, Ph_{meta}), 128.3 (s, 1 C, Ph_{para}), 125.1 (s, 1 C, Ph_{ipso}), 112.4 (s, 2 C, CH_{Cp}), 107.6 (s, 2 C, CH_{Cp}), 105.7 (s, 1 C, $C\equiv C-Si$), 103.9 (s, 1 C, C_{Cp}), 98.1 (s, 1 C, $C\equiv C-Si$), 1.3 (s, $^1J_{CSi}$ = 55 Hz, 2 C, $SiMe_2$) ppm. ^{29}Si NMR (79.5 MHz, 1.2 M in THF, 22 °C): δ = -30.4 [s, $^1J_{SiC(Me)}$ = 56 (2 C), $^1J_{SiC(C_5H_4)}$ = 80 (1 C), $^1J_{SiC(C\equiv C)}$ = 88 (1 C), $^2J_{SiC(C\equiv C)}$ = 15 Hz (1 C)] ppm.

Dimethyl(pent-1-yn-1-yl)phenylsilane (PrC $\equiv$ CMe $_2$ SiPh, 12): A solution of PhMe $_2$ SiCl (8.0 mL, 8.64 g, 50.6 mmol) in Et $_2$ O (17 mL) was added at room temperature to a solution of PrC $\equiv$ CMgBr in Et $_2$ O [prepared according to standard procedures^[88] from Mg (1.44 g, 59.2 mmol), 1,2-dibromoethane (0.15 mL), EtBr (5.3 mL, 7.74 g, 71.0 mmol), 1-pentyne (6.5 mL, 4.47 g, 65.7 mmol), and Et $_2$ O (110 mL)]. The mixture was then heated to reflux for 3 h. After cooling to room temperature, the solution was cautiously hydrolyzed with 2 M NH_4Cl solution, washed with water, and dried with Na_2SO_4 . The Et $_2$ O was evaporated by standing in the fume hood overnight. Distillation of the residue under reduced pressure furnished **12** as a colorless oil. Yield: 8.99 g (44.4 mmol, 88%). Density: 0.90 g/mL. B.p. 68–71 °C (0.2 kPa). $C_{13}H_{18}Si$ (202.373 g/mol): calcd. C 77.16, H 8.97; found C 76.92, H 8.93. 1H NMR (400.1 MHz, $CDCl_3$, 22 °C): δ = 7.63 (m, 2 H, Ph_{ortho}), 7.35 (m, 3 H, $Ph_{meta+para}$), 2.23 (t, $^3J_{HH}$ = 7.0 Hz, 2 H, $-CH_2-CH_2-CH_3$), 1.55 (apparent sext, $^3J_{HH}$ = 7.2 Hz, 2 H, $-CH_2-CH_2-CH_3$), 0.99 (t, $^3J_{HH}$ = 7.4 Hz, 3 H, $-CH_2-CH_2-CH_3$), 0.39 (s, $^1J_{HC}$ = 120.4, $^2J_{HSi}$ = 7.0 Hz, 6 H, $SiMe_2$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 22 °C): δ = 137.7 (s, $^1J_{CSi}$ = 74 Hz, 1 C, Ph_{ipso}), 133.7 (s, 2 C, Ph_{ortho}), 129.2 (s, 1 C, Ph_{para}), 127.8 (s, 2 C, Ph_{meta}), 109.4 (s, 1 C, $C\equiv C-Si$), 82.4 (s, $^1J_{CSi}$ = 91 Hz, 1 C, $C\equiv C-Si$), 22.1 (s, 1 C, $-CH_2-$), 21.9 (s, 1 C, $-CH_2-$), 13.4 (s, 1 C, $-CH_3$), -0.6 (s, $^1J_{CSi}$ = 57 Hz, 2 C, $SiMe_2$) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 22 °C): δ = -22.9 [s, $^1J_{SiC(Me)}$ = 57 (2 C), $^1J_{SiC(Ph)}$ = 73 (1 C), $^1J_{SiC(C\equiv C)}$ = 91 (1 C), $^2J_{SiC(C\equiv C)}$ = 17 Hz (1 C)] ppm.

Alkyne Complexes

$\{\mu$ -Dimethyl[(1,2- η :1,2- η)-phenylethynyl]silane}bis[dicarbonyl(η^5 -cyclopentadienyl)molybdenum(I)](*Mo–Mo*) [PhC $\equiv$ CMe $_2$ SiH-Cp $_2$ -Mo $_2$ (CO) $_4$, 13]: Cp $_2$ Mo $_2$ (CO) $_4$ (434 mg, 1.00 mmol) was dissolved

in THF (20 mL), and silane **4** (190 μ L, 180 mg, 1.12 mmol) was added. After stirring at room temperature for 6 d, the volatiles were evaporated in vacuo and the residue extracted with toluene (4 mL). The extract was concentrated in vacuo to 2 mL and layered with hexane (4 mL). On cooling to -78°C a solid precipitated, which was separated, washed with hexane, and dried in vacuo (400 mg, 67% crude yield). The solid was recrystallized from hexane (135 mL) at -20°C and then once again from benzene (3 mL)/hexane (12 mL) at -20°C to give dark brownish-red crystals, which were separated, washed with hexane, and dried in vacuo. The by-product $\text{Cp}_2\text{Mo}_2(\text{CO})_6$, which was easily recognized by its violet color, was removed mechanically under a microscope. Complex **13** is air-stable for at least some days but should be stored under argon. It is soluble in benzene, toluene, and THF but only sparingly soluble in hexane. Yield: 250 mg (0.42 mmol, 42%). M.p. $179\text{--}181^\circ\text{C}$ (argon), 165°C (dec., air). $\text{C}_{24}\text{H}_{22}\text{Mo}_2\text{O}_4\text{Si}$ (594.402): calcd. C 48.50, H 3.73; found C 48.55, H 3.73. ^1H NMR (400.1 MHz, 0.09 M in C_6D_6 , 22°C): $\delta = 7.44$ (dm, $^3J_{\text{HH}} = 7.7\text{ Hz}$, 2 H, Ph_{ortho}), 7.13 ("t", $^3J_{\text{HH}} = 7.7\text{ Hz}$, 2 H, Ph_{meta}), 6.90 (tt, $^3J_{\text{HH}} = 7.3$, $^4J_{\text{HH}} = 1\text{ Hz}$, 1 H, Ph_{para}), 4.93 (sept, $^3J_{\text{HH}} = 3.7\text{ Hz}$, 1 H, SiH), 4.82 (s, 10 H, Cp), 0.33 (d, $^3J_{\text{HH}} = 3.7$, $^1J_{\text{HC}} = 120\text{ Hz}$, 6 H, SiMe_2) ppm. ^{13}C NMR (100.6 MHz, 0.09 M in C_6D_6 , 22°C): $\delta = 230.9$ (s, CO), 230.5 (s, CO), 147.5 (s, 1 C, Ph_{ipso}), 129.8 (s, 2 C, Ph_{ortho}), 128.5 (s, 2 C, Ph_{meta}), 126.5 (s, 1 C, Ph_{para}), 111.0 (s, 1 C, $\text{C}\equiv\text{C}-\text{Si}-\text{Mo}_2$), 92.1 (s, 10 C, Cp), $^{90}\text{--}1.1$ (s, $^1J_{\text{CSi}} = 51\text{ Hz}$, 2 C, SiMe_2) ppm. ^{29}Si NMR (79.5 MHz, 0.09 M in C_6D_6 , 22°C): $\delta = -9.5$ [s (^1H -coupled: dsept), $^1J_{\text{SiH}} = 195$, $^2J_{\text{SiH}} = 7$, $^1J_{\text{SiC(Me)}} = 52$ (2 C), $^1J_{\text{SiC(C}\equiv\text{C-Mo}_2\text{)}} = 77\text{ Hz}$ (1 C)] ppm. ^{95}Mo NMR (26.0 MHz, 0.09 M in C_6D_6 , 22°C): $\delta = -1.887$ (br., $\Delta\nu_{1/2} = 500\text{ Hz}$) ppm.

$\{\mu\text{-(Cyclopenta-2,4-dien-1-yl)dimethyl[(1,2-\eta\text{-(1,2-\eta-phenylethynyl)silane}\}\text{bis[tricarboxylcobalt(0)](Co-Co)}\}$ [PhC $\equiv$ CMe $_2$ SiCp-Co $_2$ (CO) $_6$, **14a-c]:** A solution of $\text{Co}_2(\text{CO})_8$ (1.710 g, 5.00 mmol) in hexane (30 mL) was added with stirring at room temperature to a solution of **8** (1.130 g, 5.04 mmol) in hexane (25 mL). The mixture turned dark brown, and a gas evolution commenced. After 1 d, the solution was filtered, concentrated in vacuo to 10 mL, and cooled to -78°C . On warming up to -20°C a solid precipitated, which was separated, washed with hexane, and dried in vacuo. Complex **14** forms dark brown crystals, which can be handled in air but should be stored under argon. It is soluble in hexane and benzene. Yield: 990 mg (1.94 mmol, 39%). M.p. $42\text{--}45^\circ\text{C}$ (argon), $43\text{--}46^\circ\text{C}$ (air). $\text{C}_{21}\text{H}_{16}\text{Co}_2\text{O}_6\text{Si}$ (510.305 g/mol): calcd. C 49.43, H 3.16; found C 50.15, H 3.16. ^1H NMR (400.1 MHz, 0.11 M in C_6D_6 , 22°C): $\delta = 7.62$ (d, $^3J_{\text{HH}} = 7.3\text{ Hz}$, 2 H, Ph_{ortho}), 7.04 ("t", $^3J_{\text{HH}} = 7.3\text{ Hz}$, 2 H, Ph_{meta}), 6.97 (t, $^3J_{\text{HH}} = 7.3\text{ Hz}$, 1 H, Ph_{para}), 6.61 (br., $\Delta\nu_{1/2} = 15\text{ Hz}$, 2 H, CH_{Cp}), 6.48 (br., $\Delta\nu_{1/2} = 23\text{ Hz}$, 2 H, CH_{Cp}), 3.56 (br., $\Delta\nu_{1/2} = 20\text{ Hz}$, 1 H, SiCH_{Cp}), 0.20 (s, $\Delta\nu_{1/2} = 4$, $^1J_{\text{HC}} = 121\text{ Hz}$, 6 H, SiMe_2) ppm. ^{13}C NMR (100.6 MHz, 0.11 M in C_6D_6 , 22°C): $\delta = 200.3$ (br., $\Delta\nu_{1/2} = 41\text{ Hz}$, CO), 138.2 (s, $\Delta\nu_{1/2} = 4\text{ Hz}$, 1 C, Ph_{ipso}), 133.1 (br., $\Delta\nu_{1/2} = 29\text{ Hz}$, 2 C, CH_{Cp}), 131.9 (br., $\Delta\nu_{1/2} = 18\text{ Hz}$, 2 C, CH_{Cp}), 130.3 (s, $\Delta\nu_{1/2} = 5\text{ Hz}$, 2 C, Ph_{ortho}), 129.3 (s, $\Delta\nu_{1/2} = 4\text{ Hz}$, 2 C, Ph_{meta}), 128.6 (s, $\Delta\nu_{1/2} = 5\text{ Hz}$, 1 C, Ph_{para}), 106.6 (s, $\Delta\nu_{1/2} = 9\text{ Hz}$, 1 C, $\text{C}\equiv\text{C}-\text{Si}-\text{Co}_2$), 78.8 (s, $\Delta\nu_{1/2} = 7\text{ Hz}$, 1 C, $\text{C}\equiv\text{C}-\text{Si}-\text{Co}_2$), 52.4 (br., $\Delta\nu_{1/2} = 31\text{ Hz}$, 1 C, SiCH_{Cp}), -1.9 (s, $\Delta\nu_{1/2} = 5$, $^1J_{\text{CSi}} = 58\text{ Hz}$, 2 C, SiMe_2) ppm (**14a**); $\delta = 144.8$ (s, 1 C, CH_{Cp}), 139.0 (s, 1 C, CH_{Cp}), 133.2 (s, 1 C, CH_{Cp}), 130.1 (s, 2 C, Ph_{ortho}), 129.3 (s, 1 C, Ph_{meta}), 106.2 (s, 1 C, $\text{C}\equiv\text{C}-\text{Si}-\text{Co}_2$), 79.9 (s, 1 C, $\text{C}\equiv\text{C}-\text{Si}-\text{Co}_2$), 45.8 (s, 1 C, CH_2), -0.1 (s, 2 C, SiMe_2) ppm (**14b**); $\delta = 44.0$ (s, 1 C, CH_2), -0.6 (s, 2 C, SiMe_2) ppm (**14c**). ^{29}Si NMR (79.5 MHz, 0.11 M in C_6D_6 , 22°C): $\delta = -0.6$ [s, $^1J_{\text{SiC(Me/Cp)}} = 58$ (3 C), $^1J_{\text{SiC(C}\equiv\text{C-Co}_2\text{)}} = 68\text{ Hz}$ (1 C, **14a**), -10.6 (s, **14b**), -10.8 (s, **14c**) ppm. ^{59}Co NMR (94.7 MHz, 0.11 M in C_6D_6 , 22°C): $\delta = -2300 \pm 100$ (br., $\Delta\nu_{1/2} = 27\text{ kHz}$) ppm.

Trisilanes: Compounds **18** and **19** were not isolated and directly used in the next step. Silanes **20–23** were isolated, but not purified by distillation because of the small amounts and their high boiling points. Hence, elemental analyses were not carried out except for silane **23**. Nevertheless, the spectroscopic data confirm the identity of **18–23**.

1-(Diethylamino)-1,1,2,2,3,3-hexamethyl-3-phenyltrisilane [Ph-(SiMe $_2$) $_3$ -NET $_2$, **18]:** A solution of $\text{Et}_2\text{NMe}_2\text{Si-SiMe}_2\text{Cl}$ (5.1 mL, 4.57 g, 20.4 mmol) in THF (10 mL) was cooled to 0°C , and a solution of PhMe_2SiLi [21.1 mmol, prepared from PhMe_2SiCl (3.34 mL, 3.61 g, 21.1 mmol), Li (295 mg, 42.5 mmol), and THF (40 mL)]^[74b] was added within 45 min. The mixture slowly turned red. After stirring at room temperature overnight, a clear honey-colored solution of **18** in THF was obtained. As judged by ^{29}Si NMR spectroscopy it contained some impurities but was sufficiently pure for the next step. $\text{C}_{16}\text{H}_{33}\text{NSi}_3$ (323.705 g/mol). ^{29}Si NMR (79.5 MHz, THF, 22°C): $\delta = -0.6$ [s, $^1J_{\text{SiC(Me)}} = 48$, $^1J_{\text{SiSi}} = 84$, $^2J_{\text{SiSi}} = 8\text{ Hz}$, 1 Si, $-\text{SiMe}_2\text{NET}_2$], -19.5 [s, $^1J_{\text{SiC(Me)}} = 45$ (2 C), $^1J_{\text{SiC(Ph)}} = 59$ (1 C), $^1J_{\text{SiSi}} = 71$, $^2J_{\text{SiSi}} = 9\text{ Hz}$, 1 Si, $-\text{SiMe}_2\text{Ph}$], -51.0 [s, $^1J_{\text{SiC(Me)}} = 37$, $^1J_{\text{SiSi}} = 71$, $^1J_{\text{SiSi}} = 84\text{ Hz}$, 1 Si, $-\text{SiMe}_2$] ppm.

1-Methoxy-1,1,2,2,3,3-hexamethyl-3-phenyltrisilane [Ph-(SiMe $_2$) $_3$ -OMe, **19]:** Methanol (2.0 mL, 49.4 mmol) was added at room temperature with stirring to the crude THF solution obtained in the synthesis of **18**. The mixture quickly turned greenish-yellow. Evaporation of the solvent in vacuo after 1 h left a brownish-yellow oil (**19**) and a white solid (LiCl), which could be used for the next step without separation. $\text{C}_{13}\text{H}_{26}\text{OSi}_3$ (282.608 g/mol). ^{29}Si NMR (79.5 MHz, THF, 22°C): $\delta = +19.3$ [s, $^1J_{\text{SiC(Me)}} = 48$, $^1J_{\text{SiSi}} = 85$, $^2J_{\text{SiSi}} = 9\text{ Hz}$, 1 Si, $-\text{SiMe}_2\text{OMe}$], -18.8 [s, $^1J_{\text{SiC(Me)}} = 45$ (2 C), $^1J_{\text{SiC(Ph)}} = 58$ (1 C), $^1J_{\text{SiSi}} = 73$, $^2J_{\text{SiSi}} = 8\text{ Hz}$, 1 Si, $-\text{SiMe}_2\text{Ph}$], -50.4 [s, $^1J_{\text{SiC(Me)}} = 38$, $^1J_{\text{SiSi}} = 73$, $^1J_{\text{SiSi}} = 85\text{ Hz}$, 1 Si, $-\text{SiMe}_2$] ppm.

1-Chloro-1,1,2,2,3,3-hexamethyl-3-phenyltrisilane [Ph-(SiMe $_2$) $_3$ -Cl, **20]:** The mixture obtained in the synthesis of **19** was dissolved in hexane (15 mL). Then acetyl chloride (5 mL, 70.4 mmol) was added at room temperature with stirring. After 1 h, the solution was filtered and the residue washed with hexane. From the combined filtrates and washings the volatiles were removed in vacuo leaving an orange-yellow oil. According to its ^{29}Si NMR spectrum it consisted of **20** and some impurities and was sufficiently pure for further reactions. Yield: 5.42 g (18.9 mmol, 92% crude). $\text{C}_{12}\text{H}_{23}\text{ClSi}_3$ (287.027 g/mol). ^{29}Si NMR (79.5 MHz, hexane, 22°C): $\delta = +26.5$ [s, $^1J_{\text{SiC(Me)}} = 46$, $^1J_{\text{SiSi}} = 79$, $^2J_{\text{SiSi}} = 10\text{ Hz}$, 1 Si, $-\text{SiMe}_2\text{Cl}$], -19.2 [s, $^1J_{\text{SiC(Me)}} = 46$ (2 C), $^1J_{\text{SiC(Ph)}} = 59$ (1 C), $^1J_{\text{SiSi}} = 75$, $^2J_{\text{SiSi}} = 10\text{ Hz}$, 1 Si, $-\text{SiMe}_2\text{Ph}$], -45.6 [s, $^1J_{\text{SiC(Me)}} = 40$, $^1J_{\text{SiSi}} = 74$, $^1J_{\text{SiSi}} = 80\text{ Hz}$, 1 Si, $-\text{SiMe}_2$] ppm.

1,1,2,2,3,3-Hexamethyl-1-phenyltrisilane [Ph-(SiMe $_2$) $_3$ -H, **21]:** A solution of **20** (1.45 g, 5.1 mmol) in Et_2O (10 mL) was added at 0°C to excess LiAlH_4 (1.5 mmol) in Et_2O (10 mL). After warming up to room temperature, the solvent was distilled off in vacuo, and the residue was extracted with hexane. The extract was then concentrated in vacuo leaving a colorless oil. According to its ^{29}Si NMR spectrum it consisted of **21** and minor impurities. Yield: 1.16 g (4.6 mmol, 91% crude). $\text{C}_{12}\text{H}_{24}\text{Si}_3$ (252.582 g/mol). ^{29}Si NMR (79.5 MHz, Et_2O , 22°C): $\delta = -18.3$ [s, $^1J_{\text{SiC(Me)}} = 45$, $^1J_{\text{SiC(Ph)}} = 59$ (1 C), $^1J_{\text{SiSi}} = 74$, $^2J_{\text{SiSi}} = 8\text{ Hz}$, 1 Si, $-\text{SiMe}_2\text{Ph}$], -36.3 (s, $^1J_{\text{AB}}$ not observed, 1 Si, $-\text{SiMe}_2\text{H}$), -47.4 [s, $^1J_{\text{SiC(Me)}} = 39$, $^1J_{\text{SiSi}} = 74$, $^1J_{\text{SiSi}} = 71\text{ Hz}$?, 1 Si, $-\text{SiMe}_2$] ppm.

1,1,2,2,3,3-Hexamethyl-1-(pent-1-yn-1-yl)-3-phenyltrisilane [Ph-(SiMe $_2$) $_3$ -C $\equiv$ CPent, **23]:** A solution of $\text{PrC}\equiv\text{CMgBr}$ in Et_2O [prepared according to standard procedures^[88] from Mg (390 mg, 16.0 mmol), 1,2-dibromoethane (50 μ L), EtBr (2.0 mL, 2.9 g, 26.8 mmol), 1-pentyne (2.0 mL, 1.38 g, 20.2 mmol), and Et_2O

(32 mL)] was added to **20** (2.275 g, 7.9 mmol) in Et₂O (20 mL). The mixture was stirred at room temperature for 1 h and heated to reflux for another hour. Then it was cautiously hydrolyzed with 2 M NH₄Cl solution, washed with water, and dried with Na₂SO₄. After removal of the Et₂O, the residue was dissolved in hexane, filtered, and the filtrate concentrated in vacuo leaving a light yellow oil. Yield: 2.52 g (7.9 mmol, 99% crude). C₁₇H₃₀Si₃ (318.685 g/mol): calcd. C 64.07, H 9.49; found C 65.65, H 9.65. ¹H NMR (400.1 MHz, CDCl₃, 22 °C): δ = 7.46 (m, 2 H, Ph_{ortho}), 7.32 (m, 3 H, Ph_{meta + para}), 2.21 (t, ³J_{HH} = 7.0 Hz, 2 H, –CH₂–CH₂–CH₃), 1.53 (apparent sext, ³J_{HH} = 7.2 Hz, 2 H, –CH₂–CH₂–CH₃), 0.98 (t, ³J_{HH} = 7.4 Hz, 3 H, –CH₂–CH₂–CH₃), 0.41 (s, 6 H, SiMe₂), 0.11 (s, 12 H, SiMe₂) ppm. ¹³C NMR (100.6 MHz, CDCl₃, 22 °C): δ = 139.7 (s, 1 C, Ph_{ipso}), 133.8 (s, 2 C, Ph_{ortho}), 128.3 (s, 1 C, Ph_{para}), 127.7 (s, 2 C, Ph_{meta}), 109.9 (s, 1 C, C≡C–Si), 83.2 (s, 1 C, C≡C–Si), 22.2 (s, 1 C, –CH₂–), 22.1 (s, 1 C, –CH₂–), 13.5 (s, 1 C, –CH₃), –1.9 (s, ¹J_{CSi} = 50 Hz, 2 C, –SiMe₂C≡CPr), –3.1 (s, ¹J_{CSi} = 46 Hz, 2 C, –SiMe₂Ph), –6.8 (s, ¹J_{CSi} = 39 Hz, 2 C, –SiMe₂–) ppm. ²⁹Si NMR (79.5 MHz, CDCl₃, 22 °C): δ = –18.4 [s, ¹J_{SiC(Me)} = 45 (2 C), ¹J_{SiC(Ph)} = 58 (1 C), ¹J_{SiSi} = 73, ²J_{SiSi} = 9 Hz, 1 Si, –SiMe₂Ph], –35.2 [s, ¹J_{SiC(Me)} = 49 (2 C), ¹J_{SiC(C≡C)} not observed, ²J_{SiC(C≡C)} = 14 (1 C), ¹J_{SiSi} = 79, ²J_{SiSi} = 8 Hz, 1 Si, –SiMe₂C≡CPr], –47.6 [s, ¹J_{SiC(Me)} = 39, ¹J_{SiSi} = 73, ¹J_{SiSi} = 79 Hz, 1 Si, –SiMe₂–] ppm.

1,1,2,2,3,3-Hexamethyl-1-phenyl-3-(phenylethynyl)trisilane [Ph–(SiMe₂)₃–C≡CPh, **22]:** Compound **22** was prepared analogously to **23** from Mg (300 mg, 12.3 mmol), 1,2-dibromoethane (50 μL), EtBr (2.0 mL, 2.9 g, 26.8 mmol), PhC≡CH (1.4 mL, 1.30 g, 12.8 mmol), **20** (1.75 g, 6.1 mmol), and Et₂O (45 mL). It was obtained as an orange oil (2.62 g, theoretical yield: 2.15 g). According to its NMR spectra it was contaminated with PhC≡CH (ca. 15%) and minor amounts of other impurities, which could not be removed in vacuo. C₂₀H₂₈Si₃ (352.702 g/mol). ¹H NMR (400.1 MHz, CDCl₃, 22 °C): δ = 7.46 (m, 4 H, Ph_{ortho}), 7.29 (m, 6 H, Ph_{meta + para}), 0.44 (s, 6 H, SiMe₂), 0.21 (s, 6 H, SiMe₂), 0.18 (s, 6 H, SiMe₂) ppm. ¹³C NMR (100.6 MHz, CDCl₃, 22 °C): δ = 139.4 (s, 1 C, Ph_{ipso}), 133.8 (s, 2 C, Ph_{ortho}), 131.8 (s, 2 C, PhC≡C_{ortho}), 128.4 (s, 1 C, Ph_{para}), 128.3 (s, 1 C, Ph_{para}), 128.2 (s, 2 C, PhC≡C_{meta}), 127.7 (s, 2 C, Ph_{meta}), 123.4 (s, 1 C, PhC≡C_{ipso}), 107.6 (s, 1 C, C≡C–Si), 93.4 (s, 1 C, C≡C–Si), –2.2 (s, ¹J_{CSi} = 49 Hz, 2 C, –SiMe₂C≡CPh), –3.1 (s, ¹J_{CSi} = 46 Hz, 2 C, –SiMe₂Ph), –6.8 (s, ¹J_{CSi} = 39 Hz, 2 C, –SiMe₂–) ppm. ²⁹Si NMR (79.5 MHz, CDCl₃, 22 °C): δ = –18.4 [s, ¹J_{SiC(Me)} = 46 (2 C), ¹J_{SiC(Ph)} = 59 (1 C), ¹J_{SiSi} = 74, ²J_{SiSi} = 8 Hz, 1 Si, –SiMe₂Ph], –34.0 [s, ¹J_{SiC(Me)} = 49 (2 C), ¹J_{SiC(C≡C)} not observed because of impurities, ²J_{SiC(C≡C)} = 13 (1 C), ¹J_{SiSi} = 79, ²J_{SiSi} = 8 Hz, 1 Si, –SiMe₂C≡CPh], –47.2 [s, ¹J_{SiC(Me)} = 39, ¹J_{SiSi} = 74, ¹J_{SiSi} = 78 Hz, 1 Si, –SiMe₂–] ppm.

Supporting Information (see footnote on the first page of this article): GC-MS, IR, and UV/Vis data of the reported compounds as well as experimental details and spectroscopic data of **2**, **3**, **4**, **7**, **9**, and **11**; experimental details of the crystal structure determinations and tables with bond lengths and angles.

Acknowledgments

The authors thank the Fonds der Chemischen Industrie for financial support of this work.

- [1] F. Hoffmann, J. Wagler, G. Roewer in *14th International Symposium on Organosilicon Chemistry/3rd European Organosilicon Days*, Book of Abstracts, Würzburg, **2005**, p. 139.
- [2] Manuscript in preparation.
- [3] O. N. Florensova, B. A. Sokolov, L. I. Volkova, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1973**, 6, 1390–1392.

- [4] C. Eaborn, W. A. Stanczyk, *J. Chem. Soc. Perkin Trans. 2* **1984**, 12, 2099–2103.
- [5] J. Chmielecka, J. Chojnowski, C. Eaborn, W. A. Stanczyk, *J. Chem. Soc. Perkin Trans. 2* **1985**, 11, 1779–1783.
- [6] N. V. Komarov, L. I. Ol'khovskaya, K. S. Pushkareva, L. A. Soboleva, *Zh. Obshch. Khim.* **1984**, 54, 1584–1587.
- [7] B. Wrackmeyer, G. Kehr, J. Süß, *Chem. Ber.* **1993**, 126, 2221–2226.
- [8] P. Lapouyade, G. Deleris, J. Dunoguès, R. Calas, *J. Organomet. Chem.* **1974**, 80, C45–C46.
- [9] K. Tamao, E. Nakajo, Y. Ito, *Tetrahedron* **1988**, 44, 3997–4007.
- [10] S. I. Nitsche, Ph. D. Thesis, TU Bergakademie Freiberg, **2002**.
- [11] L. I. Ol'khovskaya, N. V. Komarov, K. S. Pushkareva, G. V. Pletneva, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* **1988**, 31, 29–32.
- [12] I. M. Gverdtseteli, M. I. Dzheleliya, L. V. Baramidze, *Soobshch. Akad. Nauk Gruz. SSR* **1976**, 84, 381–384.
- [13] The detour via the methoxysilane was chosen because the direct reaction of (diethylamino)silane with acetyl chloride would give *N,N*-diethylacetamide, which is a liquid with a high boiling point and hardly possible to separate from the product. Diethylamine and methyl acetate are, however, volatile liquids and easy to remove in vacuo.
- [14] Z. H. Aiube, J. Chojnowski, C. Eaborn, W. A. Stanczyk, *J. Chem. Soc., Chem. Commun.* **1983**, 9, 493–495.
- [15] V. E. Baikov, L. P. Danilkina, K. A. Ogloblin, *Zh. Obshch. Khim.* **1983**, 53, 1330–1335.
- [16] R. J. P. Corriu, J. J. E. Moreau, H. Praet, *Organometallics* **1990**, 9, 2086–2091.
- [17] E. T. Bogorodovskii, *Zh. Obshch. Khim.* **1992**, 62, 957–958.
- [18] Sh. Y. Feng, Sh. Q. Yu, Sh. J. Li, Sh. Y. Zhang, J. H. Chen, Z. D. Du, *Chin. J. Polym. Sci.* **1995**, 13, 228–234.
- [19] H. Sugita, Y. Hatanaka, T. Hiyama, *Chem. Lett.* **1996**, 5, 379–380.
- [20] H. G. Schuster, E. Hengge, *Monatsh. Chem.* **1983**, 114, 1305–1310.
- [21] U. Herrmann, H. Marsmann, F. Uhlig, *Silicon NMR Database V2.0*, Dortmund, **1999–2000**.
- [22] Three isomers: (cyclopenta-2,4-dien-1-yl)- (**8a**), (cyclopenta-2,4-dien-2-yl)- (**8b**), and (cyclopenta-2,4-dien-3-yl)dimethyl-(phenylethynyl)silane (**8c**).
- [23] R. W. Martin, General Electric Co., US 2667501, **1954**.
- [24] M. Ishikawa, H. Sugisawa, O. Harata, M. Kumada, *J. Organomet. Chem.* **1981**, 217, 43–50.
- [25] S. Kotani, T. Matsumoto, H. Yamaguchi, K. Shiina, K. Sonogashira, *Chem. Lett.* **1989**, 2, 293–296.
- [26] R. J. P. Corriu, J. J. E. Moreau, H. Praet, *J. Organomet. Chem.* **1989**, 376, C39–C43.
- [27] R. J. P. Corriu, J. J. E. Moreau, H. Praet, *Organometallics* **1989**, 8, 2779–2786.
- [28] H. Lang, U. Lay, *J. Organomet. Chem.* **1990**, 388, C1–C4.
- [29] H. Lang, U. Lay, L. Zsolnai, *J. Organomet. Chem.* **1991**, 417, 377–387.
- [30] U. Lay, H. Lang, *J. Organomet. Chem.* **1991**, 418, 79–89.
- [31] H. Lang, U. Lay, M. Weinmann, *J. Organomet. Chem.* **1992**, 436, 265–276.
- [32] H. Lang, M. Weinmann, L. Zsolnai, *J. Organomet. Chem.* **1996**, 522, 277–289.
- [33] K. H. Pannell, A. R. Bassindale, J. W. Fitch, *J. Organomet. Chem.* **1981**, 209, C65–C68.
- [34] ⁹⁵Mo NMR (26.0 MHz, C₆D₆, 22 °C): δ = –1854 (Δν_{1/2} = 470 Hz) ppm. IR (THF): ν̄ = 1983, 1925, 1840 (C≡O) cm^{–1}. UV/Vis (hexane): λ (ε) = 216 (70000, sh up to 300 nm), 363 (12000), 544 (1500 L mol^{–1} cm^{–1}) nm.
- [35] R. J. Klingler, W. Butler, M. D. Curtis, *J. Am. Chem. Soc.* **1975**, 97, 3535–3536.
- [36] J. A. Beck, S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, P. Woodward, *J. Chem. Soc., Dalton Trans.* **1982**, 1, 195–200.

- [37] D. S. Ginley, C. R. Bock, M. S. Wrighton, B. Fischer, D. L. Tipton, R. Bau, *J. Organomet. Chem.* **1978**, *157*, 41–50.
- [38] W. I. Bailey, M. H. Chisholm, F. A. Cotton, L. A. Rankel, *J. Am. Chem. Soc.* **1978**, *100*, 5764–5773.
- [39] W. I. Bailey, F. A. Cotton, J. D. Jamerson, J. R. Kolb, *J. Organomet. Chem.* **1976**, *121*, C23–C26.
- [40] P. Galow, A. Sebald, B. Wrackmeyer, *J. Organomet. Chem.* **1983**, *259*, 253–268.
- [41] G. Bor, *Chem. Ber.* **1963**, *96*, 2644–2648.
- [42] G. Varadi, I. Vecsei, A. Vizi-Orosz, G. Palyi, A. G. Massey, *J. Organomet. Chem.* **1976**, *114*, 213–217.
- [43] G. Bor, S. F. A. Kettle, P. L. Stanghellini, *Inorg. Chim. Acta* **1976**, *18*, L18–L20.
- [44] G. Peyronel, A. Ragni, E. F. Trogu, *Gazz. Chim. Ital.* **1967**, *97*, 1327–1343.
- [45] Average value of 37 crystal structures of cyclopentane solvates (CSD search).
- [46] J. A. Connor, G. A. Hudson, *J. Organomet. Chem.* **1975**, *97*, C43–C45.
- [47] J. A. Connor, G. A. Hudson, *J. Organomet. Chem.* **1978**, *160*, 159–164.
- [48] H. Kolshorn, H. Meier, E. Müller, *Tetrahedron Lett.* **1972**, *13*, 1589–1592.
- [49] A. N. Nesmeyanov, V. V. Krivikh, V. S. Kaganovich, M. I. Rybinskaya, *Koord. Khim.* **1975**, *1*, 634–640.
- [50] T. Szymanska-Buzar, T. Glowiak, *J. Organomet. Chem.* **1994**, *467*, 223–230.
- [51] G. Hogarth, J. Y. Pang, *J. Organomet. Chem.* **1996**, *515*, 193–203.
- [52] A. I. Kuramshin, A. A. Nikolaev, R. A. Cherkasov, *Mendeleev Commun.* **2005**, *4*, 155–156.
- [53] C. Hernandez, H. K. Sharma, K. H. Pannell, *J. Organomet. Chem.* **1993**, *462*, 259–264.
- [54] K. E. Ruehl, M. E. Davis, K. Matyjaszewski, *Organometallics* **1992**, *11*, 788–794.
- [55] M. Savignac, G. Jaouen, C. A. Rodger, R. E. Perrier, B. G. Sayer, M. J. McGlinchey, *J. Org. Chem.* **1986**, *51*, 2328–2332.
- [56] A. Meyer, D. J. McCabe, M. D. Curtis, *Organometallics* **1987**, *6*, 1491–1498.
- [57] M. H. Chisholm, B. K. Conroy, D. L. Clark, J. C. Huffman, *Polyhedron* **1988**, *7*, 903–918.
- [58] F. Cervantes-Lee, L. Parkanyi, R. N. Kapoor, A. J. Mayr, K. H. Pannell, Y. Pang, T. J. Barton, *J. Organomet. Chem.* **1998**, *562*, 29–33.
- [59] L. J. Todd, J. R. Wilkinson, *J. Organomet. Chem.* **1974**, *80*, C31–C34.
- [60] S. Aime, L. Milone, R. Rossetti, P. L. Stanghellini, *Inorg. Chim. Acta* **1977**, *22*, 135–139.
- [61] A. M. Montaña Pedrero, K. M. Nicholas, *Magn. Reson. Chem.* **1990**, *28*, 486–495.
- [62] D. Osella, O. Gambino, R. Gobetto, C. Nervi, M. Ravera, G. Jaouen, *Inorg. Chim. Acta* **1992**, *192*, 65–70.
- [63] B. Happ, T. Bartik, C. Zucchi, M. C. Rossi, F. Ghelfi, G. Palyi, G. Varadi, G. Szalontai, I. T. Horvath, A. Chiesi-Villa, C. Guastini, *Organometallics* **1995**, *14*, 809–819.
- [64] D. Pohl, J. Ellermann, M. Moll, F. A. Knoch, W. Bauer, *Z. Anorg. Allg. Chem.* **1996**, *622*, 283–291.
- [65] H. Lehmkuhl, F. Danowski, G. Mehler, J. Popawska, S. Pasynkiewicz, *J. Organomet. Chem.* **1989**, *363*, 387–391.
- [66] S. Pasynkiewicz, M. Poplawska, R. Mynott, *J. Organomet. Chem.* **1992**, *429*, 135–141.
- [67] H. Lehmkuhl, V. Dimitrov, *J. Organomet. Chem.* **1996**, *519*, 69–73.
- [68] Alkanes (sp³): 0 to +70 ppm; alkenes (sp²): +100 to +165 ppm; alkynes (sp): +60 to +100 ppm.^[69,70]
- [69] H.-O. Kalinowski, S. Berger, S. Braun, *¹³C-NMR-Spektroskopie*, Georg Thieme, Stuttgart, **1984**.
- [70] E. Breitmaier, W. Voelter, *Carbon-13 NMR Spectroscopy*, Wiley-VCH, Weinheim, **1987**.
- [71] Abbreviations: as asymmetric; br. broad; comb combination; d doublet; δ bending vibration; γ wagging vibration; m medium (IR), multiplet (NMR); ν stretching vibration; q quartet; ρ rocking vibration; s singlet (NMR), strong (IR), symmetric (IR); sh shoulder; t triplet; “t” apparent triplet; vs very strong; vw very weak; w weak; ? assignment ambiguous.
- [72] U. Herzog, K. Trommer, G. Roewer, *J. Organomet. Chem.* **1998**, *552*, 99–108.
- [73] T. K. Panda, M. T. Gamer, P. W. Roesky, *Organometallics* **2003**, *22*, 877–878.
- [74] a) I. Fleming in *Synthetic Methods of Organometallic and Inorganic Chemistry (Herrmann/Brauer)* (Eds.: W. A. Herrmann, N. Auner, U. Klingebiel), Georg Thieme, Stuttgart, **1996**, vol. 2, pp. 163–165; b) I. Fleming in *Synthetic Methods of Organometallic and Inorganic Chemistry (Herrmann/Brauer)* (Eds.: W. A. Herrmann, N. Auner, U. Klingebiel), Georg Thieme, Stuttgart, **1996**, vol. 2, pp. 167–169.
- [75] a) *Handbuch der Präparativen Anorganischen Chemie, Dritter Band* (Ed.: G. Brauer), Ferdinand Enke, Stuttgart, **1981**, pp. 1865–1866; b) *Handbuch der Präparativen Anorganischen Chemie, Dritter Band* (Ed.: G. Brauer), Ferdinand Enke, Stuttgart, **1981**, pp. 1683–1684.
- [76] M. D. Curtis, R. J. Klingler, *J. Organomet. Chem.* **1978**, *161*, 23–37.
- [77] H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby, I. Wender, *J. Am. Chem. Soc.* **1956**, *78*, 120–124.
- [78] *Multinuclear NMR* (Ed.: J. Mason), Plenum Press, New York, **1987**.
- [79] *The Chemistry of Functional Groups – The Chemistry of Organosilicon Compounds* (Eds.: S. Patai, Z. Rappaport), John Wiley & Sons, Chichester, **1989–2001**, vols. 1–3.
- [80] a) *Comprehensive Organometallic Chemistry – The Synthesis Reactions and Structures of Organometallic Compounds* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon Press, Oxford, **1982**; b) *Comprehensive Organometallic Chemistry – A Review of the Literature 1982–1994* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Elsevier Science, Oxford, **1995**.
- [81] C. Elschenbroich, *Organometallchemie*, B. G. Teubner, Stuttgart, **2003**.
- [82] *Studies in Inorganic Chemistry 13 – Transition Metal Nuclear Magnetic Resonance* (Ed.: P. S. Pregosin), Elsevier, Amsterdam, **1991**.
- [83] J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsfrequenzen*, Georg Thieme, Stuttgart, **1981–1986**.
- [84] *Gmelins Handbuch der Anorganischen Chemie – Cobalt-organische Verbindungen*, Verlag Chemie, Weinheim, **1973**.
- [85] *The Aldrich Library of FT-IR Spectra – Edition I* (Ed.: C. J. Pouchert), Aldrich Chemical Company, Milwaukee, **1985**.
- [86] a) G. M. Sheldrick, *SHELXS-97*, University of Göttingen, **1997**; b) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, **1997**.
- [87] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565–565.
- [88] L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, **1988**.
- [89] N. M. Sergeev, G. I. Avramenko, A. V. Kisin, V. A. Korenevsky, Yu. A. Ustynyuk, *J. Organomet. Chem.* **1971**, *32*, 55–77.
- [90] The second alkyne carbon signal is probably hidden by this peak.

Received: August 5, 2009

Published Online: January 13, 2010