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ARTICLE

Reactivity of Phenylacetylene toward Unsymmetrical Disilenes: Regiodivergent [2+2] Cycloaddition vs. CH Addition

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Dedicated to Prof. Hansgeorg Schnöckel on occasion of his 80th birthday.

We report the regiodivergent reaction of phenylacetylene with a selection of disilenes $Tip_2Si{=}SiTipR$ as well as bridged tetrasiladienes $Tip_2Si{=}SiTip{-}LU{-}SiTip{=}SiTip_2$ (Tip = 2,4,6-$^{i}Pr_3C_6H_2$, R = aryl groups; LU = arylene linkers). The regioselectivity of the [2+2] cycloaddition as determined by NMR spectroscopy and X-ray crystallography is shown to strongly depend on the nature of the substituent R. The small size of the substituents compared to the Tip groups in both cases suggests a change in mechanism between the substrates with only hydrogen in the *ortho*-positions of R and LU and those with either *ortho*-methyl groups or condensed aromatic rings. In contrast, the presence of catalytic quantities of base completely suppresses cycloaddtion in favor of the formal CH addition of phenylacetylene. Quenching reactions with either MeI or MeOH after the stoichiometric application of deprotonated phenylacetylene as well as NMR studies at low temperature prove the intermediacy of an alkynyl-substituted disilanyl lithium and thus suggest a carbolithiation pathway for the net CH addition.

Introduction

Concerted pathways for [2+2] cycloadditions of two multiple bonds are symmetry-forbidden under thermal conditions according to the Woodward-Hofmann rules.[1] Therefore, the [2+2] cycloaddition of two alkenes or alkynes requires activation by either UV irradiation or transition metal catalysts.[2] In contrast, uncatalyzed [2+2] thermal cycloadditions are among the most widely studied reactions of compounds with heavier double bonds.[3] In particular, the reactivity of species with Si=Si bond (disilenes) with alkynes to 1,2-disilacyclobutenes has been thoroughly investigated out of fundamental curiosity[4] and for its potential in polymerization.[5] Due to the above-mentioned incompatibility of the symmetries of the π and π* orbitals, these reactions typically occur in a stepwise manner. Although dipolar reaction courses have been postulated repeatedly,[6] most available evidence supports diradical pathways.[7]

[2+2] cycloadditions of transient disilenes with phenylacetylene to give 1,2-disilacyclobutenes **Ia** were reported by Sakurai and co-workers as early as 1985 (Chart 1).[8] The reaction of the stable disilene $Mes_2Si{=}SiMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$) with various polar alkynes yields air-stable disilacyclobutenes **Ib–g**.[6] As no reaction was observed with non-polar alkynes such as acetylene, diphenylacetylene, dimethyl acetylenedicarboxylate and phenyl(trimethylsilyl)acetylene, a stepwise dipolar reaction pathway was proposed. Using an elegant "radical clock" approach, however, Baines et al. have gathered evidence for a diradical pathway.[4] In case of unsymmetrically substituted disilenes, **If,g** were obtained and we had speculated that a dipolar reaction pathway might nonetheless be more favorable due to the inherent polarization of the Si=Si moiety.[9,10] In a recent collaborative effort with the Baines group, however, the diradical pathway gained significant support from experiments with the above-mentioned mechanistic probe.[11]

In collaboration with the Manners group, we had reported the application of the [2+2] cycloaddition of disilenes to alkynes for the step growth polymerization of *para*-phenylene-bridged tetrasiladienes with 1,4-diethynylbenzene to σ,π-conjugated hybridpolymers.[5] In these reactions, the two sterically less demanding ends of both substrates always ended up being adjacent to one another in the 1,2-disilacyclobutene units of the products as shown in an exemplary manner for **IIa** in Chart 1. The near perfect regioselectivity prompted us to extend the concept towards tetrasiladienes with different π-conjugated linking units.[12]

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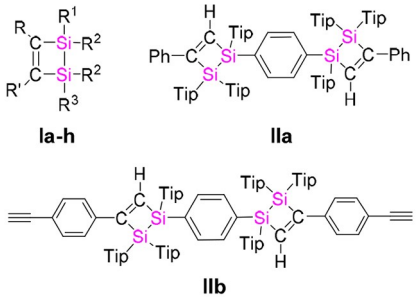


Chart 1. Reported examples of 1,2-disilacyclobutenes **Ia-h** and para-phenylene bridged bis(1,2-disilacyclobutenes) **IIa,b** (**Ia**: R = Ph, R' = H, R^1 = R^3 = Ph, R^2 = Me; **Ib**: R = Ph, R' = H, R^1 = R^2 = R^3 = Mes = 2,4,6-$Me_3C_6H_2$; **Ic**: R = OEt, R' = H, R^1 = R^2 = R^3 = Mes; **Id**: R = CO_2Me, R' = H, R^1 = R^2 = R^3 = Mes; **Ie**: R = $SiMe_3$, R' = H, R^1 = R^2 = R^3 = Mes; **If**: R = Ph, R' = H, R^1 = R^2 = Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$; R^3 = Ph; **Ig**: R=Ph, R' = H, R^1 = R^2 = Tip, R^3 = TMOP = 2,4,6-$(MeO)_3C_6H_2$; **Ih**: R = R' = Ph, R^1 = R^3 = Br, R^2 = Si^{t}Bu$_3$).[5,6,8,10,13]

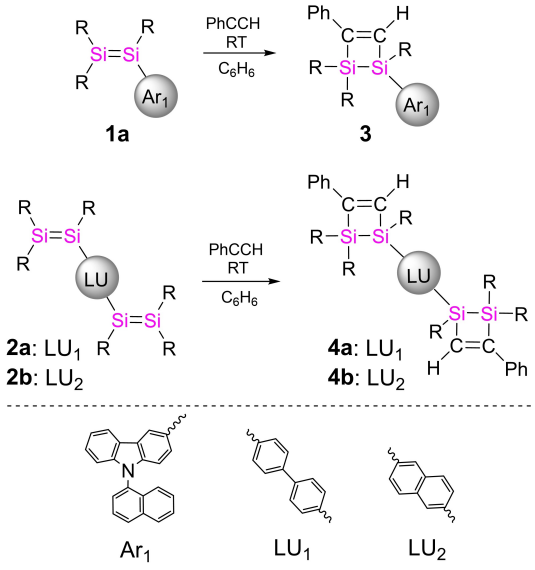
Here, we report the [2+2] cycloaddition reactions of selected species with one or two Si–Si double bonds towards phenylacetylene. As will be shown, while the regioselectivity of all reactions is indeed near-perfect, it is unexpectedly reversed in some cases. Moreover, the presence of catalytic quantities of residual base is shown to completely alter the course of the reaction towards the selective formation of a formal CH addition product.

Results and Discussion

[2+2] Cycloadditions

The addition of the appropriate number of equivalents of phenylacetylene to the aryldisilene **1a** and *para*-arylene bridged tetrasiladienes **2a,b** in benzene at room temperature results in a color change from intense red to bright yellow, indicating complete conversion to new products (Scheme 1). The targeted aryldisilacyclobutene **3** and *para*-arylene bridged bis(disilacyclobutene)s **4a,b** were isolated as air-stable colorless crystals (mp. > 230 °C) in 86-94% yield.

Table 1 compares the ^{29}Si NMR data and selected structural parameters as determined by X-ray crystallography. Compounds **3** and **4a,b** show very similar ^{29}Si NMR spectra with two high-field signals between −11.77 and −10.79 ppm in the typical range for saturated silicon atoms of disilacyclobutenes.[14] This is indicative of the clean formation of [2+2] cycloadducts with the expected regioselectivity in which the sterically less demanding ends of the two starting materials are connected as to be expected for a step-wise diradical mechanism. The ^{29}Si NMR shifts turn out to be almost independent of the substituents and can therefore be considered as diagnostic for this type of cycloadduct. The ^{1}H-NMR spectra reveal the vinylic protons of the 1,2-disilacyclobutene rings in the lowfield region as singlets between 7.73 and 7.94 ppm with satellite signals arising from coupling to the two silicon atoms (^{3}J = 29 Hz and ^{2}J = 8 Hz).[15] The ^{13}C NMR signals of the C=C bond in the disilacyclobutene moiety are observed between 155.95 and 173.22 ppm (Table 1).



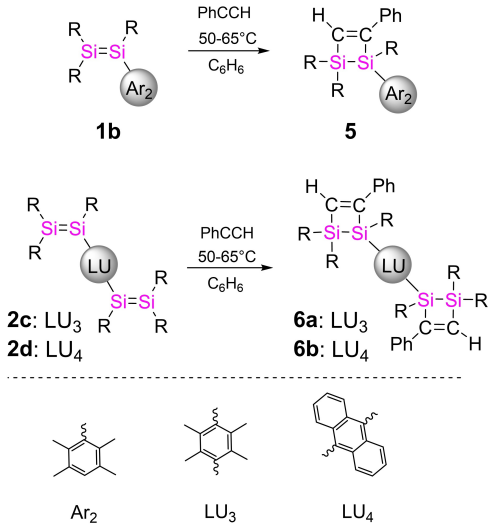
Scheme 1. Synthesis of [2+2] cycloadducts **3** and **4a,b** with regular regioselectivity (R = Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$).

Table 1. Selected ^{29}Si NMR data and solid-state structural parameters of [2+2] cycloadducts **3**, **4a,b**, **5** and **6a,b**.

	3	**4a**	**4b**
δ^{29}Si, ppm	−11.16, −11.58	−11.28, −11.77	−10.79, −11.07
Si1–Si2), Å	2.4197(8)	2.3953(15)	2.4121(11)
C1–Si1–Si2, °	73.02(7)	73.27(13)	72.75(10)
C2–Si2–Si1, °	73.95(7)	74.14(13)	74.22(9)
C1=C2, Å	1.3496(1)	1.3510(62)	1.3411(46)
	5	**6a**	**6b**
δ^{29}Si, ppm	2.89, 2.19 −10.38	3.60, 3.12 −9.32, −10.21	1.83, 1.69 −7.89, −8.89
Si1–Si2, Å	2.4535(19)	–	2.4365(7)
C2–Si1–Si2, °	73.45(14)	–	73.50(6)
C1–Si2–Si1, °	72.49(14)	–	72.72(6)
C1=C2, Å	1.3551(72)	1.3382(77)	1.3491(27)

In contrast, [2+2] cycloadditions of phenylacetylene to Si=Si substrates with a sterically more demanding fourth substituent besides the three Tip groups as in disilene **1b** or tetrasiladienes **2c,d** require considerably higher temperatures in order to achieve reasonable reaction rates (Scheme 2). Thus, after stirring overnight at 65 °C, the reaction mixtures turn yellow in case of **1b** and **2c** whereas the original yellow orange color is retained in case of **2d**. In all cases, however, full conversion to new products is achieved according to the NMR spectra.

Most of the ^{1}H NMR signals of the reaction mixtures show significant overlap and therefore do not lend themselves to straightforward interpretation. In most cases, the ^{29}Si NMR spectra disclose two sets of two signals of which the first



Scheme 2. Synthesis of [2 + 2] cycloadducts **5** and **6a,b** with reversed regioselectivity (R = Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$).

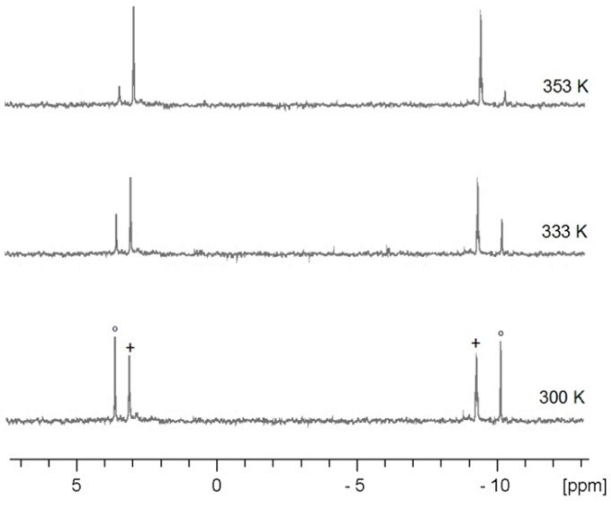


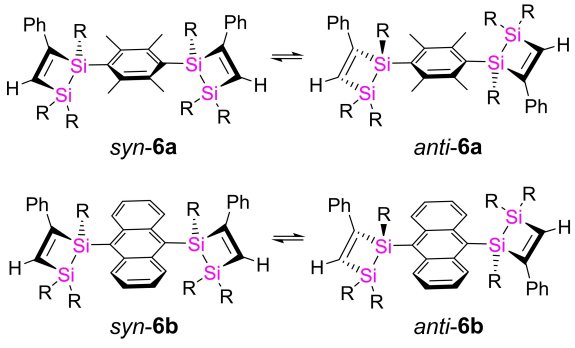
Figure 1. ^{29}Si VT-NMR of durene- bridged bis(disilacyclobutene) **6a** at different temperatures in d$_8$-toluene (333 and 353 K), and the resonances for the expected two rotamers, (°): signals are assigned to *anti*-**6a**, (+): signals are assigned to *syn*-**6a**.

resonance is located between δ = 1.7 and 3.6 ppm and the second between δ = −7.9 and −10.4 ppm, thus showing very little variance with the different Si=Si substrates employed (Table 1). The reaction mixture resulting from **1b** gives two lowfield signals at δ = 2.9 and 2.2 ppm, but only one highfield signal at δ = −10.4 ppm, which may be explained by a superposition of two coincidentally identical signals (Supporting Information, Figure S14). As the final products are unlikely to be a mixture of regioisomers given the close to invariant ^{29}Si chemical shifts of **3** and **4a,b**, either conformational isomerism or a mixture of diastereomers could be envisaged as plausible reasons for the splitting of signals. In fact, for the previously reported Si=Si starting materials **2c,d** the temperature dependence of a conformational equilibrium had been demonstrated.[12]

The high crystalline yields obtained for each product provided an initial hint at rapid equilibration between the two species present in the reaction mixture: while those derived from the reaction of duryldisilene **1b** and durylene-bridged tetrasiladiene **2c** were isolated as colorless crystals in 90% and 83% yield, respectively, the product from anthracene-bridged **2d** was obtained in 80% yield as yellow crystals. The ^{29}Si NMR spectra of the crystallized materials in C$_6$D$_6$ solution turned out to be virtually identical to those of the crude reaction mixtures in all cases (except for the disappearance of minor signals due to impurities).

In order to corroborate the hypothesis of conformational isomerism, **6a,b** were investigated by NMR at variable temperature in *d*$_8$-toluene. As in C$_6$D$_6$, the ^{29}Si NMR spectrum of compound **6a** in d$_8$-toluene at 300 K (Figure 1) exhibits two set of signals albeit slightly shifted to δ = 3.5, −10.3 ppm and δ = 3.0, −9.4 ppm (ratio 1:0.82). Even though coalescence could not be reached by increasing the temperature, a significant and reversible change in the ratio of the two isomers is observed (0.41:1 at 333 K; 0.13:1 at 353 K), which unambiguously proves the anticipated equilibrium. We tentatively assign the conformer *syn*-**6a** (C$_s$ symmetry) to the high temperature signals at δ = 3.0, −9.4 ppm and *anti*-**6a** (C$_i$ symmetry) to the two other signals at δ = 3.5, −10.3 ppm (Scheme 3).

The ^{1}H VT-NMR of **6a** (Supporting Information, Figure S20) allows for an estimation of the thermodynamic parameters of the *syn-anti* isomerization by comparison of the relative intensities of the vinylic ^{1}H NMR signals at δ = 7.75 and 7.77 ppm at various temperatures. From a van't Hoff plot of the equilibrium constants thus determined, the enthalpy was estimated to △H ≈ 29 kJ mol^{-1} and the entropy to △S ≈ 93 J mol^{-1} (Supporting Information, Figure S39 and Table S1). The strong entropic contribution vaguely supports our above hypothesis that *syn*-**6a** is increasingly favored at higher temperatures as the number of interactions with solvent molecules is minimized by the more compact arrangement in *syn*-**6a**.



Scheme 3. Equilibrium between the postulated *syn*- and *anti*-conformations of resulting bis(disilacyclobutenes) **6a,b** (R = Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$).

The ^{29}Si NMR of **6b** in d_8-toluene at 300 K (Supporting Information, Figure S23) shows one set of signals of higher intensity at $\delta = 1.5$, -8.1 ppm and a lower intensity pair at $\delta = 1.7$, -9.0 ppm in an approximate ratio of 3:1. As in the case of **6a**, both *syn*-**6b** (major) and *anti*-**6b** (minor) conformations are observed in solution due to the slow rotation about the Si–C bonds on the NMR time scale (Scheme 3). As the *syn*-conformer is already favored at room temperature, warming to 353 K led to the complete disappearance of the ^{29}Si signals of the minor conformer. Apparently, the equilibrium is shifted completely towards *syn*-**6b** at this temperature.

X-ray diffraction analysis of single crystals verified the constitutions of all products as the anticipated [2+2] cycloadducts of which 1,2-disilacyclobutenes **5** and **6a**,**b** exhibit the opposite regiochemistry of **3** and **4a**,**b** (Figure 2). Except for **6a**, which exhibited strong disorder and accordingly high R values, the quality of all other structure determinations allows for a reliable discussion of bonding parameters. Unlike the previously reported 1,2-disilacyclobutenes as well as **3** and **4a**,**b**, the [2+2] cycloadducts **5** and **6a**,**b** show a connectivity with the more sterically encumbered phenyl-substituted carbon atom of the vinyl moiety attached to the less bulkily substituted silicon atom (bonded to the aryl substituent/linking unit and one Tip group). This may indicate a change from the frequently proposed diradical pathway to a concerted mechanism. The higher temperatures and reaction times required in these cases would be in line with this assertion, although there is currently no further evidence available.

The endocyclic Si–Si single bond distances of the reversed regioisomers **5** and **6b** (2.4365(7) to 2.4535(19) Å) are significantly longer than that of disilacyclobutenes **3** and **4a**,**b** (2.3953(15) to 2.4197(8) Å) presumably due to the more pronounced steric bulk of the organic linking unit in **5** and **6b**. In all cases, however, C1 and C2, Si1, and Si2 form an almost perfectly planar trapezoid (sum of internal angles 359.59°) with relatively acute endocyclic angles at the Si atoms (Table 1).

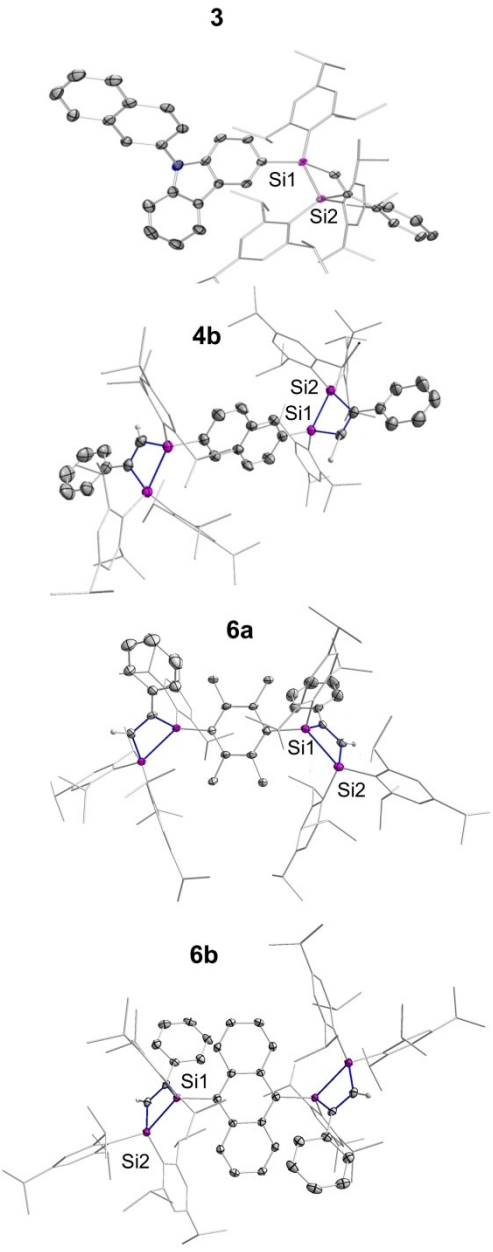
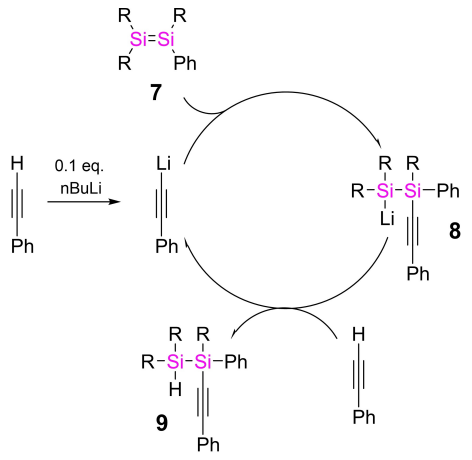


Figure 2. Molecular structures in the solid state of disilacyclobutene **3** and *para*-arylene bridged bis(disilacylobutenes) **4b** and **6a**,**b** (thermal ellipsoids at 50%, H atoms and disordered ^{i}Pr groups are omitted for clarity).

CH Additions

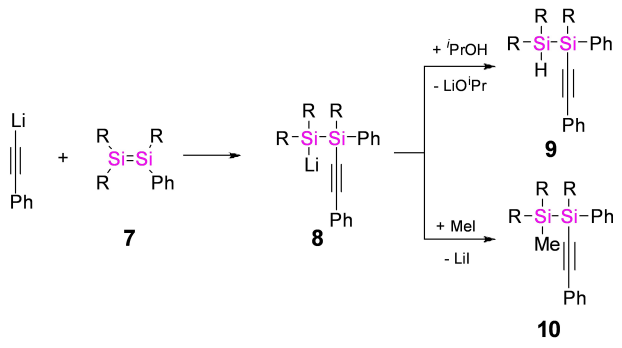
In some batches, the reaction of phenylacetylene to phenyldisilene afforded a side product in variable quantities with two ^{29}Si NMR signals at $\delta = -40.1$ and -63.2 ppm. The substantial difference to the signals of the cycloaddition product ($\delta = -11.2$ and -11.5 ppm) suggested an altogether different structural motif. After fractional crystallization, the cycloaddition product could be separated and crystals of the unknown product were grown from the mother liquor. X-ray diffraction revealed that the acetylenic CH bond of phenylacetylene had formally added across the Si=Si double bond to yield the ethinyl-substituted disilane **9**.

In case of the reaction of phenylacetylene and species with Ge=C double bond, Baines et al. found ene-addition and CH addition as competing reaction pathways. They had proposed that the catalytic influence of base would favor the CH addition pathway.[16] A plausible basic impurity would be residual disilenide, $Tip_2Si{=}SiTipLi$, which can reasonably be expected to deprotonate phenylacetylene. Indeed, samples of phenyldisilene **7** purified by crystallization never gave rise to the formation of **9**. The increased nucleophilicity of PhCCLi would kinetically favor the carbolithiation of the Si=Si bond over the otherwise observed [2+2] cycloaddition. The resulting silyllithium species should be sufficiently basic to regenerate the lithiated, thus activated alkyne and close the catalytic cycle (Scheme 4). In order to test this hypothesis, phenylacetylene was deliberately deprotonated in part by the addition of 10 mol% ^{n}BuLi prior to the reaction with **7**. Indeed, the ethynyl-substituted disilane **9** was isolated as the only product.



Scheme 4. Proposed cycle of the base-catalyzed CH-addition of phenylacetylene to phenyldisilene (R = Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$).

In view of the rich structural chemistry of ethynylsilyl lithiums[17] and in order to corroborate the mechanistic proposal, we attempted to isolate the alleged anionic intermediate. Treatment of phenyldisilene with a stoichiometric amount of phenyl acetylide in THF results in a dark brown solution (Scheme 5). The ^{29}Si NMR spectrum of the reaction mixture shows two new signals at −2.2 and −8.7 ppm, distinctly different from those of the CH-addition product **9**, which in turn is only observed in minor quantities under these conditions. The ^{1}H NMR spectrum of the mixture shows signals of coordinated THF at 3.14 ppm suggesting the presence of lithium counter-cations and thus an ionic product. This was further confirmed by ^{7}Li NMR spectroscopy with broad overlapping signals at 2.01 and 0.70 ppm. If quenched with a proton source such as ^{i}PrOH or additional phenylacetylene the reaction mixture immediately decolorizes (Scheme 5). NMR spectra of the quenching mixture show signals of the CH-addition product **9** exclusively. The formation of the trapping product **9** supports the assignment of the initial product from PhCCLi and disilene **7** as the 1,2-addition product to the Si=Si bond, **8**. To further corroborate this assignment, **8** was quenched with MeI as an electrophile in a separate experiment. ^{29}Si NMR analysis of the crude product revealed clean conversion to a product with signals at −31.5 and −40.1 ppm (1:1 ratio). Trace amounts of the CH-addition product **9** could only be detected in the ^{1}H NMR spectrum.



Scheme 5. Suggested reaction pathway of stoichiometric amounts of phenylacetylide with phenyldisilene (R = Tip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$).

Conclusions

We have shown that the cycloaddition to the Si=Si bond of these compounds with phenylacetylene provided access to various cycloadducts products. The NMR data and the crystal structure analysis of compounds **3** and **4a**,**b** revealed that substrates **1a** and **2a**,**b** undergo facile and selective [2+2] cycloaddition with the terminal alkyne.

Notably, the addition of phenylacetylene to substrates with more steric bulk such as disilene **1b** or tetrasiladienes **2c**,**d** can be achieved only at elevated temperature. The NMR data of these reactions appeared to show the formation of a mixture of products, initially suggesting that substrates **1b** and **2c**,**d** undergo an unselective [2+2] cycloaddition with the terminal alkyne. However, VT-NMR experiments of **6a**,**b** suggest that the respective two rotational *syn*- and *anti*-conformers exist in equilibrium.

Furthermore, X-ray diffraction of the final products confirmed the formation of [2+2] cycloadducts **5** and **6a**,**b**. Unlike compounds **3** and **4a**,**b** derived from the selective [2+2] cycloaddition, the crystal structure analyses of **5** and **6a**,**b** showed that the phenyl-substituted carbon atom is bonded to the sterically less congested Si(Ar)Tip moiety.

Although diradical mechanisms are generally assumed to be more favorable for the cycloaddition of unsymmetrically substituted disilenes and tetrasiladienes, the mechanism of the cycloaddition reactions in the present study seems to heavily depend on the substitution pattern so that both diradical and concerted pathways appear to be active.

Experimental Section

General. All manipulations were carried out under a protective atmosphere of argon using standard Schlenk techniques or in a drybox. Ethereal solvents were refluxed over sodium/ benzophenone and pentane, hexane, and (deuterated) benzene over sodium/ potassium alloy; toluene was refluxed over sodium. All solvents were distilled and stored under argon and degassed prior to use. **1a**,**b** and **2a**–**d**, were prepared following published procedures.[12] Phenylacetylene was purchased from Aldrich, checked for purity by NMR analysis prior to use, and distilled when necessary. The NMR spectra were recorded on a Bruker AV 500 or AV 400 FT-NMR spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to external tetramethylsilane (TMS) via the residual protons of the deuterated solvent (^{1}H) or the solvent itself (^{13}C). ^{29}Si{^{1}H} NMR spectra were referenced to external TMS. Crystallographic data (cif files including structure factors) can be retrieved free of charge form the Cambridge Crystallographic Data Centre (deposition numbers CCDC 2078102 (**5**), 2078103 (**4a**), 2078104 (**4b**), 2078105 (**6a**), 2078106 (**3**), 2078107 (**6b**).

General procedure for compounds 3 and 4 a,b

The required stoichiometric amount of neat phenylacetylene is added via syringe to a solution of the appropriate disilene **1 a** or tetrasiladiene **2 a**,**b** in 15 mL of benzene at room temperature. The reaction mixture instantaneously turns bright yellow and is stirred for additional one hour. The solvent is removed completely under vacuum. Crystallization from a minimum amount of the indicated solvent affords the corresponding product. All products are stable in air and in different solvents such as hexane or acetone for at least several weeks.

9-(Naphthalen-1-yl)-3-(4-phenyl-1,2,2-tris(2,4,6-triisopropylphenyl)-1,2-dihydro-1,2-disilet-1-yl)-9H-carbazole **3**. Phenylacetylene (0.067 g, 0.66 mmol), disilene **2 a** (0.63 g, 0.66 mmol). Colorless crystals at room temperature from concentrated solution in acetone (0.6204 mmol, 94 %, mp. > 220 °C). ^{1}H NMR (300 MHz, [D$_6$]benzene, TMS) δ = 8.33 (s, 1H, Ar–H); 7.94 (s, 1H, SiPhC=CHSi); 7.83 (d, 1H, ArH); 7.54 (m, 4H, ArH); 7.49 (s, 1H, ArH); 7.43 (m, 2H, ArH); 7.38 (s, 1H, ArH); 7.32 (m, 2H, ArH); 7.28, 7.24 (each m, each 2H, TipH); 7.22 (br., 2H, TipH); 7.16 (s, 1H, *p*-PhH); 7.08 (dd, 2H, ArH); 7.00 (m, 4H, PhH); 4.03 (hept., 2H, ^{i}PrCH); 3.83 (hept., 1H, ^{i}PrCH); 3.58 (hept., 2H, ^{i}PrCH); 3.18 (hept., 1H, ^{i}PrCH); 3.03 (hept., 1H, ^{i}PrCH); 2.84 (hept., 2H, ^{i}PrCH); 1.55 (acetone); 1.49 (t, 6H, ^{i}PrCH$_3$); 1.42 (t, 6H, ^{i}PrCH$_3$); 1.29 (m, 10H, ^{i}PrCH$_3$); 1.21 (m, 11H, ^{i}PrCH$_3$); 1.13 (m, 8H, ^{i}PrCH$_3$); 1.04 (t, 6H, ^{i}PrCH$_3$); 0.83 (d, 2H, ^{i}PrCH$_3$); 0.68 (d, 2H, ^{i}PrCH$_3$); 0.45 (d, 2H, ^{i}PrCH$_3$) ppm. ^{13}C NMR (75.46 MHz, [D$_6$]benzene, TMS) δ = 203.59 (CO, acetone); 172.91 (SiPhC=CHSi); 157.99; 156.91, 156.47, 155.62, 154,72, 154.58, 150.80, 150.43, 150.23 (Tip-C$_{o/p}$); 144.79, 141.88, 141.39, 138.25 (Ar-C$_i$); 135.20 (Ar-CH); 134.23, 133.96, 132.65, 132.54, 130.11, 129.59, 128.43 (Ar-C$_i$); 132.22 (Ar-CH; 127.88, 127.56 (Ar-C$_q$); 127.38, 126.77, 126.56, 126.29, 125.97, 125.40, 125.29, 124.17, 121.48, 121.22, 122.68, 122.35, 122.23, 121.51, 120.08, 120.33, 120.17, 109.95, 109.08 (ArCH); 36.59 to 33.88 (^{i}PrCH); 29.94 to 22.62 (^{i}PrCH$_3$) ppm. ^{29}Si NMR (59.62 MHz, [D$_6$]benzene, TMS) δ = −11.6, −11.6 ppm. Combustion Analysis: Calcd. for $C_{75}H_{89}NSi_2$: C, 84.93; H, 8.46. Found: C, 83.42; H,

4,4′-Bis(4-phenyl-1,2,2-tris(2,4,6-triisopropylphenyl)-1,2-dihydro-1,2-disilet-1-yl)-1,1′-biphenyl **4 a**. Phenylacetylene (0.067 g, 0.66 mmol), tetrasiladiene **2 a** (0.36 g, 0.33 mmol). Colorless crystals at room temperature from concentrated solution in isopropanol (0.283 mmol, 86 %, mp. > 220 °C). ^{1}H NMR (300 MHz, [D$_6$]benzene, TMS) δ = 7.77 (s, 2H, SiPhC=CHSi); 7.45 (d, 4H, *o*-PhH); 7.23, 7.19, 7.11 (br., each 4H, TipH); 7.08 (s, 8H, ArH); 6.97 (dd, 6H, PhH); 3.83 (hept., 4H, ^{i}PrCH); 3.60 (hept., 2H, ^{i}PrCH); 3.35 (hept., 4H, ^{i}PrCH); 3.84 (hept., 2H, ^{i}PrCH); 2.83 (hept., 6H, ^{i}PrCH), 1.38 (m, 12H, ^{i}PrCH$_3$); 1.28 to 1.20 (m, 41H, ^{i}PrCH$_3$); 1.17 (d, 8H, ^{i}PrCH$_3$); 1.04 to 0.99 (m, 24H, ^{i}PrCH$_3$); 0.94 (s, 4H, ^{i}PrCH$_3$); 0.74, 0.63, 0.46 (each d, 18H, ^{i}PrCH$_3$); 0.27 (s, 1H, ^{i}PrCH$_3$) ppm. ^{13}C NMR (75.46 MHz, [D$_6$]benzene, TMS) δ = 171.91 (SiPhC=CHSi); 155.94 (SiPhC=CHSi); 155.31 155.21, 154.22, 153,96, 152.88, 152.83, 149.56, 149.19, 148.94 (Tip-C$_{o/p}$); 143.51, 139.99, 137.52, 135.97 (Ar-C$_i$); 135.07 (ArCH); 132.83, 130.62 (Ar-C$_i$); 127.11 (Ar-CH); 126.94, 126.62, 126.30 (Ar-C$_q$); 126.08, 125.43, 124.68, 121.64, 121.38, 120.79, 120.59, 120.33, 119.12 (ArCH); 62.47 (^{i}PrOH-CH.); 35.32 to 32.56 (^{i}PrCH); 27.36 to 21.56 (^{i}Pr-CH$_3$) ppm. ^{29}Si NMR (59.62 MHz, [D$_6$]benzene, TMS) δ = −11.27, −11.76 ppm. Combustion Analysis: Calcd. for $C_{118}H_{158}Si_4$: C, 83.92; H, 9.43. Found: C, 81.69; H, 9.83.

2,6-Bis(4-phenyl-1,2,2-tris(2,4,6-triisopropylphenyl)-1,2-dihydro-1,2-disilet-1-yl)naphthalene **4 b**. Phenylacetylene (0.067 g, 0.66 mmol), tetrasiladiene **2 b** (0.48 g, 0.33 mmol). Colorless crystals at room temperature from concentrated ^{i}PrOH solution (0.282 mmol, 86 %, mp. > 220 °C). ^{1}H NMR (300 MHz, [D$_6$]benzene, TMS) δ = 7.73 (s, 2H, SiPhC=CHSi); 7.62 (s, 1H, ArH); 7.38 (m, 5H, ArH); 7.24 (br., 2H, *o*-PhH); 7.18 (br., 2H, *o*-PhH); 7.11, 7.07, 7.01, (each s, each 4H, TipH); 6.90 (m, 6H, PhH); 3.89 (hept., 4H, ^{i}PrCH); 3.67 (hept., 2H, ^{i}PrCH); 3.37 (hept., 4H, ^{i}PrCH); 3.08 (hept., 2H, ^{i}PrCH); 2.79 (hept., 6H, ^{i}PrCH); 1.41(m, 12H, ^{i}PrCH$_3$); 1.33 to 1.21 (m, 28H, ^{i}PrCH$_3$); 1.20 (s, 6H, ^{i}PrCH$_3$); 1.18 (d, 10H, ^{i}PrCH$_3$); 1.17 (s, 12H, ^{i}PrCH$_3$); 1.04 (d, 12H, ^{i}PrCH$_3$); 0.99 (m, 8H, ^{i}PrCH$_3$); 0.85 (d, 6H, ^{i}PrCH$_3$); 0.65(d, 4H, ^{i}PrCH$_3$); 0.60 (d, 4H, ^{i}PrCH$_3$); 0.42 (d, 4H, ^{i}PrCH$_3$) ppm. ^{13}C NMR (75.46 MHz, [D$_6$]benzene, TMS) δ = 173.22 (SiPhC=CHSi); 157.58 (SiPhC=CHSi); 156.58, 155.61, 155.15, 154,12, 154.01, 150.80, 150.51, 150.20 (Tip-C$_{o/p}$); 144.92, 137.74, 137.55 (Ar-C$_i$); 137.04 (ArCH); 134.01, 133.05, 131.52 (Ar–C$_i$); 131.44 (ArCH); 127.87, 127.55 (Ar-C$_q$); 127.12, 126.71, 121.03, 122.61, 121.95, 121.63, 121.95, 121.63, 121.27, 120.42 (TipCH); 36.65 to 33.85 (^{i}PrCH); 28.63 to 22.89 (^{i}PrCH$_3$) ppm. ^{29}Si NMR (59.62 MHz, [D$_6$]benzene, TMS) δ = −10.8, −11.1 ppm. Combustion Analysis: Calcd. for $C_{116}H_{156}Si_4$: C, 82.35; H, 9.95. Found: C, 82.11; H, 9.36.

General procedure for compounds 5, 6 a,b

The required stoichiometric amount of neat phenylacetylene is added via syringe to a solution of the appropriate disilene **1 b** or tetrasiladiene **2 c**,**d** in 20 mL of benzene at 65 °C. Stirring overnight at 65 °C resulted in a colorless reaction mixture that was thoroughly dried in vacuo. The residue is re-dissolved with a minimum amount of the indicated solvent and standing overnight at room temperature affords the corresponding product. All products are stable in air and in different solvents such as hexane or acetone for at least several weeks.

3-Phenyl-2-(2,3,5,6-tetramethylphenyl)-1,1,2-tris(2,4,6-triisopropylphenyl)-1,2-dihydro-1,2-disilete **5**. Phenylacetylene (0.067 g, 0.66 mmol), disilene **1 a** (0.52 g, 0.66 mmol). Colorless crystals at room temperature from concentrated solution in acetone (0.594 mmol, 90 %, mp. 182-188 °C). Exact integration of ^{1}H NMR spectra is impossible due to strongly overlapping resonances of two rotamers. ^{1}H NMR (300 MHz, [D$_6$]benzene, TMS) δ = 7.81 (s, 1H, SiPhC=CHSi); 7.80 (s, 1H, SiPhC=CHSi); 7.15 to 6.90 (m, 12H, TipH; 10H PhH); 6.83 (s, 1H, *p*-DurH); 6.83 (s, 1H, *p*-DurH); 4.00 to 3.22 (m, 12H, *o*-^{i}PrCH); 2.75 (hept., 6H, *p*-^{i}PrCH); 2.45, 2.24, 1.96, 1.88 (br., 24H, DurCH$_3$); 1.55 (acetone); 1.52 to 0.45 (br. m, 108H, ^{i}PrCH$_3$) ppm. ^{13}C NMR (75.46 MHz, [D$_6$]benzene, TMS) δ = 172.99 (SiPhC=CHSi); 162.41 (SiPhC=CHSi); 154.72 to 149.67 (Tip-C$_{o/p}$); 147.60, 140.63, 140.37, 137.29, 135.75, 135.6 (Ar-C$_i$); 133.11, 132.54 (ArCH); 127.87, 127.55 (duryl-C$_q$); 126.35, 126.31, 122.67, 122.30, 121.93, 121.51 (ArCH); 36.71 to 32.59 (^{i}PrCH); 27.36 to 20.37 (^{i}PrCH$_3$) ppm. ^{29}Si NMR (59.62 MHz, [D$_6$]benzene, TMS) δ = 2.9, 2.2, −10.4 ppm. Combustion Analysis: Calcd. for $C_{63}H_{88}Si_2$: C, 83.93; H, 9.84. Found: C, 80.91; H, 9.12.

2,2′-(2,3,5,6-Tetramethyl-1,4-phenylene)bis(3-phenyl-1,1,2-tris(2,4,6-triisopropylphenyl)-1,2-dihydro-1,2-disilete) **6 a**. Phenylacetylene (0.067 g, 0.66 mmol), tetrasiladiene **2 c** (0.48 g, 0.33 mmol). Colorless crystals at room temperature from concentrated solution in isopropanol (0.273 mmol, 83 %, mp. > 230 °C). Exact integration of ^{1}H NMR spectra is impossible due to strongly overlapping resonances of two rotamers. ^{1}H NMR (300 MHz, [D$_6$]benzene, TMS) δ = 7.77 (s, 2H, SiPhC=CHSi); 7.75 (s, 2H, SiPhC=CHSi); 7.13 to 7.07 (m, 20H, PhH); 7.06 to 6.98 (m, 20H, TipH); 6.97 (s, 2H, TipH); 6.95 (s, 2H, TipH); 4.10 to 3.12 (m, 24H, ^{i}PrCH); 2.65 (hept., 12H, ^{i}Pr-CH); 2.54, 2.22, 1.98, 1.87 (br., 24H, DurCH$_3$); 1.56 (acetone); 1.42 to 1.31 (br, 48H, ^{i}PrCH$_3$); 1.26 (s, 6H, ^{i}PrCH$_3$); 1.23 (d, 12H, ^{i}PrCH$_3$); 1.21 (s, 18H, ^{i}PrCH$_3$); 1.20 (s, 6H, ^{i}PrCH$_3$); 1.17 (d, 12H, ^{i}PrCH$_3$); 1.13 (d, 12H, ^{i}PrCH$_3$); 1.06 (m, 24H, ^{i}PrCH$_3$); 0.65 (br, 24H, ^{i}PrCH$_3$); 0.55 to 0.41 (br, 18H, ^{i}PrCH$_3$) ppm. ^{13}C NMR (75.46 MHz, [D$_6$]benzene, TMS) δ = 170.19 (SiPhC=CHSi); 162.44 (SiPhC=CHSi); 154.76 to 149.68 (Tip-C$_{o/p}$); 147.58, 140.61, 140.47, 137.19, 135.64, 135.63 (Ar-C$_i$); 133.12, 132.51 (ArCH); 127.87, 127.58 (Ar-C$_q$); 126.34, 126.31, 122.66, 122.31, 121.84, 121.53 (ArCH); 36.72 to 33.58 (^{i}PrCH); 27.57 to 23.92 (^{i}PrCH$_3$) ppm. ^{29}Si NMR (59.62 MHz, [D$_6$]-benzene, TMS) δ = 3.6, 3.1, −9.3,

−10.2 ppm. Combustion Analysis: Calcd. for $C_{116}H_{162}Si_4$: C, 83.48; H, 9.78. Found: C, 82.53; H, 9.04.

9,10-Bis(4-phenyl-1,2,2-tris(2,4,6-triisopropylphenyl)-1,2-dihydro-1,2-disilet-1-yl)anthracene **6b**. Phenylacetylene (0.067 g, 0.66 mmol), tetrasiladiene **2c** (0.50 g, 0.33 mmol). Yellow crystals at room temperature from concentrated solution in benzene (0.262 mmol, 80%, mp. >230 °C). Exact integration of ^{1}H NMR spectra is impossible due to strongly overlapping resonances of two rotamers. ^{1}H NMR (300 MHz, [D_8]toluene, TMS) δ = 9.11, 8.55 (each d, each 2H, ArH); 7.83 (s, 2H, PhSiC=CHSi, minor); 7.81 (s, 2H, PhSiC=CHSi, major); 7.25 to 6.54, (m, 40H, Ph–H and Tip-H); 4.2 to 2.5 (m, 18 H, ^{i}PrCH); 1.80 to −0.2 (m, 108H, ^{i}PrCH$_3$); ^{13}C NMR (75.46 MHz, [D_6]benzene, TMS) δ = 171.75 (PhSiC=CHSi); 154.86, 154.62, 150.01, 149.83 (Tip-C$_{o/p}$); 145.12, 141.52, 137.25 (Ar-C$_i$); 133.70 (ArCH); 133.44, 133.41, 132.55, 129.61 (Tip-C$_i$); 130.05, 129.15, 128.85 (ArCH); 127.85, 127.54 (Ar-C$_q$);127.71, 127.12, 126.92, 126.70, 125.90, 125.81, 121.83 (Tip-CH); 47.31, 34.46, 34.27, 34.20, 32.64, 32.01 (^{i}PrCH); 25.83, 25.51, 24.43, 23.92, 23.83, 23.82, 23.61, 23.60, 23.50 (^{i}PrCH$_3$) ppm. ^{29}Si NMR (59.62 MHz, [D_8]toluene, TMS) δ = 1.7, 1.5, −8.1, −9.0 ppm. Combustion Analysis: Calcd. for $C_{120}H_{158}Si4$: C, 84.14; H, 9.30. Found: C, 83.90; H, 9.89.

Lithium phenylacetylide. To a solution of ^{n}BuLi (40 mmol) in hexane phenylacetylene (5 g, 49 mmol) is added dropwise under vigorous stirring. The white precipitate is then filtered and repeatedly rinsed with clean hexane. Residual solvent and phenyl acetylene are then removed under reduced pressure and the product obtained as a white powder is stored in the glovebox for further use.

Spectroscopic detection of intermediate **8**. At −80 °C a solution of phenyldisilene **7** (0.991 g; 1.33 mmol) in hexane (15 mL) was added dropwise to a stirred solution of lithium phenylacetylide (0.138 g; 1.25 mmol) in THF (10 mL). After the addition was finished the reaction mixture was kept stirring for another two hours while warming to room temperature. All volatiles of the dark brown solution were then removed under reduced pressure. The residue contains the CH-addition product **9** together with the intermediate **8** ^{1}H-NMR (300.13 MHz, C_6D_6, 300 K): δ = 8.08 (d, 2H, C≡C-PhH, J = 7.1 Hz), 7.89 to 6.69 (m, 103 H, 6 TipH, 6 PhH, each of the anion and the protonated molecule, NMR solvent, impurities), 6.36 (s, 1H, SiH), 4.987 (hept, 2H, ^{i}PrCH of the anion), 4.72 to 4.08 (m, 7H, ^{i}PrCH of anion and the protonated molecule), 4.00 to 2.28 (m, 14 H altogether, ^{i}PrCH), 3.14 (br, 33 H, coordinated THF), 3.00 to 2.58 (m, 19 H, ^{i}PrCH of anion and protonated molecule), 1.86 to 0.09 (overlapping signals of **8**, **9**, hexane and minor impurities) ppm.^{29}Si-NMR (59.62 MHz, C_6D_6, 300 K): δ = −2.2 (s, **8**), −8.7 (s, **8**), −40.1 (s, **9**), −63.2 (s, **9**, Si–H) ppm.

1-Phenyl-1-(phenylethynyl)-1,2,2-tris(2,4,6-triisopropylphenyl) disilane **9**. At −80 °C a solution of phenyldisilene **7** (255 mg; 0.34 mmol) in hexane (20 mL) was added dropwise to a stirred solution of lithium phenylacetylide (38 mg, 0.35 mmol) in THF (10 mL). After the addition was finished ^{i}PrOH (0.5 mL) was added to the brown reaction mixture. While warming to room temperature the mixture was kept stirring. Then all volatiles were removed in reduced pressure and hexane was added to the slightly yellow solid remains. The solution was filtered and concentrated and a colorless solid of CH addition product **7** (110 mg; 0.13 mmol; 38%) formed overnight at room temperature. The product is stable in air and in different solvents such as hexane or isopropanol for at least several months. ^{1}H-NMR (300.13 MHz, C_6D_6, 300 K): δ = 8.09 (d, 2H, ArH, J = 7.5 Hz), 7.57 (d, 2H, ArH, J = 7.4 Hz), 7.13 to 6.92 (m, 13H, ArH), 6.37 (s, 1H, SiH), 3.79 (br, 4H, ^{i}PrCH), 3.53 (br, 2H, ^{i}PrCH), 2.71 (m, 3H, ^{i}PrCH), 1.61 to 1.01 (m, 56H, ^{i}Pr-CH$_3$), 0.89 (m, 9H, hexane), 0.54 (d, 13H, J = 5.8 Hz) ppm.^{29}Si-NMR (59.62 MHz, C_6D_6, 300 K): δ = −40.1 (s, SiC≡C–Ph), −63.2 (s, SiH) ppm.

Base catalyzed formation of 1-phenyl-1-(phenylethynyl)-1,2,2-tris (2,4,6-triisopropylphenyl)disilane **9**. At −80 °C and under constant stirring ^{n}BuLi (29 μmol) was added to a solution of phenylacetylene (36 mg, 350 μmol) in THF. To this mixture a solution of phenyl disilene **7** (345 μmol) is added. To the resulting brown mixture, a solution of phenyl acetylene in hexane is slowly added. The now decolorized solution is dried under reduced pressure and solid addition product **9** is obtained.

1-Methyl-2-phenyl-2-(phenylethynyl)-1,1,2-tris(2,4,6-triisopropyl-phenyl)disilane **10**. At −80 °C a solution of phenyldisilene **7** (252 mg; 0,34 mmol) in hexane was added dropwise to a stirred solution of lithium phenylacetylide (80 mg; 0.7 mmol) in THF. After the addition was finished an excess of MeI was added to the brown reaction mixture. While warming to room temperature the mixture was kept stirring. Then all volatiles were removed, and hexane was added to the slightly yellow solid remains. The solution was filtered and concentrated and a colorless microcrystalline product (288 mg, 0.33 mmol, 95%) precipitated overnight at room temperature. The product is stable in air and in different solvents such as hexane or isopropanol for at least several months. ^{1}H-NMR (300.13 MHz, C_6D_6, 300 K): δ = 8.12 (m, 2H, Si–C≡C–Ph–H, J = 7.1 Hz), 7.54 (d, 2H, ArH, J = 7.27 Hz), 7.26 to 6.82 (m, ArH, NMR solvent, impurities), 3.92 (hept, 1H, ^{i}PrCH, J = 6.2 Hz), 3.75 (hept, 1H, ^{i}PrCH, J = 6.2 Hz), 3.54 (hept, 2H, ^{i}PrCH, J = 6.2 Hz), 3.13 (hept, 1H, ^{i}PrCH, J = 6.5 Hz), 2.74 (m, 3H, ^{i}PrCH, THF), 1.85 to 0.03 (overlapping signals of ^{i}PrCH$_3$ and minor impurities) ppm.^{29}Si-NMR (59.62 MHz, C_6D_6, 300 K): δ = −31.5 (s, Si–C≡C–H), −40.1 ppm (s, Si–Me).

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Conflict of Interest

The authors declare no conflict of interest.

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