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Cross-coupling of vinyldisilacyclobutane with olefins catalyzed by $[RuH(Cl)(CO)(PCy_3)_2]$ ☆

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Abstract

Cross-coupling of vinyldisilacyclobutane with a variety of olefins in the presence of $[RuH(Cl)(CO)(PCy_3)_2]$ leads to stereoselective formation of functionalized vinyldisilacyclobutanes. Analogous homo-coupling of vinyldisilacyclobutane leads to the formation of *E*- and *gem*-bis(silyl)ethenes. The reaction offers a new route for synthesis of attractive monomers for ring opening polymerization (ROP).

Keywords: Silylative coupling; Ruthenium complex; Vinyldisilacyclobutane; Disilacyclobutane derivatives

1. Introduction

Recent progress in the synthetic routes leading to the substituted disilacyclobutanes has enabled the preparation of a wide range of poly(silylenemethylene)s via ring opening polymerization (ROP) (Scheme 1) [1]. By using reactive functionalities on silicon new polymers of this type bearing various side chains on the polymer backbone can be formed [2].

Four membered silacyclobutane ring is susceptible to ROP even without any catalyst present [1].

In the last two decades, we have developed two new catalytic reactions occurring between the same parent substances, i.e., silylative coupling (SC) (also called *trans*-silylation or silyl group transfer) and cross-metathesis (CM) of alkenes (Scheme 2) with vinylsilanes which have provided a universal route for the synthesis of molecular compounds with vinylsilicon functionality. While the cross-metathesis is catalyzed by well-defined Ru and Mo carbenes the silylative coupling is catalyzed by complexes initiating or generating [M]–H or [M]–Si bonds (where M = Ru, Rh, Ir) (for recent reviews, see [3–5]).

The mechanism of catalysis of SC proved by Wakatsuki et al. [6] and by us [7] involves insertion of vinylsilane into the [M]–H bond followed by β-silyl elimination which generates [M]–Si complex and ethylene, followed by insertion of alkene into [M]–Si bond followed by β-elimination with elimination of substituted vinylsilane and regeneration of [Ru]–H complex. Functionalization of vinylsubstituted cyclosiloxanes, cyclosilazane [8] and octavinylsilsesquioxane [9], stereoselective synthesis of amides [10] and boranes [11] having a vinylsilicon functionality are recent examples of this new synthetic route.

Herein, we report the effective homo-coupling of 1,1,3-trimethyl-3-vinyl-1,3-disilacyclobutane and its *cross*-coupling with olefins catalyzed by ruthenium complexes containing [Ru]–H bonds leading to respective substituted vinylsilanes.

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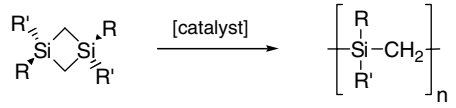
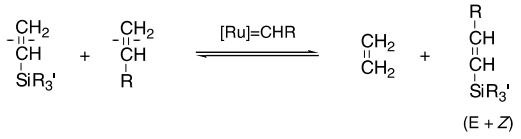
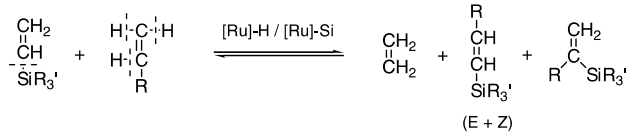


Scheme 1.

Cross-metathesis (CM)



Silylative Coupling (*trans*-silylation) (SC)



Scheme 2.

2. Results and discussion

When the solution of 1,1,3-trimethyl-3-vinyl-1,3-disilacyclobutane (**2**) in toluene was treated in the presence of $[RuH(Cl)(CO)(PCy_3)_2]$ at 110 °C for 18 h over 99% conversion was observed and the mixture of (*E* + *gem*) bis(trimethyldisilacyclobutyl)ethene was formed with the total yield 75% (Scheme 3).

The process was carried out at 110 °C for 18 h. After that time products (*E* + *gem*) was yielded. In case the reaction was performed in the presence of the first or second generation of Grubbs catalysts $[RuCl_2(PCy_3)_2$-(=CHPh)] and $[RuCl_2(PCy_3)(IMesH_2)$(=CHPh)], respectively, no conversion was observed.

Trans-silylation of **2** with a variety of olefins occurs regio- and stereoselectively and lead to exclusive formation of *E*-isomer (Scheme 4).

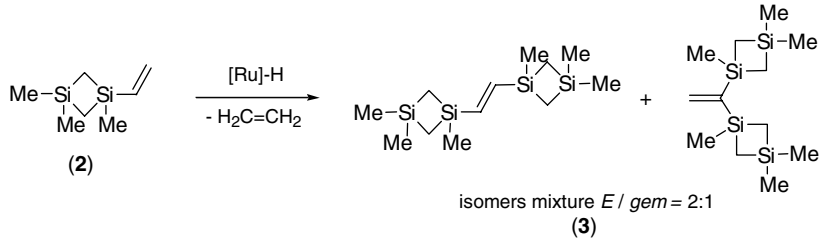
In order to avoid vinyldisilacyclobutane homo-coupling, olefins were used in excess. The experimental data for the reactions were compiled in Table 1.

In contrast to effective silylative coupling the cross-metathesis of **2** with the olefins does not proceed in the presence of Grubbs catalysts. Apparently, reported earlier decomposition of Grubbs catalyst takes place in the system [12].

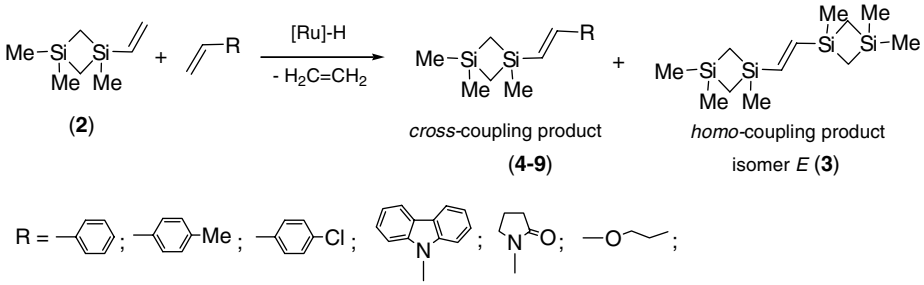
To learn more about the mechanism of the reaction, experiment with deuterium-labelled styrene-d_8 was performed. Thus, the reaction of vinyldisilacyclobutane (**2**) with styrene-d_8 permits a distinction between the mechanism of the silylative coupling (*trans*-silylation) and metallacarbene mechanism. In the case of a *trans*-silylation the formation of silyl-styrene-d_7 and ethylene-d_1 is expected (Scheme 5). In contrast, the metallacarbenes mechanism should afford silyl-styrene-d_6 and ethylene-d_2.

The GC–MS analysis of the reaction mixture after 20 min, i.e., in the initial stage of the reaction, when the conversion did not exceed 10%.

A comparison of the fragments of mass spectra of silyl-styrene-d_0 ($m/z = 232M^+$) (obtained in a control experiment, Fig. 1(a)) with the corresponding ones of silyl-styrene-d obtained in a reaction according to Scheme 5, reveals a shift of the signals of the analogous fragments by 7 units, which suggests the formation of silyl-styrene-d_7 ($m/z = 239M^+$). Moreover, the mass distribution presented in the spectrum (Fig. 1(b)) and



Scheme 3.

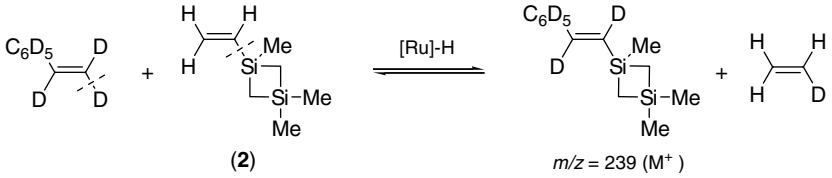


Scheme 4.

Table 1
Silylative coupling of vinyldisilacyclobutane with olefins catalyzed by $[RuH(Cl)(CO)(PCy_3)_2]$

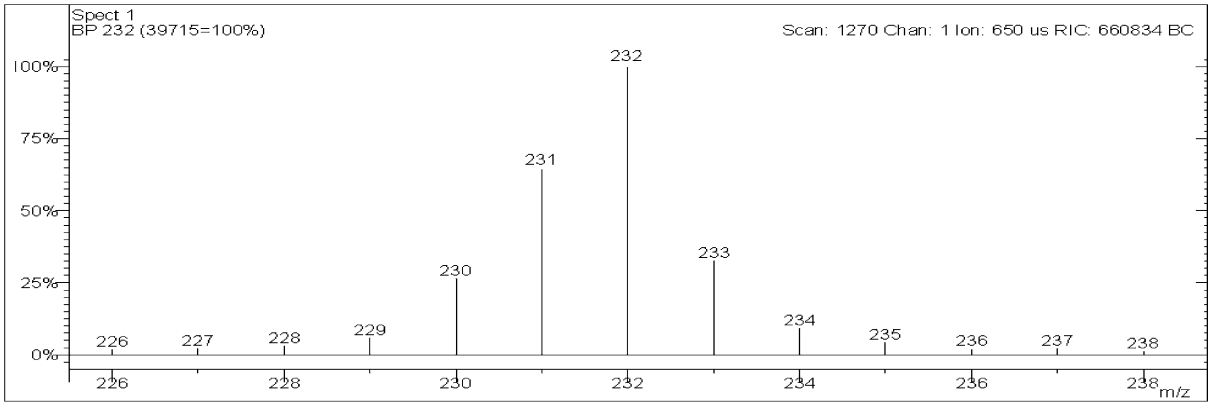
Olefin	Conversion of vinyldisilacyclobutane[b,c] (%)	Yield of *cross*-coupling products[b,c] (%)	Yield of homo-coupling product[b,c] (%)
Styrene	>99	>99 (80)[d]	0
4-Chlorostyrene	>99	94 (85)[d]	5
4-Methylstyrene	>99	92 (80)[d]	8
9-Vinylcarbazole	>99	85 (55)[d]	15
1-Vinyl-2-pyrrolidinone	40[a]	34	6
Propyl vinyl ether	>95[a]	59	7

Reaction conditions: molar ratio [Ru]:[ViSi]:[olefin] = 1:100:300; toluene (1 M); $T = 80$ °C; argon; time: 4 h.
[a] 18 h.
[b] Determined by GC and GC–MS.
[c] Determined by NMR.
[d] Isolated yield.

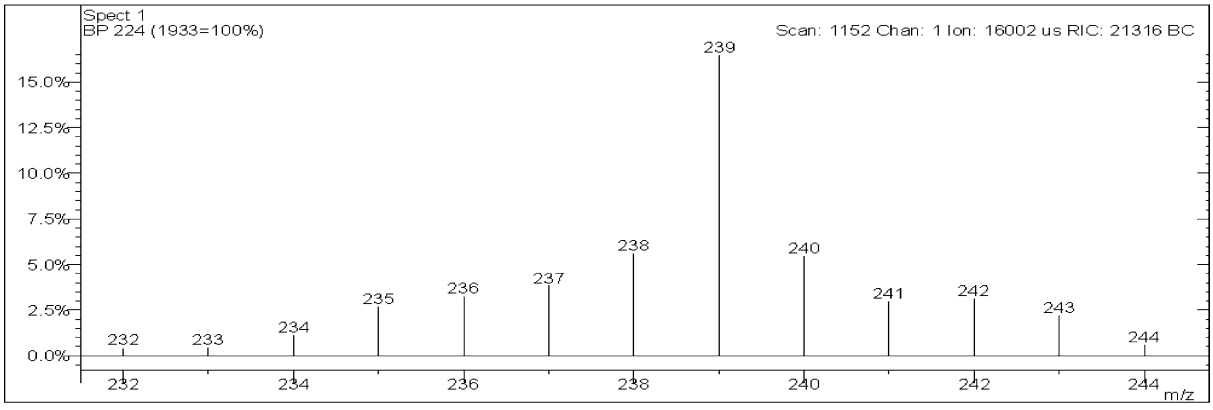


(**2**) *m/z* = 239 (M^+)

Scheme 5.

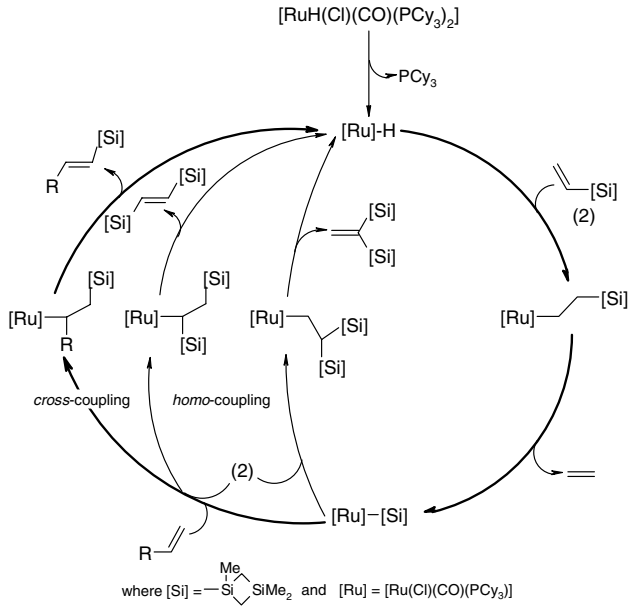


(a) The fragment of mass spectra of the silyl-styrene-d_0 ($m/z = 232M^+$)



(b) The fragment of mass spectra of the silyl-styrene-d_7 ($m/z = 239M^+$)

Fig. 1. (a) The fragment of mass spectra of the silyl-styrene-d_0 ($m/z = 232M^+$). (b) The fragment of mass spectra of the silyl-styrene-d_7 ($m/z = 239M^+$).



Scheme 6.

in particular the low intensity of the signals assigned to $M^+ - 1$ and $M^+ - 2$ do not indicate the presence of silyl-styrene-d_6 or silyl-styrene-d_5 in the system. This result supports the non-metallacarbene mechanism of the process.

On the basis of obtained results, a reasonable mechanism of homo-coupling of vinyldisilacyclobutane and its cross-coupling with which olefins in the presence of $[RuH(Cl)(CO)(PCy_3)_2]$ can be proposed (Scheme 6).

Dissociation of phosphine is postulated to generate the active catalyst. A mechanistic scheme of the *cross*-coupling of **2** with olefins involves the migratory insertion of vinylsilane into the [Ru]–H bond followed by β-Si elimination with the formation of ethylene and [Ru]–Si complex and insertion of the olefin into a [Ru]–Si bond followed by β-H elimination with the formation of substituted vinylsilane and regeneration of hydride complex. In the separate homo-coupling of **2** both modes of insertion proceed to give a mixture of *E* and *gem* products but the *cross*-coupling of olefin with **2** gives exclusively *E*-product accompanied by traces of the *E*-product of homo-coupling. Mechanism is analogous to that proved for other vinylsilicon compounds [7].

3. Conclusions

Cross-coupling of vinyldisilacyclobutanes with a variety of olefins in the presence of the ruthenium-hydride catalyst $[RuH(Cl)(CO)(PCy_3)_2]$ was found to be a general, highly selective method for the synthesis of functionalized vinyldisilacyclobutanes. The vinyldisilacyclobutane homo-coupling gives a mixture of *E* and *gem*-bis(silyl)ethenes. The reaction offers a new route for functionalized vinyldisilacyclobutanes, attractive monomers in ROP.

4. Experimental

4.1. Instrumentation

4.1.1. General procedures

^1H NMR (300 MHz), ^{13}C NMR (75 MHz) and ^{29}Si NMR (60 MHz) and DEPT spectra were recorded on Varian XL 300 MHz spectrometer in $CDCl_3$ solution. Chemical shifts are reported in δ (ppm) with reference to the residue portion solvent (CH_3Cl) peak for ^1H, ^{13}C and to TMS for ^{29}Si. Analytical gas chromatographic (GC) analyses were performed on a Varian Star 3400CX with a DB-5 fused silica capillary column (30 m × 0.15 mm) and TCD. Mass spectra of the monomers and products were obtained by GC–MS analysis (Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and an ion trap detector. High-resolution mass spectroscopic (HRMS) analyses were done on a AMD-402 mass spectrometer. Thin-layer chromatography (TLC) was performed on plates coated with 250 μm thick silica gel (Aldrich), and column chromatography was performed with silica gel 60 (70–230 mesh; Fluka). Benzene and hexane were dried, by distillation from sodium hydride, similarly toluene was distilled from sodium and hexane from calcium hydride under argon. All liquid substrates were also dried and degassed by bulb-to-bulb distillation. All the reactions were carried out under dry argon atmosphere.

4.2. Materials

The chemicals were obtained from the following sources: benzene, CH_2Cl_2, EtOAc, toluene, dodecane and hexane were purchased from Fluka, $CDCl_3$, C_6D_6 and $D_2C{=}CDC_6D_5$ from Dr Glaser A.G. Basel, the styrene, 4-chlorostyrene, 4-methylstyrene, 9-vinylcarbazol, 1-vinyl-2-pyrrolidinone and propyl vinyl ether were bought from Aldrich. CH_2Cl_2 was additionally passed through a column of aluminium oxide. The ruthenium (II) complex $[RuH(Cl)(CO)(PCy_3)_2]$ [13] (**1**) and 1,1,3-trimethyl-3-vinyl-1,3-disilacyclobutane (**2**) were prepared according to procedure described in the literature [14,15].

4.3. Catalytic examinations

In typical catalytic test, a toluene solution of the ruthenium catalyst **1** was placed in a glass ampoule under argon. Then the reagents and dodecane as internal standard (5% by volume) were added (molar ratio: [Ru]:[ViSi]:[olefin] = 1:100:300). After that, the ampoule was heated at 80 °C for 4–18 h. The composition of the

reaction mixture was analyzed by GC and GC–MS. The conversion and chemoselectivity of the reactions and yields were calculated by using the internal standard method.

4.4. Reaction of 1,1,3-trimethyl-3-vinyl-1, 3-disilacyclobutane with $CD_2{=}CDC_6D_5$ catalyzed by $[RuH(Cl)(CO)(PCy_3)_2]$

The complex $[RuH(Cl)(CO)(PCy_3)_2]$ (2 mg, 0.0028 mmol), C_6D_6 (0.28 mL), $D_2C{=}CDC_6D_5$ (94 mg, 0.84 mmol) and $H_2C{=}CHSiMe_2SiMe_2$ (43.8 mg, 0.28 mmol) were introduced to a glass ampule. The reaction mixture was heated at 80 °C. The progress of the reaction was monitored by GC–MS. The first GC–MS analysis was done after 20 min.

4.5. Synthesis of 1,1,3-trimethyl-1,3-disilacyclobutane derivatives

4.5.1. Ruthenium-catalyzed silylative coupling of 1,1,3-trimethyl-3-vinyl-1,3-disilacyclobutane

*4.5.1.1. [(gem + E)-1,2-bis(3,5,5-trimethyl-3,5-disilacyclobutane)]ethene (**3**).* A solution of $[RuH(Cl)(CO)(PCy_3)_2]$ (**1**) (9.3 mg, 0.0128 mmol), toluene (1.28 mL) and 1,1,3-trimethyl-3-vinyl-1,3-disilacyclobutane (**2**) (200 mg, 1.28 mmol) were placed in a 5 mL glass mini-reactor. The mixture was heated at 110 °C for 18 h under an argon flow. When the conversion of vinylsilane reached >99% the solvent was evaporated under vacuum. The final product was separated from residues of catalyst by column chromatography with silica, using hexane as eluent ($R_f = 0.60$). In this way we obtained 273 mg of **3** (0.96 mmol, 75% yield) as a colourless liquid. *Analytical data*: ^{1}H NMR ($CDCl_3$; δ (ppm)): 0.24 (s, 6H, Si(CH_3)); 0.27 (s, 12H, Si(CH_3)$_2$); 0.32 (s, 8H, –CH_2–); 6.41 (s, 2H, >C=CH_2, *gem*-); 6.77 (s, 2H, Si–H*C*=C*H*–Si, *trans*-). ^{13}C NMR ($CDCl_3$; δ (ppm)): 0.46 (Si(*C*H_3)); 2.33 (Si(*C*H_3)$_2$); 2.42 (–*C*H_2–, *trans*-isomer); 2.63 (Si(*C*H_3)); 3.25 (–*C*H_2–, *gem*-isomer); 140.40 (>C=*C*H_2, *gem*-); 150.45 (-Si–H*C*=*C*H–Si–, *trans*-); 154.40 (>*C*=CH$_2$). ^{29}Si NMR ($CDCl_3$; δ (ppm)): −5.28; 4.30; 4.56. HRMS for $C_{12}H_{28}Si_4$: Calculated 284.12681. Found: 284.12696.

4.5.2. Ruthenium-catalyzed silylative coupling of 1,1,3-trimethyl-3-vinyl-1,3-disilacyclobutane with olefins

*4.5.2.1. [(E)-1-phenyl-2-(3,5,5-trimethyl-3,5-disilacyclobutane)]ethene (**4**).* A solution of $[RuH(Cl)(CO)(PCy_3)_2]$ (**1**) (13.9 mg, 0.0192 mmol), toluene (1.92 mL), 1,1,3-trimethyl-3-vinyl-1,3-disilacyclobutane (**2**) (300 mg, 1.92 mmol) and styrene (600 mg, 5.76 mmol) were placed in a 5 mL glass mini-reactor. The mixture was heated at 80 °C for 8 h under an argon flow. After the vinylsilane derivative disappearance (>99% conversion), which was confirmed by GC analysis, the solvent and an excess of styrene were removed under vacuum. The final product was separated from residues of catalyst and the remains of styrene by column chromatography similarly to synthesis of **3** ($R_f = 0.45$), to afford 358 mg of **4** (1.54 mmol, 80% yield) as a colourless oily liquid. *Analytical data*: ^{1}H NMR ($CDCl_3$; δ (ppm)): 0.28 (s, 3H, Si(CH_3)); 0.31 (s, 6H, Si(CH_3)$_2$); 0.39 (s, 4H, –CH_2–); 6.59 (d, 1H, $J_{H-H} = 19.2$ Hz, Si–HC=C*H*–C$_6$H$_5$); 6.96 (d, 1H, $J_{H-H} = 19.2$ Hz, Si–*H*C=CH–C$_6$H$_5$); 7.28-7.35 (m, 3H, *m(p)*-C$_6$*H*$_5$); 7.46 (d, 2H, *o*-C$_6$*H*$_5$). ^{13}C NMR ($CDCl_3$; δ (ppm)): 1.03 (Si*C*H_3); 2.43 (–*C*H_2–); 2.77 (Si(*C*H_3)$_2$); 126.50 (*o*-*C*$_6$H$_5$); 128.09 (*p*-*C*$_6$H$_5$); 128.53 (*m*-*C*$_6$H$_5$); 129.06 (>Si–HC=*C*H–C$_6$H$_5$); 138.12 (–HC=CH–*C*<); 144.10 (>Si–H*C*=CH–). ^{29}Si NMR ($CDCl_3$; δ (ppm)): 4.71, 4.15. HRMS for $C_{13}H_{20}Si_2$: Calculated 232.11035. Found: 232.11058.

The next new compounds presented below were synthesized essentially in the same manner as **4**, by the reaction between **2** and a suitable olefin.

*4.5.2.2. [(E)-1-(4-chloro-phenyl)-2-(3,5,5-trimethyl-3,5-disilacyclobutane)]ethene (**5**). Analytical data*: ^{1}H NMR ($CDCl_3$; δ (ppm)): 0.27 (s, 3H, Si(CH_3)); 0.30 (s, 6H, Si(CH_3)$_2$); 0.38 (s, 4H, –CH_2–); 6.55 (d, 1H, $J_{H-H} = 19.2$ Hz, Si–HC=C*H*–C$_6$H$_4$–); 6.89 (d, 1H, $J_{H-H} = 18.9$ Hz, Si–*H*C=CH–C$_6$H$_4$–); 7.31 (d, 2H, *m*-C$_6$*H*$_4$–); 7.38 (d, 2H, *o*-C$_6$H$_4$–). ^{13}C NMR ($CDCl_3$; δ (ppm)): 0.89 (Si*C*H_3); 2.39 (–*C*H_2–); 2.75 (Si(*C*H_3)$_2$); 127.71 (*o*-*C*$_6$H$_5$); 128.69 (*m*-*C*$_6$H$_5$); 130.03 (>Si–HC=*C*H–C$_6$H$_4$-Cl); 133.70 (>Si–HC=CH–*C*<); 136.64 (>*C*-Cl); 142 (>Si–H*C*=CH–). ^{29}Si NMR ($CDCl_3$; (ppm)): 4.83, 4.20. HRMS for $C_{13}H_{19}ClSi_2$: Calculated 266.07138. Found: 266.07142. The isolation procedure: the reaction mixture was injected onto a silica gel column. Hexane was applied as an eluent ($R_f = 0.40$). The final product was obtained with 80% productivity as a colourless liquid.

*4.5.2.3. [(E)-1-(4-methyl-phenyl)-2-(3,5,5-trimethyl-3,5-disilacyclobutane)]ethene (**6**). Analytical data*: ^{1}H NMR ($CDCl_3$; δ (ppm)): 0.27 (s, 3H, Si(CH_3)); 0.30 (s, 6H, Si(CH_3)$_2$); 0.38 (s, 4H, –CH_2–); 2.35 (–CH_3); 6.52 (d, 1H, $J = 18.9$ Hz, Si–HC=C*H*–C$_6$H$_4$–); 6.93 (d, 1H, $J = 18.9$ Hz, Si–HC=C*H*–C$_6$H$_4$–); 7.15 (d, 2H, *m*-C$_6$*H*$_4$–); 7.37 (d, 2H, *o*-C$_6$H$_4$–). ^{13}C NMR ($CDCl_3$; δ (ppm)): 1.15 (Si*C*H_3); 2.58 (–*C*H_2–); 2.96 (Si(*C*H_3)$_2$); 21.33 (–*C*H_3); 126.35 (*o*-*C*$_6$H$_5$); 127.66 (>Si–HC=*C*H–C$_6$H$_4$–CH$_3$); 129.14 (*m*−*C*$_6$H$_5$); 135.41 (>Si–HC=CH–*C*<); 137.89 (>*C*–CH$_3$); 143.91 (>Si–H*C*=CH–C$_6$H$_4$–CH$_3$). ^{29}Si NMR ($CDCl_3$; (ppm)): 4.63, 4.03. HRMS for $C_{14}H_{22}Si_2$: Calculated 246.12600. Found: 246.12615. The isolation procedure: the reaction mixture was injected onto a silica gel column. Hexane was applied as an eluent ($R_f = 0.38$). The final product was obtained with 85% productivity as a colourless liquid.

*4.5.2.4. [(E)-1-(N-carbazole)-2-(3,5,5-trimethyl-3,5-disilacyclobutane)]ethene (**7**). Analytical data*: ^{1}H NMR ($CDCl_3$; δ (ppm)): 0.30 (s, 3H, Si(CH_3)); 0.36 (s, 6H, Si(CH_3)$_2$); 0.51 (s, 4H, –CH_2–); 6.17 (d, 1H, J_{H-H} = 17.1 Hz, ≻Si–*H*C═CH–N≺); 7.34 (t, 1H, Ph), 7.40 (d, 1H, J_{H-H} = 21.3 Hz, ≻Si–HC═C*H*–N≺); 7.49 (t, 1H, Ph); 7.70 (d, 1H, Ph), 8.11 (d, 1H, Ph). ^{13}C NMR ($CDCl_3$; δ (ppm)): 1.76 (Si*C*H$_3$); 2.59 (–*C*H$_2$–); 3.45 (Si(*C*H$_3$)$_2$); 110.39 (*C*H at Ph); 120.14 (*C*H at Ph); 120.76 (*C*H at Ph); 123.89 (*C* at C_4N); 124.14 (Si–HC═*C*H–N≺).); 126.16 (*C*H at Ph); 134.11 (*C*–N–HC═); 139.26 (Si–H*C*═CH–N≺). ^{29}Si NMR ($CDCl_3$; δ (ppm)): −21.19; 1.98; 4.71. HRMS for $C_{19}H_{23}NSi_2$: Calculated 321.13690. Found: 321.13730. The isolation procedure: the reaction mixture was injected onto a silica gel column. The mixture of hexane and EtOAc (50/1) was applied as an eluent (R_f = 0.40). The final product was obtained with 55% productivity as a less-yellow powder.

*4.5.2.5. [(E)-1-(N-2-pyrrolidinone)-2-(3,5,5-trimethyl-3,5-disilacyclobutane)]ethene (**8**). Analytical data*: ^{1}H NMR ($CDCl_3$; δ (ppm)): 0.27 (s, 3H, Si(CH_3)); 0.32 (s, 6H, Si(CH_3)$_2$); 0.48 (s, 4H, –CH_2– at disilacyclobutane); 1.17 (m, 2H, CH_2), 1.96 (t, 2H, –CH_2–); 2.78 (t, 2H, –CH_2–); 4.56 (d, 1H, J_{H-H} = 18.9 Hz, Si–*H*C═CH–N≺), 7.51 (d, 1H, J_{H-H} = 19.2 Hz, Si–HC═C*H*–N≺). ^{13}C NMR ($CDCl_3$; δ (ppm)): −1.89 (–*C*H$_2$– at disilacyclobutane1); −1.30 (Si*C*H$_3$); 3.75 (Si(*C*H$_3$)$_2$); 18.61 (–*C*H$_2$–); 31.49 (–*C*H$_2$–); 46.97 (–*C*H$_2$–); 104.29 (Si–HC═*C*H–N≺); 148.52 (Si–H*C*═CH–N≺); 172.07 (*C*═O). MS [*m*/*z* (rel. int.)]: MS [*m*/*z* (rel. int.)]: 238 (90), 224 (100), 210 (22), 198 (43), 184 (13), 168 (35), 155 (13), 143 (15), 131 (41), 117 (18), 85 (10), 73 (16), 59 (15).

*4.5.2.6. [(E)-1-(propoxy)-2-(3,5,5-trimethyl-3,5-disilacyclobutane)]ethene (**9**). Analytical data*: ^{1}H NMR ($CDCl_3$; δ (ppm)): 0.25 (s, 3H, Si(C_3)); 0.28 (s, 6H, Si(CH_3)$_2$); 0.38 (s, 4H, –CH_2– at disilacyclobutane); 0.96 (t, 3H, –CH_3); 0.96 (m, 2H, –CH_2–); 3.70 (t, 2H, –O–CH_2–); 4.63 (d, 1H, *J* = 15.0 Hz, Si–*H*C═CH–O–CH_2–); 6.49 (d, 1H, *J* = 14.5 Hz, Si–HC═C*H*–O–CH_2–). ^{13}C NMR ($CDCl_3$; (ppm)): −1.42 (Si*C*H$_3$); 0.72 (–*C*H$_2$–); 2.78 (Si(*C*H$_3$)$_2$); 10.50 (–*C*H$_3$); 21.62 (–*C*H$_2$–CH$_3$); 73.50 (-O–*C*H$_2$–); 111.47 (Si–HC═*C*H–O–CH$_2$–); 156.41 (Si–H*C*═CH–O–CH$_2$–). MS [*m*/*z* (rel. int.)]: 214 (77), 199 (11), 185 (2), 173 (3), 159 (11), 146 (2), 133 (100), 113 (9), 104 (2), 83 (22), 67 (7), 55 (30).

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