$[Me_2C(C_5H_4)_2TiMe_2]$: An Open-Bent Titanocene Catalyst for the Hydrosilylation of Bulky 1,3-Dienes

Roxana Pop,[a] Jin Lan Cui,[b] Louis Adriaenssens,[a] Virginie Comte,[a] Pierre Le Gendre*[a]

[a] Institut de Chimie Moléculaire de l'Université de Bourgogne, ICMUB-UMR CNRS 5260, Université de Bourgogne, 9 Avenue Alain Savary, BP 47870, 21078 Dijon Cedex, France
E-mail: pierre.le-gendre@u-bourgogne.fr

[b] Department of Chemistry, University of Louisville, 2320 South Brook Street, Louisville, KY 40292, USA

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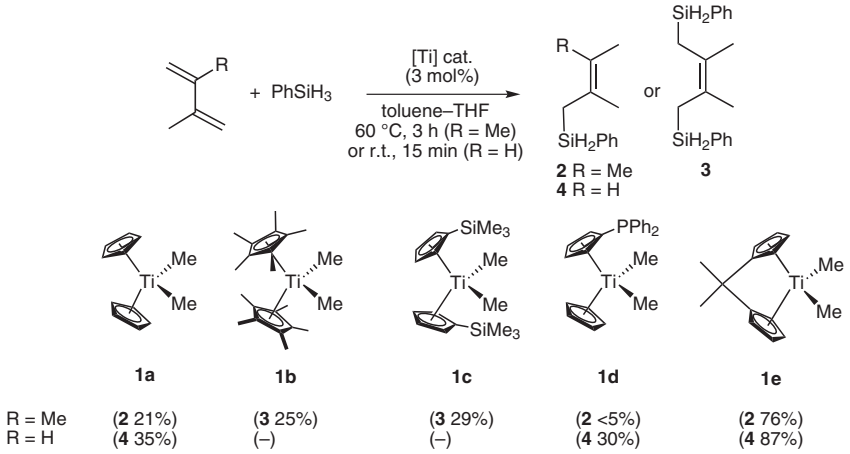
Abstract: Motivated by our preliminary results on Cp_2TiF_2-catalysed 1,4-hydrosilylation of monosubstituted dienes, we assessed the performance of several titanium complexes for the hydrosilylation of 2,3-dimethylbutadiene, a representative bulky diene. An open-bent titanocene complex $[Me_2C(C_5H_4)_2TiMe_2]$ performed the best and proved to be efficient for the hydrosilylation of a variety of substrates such as disubstituted dienes, activated alkenes, and even an acetylene.

Key words: hydrosilylation, titanium, diene, allylsilane, homogeneous catalysis

Allylsilanes are indispensable compounds widely employed as synthetic reagents in organic synthesis.[1] Among the wide number of synthetic methods to prepare these versatile reagents,[2,3] metal-catalysed hydrosilylation of 1,3-dienes is attractive as it avoids the use of highly reactive organometallic reagents and their associated limitations.[4] Several late-transition-metal complexes catalyse this reaction with those based on Rh and Pd being especially useful as they are selective, predominantly giving 1,4-addition of the hydrosilane.[5] However, when unsymmetric dienes are used, the Rh- or Pd-catalysed reaction generally leads to a mixture of regioisomers (tail or head products) via *Z*-specific 1,4-addition.

In 2005, our group described the first regio- and stereoselective *anti*-1,4-hydrosilylation of dienes using the air-stable titanium precatalyst Cp_2TiF_2.[6] This complex is the only known precatalyst capable of selectively generating (*E*)-allylsilanes.[7] The reaction proceeded well with butadiene and monosubstituted dienes such as isoprene, myrcene, and pentadiene. However, attempted hydrosilylation of sterically more demanding dienes (disubstituted dienes) met with little success. In an effort to widen the scope of this reaction we decided to investigate the catalytic properties of other titanium precatalysts, and we present the results here.

Considering our previous success with Cp_2TiF_2, we first assessed the efficacy of a series of difluoride complexes as precatalysts in the dihydrosilylation of sterically challenging dienes. Unfortunately, whereas activation of Cp_2TiF_2 by $PhSiH_3$ proceeded in a few minutes, activation periods with other complexes ranged from a few minutes to several hours at varying temperatures which rendered a comparative study risky. Taking into account that dialkyl titanocene complexes may also be good-candidates as precatalysts for the hydrosilylation of dienes,[8] we continued our investigation using a variety of titanium complexes with methyl groups as equatorial ligands. We thus assessed the efficacy of these complexes in the catalytic hydrosilylation of 2,3-dimethyl-1,3-butadiene with $PhSiH_3$ (Scheme 1).



Scheme 1 Screening of titanium complexes as precatalysts for the hydrosilylation of 2,3-dimethyl-1,3-butadiene and isoprene with $PhSiH_3$

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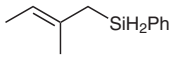
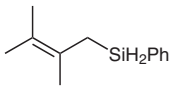
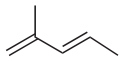
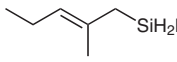
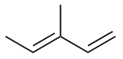
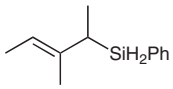
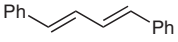
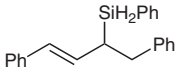
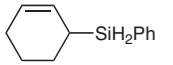
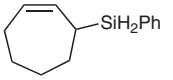
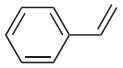
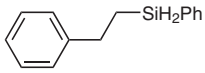
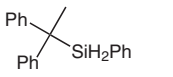
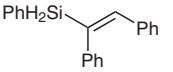
Dimethyltitanocene complexes **1a–e** were generated in situ from the corresponding dichloride complexes and two equivalents of MeLi. After stirring one hour at room temperature, phenylsilane was added to the orange solution, and the reaction mixture was briefly heated to 60 °C (1–2 min) until the colour changed to black. 2,3-Dimethylbutadiene was then added at room temperature, and the reaction was stirred at 60 °C for three hours. Volatiles were evaporated, and the products were separated by flash chromatography. Using these conditions, complex **1a** led to the formation of targeted hydrosilylated product **2** in 21% yield and also to oligomerisation of $PhSiH_3$. Complexes **1b** and **1c** with bulkier, more electron-rich cyclopentadienyl ligands did not catalyse the hydrosilylation reaction. However, both were active giving mainly doubly silylated product **3** in 25% and 29% yield, respectively. Complex **1b** also catalysed the competitive dehydropolymerisation of $PhSiH_3$ under these conditions, whereas a redistribution of 20% of $PhSiH_3$ into Ph_2SiH_2 was observed as the main side reaction when using **1c** as precatalyst. Recent studies conducted on the electrochemical properties of the complex $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4PPh_2)TiCl_2]$ have highlighted its particularly electron-poor character and thus it was of interest in our screening.[9] In the event the dimethyl variant **1d** gave only traces of the expected hydrosilylation product **2**. We next studied the ansa-complex **1e** exhibiting a pronounced bent geometry and a possibly more open reactive surface than Cp_2TiMe_2.[10] This last proved to be the most effective catalyst leading to full conversion of phenylsilane after three hours and giving allylsilane **2** in 76% yield. It should be noted that, aside from fitting nicely into a comparative study, complex **1e** was the best precatalyst studied, outperforming all other Ti complexes, whether they contained fluorine or methyl equatorial ligands, in the hydrosilylation of 2,3-dimethyl-1,3-butadiene.[11]

The comparative study was expanded to include the hydrosilylation of isoprene using **1a–e** as precatalysts. Once again the ansa-titanocene complex **1e** performed the best, promoting the *trans*-1,4-hydrosilylation of isoprene in 87% yield in 15 minutes at room temperature.[12] Cp_2TiMe_2 **1a** was a distant second giving only a 35% yield under similar conditions. Interestingly, the electron-poor diphenylphosphino-substituted dimethyltitanocene complex **1d** gave a comparable result to Cp_2TiMe_2 (30% yield) whereas both electron-rich and bulky titanium complexes **1b** and **1c** did not show any activity in hydrosilylation or silylation of isoprene at room temperature.

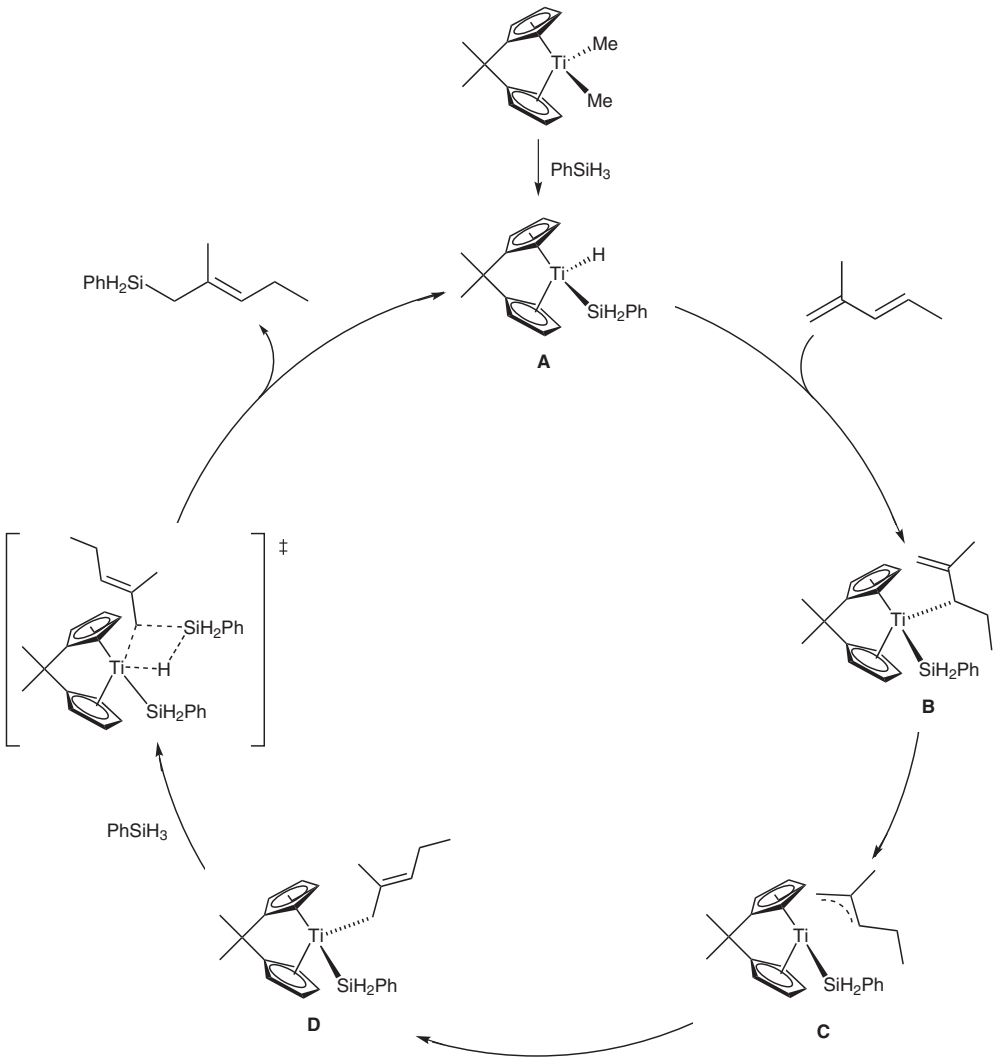
With these results in hand, we started to explore the scope of the ansa-dimethyltitanocene-catalysed hydrosilylation (Table 1). As observed for 2,3-dimethylbutadiene, hydrosilylation of 2-methyl-1,3-pentadiene and 3-methyl-1,3-pentadiene required higher reaction temperature and longer reaction time with respect to isoprene (Table 1, entries 2–4 vs. entry 1). In both cases, the hydrosilylation took place regio- and stereoselectively to give (*E*)-allylsilanes **5** and **6** in 83% and 85% yields, respectively.[13] We next attempted the hydrosilylation of 1,4-diphenyl-1,3-butadiene, an example of a 1,4-disustituted diene. The hydrosilylation took place smoothly but with different regioselectivity, furnishing only the 1,2-addition product **7** (entry 5). Cyclic dienes such as 1,3-cyclohexadiene and 1,3-cycloheptadiene also underwent hydrosilylation to yield (2-cyclohexenyl)(phenyl)silane **8** and (2-cycloheptenyl)(phenyl)silane **9** albeit in only modest yields.

Table 1 Scope of $[Me_2C(C_5H_4)_2TiMe_2]$ (**1e**) Catalysed Hydrosilylation[a]

Entry	Substrate	Product	Time (h)	Yield (%)
1		 **4**	0.25	87[b]
2		 **2**	3	76
3		 **5**	2	83
4		 **6**	6	85
5		 **7**	4.5	75
6		 **8**	4	34
7			21	40
8		 **10**	4	87[b]
9		 **11**	3	75
10		 **12**	24	72

[a] Conditions: ansa-Cp_2TiCl_2 (**1e**, 0.036 mmol), MeLi (0.072 mmol), $PhSiH_3$ (1.2 mmol), substrate (3 mmol), 60 °C.
[b] Reaction at r.t.

A proposed mechanism of the reaction using 2-methyl-1,3-pentadiene as a representative substrate is reported in Scheme 2. Initially, as proposed by Harrod, $[Me_2C(C_5H_4)_2TiH(SiPhH_2)]$ (**A**) is generated from $[Me_2C(C_5H_4)_2TiMe_2]$ **1e** and phenylsilane.[14] Then, hydrotitanation of the internal double bond of the diene occurs leading to the η^1-allyl titanium complex (**B**). Isomerisation, via a *syn*-π-allyltitanium complex (**C**), to



Scheme 2 Postulated mechanism of the $[Me_2C(C_5H_4)_2TiMe_2]$-catalyzed hydrosilylation of 2-methyl-1,3-pentadiene as representative substrate

the less congested and, thus, more stable η^1-allyl complex (**D**) followed by subsequent σ-bond metathesis with a molecule of phenylsilane leads to the desired allylsilane and regenerates the active catalyst (**A**). As mentioned above, the hydrosilylation of 1,4-diphenyl-1,3-butadiene led preferentially to 1,2-addition product whereas other dienes led to 1,4-addition. This regioselectivity is consistent with the formation of the more stable allyltitanium intermediate.

The reaction was then extended to substrates other than dienes such as styrene, 1,1-diphenylethylene, and diphenylacetylene. The reaction between styrene and phenylsilane led to rapid and regioselective hydrosilylation at room temperature leading to the linear product in 87% yield (entry 8). Surprisingly, a complete change of regioselectivity was observed in the hydrosilylation of diphenylethylene, which gave the 2,1-addition product. This regioselectivity was reported earlier by other groups in the hydrosilylation of the same substrate using Ca-, Sr-, and Yb-based catalysts.[15] Finally, the ansa-dimethyltitanocene complex also proved effective for the hydrosilylation of alkynes. Phenylsilane added to diphenylacetylene in the presence of 3 mol% **1e** giving exclusively (*E*)-vinylsilane **12** in good yield (entry 10).

In summary, we have shown that the ansa-dimethyltitanocene complex is a very efficient catalyst for the hydrosilylation of 1,3-dienes. It gives (*E*)-allylsilanes with high regio- and stereoselectivities from isoprene and a variety of disubstituted dienes. Cyclic dienes also underwent hydrosilylation under similar conditions. In addition, the complex is also able to promote hydrosilylation of styrene, 1,1-diphenylethylene, and diphenylacetylene in good yields, making it a versatile addition to the toolbox of hydrosilylation catalysts.

General Considerations

All experiments were carried out under an atmosphere of purified argon using vacuum line techniques. Glassware was flame-dried before use. Solvents were dried and distilled under argon from sodium and benzophenone before use. Elemental analyses were performed on a EA 1108 CHNS-O FISONS. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 300 MHz Avance spectrometer. Chemical

shifts are denoted in ppm (δ) relative to TMS (^{1}H). Coupling constants are reported in Hz. Dienes were purchased from Aldrich and distilled under an argon atmosphere. Silanes were purchased from Aldrich and used without further purification. Dichloride precursors of complexes **1c**,[16] **1d**,[17] and **1e**[10a] were prepared as reported in the literature. Titanocene dichloride and bis(pentamethylcyclopentadienyl)titanium dichloride were purchased from Aldrich.

Procedure for the Catalytic Hydrosilylation

Methyllithium (1 M in Et_2O, 0.072 mL, 0.072 mmol) was added to a stirred, black solution of ansa-Cp_2TiCl_2 (10 mg, 0.036 mmol) in dry toluene (0.5 mL) at 0 °C. The cooling bath was removed, and the reaction was stirred for 1 h at r.t. A solution of phenylsilane (0.15 mL, 1.2 mmol) in dry THF (0.5 mL) was added, and the orange solution was heated to 60 °C until the color turned to dark blue. After cooling to r.t., diene (3 mmol) was added, and the reaction proceeded under the conditions described in Table 1. The reaction was monitored by GC. After consumption of the silane, the solvent was removed by evaporation, and the product was purified by silica gel chromatography (pentane).

(2,3-Dimethyl-2-butenyl)phenylsilane (2)

Yield 174 mg, 76%. IR (neat): ν_{Si-H} = 2169 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3), 1.72 (m, 3 H, CH_3), 1.94 (m, 2 H, CH_2), 4.36 (t, 2 H, $^3J_{H-H}$ = 3.9 Hz, SiH_2), 7.41 (m, 3 H, Ph), 7.61 (m, 2 H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 18.9, 20.0, 20.4, 24.0, 122.5, 123.1, 127.7, 129.3, 132.7, 135.0. Anal. Calcd for $C_{12}H_{18}Si$: C, 75.71; H, 9.53. Found: C, 75.52; H, 9.27.

(2,3-Dimethyl-2-butene-1,4-diyl)bis(phenylsilane) (3)

Yield 52 mg, 29%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 6 H, CH_3), 1.90 (t, 4 H, $^3J_{H-H}$ = 3.9 Hz, CH_2), 4.31 (t, 4 H, $^3J_{H-H}$ = 3.9 Hz, SiH_2), 7.38 (m, 6 H, Ph), 7.41 (m, 4 H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 19.4, 20.4, 122.7, 127.9, 129.6, 132.8, 135.2. Anal. Calcd for $C_{18}H_{24}Si_2$: C, 72.90; H, 8.16. Found: C, 72.97; H, 8.31.

(*E*)-(2-Methyl-2-butenyl)phenylsilane (4)

Yield 183 mg, 87%. IR (neat): ν_{Si-H} = 2138 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 (d, 3 H, $^3J_{H-H}$ = 7 Hz, C*H*$_3$CH), 1.57 (s, 3 H, CH_3C), 1.78 (d, 2 H, $^3J_{H-H}$ = 3.9 Hz, CH_2Si), 4.24 (t, 2 H, $^3J_{H-H}$ = 3.9 Hz, SiH_2), 5.07 (q, 1 H, $^3J_{H-H}$ = 7.0 Hz, CH=C), 7.30 (m, 3 H, Ph), 7.48 (m, 2 H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 13.6, 17.6, 23.0, 118.3, 128.0, 129.6, 132.0, 132.7, 135.2. Anal. Calcd for $C_{11}H_{16}Si$: C, 74.93; H, 9.15. Found: C, 75.12; H, 9.31.

(*E*)-(2-Methyl-2-pentenyl)phenylsilane (5)

Yield 190 mg, 83%; *Z*/*E* = 22:78). IR (neat): ν_{Si-H} = 2147 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 (t, 3 H, $^3J_{H-H}$ = 7 Hz, C*H*$_3$CH$_2$), 1.69 (s, 3 H, CH_3C), 1.89 (m, 2 H, CH_2Si), 2.02 (qt, 2 H, $^3J_{H-H}$ = 7.0 Hz, C*H*$_2$CH$_3$), 4.38 (t, 2 H, $^3J_{H-H}$ = 7.0 Hz, SiH_2), 5.12 (t, 1 H, $^3J_{H-H}$ = 7.0 Hz, CH=C), 7.40 (m, 3 H, Ph), 7.60 (m, 2 H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 14.2, 17.5, 21.2, 22.7, 126.2, 127.7, 129.3, 130.3, 132.4, 135.1. Anal. Calcd for $C_{12}H_{18}Si$: C, 75.71; H, 9.53. Found: C, 75.70; H, 9.53.

(*E*)-(3-Methyl-3-penten-2-yl)phenylsilane (6)

Yield 193 mg, 85%. IR (neat): ν_{Si-H} = 2143 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (d, 3 H, $^3J_{H-H}$ = 7.2 Hz, C*H*$_3$CH), 1.51 (d, 3 H, $^3J_{H-H}$ = 6.6 Hz, C*H*$_3$CH=), 1.57 (s, 3 H, CH_3C), 1.87 (m, 1 H, C*H*CH$_3$), 4.14 (m, 1 H, SiH_2), 4.19 (m, 1 H, SiH_2), 5.04 (q, 1 H, $^3J_{H-H}$ = 6.6 Hz, CH$_3$C*H*=C), 7.29 (m, 3 H, Ph), 7.46 (m, 2 H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 13.5, 15.4, 16.5, 28.0, 116.6, 127.8, 129.5, 132.4, 135.6, 137.6. Anal. Calcd for $C_{12}H_{18}Si$: C, 75.71; H, 9.53. Found: C, 75.91; H, 9.88.

(*E*)-(1,4-Diphenyl-3-buten-2-yl)phenylsilane (7)

Yield 283 mg, 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.47 (m, 1 H, C*H*CH$_2$), 2.88 (m, 2 H, CH_2), 4.26 (m, 2 H, SiH_2), 6.13 (m, 1 H, =CH), 6.25 (s, 1 H, =CH), 7.16 (m, 15 H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 31.3, 36.8, 125.8, 126.0, 126.4, 126.6, 127.6, 128.3, 128.5, 128.7, 129.9, 130.8, 131.1, 135.9, 137.9, 141.2. Anal. Calcd for $C_{22}H_{22}Si$: C, 84.02; H, 7.05. Found: C, 84.12; H, 7.28.

(2-Cyclohexenyl)phenylsilane (8)

Yield 76 mg, 34%. IR (neat): ν_{Si-H} = 2132 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.55 (m, 3 H, CH_2 + CH), 2.02 (m, 4 H, CH_2), 4.29 (m, 2 H, SiH_2), 7.41 (m, 3 H, Ph), 7.63 (m, 2 H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 21.7, 22.1, 24.7, 24.9, 126.4, 127.3, 128.0, 129.7, 131.8, 135.6. Anal. Calcd for $C_{12}H_{16}Si$: C, 76.53; H, 8.56. Found: C, 76.84; H, 8.91.

(2-Cycloheptenyl)phenylsilane (9)

Yield 97 mg, 40%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.74 (m, 4 H, CH_2), 2.25 (m, 4 H, CH_2), 4.49 (m, 2 H, SiH_2), 5.79 (m, 2 H, CH), 7.40 (m, 3 H, Ph), 7.60 (m, 2 H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 21.0, 21.7, 26.1, 26.7, 126.9, 128.5, 130.5, 131.1, 134.6, 141.1. Anal. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97. Found: C, 76.80; H, 8.43.

(Phenylethyl)phenylsilane (10)

Yield 221 mg, 87%. IR (neat): ν_{Si-H} = 2133 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (m, 2 H, C*H*$_2$CH$_2$), 2.70 (m, 2 H, CH$_2$C), 4.23 (t, 2 H, $^3J_{H-H}$ = 3.6 Hz, SiH_2), 7.23 (m, 10 H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 12.2, 31.2, 125.8, 127.9, 128.1, 128.4, 129.7, 132.2, 135.3, 144.0. ^{29}Si NMR ($CDCl_3$): δ = –31.0. Anal. Calcd for $C_{14}H_{16}Si$: C, 79.18; H, 7.59. Found C, 79.39; H, 7.88.

(1,1-Diphenylethyl)phenylsilane (11)

Yield 258 mg, 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.79 (s, 3 H, CH_3), 4.70 (s, 2 H, SiH_2), 7.28 (m, 15 H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 25.5, 37.6, 125.6, 127.6, 128.3, 129.8, 131.0, 136.4, 147.3. ^{29}Si NMR ($CDCl_3$): δ = –19.1. Anal. Calcd for $C_{20}H_{20}Si$: C, 83.28; H, 6.99. Found: C, 82.93; H, 6.09.

(*E*)-(1,2-Diphenylvinyl)phenylsilane (12)

Yield 247 mg, 72%. IR (neat): ν_{Si-H} = 2134 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.5 (s, 2 H, SiH_2), 7.24 (m, 10 H, Ph), 7.62 (s, 1 H, CH=C), 7.74 (m, 4 H, Ph), 8.22 (m, 1 H, Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 123.3, 128.3, 129.9, 131.6, 135.7. ^{29}Si NMR ($CDCl_3$): δ = –11.7. Anal. Calcd for $C_{20}H_{18}Si$: C, 83.86; H, 6.33. Found: C, 83.45; H, 6.41.

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