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*Articles*

# First Titanium-Catalyzed *anti*-1,4-Hydrosilylation of Dienes

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1,4-Hydrosilylation of dienes catalyzed by late transition metals constitutes a straightforward access to allylsilanes. However, when unsymmetric dienes are used, it generally leads to a mixture of regioisomers (tail or head products) via *Z*-specific 1,4-addition. Here we describe the first catalytic *anti*-1,4-hydrosilylation of dienes using the cheap and stable $Cp_2TiF_2$ complex as catalyst. It affords *E*-allylsilanes in good to excellent yields with an unprecedented regio- and diastereoselectivity. Dehydrogenative double silylation of dienes can be selectively obtained by simply changing the activation protocol of the precatalyst.

## Introduction

Allylsilanes have been extensively used in many areas of organic synthesis.[1] For example, the Lewis acid-promoted reaction of allylsilanes with aldehydes or ketones (so-called Hosomi−Sakurai reaction) has become a fundamental synthetic process in organic synthesis.[2] In addition, the cycloaddition reaction of allylsilanes with olefins, carbonyl compounds, or imines has provided a powerful tool for the construction of carbo- and heterocycles.[3] In response to the growing interest in this chemistry, a number of ways have been developed to prepare allyl silicon compounds.[4] Among them, the metal-catalyzed hydrosilylation of 1,3-dienes appeared to be very attractive since it avoids the use of highly reactive organometallic reagents and the limitation associated with them.[5] Several late transition metal complexes catalyze this reaction, but those based on Rh and Pd seem to be the most appropriate since they predominantly give 1,4-addition of the hydrosilane.[6] To the best of our knowledge, almost no result using early transition metal has been described.[7,8] However, catalysts based on cheap and easily available complexes would clearly offer significant advantages. In this paper, we report the first and unique regio- and diastereoselective *anti*-1,4-hydrosilylation of dienes using the air-stable titanium precatalyst $Cp_2TiF_2$. A surprising diversity of products leading to either allylsilanes or silacyclopentenes can be obtained by simply changing the activation protocol of $Cp_2TiF_2$.

## Results and Discussion

Some time ago, Buchwald and co-workers have shown that the reaction of $Cp_2TiF_2$ with polymethylhydrosiloxane (PMHS) provides an active titanium hydride (or silyltitanium hydride) that undergoes hydrosilylation of lactones, ketones, and esters.[9] As a part of our ongoing program on catalytic allyltitanation, we recently

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(1) Reviews: (a) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. (b) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200. (c) Langkopf, E.; Shinzer, D. *Chem. Rev.* **1995**, *95*, 1375. (d) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063. (e) Chabaud, L.; James, P.; Landais, Y. *Eur. J. Org. Chem.* **2004**, 3173.

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(4) Sarkar, T. K. *Synthesis* **1990**, 1101.

(5) (a) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 441. (b) Marciniec, B. In *Comprehensive Handbook on Hydrosilylation*; Pergamon Press: Oxford, 1993; pp 110−114.

(6) (a) Ojima, I.; Kumagai, M. *J. Organomet. Chem.* **1978**, *157*, 359. (b) Ojima, I. *J. Organomet. Chem.* **1977**, *134*, C1. (c) Ojima, I.; Kumagai, M. *J. Organomet. Chem.* **1977**, *134*, C6. (d) Tsuji, T.; Hara, M.; Ohno, K. *Tetrahedron* **1994**, *30*, 2143. (e) Gustafsson, M.; Frejd, T. *J. Chem. Soc., Perkin Trans. 1* **2002**, 102. (f) Gustafsson, M.; Frejd, T. *J. Organomet. Chem.* **2004**, *689*, 438.

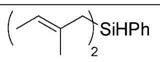
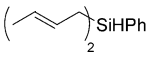
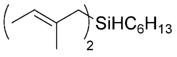
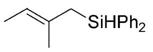
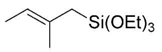
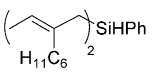
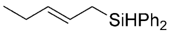
(7) Harrod only mentioned that $Cp_2TiMe_2$ catalyzes the hydrosilylation of dienes, but he specified that the reactions are generally complicated by the simultaneous catalytic oligomerization of silane: Harrod, J. F. *Coord. Chem. Rev.* **2000**, 493.

(8) For metallocene-catalyzed hydrosilylation of alkenes and alkynes, see: (a) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564. (b) Kesti, M. R.; Waymouth, R. M.; *Organometallics* **1992**, *11*, 1095. (c) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381. (d) Corey, J. Y.; Zhu, X. H. *Organometallics* **1992**, *11*, 672. (e) Ura, Y.; Gao, G.; Bao, F.; Ogasawara, M.; Takahashi, T. *Organometallics* **2004**, *23*, 4804. (f) Takahashi, T.; Bao, F.; Gao, G.; Ogasawara, M. *Org. Lett.* **2003**, *5*, 3479.

(9) (a) Carter, M. B.; Schiøtt, B.; Gutiérrez, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11667. (b) Barr, K. J.; Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1994**, *59*, 4323. (c) Verdaguer, X.; Hansen, M. C.; Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1997**, *62*, 8522.

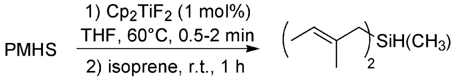
10.1021/om050533m CCC: $30.25

**Table 1. Titanium-Catalyzed *trans*-1,4-Hydrosilylation of 1,3-Dienes**[a]

| Entry | Diene | Silane | Product | | Time | Yield [%] |
|---|---|---|---|---|---|---|
| 1 | isoprene | $PhSiH_3$ |  | **2** | 20 min | 85 |
| 2 | 1,3-butadiene | $PhSiH_3$ |  | **3** | 5 h | 88[b] |
| 3 | isoprene | hexylsilane |  | **4** | 5 h | 81 |
| 4 | isoprene | $Ph_2SiH_2$ |  | **5** | 3 h | 81 |
| 5 | isoprene | $(EtO)_3SiH$ |  | **6** | 5 h | 30 |
| 6 | myrcene | $PhSiH_3$ |  | **7** | 5 h | 56 |
| 7 | pentadiene | $Ph_2SiH_2$ |  | **8** | 3 h | 95 |

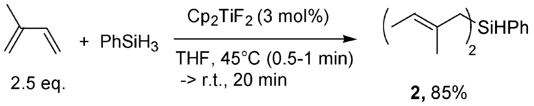
[a] $Cp_2TiF_2$ (0.0625 mmol), diene (5 mmol), silane (1.9 mmol), THF (1.5 mL). The reaction mixture is heated first at 45 °C until the color changes from yellow to dark purple, then is stirred at room temperature. [b] Reaction conducted at −4 °C.

**Scheme 1. Sequential $Cp_2TiF_2$-Catalyzed Redistribution of PMHS and Double 1,4-Hydrosilylation of Isoprene with in Situ Generated $MeSiH_3$**



**1**

**Scheme 2. Double $Cp_2TiF_2$-Catalyzed 1,4-Hydrosilylation of Isoprene with $PhSiH_3$**



**2**, 85%

started to explore the reaction of titanium hydride thus generated with dienes.[10] In initial experiments we carried out the reaction of isoprene with PMHS as substrates in the presence of $Cp_2TiF_2$ (1 mol %) as precatalyst (Scheme 1). The titanium catalyst was first briefly heated with PMHS at 60 °C (0.5−2 min) in THF, resulting in a color change from yellow to dark blue. The flask was then cooled at 0 °C, and isoprene was added dropwise via a syringe. The reaction mixture was stirred at room temperature for 1 h, during which time the color slowly changed from blue to dark purple. Evaporation of the solvent and flash chromatography afforded a small amount of the unexpected methylbis(2-methylbut-2-enyl)silane **1**, which have been unambiguously identified by NMR spectroscopy. With regard to the formation of **1**, we propose that it is generated by a 1,4-hydrosilylation of two molecules of isoprene with $MeSiH_3$, which results from a partial redistribution of PMHS.[11] The NMR analysis of the residual polymeric material confirmed that a redistribution of PMHS occurred, generating a methylsilsequioxane polymer as reported by Harrod with some of the silicon atoms bearing allylic groups. Therefore $Cp_2TiF_2$ seems to be a very effective precatalyst for the hydrosilylation since it is able to make react almost 50% of the $MeSiH_3$ potentially formed and to functionalize the polysilsesquioxane.

To confirm the ability of $Cp_2TiF_2$ to catalyze the hydrosilylation of dienes, we next examined the reaction with the less volatile $PhSiH_3$, isoprene, and 3 mol % of $Cp_2TiF_2$ (Scheme 2). The procedure was even simpler than for **1** since the precatalyst was activated in the presence of isoprene. After a few minutes at 45 °C, the color of the solution changed spontaneously from yellow to dark purple. The flask was then removed from the oil bath and the solution stirred at room temperature for 20 min. Evaporation of the solvent followed by flash chromatography provided the bis(2-methylbut-2-enyl)phenylsilane **2** in 85% yield. The NMR data of **2**, in the 2-methylbuten-2-yl region, compare well with the respective data for **1** and also indicate the presence of a single isomer. Thus, contrary to the late transition metals such as Rh and Pd, which generally give a mixture of regioisomers when unsymmetric dienes are used (tail or head products),[6] the titanocene complex catalyzes the 1,4-hydrosilylation of two molecules of isoprene to afford exclusively the head products. Moreover, considering that the diallylsilanes formed (**1** and **2**) could *a priori* consist of three diastereoisomers ((*E*,*E*), (*E*,*Z*), or (*Z*,*Z*)), it appears that this reaction is extremely stereoselective.

The geometry of the diallylsilanes formed was elucidated using 1,3-butadiene and $PhSiH_3$ as substrates (Table 1, entry 2). The titanium precatalyst was first briefly activated with $PhSiH_3$ at 45 °C (0.5−1 min) in THF under a 1,3-butadiene atmosphere. The flask was then cooled at −4 °C and reloaded with 1,3-butadiene via a syringe. At this temperature, the reaction even proceeded and afforded after 5 h and usual workup the bis(but-2-enyl)phenylsilane **3** in 88% yield. The geometry of **3** was determined to be (*E*,*E*) on the basis of the

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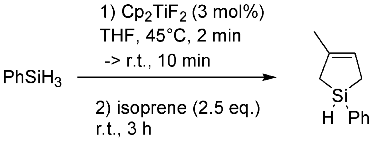
[10] Bareille, L.; Le Gendre, P.; Moïse, C. *Chem. Commun.* **2005**, 775.

[11] Harrod and Laine have reported that dimethyl titanocene catalyzes the partial redistribution of PMHS into $MeSiH_3$ and polymeric material $\{-[MeHSiO]_{0.3}[MeSi(O)_{1.5}]_{0.7}-\}$: Laine, R. M.; Rahn, J. A.; Youngdahl, K. A.; Babonneau, F.; Hoppe, M. L.; Zhang, Z. F.; Harrod, J. F. *Chem. Mater.* **1990**, *2*, 464.

**Scheme 3. $Cp_2TiF_2$-Catalyzed Dehydrogenative Silylation of Isoprene with $PhSiH_3$**

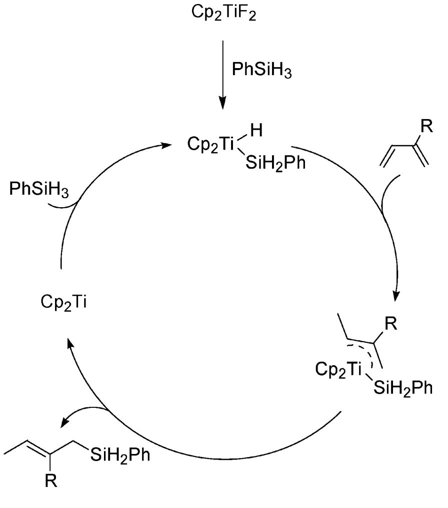


**10**, 72%

coupling constant between the olefinic protons observed in the $^1H$ NMR spectrum of the isolated product. Indeed, by irradiating the methyl protons (at $\delta = 1.66$ ppm), the signals of the olefinic protons of **3** became simpler and a large value of $^3J = 15$ Hz of the coupling constant could be attributed unambiguously. Thus the titanium-catalyzed 1,4-hydrosilation reaction was shown to be not only competitive with regard to those reported with palladium or rhodium complexes but also complementary since the latter give *Z*-allylsilanes as major products. As reported in Table 1, the highly head- and *E*-specific 1,4-hydrosilylation of isoprene could be applied to several silanes such as hexylsilane, diphenylsilane, and even triethoxysilane. The single hydrosilylation products were expectedly obtained in the last two cases. We also demonstrated the feasibility of this reaction with a more complicated diene such as myrcene. The reaction of 1,3-pentadiene with diphenylsilane led to the (*E*)-pent-2-enyldiphenylsilane **8** in 95% yield. Finally, attempts to extend this methodology to the hydrosilylation of "disubstituted butadienes" such as 2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, or 2,3-dimethyl-1,3-butadiene were unsuccessful.

Further investigations on this unique regio- and diastereoselective hydrosilylation using isoprene and $PhSiH_3$ were then attempted. A large temperature effect was first observed. Indeed, by just cooling the reaction mixture immediately after activation (45 °C to 0 °C), the reaction was considerably slowed and led after 3 h at room temperature to a mixture of (2-methylbut-2-enyl)phenylsilane **9** and bis(2-methylbut-2-enyl)phenylsilane **2** in 30 and 55% yields, respectively. Therefore it can be assumed that the monoallylsilane **9** is an intermediate in the formation of the diallylsilane **2**. Then, it was found that the presence of isoprene in the reaction mixture during the activation period is also crucial. Indeed when $Cp_2TiF_2$ was first activated in a THF solution of $PhSiH_3$ (0.5−1 min at 45 °C) and then isoprene subsequently added, the monoallylsilane **9** was obtained together with the unexpected 1-phenyl-3-methyl-3-silacyclopentene **10** in 60 and 20% yields, respectively. By prolongating the activation period (i.e., 2 min at 45 °C, then 10 min at room temperature) before adding isoprene, the silacyclopentene **10** was obtained in 72% yield after 3 h without any trace of di- or monoallylsilane (Scheme 3). However, a careful study of the $^1H$ NMR spectrum of the crude product revealed that a partial oligomerization of $PhSiH_3$ is concomitant with this reaction.[12] Finally, the reaction of myrcene with $PhSiH_3$ in similar conditions led also to the silacyclopentene **11** (74% yield), whereas it could not be detected in the reaction of hexylsilane or PMHS with isoprene.

**Scheme 4. Postulated Mechanism of the $Cp_2TiF_2$-Catalyzed *anti*-1,4-Hydrosilylation of Dienes**



Thus using the same precatalyst species, either hydrosilylation or dehydrogenative double silylation[13] could be selectively obtained by simply activating the precatalyst in the presence of the diene or not. With regard to the mechanism of the hydrosilylation reaction, a proposed catalytic cycle is reported in Scheme 4.[14] This involves the formation of $Cp_2TiH(SiH_2Ph)$ generated from $Cp_2TiF_2/PhSiH_3$, followed by the formation of a $\pi$-allylic intermediate via a regiospecific hydrogen transfer to the diene (Chalk−Harrod).[15] It is reasonable to assume that the most sterically favorable isomer is the *E*-allyltitanium complex. Therefore, subsequent silicon−carbon bond formation gives the *E*-allylsilane and titanocene, which undergoes oxidative addition with $PhSiH_3$, thus regenerating $Cp_2TiH(SiH_2Ph)$ in the process. To support this mechanism, we synthesized the binuclear complex $[Cp_2Ti]_2(\mu\text{-}H)(\mu\text{-}HSiPhH)$, which is known to have a propensity to disproportionate to $Cp_2Ti^{II}$ and $Cp_2Ti^{IV}H(SiH_2Ph)$.[16] Then we carried out the reaction of $PhSiH_3$ with isoprene using either the binuclear complex $[Cp_2Ti]_2(\mu\text{-}H)(\mu\text{-}HSiPhH)$ (1.5 mol %) or $Cp_2Ti(PMe_3)_2$ (3 mol %) as precatalysts. In both cases we obtained a mixture of monoallylsilane **9** (78−80%) and diallylsilane **2** (8−10%) after 3 h at room temperature. Even though these two complexes were shown to be less active than $Cp_2TiF_2$, the reactions for the latter are conducted between 45 and 20 °C and this may account for the differences.

Considering now the dehydrogenative double silylation reaction, it can be assumed that $Cp_2TiH(SiH_2Ph)$

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[12] Harrod, J. F. In *Organometallic and Inorganic Polymers*; American Chemical Society: Washington, DC, 1988; pp 89−100. (b) Lunzer, F.; Marschner, C.; Landgraf, S. *J. Organomet. Chem.* **1998**, *568*, 253. (c) Wang, Q.; Corey, J. *Can. J. Chem.* **2000**, *78*, 1434.

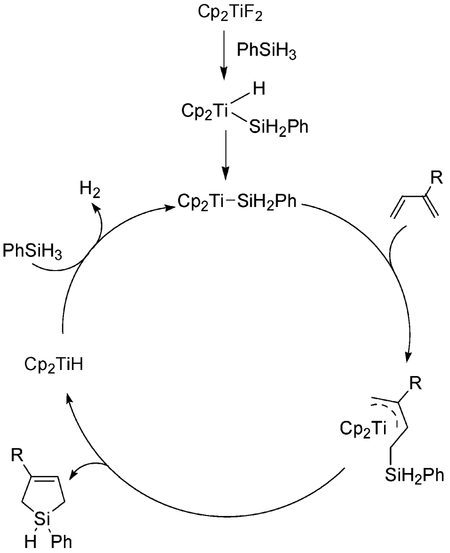
[13] (a) Tamao, K.; Miyake, N.; Kiso, Y.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5603. (b) Tanaka, M.; Uchimaru, Y.; Lautenschlager, H. J. *J. Organomet. Chem.* **1992**, *428*, 1. (c) Takaki, K.; Sonoda, K.; Kousaka, T.; Koshoji, G.; Shishido, T.; Takehira, K. *Tetrahedron Lett.* **2001**, *42*, 9211. (d) Takaki, K.; Komeyama, K.; Takehira, K. *Tetrahedron* **2003**, *59*, 10381.

[14] Another plausible pathway involving the addition of $Cp_2TiH$ to isoprene and the $\sigma$-bond metathesis of the resultant complex $[Ti(Cp)_2(\eta^3\text{-}1,2\text{-dimethylallyl})]$ with $PhSiH_3$ to form the allysilane has been also envisioned. Nevertheless, the fact that only traces of mono- or diallylsilane have been detected using isoprene and $PhSiH_3$ as substrates and $[Ti(Cp)_2(\eta^3\text{-}1,2\text{-dimethylallyl})]$ as catalyst excluded this possibility.

[15] Harrod, J. F.; Chalk, A. J. In *Organic Syntheses via Metal Carbonyls, Vol. 2*; Wiley: New York, 1977; pp 673−704.

[16] Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059.

**Scheme 5. Postulated Mechanism of the $Cp_2TiF_2$-Catalyzed Dehydrogenative Silylation of Dienes**



in the absence of diene is converted to $Cp_2Ti(SiH_2Ph)$ by reaction with an excess of silane (Scheme 5).[16] Olefin insertion ensues, providing a $\pi$-allyltitanium complex that undergoes an intramolecular $\sigma$-bond metathesis to release the silacyclopentene and $Cp_2TiH$. Finally $Cp_2Ti(SiH_2Ph)$ can be regenerated by the reaction of $Cp_2TiH$ with $PhSiH_3$ with hydrogen evolution. Also in support of this mechanism is the reaction of $PhSiH_3$ with isoprene using the binuclear titanium(III) silyl complex $[Cp_2Ti(SiH_2Ph)]_2$[16] as precatalyst, which afforded after 3 h at room temperature the silacyclopentene in 77% yield. Thus we have shown that the complexes $[Cp_2Ti]_2(\mu\text{-H})(\mu\text{-HSiPhH})$and $[Cp_2Ti(SiH_2Ph)]_2$ described by Harrod in the titanocene-catalyzed dehydrogenative coupling of primary silanes catalyze either the hydrosilylation or the dehydrogenative silylation of dienes. These results suggest that similar catalytically active species are formed from $Cp_2TiF_2$ under the reaction conditions.[17] Finally, we have shown that the presence of dienes in the reaction mixture prevents the polymerization of silanes.

## Conclusion

We have developed a novel catalytic hydrosilylation of dienes using the cheap and stable $Cp_2TiF_2$ complex as precatalyst. The reaction proceeds with an unprecedented regio- and diastereoselectivity to give *E*-allylsilanes in good to excellent yields. Pleasingly, by varying the activation protocol of the precatalyst, we have found that $Cp_2TiF_2$ can also promote the dehydrogenative double silylation of dienes.

## Experimental Section

**General Considerations.** All reactions were carried out under an atmosphere of purified argon using vacuum line techniques. Solvents were dried and distilled under argon from sodium and benzophenone before use. Elemental analyses were performed on a EA 1108 CHNS-O FISONS. $^1H$ and $^{13}C$ NMR spectra were recorded on Bruker 300 MHz Avance and Bruker 500 MHz Avance spectrometers. Chemical shifts are denoted in ppm ($\delta$) relative to TMS ($^1H$). Coupling constants are reported in Hz. Dienes were distilled under an argon atmosphere. Silanes were used without further purification. $Cp_2TiF_2$,[18] $Cp_2Ti(PMe_3)_2$,[19] $[Cp_2Ti]_2(\mu\text{-H})(\mu\text{-HSiPhH})$,[16] and $[Cp_2Ti(SiH_2Ph)]_2$[16] were prepared as reported in the literature. The NMR data collected for the silacyclopentene **10** are consistent with those reported in the literature.[13d]

**Synthesis of Methylbis(2-methylbut-2-enyl)silane, 1.** To a yellow, stirred solution of $Cp_2TiF_2$ (27 mg, 0.125 mmol) in dry THF (3 mL) was added PMHS (0.75 mL, 12.5 mmol). The resulting mixture was warmed to 60 °C until the color changed to dark blue. The solution was immediatly dipped into an ice cold water bath for 15 min. After this time isoprene (1 mL, 10 mmol) was slowly added. The reaction mixture was allowed to stir at room temperature for 1 h, during which time the color changed to purple. Then the solvent was removed by mild evaporation. The product was purified by column chromatography (pentane) and finally obtained as a colorless oil (0.2 g, 1.09 mmol). IR (neat): 2126 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 0.05 (d, $J = 3.6$ Hz, 3H), 1.51 (m, 4H), 1.55 (d, $J = 6.5$ Hz, 6H), 1.61 (s, 6H), 3,85 (m, 1H), 5,07 (q, $J = 6.5$ Hz, 2H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ −5.5, 14.0, 18.5, 26.4, 117.4, 133.2. Anal. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16. Found: C, 72.62; H, 12.65.

**General Procedure for the Catalytic Hydrosilylation (2−8).** To a stirred, yellow solution of $Cp_2TiF_2$ (13.5 mg, 0.0625 mmol) in dry THF (1.5 mL) was added diene (0.5 mmol), then silane (1.9 mmol). The mixture was warmed without stirring at 45 °C until the color changed from yellow to purple. The Schlenk tube was then immediately removed from the bath, and the mixture was stirred at room temperature. The reaction was monitored by TLC and GC. After consumption of the silane, the solvent was removed by evaporation and the product was purified by column chromatography (pentane).

**Bis(2-methylbut-2-enyl)phenylsilane, 2:** colorless oil, 0.4 g, 85% yield. IR (neat): 2122 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 1.47 (d, $J = 6.6$ Hz, 6H), 1.51 (s, 6H), 1.74 (m, 4H), 4.31 (quint, $J = 3.6$ Hz, 1H), 5.04 (q, $J = 6.6$ Hz, 2H), 7.26−7.28 (m, 3H, Ph), 7.44−7.46 (m, 2H, Ph). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 14.0, 18.3, 25.5, 118.3, 128.1, 129.7, 132.6, 135.1, 136.1. Anal. Calcd for $C_{16}H_{24}Si$: C, 78.61; H 9.90. Found: C, 78.80; H, 10.18.

**Bis(but-2-enyl)phenylsilane, 3:** colorless oil, 0.36 g, 88% yield. IR (neat): 2121 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 1.66 (dd, $J = 6.1$, 1.3 Hz, 6H), 1.80 (m, 4H), 4.27 (quint, $J = 3.2$ Hz, 1H), 5.37 (dqt, $J = 15.1$, 6.1, 0.9 Hz, 2H), 5.45 (dtq, $J = 15.1$ Hz, 7.6, 1.3 Hz, 2H), 7.38−7.40 (m, 3H), 7.54−7.56 (m, 2H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 17.8, 18.8, 125.5, 126.5, 128.4, 130.1, 135.4, 135.4. Anal. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32. Found: C, 78.42; H, 9.14.

**Hexylbis(2-methylbut-2-enyl)silane, 4:** colorless oil, 0.38 g, 81% yield. IR (neat): 2112 $cm^{-1}$. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 0.56−0.60 (m, 2H), 1.23−1.33 (m, 11H), 1.53−1.56 (m, 10H), 1.61 (s, 6H), 3.78 (m, 1H), 5.07 (q, $J = 6.6$ Hz, 1H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 11.9, 13.9, 14.5, 18.2, 22.3, 25.0, 31.9, 33.4, 34.5, 117.3, 133.3. Anal. Calcd for $C_{16}H_{32}Si$: C, 76.10; H, 12.77. Found: C, 75.30; H, 12.75.

**(2-Methylbut-2-enyl)diphenylsilane, 5:** colorless oil, 0.39 g, 81% yield. IR (neat): 2123 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 1.51 (d, $J = 6.7$ Hz, 3H), 1.58 (s, 3H), 2.08 (app s, 2H), 4.89 (m, 1H), 5.12 (q, $J = 6.7$ Hz, 1H), 7.26−7.39 (m, 6H), 7.54−7.56 (m, 4H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 14.2, 18.6, 26.1, 119.1, 128.4, 130.5, 132.2, 134.6, 135.7. Anal. Calcd for $C_{17}H_{20}Si$: C, 80.89; H, 7.99. Found: C, 80.45; H, 7.83.

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[17] The $^1H$ NMR spectrum of a TDF solution of $[Cp_2TiF_2]$ with $PhSiH_3$ (briefly heated at 45 °C until the color change from yellow to dark blue) revealed the presence of $\{[Cp_2Ti]_2(\mu\text{-H})(\mu\text{-HSiPhH})\}$ and $[Cp_2Ti(SiH_2Ph)]_2$.[12c]

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**(2-Methylbut-2-enyl)triethoxysilane, 6:** colorless oil, 0.13 g, 30% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.19 (t, $J$ = 7.0 Hz, 9H), 1.55 (d, $J$ = 6.7 Hz, 3H), 1.59 (s, 2H), 1.67 (s, 3H), 3.81 (q, $J$ = 7.0 Hz, 6H), 5.16 (q, $J$ = 6.7 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 13.9, 18.1, 18.6, 23.7, 58.7, 118.4, 131.3. Anal. Calcd for $C_{11}H_{24}SiO_3$: C, 56.85; H, 10.41. Found: C, 56.67; H, 10.07.

**Bis(2-ethylidene-6-methylhept-5-enyl)phenylsilane, 7:** colorless oil, 0.4 g, 56% yield. IR (neat): 2122 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.53 (d, $J$ = 6.7 Hz, 6H), 1.58 (s, 6H), 1.66 (s, 6H), 1.78 (m, 4H), 2.00 (m, 8H), 4.35 (quint, $J$ = 3.5 Hz, 1H), 5.06 (m, 2H), 5.07 (quint, $J$ = 6.7 Hz, 2H), 7.31−7.34 (m, 3H), 7.49−7.51 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 13.8, 18.0, 22.7, 26.1, 26.9, 32.1, 118.9, 124.7, 128.1, 129.6, 131.9, 135.1, 136.2, 136.7. Anal. Calcd for $C_{26}H_{40}Si$: C, 82.03; H, 10.59. Found: C, 82.06; H, 10.84.

**Pent-2-enyldiphenylsilane, 8:** colorless oil, 0.45 g, 95% yield. IR (neat): 2122 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 0.97 (t, $J$ = 7.4 Hz, 3H), 2.04 (app quint, $J$ = 7.4 Hz, 2H), 2.12−2.14 (m, 2H), 4.99 (m, 1H), 5.47 (dt, $J$ = 15.2, 6.3 Hz, 1H), 5.54 (dt, $J$ = 15.2, 7.4 Hz, 1H), 7.41−7.47 (m, 6H), 7.63−7.65 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 15.1, 18.8, 26.8, 124.4, 128.9, 130.5, 133.7, 134.9, 136.5. Anal. Calcd for $C_{17}H_{20}Si$: C, 80.89; H, 7.99. Found: C, 80.36; H, 8.01.

**Synthesis of (2-Methylbut-2-enyl)phenylsilane, 9.** To a stirred brown solution of Cp$_2$Ti(PMe$_3$)$_2$ (19 mg, 0.0625 mmol) in dry THF (1.5 mL) was added isoprene (0.5 mL, 0.34 g, 5 mmol), then PhSiH$_3$ (0.24 mL, 0.20 g, 1.9 mmol). The mixture was allowed to stir at room temperature for 3 h. After the removal of the volatiles under reduced pressure and chromatography (pentane), the product was finally obtained as a colorless oil (0.26 g, 80% yield). IR (neat): 2137 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.57 (d, $J$ = 7.5 Hz, 3H), 1.64 (s, 3H), 1.86 (m, 2H), 4.31 (m, 2H), 5.16 (q, $J$ = 7.5 Hz, 1H), 7.26−7.37 (m, 3H, Ph), 7.56 (d, $J$ = 6.5 Hz, 2H, Ph). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 14.3, 18.3, 23.7, 119.0, 128.6, 130.3, 132.7, 133.36, 135.9. Anal. Calcd for $C_{11}H_{16}Si$: C, 74.93; H 9.15. Found: C, 75.20; H, 9.40.

**General Procedure for the Catalytic Dehydrogenative Silylation (10, 11).** To a yellow, stirred solution of Cp$_2$TiF$_2$ (13.5 mg, 0.0625 mmol) in dry THF (1.5 mL) was added a silane (1.9 mmol). The mixture was warmed, without stirring, at 45 °C until the color changed from yellow to dark blue and then stirred 1 min at this temperature. After 10 min stirring at room temperature, a diene (5 mmol) was added. The color changed slowly from dark blue to purple. The reaction was followed by TLC and GC. After consumption of the silane the solvent was removed by evaporation and the product was purified by column chromatography (pentane).

**1-Phenyl-3-methyl-3-silacyclopentene, 10:** colorless oil, 0.24 g, 72% yield. IR (neat): 2133 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.53−1.68 (m, 4 H), 1.84 (s, 3H), 4.75 (app quintd, $J$ = 3.1, 0.8 Hz, 1H), 5.61 (m, 1H), 7.36−7.38 (m, 3H), 7.58−7.60 ppm (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 16.7, 20.9, 23.0, 125.4, 128.6, 130.3, 135.1, 136.4, 141.0.

**1-Phenyl-3-(4-methylpent-3-enyl)-3-silacyclopentene, 11:** colorless oil, 0.34 g, 74% yield. IR (neat): 2131 cm$^{-1}$. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.61−1.89 (m, 4H), 1.72 (s, 3H), 1.80 (s, 3H), 2.27 (app s, 4H), 4.86 (quint, $J$ = 3.0 Hz), 5.22 (m, 1H), 5.75 (m, 1H), 7.41−7.48 (m, 3H), 7.65−7.69 (m, 2H). $^{13}$C NMR (75. MHz, CDCl$_3$): $\delta$ 16.2, 18.4, 18.8, 26.3, 26.9, 36.9, 124.7, 124.9, 128.5, 130.1, 132.1, 134.9, 136.7, 144.6. Anal. Calcd for $C_{16}H_{22}Si$: C 79.27, H 9.15. Found: C 79.01, H 9.43.

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**Supporting Information Available:** $^1$H NMR spectra of **3** with or without irradiation at the frequency of the methyl protons; the GC-MS and $^1$H and $^{13}$C NMR spectra of the allylsilane **5** obtained after evaporation of the solvent without any purification. This material is available free of charge via the Internet at http://pubs.acs.org.

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