

Homogeneous Catalysis

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Regioselective Hydrosilylation of Olefins Catalyzed by a Molecular Calcium Hydride Cation

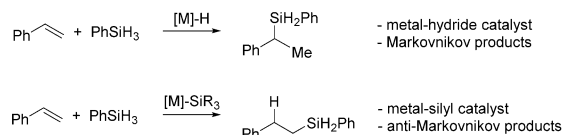
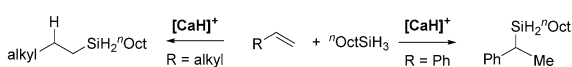
Danny Schuhknecht, Thomas P. Spaniol, Laurent Maron, and Jun Okuda*

Abstract: Chemo- and regioselectivity are often difficult to control during olefin hydrosilylation catalyzed by *d*- and *f*-block metal complexes. The cationic hydride of calcium $[\text{CaH}]^+$ stabilized by an NNNN macrocycle was found to catalyze the regioselective hydrosilylation of aliphatic olefins to give anti-Markovnikov products, while aryl-substituted olefins were hydrosilylated with Markovnikov regioselectivity. Ethylene was efficiently hydrosilylated by primary and secondary hydrosilanes to give di- and monoethylated silanes. Aliphatic hydrosilanes were preferred over other commonly employed hydrosilanes: Arylsilanes such as PhSiH_3 underwent scrambling reactions promoted by the nucleophilic hydride, while alkoxy- and siloxy-substituted hydrosilanes gave isolable alkoxy and siloxy calcium derivatives.

Hydrosilylation of olefins is of considerable importance, since organosilicon intermediates and fine chemicals can be synthesized by addition of a Si–H function to unsaturated C=C double bonds.^[1] This reaction is efficiently catalyzed by transition metal catalysts,^[2] in particular platinum complexes (Speier and Karstedt catalysts).^[3] In the context of current quests for inexpensive, innocuous, and earth-abundant alternatives, base metal catalysts containing Mn, Fe, Co, and Ni have been reported.^[2b,4] Systems based on rare earth metals^[5] were also introduced as hydrosilylation catalysts, but operate through the combination of hydrometalation and σ -bond metathesis steps instead of the sequence of oxidative addition/reductive elimination as commonly observed for late transition metal catalysts (Chalk–Harrod mechanism).^[6] Catalysts based on p-block elements also promote this reaction.^[7] Harder et al. reported on the use of Group 1 and Group 2 metal benzyl complexes for the hydrosilylation of styrene derivatives with arylsilanes (Scheme 1);^[8] the molecular calcium hydride $[(^{\text{DIPP}}\text{BDI})(\text{thf})\text{Ca}(\mu\text{-H})_2]$ ($^{\text{DIPP}}\text{BDI} = \text{CH}[\text{C}$

a) Previously reported hydrosilylation by s-block metal catalysts

M = Li, Na, K, Mg, Ca, Sr Hydrosilanes limited to aryl hydrosilanes

b) This work: Hydrosilylation of α -olefins and styrene derivatives with alkyl hydrosilanes

Scheme 1. a) Previous reports of s-block metal catalyzed hydrosilylation. b) Hydrosilylation catalyzed by calcium hydride cation $[\text{CaH}]^+$.

(Me)N-DIPP)₂, DIPP = 2,6-*i*Pr₂C₆H₃) was found to catalyze the hydrosilylation of 1,1-diphenylethylene (1,1-DPE) with phenylsilane.^[9] The triphenylsilyl complex $[\text{Ca}(\text{SiPh}_3)_2(\text{thf})_4]$ hydrosilylated styrene derivatives with anti-Markovnikov selectivity as did related alkali metal silanide and hydrosilicate complexes.^[10] Although simple $\text{Na}[\text{HBET}_3]$ was reported to hydrosilylate styrene derivatives with aryl hydrosilanes, no activity was observed when aliphatic olefins like 1-hexene or silanes such as Et_3SiH were used.^[11]

In contrast to olefin hydrogenation by molecular alkaline earth metal hydrides,^[13] hydrosilylation of unactivated alkenes using aliphatic silanes by s-block metal catalysts remains elusive.^[12] Herein we report on the hydrosilylation of ethylene, α -olefins, and styrene derivatives using a molecular calcium hydride cation $[\text{CaH}]^+$ stabilized by the macrocyclic polyamine ligand Me_4TACD (1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane).

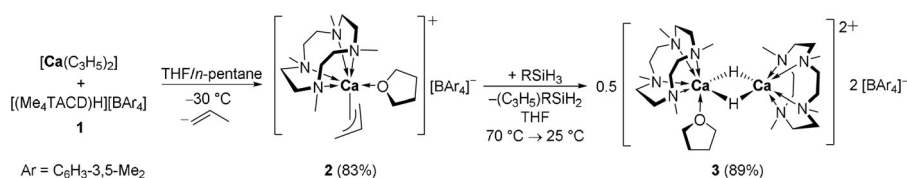
Recently we isolated cationic calcium hydrides by hydrogenolysis of benzyl complexes $[(\text{L})\text{Ca}(\eta^1\text{-CH}_2\text{Ph})_x(\text{thf})_{(2-x)}][\text{BAR}_4]_{(2-x)}$ ($\text{L} = \text{Me}_4\text{TACD}$; $x = 1, 2$; $\text{Ar} = \text{C}_6\text{H}_3\text{-}3,5\text{-Me}_2$), which were limited by their solubility, stability, and scalability.^[13a] When bis(allyl)calcium^[14] was treated with the conjugated Brønsted acid of the macrocyclic ligand $[\text{LH}][\text{BAR}_4]$ (**1**),^[15] the allyl calcium cation $[(\text{L})\text{Ca}(\eta^3\text{-C}_3\text{H}_5)(\text{thf})][\text{BAR}_4]$ (**2**) was obtained in high yield (Scheme 2 and Figure 1).^[16] Although **2** was inert towards H_2 even at 70 °C, the stoichiometric reaction with RSiH_3 ($\text{R} = \text{Ph}$, $n\text{Oct}$) in THF gave the dimeric calcium hydride cation $[(\text{L})_2\text{Ca}_2(\mu\text{-H})_2(\text{thf})][\text{BAR}_4]_2$ (**3**) alongside the corresponding allylsilane (C_3H_5) RSiH_2 after 5 min at 25 °C. A crystal structure analysis of **3** by X-ray diffraction revealed a nonsymmetrical dimer with one coordinated THF as observed for the Me_4TACD -stabilized hydride of divalent ytterbium.^[17] The ¹H NMR spectrum of **3** in $[\text{D}_8]\text{THF}$ shows a C_i -symmetric structure even at –80 °C, indicating fast reversibility of the THF

* D. Schuhknecht, Dr. T. P. Spaniol, Prof. Dr. J. Okuda
Institute of Inorganic Chemistry, RWTH Aachen University
Landoltweg 1, 52074 Aachen (Germany)
E-mail: jun.okuda@ac.rwth-aachen.de

Prof. Dr. L. Maron
CNRS, INSA, UPS, UMR 5215, LPCNO, Université de Toulouse
135 avenue de Rangueil, 31077 Toulouse (France)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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Scheme 2. Improved synthesis of the cationic calcium hydride **3** starting from the allyl calcium cation **2**.

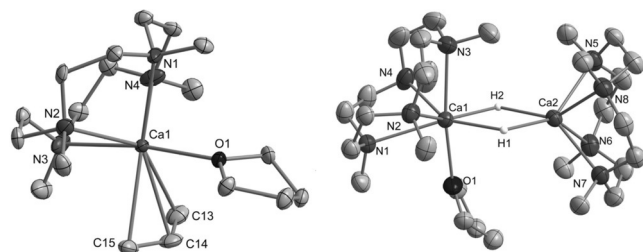


Figure 1. Structure of the molecular cations in **2** and **3**. Displacement parameters are shown at the 50% probability level. Anions, lattice solvents, and hydrogen atoms except for the hydrides are omitted for clarity.

coordination (see the Supporting Information). Calculations on the DFT level suggest exothermic THF coordination (ca. 33 kJ mol⁻¹, see the Supporting Information) to the solvent-free dimer,^[13a] in line with labile solvation of other molecular calcium hydrides.^[18]

The molecular cation in **3** was highly reactive toward hydrosilanes: Treating a solution of **3** with the commonly employed hydrosilylane PhSiH₃ led to broad resonances for the calcium- and silicon-bonded hydrides in the ¹H NMR spectrum. Cross peaks appeared in an EXSY NMR experiment (see the Supporting Information), indicating their exchange on the NMR timescale. After 30 min, signals for SiH₄ and Ph₂SiH₂ were observed as the result of reversible aryl exchange.^[19] Addition of D₂ (1 bar) lowered the intensity of the hydride resonances and signals of H₂ and HD appeared within 3 d. These exchange processes may be explained by reversible coordination of the metal hydride to the silicon center to form a hypervalent silicate.^[20] Although such a species was not observed by ¹H and ²⁹Si NMR spectroscopy even at -90 °C, NOESY signals indicate close proximity of the silicon hydrides to the methyl protons in the Me₄TACD ligand (see the Supporting Information). Transfer of a hydride from [CaH]⁺ to the hydrosilane to give a solvent-separated ion pair with [PhSiH₄]⁻ anion remains undetected but cannot be ruled out.^[8] An experiment performed with ¹⁸OOctSiH₃ under identical conditions did not show any formation of

¹⁸OOct₂SiH₂ or SiH₄ after 24 h; however, deuteration of ¹⁸OOctSiH₃ in the presence of **3** (10 mol %) to give ¹⁸OOctSiH_{3-x}D_x (x = 0–3) and HD/H₂ was observed after 7 d at 25 °C under 1 bar of D₂. When alkoxy hydrosilanes were used, irreversible hydride transfer from calcium to silicon occurred (Scheme 3). Reaction with

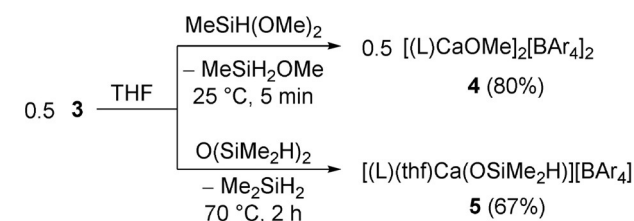
MeSiH(OMe)₂ gave the dimeric methoxy calcium complex **4**, which was independently synthesized from **3** and methanol. Commonly used O(SiMe₂H)₂ also underwent Si–O cleavage to selectively give the dimethylsiloxy complex **5** and Me₂SiH₂ within 2 h at 70 °C. Coordination of the silyl ether to the Lewis acidic calcium center, as recently observed for a cationic magnesium complex, might facilitate the ether cleavage.^[21]

To assess the suitability of different hydrosilanes, complex **3** was tested in the hydrosilylation of ethylene. At ambient conditions (25 °C, 1 bar ethylene), PhSiH₃ gave Et₂PhSiH within 6 h (Table 1, entry 1). Because of competing aryl exchange, ca. 5 % of Ph₂EtSiH and Et₃SiH were also formed at 70 °C (Table 1, entry 2). Higher selectivity was observed with electron-rich (*para*-R-C₆H₄)SiH₃ (Table 1, entry 3, R = MeO and **4**, R = Me₂N), while electron-deficient (*para*-F₃C-C₆H₄)SiH₃ showed immediate scrambling followed by decomposition of the catalyst (Table 1, entry 5). Alkyl-substituted primary hydrosilanes were selectively converted within 30–35 min (Table 1, entries 6–9). Monitoring the reaction by

Table 1: Hydrosilylation of ethylene by complex **3**.^[a]

Entry	Hydrosilane	Product ^[b]	<i>t</i> [min]	Conv. [%] ^[c]	TOF [h ⁻¹] ^[d]
1 ^[e]	PhSiH ₃	Et ₂ PhSiH	360	90	12
2	PhSiH ₃	Et ₂ PhSiH	30	90	144
3	(<i>para</i> -MeO-C ₆ H ₄)SiH ₃	Et ₂ (<i>para</i> -MeO-C ₆ H ₄)SiH	30	99	160
4	(<i>para</i> -Me ₂ N-C ₆ H ₄)SiH ₃	Et ₂ (<i>para</i> -Me ₂ N-C ₆ H ₄)SiH	30	99	160
5 ^[e]	(<i>para</i> -F ₃ C-C ₆ H ₄)SiH ₃	– ^[f]	30	0	0
6	ⁿ BuSiH ₃	Et ₂ ⁿ BuSiH	35	99	144
7	ⁿ HexSiH ₃	Et ₂ ⁿ HexSiH	30	99	160
8	ⁿ OctSiH ₃	Et ₂ ⁿ OctSiH	30	99	160
9	CySiH ₃	Et ₂ CySiH	30	90	144
10	Ph ₂ SiH ₂	EtPh ₂ SiH	15	90	144
11	PhMeSiH ₂	EtPhMeSiH	15	99	160
12	ⁿ OctMeSiH ₂	Et ⁿ OctMeSiH	15	99	160
13	CyMeSiH ₂	EtCyMeSiH	15	99	160
14	Et ₂ SiH	Et ₃ SiH	20	99	120
15	^t Bu ₂ SiH ₂	Et ^t Bu ₂ SiH	60	28	11
16	Me ₂ SiH ₂ / ^t Bu ₂ SiH ₂	–	60	0	0
17	Et ₃ SiH/ Me ₂ EtSiH	–	60	0	0

[a] 0.1 mmol of substrate in 0.6 mL of [D₈]THF, 1,4-(SiMe₃)₂C₆H₄ (25 μmol) as internal standard. [b] Characterized by NMR spectroscopy and GC-MS. [c] Determined by ¹H NMR spectroscopy. [d] Calculated based on the amount of ethylene consumed. [e] 25 °C. [f] Decomposition of catalyst.



Scheme 3. Reaction of calcium hydride **3** with alkoxy- and siloxy-substituted hydrosilanes.

NMR spectroscopy revealed full consumption of the primary hydrosilane prior to the second addition of ethylene. While the selectivity with Ph₂SiH₂ was lower due to scrambling (Table 1, entry 10), alkyl-substituted secondary silanes were fully converted within 15–20 min (Table 1, entries 11–14). Hydrosilylation of sterically more demanding ^tBu₂SiH₂ was incomplete after 60 min (Table 1, entry 15), while bulkier hydrosilanes Mes₂SiH₂ and ^tBu₂SiH₂ as well as tertiary hydrosilanes Et₃SiH and Me₂EtSiH did not react at all (Table 1, entries 16 and 17).

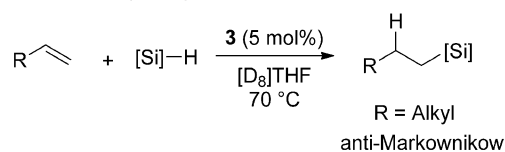
The Lewis acidity of the silicon center of the hydrosilane could promote the nucleophilic addition of the metal hydride to form a hypervalent silicate, but also facilitates the aryl exchange.^[19b] Alkyl groups that lower the Lewis acidity increase the chemoselectivity and are favored for hydrosilylation catalyzed by **3**. As the homologous magnesium hydride cation [MgH]⁺ did not show any reaction with PhSiH₃ under comparable conditions,^[22] the combination of the Lewis acidic metal center with the nucleophilicity of the hydride ligand appears crucial.

While monitoring the catalysis by ¹H NMR spectroscopy, we observed no calcium ethyl species. Only after the hydrosilane was fully consumed or when hydride **3** was dissolved in [D₈]THF and pressurized with ethylene (1 bar), was formation of an ethyl calcium species detected by characteristic signals at δ –1.02 (q) and 1.26 (t) ppm for the methylene and methyl protons, respectively.^[24] After 10 min at 25 °C, higher *n*-alkyl calcium species were also evident from their charac-

teristic resonances, indicating additional insertion of ethylene into the calcium–*n*-alkyl bond (see the Supporting Information). While oligomerization of ethylene was not observed for solid [CaH₂]_∞^[23] and [(^DI^{PP}B^DI)Ca(μ-H)]₂,^[24] strontium hydride [(^DI^{Pe}P^BD^I)Sr(μ-H)]₂ (DI^{Pe}P = 2,6-(pent-3-yl)₂-phenyl) formed oligoethylene at room temperature.^[20a] Unlike the BDI-stabilized ethyl complexes, the highly reactive cationic *n*-alkyl calcium derivative of **3** could not be isolated as it readily decomposed in THF solution (*t*_{1/2} < 10 min at 25 °C, 20 min at –20 °C) to give short alkanes (C₂–C₆) and other undefined species. Only fully protonated alkanes were detected when the reaction was carried out in [D₈]THF, indicating that the reaction with the ligand backbone as in related lanthanide complexes^[25] is favored over solvent deprotonation.

Higher α-olefins such as 1-octene and 1-hexene were hydrosilylated at 70 °C to give the anti-Markovnikov products with high regioselectivity. Depending on the stoichiometry and the hydrosilane, secondary (Table 2, entries 1 and 2) or tertiary (Table 2, entries 3 and 4) silanes formed, while no reaction occurred with the tertiary products or Et₃SiH (Table 2, entry 5). The silanes could be readily isolated after the catalyst **3** was precipitated with *n*-pentane and filtered off (see the Supporting Information). Hydrosilylation of 1,4-hexadiene only gave the 4-alkenylsilane, and as for 2-hexene, no reaction of the internal double bond was detected even after prolonged reaction time or with an excess of hydrosilane (Table 2, entries 6 and 7). Likewise, the internal double bond

Table 2: Regioselective hydrosilylation of aliphatic olefins by complex **3**.^[a]



Entry	Olefin	Hydrosilane	Product ^[b]	<i>t</i> [h]	Conv. [%] ^[c]	TOF [h ^{–1}]
1	ⁿ Bu-CH=CH ₂	Et ₂ SiH ₂	Et ₂ ⁿ HexSiH	24	96	0.8
2		ⁿ OctSiH ₃	ⁿ Oct ₂ SiH ₂	24	95	0.8
3 ^[d]		ⁿ OctSiH ₃	ⁿ Oct ₃ SiH	24	87	0.7
4	ⁿ Hex-CH=CH ₂	Et ₂ SiH ₂	Et ₂ ⁿ OctSiH	24	95	0.8
5		Et ₃ SiH	–	24	0	0
6		Et ₂ SiH ₂		24	95	0.8
7		ⁿ OctSiH ₃	–	24	0	0
8		ⁿ OctSiH ₃		24	70	0.6
9		ⁿ OctSiH ₃	–	24	0	0
10		ⁿ OctSiH ₃	–	24	0	0
11		ⁿ OctSiH ₃	–	24	0	0
12		ⁿ OctSiH ₃	– ^[e]	0.1	0	0

[a] Substrate (0.1 mmol) in [D₈]THF (0.6 mL), 1,4-(SiMe₃)₂C₆H₄ (25 μmol) as internal standard. [b] Characterized by NMR spectroscopy and GC-MS. [c] Determined by ¹H NMR spectroscopy. [d] 0.5 equiv of silane [e] Formation of methoxide complex **4** and propene.

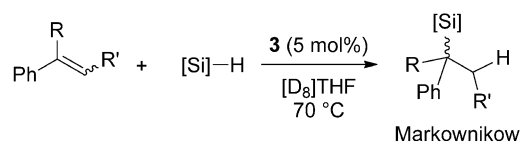
in 4-vinylcyclohexene, cyclohexene, and norbornene, as well as the 1,1-disubstituted double bond in 2-ethyl-1-butene (Table 2, entries 8–11) were not hydrosilylated. Allyl methyl ether was not hydrosilylated as the nucleophilic hydride was readily converted into the methoxy complex **4** under formation of propene (Table 2, entry 12).

Styrene and PhSiH₃ reacted with moderate selectivity to give the Markovnikov-silylated product, while by-products included unreacted Ph₂SiH₂ and the dibenzylsilane (PhCHMe)₂SiH₂, which were formed from SiH₄ through competing silane scrambling (Table 3, entry 1). Electron-rich (*para*-MeO-C₆H₄)SiH₃ gave a similar product mixture with higher selectivity for the expected monoalkylated arylsilane (Table 3, entry 2). Slower, but highly selective conversion was observed for ⁿOctSiH₃, as no silane scrambling was evident after 90 min (Table 3, entry 3). In contrast to the hydrosilylation of α -alkenes, no hydrosilylation was detected with the secondary silane Et₂SiH₂, and only oligostyrene was obtained after 6 h (Table 3, entry 4). 1,1-DPE was selectively hydrosilylated with primary ⁿOctSiH₃ after 4 h at 70 °C (Table 3, entry 5), which is slower than hydrosilylation by

[(DMAT)₂Ca(thf)₂] (DMAT = α -Me₃Si-2-Me₂N-benzyl) using PhSiH₃ in benzene.^[8] While this calcium catalyst gave the anti-Markovnikov product when the reaction was carried out in THF, complex **3** gave the Markovnikov product exclusively. This indicates that the hydride-insertion mechanism is operative for **3** even in THF.^[8,10c] Again, the sterically demanding tertiary carbanion [Ph₂CMe]⁻ readily formed by insertion remained unreacted after 6 h in the presence of secondary Et₂SiH₂ (Table 3, entry 6), in line with a metal-centered σ -bond metathesis. α -Methylstyrene was also selectively hydrosilylated as were the internal double bonds in *E*- and *Z*-stilbene, but longer reaction times were required (Table 3, entries 7–9). Higher substituted 1-phenylcyclohexene as well as tri- and tetraphenylethylene did not show any conversion (Table 3, entries 10–12). Triphenyl(vinyl)silane gave a mixture of both regioisomers (Table 3, entries 13), formed through competing insertion to give either the sterically favored linear or the α -silicon-stabilized branched carbanion (Ph₃SiCHCH₃)⁻.^[11,26]

In conclusion, the cationic calcium hydride **3** catalyzed the hydrosilylation of ethylene and α -olefins with anti-Markov-

Table 3: Regioselective hydrosilylation of activated olefins by complex **3**.^[a]



Entry	Olefin	Hydrosilane	Product ^[b]	<i>t</i> [h]	Conv. [%] ^[c]	TOF [h ⁻¹]
1		PhSiH ₃	[Si]	0.5	60 ^[d]	24
2	Ph-CH=CH ₂	(<i>para</i> -MeO-C ₆ H ₄)SiH ₃	Ph-CH(Si)-CH ₃	0.5	81 ^[d]	32
3	Ph-CH=CH ₂	ⁿ OctSiH ₃	Ph-CH(Si ⁿ Oct)-CH ₃	1.5	99	13.3
4	Ph-CH=CH ₂	Et ₂ SiH ₂	oligostyrene	6	0	0
5	Ph-CH=C(Ph) ₂	ⁿ OctSiH ₃	Ph-CH(Si ⁿ OctH ₂)-C(Ph) ₂	4	99	5
6	Ph-CH=C(Ph) ₂	Et ₂ SiH ₂	–	6	0	0
7	Ph-CH=C(Ph)Me	ⁿ OctSiH ₃	Ph-CH(Si ⁿ OctH ₂)-C(Ph)Me	48	94	0.6
8	Ph-CH=CH-Ph	ⁿ OctSiH ₃	Ph-CH(Si ⁿ OctH ₂)-CH ₂ -Ph	22	99	0.9
9	Ph-CH=CH-Ph	ⁿ OctSiH ₃	Ph-CH(Si ⁿ OctH ₂)-CH(Ph)-Ph	22	99	0.9
10	Ph-1-cyclohexene	ⁿ OctSiH ₃	–	24	0	0
11	Ph-1,1-diphenylethylene	ⁿ OctSiH ₃	–	24	0	0
12	Ph-1,1,1-triphenylethylene	ⁿ OctSiH ₃	–	24	0	0
13	Ph ₃ Si-CH=CH ₂	ⁿ OctSiH ₃	Ph ₃ Si-CH(Si ⁿ OctH ₂)-CH ₃ / Ph ₃ Si-CH ₂ -CH ₂ -Si ⁿ OctH ₂	16	72/28	1.3

[a] Substrate (0.1 mmol) in [D₈]THF (0.6 mL) 1,4-(SiMe₃)₂C₆H₄ (25 μ mol) as internal standard. [b] Characterized by NMR spectroscopy and GC-MS. [c] Determined by ¹H NMR spectroscopy. [d] Ar₂SiH₂ and (MeCHPh)₂SiH₂ (diastereomers) as by-products.

nikov selectivity as well as styrene derivatives with Markovnikov selectivity. Selective catalysis was observed with (alkyl)hydrosilanes, whereas PhSiH_3 as well as alkoxy- and siloxy-substituted hydrosilanes underwent nucleophilic substitution of the hydride. Using $^n\text{OctSiH}_3$, the following order of reactivity for **3** was established: ethylene > styrene > 1-octene. All experimental evidence suggests that $[\text{CaH}]^+$ forms an alkyl calcium complex^[24] as the result of hydrometalation of olefin followed by σ -bond metathesis with the hydrosilane to give the hydrosilylated product and $[\text{CaH}]^+$.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkaline earth metals · calcium hydride · hydrosilylation · Lewis acids · regioselective catalysis

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