A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition

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Accepted Article

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201909585
Angew. Chem. 10.1002/ange.201909585

Link to VoR: http://dx.doi.org/10.1002/anie.201909585
http://dx.doi.org/10.1002/ange.201909585

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10.1002/anie.201909585

Regioselective Hydrosilylation of Olefins Catalyzed by a Molecular Calcium Hydride Cation

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Keywords: calcium hydride • hydrosilylation • alkaline earth metal • regioselective catalysis • Lewis acids

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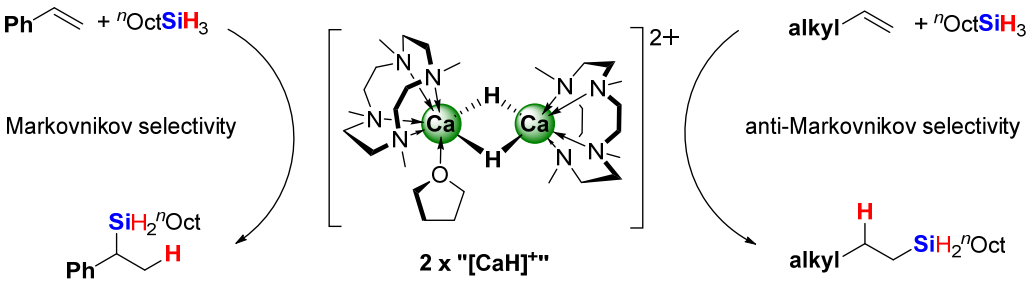

The calcium hydride cation $[CaH]^+$ catalyzes the regioselective hydrosilylation of ethylene, α-olefins and styrene derivatives. Aliphatic hydrosilanes are preferred over commonly employed silanes such as $PhSiH_3$ as the latter undergoes scrambling reactions.

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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 $[CaH]^+$ 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 hydrosilyated with Markovnikov regioselectivity. Ethylene was efficiently hydrosilylated by primary and secondary hydrosilanes to give di- and mono-ethylated 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 (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 2 metal benzyl complexes for the hydrosilylation of styrene derivatives with arylsilanes (Scheme 1);[8] the molecular calcium hydride $[(^{DIPP}BDI)(thf)Ca(\mu\text{-}H)]_2$ (^{DIPP}BDI = $CH[C(Me)N\text{-}DIPP]_2$, DIPP = 2,6-$^iPr_2C_6H_3$) was found to catalyze the hydrosilylation of 1,1-diphenylethylene (1,1-DPE) with phenylsilane.[9] The triphenylsilyl complex $[Ca(SiPh_3)_2(thf)_4]$ hydrosilylated styrene derivatives with anti-Markovnikov selectivity as did related alkali metal silanide and hydrosilicate complexes.[10] Although simple $Na[HBEt_3]$ 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]

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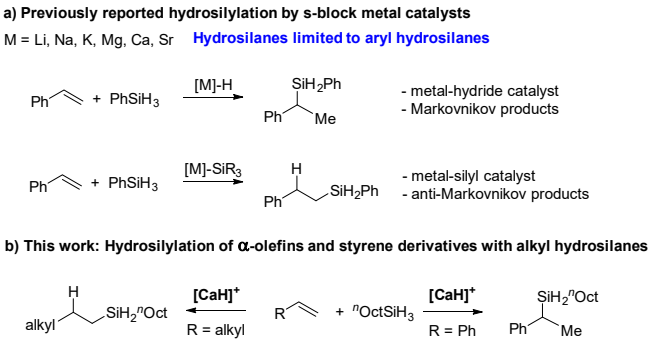
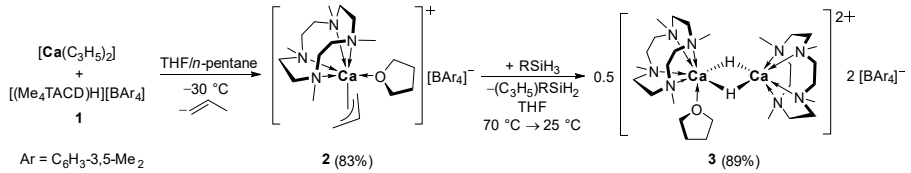


Scheme 1. a) Previous reports of s-block metal catalyzed hydrosilylation. b) Hydrosilylation catalyzed by calcium hydride cation $[CaH]^+$.

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 $[CaH]^+$ stabilized by the macrocyclic polyamine ligand Me_4TACD (1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane).



Scheme 2. Improved synthesis of the cationic calcium hydride **3** starting from the allyl calcium cation **2**.

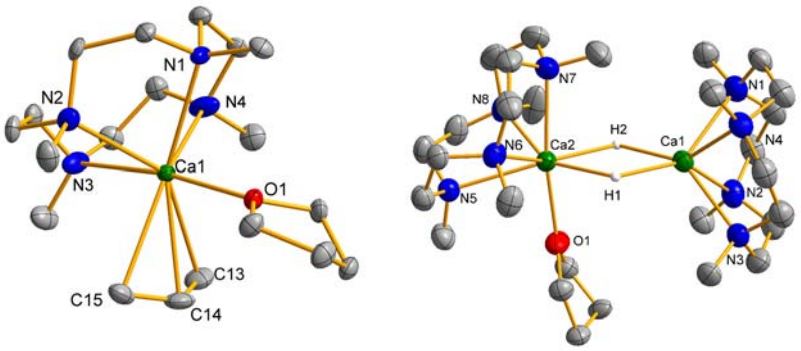


Figure 1. Structure of the molecular cations in **2** and **3**. Displacement parameters are shown at the 50% probability level. Anions, lattice solvents, and hydrogen atoms except for the hydrides are omitted for clarity.

Recently we isolated cationic calcium hydrides by hydrogenolysis of benzyl complexes $[(L)Ca(\eta^1\text{-}CH_2Ph)_x(thf)_{(2-x)}][BAr_4]_{(2-x)}$ (L = Me_4TACD; x = 1,2; Ar = C_6H_3-3,5-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 $[LH][BAr_4]$ (**1**),[15] the allyl calcium cation $[(L)Ca(\eta^3\text{-}C_3H_5)(thf)][BAr_4]$ (**2**) was obtained in high yield (Scheme 2).[16] Although **2** was inert towards H_2 even at 70 °C, the stoichiometric reaction with $RSiH_3$ (R = Ph, ^{n}Oct) in THF gave the dimeric calcium hydride cation $[(L)_2Ca_2(\mu\text{-}H)_2(thf)][BAr_4]_2$ (**3**) alongside the corresponding allylsilane $(C_3H_5)RSiH_2$ after 5 min at 25 °C. A crystal structure analysis of **3** by

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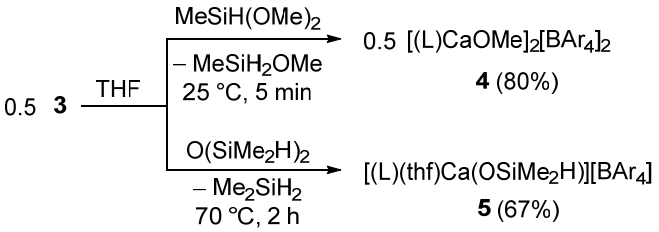
X-ray diffraction revealed a non-symmetrical dimer with one coordinated THF as observed for the Me_4TACD-stabilized hydride of divalent ytterbium.[17] The ^{1}H NMR spectrum of **3** in [D_8]THF shows a C_i symmetric structure even at –80 °C, indicating fast reversibility of the THF coordination (see SI). Calculations on the DFT level suggest exothermic THF coordination (ca. 33 kJ/mol, see SI) 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 hydrosilylation reagent $PhSiH_3$ led to broad resonances for the calcium- and silicon-bonded hydrides in the ^{1}H NMR spectrum. Cross peaks appeared in an EXSY NMR experiment (see SI), indicating their exchange on the NMR time scale. After 30 min, signals for SiH_4 and Ph_2SiH_2 were observed as the result of reversible aryl exchange.[19] Addition of D_2 (1 bar) lowered the intensity of the hydride resonances and signals of H_2 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 ^{1}H and ^{29}Si NMR spectra even at –90 °C, NOESY signals indicate close proximity of the silicon hydrides to the methyl protons in the Me_4TACD ligand (see SI). Transfer of a hydride from $[CaH]^+$ to the hydrosilane to give a solvent-separated ion pair with $[PhSiH_4]^-$ anion remains undetected but cannot be ruled out.[8] An experiment performed with ^{n}OctSiH$_3$ under identical conditions did not show any formation of ^{n}Oct$_2$SiH$_2$ or SiH_4 after 24 h; however, deuterolysis of ^{n}OctSiH$_3$ in the presence of **3** (10 mol%) to give ^{n}OctSiH$_{3-x}$D$_x$ (x = 0–3) and HD/H_2 was observed after 7 d at 25 °C under 1 bar of D_2. 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 $O(SiMe_2H)_2$ also underwent Si-O cleavage to selectively give the dimethylsiloxy complex **5** and Me_2SiH_2 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]



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

To assess the suitability of different hydrosilanes, complex **3** was tested in the hydrosilylation of the parent olefin ethylene. At ambient conditions (25 °C, 1 bar ethylene), $PhSiH_3$ gave Et_2PhSiH within 6 h (Table 1, entry 1). Because of competing aryl exchange, ca. 5% of Ph_2EtSiH and Et_3SiH were also formed at 70 °C (Table 1, entry 2). Higher selectivity was

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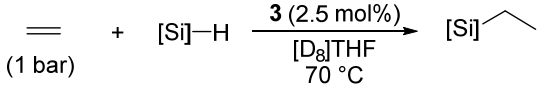
observed with electron-rich (*para*-R-C_6H_4)SiH_3 (Table 1, entry 3, R = MeO and 4, R = Me_2N), while electron-deficient (*para*-CF_3-C_6H_4)SiH_3 showed immediate scrambling followed by decomposition of the catalyst (Table 1, entry 5). Alkyl-substituted primary hydrosilanes were selectively converted within 30–35 min (Table 1, entries 6–9). Monitoring the reaction by NMR spectroscopy revealed full consumption of the primary hydrosilane prior to the second addition of ethylene. While the selectivity with Ph_2SiH_2 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 $^{i}Bu_2SiH_2$ was incomplete after 60 min (Table 1, entry 15), while bulkier hydrosilanes Mes_2SiH_2 and $^{t}Bu_2SiH_2$ as well as tertiary hydrosilanes Et_3SiH and Me_2EtSiH did not react at all (Table 1, entries 16 and 17).

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



Entry	Silane	Product[b]	*t* [min]	Conv. [%][c]	TOF [h^{-1}][d]
1[e]	$PhSiH_3$	Et_2PhSiH	360	90	12
2	$PhSiH_3$	Et_2PhSiH	30	90	144
3	(*para*-MeO-C_6H_4)SiH_3	Et_2(*para*-MeO-C_6H_4)SiH	30	99	160
4	(*para*-Me_2N-C_6H_4)SiH_3	Et_2(*para*-Me_2N-C_6H_4)SiH	30	99	160
5[e]	(*para*-CF_3-C_6H_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_2CySiH	30	90	144
10	Ph_2SiH_2	$EtPh_2SiH$	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_2SiH	Et_3SiH	20	99	120
15	$^{i}Bu_2SiH_2$	$Et{}^{i}Bu_2SiH$	60	28	11
16	Mes_2SiH_2 / $^{t}Bu_2SiH_2$	–	60	0	0

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17	Et_3SiH / Me_2EtSiH	–	60	0	0	

a) 0.1 mmol of substrate in 0.6 mL of [D_8]THF, 25 μmol 1,4-($SiMe_3$)$_2C_6H_4$. b) Characterized by NMR spectroscopy and GC MS. c) Determined by ^{1}H NMR spectroscopy. d) Calculated based on the amount of ethylene consumed. e) 25 °C. f) Decomposition of catalyst.

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 $PhSiH_3$ 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 ^{1}H NMR spectroscopy, no calcium ethyl species was observed. Only after the hydrosilane was fully consumed or when hydride **3** was dissolved in [D_8]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 characteristic resonances, indicating additional insertion of ethylene into the calcium-*n*-alkyl bond (see SI). While oligomerization of ethylene was not observed for solid $[CaH_2]_\infty$[23] and [(^{DIPP}BDI)Ca(μ-H)]$_2$,[24] strontium hydride [(^{DIPeP}BDI)Sr(μ-H)]$_2$ (DIPeP = 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 (C_2–C_6) and other undefined species. Only fully protonated alkanes were detected when the reaction was carried out in [D_8]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 3, entries 1 and 2) or tertiary (Table 3, entries 3 and 4) silanes formed, while no reaction occurred with the tertiary products or Et_3SiH (Table 3, entry 5). The silanes could be readily isolated after the catalyst **3** was precipitated with *n*-pentane and filtered off (see SI). Hydrosilylation of 1,4-hexadiene only gave 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 3, entries 6 and 7). Likewise, the internal double

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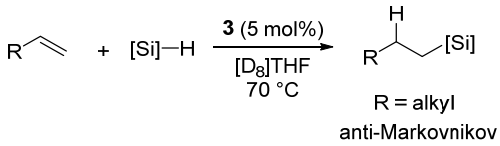
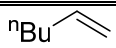
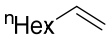
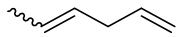
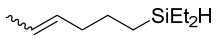
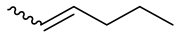
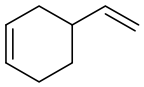
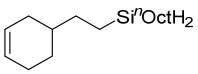
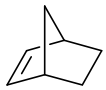
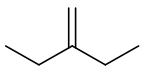
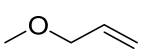
bond in 4-vinylcyclohexene, cyclohexene, norbornene, as well as the 1,1-disubstituted double bond in 2-ethyl-1-butene (Table 3, entries 8–11) were not hydrosilylated. Allyl ethers were not hydrosilylated as the nucleophilic hydride was readily converted into the methoxy complex **4** under formation of propene (Table 3, entry 12).

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



Entry	Olefin	Silane	Product[b]	*t* [h]	Conv. [%][c]	TOF [h^{-1}]
1		Et_2SiH_2	$Et_2{}^nHexSiH$	24	96	0.8
2		$^nOctSiH_3$	$^nOct_2SiH_2$	24	95	0.8
3[d]		$^nOctSiH_3$	$^nOct_3SiH$	24	87	0.7
4		Et_2SiH_2	$Et_2{}^nOctSiH$	24	95	0.8
5		Et_3SiH	–	24	0	0
6		Et_2SiH_2		24	95	0.8
7		$^nOctSiH_3$	–	24	0	0
8		$^nOctSiH_3$		24	70	0.6
9		$^nOctSiH_3$	–	24	0	0
10		$^nOctSiH_3$	–	24	0	0
11		$^nOctSiH_3$	–	24	0	0
12		$^nOctSiH_3$	–[e]	0.1	0	0

a) Substrate (0.1 mmol) in $[D_8]THF$ (0.6 mL), 1,4-$(SiMe_3)_2C_6H_4$ (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.

Styrene and $PhSiH_3$ reacted with moderate selectivity to the Markovnikov-silylated product, while by-products included unreacted Ph_2SiH_2 and the dibenzylsilane $(PhCHMe)_2SiH_2$, which were formed from SiH_4 through competing silane scrambling (Table 3, entry 1). Electron-rich

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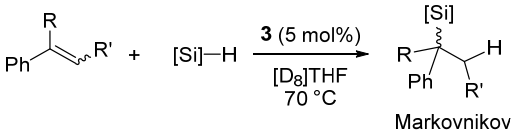
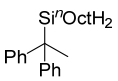
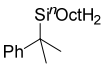
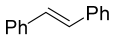
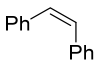
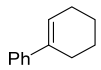
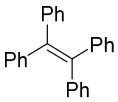
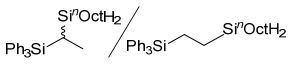
(*para*-MeO-C_6H_4)SiH_3 gave a similar product mixture with higher selectivity for the expected monoalkylated arylsilane (Table 3, entry 2). Slower, but highly selective conversion was observed for ^{n}OctSiH_3, as no silane scrambling was evident after 90 min (Table 3, entry 3). In contrast to the hydrosilylation of α-alkenes, no hydrosilylation using secondary Et_2SiH_2 was detected, giving only oligostyrene after 6 h (Table 3, entry 4). 1,1-DPE was selectively hydrosilylated with primary ^{n}OctSiH_3 after 4 h at 70 °C (Table 3, entry 5), slower than hydrosilylation by [(DMAT)$_2$Ca(thf)$_2$] (DMAT = α-Me_3Si-2-Me_2N-benzyl) using $PhSiH_3$ 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 $[Ph_2CMe]^-$ readily formed by insertion remained unreacted after 6 h in presence of secondary Et_2SiH_2 (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 $(Ph_3SiCHCH_3)^-$.[11, 26]

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



Entry	Olefin	Silane	Product[b]	*t* [h]	Conv. [%][c]	TOF [h^{-1}]
1		$PhSiH_3$		0.5	60[d]	24
2		(*para*-MeO-C_6H_4)SiH_3		0.5	81[d]	32
3		^{n}OctSiH_3		1.5	99	13.3
4		Et_2SiH_2	oligostyrene	6	0	0
5		^{n}OctSiH_3		4	99	5
6		Et_2SiH_2	–	6	0	0
7		^{n}OctSiH_3		48	94	0.6
8		^{n}OctSiH_3		22	99	0.9
9		^{n}OctSiH_3		22	99	0.9

10		^{n}OctSiH$_3$	–	24	0	0
11		^{n}OctSiH$_3$	–	24	0	0
12		^{n}OctSiH$_3$	–	24	0	0
13		^{n}OctSiH$_3$		16	72/28	1.3

a) Substrate (0.1 mmol) in [D$_8$]THF (0.6 mL) 1,4-(SiMe$_3$)$_2$C$_6$H$_4$ (25 µmol) as internal standard. b) Characterized by NMR spectroscopy and GC MS. c) Determined by ^{1}H NMR spectroscopy. d) Ar$_2$SiH$_2$ + (MeCHPh)$_2$SiH$_2$ (diastereomers) as by-products.

In conclusion, the cationic calcium hydride **3** catalyzed the hydrosilylation of ethylene and α-olefins with anti-Markovnikov 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}OctSiH$_3$, the following order of TOF for **3** was established: ethylene > styrene > 1-octene. All experimental evidence suggests that [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 [CaH]$^+$.

Notes

The authors declare no competing financial interest.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft through the International Research Training Group “Selectivity in Chemo- and Biocatalysis” (GRK 1628) for financial support, F. Ritter and M. Paul for assistance with X-ray crystallography, and Dr. G. Fink for NMR measurements.

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