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Silicon(II) Cation Cp*Si:$^+$ X$^-$: A New Class of Efficient Catalysts in Organosilicon Chemistry

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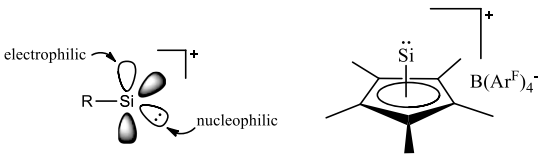
Supporting Information

ABSTRACT: The catalytic activity of the pentamethylcyclopentadienylsilicon(II) cation Cp*Si:$^+$ was investigated. It was shown that Cp*Si:$^+$ efficiently catalyzes reactions of technical relevance in organosilicon chemistry: Cp*Si:$^+$ proved to be a very efficient nonmetallic catalyst for the hydrosilylation of olefins at low catalyst amounts of <0.01 mol % and for the Piers−Rubinsztajn reaction in order to make controlled silicone topologies. The thermal induction of hydrosilylation which is important for the manufacturing of silicone rubber can be achieved by small amounts of alkoxysilanes.

KEYWORDS: *hydrosilylation, cationic silicon(II) compounds, homogeneous catalysis, Piers−Rubinsztajn reaction, polysiloxanes, copolymers*

INTRODUCTION

Silyliumylidene cations RSi:$^+$ (**1**, Figure 1) are of increasing interest in chemistry. Two vacant orbitals and a lone pair of electrons formally combine the characters of both strongly electrophilic silylium cations[1] R_3Si^+ and nucleophilic silylenes R_2Si:.[2]

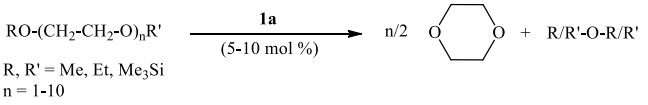


1 **1a**

Figure 1. Left: Electronic structure of silyliumylidene cations **1**; Right: structure of Jutzi's Cp*Si:$^+$ B(Ar^F)$_4^-$, with Ar^F = C_6F_5 and Cp* = pentamethylcyclopentadienyl (**1a**).

The reactivity of silylenes R_2Si: was investigated in detail in the past 20 years[2] and interesting reactivities and potential applications, for example, as ligands in transition metal catalysis,[3] have been found. The catalytic potential of silylenes, however, seems to be low due to their pronounced tendency to undergo irreversible addition and insertion reactions leading to tetravalent Si(IV) compounds.[4] Silylium cations R_3Si^+,[1] on the other hand, are very strong Lewis acids and some catalytic activities have been demonstrated in hydrodefluorinations[5] and Diels−Alder reactions,[6] and furthermore in Friedel−Crafts reactions.[7] Reactivity studies of silyliumylidene cations RSi:$^+$, however, are still at their very beginning. Several stable silyliumylidene cations[8−12] have been synthesized in the last 14 years by applying principles of thermodynamic and kinetic stabilization originally applied on silylenes.[12,13] Silyliumylidene cations bearing sterically demanding donor ligands for stabilization have, for instance, been synthesized by Driess,[8] Filippou,[9] So,[10] and Sasamori.[11] Until now, a catalytic activity of these compounds has not been found. Jutzi's Cp*Si:$^+$ B(Ar^F)$_4^-$ (**1a**, Ar^F = C_6F_5, Cp* = pentamethylcyclopentadienyl, Figure 1),[12,14] however, represents a unique cationic silyliumylidene structure because the cationic silicon center is only stabilized by a Cp* residue and therefore the positively charged silicon center has free coordination sites which was proved by crystal structure analysis.[14] Cp*Si:$^+$ is stable in combination with an inert non-nucleophilic anion, usually the perfluorinated tetraarylboranate anion, B(Ar^F)$_4^-$ (Ar^F = $C_6F_5^-$). The catalytic potential of this interesting cation is almost unknown, whereas irreversible reactions of Cp*Si:$^+$ with nucleophilic reagents have been reported.[12] It was found that the formation of cyclic ethers from oligoethyleneglycol ethers can be catalyzed by 5−10 mol % of **1a** in a slow reaction at room temperature (rt) (Scheme 1),[15] but to date this remains the only example of using a silyliumylidene cation as a catalyst.

Scheme 1. Formation of Cyclic Ethers Catalyzed by 1a[15]



RESULTS AND DISCUSSION

Synthesis of Cp*Si:$^+$ B(Ar^F)$_4^-$ (1a). **1a** was originally prepared from decamethylsilicocene[16,17] **2** in a comparatively complicated synthesis by a selective protonation reaction using the pentamethylcyclopentenyl cation **3a** at −78 °C (Scheme 2).[14] This strategy, however, affords the preparation of **3a** separately in a two-step procedure at low temperatures. Recently, Filippou and coworkers[17] reported that the selective protonation can be simplified using H$^+$(OEt$_2$)$_2$ B(Ar^F)$_4^-$ (**3b**, Scheme 2). **1a** was isolated in pure form by crystallization from fluorobenzene/pentane at −30 °C.

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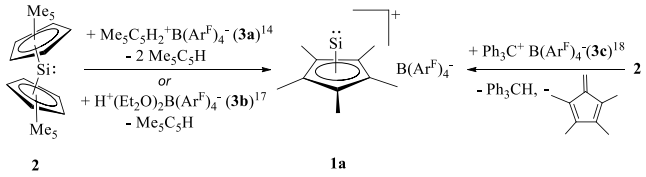
Scheme 2. Synthesis of 1a.[14,17,18]

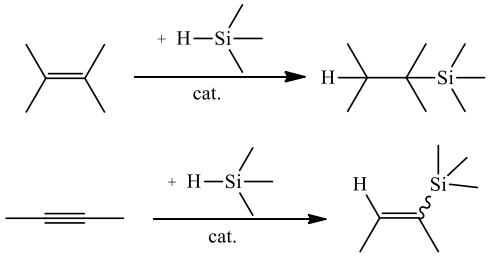


A novel synthetic strategy with hydride abstraction from the methyl group of one Cp* residue using the tritylium salt **3c**[18] at rt (Scheme 2) is even more attractive under technical aspects because **3c** is already produced in batches of more than 100 kg. The tetramethyl fulvene formed in the reaction can be removed by simple crystallization from dichloromethane/*n*-decane which gives the product **1a** in good yields of 89%. The improved availability under technical aspects makes **1a** an attractive candidate for catalysis in large-scale processes. Herein, we report about the catalytic potential of **1a** in technical organosilicon chemistry.

HYDROSILYLATION OF UNSATURATED CARBON−CARBON BONDS

Hydrosilylation of carbon−carbon double bonds and triple bonds[19] using silicon hydrides is an important approach to prepare organosilicon compounds (Scheme 3). The reaction is widely applied in the industry to produce various silanes and siloxanes.

Scheme 3. Hydrosilylation of Unsaturated Carbon−Carbon Bonds



The reaction requires catalysis, and noble metal complexes, for example, of platinum, are the most efficient catalysts.[19,20] In most cases, products according to the *anti*-Markovnikov rule are formed.[19] The high and volatile price of platinum, environmental issues associated with mining, and the persistence of platinum, however, have inspired the development of alternative catalysts.[21−24] Complexes of earth-abundant first-row transition metal complexes of iron, cobalt, nickel,[21−23] and manganese[24] have been developed. However, catalysts free of transition metals are the most attractive target. Tris(pentafluorophenyl)borane, $B(Ar^F)_3$, proved to be a highly active nonmetal catalyst for the hydrosilylation of carbon−carbon double bonds,[25−27] but catalyst amounts of 1−5 mol % are necessary to obtain full conversion due to deactivation processes of the catalyst during hydrosilylation.[28]

Here, we could demonstrate that $Cp^*Si:^+$ efficiently catalyzes the hydrosilylation of olefins (Table 1).[29]

Terminal olefins (Table 1, entries 1−19) give the *anti*-Markovnikov adducts. As can be seen from Table 1 full conversion can be achieved with as low as 0.0013 mol % of **1a**, which was demonstrated by the hydrosilylation of α-methylstyrene with pentamethyldisiloxane (Table 1, entry 3). This corresponds to a TON in the range of 80 000. In another experiment with 0.01 mol % of **1a,** we were able demonstrate that the product mixture still contains the active catalyst by repeated addition of a mixture of the starting materials which react to full conversion (see Experimental Section). Therefore, **1a** may be recovered and used in further hydrosilylation reactions. The stability and high activity make the catalyst **1a** especially interesting for technical applications.

As can be seen from Table 1, olefins with internal double bonds can also be hydrosilylated but are less reactive than terminal olefins and need higher reaction temperatures and more catalysts (Table 1, entries 20 and 21). The hydrosilylation of double bonds attached to silicon, however, proceeds slowly (Table 1, entry 22). In this case, a competing redistribution reaction of the Si bound H and the Si bound vinyl group was detected, and, as a consequence, a mixture of coupling products is formed, see Scheme 4.

The $Cp^*Si:^+$ catalyzed reaction between alkynes and hydrosilanes gives a mixture of hydrosilylation products and dehydrogenative silylation products (Scheme 5, eqs 1 and 2, Table 1, entries 23 and 24), and therefore is of limited practical use. Interestingly, Luo, Hou, and coworkers[30] found that $B(Ar^F)_3$ is completely inactive as a catalyst for the hydrosilylation of carbon−carbon triple bonds, but dehydrogenative silylation can be achieved by using large amounts of $B(Ar^F)_3$ (10 mol %) in a 1:1 mixture with DABCO.

Si bound alkynes can be hydrosilylated with **1a** as was shown for the reaction between trimethylsilyl acetylene and triethyl silane (Table 1, entry 25). Dehydrogenative silylation products were only observed in traces (1%). As in the case of Si vinyl groups, the addition reaction is accompanied by a redistribution process of Si H and Si alkyne (Scheme 5, eq 3).

It is assumed that the hydrosilylation catalyzed by **1a** follows a cationic mechanism similar to the mechanism suggested by Gevorgyan[25] and Oestreich[31] for $B(C_6F_5)_3$ as outlined in Scheme 6.

In analogy to Oestreich[31] and Piers[32] in the first step the silicon hydrogen bond is activated by $Cp^*Si:^+$ forming a hydrogen-bridged complex.

Evidence for Si−H activation is provided by the ^1H NMR spectrum of triethylsilane, Figure 2, where the Si−H signal shows coalescence after the addition of 0.10 mol % **1a**.

A cationic mechanism is in accordance with the fact that the electronically deficient methyl dichlorosilane does not react, whereas dimethyl chlorosilane still forms a hydrosilylation product (Table 1, entries 14 and 15).

The new hydrosilylation procedure requires chlorinated solvents such as dichloromethane or 1,2-dichloroethane to proceed at a high reaction rate. Hydrosilylations are much slower in benzene (entry 13) and under solvent-free conditions (entries 8 and 9). This can be attributed to a better ion pair separation in dipolar solvents.

Next, we studied the influence of different anions of $Cp^*Si:^+$ on the catalytic activity. The combinations of $Cp^*Si:^+$ with perfluorinated aluminates $Cp^*Si:^+$ $Al[OCH(CF_3)_2]_4^-$ (**1b**) and $Cp^*Si^+Al[OC(CF_3)_3]_4^-$ (**1c**) exhibited a very low catalytic activity (Table 1, entries 6 and 7) though they were soluble in the reaction mixture. Then, in order to improve ion pair separation even in a less polar reaction medium, we combined $Cp^*Si:^+$ with the more bulky and more lipophilic $B[C_6F_4\text{-}(4\text{-}SiMe_2t\text{-}Bu)]_4^-$ anion. $Cp^*Si:^+$ $B[C_6F_4\text{-}(4\text{-}SiMe_2t\text{-}Bu)]_4^-$ (**1d**) was more active under neat conditions (entries 8 and 9) thus principally verifying this concept.

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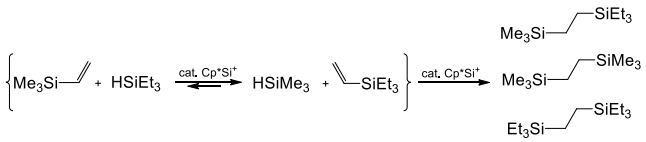
Table 1. Hydrosilylations of Alkenes and Alkynes Catalyzed by 1a to 1d

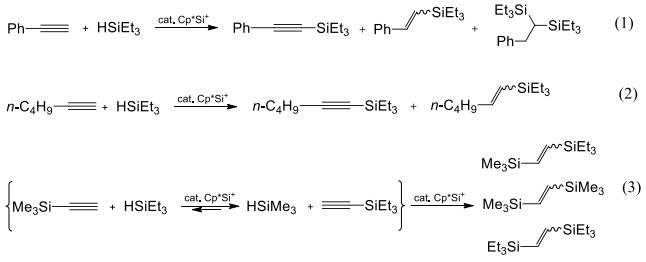
entry	alkene/alkyne	sil(ox)ane	catalyst (mol %)	solvent	T (°C)	t (h)/conversion (%)[a]	yield[b] (%, method)
1	α-methylstyrene	TMS[c]-O-$SiMe_2$-H	**1a** (0.012)	CD_2Cl_2	25	2/50, 25/100	>97 (NMR)
2	α-methylstyrene	TMS-O-$SiMe_2$-H	**1a** (0.012)	CD_2Cl_2	50	2/95	>97 (NMR)
3	α-methylstyrene	TMS-O-$SiMe_2$-H	**1a** (0.0013)	CD_2Cl_2	25	24/90, 48/98	>97 (NMR)
4	α-methylstyrene	TMS-O-$SiMe_2$-H	**1a** (0.012)	DCE[d]	80	0.16/100	>97 (NMR)
5	α-methylstyrene	TMS-O-$SiMe_2$-H	**1a** (0.004)	DCE	80	0.16/33, 1/100	>97 (NMR)
6	α-methylstyrene	TMS-O-$SiMe_2$-H	**1b** (0.50)	CD_2Cl_2	25	72/3	>97 (NMR)
7	α-methylstyrene	TMS-O-$SiMe_2$-H	**1c** (0.50)	CD_2Cl_2	25	72/14	>97 (NMR)
8	α-methylstyrene	TMS-O-$SiMe_2$-H	**1a** (0.012)	neat	25	2/4, 20/25, 120/32	>90 (NMR)[e]
9	α-methylstyrene	TMS-O-$SiMe_2$-H	**1d** (0.0096)	neat	25	2.5/18, 20/35, 72/51	>98 (NMR)[e]
10	α-methylstyrene	Et_3Si–H	**1a** (0.1)	CD_2Cl_2	50	28/100	>98 (NMR)
11	α-methylstyrene	$PhMe_2Si$–H	**1a** (0.06)	CD_2Cl_2	50	4/100	>98 (NMR)
12	α-methylstyrene	TMS-O-SiMeH-O-TMS	**1a** (0.20)	CD_2Cl_2	25	24/98	>98 (GC)
13	α-methylstyrene	TMS-O-SiMeH-O-TMS	**1a** (0.20)	benzene-d_6	25	5/2, 23/25	>90 (NMR)[e]
14	α-methylstyrene	Me_2ClSi-H	**1a** (0.10)	CD_2Cl_2	25	21/100	90 (GC)
15	α-methylstyrene	$MeCl_2Si$-H	**1a** (0.10)	CD_2Cl_2	25	48/0	0 (NMR)
16	n-C_4H_9–CH=CH_2	TMS-O-$SiMe_2$-H	**1a** (0.09)	CD_2Cl_2	25	0.8/100[f]	98 (NMR)
17	n-C_4H_9–CH=CH_2	TMS-O-SiMeH-O-TMS	**1a** (0.050)	CD_2Cl_2	25	24/100[g]	81 (GC)
18	n-C_4H_9–CH=CH_2	Me_2ClSi-H	**1a** (0.20)	CD_2Cl_2	50	6/100[g]	>90 (GC)
19	n-C_4H_9–CH=CH_2	$PhMe_2Si$-H	**1a** (0.10)	CD_2Cl_2	25	1.5/100[g]	94 (NMR)
20	*cyclo*-hexene	Et_3Si-H	**1a** (0.26)	CD_2Cl_2	50	4/100	96 (GC)
21	norbornene	Et_3Si-H	**1a** (0.20)	CD_2Cl_2	50	11/99	97 (GC)
22	Me_3Si–CH=CH_2	Et_3Si-H	**1a** (0.48)	CD_2Cl_2	50	50/30	50[h], 40[i], 20[k] (GC)
23	Ph–C≡CH	Et_3Si-H	**1a** (0.040)	CD_2Cl_2	25	18/70	34[l], 41[m], 20[n] (GC)
24	n-C_4H_9–C≡CH	Et_3Si-H	**1a** (0.10)	CD_2Cl_2	50	5/30	27[o], 37[p] (GC)
25	Me_3Si–C≡CH	Et_3Si-H	**1a** (0.10)	CD_2Cl_2	50	40/44	43[q], 30[r], 7[s] (GC)

[a]Determined by ^{1}H NMR. [b]*Anti*-Markovnikov product. [c]Trimethylsilyl. [d]1,2-Dichloroethane. [e]Referring to conversion. [f]4.5 equiv of n-C_4H_9–CH=CH_2 were used. [g]4.5 equiv of n-C_4H_9–CH=CH_2 were used, excess hexene was removed in vacuo for analysis. [h]Me_3Si–CH_2–CH_2–$SiEt_3$. [i]Me_3Si–CH_2–CH_2–$SiMe_3$. [k]Et_3Si–CH_2–CH_2–$SiEt_3$. [l]Ph–CH=CH–$SiEt_3$. [m]Ph–C≡C–$SiEt_3$. [n]Ph–CH_2–$CH(SiEt_3)_2$. [o]n-C_4H_9–CH=CH–$SiEt_3$. [p]n-C_4H_9–C≡C–$SiEt_3$. [q]Me_3Si–CH=CH–$SiEt_3$. [r]Me_3Si–CH=CH–$SiMe_3$. [s]Et_3Si–CH=CH–$SiEt_3$.

Scheme 4. Redistribution Reaction and Hydrosilylation of a Vinylsilane (see Table 1, Entry 22, for Product Distribution)



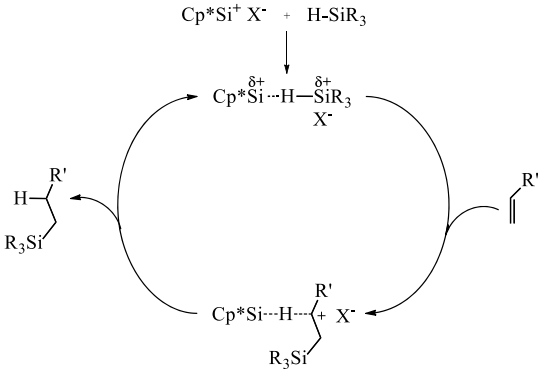
Scheme 5. Different Reactivity of Alkynes toward Triethylsilane (for Conditions and Product Distributions see Table 1)



Crosslinking of hydridosiloxanes and vinyl siloxanes (Scheme 7), which is the basis of the technical silicone elastomer syntheses, could be demonstrated using **1d** (0.27% w/w) at elevated temperatures, but it still needs some dichloromethane to proceed.

The new catalysts **1** are sensitive to air and moisture. After 19 h under open-air conditions at rt 44% of a 20 mg sample of crystalline **1a** had decomposed (^{1}H NMR measurement).

Scheme 6. Mechanism Suggested for the Hydrosilylation Catalyzed by 1a



Therefore, the preparation and handling of the catalysts **1** have to be performed in an inert Ar atmosphere. The crosslinking experiment, however, can be performed successfully under open-air conditions. It seems that in this case the catalyst is sufficiently protected by the silicone matrix.

Furthermore, we prepared a new compound Cp^*Si^+ $HB(C_6F_5)_3^-$ (**1e**) by reaction of decamethylsilicocene with $B(Ar^F)_3$.[33] Interestingly, **1e** is less active than **1a** as a catalyst in hydrosilylations by more than two orders of magnitude though it is much better soluble in the reaction medium than **1a**. This can be rationalized by a comparison of the crystal structures of **1a** and **1e**. The crystal structure of **1e** (Figure 3) revealed that the ion pair of **1e** is packed much more tightly than in **1a**.[14] The distance between the silicon center and the boron center

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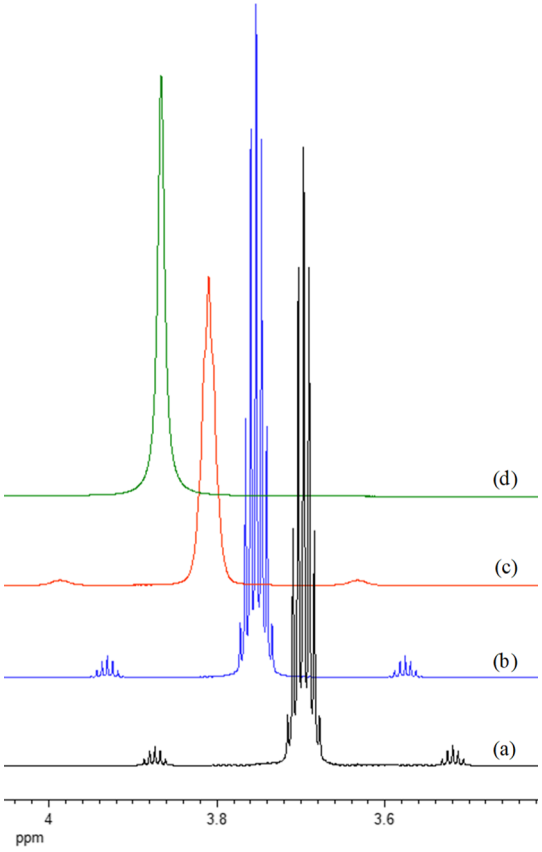
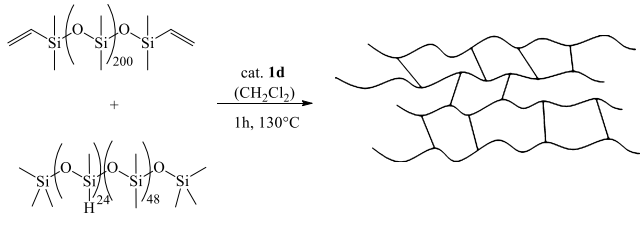


Figure 2. Time-dependent ^{1}H NMR spectrum of triethylsilane (32% w/w solution in CD_2Cl_2) with 0.10 mol % of **1a**, T = 25 °C, coalescence of the Si−H signal (a) 6, (b) 12, (c) 18, and (d) 24 h after the addition of **1a**. The chemical shift of the NMR signal remains constant.

Scheme 7. Schematic Metal-Free Elastomer Synthesis Using 1d as a Catalyst



is much smaller in **1e** (3.64 Å) than in **1a** (5.39 Å)[14] which suggests that the solvent-induced separation of the intimate ion pair of **1e** is even more difficult in dichloromethane because it is more densely packed than **1a**. The distance between the boron bound hydrogen and silicon is 2.79 Å, thus ruling out Si−H hydrogen bridging.

PIERS−RUBINSZTAJN (PR) REACTION

Piers[34] and Rubinsztajn[35] found that $B(Ar^F)_3$ catalyzes the reaction between silyl ethers and SiH to give siloxanes and the corresponding alkanes (Scheme 8). This process is called the PR reaction.[36]

Whereas the classical acid or base catalyzed condensation processes to make siloxanes are often accompanied by uncontrolled equilibration reactions, the PR reaction allows for the synthesis of well-defined siloxane architectures.

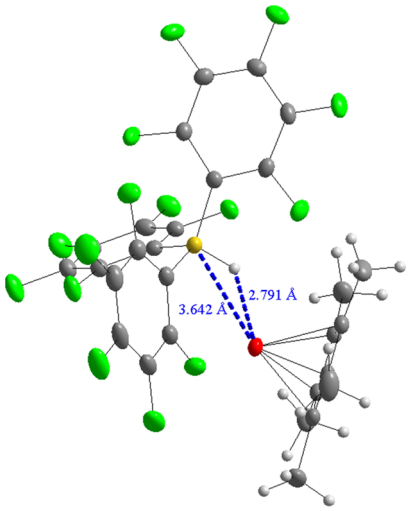
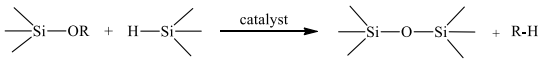


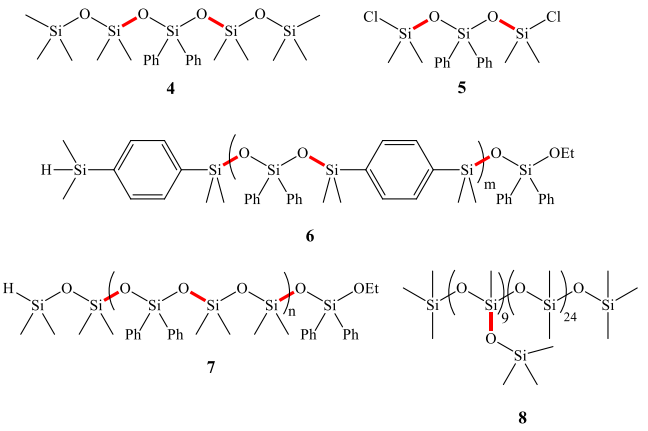
Figure 3. Diamond plot of the molecular structure of **1e** in a single crystal lattice at T = 123.00(10) K. Thermal ellipsoids are set to 30% probability.

Up to now, $B(Ar^F)_3$ is the only catalyst reported for the PR reaction which is mainly attributed both to its high electrophilicity and to its good solubility in a hydrophobic environment.[36] Now, we found that Cp*Si:$^+$ catalyzes the PR reaction very efficiently with ∼0.1 mol % in a minimum amount of solvent without significant catalyst deactivation.[37]

Scheme 8. Piers−Rubinsztajn (PR) Reaction



Scheme 9. Products of the PR reaction Catalyzed by 1e. Bonds Marked in Bold Red are Formed During the Reaction



Scheme 9 and Table 2 shows the products we obtained. First, to test the performance of the reaction, compound **4** was made on a preparative scale by reaction of diethoxydiphenylsilane with pentamethyldisiloxane and isolated in 86% yield (Table 2, entry 1). Chlorosubstituted siloxanes, for example, **5** (Table 2, entry 4) can efficiently be prepared and used as building blocks, for example, to prepare siloxane copolymers. It is reported[38] that chlorosiloxanes with a definite structure can

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Table 2. Piers–Rubinsztajn (PR) Reaction of Ethoxysilanes and Hydrido Sil(ox)anes Catalyzed by 1a, 1d, and 1e

entry	alkoxysilane	hydrido sil(ox)ane	catalyst (mol %[a])	CH_2Cl_2 (%[b])	T (°C)	t (h)/conversion (%)[c]	product (M_w, M_n, D[d])
1	$Ph_2Si(OEt)_2$	TMS[e]-O-$SiMe_2$-H[f]	**1e** (0.014)	5	60	4/>95[g]	**4**[h]
2	$Ph_2Si(OEt)_2$	TMS-O-$SiMe_2$-H[f]	**1a** (0.11)	5	55	4/0	
				40	55	2/>95	**4**
3	$Ph_2Si(OEt)_2$	TMS-O-$SiMe_2$-H[f]	**1d** (0.11)	5	55	4/0	
				40	55	2/>95	**4**
4	$Ph_2Si(OEt)_2$	Me_2ClSi-H[f]	**1e** (0.13)	5	60	2/>95[i]	**5**
5	$Ph_2Si(OEt)_2$	1,4-($SiMe_2H$)benzene	**1e** (0.11)	10	60	2/>95	**6** (18 600, 5040, 3.69)
6	$Ph_2Si(OEt)_2$	H-$SiMe_2$-O-$SiMe_2$-H[f]	**1e** (0.10)	10	60	2/>95	**7** (8100, 4300, 1.9)
7	Me_3SiOEt	TMS-O-D_9-D^H_{24}-TMS[j]	**1e** (0.033)	10	60	1/>95	**8**

[a]Based on the amount of Si–H. [b](w/w). [c]Residual Si–H was determined in the ^{1}H NMR spectrum. [d]Dispersity $D = M_w/M_n$. [e]Trimethylsilyl. [f]Si–H/Si–OEt = 1:1. [g]GC: 80 area % **4**, 10 area % 1-ethoxy-1,1-diphenyl-3,3,5,5,5-pentasiloxane). [h]Preparative example, see Experimental Section, yield 86%. [i]GC: 72 area % **5**, 10 area % 1-chloro-1,1-dimethyl-3-ethoxy-3,3-diphenyl-trisiloxane). [j]D = Me_2SiO, D^H = MeHSiO, statistical distribution of Si–H, Me_3SiOEt was used in 10% excess (Si–H/Si–OEt = 1:1.1).

also be prepared very selectively by stepwise reactions of silanols with dichlorosilanes. This transformation, however, affords a base to remove the HCl in order to prevent the self-condensation of silanols and therefore might be of limited technical use.

Most interesting on technical aspects, however, is to prepare siloxane copolymers directly by a combination of bifunctional alkoxysilanes with bifunctional hydrido sil(ox)anes (Table 2, compounds **6**,**7**, entries 5 and 6). Furthermore, it is possible to prepare branched silicones, for example, compound **8** (Table 2, entry 7).

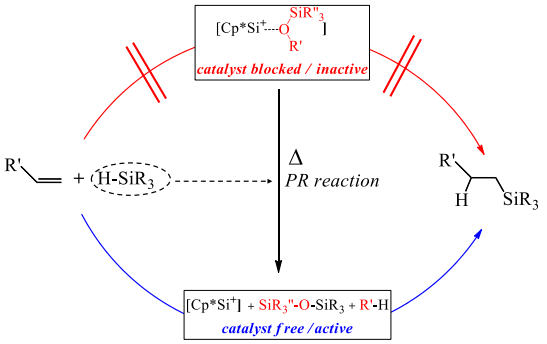
Interestingly, compound **1e** is highly active in the PR reaction, even with less than 10% of dichloromethane (Table 2, entry 1), whereas **1a** and **1d** showed no catalytic activity under these conditions, but the PR reaction took place with 40% dichloromethane solvent (Table 2, entries 2 and 3). This is quite different from the hydrosilylation reaction, where **1a** is by far more active than **1e**, which was attributed to an inefficient separation of the intimate ion pair in **1e**. We assume that the alkoxysilane coordinates at the cationic silicon center similar to the Cp*Si:$^+$ coordination of ethers reported by Jutzi,[15] and this coordination facilitates the separation of the intimate ion pair.

In a further experiment, we could show that small amounts of an alkoxysilane (e.g. ~2% w/w 1-ethoxy pentamethyldisiloxane or ethoxy trimethylsilane) completely suppress the hydrosilylation of α-methylstyrene at rt for more than a week. This is a further indication that the catalytically active cationic silicon center is masked by the alkoxysilane. Interestingly, inhibition by alkoxysilanes fails with the $B(C_6F_5)_3$ catalyst.

The use of reversible inhibitors is a well-established technology in the platinum-catalyzed silicone rubber manufacturing in order to guarantee a certain pot life of the hydrosilylation mixture, which means that the mixture of all components remains stable at ambient temperature. Curing can be performed on demand by an increase of temperature. For the platinum-catalyzed hydrosilylation, small amounts of alkynes are often used which block the hydrosilylation reaction by coordination to the metal center.[39]

In the Cp*Si:$^+$ catalyzed hydrosilylation, alkoxysilanes play the role of reversible inhibitors,[40] see Scheme 10. At ambient temperatures the PR reaction which consumes the alkoxysilane is very slow (see Experimental Section for details). At higher temperatures (>60 °C), however, the alkoxysilane is quickly consumed by the PR reaction because it has a pronounced

Scheme 10. Reversible Inhibition of the Hydrosilylation by Means of Alkoxysilanes



temperature dependence. The catalyst becomes active again and the hydrosilylation proceeds at a regular reaction rate.

CONCLUSIONS

New catalysts based on a cationic silicon(II) center, Cp*Si:$^+$, have been developed and their potential in technically relevant processes of organosilicon chemistry was demonstrated. Hydrosilylation still proceeds at catalyst amounts of 0.0013 mol % (TON ≈ 80 000) which is in the range of platinum catalysts. Separation of the catalysts' intimate ion pair is considered important for activity and can be enhanced by the introduction of lipophilic counter anions which allows for syntheses without polar solvents. Si bound vinyl groups are less reactive than C bound vinyl groups. Nevertheless, silicone elastomer curing was achieved by Cp*Si:$^+$ catalyzed hydrosilylation of vinyl substituted siloxanes. Furthermore, Cp*Si:$^+$ efficiently catalyzes the PR reaction between the Si–OR and Si–H groups and gives access to well-defined siloxane structures. Cp*Si:$^+$ is a good alternative to the well-known $B(Ar^F)_3$ catalyst as it shows no deactivation during the reaction. Finally, the Cp*Si:$^+$ catalyzed hydrosilylation can be reversibly blocked by low amounts of an alkoxysilane offering a way to temperature-induced hydrosilylation.

The present work gives insights into the reactivity of cationic silicon(II) compounds and their catalytic behavior and therefore may also pave the way towards further development.

EXPERIMENTAL SECTION

Analytical Methods. All ^{1}H NMR spectra were measured by using a Bruker AVANCE 500 spectrometer. GC: Agilent Technologies, HP 5 column (polydimethylsiloxane with 5%

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Table 3. Hydrosilylation of α-Methylstyrene with Pentamethyldisiloxane at 25 °C with 0.1 mol % 1a and 2.0 mol % of an Alkoxysilane as Inhibitor[a]

t (h)	ethoxy group	hydrosilylation product	1a Cp*
0.3	1.96	n.d.[b]	0.083
1	1.95	0.1	0.081
4	1.96	0.15	0.083
24	1.67	0.28	0.083
48	1.56	0.45	0.083
72	1.45	0.52	0.084
120	1.00	0.78	0.091
168	0.04	1.13	0.071
192	n.d.[b]	1.27	0.071
216	n.d.	95	0.082
240	n.d.	100	0.067

	ethoxy groups			
t (h)	EtO-TMS	EtO-PDMS[c]	hydrosilylation product	1a Cp*
0.3	1.48	0.16	0.11	0.085
1	1.44	0.21	0.10	0.078
4	1.35	0.33	0.17	0.080
24	0.83	0.60	0.40	0.077
48	0.50	0.93	0.79	0.081
72	n.d.	0.30	1.04	0.081
120	n.d.	0.11	1.70	0.075
168	n.d.	n.d.	2.10	0.080
192	n.d.	n.d.	93	0.088
216	n.d.	n.d.	98	0.090

[a]Figures are given in mol %; top: ethoxy pentamethyldisiloxane was used as the inhibitor, bottom: ethoxy trimethylsilane was used as the inhibitor. [b]Not detected. [c]Because of SiH/SiOEt exchange reaction.

phenyl groups); length, 30 m; internal diameter, 0.25 mm; film thickness, 0.25 μm; injector temp., 290 °C; detector FID, 320 °C; carrier gas, He. GC–MS: Agilent Technologies; GC unit, 6890N; column, Agilent HP-5MS UI; injector temperature, 250 °C; MS unit, 5975C; EI, 70 eV. Relative molecular masses of silicone copolymers were measured by GPC using an Agilent MesoPore and OligoPore column; length, 300 mm; internal diameter, 7.5 mm; particle size, 3 and 6 μm respectively, at 35 °C; eluent, toluene; RI Detektor; PDMS calibration.

Materials. $(C_6H_5)_3C^+B(Ar^F)_4^-$ (**3c**) and $B(Ar^F)_3$ were commercially available and were used without further purification. $(C_6H_5)_3C^+Al[OCH(CF_3)_2]_4^-$ and $(C_6H_5)_3C^+Al[OC(CF_3)_3]_4^-$[41] were provided by Prof. Dr. I. Krossing, University of Freiburg/Germany. Decamethylsilicocene (**2**) was synthesized according to the literature.[17] $(C_6H_5)_3C^+B[C_6F_4–SiMe_2t\text{-}Bu]_4^-$ was synthesized according to the literature.[42]

Synthesis of 1a–d. A solution of 0.336 mmol of the tritylium salt in 3.5 mL of dichloromethane was mixed with a solution of 102 mg (0.342 mmol) of decamethylsilicocene (**2**) in 3.5 mL of dichloromethane at rt in an argon atmosphere. *n*-Decane was added dropwise to the homogeneous solution until the product precipitates as a solid. The mother liquor was decanted off and the solid was washed 3 times with *n*-hexane and dried in vacuo. **1a**: Yield 89%, off-white crystalline solid. ^{1}H NMR δ (CD_2Cl_2): 2.24 (s, Cp*). ^{29}Si NMR δ (CD_2Cl_2): −398.8. ^{19}F NMR δ (CD_2Cl_2): −167.5 (mc, 8F, 3,5-F), −163.6 (mc, 4F, 4-F), −133.0 (mc, 8F, 2,6-F). **1b:** Yield 62%. ^{1}H NMR δ (CD_2Cl_2): 2.25 (s, 15H, Cp*), 4.52 [mc, 4H, −$CH(CF_3)_2$]. ^{19}F NMR δ (CD_2Cl_2): −77.2 (s, CF_3). ^{29}Si NMR δ (CD_2Cl_2): −399.3. **1c:** Yield 76%, ^{1}H NMR δ (CD_2Cl_2): 2.26 (s, Cp*). ^{19}F NMR δ (CD_2Cl_2): −75.7 (s, CF_3). ^{29}Si NMR δ (CD_2Cl_2): −398.9. **1d**: Yield 92%. ^{1}H NMR δ (CD_2Cl_2): 0.35 (s, 24H, 4 $SiMe_2$), 0.91 (s, 36H, 4-*tert*-butyl), 2.18 (s, 15H, Cp*). ^{19}F NMR δ (CD_2Cl_2): −132.3 (mc, 8F), −130.6 (mc, 8F). ^{29}Si NMR δ (CD_2Cl_2): −398.9 (s, Cp*Si), 5.58 [s, Si(Me_2*tert*-butyl)].

Synthesis of 1e. A solution of $B(Ar^F)_3$ (172 mg, 335 mmol) in 1 mL of dichloromethane was added dropwise to a solution of 100 mg (335 mmol) of decamethylsilicocene in 1 mL of dichloromethane at rt in an argon atmosphere. The color of the solution turned dark orange indicating the formation of tetramethylfulvene. *n*-Decane was added, the precipitate was washed twice with *n*-decane and dried in vacuo. Yield: 155 mg (64%), colorless solid. ^{1}H NMR δ (CD_2Cl_2): 2.10 (s, 15H, Cp*), 3.48 [q, broad, 1H, H–$B(C_6F_5)_3^-$]. ^{19}F NMR δ (CD_2Cl_2): −167.3 (mc, 8F, 3,5-F), −163.6 (mc, 4F, 4-F), −133.7 (mc, 8F, 2,6-F). ^{29}Si NMR δ (CD_2Cl_2): −399.9.

Hydrosilylation of α-Methylstyrene with Pentamethyldisiloxane in CD_2Cl_2—Standard Procedure. Under an argon atmosphere, a solution of **1a** (16.9 mg, 2.00 μmol) in 1.76 g of dichloromethane was prepared. A mixture of α-methylstyrene (2.37 g, 20.0 mmol) and pentamethyldisiloxane (2.97 g, 20.0 mmol) in 1.77 g of dichloromethane was added at 20 °C. The colorless solution was stirred at rt overnight. ^{1}H NMR (CD_2Cl_2) indicated a complete conversion into Ph–$CH(CH_3)$–CH_2–$SiMe_2O$–$SiMe_3$.[22] ^{1}H NMR δ (CD_2Cl_2): 0.00 (2s, 2 CH_3), 0.12 (s, TMS), 1.01 (mc, CH_2), 1.33 (d, J = 7 Hz, CH_3), 2.98 (mc, CH), 7.15–7.34 (5 aromat. H); ^{29}Si NMR δ (CD_2Cl_2): 6.58 (s), 7.32 (s). GC–MS *m/z*: 266 (5, M^+), 251 (19, $M^+ - CH_3$), 209 (12), 147 [100, $(Me_2SiOTMS)^+$], 133 (45, Ph–$C_4H_7^+$), 105 (13, $C_8H_9^+$).

Repeated Addition of Educts. A further mixture of α-methylstyrene (2.37 g, 20.0 mmol) and pentamethyldisiloxane (2.97 g, 20.0 mmol) in 1.77 g of dichloromethane was then added to the product mixture at 20 °C. After 1 h, the hydrosilylation reaction was complete (^{1}H NMR) indicating that the catalyst was still active in the product mixture. The same procedure was repeated twice; for each repetition complete conversion was reached after 1 h. The catalyst was deactivated by the addition of pyridine (∼20 mg of a ∼10% solution in dichloromethane) and the mixture was fractionally distilled. Yield of the isolated product: 14 g (66%), bp 56 °C/0.3 mbar.

The following products were prepared according to the standard procedure (for further details see Table 1) and identified directly in the product solution.

Ph–$CH(CH_3)$–CH_2–$SiEt_3$[25] (entry 10)—^{1}H NMR δ (CD_2Cl_2): 0.83 (mc, 3 Si–C$\underline{H}_2$–CH_3), 1.29 (t, J = 8 Hz, 3 Si–CH_2–C$\underline{H}_3$), 1.36 (mc, $-CH_2-$), 1.67 (d, J = 7 Hz, C$\underline{H}_3$–CH), 3.27 (mc, CH_3–C$\underline{H}$), 7.45–7.51 (m, 1 aromat. H), 7.54–7.63 (m, 4 aromat. H). ^{29}Si NMR δ (CD_2Cl_2): 6.18, GC–MS *m/z*: 234, 219 (∼0.1, $M^+ - CH_3$), 205 (77, $M^+ - C_2H_5$), 163 (100, $C_6H_5SiEt_2^+$), 135 (55, 163 $-C_2H_4$).

Ph–$CH(CH_3)$–CH_2–$SiMe_2$Ph (entry 11)[43]—^{1}H NMR δ (CD_2Cl_2): δ 0.71 (s, Si–CH_3), 0.76 (s, Si–CH_3), 1.79 (mc, 2H, CH_2), 1.83 (d, J = 7 Hz, CH_3), 3.46 (mc, J = 7.5 Hz, C$\underline{H}$–CH_3), 7.6–8.1 (10 aromat. H). ^{29}Si NMR δ (CD_2Cl_2): −3.87. GC–MS *m/z*: 254 (∼0.1, M^+), 239 (8, $M^+ - CH_3$), 197 (16), 176 (47), 135 (100, $PhSiMe_2^+$).

Ph–$CH(CH_3)$–CH_2–$SiMe(OTMS)_2$[21c] (entry 12)—^{1}H NMR δ (CD_2Cl_2): 0.09 (s, SiMe), 0.31 (s, TMS) 0.32 (s, TMS), 1.12 (mc, Si–CH_2), 1.49 (d, J = 6.5 Hz, CH_3), 3.15

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[mc, −C<u>H</u>(CH$_3$)], 7.30−7.34 (m, 1 aromat. H), 7.39−7.46 (m, 4 aromat. H). ^{29}Si NMR δ (CD_2Cl_2): −22.8, 7.13, 7.26. GC−MS m/z: 340 (5, M^+), 325 (12, $M^+ - CH_3$), 221{100, [SiMe(TMS)$_2$]$^+$}, 207 (70), 73 (58).

Ph−CH(CH$_3$)−CH$_2$−SiMe$_2$Cl[43] (entry 14)—^{1}H NMR δ (CD_2Cl_2): 0.67 (2s, 2 CH_3), 1.45 (mc, CH_2), 1.50 (d, J = 7 Hz, CH_3), 3.21 (mc, CH), 7.1−7.6 (aromat. H), GC−MS m/z: 212 (5, M^+), 197 (12, $M^+ - CH_3$), 93 [100, (SiMe$_2$Cl)$^+$].

C$_5$H$_{11}$-CH$_2$-SiMe$_2$-O-TMS[44] (entry 16)—^{1}H NMR δ (CD_2Cl_2): 0.11 (s, $SiMe_2$), 0.13 (s, TMS), 0.54 (mc, Si−CH_2), 0.90 (mc, CH_3), 1.2−1.4 (4 CH_2). ^{29}Si NMR δ (CD_2Cl_2): 7.00, 7.64. GC−MS m/z: 232 (0.1, M^+), 217 (15, $M^+ - CH_3$), 159 (2, M^+ − TMS), 147 (100, TMS-O-SiMe$_2$), 133 (50).

C$_5$H$_{11}$−CH$_2$−SiMe(TMS)$_2$ (entry 17)—^{1}H NMR δ (CD_2Cl_2): 0.035 (s, 3H, SiMe), 0.13 (s, 18H, 2 TMSO), 0.50 (mc, 2H, Si−CH_2), 0.92 (mc, 3H, CH_3), 1.2−1.4 (m, 8H, 4 CH_2). GC−MS m/z: 306 (∼0.1, M^+), 291 (30, $M^+ - CH_3$), 221 {100, [SiMe(TMS)$_2$]$^+$}, 207 (57).

C$_5$H$_{11}$−CH$_2$−SiMe$_2$Cl (entry 18)—^{1}H NMR δ (CD_2Cl_2): 0.50 (s, 6H, $SiMe_2$), 0.94 (mc, 2H, Si−CH_2), 1.03 (mc, 3H, CH_3), 1.2−1.5 (m, 8H, 4 CH_2). GC−MS m/z: 178 (2, M^+), 163 (36, $M^+ - CH_3$), 121 (18), 93 (100, Me$_2$SiCl$^+$).

C$_5$H$_{11}$−CH$_2$−SiMe$_2$Ph[43] (entry 19)—^{1}H NMR δ (CD_2Cl_2): 0.27 (s, 6H, 2 Si−CH_3), 0.77 (mc, 2H, 2 Si−CH_2), 0.89 (mc, 3H, CH_2−C<u>H</u>$_3$), 1.24−1.37 (m, 10H), 7.33−7.38 (m, 3 aromat. H), 7.50−7.55 (m, 2 aromat. H). ^{29}Si NMR δ (CD_2Cl_2): −3.10.

cyclo-C$_6$H$_{11}$−SiEt$_3$ (entry 20)[45,46]—^{1}H NMR δ (CD_2Cl_2): 0.61 (q, J = 8 Hz, 6H, Si−C<u>H</u>$_2$−CH_3), 0.82 (mc, 1H, C<u>H</u>−$SiEt_3$), 1.02 (t, J = 8 Hz, 9H, Si−CH_2−C<u>H</u>$_3$), 1.29−1.38 (m, 5H, cyclohexyl), 1.71−1.86 (m, 5H, cyclohexyl). ^{29}Si NMR δ (CD_2Cl_2): 5.64. GC−MS m/z: 198 (9, M^+), 169 (41, $M^+ - C_2H_5$), 141 (4, 169 $-C_2H_4$), 115 (53, Et_3Si^+), 87 (100, $Et_3Si^+ - C_2H_4$).

exo-2-Norbornyl-SiEt$_3$ (entry 21)[45,46]—^{1}H NMR δ (CD_2Cl_2): 0.56 (q, J = 8 Hz, 6H, Si−C<u>H</u>$_2$−CH_3), 0.72 (t, J = 8.5 Hz, 1H), 1,00 (t, J = 8 Hz, 9H, Si−CH_2−C<u>H</u>$_3$), 1.14−1.33 (m, 4H), 1.38−1.64 (m, 4H), 2.23 (m, 1H), 2.27 (m, 1H). ^{13}C NMR δ (CD_2Cl_2): 0.90 (Si−<u>C</u>H$_2$−CH_3), 5.67 (Si−CH_2−<u>C</u>H$_3$), 24.4 (Si−<u>C</u>H), 27.0, 31.0, 32.5, 35.1, 36.1, 36.2 (ring carbons of norbornyl). ^{29}Si NMR δ (CD_2Cl_2): 5.63 (s, $SiEt_3$).

Products from the reaction of Me$_3$Si−CH=CH$_2$ with Et$_3$Si−H (entry 22): Et$_3$Si−CH=CH$_2$—GC−MS m/z: 142 (∼1, M^+), 113 (69, $M^+ - C_2H_5$), 85 (100, 113 $-C_2H_4$). Me$_3$Si−CH$_2$−CH$_2$−SiEt$_3$—GC−MS m/z: 216 (0.1, M^+), 201 (6, $M^+ - CH_3$), 187 (100, $M^+ - C_2H_5$), 159 (43, 187 $-C_2H_4$), 115 (16, Et_3Si^+), 99 (46), 87 (97). Me$_3$Si−CH$_2$−CH$_2$−SiMe$_3$—GC−MS m/z: 174 (2, M^+), 159 (42, $M^+ - CH_3$), 85 (43), 73 (100, Me_3Si^+). Et$_3$Si−CH$_2$−CH$_2$−SiEt$_3$—GC−MS m/z: 258 (7, M^+), 229 (31, $M^+ - C_2H_5$), 201 (14, 229 $-C_2H_4$), 115 (100, Et_3Si^+), 87 (63).

Products from the reaction of Ph−C≡CH with Et$_3$Si−H (entry 23): Ph−CH=CH−SiEt$_3$—GC−MS m/z: 218 (2, M^+), 189 (100, $M^+ - C_2H_5$), 161 (59), 131 (67), 105 (33), 59 (30). Ph−C≡C−SiEt$_3$—GC−MS m/z: 216 (8, M^+), 187 (100, $M^+ - C_2H_5$), 159 (95), 131 (99), 105 (30). Ph−CH$_2$−CH(SiEt$_3$)$_2$—GC−MS m/z: 334 (<1, M^+), 305 (45, $M^+ - C_2H_5$), 189 (100), 161 (20), 115 (48), 87 (48).

Products from the reaction of *n*-C$_4$H$_9$−C≡CH with Et$_3$Si−H (entry 24): *n*-C$_4$H$_9$−CH=CH−SiEt$_3$—GC−MS m/z: 198 (1, M^+), 169 (100, $M^+ - C_2H_5$), 141 (95, 169 $-C_2H_4$), 113 (30). *n*-C$_4$H$_9$−C≡C−SiEt$_3$—GC−MS m/z: 196 (1, M^+), 167 (100, $M^+ - C_2H_5$), 139 (95, 169 $-C_2H_4$), 111 (30).

Products from the reaction of Me$_3$Si−C≡CH with Et$_3$Si−H (entry 25): Me$_3$Si−CH=CH−SiEt$_3$—GC−MS m/z: 214 (3, M^+), 199 (4, $M^+ - CH_3$), 185 (86, $M^+ - C_2H_5$), 157 (43, 185 $-C_2H_4$), 115 (7, $SiEt_3^+$), 101 (56), 87 (100, $Me_3SiCH_2^+$). Me$_3$Si−CH=CH−SiMe$_3$—GC−MS m/z: 172 (11, M^+), 157 (33, $M^+ - CH_3$), 99 (4, $M^+ - SiMe_3$), 73 (100, $SiMe_3^+$). Et$_3$Si−CH$_2$−CH$_2$−SiEt$_3$—GC−MS m/z: 256 (1, M^+), 227 (56, $M^+ - C_2H_5$), 199 (32, 227 $-C_2H_4$), 115 (100, $SiEt_3^+$), 87 (54).

Crosslinking Experiment. Catalyst component A: a solution of 10.0 mg of **1d** in 600 mg of CH_2Cl_2 was mixed with 1.54 g of α,ω vinyl terminated polydimethylsiloxane (see Scheme 9) in a speed mixer. Crosslinking component B: 1.97 g of the α,ω vinyl terminated polydimethylsiloxane was mixed with a polysiloxane having lateral Si−H functions (see Scheme 9) in a speed mixer. A and B were mixed in a speed mixer and heated to 130 °C for 1 h. Most of the CH_2Cl_2 evaporates first, then—at higher temperatures—crosslinking takes place. A colorless and clear elastomer was formed.

PR Reaction—Preparative Example. Diethoxydiphenylsilane (5.66 g, 20.8 mmol) and pentamethyldisiloxane (6.29 g, 42.4 mmol) were mixed at rt in an argon atmosphere, a solution of 2.9 mg (4.3 μmol, 0.02 mol %) of **1e** in 0.9 g of dichloromethane was slowly added under stirring. An exothermic reaction set in, the temperature reached a maximum of 100 °C and was accompanied by the evolution of gas (ethane). The temperature reached rt again after about 1 h, GC-analysis of the reaction mixture yielded 84 area % *1,1,1,3,3,7,7,9,9,9-decamethyl-5,5-diphenyl-pentasiloxane*[47] (**4**) and 8.2 area % *1-ethoxy-1,1-diphenyl-3,3,5,5,5-pentasiloxane*. The mixture (12.8 g) was fractionally distilled in vacuo using a short column filled with glass spirals to give 3.7 g of a mixture of **4** (66 GC-area %) and *1-ethoxy-1,1-diphenyl-3,3,5,5,5-pentasiloxane* (33 GC-area %) with bp 54−62 °C/0.02 mbar and 6.7 g of **4** (99 GC area %) with bp 91 °C/0.03 mbar. Yield 86%. ^{1}H NMR δ (CD_2Cl_2): 0.16 (s, 2 TMS), 0.21 (s, 2 $OSiMe_2$), 7.4−7.5 (m, 3 aromat. H), 7.7−7.8 (m, 2 aromat. H). ^{13}C NMR δ (CD_2Cl_2): 0.49 (2 $OSiMe_2O$), 0.90 (2 TMS), 127.0, 129.2, 133.7, 135.8 (2 Phenyl-Si). ^{29}Si NMR δ (CD_2Cl_2): −48.2 ($SiPh_2$), −20.2 (2 TMS-<u>Si</u>Me$_2$), 7.74 (2 Me_3Si).

PR Reaction—Typical Procedure. Alkoxysilane (1.0 mmol) and hydrido sil(ox)ane (1.0 mmol) were mixed stoichiometrically (Si−OEt/SiH = 1:1), 30 mg of a 3.6 × 10^{-5} mmol/mg solution of the catalyst **1e** in dichloromethane (1.1 μmol, 0.11 mol % **1e**) was added to the mixture at rt in an inert atmosphere (Ar), and the mixture was heated (for individual starting materials, catalyst amounts, reaction times, temperatures, and yields see individual products). *1,5-Dichloro-1,1,5,5-tetramethyl-3,3-diphenyl-trisiloxane*[48] (**5**)—^{1}H NMR δ (CD_2Cl_2): 0.55 (s, 12H, 2 $SiMe_2$), 7.35−7.55 (m, 3 aromat. H), 7.66−7.75 (m, 2 aromat. H). *Siloxane copolymer* **6**[35]—^{29}Si NMR δ (CD_2Cl_2): −46.2 ($OSiPh_2O$), 0.1 (Me_2SiPh); GPC: M_w = 18 600, M_n = 5040, M_w/M_n = 3.69. *Siloxane copolymer* **7**[48]—^{29}Si NMR δ (CD_2Cl_2): −48.1 ($OSiPh_2O$), −20.1 (Me_2SiPh); GPC: M_w = 8100, M_n = 4300, M_w/M_n = 1.9. *Branched polysiloxane* **8**—^{29}Si NMR δ (CD_2Cl_2): −69.1—(−67) ($MeSiO_3$), −21.9 (Me_2SiO_2), 7.2 ($SiMe_3$).

Inhibition of Hydrosilylation by Alkoxysilanes. Under an argon atmosphere, a solution of **1a** (1.7 mg, 2.0 μmol) in 755 mg of d_2-dichloromethane and ethoxy trimethylsilane (5.2

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mg, 44 μmol, 2 mol %) were added to a mixture of α-methylstyrene (240 mg, 2.03 mmol) and pentamethyldisiloxane (302 mg, 2.03 mmol). After 3 h at 25 °C no hydrosilylation product was detected by ^{1}H NMR spectroscopy. Then the mixture was heated to 50 °C for 1 h. The hydrosilylation product was detected quantitatively. The experiment was repeated without ethoxy trimethylsilane. After 2 h at 25 °C the hydrosilylation product was detected quantitatively.

Determination of Pot Life. Under an argon atmosphere, a solution of 1.7 mg (2.0 μmol) of **1a** in 540 mg of d_2-dichloromethane and 7.8 mg (40 μmol, 2 mol %) of ethoxy 1,1,2,2,2-pentamethyldisiloxane were added to a mixture of 239 mg (2.02 mmol) of α-methylstyrene and 300 mg (2.02 mmol) of 1,1,2,2,2-pentamethyldisiloxane with stirring. The slow disappearance of the ethoxy group of the alkoxysilane was monitored by ^{1}H NMR spectroscopy, see Table 3 (top), the aromatic signals were taken as a reference. Hydrosilylation starts after 8 days when the alkoxysilane was completely used up.

The experiment was repeated with **1a** (1.8 mg, 2.1 μmol) and ethoxy trimethylsilane (4.8 mg, 40 μmol, 2 mol %). The slow disappearance of the ethoxy group of the alkoxysilane was monitored by ^{1}H NMR spectroscopy, see Table 3 (bottom), and the aromatic signals were taken as reference. Ethoxypentamethyldisiloxane was formed as an intermediate (see Table 3, bottom) by the H/OEt exchange reaction.[49] Hydrosilylation started after ∼7 days when the alkoxysilanes are completely used up.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.oprd.9b00260.

NMR spectra, X-ray crystal structure data of **1e** (PDF)

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Notes

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