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Novel Si(II)$^+$ and Ge(II)$^+$ Compounds as Efficient Catalysts in Organosilicon Chemistry: Siloxane Coupling Reaction[†]

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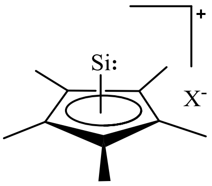
ABSTRACT: Novel catalytically active cationic Si(II) and Ge(II) compounds were synthesized and isolated in pure form. The Ge(II)$^+$-based compounds proved to be stable against air and moisture and therefore can be handled very easily. All compounds efficiently catalyze the oxidative coupling of hydrosil(ox)anes with aldehydes and ketones as oxidation reagents and simultaneously the reductive ether coupling at very low amounts of <0.01 mol %. Because the catalysts also catalyze the reversible cyclotrimerization of aldehydes, paraldehyde can be used as a convenient source for acetaldehyde in siloxane coupling. It is shown that the reaction is especially suitable to make siloxane copolymers. Moreover, a new fluorine-free weakly coordinating boronate anion, $B(SiCl_3)_4^-$, was successfully combined with the Si(II) and Ge(II) cations to give the stable catalytically active ion pairs $Cp^*Si:^+B(SiCl_3)_4^-$, $Cp^*Ge:^+B(SiCl_3)_4^-$, and $[Cp(SiMe_3)_3Ge:^+]B(SiCl_3)_4^-$.

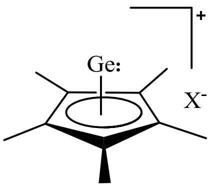
KEYWORDS: *hydrosil(ox)anes, aldehydes and ketones as oxidants, Si(II)$^+$/Ge(II)$^+$ catalysts, cyclotrimerization of aldehydes, siloxane copolymers, WCA*

■ INTRODUCTION

Recently, we reported the high catalytic activity of silyliumylidene compounds $Cp^*Si:^+X^-$ (**1a**) [Cp* = pentamethylcyclopentadienyl, X = $B(Ar^F)_4$, $Ar^F = C_6F_5$] and related compounds as efficient catalysts for the hydrosilylation of olefins at low amounts of <0.01 mol %.[1] In our further work,[2] we were able to demonstrate that $Cp^*Ge:^+B(Ar^F)_4^-$ (**2a**) is also catalytically active in olefin hydrosilylations.



1a [X = $B(Ar^F)_4$]



2a [X = $B(Ar^F)_4$]

These results prompted us to investigate the catalytic potential of various cationic Si(II) and Ge(II) compounds in further reactions of organosilicon chemistry.

Siloxane coupling reaction is a very important process. Hydrolysis and condensation of chlorosilanes (Scheme 1, eq 1) are widely applied but require special technologies to remove hydrogen chloride or stoichiometric amounts of a base, which makes the process laborious. The acid-catalyzed aqueous condensation of alkoxysilanes (Scheme 1, eq 2) is also common but may suffer from equilibration reactions catalyzed by the acid necessary for the process. A strategy that avoids these problems is the Piers–Rubinsztajn (PR) reaction[3,4] (Scheme 1, eq 3). In this process, alkoxysilanes are combined with hydrosilanes in the presence of catalytic amounts of $B(Ar^F)_3$ ($Ar^F = C_6F_5$) to give siloxanes and the corresponding hydrocarbons. As we recently demonstrated, $Cp^*Si:^+$[1] and $Cp^*Ge:^+$[5] are favorable catalysts for the PR process. One issue, however, arises, especially for bulk procedures: usually alkoxysilanes of lower alcohols are used because of their availability, and therefore the reaction produces gaseous hydrocarbons, which makes bulk procedures difficult to be performed in a safely controlled manner. So, alternatives are still of technical interest.

Oxidative coupling (Scheme 1, eq 4) is a further alternative. However, whereas it is well known that SiH_4 reacts violently to give SiO_2 when exposed to air, monohydrosilanes are air-stable and moisture-insensitive, so that catalytic activation for their oxidative coupling is required.[6b] Activation of this reaction, however, was attained by various transition-metal complexes in combination with various oxidants,[6] such as Ir/CO_2, Rh/CH_3NO_2, Au/H_2O, Pt/H_2O, Co/H_2O, Fe/dimethylformamide (DMF), and Ni/air, as well as $InBr_3$/air[7] and KO_2/18-crown-6.[8] On the other hand, it is known that triethylsilane and other silanes can be used in excess as reductants for aldehydes,[9] which then play the role of oxidants. This reaction, however, was developed for the synthesis of symmetrical ethers but not for the synthesis of siloxanes from hydrosilanes. Large amounts of Lewis acids[9] are necessary as catalysts for this transformation, for example, 5–10 mol % tritylium perchlorate,[10] 11% $BiCl_3$,[11] 1–3 mol % $BiBr_3$,[12] 5 mol % trimethylsilyl triflate,[13] ~5 mol % trimethylsilyl trifluoromethanesulfonate,[14] 5 mol % 1-diphenylphosphinonaphthyl-8-triphenylstibonium

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Scheme 1. Known Types of Siloxane Coupling

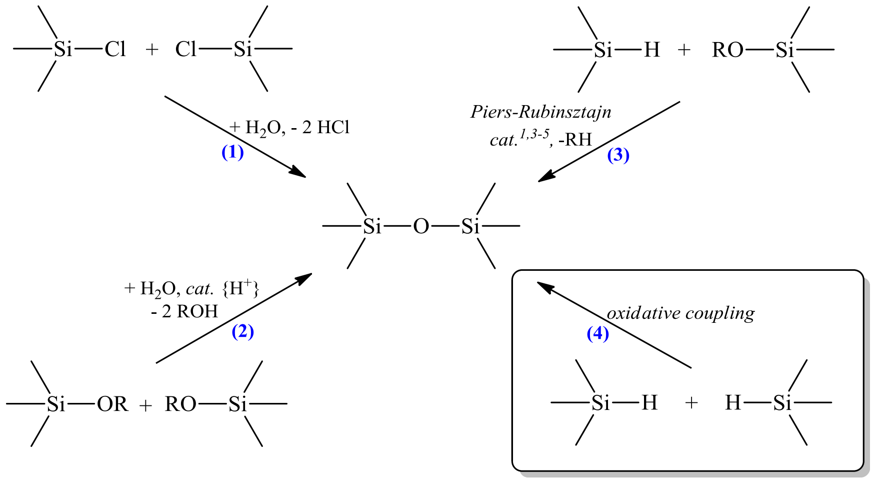


Table 1. Synthesis of Cationic Si:$^+$ and Ge:$^+$ Catalysts

compound	Z	Cp ligand	X	method[a]	isol. yield (%)	mp (°C)
1a	Si	Cp*	$B(Ar^F)_4$	(a)	95 (89[b])	250[c]
1b	Si	Cp*	$Al[OC(CF_3)_3]_4$	(a)	76[b]	216 (dec)[d]
2a	Ge	Cp*	$B(Ar^F)_4$	(a)	97	237[d,e]
2b	Ge	Cp*	$Al[OC(CF_3)_3]_4$	(a)	90	180 (dec)[d]
2c	Ge	$Cp(SiMe_3)_3$	$B(Ar^F)_4$	(b)	90	87[f]
1c	Si	Cp*	$B(SiCl_3)_4$	(b)	55	323 (dec)[d,g]
2d	Ge	Cp*	$B(SiCl_3)_4$	(b)	65	230 (dec)[d]
2e	Ge	$Cp(SiMe_3)_3$	$B(SiCl_3)_4$	(b)	58	299 (dec)[d]

[a] For methods (a) and (b), see Scheme 2. [b] Isolated yields according to the literature.[1] [c] Recrystallization from CD_2Cl_2/*n*-hexane. [d] Recrystallization from CD_2Cl_2/*n*-heptane. [e] Discoloration begins at ~230 °C. [f] Recrystallization from CD_2Cl_2/*n*-pentane. [g] Discoloration begins at ~250 °C.

triflate,[15] 4% w/w heterogeneous molybdenium-dioxo catalyst,[16] and stoichiometric amounts of SbI_3.[17]

Herein, we report a very efficient procedure to make siloxanes by oxidative coupling of hydrosil(ox)anes using aldehydes as oxidants and cationic Si(II) and Ge(II) compounds as catalysts. Moreover, we further develop the basic structural motifs of **1a** and **2a** under the aspects of accessibility and practical use for this reaction.

RESULTS AND DISCUSSION

Synthesis of Cationic Si:$^+$ and Ge:$^+$ Catalysts. $Cp^*Si:^+B(Ar^F)_4^-$ (**1a**) and $Cp^*Si:^+Al[OC(CF_3)_3]_4^-$ (**1b**) (Table 1) were made from decamethylsilicocene (**3a**, Z = Si) by hydride transfer from one of the Cp* residues to the corresponding tritylium salts **4a** [X = $B(Ar^F)_4$] and **4b** {X = $Al[OC(CF_3)_3]_4$}[1] [see Scheme 2, method (a)]. This procedure was now successfully applied on the synthesis of new cationic germanium compounds $Cp^*Ge:^+B(Ar^F)_4^-$ (**2a**) and $Cp^*Ge:^+Al[OC(CF_3)_3]_4^-$ (**2b**) (see Scheme 2 and Table 1) from decamethylgermanocene (**3a**, Z = Ge).[18] Compounds **2a** and **2b** were isolated in pure form by crystallization and characterized by NMR spectroscopy. In addition, the structure of **2a** was verified by crystal structure analysis (see Figure 1). The Ge–B distance is 5.91 Å, in accordance with the Si–B distance of 5.39 Å in the analogous Si compound **1a**.[19]

Furthermore, we were able to introduce a novel silylated Cp ligand, tris(trimethylsilyl)cyclopentadienyl, which is readily available in only two steps from cyclopentadiene[20] (Scheme 2), leading to hexakis(trimethylsilyl)germanocene **3b**[21] and subsequently to the new catalyst structure **2c** [Scheme 2, method (b)] by selective protonation with 1 equiv of $H^+(OEt_2)_2B(Ar^F)_4^-$ in analogy to the literature.[22]

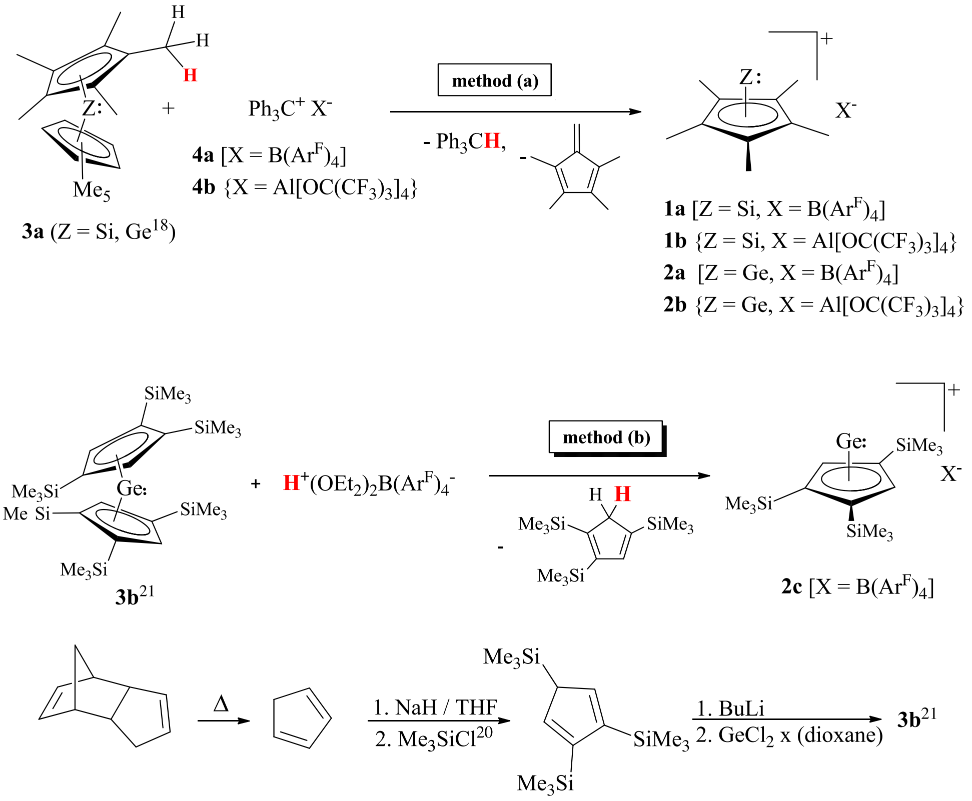
The cationic Ge(II) compounds **2a–c** are bench stable in contrast to the cationic Si(II) compounds.[1] A crystalline sample of **2c** was exposed to air for 30 days and showed no change in the NMR spectrum. Therefore, the germanium compounds are particularly useful for practical applications.

OXIDATIVE COUPLING OF HYDROSILANES

When we treated triethylsilane (**5**, $R^1 = R^2 = R^3$ = ethyl) with stoichiometric amounts of hexanal (**6**, R′ = *n*-C_5H_{11}, R″ = H) in the presence of 0.06 mol % of the cationic silyliumylidene compound **1a** (Table 2, entry 1; Scheme 3), hexaethyldisiloxane and di-*n*-hexyl ether were both formed nearly quantitatively, as can be seen from the ^1H NMR spectra of both products in the reaction mixture after almost complete conversion of the educts triethylsilane and hexanal (Figure 2).[23] A significant excess of one of the reaction partners is not necessary, and this makes the method suitable both for the synthesis of symmetrical ethers and for siloxanes.

The results are summarized in Table 2. It shows that both cationic Si(II) and Ge(II) compounds are catalytically active, and no pronounced influence of the anionic counterion on the catalytic activity is observed. This is in contrast to the hydrosilylation reaction where compound **1b** with the aluminate anion[1] exhibits a very low catalytic activity, which can be attributed to a weak ion-pair separation.[1] In the siloxane/ether redox coupling, however, we assume that the carbonyl compound coordinates to the cationic center, thus

Scheme 2. Synthesis of Si(II):$^+$- and Ge(II):$^+$-Based Catalysts[a]



[a] Method (a): hydride transfer reaction from Cp to tritylium cation. Method (b): selective protonation of Cp by H$^+$.

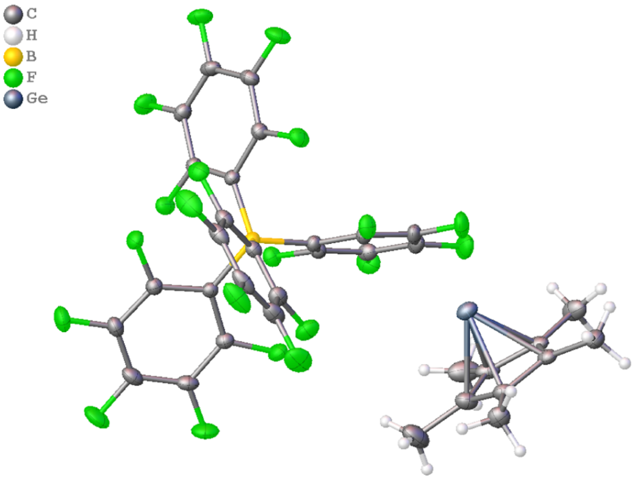


Figure 1. OLEX2 plot of the molecular structure of **2a** in the single-crystal lattice at T = 123.00(10) K. Ge−B distance: 5.91 Å. Thermal ellipsoids are set at 20% probability.

facilitating the ion-pair separation and thus playing a role in the activation process.

Table 2 shows that also ketones can be used for the siloxane coupling reaction (entries 7 and 8), but they are less reactive and therefore aldehydes are preferred as coupling reagents for siloxanes.

The new method also gives ethers from the corresponding aldehydes or ketones under neutral, anhydrous, and homogeneous conditions without producing salts. This facilitates workup and may be advantageous compared to the well-known ether syntheses such as Williamson ether synthesis or

Table 2. Oxidative Coupling of Et_3SiH (5, $R^1 = R^2 = R^3$ = Et) to $Et_3SiOSiEt_3$ by Aldehydes and Ketones, and Simultaneous Reductive Coupling to Ethers[a]

entry	aldehyde[b]/ ketone 6 R′, R″ (equiv)	catalyst (mol %)	t (h)/conversion of silane [aldehyde/ketone] (%)[c]	yield[d] (% siloxane, ether)
1	H, n-C_5H_{11} (1.0)	**1a** (0.059)	0.3/97[96]	96, 96
2	H, n-C_5H_{11} (1.2)	**1a** (0.050)	0.3/97[83]	96, 96
3	H, n-C_5H_{11} (1.0)	**1b** (0.061)	5.7/91[94]; 19/94[97]	97, 97
4	H, n-C_5H_{11} (1.0)	**2a** (0.062)	0.5/96[99]	>95, >95[e]
5	H, n-C_5H_{11} (1.0)	**2b** (0.062)	5.5/89[93]; 22.5/94[98]	97, 97
6	H, n-C_5H_{11} (1.1)	**2c** (0.059)	3.5/95[91]	97, 97
7	CH_3, C_2H_5	**1a** (0.050)	0.5/93[95]; 4/99[99]	79, 79[f]
8	cyclobutanone (0.9)[g]	**2a** (0.01)	15/98[92]	95, >90[h]
9	H, n-C_5H_{11} (1.0)	**1c** (0.065)	3.7/95[95]; 19.5/97[98]	97, 97
10	H, n-C_5H_{11} (1.0)	**2d** (0.065)	3.5/92[95]; 22.5/96[98]	98, 98
11	H, n-C_5H_{11} (1.1)	**2e** (0.059)	0.3/99[92]	98, 98

[a] In 60% (w/w) CD_2Cl_2, according to the standard procedure in an NMR tube. [b] The reaction was started at rt (23−25 °C); initially, the temperature increased to ∼40 °C for ∼20 min after adding the catalyst solution and then reached rt again. [c] Of Si−$\underline{H}$ and C$\underline{H}$O measured by ^1H NMR. [d] By gas chromatography (GC) measurement. [e] By ^1H NMR. [f] 21% $Et_3SiOCH(CH_3)CH_2{-}CH_3$ was formed. [g] Reaction performed at 45 °C. [h] The reaction was also performed on a preparative scale, isolated yield 75%.

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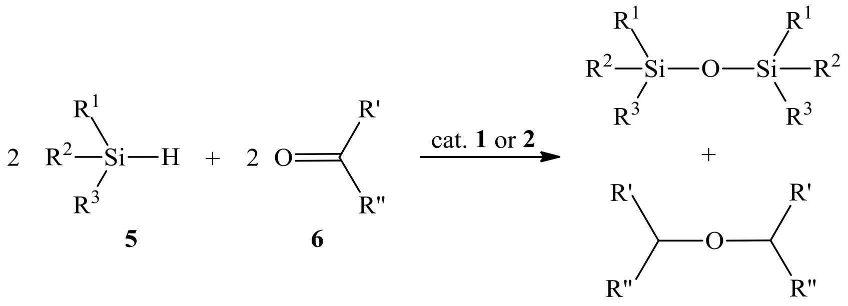
Scheme 3. Oxidative Siloxane Coupling and Simultaneous Ether Formation Catalyzed by Si(II)$^+$ (1) and Ge(II)$^+$ (2) Compounds



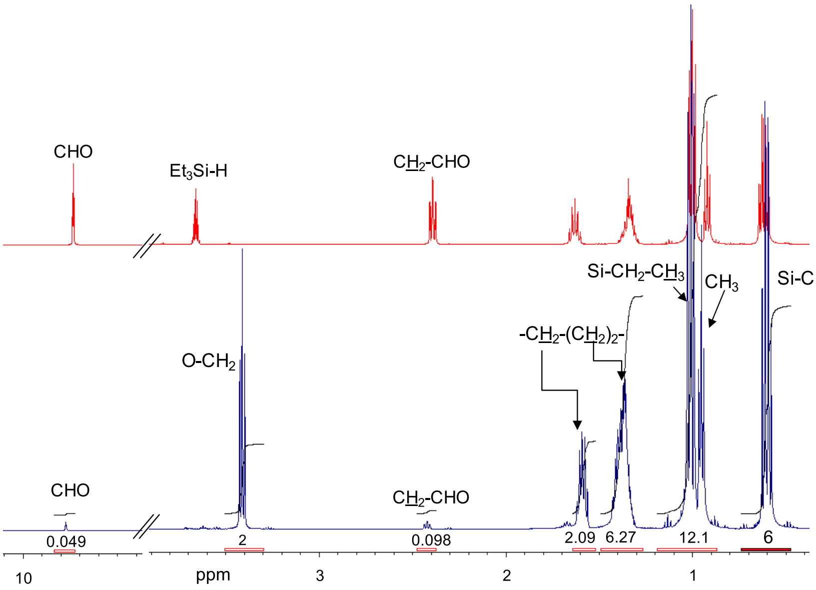
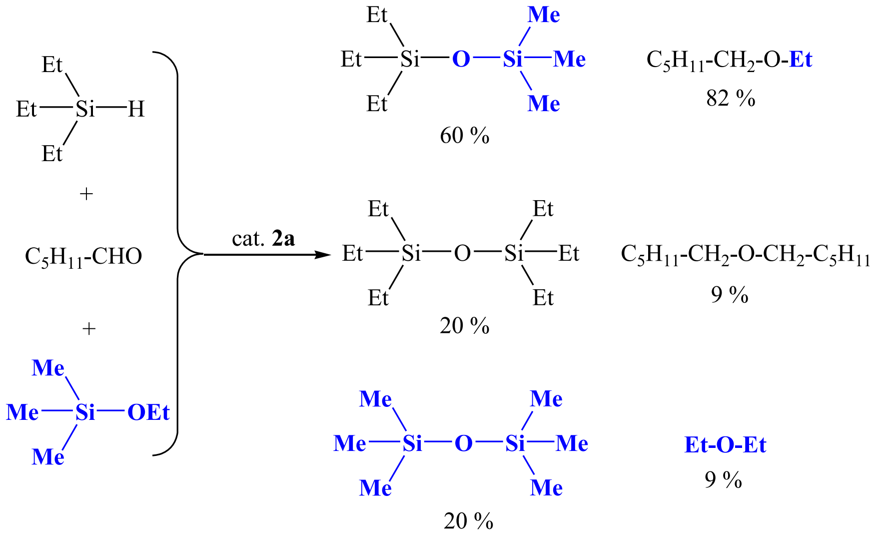


Figure 2. Red: mixture of triethylsilane and hexanal; blue: product mixture of hexaethyldisiloxane and di-*n*-hexyl ether (Table 2, entry 1).

Scheme 4. Products of the Reaction of a 1:1:1 Mixture of Triethylsilane, Hexanal, and Me_3SiOEt with 0.02 mol % 2a in CD_2Cl_2[a]

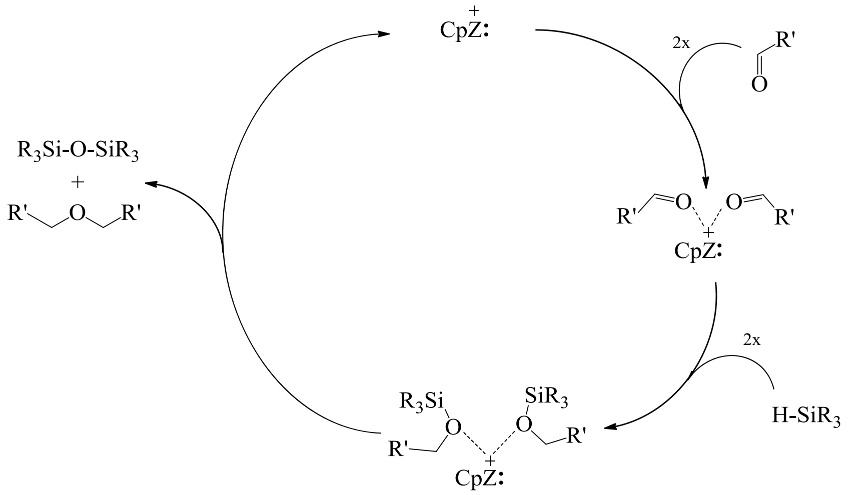


[a] Product ratio measured by ^1H NMR.

dehydration of alcohols.[24] As a preparative example, the synthesis of dicyclobutyl ether from cyclobutanone is given (Table 2, entry 8).

Although the other electrophilic catalysts $B(Ar^F)_3$[25] and the Lewis acidic bis(perfluorocatecholato)silane[26] give alkoxysilanes as reaction products from Si−H and C=O, with

Scheme 5. Mechanism Supposed for the Oxidative Coupling Reaction Catalyzed by 1 and 2



catalysts **1** and **2**, alkoxysilane was only observed in the range of 0.1−0.2 mol % from triethylsilane and hexanal (Table 2, entries 1−6, in 20 mol % yield in the reaction between triethylsilane and methylethylketone (Table 2, entry 7) and not observed in the transformation of triethylsilane and cyclobutanone (Table 2, entry 8).

Alkoxysilanes might be formed as intermediates during the redox process; however, they are not stable under the conditions and react further: When we performed the oxidative coupling of triethylsilane and hexanal (1:1) in the presence of 1 equiv of $Me_3Si{-}OEt$ the alkoxysilane was completely consumed during the reaction and mixed products were detected (Scheme 4).

In analogy to the literature,[25,26] we assume that the carbonyl groups are activated by coordination to the cationic Si(II) and Ge(II) centers. The alkoxysilanes formed by hydrosilylation remain coordinated, as was already shown for $Cp^*Si:^+$,[1,27] and this facilitates the formation of siloxane and ether (Scheme 5). Evidence for the suggested mechanism is given by the fact that triisopropylsilane and acetaldehyde react to give mainly triisopropylethoxysilane (Table 4, entry 4). In this case, the complexation of two alkoxysilane units may be hindered due to steric reasons.

Reversible Cyclotrimerization of Aldehydes. For the siloxane coupling reaction, aldehydes are generally preferred because they are more reactive than ketones, but the most attractive aldehyde under economical aspects is acetaldehyde. When we tried to react triethylsilane with acetaldehyde, a very vigorous and exothermic reaction took place, which was difficult to control. A further disadvantage of acetaldehyde is its low boiling point of 20−21 °C, which would require pressurized conditions.

Here, we found that the cationic Si(II) and Ge(II) catalysts catalyze the reversible cyclotrimerization of aldehydes (Scheme 6), as was shown for the catalysts **1a** and **2a** (Table 3, entries 1 and 2).[28] Side reactions were not observed. As shown below, the equilibrium reaction can be used to control the oxidative coupling reaction because it renders low stationary concentrations of acetaldehyde.

Scheme 6. Reversible Cyclotrimerization of Aldehydes Catalyzed by 1a and 2a

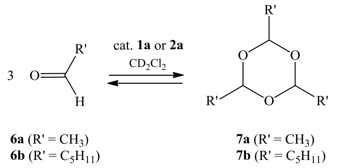


Table 3. Reversible Cyclotrimerization and Equilibrium Concentrations of Aldehydes 6 at Different Temperatures

entry	catalyst (mol %)[a]	starting from	c (mmol/g)[b]	T (°C)	mol % **6**[c]
1	**2a** (0.0050)	**6a**	2.00	25	53
2	**2a** (0.0050)	**7a**	1.96	25	53
3	**2a** (0.0050)	**6a** + **7a**[d]	1.96	0	19
4	**2a** (0.0050)	**6a** + **7a**[e]	1.96	−20	7.5
5	**2a** (0.0051)	**7a**	3.99	23	37
6	**2a** (0.0051)	**7a**	7.74	23	23
7	**2a** (0.039)	**6a**	0.179	23	99
8	**1a** (0.020)	**6b**	1.77	23	78
9	**2a** (0.021)	**6b**	1.74	23	77
10	**2a** (0.016)	**6b**	7.11	−10	8[f]

[a] Calculated for aldehyde units of **6** + **7**. [b] Calculated as aldehyde units, in CD_2Cl_2. [c] Measured by ^1H NMR, relative amounts. [d] Equilibrium mixture of **6a** + **7a** at 25 °C was used. [e] Equilibrium mixture of **6a** + **7a** at 0 °C was used. [f] This transformation was also run on a preparative scale, 85% yield.

Various catalysts have been already described for the cyclotrimerization of aldehydes, such as ionic liquids (0.1 mol %),[29] $FeCl_3$ (20 mol %),[30] ZnO (12 mol %),[31] UO_2^{2+} (1−5 mol %),[32] Sb(V)$^+$ (0.5 mol %),[15] and $InCl_3$ (5 mol %).[33] The cationic Si(II) and Ge(II) catalysts, however, give fast and completely reversible cyclotrimerization reactions at catalytic amounts of only 0.005 mol %.

Independent kinetic measurements starting from acetaldehyde and from paraldehyde with **2a** (0.0050 mol %) gave the same equilibrium mixture of 53 ± 1 mol % acetaldehyde (**6a**, R′ = H, R″ = Me) and 47 ± 1 mol % paraldehyde (2,4,6-trimethyl-1,3-5-trioxane, **7a**, R′ = H, R″ = Me) (Figure 3 and Table 3, entries 1 and 2), indicating complete reversibility (25 °C, initial concentrations $c_{\text{acetaldehyde}} = 2.00$ mmol/g, $c_{\text{paraldehyde}} = 0.654$ mmol/g).

As expected, the aldehyde−trioxane equilibrium strongly depends on temperature (Table 3, entries 2−4) and on concentration (Table 3, entries 4−7). A 92% cyclotrimeriza-

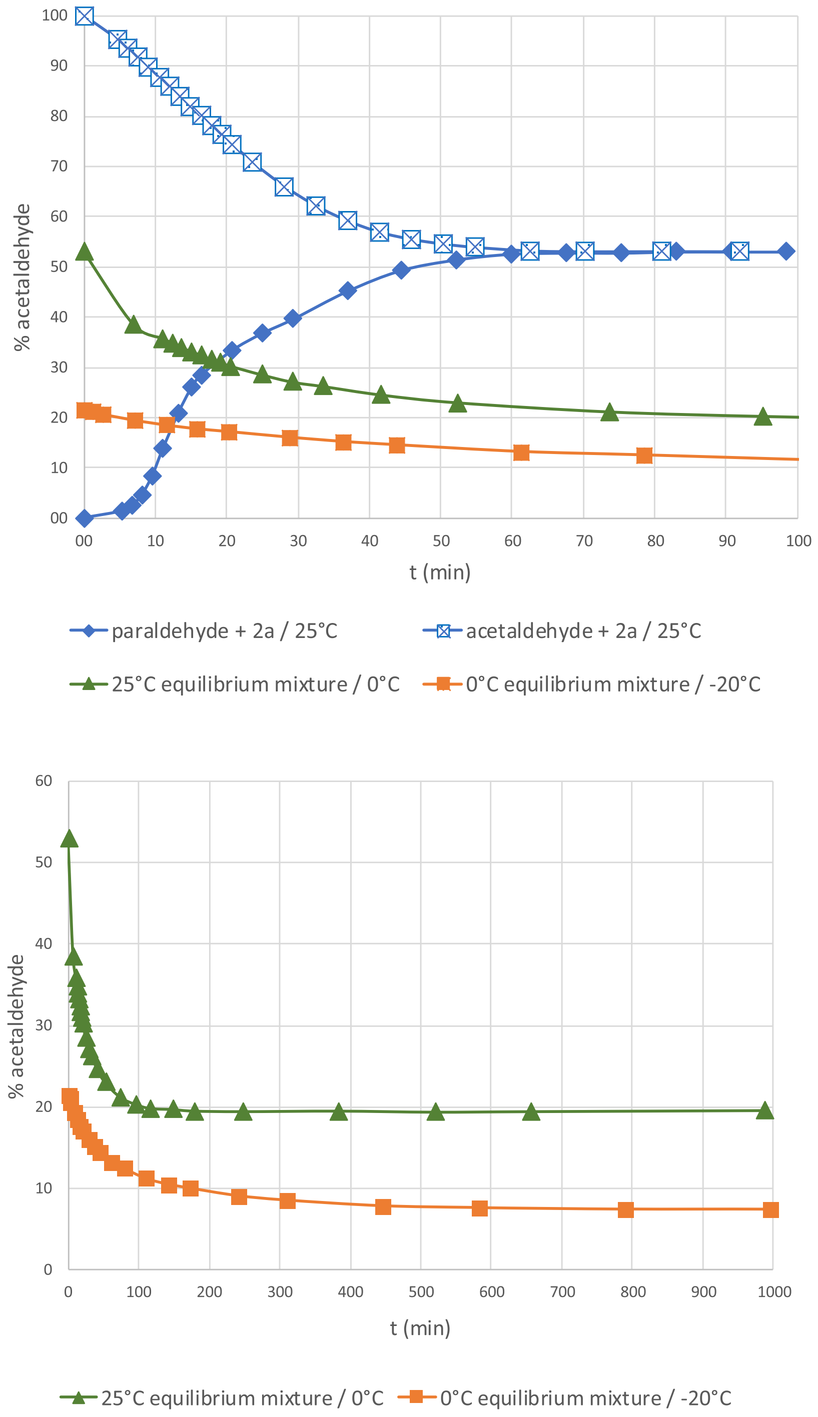


Figure 3. Top: kinetic measurement of the equilibration starting from acetaldehyde (**6**, R′ = Me), c = 2.00 mmol/g in CD_2Cl_2 (blue, Table 3, entry 1) and independently from paraldehyde (**7**, R′ = Me), c = 0.654 mmol/g in CD_2Cl_2 at 25 °C (blue, Table 3, entry 2). Kinetic measurement of the equilibration at 0 °C starting from the equilibrium mixture at 25 °C (green, Table 3, entry 3) and at −20 °C starting from the equilibrium mixture at 0 °C (orange, Table 3, entry 4). Bottom: extended time scale. All experiments were performed with 0.0050 mol % **2a**.

tion was achieved for hexanal at a high concentration and T = −10 °C (Table 3, entry 10).

Oxidative Siloxane Coupling Using Paraldehyde. Because of the reversible cyclotrimerization of acetaldehyde, paraldehyde is advantageously used instead of acetaldehyde in the oxidative siloxane coupling process. Acetaldehyde is formed in situ during the reaction and consumed by the redox process (Scheme 7). The results are summarized in Table 4.

High yields of siloxanes are achieved using paraldehyde and the Ge(II)$^+$ catalyst **2a** at amounts of 0.005 mol % or even lower (Table 4, entries 1−3). Interestingly, hydrosilylation of the vinyl groups of methylphenylvinylsilane was not observed (Table 4, entry 3) because the catalyst is masked by the oxygen ligands, as was already demonstrated for Cp*Si(II)$^+$.[1] Triisopropylsilane (Table 4, entry 4) gives mainly triisopropylethoxysilane (68%) and smaller amounts of triisopropylsilanol (15%). Complexation of two alkoxysilane units, which is

Scheme 7. Oxidative Siloxane Coupling Using Paraldehyde

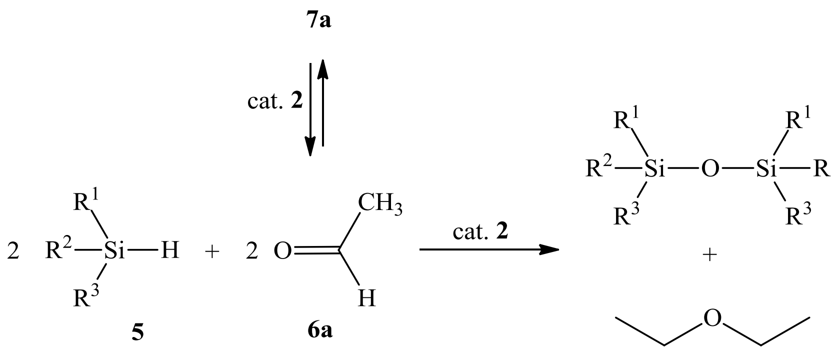
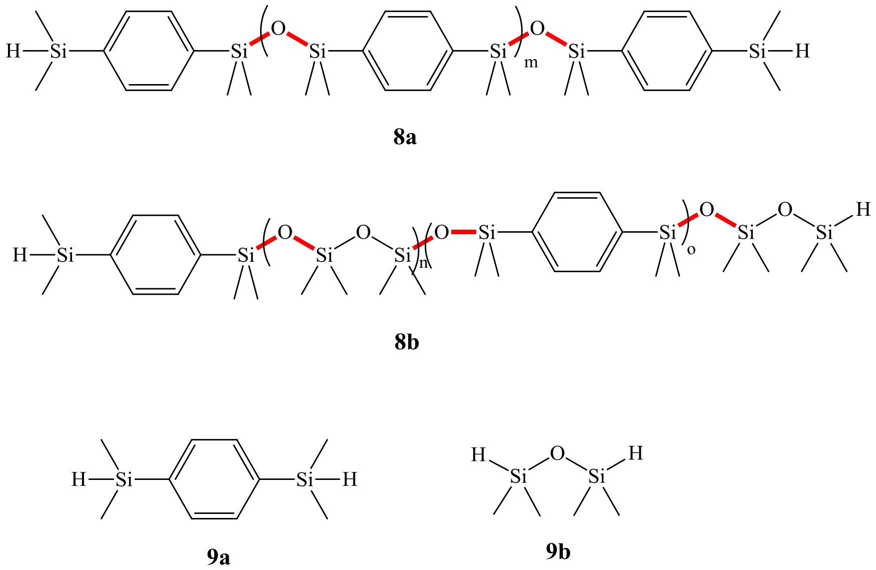


Table 4. Oxidative Coupling of Si−H to Si−O−Si Using Paraldehyde 7a[a]

entry	hydrosilane **5**,[b] R^1, R^2, R^3	equiv. of paraldehyde (**7a**)	catalyst (mol %)	*t* (h)/conversion (%)[c]	siloxane yield (%)[d]
1	Me, Me, Ph	1.13	**2a** (0.0055)	1/99	97
2	Me, Ph, Ph	1.08	**2a** (0.0065)	1/99	96
3	Me, Ph, Vi	1.13	**2a** (0.0029)	1/93; 3/99	95
4	*i*-C_3H_7, *i*-C_3H_7, *i*-C_3H_7	1.11	**2a** (0.0058)	4/89	[e]
5	Et, Et, Et	1.10	**2e** (0.0050)	0.5/96; 4/98	98
6	Me, Me, Ph	1.11	**2e** (0.0027)	1/99	97
7	Me, Me, Ph	1.13	**2e** (0.0001)	1.5/84; 5/88[f]	98
8	Me, Ph, Vi	1.11	**2e** (0.0054)	1/99[g]	94
9	Me, Ph, Vi	1.13	**2e** (0.0027)	0.5/81; 3/93	95

[a] In 55% (w/w) CD_2Cl_2, $T = 50$ °C, according to the standard procedure in an NMR tube. [b] Et = ethyl, Me = methyl, Ph = phenyl, and Vi = vinyl. [c] Of Si−H measured by ^{1}H NMR. [d] Area % by GC. [e] 68% triisopropylethoxysilane, 15% triisopropylsilanol, 5% **6**, R^1, R^2, R^3 = *i*-C_3H_7, and 1% bis-triisopropylsiloxane. [f] Full conversion after ~10 days. [g] This transformation was also run on a preparative scale, 89% yield.

Scheme 8. Synthesis of Phenyl-Siloxane Copolymers 8a and 8b by Oxidative Coupling of Monomers 9a and 9b[a]



[a] Bonds in red are formed by the oxidative coupling process.

a prerequisite of siloxane coupling according to the mechanism in Scheme 5, may be disfavored in this case due to the steric demand of the alkyl groups.

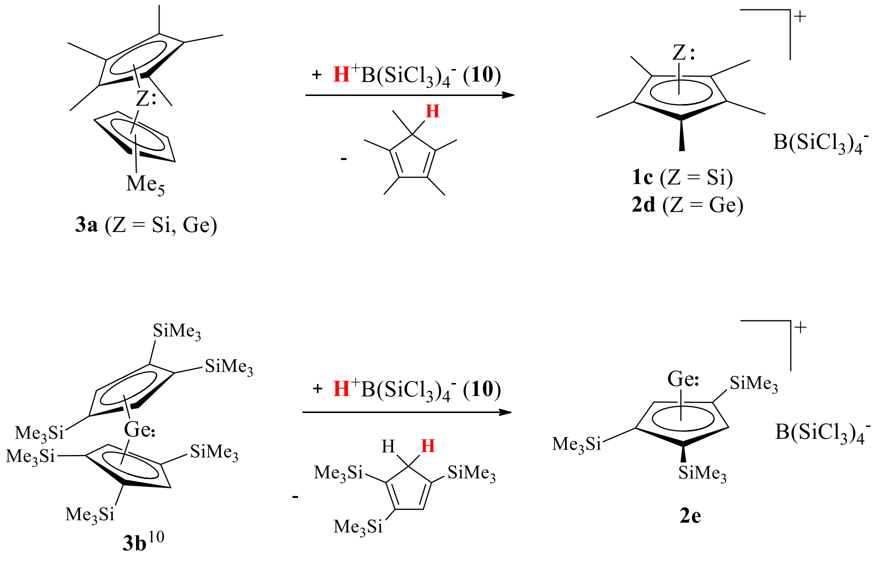
Synthesis of Phenyl-Siloxane Copolymers. The incorporation of phenyl units into siloxane polymers is especially important because phenyl groups may improve the mechanical properties and make the siloxanes more compatible with organic polymers. Moreover, phenyl groups are often introduced to modify the optical properties of polysiloxanes, such as light absorption and refractive index. The oxidative siloxane coupling is especially useful for the synthesis of siloxane copolymers because it is a very fast and selective reaction: a prerequisite for polymer synthesis. By this method, the phenyl-siloxane copolymer **8a** (Scheme 8) was prepared from the readily available bis(1,4-dimethylsilyl)benzene (**9a**) using acetaldehyde (**6a**) in a fast and exothermic reaction (Table 5, entries 1 and 2), or, advantageously, in a more moderate reaction using paraldehyde (**7a**) (Table 5, entry 3).

Table 5. Synthesis of Phenyl-Siloxane Copolymers 8a and 8b from the Monomers 9a and 9b by Oxidative Coupling[a]

entry	monomer(s)[b]	catalyst (mol %[c])	oxidant (equiv); CH_2Cl_2 (% w/w)	polymer (T_g;[d] M_w, M_n, D;[e] n_D^{20}[f])
1[g]	**9a**	**2a** (0.0069)	**6a** (1.10); 38	−33;[h] 22 600, 15 000, 1.51; –
2[h]	**9a**	**2c** (0.0014)	**7a** (1.34); 45	−25;[i] 12 800, 51 300, 4.02; –
3	**9a**, **9b** (1:1)	**2a** (0.011)	**7a** (1.40); 26	−77; 96 200, 30 300, 3.18; 1.476
4	**9a**, **9b** (1:1)	**2c** (0.010)	**7a** (1.41); 36	−77; 100 700, 30 000, 3.39; 1.476
5	**9a**, **9b** (1:3)	**2c** (0.014)	**7a** (1.40); 44	−104; 26 400, 82 200, 3.11; 1.445
6	**9a**, **9b** (1:6)	**2c** (0.010)	**7a** (1.40); 44	−113; 40 000, 159 000, 4.00; 1.430
7	**9a**, **9b** (1:6)	**2c** (0.014)	**7a** (1.30); 60	−113; 22 300, 66 200, 2.96; 1.429
8[k]	H-$(SiMe_2O)_{47}$-$SiMe_2H$	**2a** (0.044[l])	**6a** (4.0); 20	−39;[m] 242 000, 980 000, 4.05;[n] 1.403

[a] 15 h at 45 °C. [b] Molar ratio in brackets. [c] Based on Si−H. [d] Glass temperature in °C. [e] Dispersity $D = M_w/M_n$. [f] Refractive index at 20 °C. [g] Exothermic reaction, reaction completes after ∼30 min. [h] Melting range: 108.5−114 °C. [i] Melting range: 119−128 °C. [k] At rt. [l] % w/w. [m] Crystallization. [n] Viscoelastic polymer.

Scheme 9. Synthesis of Tetrakis(trichlorsilyl) Boronates of Si(II) and Ge(II) Cations using Bochmann's Acid 10



Compound **8a** is a partially crystalline solid, with a melting range of 109−114 °C [measured by differential scanning calorimetry (DSC); see the Supporting Information (SI)], which varies depending on the molecular weight of the polymer, and glass transition at ∼−30 °C (Table 5, entries 1 and 2; for DSC, see the SI), which is due to the rigidity of the chain. However, to make the polymer chain more flexible, we copolymerized **9a** and the similar reactive tetramethyldisiloxane (**9b**) to get the copolymer fluids **8b** (Scheme 8 and Table 5, entries 3−7). As expected, the glass temperature of the fluids **8b** (measured by DSC, see SI) decreases with the amount of dimethylsiloxane units in the chain, whereas the refractive index (n_D^{20}) increases with the amount of phenyl units (Table 5).

Finally, we coupled a polymeric hydrosiloxane (Table 5, entry 8) to make a linear high-molecular-weight siloxane.

Introduction of the $B(SiCl_3)_4^-$ Counterion. Highly electrophilic cations such as Cp*Si:$^+$ and Cp*Ge:$^+$ are only stable in combination with non-nucleophilic weakly coordinating anions (WCAs), which are usually perfluorinated boronate or perfluorinated aluminate anions.[34] However, in the context of environmental issues associated with persistent organofluorine compounds, it would be advantageous to develop catalysts with fluorine-free counterions.

Here, we were able to introduce a new fluorine-free weakly coordinating anion (WCA), tetrakis(trichlorosilyl) boronate, $B(SiCl_3)_4^-$, by reacting silicocene and germanocene (**3a**, Z = Si, Ge) with $H^+B(SiCl_3)_4^-$,[35] Bochmann's acid (**10**), which protonates one of the Cp* residues selectively to give Cp*H and the compounds Cp*Si:$^+B(SiCl_3)_4^-$ (**1c**), Cp*Ge:$^+B(SiCl_3)_4^-$ (**2d**), and $[Cp(SiMe_3)_3Ge:^+]$ $B(SiCl_3)_4^-$ (**2e**, Scheme 9). Compounds **1c**, **2d**, and **2e** were isolated in pure form and characterized by electrospray ionization (ESI)-MS (see the SI) and their ^1H, ^{13}C, ^{29}Si, and ^{11}B NMR spectra. The Si(II)$^+$ compound **1c** was stable for more than 6 months under inert conditions, and the Ge(II)$^+$ compounds **2d** and **2e** were completely bench stable for more than several weeks. They had about the same catalytic activity and selectivity as compounds **1** and **2** with the $B(Ar^F)_4^-$ counterion (see Table 2, entries 9−11, and Table 4, entries 5−9). Only with the minimal catalytic amount of 0.0001 mol %, the reaction becomes slower at high conversion, indicating some loss of catalytic activity (Table 4, entry 7). Therefore, the new tetrakis(trichlorosilyl) boronate anion is an environmentally friendly, fluorine-free alternative to the well-established perfluorinated boronate anions.

■ CONCLUSIONS

New cationic Si(II) and Ge(II) compounds are synthesized and applied as efficient catalysts for the oxidative coupling of hydrosil(ox)anes using aldehydes, thus offering an efficient method to make siloxanes. The cationic Ge(II) compounds are completely stable toward air and moisture and readily available, making them particularly useful under synthetic aspects.

Paraldehyde can be advantageously used instead of low-boiling acetaldehyde for the coupling reaction because the catalysts also catalyze the formation of acetaldehyde from paraldehyde. The oxidative coupling method was successfully used to make a new class of siloxane-*p*-phenylene copolymers. Finally, the tetrakis(trichlorosilyl) boronate anion, $B(SiCl_3)_4^-$, was successfully introduced into the cationic Si(II) and Ge(II) structures as a new stable fluorine-free weakly coordinating anion, which is readily available from chlorosilanes and boron trichloride, thus improving the availability of the catalysts considerably. Furthermore, it may be useful for the stabilization of further cations of p-block elements.

■ EXPERIMENTAL SECTION

Analytical Methods. All ^1H NMR spectra were measured with a Bruker Avance 500 spectrometer. GC: Agilent Technologies, HP 5 column (polydimethylsiloxane) (PDMS) with 5% phenyl groups), length 30 m, internal diameter 0.25 mm, film thickness 0.25 μm, injector temperature 290 °C, flame ionization detector (FID), 320 °C, carrier gas He. GC-MS: Agilent Technologies, GC unit 6890N, Agilent HP-5MS UI column, injector temperature 250 °C, MS unit 5975C, EI, 70 eV. Relative molecular masses of silicone copolymers were measured by gel permeation chromatography (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 detector, PDMS calibration. ESI-MS: Bruker Daltonics Amazon SL Ion-Trap mass spectrometer, direct infusion with syringe pump 4 μL/min, ESI-alternating (±) full-scan mode and tandem mass spectrometry (MS/MS) mode, ionization voltage 5000 V, dry gas temperature 300 °C, dry gas flow 4 L/min, nebulizer gas pressure 10 psi, sample concentration 1 mg/mL in anhydrous acetonitrile.

Materials. $(C_6H_5)_3C^+B(Ar^F)_4^-$ (**4a**) was commercially available and used without further purification. $(C_6H_5)_3C^+Al[OC(CF_3)_3]_4^-$ (**4b**)[36] was provided by Prof. Dr. I. Krossing, University of Freiburg/Germany. $GeCl_2$−dioxane complex,[37] decamethylgermanocene (**3a**, Z = Ge),[18] $H^+(OEt_2)_2B(Ar^F)_4^-$,[10] tris(trimethylsilyl)cyclopentadiene,[20] hexakis(trimethylsilyl)germanocene,[21] **1a**, and **1b** were synthesized according to the literature procedure. $H^+B(SiCl_3)_4^-$ (**10**, Bochmann's acid)[35] was provided by Dr. S. Bochmann, Wacker Chemie AG, Nünchritz, Germany. Bis-1,4-dimethylsilylbenzene from ABCR was purified by fractional distillation in vacuo.

Synthesis of 2a. A solution of 1.70 g (1.84 mmol) of the tritylium salt **4a** in 5 mL of dichloromethane was slowly added to a solution of 701 mg (2.04 mmol) decamethylgermanocene (**3a**, Z = Ge) in 5 mL dichloromethane at rt in an argon atmosphere. *n*-Heptane was added dropwise to the homogeneous solution until no more solid precipitates. After decanting off the mother liquor, the solid was washed with *n*-heptane, dissolved in dichloromethane, precipitated with *n*-heptane again, and dried in vacuo. Yield 1.63 g (97%) off-white crystalline solid, mp 237 °C. ^1H NMR δ (500 MHz, CD_2Cl_2): 2.23 (s, Cp*). ^{11}B NMR δ (160.4 MHz, CD_2Cl_2): −16.7 [s, $B(Ar^F)_4^-$]. ^{13}C NMR δ (125.8 MHz, CD_2Cl_2): 8.82 (5 CH_3), 123.1 (5 $\underline{C}$−CH_3), 124 (broad, C−B), 136.3 (m, $^1J_{C,F}$ = 243 Hz, *ortho*-C), 138.2 (m, $^1J_{C,F}$ = 243 Hz, *para*-C), 148.3 (m, $^1J_{C,F}$ = 243 Hz, *meta*-C). ^{19}F NMR δ (470.5 MHz, CD_2Cl_2): −167.4 (mc, 8F, 3,5-F), −163.5 (mc, 4F, 4-F), −132.9 (mc, 8F, 2,6-F). A small sample of the product was exposed to air for 4 days and then analyzed by ^1H NMR spectroscopy. No decomposition products were detected.

Synthesis of 2b. A solution of 117 mg (97.0 μmol) of the tritylium salt **4b** in 0.3 mL of dichloromethane was slowly added to a solution of 32.8 mg (95.6 μmol) of decamethylgermanocene (**3a**, Z = Ge) in 0.3 mL dichloromethane at rt in an argon atmosphere. The mixture was allowed to stand for 30 min at rt. *n*-Heptane was added dropwise to the homogeneous solution until no more solid product precipitates. After removing the mother liquor by means of a syringe, the solid was washed with *n*-heptane, dissolved in dichloromethane, precipitated with *n*-heptane for the second time, and dried in vacuo. Yield 102 mg (90%) slightly rose-colored crystalline solid, mp 180 °C (dec.). ^1H NMR δ (500 MHz, CD_2Cl_2): 2.26 (s, Cp*). ^{19}F NMR δ (470.5 MHz, CD_2Cl_2): −75.7 (s, CF_3). ^{27}Al NMR δ (130.3 MHz, CD_2Cl_2): 34.6.

Synthesis of 2c. A solution of 195 mg (236 μmol) of $H^+(OEt_2)_2B(Ar^F)_4^-$ in 910 mg of dichloromethane was slowly added to a solution of 151 mg (237 μmol) hexakis(trimethylsilyl)germanocene (**3b**) in 520 mg dichloromethane at rt in an argon atmosphere. The slightly turquoise mixture was allowed to stand for 15 min at rt. *n*-Pentane was added dropwise to the solution until no more solid precipitated (~3 mL). The mother liquor was removed by means of a syringe and the off-white solid was washed three times with ~0.5 mL *n*-pentane. The solid was dissolved in ~0.2 mL dichloromethane, precipitated by adding *n*-pentane, and dried in vacuo. It yielded 220 mg (90%) of an off-white crystalline solid, mp 87 °C. ^1H NMR δ (500 MHz, CD_2Cl_2): 0.41 (s, 9H, Si−CH_3), 0.47 (s, 18H, Si−CH_3), 7.00 (s, 2H, Cp−H). ^{11}B NMR δ (CD_2Cl_2): −16.7 [s, $B(Ar^F)_4^-$]. ^{19}F NMR δ (CD_2Cl_2): −167.4 (mc, 8F, 3,5-F), −163.7 (mc, 4F, 4-F), −133.0 (mc, 8F, 2,6-F). ^{29}Si NMR δ (CD_2Cl_2): −4.39 [s, $1Si(CH_3)_3$], −3.55 [s, $2Si(CH_3)_3$]. For ESI-MS, see SI.

Synthesis of 1c. A solution of 167 mg (303 μmol) of $H^+B(SiCl_3)_4^-$ (Bochmann's acid, **10**) in 2.35 g of dichloromethane was slowly added to a solution of 101 mg (338 μmol) of decamethylsilicocene (**3a**, Z = Si) in 810 mg of dichloromethane at rt in an argon atmosphere. The color of the mixture immediately turned red. *n*-Heptane was added dropwise to the solution until no more solid precipitates. After cooling the suspension to −38 °C for 30 min, the mother liquor was removed by means of a syringe, and the solid was washed with *n*-heptane, dissolved in dichloromethane, precipitated by adding *n*-heptane again, and dried in vacuo. Yield 118 mg (55%) rose-colored crystalline solid, which decomposes at ~323 °C. ^1H NMR δ (500 MHz, CD_2Cl_2): 2.27 (s, Cp*). ^{11}B NMR δ (160.4 MHz, CD_2Cl_2): −30,7 [s, $B(SiCl_3)_4^-$], ^{29}Si satellites at −30.9 and −30.4. ^{29}Si NMR δ (99.3 MHz, CD_2Cl_2): 21.6 (q, 4 $SiCl_3$, $^1J_{Si,B}$ = 89 Hz), −399.4 (s, Cp*Si:$^+$). For ESI-MS, see SI.

Synthesis of 2d. A solution of 146 mg (266 μmol) of $H^+B(SiCl_3)_4^-$ (Bochmann's acid, **10**) in 3.18 g of dichloromethane was slowly added to a solution of 103 mg (299 μmol) of decamethylgermanocene (**3a**, Z = Ge) in 540 mg of dichloromethane at rt in an argon atmosphere. The color of the mixture immediately turned yellow. After 30 min at rt, *n*-heptane was added dropwise to the solution until no more solid precipitates. The mother liquor was removed by means of a syringe, and the solid was washed with *n*-heptane, dissolved in dichloromethane, precipitated by adding *n*-heptane again, and dried in vacuo. Yield 130 mg (65%) of a slightly yellowish crystalline solid, which decomposes at ~230 °C. ^{1}H NMR δ (500 MHz, CD_2Cl_2): 2.25 (s, Cp*). ^{11}B NMR δ (160.4 MHz, CD_2Cl_2): −30,6 [s, $B(SiCl_3)_4^-$], ^{29}Si satellites at −30.9 and −30.4. ^{29}Si NMR δ (99.3 MHz, CD_2Cl_2): 21.6 (q, 4 $SiCl_3$, $^1J_{Si,B}$ = 89 Hz). For ESI-MS, see SI.

Synthesis of 2e. A solution of 249 mg (453 μmol) of $H^+B(SiCl_3)_4^-$ (Bochmann's acid, **10**) in 2.4 mL of dichloromethane was slowly added to a solution of 305 mg (479 μmol) of hexakis(trimethylsilyl)germanocene (**3b**) in 0.8 mL of dichloromethane at rt in an argon atmosphere. The orange-colored mixture was allowed to stand for 30 min at rt. Then, 3.6 g of *n*-heptane was added dropwise to the solution until no more solid precipitated (~3.6 g). The mother liquor was removed by means of a syringe, and the off-white solid was washed two times with ~0.8 mL *n*-pentane and dried in vacuo. Yield 238 mg (58%) of an off-white crystalline solid, mp 299 °C (dec.).

^{1}H NMR δ (500 MHz, CD_2Cl_2): 0.44 (s, 9H, Si−CH_3), 0.49 (s, 18H, Si−CH_3), 7.00 (s, 2H, Cp−H). ^{11}B NMR δ (160.4 MHz, CD_2Cl_2): −30.7 [s, $B(SiCl_3)_4^-$], ^{29}Si satellites at −30.4 and −30.9. ^{29}Si NMR δ (99.3 MHz, CD_2Cl_2): −4.50 [s, 1 $Si(CH_3)_3$], −3.68 [s, 2$Si(CH_3)_3$]. For ESI-MS, see SI.

Oxidative Coupling of Triethylsilane (5, $R^1 = R^2 = R^3$ = Et) with Hexanal (6, R′ = H, R″ = *n*-C_5H_{11})—Standard Procedure. In an NMR tube, 305 mg (2.62 mmol) of triethylsilane and 282 mg (2.81 mmol, 1.07 equiv) of hexanal were mixed under an argon atmosphere. A solution of 1.6 mg (1.5 μmol, 0.059 mol %) of **2c** in 853 mg of CD_2Cl_2 was added to the tube. The contents of the tube were immediately mixed by turning the NMR tube upside down several times. The reaction was then monitored by ^{1}H NMR spectroscopy (see Figure 2 and Table 2 for results).

Hexaethyldisiloxane (Table 2, entries 1−6 and 9−11): ^{1}H NMR δ (500 MHz, CD_2Cl_2): 0.60 (q, $^3J_{H,H}$ = 8 Hz, 12H, Si−CH_2), 1.01 (t, $^3J_{H,H}$ = 8 Hz, 18H, Si−CH_2−CH_3). GC/MS: m/z = 246 (1, M^+), 217 (100, $M^+ - C_2H_5$), 189 (90, 217-C_2H_4), 161 (60, 189-C_2H_4), 115 (2, Et_3Si^+).

Di-*n*-hexyl ether (Table 2, entries 1−6 and 9−11): ^{1}H NMR δ (500 MHz, CD_2Cl_2): 0.95 (t, $^3J_{H,H}$ = 8 Hz, 6H, 2CH_3), 1.30−1.45 [m, 12H, 2(−CH_2−)$_3$], 1.59 (mc, 4H, O−CH_2−C$\underline{H}_2$), 3.41 (t, $^3J_{H,H}$ = 6.7 Hz, 4H, 2CH_2−O). GC/MS: m/z = 186 (1, M^+), 157 (1, M^+ −CH_3), 85 (100, $C_6H_{13}^+$), 43 (70, $C_3H_7^+$).

Further coupling reactions (Table 2, entries 2−7 and 9−11) were performed according to the standard procedure.

Di-2-butyl ether (Table 2, entry 7): ^{1}H NMR δ (500 MHz, CD_2Cl_2): 0.94 (2t, 6H, 2CH_3), 1.11 (mc, 6H, CH_3), 1.38−1.59, 3.39 (mc, 2H, 2CH−O). GC/MS: m/z = 130 (1, M^+), 115 (2, $M^+ - CH_3$), 101 (30, $M^+ - C_2H_5$), 57 (80, C_4H_9), 45 (100).

Di-*cyclo*-butyl Ether[13c] (Table 2, Entry 8)—Preparative Example. A mixture of 5.94 g (84.7 mmol) of cyclobutanone, 10.4 g (89.5 mmol) of triethylsilane, and 4 g of dichloromethane was prepared and warmed to 45 °C. A solution of 8.0 mg (9.0 μmol, 0.011 mol %) of **2a** in 0.5 mL of dichloromethane was added to the mixture under stirring. After 3 h at 45 °C, a second portion of 8.0 mg (9.0 μmol, 0.011 mol %) of **2a** in 0.5 mL of dichloromethane was added and heating was continued for further 6 h. After standing overnight at rt, a small amount of sodium carbonate was added and the di-*cyclo*-butyl ether was isolated by distillation using a Vigreux column. Yield 9.6 g [purity 83% (GC), 75%], bp 75 °C/60 mbar. ^{1}H NMR δ (500 MHz, CD_2Cl_2): 1.48 (qt, J = 10.7, 8.0 Hz, 1H), 1.65 (mc, 1H), 1.88 (mc, 2H), 2.14 (mc, 2H), 3.87 (mc, 1H). ^{13}C{^{1}H} NMR δ (125.8 MHz, CD_2Cl_2): 11.0, 29.1, 69.1. GC/MS: m/z = 126 (1, M^+), 98 (40, $M^+ - C_2H_4$), 70 (70, $C_4H_6O^+$), 55 (100, $C_4H_7^+$).

2,4,6-Tri-*n*-pentyl-1,3,5-trioxane (7b)[32] – Preparative Example. A solution of 5.0 mg (4.8 mmol, 0.016 mol %) of **2c** and 0.7 mL of dichloromethane was added to 3.00 g (30.0 mmol) of hexanal under stirring. The solution was cooled to −20 °C for 24 h. The product was partially crystallized. 2 N NaOH (10 μL) was under stirring, and the mixture was warmed to rt. After filtration through silica to remove the catalyst, residual hexanal and dichloromethane were removed in vacuo at 50 °C/0.1 mbar. Yield 2.55 g of **7b**, purity 96% (GC), 85%. ^{1}H NMR δ (500 MHz, CD_2Cl_2): 0.90 (t, J = 7.0 Hz, 9H, CH_3), 1.26−1.44 [m, 18H, CH_3−(C$\underline{H}_2$)$_3$], 1.59−1.66 (m, 6H, C$\underline{H}_2$−CHO), 4.84 (t, J = 5.0 Hz, 3H, O−CH−O). ^{13}C{^{1}H} NMR δ (125.8 MHz, CD_2Cl_2): 13.77 (CH_3), 22.56 (C5), 23.22 (C4), 31.61 (C3), 34.43 (C2), 101.54 (C1). GC/MS: m/z = 299 (1, M^+), 229 (3, $M^+ - C_5H_{10}$), 201 (70, $M^+ - C_6H_{10}O$), 101 (100, $C_5H_{11}CH_2O$).

Oxidative Coupling of Hydrosilanes with Paraldehyde—Standard Procedure. Hydrosilane (2 mmol), paraldehyde (101 mg, 0.76 mmol), and 300 mg of CD_2Cl_2 were mixed. A solution of the catalyst in ~50 mg of CD_2Cl_2 was added under stirring. The solution was placed in an NMR tube and warmed to 50 °C. From time to time, the formation of the coupling product was monitored by ^{1}H NMR spectroscopy. See Table 4 for details.

1,1,3,3-Tetramethyl-1,3-diphenyl-disiloxane[6f] (Table 4, entries 1, 6, and 7): ^{1}H NMR δ (500 MHz, CD_2Cl_2): 0.35 (s, 12H, CH_3), 7.3−7.4 (m, 6H, phenyl), 7.5−7.6 (m, 4H, phenyl). GC/MS: m/z = 286 (10, M^+), 271 (100, M^+ −CH_3), 193 (90), 89 (10).

1,3-Dimethyl-1,1,3,3-tetraphenyldisiloxane[6k] (Table 4, entry 2): ^{1}H NMR δ (500 MHz, CD_2Cl_2): 0.62 (s, 6H, CH_3), 7.32−7.36 (m, 8H, phenyl), 7.38−7.42 (m, 4H, phenyl), 7.53−7.57 (m, 8H, phenyl). GC/MS: m/z = 410 (10, M^+), 395 (100, M^+ −CH_3), 332 (15), 317 (90), 255 (20), 195 (55).

1,3-Dimethyl-1,3-diphenyl-1,3-divinyldisiloxane[38]—Preparative Example. To a mixture of 6.64 g (44.8 mmol) of methylphenylvinylsilane and 2.37 g (17.9 mmol) of paraldehyde (**7a**) in 1.9 g of dichloromethane was added a solution of 1.28 mg (1.24 μmol, 0.0028 mol %) of **2c** in 130 mg of dichloromethane. The mixture was heated to 50 °C for 2 h, and further, 0.51 g (3.86 mmol) of **7a** was added. After 6 h at 50 °C, the reaction mixture was filtered through a small amount of silica and volatiles were removed in vacuo. Yield 6.7 g of a colorless liquid, purity 92% (GC), 89%. ^{1}H NMR δ (500 MHz, CD_2Cl_2): 0.44 (s, 6H, CH_3), 5.83 (dd, $^3J_{HH}$(trans) = 20 Hz, $^2J_{HH}$(gem) = 3.5 Hz, 1H), 6.08 (dd, $^3J_{HH}$(cis) = 15 Hz, $^2J_{HH}$(gem) = 3.5 Hz, 1H), 6.28 (dd, $^3J_{HH}$(cis) = 20 Hz, $^3J_{HH}$(trans) = 15 Hz, 1H, Si−C$\underline{H}$=CH_2), 7.33−7.41 (m, 6H, phenyl), 7.54−7.58 (m, 4H, phenyl). ^{13}C{^{1}H} NMR δ (125.8 MHz, CD_2Cl_2): 129.76, 131.55, 135.61, 135.72, 139.38, 139.80. ^{29}Si NMR δ (99.3 MHz, CD_2Cl_2): −11.69. GC/MS: m/z = 312 (5, M^+), 297 (5, $M^+ - CH_3$), 283 (100), 205 (70), 179 (45). For further results, see Table 4, entries 3, 8, and 9.

Triisopropylethoxysilane[38] (Table 4, entry 4): ^{1}H NMR δ (500 MHz, CD_2Cl_2): 1.04−1.09 (m, 21H, isopropyl), 1.19 (t, J = 7 Hz, 3H, CH_3), 3.76 (q, J = 7 Hz, 2H, CH_2).

Synthesis of Phenyl-Siloxane Copolymers—Standard Procedure. A solution of 0.75 mg (0.72 μmol, 0.0070 mol %)

of **2c** in 0.6 g of dichloromethane was added to a mixture of 2.00 g (10.3 mmol) of bis-1,4-dimethylsilylbenzene (**9a**), 1.06 g (8.01 mmol, 1.17 equiv) of **7a**, and 1.4 g of dichloromethane under stirring at rt. The mixture was kept at 40 °C for 4.5 h. Then, a further amount of 0.15 g (1.14 mmol, 0.17 mol %) of **7a** and a solution of 0.67 mg (0.65 mmol, 0.0063 mol %) of **2c** in 0.5 g of dichloromethane and 1.2 g of dichloromethane were added and heating was continued overnight. After removal of volatiles at 110−115 °C/0.2 mbar, 2.10 g (quantitative yield) of the phenyl-siloxane polymer **8a** was obtained. ^{1}H NMR δ (500 MHz, CD_2Cl_2): 0.34 (s, 12H, $SiMe_2$), 7.55 (s, 4H, phenyl).

Phenyl-siloxane copolymers **8b** were obtained by the same procedure using mixtures of **9a** and 1,1,3,3-tetramethyldisiloxane (**9b**).

8b (from **9a**/**9b** = 1:1): ^{1}H NMR δ (500 MHz, CD_2Cl_2): 0.08−0.16 (12H, $SiMe_2O_{2/2}$), 0.35−0.44 (12H, Ph−$SiMe_2$), 7.58−7.63 (4H, phenyl).

8b (from **9a**/**9b** = 1:3): ^{1}H NMR δ (500 MHz, CD_2Cl_2): 0.05−0.11 (36H, $SiMe_2O_{2/2}$), 0.32−0.36 (12H, Ph−$SiMe_2$), 7.55−7.57 (4H, phenyl).

8b (from **9a**/**9b** = 1:6): ^{1}H NMR δ (500 MHz, CD_2Cl_2): 0.04−0.15 (64H, $SiMe_2O_{2/2}$), 0.32−0.37 (12H, Ph−$SiMe_2$), 7.54−7.59 (4H, phenyl).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.oprd.0c00214.

> NMR spectra of catalysts **1** and **2**; ESI-MS data of catalysts **1c** and **2c−e**; DSC measurements of copolymers; and X-ray crystal structure data of **2a** (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

[†] In memoriam Prof. Dr. Rolf Huisgen (1920−2020).

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