

# $[(\eta^5\text{-Cp}^R)\text{Ge}]^+ [\text{BAr}^F_4]^- / \text{O}_2$ – A Sustainable and Efficient Catalytic System for the Hydrosilylation of Selected Olefins

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The cationic Ge(II) borates  $[(\eta^5\text{-Cp}^R)\text{Ge}]^+ [\text{BAr}^F_4]^-$  ( $\text{Cp}^R$  = substituted cyclopentadienyl) efficiently catalyze the *anti*-Markovnikov hydrosilylation of alkenes in the presence of oxygen which is investigated using the examples of  $\alpha$ -methylstyrene and 1-hexene. Full conversion is achieved with a minimal amount of 0.01 mol% of the cationic Ge(II) borate even at rt. The effect of oxygen is investigated and quantified by kinetic measurements

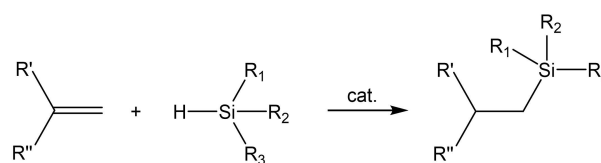
which demonstrate that oxygen is an activator which interacts directly with the germanium complex. Solvent-free hydrosilylation conditions are realized by the introduction of a more lipophilic silylated borate counteranion. Thus, the novel catalytic system is an efficient, sustainable and air-stable catalyst alternative for the established hydrosilylation catalysts based on noble metal complexes.

## Introduction

The *anti*-Markovnikov hydrosilylation of carbon-carbon double bonds<sup>[1–11]</sup> (Scheme 1) is one of the most useful reaction in organosilicon chemistry in order to form silicon-carbon bonds. It is widely used to introduce organic residues into silanes and (poly)siloxanes by stable Si–C linkers and also for the industrially important process of silicone elastomer cross-linking which is the basis of a great variety of consumer products.<sup>[4–6]</sup>

*Anti*-Markovnikov hydrosilylations are very exothermic reactions, but they are kinetically inhibited and therefore require catalysis. Various noble metal complexes, mainly of platinum,<sup>[1–6]</sup> are well established catalysts for the process. Recent developments for their replacement include first-row transition metal complexes,<sup>[7–11]</sup> e.g. of cobalt, nickel,<sup>[10]</sup> iron,<sup>[10]</sup> and manganese.<sup>[11]</sup> However, their comparably complicated synthesis and extreme sensitivity against air and moisture still limit applications. Moreover, the increased environmental awareness has intensified the demand to find alternatives for catalysts based on heavy metals because of their potential environmental impacts mainly related to mining, toxicity and persistency. These problems may be amplified by the fact that the catalysts often remain in the products and cannot be recycled. Therefore, attractive alternatives would be catalysts based on the lighter p-block compounds.

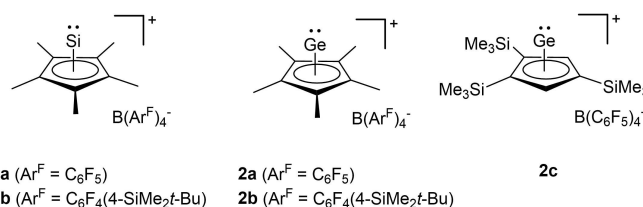
The Lewis-acidic compounds  $\text{B}(\text{C}_6\text{F}_5)_3$ ,<sup>[12]</sup>  $\text{Al}(\text{C}_6\text{F}_5)_3$ ,<sup>[13]</sup> and cationic phosphorus(III)<sup>[14]</sup> and (V) compounds<sup>[15]</sup> are de-



**Scheme 1.** *Anti*-Markovnikov hydrosilylation of carbon-carbon double bonds.<sup>[1–11]</sup>

scribed to catalyze hydrosilylation reactions of alkenes. However, catalyst amounts of 5 mol% or even more are required to achieve full conversion. Furthermore, it was demonstrated that cationic Si(IV)<sup>[16]</sup> and Ge(IV) hydronium structures<sup>[17]</sup> also catalyze C=C hydrosilylation reactions acceptably.<sup>[18]</sup>

We have found in preceding work that the cationic Si(II) compounds  $[(\eta^5\text{-Cp}^*)\text{Si}]^+ [\text{BAr}^F_4]^-$  **1a** and **1b** ( $\text{Cp}^*$  = pentamethylcyclopentadienyl,  $\text{Ar}^F = \text{C}_6\text{F}_5$ ,  $\text{C}_6\text{F}_4(4\text{-SiMe}_2\text{-t-Bu})$ ) which are stabilized by weakly coordinating polyfluorinated borate anions (Scheme 2) catalyze C=C hydrosilylation reactions with an unprecedented stability, selectivity and efficiency.<sup>[19,20]</sup> With very low amounts of < 0.01 mol% of **1** we achieved high yields of the *anti*-Markovnikov hydrosilylation products.

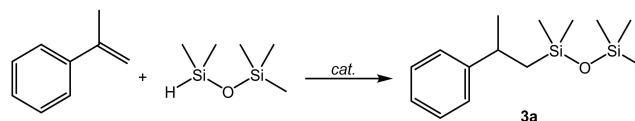


**Scheme 2.**  $\text{Cp}^*$ -coordinated ( $\text{Cp}^*$  = pentamethylcyclopentadienyl) cationic Si(II) compounds **1a**, **1b**<sup>[19,20]</sup> and  $\text{Cp}^R$ -coordinated [ $\text{Cp}^R$  = pentamethylcyclopentadienyl, tris(trimethylsilyl)cyclopentadienyl] Ge(II) compounds **2a–c**<sup>[20,21]</sup> stabilized by weakly coordinating perfluorinated borate anions.

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However, the rather complicated synthesis of **1a**<sup>[19,22,23]</sup> and **1b**<sup>[19,20]</sup> and their high sensitivity against air and moisture limit their broader application in hydrosilylation reactions. Therefore, further improvements would be desirable.



**Scheme 3.** Hydrosilylation of  $\alpha$ -methylstyrene with pentamethyldisiloxane (PMDS), formation of the *anti*-Markovnikov product **3a**.

## Results and Discussion

Herein, we extend our search for hydrosilylation catalysts to the heavier congeners of the promising Si(II)<sup>+</sup> compounds, the Ge(II)<sup>+</sup> compounds. This class of compounds is already known to be more tolerant against moisture.<sup>[20,21]</sup> To-date, however, there are only few reports of homogeneous catalysis based on this class of compounds which only cover hydroboronation<sup>[24,25]</sup> and Si–O–Si coupling reactions.<sup>[20,21]</sup>

The cationic Ge(II) borates  $[(\eta^5\text{-Cp}^R)\text{Ge}]^+[\text{BAR}^F]_4^-$  [Cp<sup>R</sup> = substituted cyclopentadienyl, Ar<sup>F</sup> = C<sub>6</sub>F<sub>5</sub>, C<sub>6</sub>F<sub>4</sub>(4-SiMe<sub>2</sub>*t*-Bu)] **2a–c** (Scheme 2) are especially attractive as catalysts because they are readily available from GeCl<sub>4</sub>.<sup>21</sup> This makes these compounds particularly interesting for the hydrosilylation of carbon-carbon double bonds.

We have chosen the standard hydrosilylation reaction<sup>19</sup> of  $\alpha$ -methylstyrene by pentamethyldisiloxane (PMDS) (Scheme 3) for our investigation. Following the hydrosilylation protocol developed for the catalysts **1a** and **1b**,<sup>[19]</sup> all steps were performed in Ar atmosphere (mode A in Table 1).

However, with **2a** (Table 1, entry 1) and also with the modified compounds **2b** and **2c** (entries 2, 3) instead of **1a** we observed only minimal product formation. Neither the 10-fold molar amount of the cationic Ge(II)<sup>+</sup> borate **2a** (Table 1, entry 4) nor higher temperatures of 70 and 100 °C (entries 5, 6) caused hydrosilylation. A hydrosilylation reaction was also not achieved by using toluene-*d*<sub>8</sub> (Table 1, entry 7) instead of CD<sub>2</sub>Cl<sub>2</sub> as a solvent. Neither removing the 4-*tert*-butylcatechol which is present in the commercial  $\alpha$ -methylstyrene in small amounts as stabilizer (Table 1, entry 8), nor the addition of small amounts of water (entry 9) had a noticeable effect.

The Si–H bond activation through formation of a Si–H–Si bridge was assumed to be the initial step in the catalytic cycle for **1a**, and evidence was given by coalescence of the Si–H signal in the <sup>1</sup>H NMR after addition of 0.1 mol % **1a** to a solution of PMDS.<sup>[19]</sup> Similar activating complexes are formulated with the electrophilic hydrosilylation catalysts B-

**Table 1.** Hydrosilylations of alkenes catalyzed by **2a**, **2b** and **2c**.

entry	alkene	sil(ox)ane <sup>[a]</sup>	catalyst (mol %)	solvent (w/w %)	mode	T (°C)	t (h)/ conversion (%) <sup>[b]</sup>	yield (%) <sup>[c]</sup>
1	$\alpha$ -methylstyrene	PMDS <sup>[d]</sup>	<b>2a</b> (0.11)	CD <sub>2</sub> Cl <sub>2</sub> (40)	A <sup>[e]</sup>	24	47/0	–
2	$\alpha$ -methylstyrene	PMDS	<b>2b</b> (0.11)	CD <sub>2</sub> Cl <sub>2</sub> (60)	A	24	0.3/0.5; 3.3/0.7; 28/2	–
3	$\alpha$ -methylstyrene	PMDS	<b>2c</b> (0.10)	CD <sub>2</sub> Cl <sub>2</sub> (61)	A	25	1/1; 5/1; 28/7	–
4	$\alpha$ -methylstyrene	PMDS	<b>2a</b> (1.01)	CD <sub>2</sub> Cl <sub>2</sub> (40)	A	24	12/1.4; 24/2.6	–
5	$\alpha$ -methylstyrene	PMDS	<b>2a</b> (0.11)	CD <sub>2</sub> Cl <sub>2</sub> (40)	A	70	22/0.6	–
6	$\alpha$ -methylstyrene	PMDS	<b>2a</b> (0.10)	CD <sub>2</sub> Cl <sub>2</sub> (10)	A	100	6/0	–
7	$\alpha$ -methylstyrene	PMDS	<b>2a</b> (0.11)	toluene- <i>d</i> <sub>8</sub> (40)	A	24	24/0; 48/0	–
8	$\alpha$ -methylstyrene <sup>[f]</sup>	PMDS	<b>2a</b> (0.10)	CD <sub>2</sub> Cl <sub>2</sub> (40)	A	70	26/0	–
9	$\alpha$ -methylstyrene	PMDS	<b>2a</b> (0.10)	CD <sub>2</sub> Cl <sub>2</sub> (60)	A <sup>[g]</sup>	24	24/0	–
10	$\alpha$ -methylstyrene	PMDS	<b>2b</b> (0.10)	CD <sub>2</sub> Cl <sub>2</sub> (51)	B <sup>[h],[i]</sup>	22	0.3/1; 3/91; 27/99 <sup>[k]</sup>	> 97
11	$\alpha$ -methylstyrene	PMDS	<b>2b</b> (0.11)	CD <sub>2</sub> Cl <sub>2</sub> (57)	C1 <sup>[l]</sup>	24	0.3/1; 3/28; 27/85; 51/96; 75/98 <sup>[m]</sup>	> 97
12	$\alpha$ -methylstyrene	PMDS	<b>2a</b> (0.10)	CD <sub>2</sub> Cl <sub>2</sub> (60)	C2 <sup>[n]</sup>	24	4/9; 20/90	> 97
13	$\alpha$ -methylstyrene	PMDS	<b>2c</b> (0.11)	CD <sub>2</sub> Cl <sub>2</sub> (61)	C2	50	1/82; 5/99	> 97
14	$\alpha$ -methylstyrene	PMDS	<b>2a</b> (0.10)	CD <sub>2</sub> Cl <sub>2</sub> (60)	D <sup>[o]</sup>	[p]	1/100	> 97
15	$\alpha$ -methylstyrene	PMDS	<b>2b</b> (0.010)	CD <sub>2</sub> Cl <sub>2</sub> (50)	E	24	24/99	> 97
16	$\alpha$ -methylstyrene	PhMe <sub>2</sub> SiH	<b>2a</b> (0.11)	CD <sub>2</sub> Cl <sub>2</sub> (64)	C2	21	4/0; 27/95	95 <sup>[q]</sup>
17	$\alpha$ -methylstyrene	PhMe <sub>2</sub> SiH	<b>2b</b> (0.093)	CD <sub>2</sub> Cl <sub>2</sub> (64)	C2	21	2/20; 6/93; 29/95	95 <sup>[q]</sup>
18	1-hexene <sup>[r]</sup>	PMDS	<b>2b</b> (0.10)	CD <sub>2</sub> Cl <sub>2</sub> (65)	C2	22	29/0	–
19	1-hexene <sup>[r]</sup>	PMDS	<b>2b</b> (0.23)	CD <sub>2</sub> Cl <sub>2</sub> (66)	C2	50	4/89; 22/95	75 <sup>[s]</sup>
20	$\alpha$ -methylstyrene	PMDS	<b>2a</b> (0.012)	no solvent <sup>[t]</sup>	C2	21	3/0; 27/19; 49/78; 73/90	> 95
21	$\alpha$ -methylstyrene	PMDS	<b>2b</b> (0.011)	no solvent <sup>[t]</sup>	C2	22	0.3/0; 3/23; 27/79; 50/99	> 95
22	$\alpha$ -methylstyrene	PMDS	<b>2b</b> (0.019)	no solvent <sup>[t]</sup>	C2	50	1/17; 4/69; 10/89; 22/99	> 95
23	$\alpha$ -methylstyrene	PMDS	<b>2b</b> (0.0042)	no solvent <sup>[t]</sup>	C2	22	0.3/0; 3.5/7; 8/36; 51/37; 71/37	> 95

[a] Molar ratio alkene: sil(ox)ane = 1 : 1, standard procedure with 1.71 mmol alkene. [b] Conversion of alkene, monitored by <sup>1</sup>H NMR. [c] Determined by <sup>1</sup>H NMR. [d] Pentamethyldisiloxane. [e] Synthesis of **2a** and all further steps performed in Ar atmosphere. [f] 4-*tert*-Butylcatechol was removed by filtration over neutral alumina. [g] **2a** was dissolved in water-saturated CD<sub>2</sub>Cl<sub>2</sub> which contained ~0.15 w/w % of water. [h] 6.81 mmol  $\alpha$ -methylstyrene and 6.80 mmol PMDS. [i] Synthesis of **2b** and all further steps performed in Ar atmosphere, the reaction was performed in air. [k] After 27 h  $\alpha$ -methylstyrene and PMDS (molar ratio 1 : 1) were added again. [l] 1 mL of air (~9  $\mu$ mol O<sub>2</sub>, ~5 eq. in relation to **2b**) were added to the reaction mixture prepared in Ar atmosphere. [m] After 75 h  $\alpha$ -methylstyrene and PMDS (molar ratio 1 : 1) were again added. [n] 3 mL of air (~27  $\mu$ mol O<sub>2</sub>, ~15 eq. in relation to **2a**) were added to the reaction mixture prepared in Ar atmosphere. [o] The solid **2a** was in air for 23 h before it was used in the reaction. [p] Exothermic reaction. [q] 4% of dimethyldiphenylsilane were formed by Si–H/Si–Ph redistribution reaction, see Scheme 4. [r] 1.1 Equiv of 1-hexene. [s] Lower yield caused by a competing redistribution reaction of PMDS, the following products were identified by GC/MS analysis: dimethylsilane, trimethylsilane, hexamethyldisiloxane, octamethyltrisiloxane, hexyldimethylsilane, hexyltrimethylsilane. [t] The solid catalyst was added to the reaction mixture.

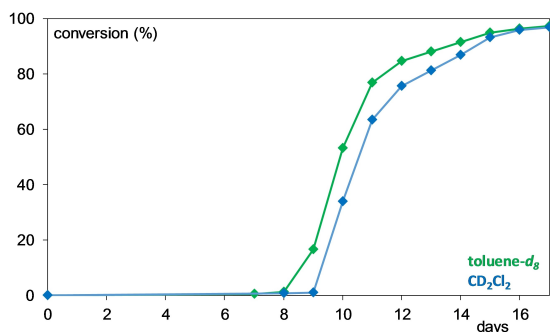
(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>[12]</sup> and Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>[13]</sup>. However, in contrast to **1a**, the addition of compound **2a** to a PMDS solution did not have a broadening effect on the Si–H signal which is a first indication that there may be basic differences in the behavior of the cationic Si(II)<sup>+</sup> compound **1a** and the corresponding Ge(II)<sup>+</sup> compound **2a**.

However, when we allowed air contact of the complete reaction mixture prepared in Ar atmosphere (mode B in Table 1), the hydrosilylation proceeded and was almost complete after 3 h (Table 1, entry 10) rendering the *anti*-Markovnikov adduct **3a** with a selectivity of more than 97% (Scheme 3). Also the addition of air in certain small amounts (molar 5-fold and 15-fold amount of oxygen, mode C1 and C2 in Table 1) with respect of compounds **2a–c** (Table 1, entries 11, 12, 13) to the reaction mixture by a syringe induced the hydrosilylation reaction. It should be mentioned here that neither air nor oxygen alone does cause any hydrosilylation reaction when the cationic Ge(II)<sup>+</sup> compounds **2a** or **2b** are not present.

The influence of oxygen may be also impressively shown by the following experiment: NMR samples of the complete reaction mixture in CD<sub>2</sub>Cl<sub>2</sub> and in toluene-*d*<sub>8</sub>, respectively, were prepared in Ar, sealed with a standard plastic stopper and then kept in ambient air at rt. The hydrosilylation started after ~8 or 9 days – that was obviously the time when sufficient oxygen has managed to diffuse into the NMR tube to start the reaction (Figure 1).

Moreover, when **2a** was in contact with air as a solid for 23 h and then added to the reaction mixture under Ar (mode D in Table 1) a spontaneous exothermic hydrosilylation reaction was observed which was already complete within one hour (Table 1, entry 14), indicating that oxygen directly activates **2a**. In the NMR spectrum of the solid **2a**, however, there were no additional signals visible. As a consequence, the catalytic system is expected to be active in minimal amounts.

Our results prompted us to investigate the effect of oxygen activation of the cationic Ge(II)<sup>+</sup> borates **3** more closely. For that purpose, solutions of compound **2a** in CD<sub>2</sub>Cl<sub>2</sub> were treated for individual times (1 min – 23 h), with a constant flow of pure oxygen in order to maintain a defined constant oxygen concentration of ~0.18 mg/mL O<sub>2</sub> (5.6 μmol/mL O<sub>2</sub>) in CD<sub>2</sub>Cl<sub>2</sub>,<sup>[26]</sup>



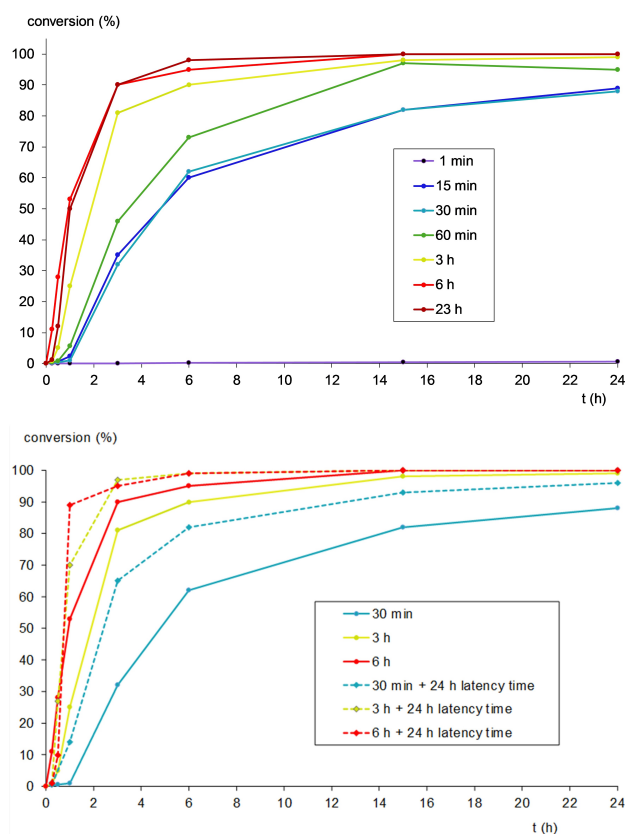
**Figure 1.** Course of the hydrosilylation reaction of 1:1 mixtures of  $\alpha$ -methylstyrene and PMDS in toluene-*d*<sub>8</sub> (60% w/w) and in dichloromethane-*d*<sub>2</sub> (60% w/w) at rt in the presence of 0.11 mol% **2a** in NMR tubes sealed by a standard plastic stopper.

then degassed and added to an equimolar test mixture of  $\alpha$ -methylstyrene and PMDS in CD<sub>2</sub>Cl<sub>2</sub> under Ar.

The propagation of the catalyzed hydrosilylation reaction was then monitored by <sup>1</sup>H NMR spectroscopy. Figure 2 shows the results. Oxygen contact of **2a** for 1 min was not sufficient to initiate the reaction. Longer times, such as 15 min or more, were effective, and the hydrosilylation reaction proceeded almost without an induction period (Figure 2, top). The time of oxygen treatment had a positive influence on the reaction rate, whereas longer treatment times > 6 h had no further accelerating effect on the hydrosilylation reaction. As can be seen from Figure 2, bottom, the catalytic activity of the combination **2a**/O<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub> further increased when it was stored in Ar for 24 hours (latency time) before it was added to the reaction mixture.

The product solution was still catalytically active as was shown by repeated addition of the educts which reacted to completion (Table 1, entries 10, 11 and experimental section). That means that the catalytic system is not deactivated during the reaction.

For preparative applications the hydrosilylation procedure can be simplified by allowing air contact during all steps of the procedure. Under these conditions full conversion was reached after 24 h already with 0.01 mol% of **2b** (Table 1, entry 15).



**Figure 2.** Top: Kinetics of the hydrosilylation reaction between  $\alpha$ -methylstyrene and PMDS after treatment of **2a** (0.11 mol%) in CD<sub>2</sub>Cl<sub>2</sub> with O<sub>2</sub> for individual times; Bottom: Solutions of **2a** in CD<sub>2</sub>Cl<sub>2</sub> were allowed to stand at rt for 24 h (latency time) after O<sub>2</sub> treatment and then added to the hydrosilylation mixture at rt. See experimental section for details.

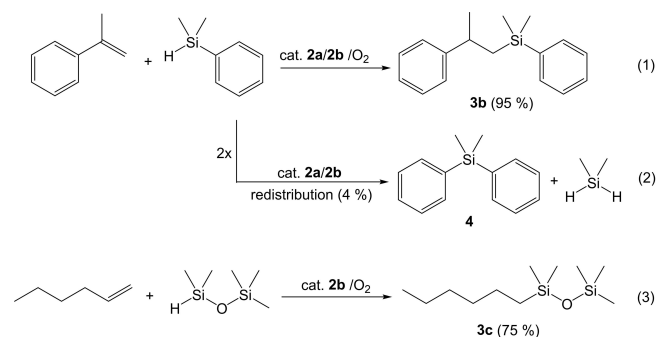
All hydrosilylation experiments of  $\alpha$ -methylstyrene and PMDS gave the *anti*-Markovnikov product **3a** (Scheme 3) in high yields > 97%.

There is no evidence that  $\text{Cp}^R\text{Ge(II)}/\text{O}_2$  promotes the formation of radical intermediates. EPR signals were not detected neither in a solution of **2a** activated by oxygen nor in the complete reaction mixture containing  $\alpha$ -methylstyrene and PMDS. Moreover, the *tert*-butylcatechol in the commercial  $\alpha$ -methylstyrene as a radical trap to inhibit polymerization did not have any noticeable effect on the course of the hydrosilylation reaction.

The reaction between  $\alpha$ -methylstyrene and dimethylphenylsilane at rt also rendered the *anti*-Markovnikov product **3b** in high yields (Table 1, entries 16 and 17, Scheme 4). Small amounts (4%) of dimethyldiphenylsilane **4** were identified as a side product due to a so-called redistribution reaction between the Si–H and Si–phenyl groups which is already known for various Si–H compounds in the presence of electrophilic reagents.<sup>[20,27,28]</sup>

1-Hexene needed higher temperatures ( $\sim 50^\circ\text{C}$ ) to be hydrosilylated by PMDS (Table 1, entries 18 and 19, Scheme 4). Under these conditions the *anti*-Markovnikov product **3c** was formed in good yields (75%). We detected the already known redistribution products of PMDS<sup>[20,27,28]</sup> as side products.

The compounds **2a–c** are completely dissolved in the reaction mixtures in the presence of dichloromethane as a solvent. Solvent free conditions, however, would be preferred under environmental aspects and sustainability. Under neat conditions, the catalysts did not dissolve completely and the hydrosilylation reaction was slower than in the presence of  $\text{CD}_2\text{Cl}_2$  (Table 1, entries 20–23). Whereas we observed no larger difference in activity between the compounds **2a** and **2b** in  $\text{CD}_2\text{Cl}_2$ , compound **2b** with the borate anion  $\{\text{B}[\text{C}_6\text{F}_4(4\text{-SiMe}_2\text{tBu})_4]_4\}^-$ , however, proved to be more active than **2a** which can be attributed to the higher lipophilicity of the anion thus enhancing the solubility of the precatalyst. The reaction mixtures were homogeneous at  $50^\circ\text{C}$  (Table 1, entry 22), and the reaction went to completion in  $\sim 22$  h with only 0.019 mol% **2b**. As can be seen from Table 1, the



**Scheme 4.** Hydrosilylation of  $\alpha$ -methylstyrene with dimethylphenylsilane [Equation (1), Table 1, entries 16 and 17], competing redistribution reaction leading to dimethyldiphenylsilane **4** [Equation (2)]; hydrosilylation of 1-hexene with PMDS [Equation (3), Table 1, entries 18 and 19].

amount of the catalyst system necessary for complete conversion is in the range of  $\sim 0.01$  mol% which corresponds to turnover numbers (TON) of 10000 demonstrating the high potential of  $[(\eta^5\text{-Cp}^R)\text{Ge}]^+[\text{BAR}^F_4]^-/\text{O}_2$  as a novel catalytic system for the *anti*-Markovnikov hydrosilylation of olefins.

## Conclusion

$[(\eta^5\text{-Cp}^R)\text{Ge}]^+[\text{BAR}^F_4]^-/\text{O}_2$  ( $2/\text{O}_2$ ) is a novel air-stable catalyst system for the regioselective *anti*-Markovnikov hydrosilylation of carbon-carbon double bonds at rt. Whereas the compounds **2** proved to be catalytically inactive in an oxygen-free environment, they can be activated by small amounts of oxygen. The unprecedented oxygen effect was further investigated by kinetic measurements which demonstrate the high reactivity of  $[(\eta^5\text{-Cp}^R)\text{Ge}]^+[\text{BAR}^F_4]^-/\text{O}_2$ .

In contrast to the established catalysts based on platinum, the hydrosilylation reaction with  $[(\eta^5\text{-Cp}^R)\text{Ge}]^+[\text{BAR}^F_4]^-/\text{O}_2$  can be performed at rt without an induction period which may be important on safety reasons. Solvent-free hydrosilylation conditions are advantageously realized when the cation  $[(\eta^5\text{-Cp}^R)\text{Ge}]^+$  is combined with the lipophilic silylated borate  $\{\text{B}[\text{C}_6\text{F}_4(4\text{-SiMe}_2\text{tBu})_4]_4\}^-$ .

Since the cationic Ge(II) compounds **2** are readily available from  $\text{GeCl}_4$  which is a by-product in the production of zinc<sup>[29]</sup> and are considered as non-toxic,<sup>[30–32]</sup> the new catalyst system contributes to the growing demand to use environmentally friendly catalyst systems instead of heavy metals in applications based on C=C hydrosilylation and opens new perspectives in main group catalysis.

## Experimental Section

**Analytical Methods.** All  $^1\text{H}$  NMR spectra were measured with a Bruker Avance 500 spectrometer. EPR experiments were performed on a Magnettech MiniScope MS 5000 bench-top spectrometer. Baseline corrections were done by subtracting a spectrum of the solvent  $\text{CD}_2\text{Cl}_2$ . GC: Agilent Technologies, HP 5 column (polydimethylsiloxane with 5% phenyl groups), length 30 m, internal diameter 0.25 mm, film thickness 0.25  $\mu\text{m}$ , injector temp.  $290^\circ\text{C}$ , detector FID,  $320^\circ\text{C}$ , carrier gas He. GC-MS: Agilent Technologies, GC unit 6890 N, column Agilent HP-5MS UI, injector temperature  $250^\circ\text{C}$ , MS unit 5975 C, EI, 70 eV.

**Materials.** Pentamethyldisiloxane (PMDS), 1-hexene,  $\alpha$ -methylstyrene and dimethylphenylsilane were commercially available from Sigma-Aldrich and used without further purification. For the experiment of entry 8 in Table 1 the 4-*tert*-butylcatechol inhibitor in the  $\alpha$ -methylstyrene was removed by filtration over a short column of neutral alumina. Compounds **2a**, **2b** and **2c** were made according to ref.<sup>[21]</sup> Oxygen gas (purity > 99.5%) was available from Linde.

**Hydrosilylation reaction in  $\text{CD}_2\text{Cl}_2$ -standard procedure** (Table 1). A mixture of the olefin (1.71 mmol) and hydridosil(ox)ane (1.72 mmol) in 680 mg of  $\text{CD}_2\text{Cl}_2$  was prepared in an NMR tube at rt. Then, a solution of the compound **2** (1.94  $\mu\text{mol}$ , 0.11 mol%) in 150 mg  $\text{CD}_2\text{Cl}_2$  was added by a syringe, and the contents of the NMR tube were mixed by shaking the tube. At definite times  $^1\text{H}$  NMR spectra were recorded. For individual reaction conditions see Table 1.

Ph-CH(CH<sub>3</sub>)-CH<sub>2</sub>-SiMe<sub>2</sub>O-SiMe<sub>3</sub> (**3a**, entries 10–14): <sup>1</sup>H NMR δ (CD<sub>2</sub>Cl<sub>2</sub>): 0.00 (2 s, 2 CH<sub>3</sub>), 0.12 (s, 3 CH<sub>3</sub>), 1.00 (mc, CH<sub>2</sub>), 1.33 (d, *J* = 7 Hz, CH<sub>3</sub>), 2.98 (mc, CH), 7.15–7.34 (5 arom. H); <sup>29</sup>Si NMR δ (CD<sub>2</sub>Cl<sub>2</sub>): 6.58 (s), 7.32 (s).

Ph-CHMe-CH<sub>2</sub>-SiMe<sub>2</sub>Ph (**3b**, entries 16 and 17) <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 0.43 (s, 3H, Si-CH<sub>3</sub>), 0.49 (s, 3H, Si-CH<sub>3</sub>), 1.56 (d, 3H, *J* = 7.0, CH<sub>3</sub>), 1.47–1.57 (mc, 2H, CH<sub>2</sub>), 3.19 (mc, 1H, *J* = 7.5 Hz, CH), 7.41–7.48 (mc, 3H, o/p C-phenyl), 7.51–7.55 (m, 2H, m-C-phenyl), 7.61–7.63 (m, 3H, o/p Si-phenyl), 7.78–7.80 (m, 2H, m-Si-phenyl).

C<sub>5</sub>H<sub>11</sub>-CH<sub>2</sub>-SiMe<sub>2</sub>-O-TMS (**3c**, entries 18 and 19) <sup>1</sup>H NMR δ (CD<sub>2</sub>Cl<sub>2</sub>): 0.10 (s, SiMe<sub>2</sub>), 0.13 (s, TMS), 0.54 (mc, Si-CH<sub>2</sub>), 0.90 (mc, CH<sub>3</sub>), 1.2–1.4 (4 CH<sub>2</sub>). <sup>29</sup>Si NMR δ (CD<sub>2</sub>Cl<sub>2</sub>): 7.00, 7.64. GC-MS: *m/z* = 232 (0.1, M<sup>+</sup>), 217 (15, M<sup>+</sup>-CH<sub>3</sub>), 159 (2, M<sup>+</sup>-TMS), 147 (100, TMS-O-SiMe<sub>2</sub>), 133 (50).

**Mode A** (Table 1, entries 1–9): synthesis of compounds **2a–c** and all following steps were performed in Ar atmosphere.

**Mode B** (Table 1, entry 10): **2b** and reaction mixture prepared in Ar atmosphere, reaction performed under air.

**Mode C1** (Table 1, entry 11): 1 mL of air (~9 μmol O<sub>2</sub>) was added to the complete reaction mixture in Ar atmosphere.

**Mode C2** (Table 1, entry 12 and 13): 3 mL of air (~26 μmol O<sub>2</sub>) were added to the complete reaction mixture in Ar atmosphere.

**Mode D** (Table 1, entry 14): solid **2a** was in contact with air for 23 h and added to the reaction mixture as a solid in Ar atmosphere.

**Mode E** (Table 1, entry 15): all steps were performed in air.

**Repeated Addition of Educt Mixture** (Table 1, entries 10 and 11).

**Entry 10:** In Ar atmosphere 804.7 mg (6.81 mmol) *α*-methylstyrene and 1009 mg (6.80 mmol) PMDS were mixed and dissolved in 924 mg of CD<sub>2</sub>Cl<sub>2</sub> in a round bottom flask equipped with a reflux condenser to minimize losses of solvent by evaporation. A solution of 9.2 mg (7.23 μmol) **2b** in 940 mg CD<sub>2</sub>Cl<sub>2</sub> was added under stirring at 22 °C. The mixture was then allowed to react in air (**Mode B**) for 27 h. At that time the formation of the hydrosilylation product **3a** was complete. Then, a mixture of 301 mg (2.55 mmol) of *α*-methylstyrene and 376 mg (2.53 mmol) of PMDS was added. The reaction ran to completion after 28 h. Then, a mixture of 805 mg (6.81 mmol) *α*-methylstyrene and 1003 mg (6.76 mmol) of PMDS was added. After 24 h the conversion was 93%.

**Entry 11:** To the product mixture according to Table 1, entry 11, obtained by the standard procedure, was added a mixture of 74.5 mg (0.63 mmol) of *α*-methylstyrene and 91.5 mg (0.62 mmol) of PMDS and 1 mL air (~9 μmol O<sub>2</sub>). T (h) / conversion (%): 0.3/74; 4/97; 28/98; 76/99. Then, a mixture of 75.7 mg (0.64 mmol) *α*-methylstyrene and 93.5 mg (0.63 mmol) PMDS and 1 mL air (~9 μmol O<sub>2</sub>) were added, t (h) / conversion (%): 0.3/79; 4/89; 28/96.

**Table 2.** Conversion of hydrosilylation reaction after oxygen treatment of **2a**.

t(h) <sup>a</sup>	1 min <sup>b</sup>	15 min	30 min	60 min	3 h	6 h	23 h
0	0	0	0	0	0	0	0
0.25	0	0.6	0.3	0.5	0.8	11	1.2
0.5	0	0.6	0.5	0.8	5.0	28	12
1	0.1	2.3	1.0	5.6	25	53	50
3	0.1	35	32	46	81	90	90
6	0.2	60	62	73	90	95	98
15	0.5	82	82	97	98	100	100
24	0.6	89	88	95	99	100	100

<sup>a</sup>time of hydrosilylation reaction, <sup>b</sup>time of oxygen treatment

**Table 3.** Conversion of hydrosilylation reaction after oxygen treatment of **2a**. Influence of latency time.

t(h) <sup>a</sup>	30 min	30 min + 24 h <sup>b</sup>	3 h	3 h + 24 h	6 h	6 h + 24 h <sup>b</sup>
0	0	0	0	0	0	0
0.25	0.3	0.6	0.8	1.2	11	0.9
0.5	0.5	–	5.0	27	28	9.9
1	1.0	14	25	70	53	89
3	32	65	81	97	90	95
6	62	82	90	99	95	99
15	82	93	98	100	100	100
24	88	96	99	100	100	100

<sup>a</sup>time of hydrosilylation reaction, <sup>b</sup>time of oxygen treatment + latency time (under Ar)

**Entry 15:** All steps were performed in ambient air (**Mode E**). A 5 mL round-bottom flask was equipped with a magnetic stirrer and a reflux condenser to minimize losses of solvent by evaporation. 801 mg (6.78 mmol) *α*-methylstyrene and 1005 mg (6.78 mmol) PMDS were mixed in the flask and diluted with 900 mg CD<sub>2</sub>Cl<sub>2</sub> under stirring at rt. Then, a solution of 0.9 mg (0.708 μmol, 0.010 mol%) **2b** in 922 mg CD<sub>2</sub>Cl<sub>2</sub> was added with stirring. The mixture was allowed to stand at rt for 24 h to reach complete conversion.

**Activation of 2a by oxygen treatment, kinetic experiments.** **2a** (1.6 mg, 1.7 μmol) was dissolved in 120 mg of CD<sub>2</sub>Cl<sub>2</sub>. A constant flow of 0.05 mL min<sup>-1</sup> O<sub>2</sub> (2 μmol min<sup>-1</sup>) was bubbled through the solution by means of a needle for a definite time, see Table 2. Then, the solution was degassed by means of Ar and added to a solution of 203 mg (1.72 mmol) of *α*-methylstyrene and 254 mg (1.71 mmol) of PMDS in 900 mg CD<sub>2</sub>Cl<sub>2</sub>. The hydrosilylation reaction was monitored by <sup>1</sup>H NMR spectroscopy. For results see Table 2 and Figure 2 (top).

In a further series of experiments, after oxygen treatment and degassing, the solution of **2a** in CD<sub>2</sub>Cl<sub>2</sub> was allowed to stand for definite times and was then added to the mixture of *α*-methylstyrene and PMDS in CD<sub>2</sub>Cl<sub>2</sub>. The hydrosilylation reaction was monitored by <sup>1</sup>H NMR spectroscopy. For results see Table 3 and Figure 2 (bottom).

**EPR experiments.** O<sub>2</sub> was bubbled through a solution of 16 mg (17 μmol) of **2a** in 1.3 g of CD<sub>2</sub>Cl<sub>2</sub> for 6 h, the solution was then degassed by means of Ar. In the EPR measurement there were no EPR signals visible. Then, 200 μL of the catalyst solution were added to a solution of 205 mg (1.73 mmol) of *α*-methylstyrene and 259 mg (1.75 mmol) of PMDS in 900 mg of CD<sub>2</sub>Cl<sub>2</sub>. EPR measurements were performed after ~30 min. and after ~1 h. There were no EPR signals visible.

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## Conflict of Interests

The author declares no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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