Main Group Catalysis: Cationic Si(II) and Ge(II) Compounds as Catalysts in Organosilicon Chemistry

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Abstract: Cyclopentadienyl (Cp)-coordinated cationic Si(II) (1) and Ge(II) compounds (2) are a new class of catalysts for various transformations in organosilicon chemistry. This review demonstrates that these compounds effectively catalyze technically important reactions, such as the hydrosilylation of carbon-carbon multiple bonds and various types of siloxane-coupling reactions, e.g., the Piers-Rubinsztajn reaction and the oxidative siloxane coupling reaction. Whereas the cationic Si(II) compounds are sensitive to air and moisture, the corresponding cationic Ge(II) compounds are bench stable, thus offering further advantages. The new catalysts contribute to the growing need for the substitution of transition metals and heavier main group metals by their lighter congeners, especially in industrially relevant organosilicon chemistry.

Keywords: cationic Cp-coordinated Si(II) and Ge(II) compounds; main group catalysis; silanes; (poly)siloxanes; hydrosilylation; Piers-Rubinsztajn (PR) reaction; redistribution; siloxane coupling reaction; condensation; copolymers; crosslinking

1. Introduction

Transition metal complexes, often of precious metals, have for a long time been thought to be unique as catalysts because of their open coordination sphere and their capability to reversibly change their oxidation states [1]. Later on, catalytically active main group compounds were found [1,2]. Whereas the heavier main-group elements more resemble transition metals [3,4] and are favored in research, their lighter congeners, however, are far more attractive for practical applications because they are more abundant on earth. More recently, even early main group organometallic compounds were found to be catalytically active, thus contradicting the traditional view that the prevalence of various oxidation states is a prerequisite for catalysis [5,6].

Moreover, there is a growing need to find alternatives for catalysts based on heavy metals because of their environmental issues related to mining, toxicity and persistency. These aspects are especially to be considered in industrial organosilicon chemistry, where catalysts based on heavy metals are of growing concern.

In order to move towards sustainable and environmentally friendly catalyst systems, attractive candidates would be the lighter p-block compounds. In the last decade, Lewis-acidic compounds based on boron (recent articles and reviews [7–10]), carbocations (recent articles and reviews [11–14]), phosphorus(III) and (V) cations (recent articles and reviews [15–18]), including frustrated Lewis pairs (FLPs) (recent articles and reviews [19–21]), have moved into the focus of catalysis.

Up to now, there are only few examples of catalysts based on electrophilic silicon or germanium compounds. Various electrophilic Si(IV) compounds are known to catalyze the hydrosilylation of aldehydes [22], hydrodefluorination reactions [23] and the crosscoupling of arylsilanes and fluorohydrocarbons [24]. Cationic Ge(II) compounds stabilized by iminato- [25] and carbene-ligands [26] catalyze hydroboration reactions of aldehydes and ketones with pinacolborane (H-Bpin). Moreover, hydrogen-bridged cationic bis(silylium)
and bis(germylium) compounds are known to catalyze the hydrosilylation of carbon-carbon double bonds [27,28].

The cyclopentadienyl (Cp)-coordinated cationic Si(II) and Ge(II) compounds 1 and 2, respectively (Scheme 1), however, should be good candidates for catalysis because of their open coordination sphere [29,30] which facilitates the interaction with various substrates being a good prerequisite for catalysis. In 2011, Jutzi [31] reported the first example of a reaction with Me₅CpSi⁺ B(ArF)₄⁻ (1a, Ar⁺ = C₆F₅) as a catalyst: the degradation of oligo(ethyleneglycol) ethers with 5-10 mol% of this compound (Scheme 2). But for several years this remained the only example for using this class of compounds as catalysts.

\[
\begin{align*}
\text{Si:} & \quad \text{WCA}^- \\
\text{Ge:} & \quad \text{WCA}^- \\
R_n & = \text{Me₅} \\
R_n & = \text{Me₅, 1,2,4-(TMS)}_3
\end{align*}
\]

Scheme 1. Catalytically active cyclopentadienyl (Cp)-coordinated cationic Si(II) and Ge(II) compounds 1 and 2. Me = methyl, TMS = trimethylsilyl, WCA = weakly coordinating anion.

\[
\text{RO-(CH₂CH₂)ₙ}R' \xrightarrow{1a \text{ 5-10 mol%}} \frac{n}{2} \frac{\text{O} + R/R'-O-R/R'}{\text{C₂H₄} + \text{R/R'-O-R/R'}}
\]

R, R' = Me, Et, Me₅Si
n = 1-10

Scheme 2. Degradation of oligo(ethyleneglycol) ethers using Me₅CpSi⁺ B(ArF)₄⁻ (1a) as catalyst [31].

This review covers the use of Cp-coordinated cationic Si(II) compounds 1 and their heavier analogs, the cationic Ge(II) compounds 2, as catalysts for important reactions in the field of organosilicon chemistry: the hydrosilylation of carbon-carbon multiple bonds, Si-H/Si-O-Si redistribution processes, and various siloxane coupling reactions.

2. Synthesis and Properties of Cp-Coordinated Cationic Si(II)⁺ (1) and Ge(II)⁺ Compounds (2)

Precursors of 1 and 2 are the corresponding tetralcenes 3 and 4, which are made by various organometallic transformations [32–35].

\[
\begin{align*}
\text{Si:} & \quad R_n \\
\text{Ge:} & \quad R_n \\
R_n & = \text{Me₅} \\
R_n & = \text{Me₅, 1,2,4-TMS}_3
\end{align*}
\]

The conversion of 3 and 4 into the cationic species 1 and 2 can be performed by selective protonation of one of the Cp residues [29,30,33] using a Brønsted acid with a weakly-coordinating anion (WCA) which is essential to stabilize the cationic center of the products 1 and 2, see Equations (1a) and (1b), and Table 1.
Table 1. Synthesis of catalysts 1 and 2 by selective protonation of tetracenes 3 and 4.

| Entry | Educt | Rₙ | H⁺[WCA]⁻ | Product | Number | Ref. |
|-------|-------|----|----------|---------|--------|------|
| 1     | 3     | Me₅ | H⁺(OEt)₂B(ArF)₄⁻ | Me₅CpSi⁺B(ArF)₄⁻ | 1a     | [33] |
| 2     | 3     | Me₅ | H⁺B(SiCl₃)₄⁻ | Me₅CpSi⁺B(SiCl₃)₄⁻ | 1b     | [30] |
| 3     | 4     | Me₅ | H⁺B(SiCl₃)₄⁻ | Me₅CpGe⁺B(SiCl₃)₄⁻ | 2b     | [30] |
| 4     | 4     | 1,2,4-TMS₃ | H⁺(OEt)₂B(ArF)₄⁻ | (1,2,4-TMS)₂CpGe⁺B(ArF)₄⁻ | 2c     | [30] |
| 5     | 4     | 1,2,4-TMS₃ | H⁺B(SiCl₃)₄⁻ | (1,2,4-TMS)₃CpGe⁺B(SiCl₃)₄⁻ | 2d     | [30] |

¹ Protonated pentamethycyclopentadiene, Me₅C₅H₅⁺B(ArF)₄⁻, was originally used instead of H⁺(OEt)₂B(ArF)₄⁻, for the synthesis of 1a [29]. ² Bochmann’s acid [30], for synthesis see ref. [36].

\[(\text{Me}_5\text{Cp})_2\text{Si} : \text{H}^+ [\text{WCA}]^{-} \rightarrow (\text{Me}_5\text{Cp})\text{Si}^{+} [\text{WCA}]^{-} + R_1\text{CpH} \quad (1a)\]

\[(\text{R}_3\text{Cp})_2\text{Ge} : \text{H}^+ [\text{WCA}]^{-} \rightarrow (\text{R}_3\text{Cp})\text{Ge}^{+} [\text{WCA}]^{-} + R_1\text{CpH} \quad (1b)\]

\[\begin{align*}
(\text{Me}_5\text{Cp})_2\text{Si} : &\quad \text{Ph}_3\text{C}^+ [\text{WCA}]^{-} + \text{Ph}_3\text{CH} + \quad (2a) \\
(\text{Me}_5\text{Cp})_2\text{Ge} : &\quad \text{Ph}_3\text{C}^+ [\text{WCA}]^{-} + \text{Ph}_3\text{CH} + \quad (2b) \\
(\text{Me}_5\text{Cp})_2\text{Si} : &\quad \text{B}(\text{ArF})_3^{-} \rightarrow (\text{Me}_5\text{Cp})\text{Si}^{+} [\text{HB}(\text{ArF})_3]^{-} + \quad (3)
\end{align*}\]

The perfluorinated phenylboranate and aluminate anions are well established as WCAs. Recently, however, a novel fluorine-free WCA, the tetrakis(trichlorosilyl) boronate anion, B(SiCl₃)₄⁻, was successfully introduced for the first time by reacting the tetracenes 3 and 4 with H⁺B(SiCl₃)₄⁻, Bochmann’s acid [30,36] (Table 1, entries 2, 3 and 5).

For Me₅Cp-ligands, an attractive alternative to the protonation reaction is the hydride abstraction from one of the methyl groups using an electrophilic tritylium salt, Ph₃C⁺[WCA]⁻ (Equations (2a) and (2b), Table 2) [37]. In this case, 1,2,3,4-tetramethylfulvene is formed from one of the permethylated Cp residues. B(ArF)₃ can also be used as a hydride acceptor in order to make Me₅CpSi⁺[HB(ArF)₃]⁻ from decamethylsilicocene 3 (Rₙ = Me₅) (Equation (3), and Table 2, entry 7).

Scheme 3 gives an overview of the synthesized structures.

Table 2. Synthesis of catalysts 1 and 2, by hydride transfer reaction from the corresponding tetracenes 3 and 4 to electrophiles [30,37].

| Entry | Educt | Electrophile | Product | Number | Ref. |
|-------|-------|--------------|---------|--------|------|
| 1     | Si    | Ph₃C⁺B(ArF)₄⁻ | Me₅CpSi⁺B(ArF)₄⁻ | 1a     | [37] |
| 2     | Ge    | Ph₃C⁺B(ArF)₄⁻ | Me₅CpGe⁺B(ArF)₄⁻ | 2a     | [30] |
| 3     | Si    | Ph₃C⁺B(C₆F₅)₄⁻ | Me₅CpSi⁺[C₆F₅]₄⁻ | 1e     | [37] |
| 4     | Si    | Ph₃C⁺Al[OCC(CF₃)₃]₁⁻ | Me₅CpSi⁺[Al[OCC(CF₃)₃]₁⁻ | 1f     | [37] |
| 5     | Ge    | Ph₃C⁺Al[OCC(CF₃)₃]₁⁻ | Me₅CpGe⁺[Al[OCC(CF₃)₃]₁⁻ | 2f     | [37] |
| 6     | Si    | Ph₃C⁺Al[OCC(CF₃)₃]₁⁻ | Me₅CpSi⁺[Al[OCC(CF₃)₃]₁⁻ | 1g     | [37] |
| 7     | Si    | B(ArF)₃ | Me₅CpSi⁺[HB(ArF)₃]⁻ | 1h     | [37] |
Whereas the compounds 1 are sensitive to air and moisture [37], the corresponding Ge(II) compounds 2 are completely bench-stable for several days. A crystalline sample of 2a, for example, was exposed to ambient air for 30 days and showed no change in the NMR spectrum [30].

3. Cp-Coordinated Si(II) and Ge(II) Compounds 1 and 2 as Catalysts in Organosilicon Chemistry

3.1. Hydroisilylation of Carbon-Carbon Double Bonds

The hydroisilylation of carbon-carbon double bonds (Scheme 4) is the most important reaction to introduce organic residues into silanes and siloxanes. Furthermore, it is the basis for the industrially performed elastomer crosslinking process. Noble metal complexes, mainly of platinum, rhodium and iridium, are widely used as hydroisilylation catalysts leading to anti-Markovnikov products [38–41]. Some progress has been made in the development of catalysts based on first-row transition metals, especially Co and Ni [42,43]. However, the limited options of recycling and the possible environmental and toxicological impacts of heavy metals, especially in consumer products, now stimulate the development of transition metal free hydroisilylation catalysts. It was already shown that the highly electrophilic B(ArF)3 [44,45] and a phosphorus(III) dication [46] catalyze C-C hydroisilylations, but catalyst amounts of 5 mol% are necessary in both cases to get full conversion. For B(ArF)3 this can be attributed to its chemical instability against Si-H groups, and various catalytically inactive follow-up products of B(ArF)3 were detected [47].
Scheme 4. Hydrosilylation of carbon-carbon double bonds [38].

It was found recently [37], that the cationic Cp-coordinated Si(II) compounds 1a and 1e very efficiently catalyze the hydrosilylation of terminal olefins with various silicon hydrides to give selectively the anti-Markovnikov products in high yields (Scheme 5). Amounts of less than 0.1 mol% are sufficient in most cases to achieve full conversion at temperatures between 25 and 50 °C (Table 3). For the very reactive combination of α-methylstyrene (R1 = Ph, R2 = Me) and pentamethyldisiloxane (R3 = R4 = Me, R5 = OTMS) the hydrosilylation product is formed quantitatively with only 0.0013 mol% of 1a (Table 3, entry 8) which corresponds to a turnover number (TON) of about 80,000 and is in the range obtained with platinum-based catalysts. When 0.012 mol% of 1a are used for this transformation, the product mixture still contains the active catalyst (Table 3, entry 9) thus offering the opportunity of catalyst recycling.

Scheme 5. Hydrosilylation of C-C double bonds using the cationic Cp-coordinated Si(II) compounds 1a and 1e [37].

Table 3. Selected hydrosilylations [37] catalyzed by 1a in CD2Cl2.

| Entry | R1   | R2   | R3  | R4  | R5  | Mol% 1a | T (°C) | Yield (%) |
|-------|------|------|-----|-----|-----|---------|--------|-----------|
| 1     | Ph   | Me   | Et  | Et  | Et  | 0.1     | 50     | >98       |
| 2     | Ph   | Me   | Me  | Me  | Ph  | 0.06    | 50     | >98       |
| 3     | Ph   | Me   | Me  | OSiMe3 | OSiMe3 | 0.2     | 25     | >98       |
| 4     | Ph   | Me   | Me  | Me  | Cl  | 0.1     | 25     | 90        |
| 5     | n-C4H9 | H  | Me  | Me  | OSiMe3 | OSiMe3 | 0.09    | 25     | 98        |
| 6     | n-C4H9 | H  | Me  | OSiMe3 | OSiMe3 | 0.05    | 25     | 81        |
| 7     | n-C4H9 | H  | Me  | Me  | Cl  | 0.1     | 50     | >90       |
| 8     | Ph   | Me   | Me  | Me  | OSiMe3 | 0.0013  | 25     | >97.1     |
| 9     | Ph   | Me   | Me  | Me  | OSiMe3 | 0.012   | 25     | >90       |
| 10.2  | Ph   | Me   | Me  | Me  | OSiMe3 | 0.012   | 25     | >90       |
| 11.2  | Ph   | Me   | Me  | Me  | OSiMe3 | 0.0096  | 25     | >98.3     |

1 Product mixture contains the active catalyst 1a [37]; 2 neat conditions; 3 catalyst 1e used under neat conditions.

The catalytic activity of the cationic Si(II) compound 1a depends on the reaction medium. Chlorinated solvents enhance the catalytic activity of 1a, probably because they support the separation of ion pairs. In this context, the nature of the anion is also important for catalytic activity. Whereas 1a and 1e are highly active, the tetrakis(trichlorosilyl)boronate 1b, the perfluorosilyl aluminates 1f and 1g and the hydrogen boronate 1h are only weakly active as catalysts [37]. Internal double bonds are less reactive than terminal double bonds, as was shown for cyclohexene and norbornene using 1a [37], but they can be completely hydrosilylated at higher temperatures [37]. The hydrosilylations of vinyl and ethynyl groups directly attached to silicon proceed comparatively slowly and give a mixture of coupling products due to a competing redistribution reaction, as outlined in Scheme 6 (1) and (2) (for further redistribution reactions see Section 3.2). Nevertheless, the technically important silicone elastomer crosslinking, which is based on the hydrosilylation...
of polysiloxanes with terminal vinyl groups and hydridosiloxanes, could be demonstrated successfully with the more lipophilic 1e under adapted conditions (Scheme 6 (3)) [37].

\[
\begin{align*}
\text{Me}_2\text{Si} & \quad + \quad \text{HSiEt}_3 \\
\text{cat.} 1e & \quad \xrightarrow{\text{redistribution}} \\
{\text{cat.} 1e} & \quad \xrightarrow{\text{catalyst}} \quad \text{Me}_2\text{Si}^{-} \quad + \quad \text{HSiMe}_3 \\
\text{redistribution} & \quad \xrightarrow{\text{catalyst}} \quad \text{Me}_2\text{Si}^{-} \quad + \quad \text{SiEt}_3
\end{align*}
\]

(1)

\[
\begin{align*}
\text{Me}_2\text{Si} & \quad + \quad \text{HSiEt}_3 \\
\text{cat.} 1e & \quad \xrightarrow{\text{redistribution}} \\
{\text{cat.} 1e} & \quad \xrightarrow{\text{catalyst}} \quad \text{Me}_2\text{Si}^{-} \quad + \quad \text{HSiMe}_3 \quad + \quad \text{SiEt}_3
\end{align*}
\]

(2)

\[
\begin{align*}
\text{Me}_2\text{Si}^{-} & \quad + \quad \text{HSiEt}_3 \\
\text{cat.} 1e & \quad \xrightarrow{\text{redistribution}} \\
{\text{cat.} 1e} & \quad \xrightarrow{\text{catalyst}} \quad \text{Me}_2\text{Si}^{-} \quad + \quad \text{HSiMe}_3 \quad + \quad \text{SiEt}_3
\end{align*}
\]

(3)

Scheme 6. Hydrosilylation of Si-bound vinyl and ethynyl groups in CD$_2$Cl$_2$ [24]. (1): 0.48 mol% 1a, after 50 h at 50 °C 30% conversion; (2): 0.1 mol% 1a, after 40 h at 50 °C 44% conversion; (3): elastomer crosslinking with 0.27% w/w 1e, 1 h at 130 °C, and a picture of the elastomer product [48].

It is assumed that the hydrosilylation follows a cationic mechanism [37], as was also proposed for the electrophilic catalyst B(ArF)$_3$ [44,45,49]. The initial Si-H bond activation by the cationic Si(II) compound can be rationalized by NMR where the Si-H coupling of triethylsilane broadens after addition of 0.1 mol% 1a indicating the formation of a hydrogen-bridged complex (Scheme 7) [37]. Interestingly, for the corresponding cationic Ge(II) compounds 2 there is no evidence in the NMR for a Si-H interaction with the cationic Ge(II) center, and, in accordance with this, these compounds are catalytically inactive in the hydrosilylation of C-C multiple bonds. However, it was found recently that cationic Ge(II) compounds 2 can be activated in the presence of oxygen [50].

Scheme 7. Activation of Si-H by a Me$_5$CpSi$^+$ catalyst, reversible deactivation of Me$_5$CpSi$^+$ by alkoxysil(ox)ane inhibitor, re-activation of the catalyst by the Piers-Rubinsztajn (PR) reaction which consumes the alkoxysil(ox)ane at higher temperatures [37].

Furthermore, it was found that the hydrosilylation catalyzed by the Me$_5$CpSi$^+$ can be completely inhibited at room temperature by small amounts of an alkoxysil(ox)ane which is coordinatively bound to the cationic center of the catalyst (Scheme 7) [37]. At higher temperatures, however, the alkoxysil(ox)ane is quickly consumed by a Piers-Rubinsztajn (PR) reaction (see Section 3.3) with the hydrosil(ox)ane present in the mixture [37], thus
offering a simple way to thermally induce hydrosilylation. This is an established technology in Pt-catalyzed silicone rubber manufacturing in order to guarantee a certain pot life of the fluid hydrosilylation mixture at ambient temperatures, so that on-demand curing can be performed by increasing the temperature [38].

3.2. Redistribution Reactions of Hydridosil(ox)anes

In the presence of catalyst 1a, hydridosil(ox)anes may undergo redistribution (exchange) reactions with various reactive groups X bound to a Si center (Scheme 8, top). As was already outlined in Section 3.1, the hydrosilylation of Si bound carbon-carbon double and triple bonds is accompanied by competing Si-H/Si-vinyl and Si-H/Si-ethynyl redistribution reactions (Scheme 6 (1) and (2)). Further redistribution reactions can be observed with Si-bound phenyl groups (Scheme 8 (1)) and alkoxy groups (Scheme 8 (2)) [37] for pentamethyldisiloxane (5a) in the presence of catalytic amounts of 1a when reactive hydrosilylatable multiple bonds are not available as reaction partners.

![Scheme 8](image_url)

Scheme 8. Redistribution reactions catalyzed by 1a. (1): Si-H/Si-Ph redistribution, equilibrium mixture after 24 h at rt in CD₂Cl₂ contains 27 mol% dimethyldiphenylsilane and 27 mol% dimethyldisiloxane (6); (2): Si-H/Si-OEt redistribution [37]; (3) and (4): multistep Si-H/Si-O-Si redistribution of siloxanes with terminal Si-H groups leading to polysiloxanes [31].

In the absence of hydrosilylatable olefins, the Si-H/Si-O-Si redistribution proceeds in a cascade-like manner in the presence of 0.1 mol% 1a and 1h, finally leading to linear polysiloxanes and hydridosilanes (Scheme 8 (3) and (4)) [51]. This redistribution reaction was also observed with catalytic amounts of B(ArF)₃ [52]. In contrast to B(ArF)₃, however, the formation of cyclosiloxanes advantageously was not observed with 1a [52]. Pentamethyldisiloxane 5a (Scheme 8) gives a mixture of polysiloxanes with Si-Me and Si-H end groups, dimethyl- (6) and trimethylsiloxane (7) [51]. Tetramethyldisiloxane 5b, selectively gives a polysiloxane with Si-H end groups on both sides and dimethylsiloxane (6). Therefore, this transformation is practically useful to make H-terminated polysiloxanes, and moreover for a non-hazardous production of gaseous 6.

The proposed mechanism of the complex multistep Si-H/Si-O-Si redistribution reaction of hydridosiloxanes is outlined in Scheme 9 in a simplified manner. After the activation of Si-H groups by the catalyst 1a, stabilized oxonium ions and Me₅CpSiH are formed. Finally, hydride transfer from Me₅CpSiH gives silanes and oligosiloxanes, which react further to give the final products.
Scheme 9. Proposed mechanism for the redistribution of siloxanes with terminal Si-H groups 5a (X = Me) and 5b (X = H) in the presence of catalytic amounts of 1a or, alternatively, 1h; AC = activated complex [37,51,52].

Hydridosiloxanes with Si-H side groups give crosslinked siloxanes and hydridosilanes [53,54]. The reaction course is represented in simplified form in Scheme 10. However, when the disproportionation reaction is performed in the presence of an excess of hexamethyldisiloxane, TMS-branched polysiloxanes can be made selectively (Scheme 10) [55].

Scheme 10. Redistribution reactions of linear siloxanes with lateral Si-H groups give branched and finally crosslinked siloxanes in the presence of 1a [53]. With excess hexamethyldisiloxane, however, linear TMS branched siloxanes are formed [55].
3.3. Siloxane Coupling Reactions

Making siloxanes is probably the most important technical process in organosilicon chemistry. The hydrolysis and condensation of chlorosilanes (Scheme 11) is widely applied especially for the production of silicone fluids, but it requires special techniques to recycle hydrogen chloride quantitatively, to remove excess water in order to achieve complete condensation of silanol groups, and to neutralize small amounts of acid which would cause unwanted degradation processes in the products. Siloxanes are also made from alkoxysilanes, which are produced by counter flow processes from chlorosilanes and then condensed hydrolytically. It is necessary to catalyze this process by acid or, alternatively, by organometallic tin compounds which are now banned due to environmental issues [56,57].

![Scheme 11](image)

Scheme 11. Hydrolytic siloxane condensation processes.

Therefore, siloxane coupling reactions which proceed under non-aqueous conditions are an important target.

A reaction which meets this target is the condensation of alkoxysil(ox)anes and hydridosil(ox)anes which is called the Piers-Rubinsztajn (PR) reaction (Scheme 12). The state-of-the-art catalyst for this reaction is B(ArF)_3 [9]. However, it was found recently that the Si(II) based catalysts 1a, 1e and 1h catalyze the PR reaction very efficiently with only ~0.1 mol% of catalyst in a minimum of solvent without significant catalyst deactivation [37]. Table 4 and Scheme 12 display some products obtained with the most efficient catalyst 1h. Important products obtained by the PR reaction are siloxane copolymers such as 8 and 9 from bifunctional building blocks and a regularly branched linear siloxane 10.

![Scheme 12](image)

Scheme 12. The Piers-Rubinsztajn (PR) reaction (top) and products 8-10 obtained by use of 1h as a catalyst. Bonds marked bold red are formed during the reaction. For starting materials and conditions, see Table 4.
Reactions

Reactions

PEER REVIEW at not the Table 37), pylethoxysilane was already shown in Section 3.1, Scheme 7, they remain coordinated, which facilitates Table 4. gives 21% of Et3SiMe2-H (Equiv.)

The further transformation into siloxane and ether (Scheme 13) [30]. Evidence for the further transformation into siloxane and ether (Scheme 13) [30]. Alkoxysilanes are formed in the first step of the redox reaction, but, as was already shown in Section 3.1, Scheme 7, they remain coordinated, which facilitates the further transformation into siloxane and ether (Scheme 13) [30]. Evidence for the suggested mechanism is also given by the fact that tri-i-propylsilane gives mainly tri-i-propylethoxysilane (Table 5, entry 14), and the reductive coupling of methylmethyleketone gives 21% of Et3Si-O-CH(CH3)CH2CH3 as a second product. Here, the complexation of two alkoxysilane units is sterically disfavored.

Table 4. Piers-Rubinsztajn (PR) reaction of ethoxysilanes (Si-OEt) and hydridosil(ox)anes (Si-H) catalyzed by 1h in the presence of 5–10% w/w dichloromethane as a solvent [37].

| Product | Si-OEt | Si-H | Mol% 1e | T (°C)/t (h) | Yield (%) |
|---------|--------|------|---------|-------------|-----------|
| (PMDSI)2SiPh2 | Ph2Si(OEt)2 | TMS-O-SiMe2-H | 0.0014 | 60/4 | >95 |
| (ClMe2SiO)2SiPh2 | Ph2Si(OEt)2 | Me3 CSI-H | 0.13 | 60/2 | >95 |
| 8 | Ph2Si(OEt)2 | 1,4-(SiMe2H)benzene | 0.11 | 60/2 | >95 |
| 9 | Ph2Si(OEt)2 | H-SiMe2-O-SiMe2-H | 0.10 | 60/2 | >95 |
| 10 | Me3SiOEt | TMS-O-D₈ | 0.033 | 60/1 | >95 |

1 PMDSI = pentamethylsiloxanylidene; 2 Mν = 18,600, Mn = 5040; 3 Mν = 8100, Mn = 4300; 4 D = Me2SiO, D Hip = MeH2SiO.

One issue with the PR reaction, however, arises especially in large-scale processes. Usually, alkoxysilanes of lower alcohols are used, and therefore the PR reaction produces gaseous hydrocarbons, which makes bulk procedures difficult to be managed in a safely controlled manner.

The oxidative coupling of hydridosil(ox)anes which is catalyzed by the Cp-coordinated cationic Si(II) and Ge(II) compounds 1 and 2 (Scheme 13) however, is a further anhydrous alternative which avoids safety issues [17]. In this procedure, aldehydes are used as oxidants for Si-H groups which are themselves reduced to ethers. The reaction is very fast, with catalyst amounts of ~0.06 mol% and gives the corresponding siloxanes in high yields. Because Si-H and carbonyl reactants can be used stoichiometrically, this method is also suitable to make symmetrical ethers from aldehydes, see Table 5. For example, cyclobutanone was successfully coupled to bis(cyclobutyl) ether (Table 5, entry 10).

Scheme 13. Anhydrous oxidative siloxane coupling using aldehydes or ketones and simultaneous formation of ethers catalyzed by Cp-coordinated cationic Si(II) and Ge(II) compounds 1 and 2. Paraldehyde (R = Me, R’ = H) can be used as an in situ source for acetaldehyde [30].

As can be seen from Table 5, both cationic Si(II) and Ge(II) compounds are catalytically active, and, in contrast to the findings for the hydrosilylation reaction (Section 3.1, [37]), there is no pronounced influence of the counter anion on the catalytic activity.

The supposed mechanism of the redox coupling with aldehydes is given in Scheme 14. The carbonyl groups of R’CH=O are activated by coordination to the electrophilic catalytic center [30]. Alkoxysilanes are formed in the first step of the redox reaction, but, as was already shown in Section 3.1, Scheme 7, they remain coordinated, which facilitates the further transformation into siloxane and ether (Scheme 13) [30]. Evidence for the suggested mechanism is also given by the fact that tri-i-propylsilane gives mainly tri-i-propylethoxysilane (Table 5, entry 14), and the reductive coupling of methylmethyleketone gives 21% of Et3Si-O-CH(CH3)CH2CH3 as a second product. Here, the complexation of two alkoxysilane units is sterically disfavored.
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Table 5. Oxidative coupling of hydridosil(ox)anes (Si-H) by aldehydes and ketones (C=O) and simultaneous reductive coupling to ethers in the presence of catalysts 1 and 2 [30]. Entries 1–9 performed at room temperature, entries 10–19 at 50 °C.

| Entry | Si-H              | Oxidant (Equiv.)          | Catalyst (Mol%) | Yield (%) |
|-------|-------------------|---------------------------|-----------------|-----------|
| 1     | Et3Si-H           | hexanal (1.0)             | 1a (0.059)      | 96/96     |
| 2     | Et3Si-H           | hexanal (1.0)             | 1f (0.061)      | 97/97     |
| 3     | Et3Si-H           | hexanal (1.0)             | 2a (0.062)      | >95/>95   |
| 4     | Et3Si-H           | hexanal (1.0)             | 2f (0.062)      | 97/97     |
| 5     | Et3Si-H           | hexanal (1.1)             | 2c (0.059)      | 97/97     |
| 6     | Et3Si-H           | hexanal (1.0)             | 1b (0.065)      | 97/97     |
| 7     | Et3Si-H           | hexanal (1.0)             | 2b (0.065)      | 98/98     |
| 8     | Et3Si-H           | hexanal (1.1)             | 2d (0.059)      | 98/98     |
| 9     | Et3Si-H           | methylethylketone         | 1a (0.050)      | 79/79 2   |
| 10    | Et3Si-H           | cyclobutanone (0.9)       | 2a (0.01)       | 95/>90    |
| 11    | Ph3MeSi-H         | paraldehyde (1.1)         | 2a (0.0055)     | 97 4      |
| 12    | Ph2MeSi-H         | paraldehyde (1.1)         | 2a (0.0065)     | 96 4      |
| 13    | PhVi3MeSi-H       | paraldehyde (1.1)         | 2a (0.0029)     | 95 4      |
| 14    | (i-C3H7)2Si-H     | paraldehyde (1.1)         | 2a (0.0058)     | 6         |
| 15    | Et3Si-H           | paraldehyde (1.1)         | 2d (0.0500)     | 98        |
| 16    | PhMe2Si-H         | paraldehyde (1.1)         | 2d (0.0027)     | 97 4      |
| 17    | PhMe2Si-H         | paraldehyde (1.1)         | 2d (0.0001)     | 98 4      |
| 18    | PhViMeSi-H        | paraldehyde (1.1)         | 2d (0.0054)     | 94 4      |
| 19    | PhViMeSi-H        | paraldehyde (1.1)         | 2d (0.0027)     | 95 4      |

1 Formed products siloxane/ether; 2 21% Et3Si-O-CH(CH3)CH2CH3; 3 phenyl; 4 yield of diethylether not determined; 5 vinyl; 6 main products: 68% (i-C3H7)Si-OEt and 15% (i-C3H7)Si-OH.

Scheme 14. Catalytic cycle of the oxidative coupling reaction of R3Si-H using aldehydes R’CHO in the presence of cationic Cp-coordinated Si(II) and Ge(II) compounds 1 and 2, with Cp* = substituted Cp residue, such as Me5Cp or (SiMe3)3Cp [30].

Aldehydes are generally preferred for the coupling of siloxanes because they are more reactive than ketones, and the simplest aldehyde for that purpose would be acetaldehyde. However, with acetaldehyde, the coupling proceeds very vigorously and is very exothermic and therefore difficult to control. Because the catalysts 1 and 2 very efficiently catalyze the reversible cyclotrimerization of aldehydes, paraldehyde can be advantageously used as a source for the in situ production of acetaldehyde, which is continuously consumed by the redox process (Scheme 13). Entries 11–19 in Table 5 demonstrate that high yields
of siloxane coupling products are obtained at very low catalyst amounts in the range of 0.005 mol%.

Because the oxidative coupling reaction is a very fast and selective reaction, it is especially suitable for the synthesis of siloxane copolymers. The incorporation of phenyl units into siloxane polymers is an important target because phenyl groups have an influence on the mechanical properties and make siloxanes compatible with organic polymers. Moreover, phenyl groups modify the optical properties of polysiloxanes. They enhance the light absorption and refractive index of a siloxane polymer. By the oxidative coupling reaction, the novel phenyl-siloxane copolymer 11a was made from the monomer 12 (Scheme 15). For the optimization of the polymer properties, e.g., chain flexibility, the siloxane monomer 13 was successfully copolymerized with 12 to give the copolymer 11b with a quasi-statistical distribution of phenyl and siloxane groups controlled by the ratio of 12 and 13.

Scheme 15. Synthesis of phenyl siloxane copolymers 11a and 11b by oxidative coupling of monomers 12 and 13 using paraldehyde and catalysts 1 or 2. Bonds in red are formed during the oxidative coupling process [30].

4. Conclusions

The synthesis and catalytic potential of cationic Cp-coordinated Si(II) and Ge(II) compounds is reviewed for the first time. These compounds proved to be efficient catalysts for various transformations in organosilicon chemistry.

Cp-coordinated cationic Si(II) compounds are very efficient catalysts for the hydrosilylation of carbon-carbon double bonds and for the Piers-Rubinsztajn reaction. Redistribution processes of hydridosiloxanes in the presence of cationic Si(II) compounds are useful to make hydridosilanes, Si-H terminated linear siloxanes, and for the crosslinking of siloxanes with lateral Si-H groups.

The cationic Si(II) and Ge(II) compounds 1 and 2 efficiently catalyze the oxidative coupling of siloxanes using aldehydes as oxidants—a non-hazardous alternative to the Piers–Rubinsztajn reaction. Paraldehyde can be advantageously used as an in situ source for acetaldehyde. This procedure was successfully applied to make a new class of siloxane-p-phenylene copolymers.

In contrast to the cationic Si(II) compounds, the corresponding Ge(II) compounds are stable against air and moisture and readily available, making them particularly useful under synthetic aspects. Finally, the tetrakis(trichlorosilyl) boronate anion, B(SiCl3)4–, was successfully introduced into the cationic Si(II) and Ge(II) structures as a novel stable fluorne-free weakly coordinating anion. Since germanium compounds are regarded as non-toxic [58], this combination perfectly meets the target of modern environmentally friendly catalyst systems.
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