

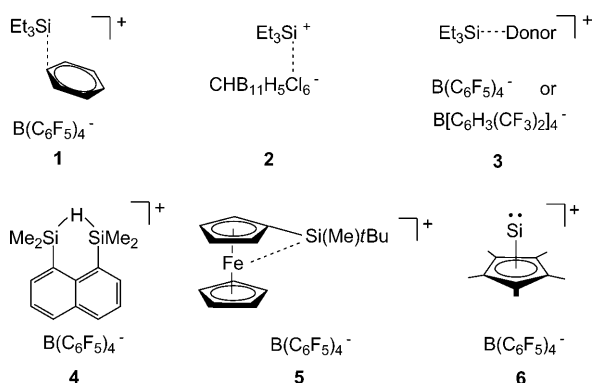
Silicon(II) Compounds

The Pentamethylcyclopentadienylsilicon(II) Cation as a Catalyst for the Specific Degradation of Oligo(ethyleneglycol) Diethers**

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Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 70th birthday

Covalent silicon(IV) compounds of the type R_3SiX (R = organic substituent, X = electronegative group) have long been used as catalysts for several organic reactions, mainly in carbon–carbon bond-forming processes (such as Diels–Alder reactions, aldol condensations).^[1] Some ionic silicon(IV) compounds containing R_3Si^+ cations have also been applied as catalysts in C–C bond formation reactions and in some other transformations.^[2] The most important examples are collected in Scheme 1.



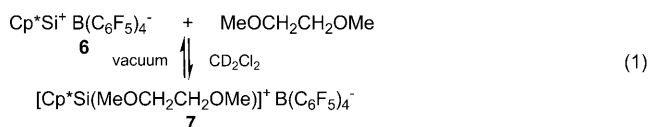
Scheme 1. Organosilicon cations in catalysis.

Compound **1**, containing the benzene-stabilized triethylsilyl cation,^[3] was used as a catalyst for the hydrosilylation of 1,1-diphenylethene^[4] and later as a catalyst in aldol and in Diels–Alder reactions.^[5] Furthermore, compound **1** was chosen as the catalytic component in the hydrodefluorination

of fluoroalkyl groups in the presence of excess triethylsilane.^[6] The closely related compound **2** containing a triethylsilyl cation weakly interacting with a halocarbollide anion^[7] was used as an intermediate catalyzing several hydrodefluorination processes.^[8] Donor-stabilized cations in compounds of type **3** catalyze the deoxygenation of ketones with hydrosilanes.^[9] The hydrogen-bridged disilyl cation in compound **4**, comprising an electrophilic silicon center and the hydrogen source in one molecule, catalyzes the hydrodefluorination of alkyl and benzyl fluorides.^[10] Finally, the ferrocenyl-stabilized R_3Si^+ cation in compound **5** catalyzes selectively several Diels–Alder reactions even at low temperature;^[11] furthermore, it is the catalytic species in the reduction of ketones to alkyl(silyl) ethers.^[12] Only very recently, the role of ionic silicon(IV) compounds in catalysis was comprehensively reviewed by Klare and Oestreich.^[13]

During the last decade, the first ionic silicon(II) compounds that are stable at room temperature have been prepared that contain electrophilic RSi^+ cations with $\text{R} = \text{Me}_3\text{C}_5$ (Cp^+ ; **6**),^[14] $i\text{Pr}_5\text{C}_5$,^[15] and $\text{HC}(\text{CMeNAryl})_2$ ($\text{Aryl} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$)^[16] and $\text{B}(\text{C}_6\text{F}_5)_4^-$ as the anion. Herein we describe the function of the half-sandwich Cp^*Si^+ cation (Scheme 1) as a catalyst for a novel type of a catalyzed reaction, namely for the controlled degradation of oligo(ethylene glycol) dialkyl and disilyl ethers and of cyclic diethers (crown ethers). Oligo(ethylene glycol) diethers serve as conducting liquid organic electrolytes in lithium batteries.^[17]

In the reaction of the compound $[\text{Cp}^*\text{Si}]^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (**6**) with dimethoxyethane (DME), which is regarded as the first member in the series of oligo(ethylene glycol) dimethyl ethers, we were able to isolate the crystalline, highly air- and moisture sensitive and thermolabile 1:1 complex $[\text{Cp}^*\text{Si}(\text{dme})]^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (**7**) [Eq. (1)]. Brief treatment of **7** with vacuum from an oil pump resulted in the reverse reaction.



Despite the instability of complex **7**, we could ascertain its structure by X-ray analysis (Figure 1).^[18] The DME molecule coordinates rather weakly in an asymmetric bidentate fashion to the silicon atom, and the Cp* ligand shows some deviation from η^5 bonding towards η^3 bonding. The average Si–C

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Supporting information for this article, including experimental details, time-dependent NMR spectra, and computational data, is available on the WWW under <http://dx.doi.org/10.1002/anie.201101139>.

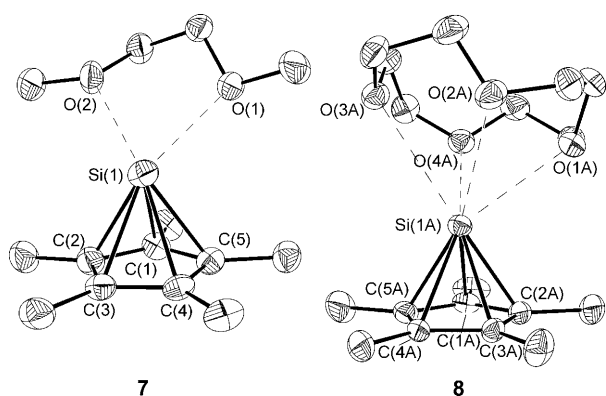
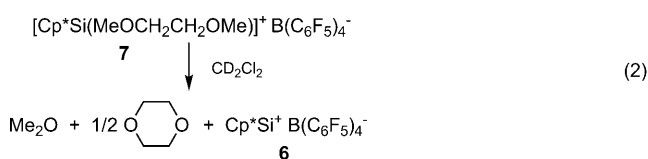


Figure 1. ORTEP plots of the $[\text{Cp}^*\text{Si}(\text{dme})]^+$ cation in compound **7** and of the $[\text{Cp}^*\text{Si}([12]\text{crown-4})]^+$ cation in compound **8**; ellipsoids set at 50% probability and hydrogen atoms omitted for clarity. Bond lengths [Å] in $[\text{Cp}^*\text{Si}(\text{dme})]^+$: Si1–O1 2.8208(14), Si1–O2 2.9055(14), Si1–C1 2.1251(17), Si1–C2 2.1604(18), Si1–C3 2.2156(17), Si1–C4 2.2164(16), Si1–C5 2.1572(17). $[\text{Cp}^*\text{Si}([12]\text{crown-4})]^+$: Si1A–O1A 2.8200(12), Si1A–O2A 2.9747(12), Si1A–O3A 3.0588(12), Si1A–O4A 2.8959(12), Si1A–C1A 2.1743(12), Si1A–C2A 2.1766(12), Si1A–C3A 2.1981(11), Si1A–C4A 2.2184(11), Si1A–C5A 2.1894(12).

distances (2.176 Å) are longer than those of the ether-free Cp^*Si^+ cation (2.147 Å). The long Si–F distances (> 3.34 Å) are in accord with an ionic structure. The structural parameters of the $[\text{Cp}^*\text{Si}(\text{dme})]^+$ cation calculated at the ab initio MP2/TZVPP level are nearly identical to those found experimentally for the cation in compound **7**; the weak Si–O bonding is based on purely electrostatic and van der Waals type interactions.^[19]

Interestingly, the complex $[\text{Cp}^*\text{Si}(\text{dme})]^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (**7**) decomposed in CD_2Cl_2 solution within several days, whereby the DME molecule was transformed into dimethyl ether and 1,4-dioxane [see Eq. (2)], as shown by NMR and GC-MS investigations (see the Supporting Information). From the reaction mixture, pure **6** could be recovered by evaporating all volatiles under vacuum from an oil pump.



As expected from these observations, the transformation of DME could also be performed in the presence of only catalytic amounts of **6**. According to the ^1H , ^{13}C , and ^{29}Si NMR spectroscopic data, almost complete reaction occurred with about 7 mol % of **6** within 15 days in CD_2Cl_2 as solvent. The catalytic process also takes place in neat DME, and a high conversion is observed even with a low catalyst loading (ca. 0.5 mol %).

To check the generality of the observed transformation, reactions with other oligo(ethyleneglycol) diethers were performed with 5–10 mol % of the catalyst and were followed by NMR spectroscopy (for NMR spectra, see the Supporting Information). They showed the tolerance of the degradation

against several modifications in the ether framework. Thus, the oligoethers diglyme, triglyme, and tetraglyme were degraded to dimethyl ether and to 1,4-dioxane in the expected ratio [Eq. (3)]. Figure 2 shows the time-dependent ^1H NMR spectra of the diglyme decomposition: after 30 h, small amounts of DME remain; the degradation process for DME is slower.

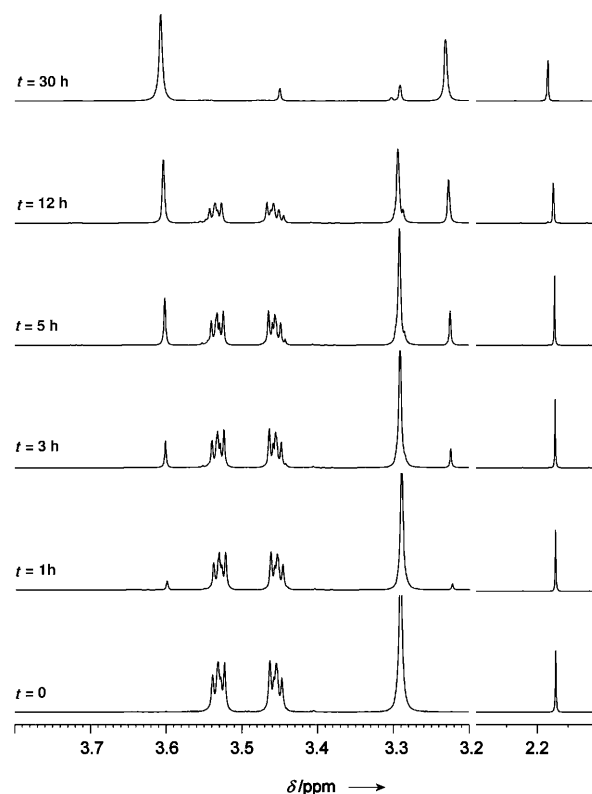
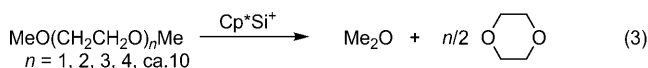
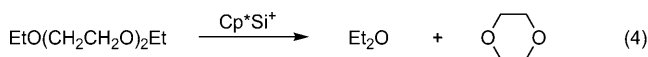
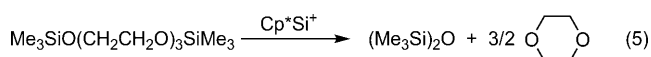


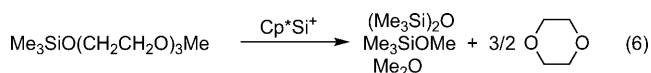
Figure 2. Time-dependent ^1H NMR investigation of the $\{\text{Cp}^*\text{Si}\}^+$ -catalyzed degradation of diglyme ($\text{MeO}(\text{CH}_2\text{CH}_2\text{O})_2\text{Me}$; 3.29, 3.46 (m), 3.53 ppm (m)) to dimethyl ether (3.23 ppm) and 1,4-dioxane (3.61 ppm). Small amounts of DME (3.30, 3.46 ppm) still remain after 30 h, and full conversion requires even longer reaction times. The $\{\text{Cp}^*\text{Si}\}^+$ catalyst (ca. 2.18 ppm) remains intact.

Similarly, a poly(ethyleneglycol) dimethyl ether containing about 10 ethylene glycol units (ca. 500 Da) was nearly quantitatively transformed [Eq. (3)], but with some decomposition of the catalyst.^[20] In case of the di(ethyleneglycol) diethyl ether and of the tri(ethyleneglycol) bis(trimethylsilyl) ether, the transformation led to 1,4-dioxane and to diethyl ether and hexamethyldisiloxane, respectively [Eqs. (4) and (5)]. In the reaction of the methyl and trimethylsilyl substituted tri(ethyleneglycol) diether, three ether species





were observed after a short reaction time [Eq. (6)]. After a longer reaction time, only the symmetric ethers were present.^[21]



Interestingly, cyclic ethyleneglycol diethers can also be catalytically decomposed, as demonstrated by the transformation of the crown ether [12]crown-4 [Eq. (7)]; a 35 %



conversion into 1,4-dioxane was obtained after reaction for 7 days in CD_2Cl_2 solution. Crystals of the air-sensitive ionic complex $[\text{Cp}^*\text{Si}(\text{[12]crown-4})]^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (**8**) were obtained from a solution of **6** and [12]crown-4 in a CH_2Cl_2 /hexane mixture. An X-ray analysis of **8**^[18] shows that four oxygen atoms of the crown ether molecule are weakly coordinated to the silicon atom of the Cp^*Si unit; the latter shows only small deviations from η^5 bonding, but longer Si–C distances (average value 2.191 Å) compared with the situation in the ether-free Cp^*Si^+ cation (2.147 Å; see Figure 1). Such a half-sandwich-like crown ether coordination to a silicon atom is thus presented herein for the first time. The quantitative degradation of complex **8** in CD_2Cl_2 takes place within about 20 days.

Concerning the mechanism of the catalytic reactions,^[23] a plausible pathway will be discussed for the simplest process, the transformation of DME. Two DME molecules are expected in the coordination sphere of the catalyst. The respective complex $[\text{Cp}^*\text{Si}(\text{dme})_2]^+\text{B}(\text{C}_6\text{F}_5)_4^-$ (**9**) could neither be isolated nor observed by NMR spectroscopy. Therefore, we performed ab initio calculations of the cation in **9** at the SCS-MP2/TZVPP level of theory. As portrayed in Figure 3, the four Si–O distances are in the range 2.900–3.037 Å, indicating rather weak contacts, and the Si–Cp* bonding shows a small deviation from an η^5 situation. Further calculations have shown that the coordination of the first DME ligand is exothermic by 15 kcal mol^{−1}, and that of a second DME molecule is exothermic by 8 kcal mol^{−1}. The transformation of two DME molecules into two molecules of dimethyl ether and one molecule of 1,4-dioxane is slightly endothermic by 2.4 kcal mol^{−1}.

A proposal of the catalytic cycle of the DME transformation is presented in Scheme 2. Two DME molecules are weakly coordinated, with up to four contacts to the silicon atom, which is similar to the coordination in the ground-state structure of the cation **9**⁺, but presumably with a smaller distance between the DME molecules. In this activated state, weak Si–O interactions (dotted line) will induce a rearrangement of σ -bond and lone-pair electrons in the ether frame-

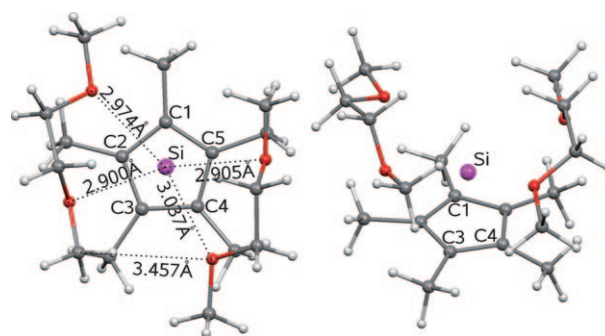
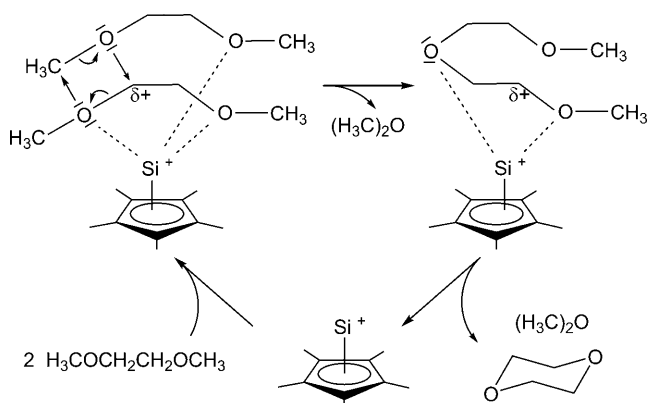


Figure 3. Calculated molecular structure of the $[(\text{Me}_5\text{C}_5)\text{Si}(\text{dme})_2]^+$ cation (**9**⁺) at the SCS-MP2/TZVPP level of theory. Two different perspectives are shown. Si–C distances [Å]: Si–C1 2.193, Si–C2 2.167, Si–C3 2.159, Si–C4 2.180, Si–C5 2.199.



Scheme 2. Suggested catalytic cycle in the transformation of DME into 1,4-dioxane and dimethyl ether. Conceivable weak Si–O interactions are represented by a dotted line.

work, which leads to the formation of dimethyl ether and of diglyme, the latter being still coordinated to the silicon atom. In a second step, the diglyme molecule is degraded in a similar fashion to dimethyl ether and 1,4-dioxane, and the catalytic cycle can start again. The possibility that R_2O or dioxane molecules coordinate weakly to the silicon atom during the catalytic cycle cannot be excluded, but the chelate effect favors DME or diglyme coordination.

More complicated multistep processes have to be discussed for the transformation of the oligoethers $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n\text{R}$ with $n \geq 2$ owing to several possible coordination arrangements.^[20] Even in the case of the di(ethyleneglycol) diethers $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_2\text{R}$ ($\text{R} = \text{Me}$ or Et), a purely intramolecular process analogous to the second step in Scheme 2 can be excluded owing to the presence of DME or di(ethoxy)ethane in the reaction mixture (see Figure 2 and ¹H NMR data in the Supporting Information). The coordination features in the cations of **7** and **8** and in **9**⁺ are regarded as an indication that up to four oxygen atoms can interact with the silicon atom in the catalytic cycle.

In summary, the half-sandwich cation in the silicon(II) compound $\text{Cp}^*\text{Si}^+ \text{B}(\text{C}_6\text{F}_5)_4^-$ catalyzes the specific degradation of open-chain and cyclic oligo(ethyleneglycol) diethers. The open coordination sphere at the silicon atom in the half-

sandwich cation enables up to four weak and thus flexible interactions with oxygen atoms from oligoether molecules. Such interactions are strong enough to induce rearrangement processes in the ether framework. The flexible $\text{Cp}^*\text{-Si}$ bonding is regarded as a prerequisite for the observed catalyzed reactions.

The splitting of C–O bonds in ethers and polyethers is a key step in organic synthesis.^[24] To the best of our knowledge, reactions comparable to those described in Equations (3)–(7) have not been reported to date in the literature.^[25] In future work, it needs to be determined whether the Cp^*Si^+ cation can also catalyze other so far unknown reaction types; the possible formation of several weak contacts between the silicon atom and the respective substrate has to be utilized.

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