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Catalytic Degradation of Aliphatic Ethers using the Lewis Superacidic Bis(perfluoropinacolato)silane

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The exceptional catalytic activity of a neutral Si(IV) Lewis superacid was highlighted on the degradation of oligo- and polyethers *via* ring closing metathesis. Model reaction experiments with diglyme and 1,5-dimethoxypentane outlined a significantly increased reactivity surpassing comparable Lewis acid catalyst presented in the literature. The high observed activity was explained by the kinetic effect of the bulky perfluorinated substituents, blocking a second coordination site that is responsible for catalyst deactivation by substrate chelation. Further experiments with aliphatic oligoethers outlined a gradual activity loss of the catalyst due to mechanistic disparities favoring side-reactions when more than one internal product unit is present. The extraordinary affinity for the cleavage of etheric C–O bonds was ultimately demonstrated by the reaction with diethylether, producing a pentavalent silicate species that was fully characterized including SC-XRD analysis.

Introduction

The demand for sustainable products and environmentally friendly industrial processes increased significantly in recent years, leading to challenging changes but also opportunities especially in the chemical and polymer industry.[1] For the production of plastic commodities, for instance, a clear tendency towards circular and recyclable materials can be traced. Nevertheless, this transition is rather slow and the majority of plastic waste still ends up in landfills or is thermally converted for energy recovery.[2] In this regard chemical depolymerization introduces an alternative solution to recover valuable building blocks and chemicals from waste-materials.[3] Especially aliphatic polyethers are produced on a megatong scale and can be found in a wide range of commodities as well as functionalized materials like fibers, foams, or medical surfactants.[4] The predominant repeating units of those polymers are composed of aliphatic ethers, that can be degraded in the presence of strong Lewis acids thus enabling a strategy for targeted depolymerization.[5] The early work of Enthaler *et al.* demonstrated that Lewis acidic iron and zinc catalysts successfully convert various oligo- and poly(ethylene)glycols with stoichiometric amounts of acyl chlorides.[6] Additional studies showed the suitability of various Lewis and Brønsted acids for the degradation of poly(THF) substrates with no additional reactants, but harsh reaction conditions required.[7] The Morandi group investigated $Fe(OTf)_3$ for the catalytic ring-closing metathesis of 1,5-dimethoxypentane and resembling aliphatic ethers to form cyclic reaction products.[8] A metal-free version of this reaction was further outlined by Liu *et al.* using imidazolium-based ionic liquids as catalysts under biphasic and solvent-free conditions.[9] Persuing an environmentally friendly polymer degradation, Cantat and coworkers applied the multi-talent $B(C_6F_5)_3$ as well as transition-metal catalysts for the reductive degradation of polyethers, polyesters and polycarbonates with hydrosilanes.[10] As shown by the Jutzi group also low-valent silicon cations can be used for the C–O metathesis of oligo(ethyleneglycol)diethers (Figure 1, b), thus introducing the second most abundant

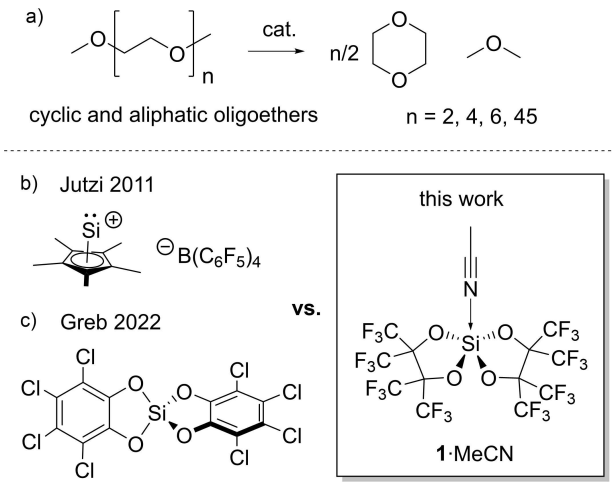

Figure 1. (a) Reported ring closing metathesis of oligoethers catalysed by the low-valent Si(II) cation (b) and the neutral Lewis superacid $Si(cat^{Cl})_2$ (c), compared to the catalyst system studied in this work.[11–12]

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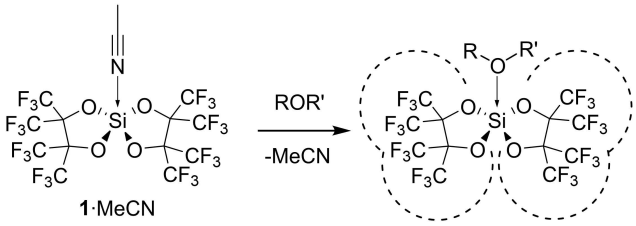
element of the earth's crust as a potential catalyst for polymer degradation.[11]

A recent study from the Greb group comprehensively investigated the catalytic C–O metathesis reactions of oligo- and polyethers using the neutral Si(IV) Lewis superacid $Si(cat^{Cl})_2$ that possesses a polymeric structure ($[Si(cat^{Cl})_2]_n$).[12] The compound catalytically converted chelating substrates like 1,5-dimethoxypentane, diglyme and crown ethers while outperforming previously established catalysts with ease (Figure 1, c). Even polymeric ethylene- and propyleneglycol diethers could be degraded, however high catalyst loadings were required. Our group published a related acetonitrile-adduct of a Lewis superacidic silane ($Si(pin^F)_2 \cdot MeCN$) that showed significant catalytic behavior for carbonyl reduction reactions and even activated Si–F bonds.[13] In this study we present the compound's tremendous activity in the degradation of oligo- and polyethers and discuss reaction differences for etheric substrates that affect the catalyst's performance. We additionally give a full characterization of a pentaoxo-coordinate silicate species as a potential reaction intermediate derivative that was isolated by the cleavage of diethyl ether.

Results and Discussion

In 2021 we presented the synthesis and characterization of bis(perfluoropinacolato)silane as its acetonitrile mono-adduct $Si(pin^F)_2 \cdot MeCN$ (**1**·MeCN).[13] Lewis acidity investigations by competitive abstraction experiments outlined a Lewis superacidic nature and several reactions like hydrodefluorination or carbonyl reduction were successfully catalyzed by **1**·MeCN. While assessing the Lewis acidity by the Gutmann-Beckett (GB) method only mono-coordinated Lewis pairs were formed and no double-coordinated product could be observed, even when surplus Et_3PO was present. This inclination is rather uncommon among Lewis acids like in the case of catecholato silanes and related systems, where twofold coordination is the prevalent structural motif.[14] An explanation for this phenomenon can be found in the steric bulk of the perfluorinated pinacolato groups that shield a second coordination site when one donor molecule is already attached to the silicon center. The resulting pentacoordinate geometry was already visualized in case of the acetonitrile-coordinated **1**·MeCN by SC-XRD analysis.[13]

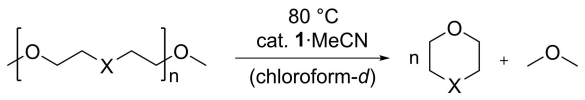
Due to this geometric effect, the pinacolato silane could act as a potent catalyst for the ring closing metathesis of oligoethers, as recently published mechanistic investigations for the related Lewis superacid $[Si(cat^{Cl})_2]_n$ would suggest.[12] In that study the catalytic ether degradation initiated *via* the mono-coordination of one etheric oxygen followed by the cleavage of a C–O bond while forming a zwitterionic intermediate. As reported, a twofold coordination by the chelating reactant, however, leads to catalyst deactivation because of the strong thermodynamic stabilization.[12] For this reason, catalysts with two or three potential coordination sites for multidentate substrates were found less active for the ring-closing metathesis, whereas catalysts with blocked or less favorable multiple-coordination sites showed increased activity. This was underpinned by an experiment with bis(perfluoro-*N*-phenylamidophenolato)silane,[15] where the double coordination of diglyme is even less stabilized as for $[Si(cat^{Cl})_2]_n$.[12] Following this reasoning, we expected that our pinacolato silane **1**·MeCN shows even higher reactivity as acetonitrile should be exchanged in solution with the employed etheric substrate (Scheme 1) Furthermore, the liberated silane **1** possesses a similar Lewis acidity compared to $[Si(cat^{Cl})_2]_n$ in case of fluoride ion affinity calculations (FIA: 474 kJ mol^{-1} (**1**) vs. 507 kJ mol^{-1}) as well as GB measurements ($\Delta\delta(^{31}P) = 35.8$ ppm (**1**) vs. 35 ppm).[13,14e] Deactivating effects caused by twofold coordination of the substrate should be sufficiently diminished by steric protection of the perfluoropinacolato groups.



Scheme 1. Schematic depiction of catalyst mono-coordination by etheric substrate substituting acetonitrile in solution.

In fact, reactions with 1,5-dimethoxypentane and diglyme revealed an outstanding performance of **1**·MeCN for the catalytic C–O metathesis reaction under mild condition and low catalyst loadings, thus outperforming established catalyst systems (Table 1).[8,12] For both substrates full conversion was observed quantitatively yielding the cyclic reaction products already after 1 hour at 80 °C for 1,5-dimethoxypentane and 2.5 hours at 80 °C for diglyme, when using a catalyst loading of 5 mol%. Unlike in the case of $[Si(cat^{Cl})_2]_n$ no deactivation was observed for reactions with 1,5-dimeth-

Table 1. Ring closing metathesis experiments of 1,5-dimethoxypentane (1,5-DMP), diglyme, poly(ethyleneglycol)dimethylether (PEG-DME) and 18-crown-6 at 80 °C using **1**·MeCN as reaction catalyst.



1,5-DMP: X = CH_2, n = 1 Diglyme: X = O, n = 1

PEG-DME: X = O, n = 22.5 18-crown-6: X = O, n = 3, no Me_2O

Entry	Substrate	cat. (mol%)	Time [h]	Yield [%][a]	TON[b]
1	1,5-DMP	1	20	97	97.0
2	1,5-DMP	5	1	96	19.2
3	Diglyme	1	20	96	96.0
4	Diglyme	5	2.5	96	19.2
6	Diglyme	10	96	99	9.9
7	18-crown-6	30	30	88	8.8
8	PEG-DME	225	18	87	8.7

[a] Yield determination of reaction products tetrahydropyran and 1,4-dioxane was conducted by ^{1}H NMR *via* integration against internal standard mesitylene. [b] Calculation: TON = n(cyclic product)/n(catalyst).

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oxypentane and diglyme, even allowing quantitative conversions with catalyst loadings of only 1 mol%.[12]

Both reactions also proceeded at room temperature but required significantly elongated reaction periods for full conversion (see SI Table S1 and S2). Further screenings of **1**·MeCN for the degradation of 18-crown-6 and poly(ethyleneglycol)-dimethylether (Mw = ~2000 g mol^{-1}) revealed that significantly higher catalyst amounts were required for those substrates. In case of 18-crown-6, 30 mol% of the catalyst were used to ensure quantitative conversion. This correlates to the 21 mol% of catalyst [Si(cat^{Cl})$_2$] that were applied in the literature.[12,16] A similar result was observed for PEG-DME where 225 mol% of **1**·MeCN were necessary for full conversion.[12,17] The decreased turn over number (TON) in the case of 18-crown-6 and PEG-DME indicates a catalyst deactivation, that is more pronounced for substrates with more than one internal C–O metathesis cycle per molecule. To verify this hypothesis, fragmentation experiments with tetra(ethyleneglycol)dimethyl ether (TEG-DME) were conducted. In that case full conversion was not reached with catalyst loadings of 5–10 mol% and reaction times up to 6 days (Table 2).

However, quantitative conversion was reached with 20 mol% of the catalyst. Even though the number of metathesis cycles per catalyst molecule is the same as for experiments with diglyme when 10 mol% of **1**·MeCN were used, significantly decreased turnover rates were observed. As outlined in Figure 2 most catalytic activity for those reactions was lost already during the first 20 h. Experiments with 5 mol% at 80 °C and at room temperature even demonstrated a faster catalyst deactivation at elevated temperatures (see SI Figure S5). This effect, however, was canceled out at higher catalyst loadings, due to solubility influences.

The observed deactivation can be explained by a mechanistic investigation of this reaction. According to literature findings, the reaction initiates *via* the mono-coordination of the ether substrate, followed by an intramolecular S_N2 attack forming an *O*-substituted dioxane cation as well as a pentavalent silicate anion (Figure 3).[12] A subsequent S_N2 attack of the methoxy group on the methyl moiety of the cation releases 1,4-dioxane while forming Me_2O in case of diglyme. When substrates with more than one internal dioxane unit are degraded, the second S_N2 reaction encounters a kinetically less favored secondary carbon center, thus lowering the overall reaction speed .[18] In that case the extended population of the highly electrophilic oxonium species caused by the less favored S_N2 reaction facilitates the likelihood for side-reactions. As oxonium species are prone for nucleophilic substitution an attack could also occur on one of the other secondary carbon atoms, leading to the irreversible deactivation of the catalyst.[19]

The tremendous oxophilicity of **1**·MeCN and reactivity for oxygen containing substrates was ultimately demonstrated by the cleavage of Et_2O. In this experiment **1**·MeCN was

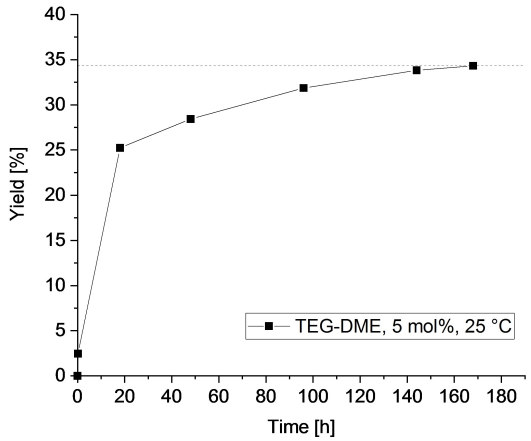
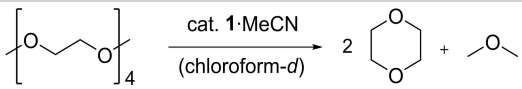


Figure 2. Yield of 1,4-dioxane during a degradation experiment of TEG-DME with 5 mol% of catalyst **1** at 25 °C over the course of 7 days.

Table 2. Ring closing metathesis experiments of TEG-DME at various conditions using **1**·MeCN as reaction catalyst.



Entry	cat. (mol%)	Temp. [°C]	Time [h]	Yield [%][a]	TON[b]
1	5	80	120	26	10.4
2	5	25	144	34	13.4
3	10	80	120	58	11.6
4	10	25	144	39	7.8
5	20	80	48	75	15.0

[a] Yield determination of reaction product 1,4-dioxane was conducted by ^{1}H NMR *via* integration against internal standard mesitylene. [b] Calculation: TON = n(1,4-dioxane)/n(catalyst).

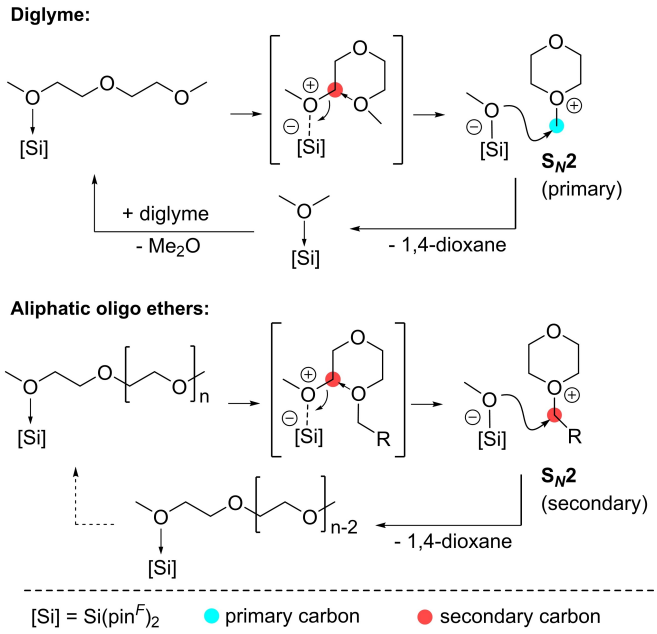


Figure 3. Potential reaction pathway of the ring-closing metathesis of diglyme and longer oligo(ethyleneglycol) catalysed by *in situ* liberated **1** ([Si]) starting from the terminal ether bonds. The reaction determining S_N2 reaction are highlighted in red for secondary carbons and blue for primary carbons.

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precipitated from a saturated diethylether solution at room temperature, yielding the salt of the ethoxy substituted silicate species with the respective triethyl oxonium counterion [Et_3O][**1**-OEt] (Figure 4). The NMR analysis of the product in acetonitrile-d_3 showed the presence of the characteristic species [Et_3O]$^+$ when measured 10 min after solvent addition (see SI Figure S1). Another ^{1}H NMR spectrum of the same sample obtained 3 hours later, however, revealed the presence of Et_2O and another species that was attributed to the deuterated *N*-ethylacetonitrilium cation [MeCN–Et]$^+$. Despite this conversion, the characteristic ^{1}H-, ^{19}F- and ^{29}Si ($\delta = -106.6$ ppm) NMR signals of the silicate species [**1**-OEt]$^-$ were not affected (see SI for details). Interestingly, this characteristic ^{29}Si NMR signal at around $\delta = -106.6$ ppm was also observed during reactions of 1,5-dimethoxypentane and diglyme with **1**·MeCN. This evidently demonstrated the presence of alkoxy-substituted pentacoordinate silicate anions as intermediates during ether degradation reactions (see SI chapter 3.3).

Single crystals suitable for SC-XRD analysis of [MeCN–Et][**1**-OEt] were obtained from a saturated solution of [Et_3O][**1**-OEt] in MeCN/Et_2O. As can be seen in Figure 4 the silicon is pentaoxo-coordinate with two perfluoropinacolato groups and one ethoxy substituent attached. The Si–O(pin^F) bond lengths range from 1.7070(19) Å to 1.7613(19) Å and align well with the bond lengths already observed for the chloro-, fluoro and hydrido-substituted perfluoropinacolato silicates, published by our group.[13] The Si1–O5 length of 1.6210(19) Å is slightly shorter as for comparable non-fluorinated bis(pinacolato)silicates holding MeO-, EtO-, *i*PrO- and *t*BuO-substituents (Si–O: 1.661(4)–1.670(3) Å).[20] The perfluoropinacolato groups of [**1**-OEt]$^-$ arrange in a distorted see-saw geometry with bond angles of 124.54(9)° for O1–Si1–O4 and 170.95(9)° for the O2–Si1–O3 axis. A similar geometry was observed for previously reported silicate anions with two perfluorinated pinacolato groups and a hydride, fluoride or chloride substituent.[13] Related geometries were also found in the case bis(catecholato)silicates with different sterically demanding substituents attached to the silicon center.[21]

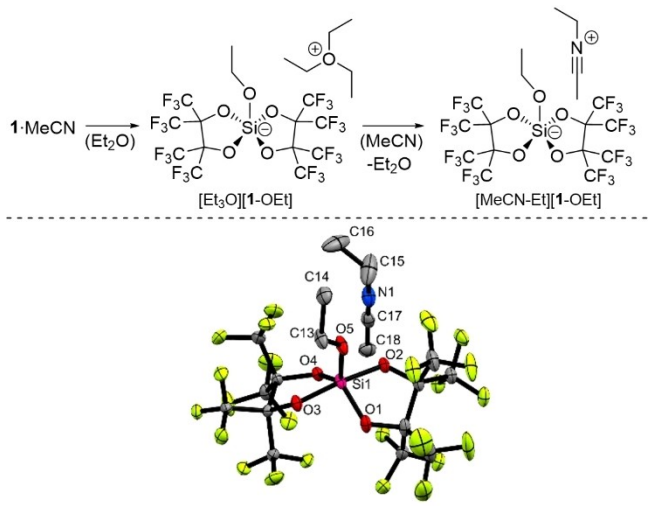

Figure 4. Top: Degradation experiment of diethyl ether in the presence of **1**·MeCN, yielding the ethoxy substituted perfluoropinacolato silicate with respective triethyloxonium or *N*-ethylacetonitrilium cation; Bottom: Molecular structure of [MeCN–Et][**1**-OEt] obtained by SC-XRD analysis (ellipsoids at 50% probability level). Selected bond lengths (Å): Si1–O5 1.6210(19), Si1–O1 1.7165(19), Si1–O2 1.7613(19), Si1–O3 1.7529(19), Si1–O4 1.7070(19); N1–C15 1.446(4), N1–C17 1.124(4).[22]

Conclusion

In conclusion we demonstrated that the neutral Lewis superacid **1**·MeCN efficiently catalyzed the degradation of oligo- and polyethers *via* C–O metathesis. The unmatched reactivity of **1**·MeCN was explained by the sterically predefined monocoordination of the corresponding adduct that is formed between the Lewis acid **1** and the employed etheric substrate, under the displacement of acetonitrile. The obtained reactivity aligned well with calculation on the reaction mechanism for related catecholato silanes that were given in the literature.[12] With the isolation of an anionic ethoxy substituted silicate anion, we further presented a potential reaction intermediate derivative that supports the published mechanistic investigation. Additional degradation studies with TEG-DME revealed a gradual deactivation of catalytic activity which could be explained by an overall deceleration of the metathesis reaction caused by the slower substitution reactions on secondary carbon atoms for substrates holding more than one cyclic product unit. The striking oxophilicity of **1**·MeCN was ultimately demonstrated by the cleavage of Et_2O, yielding the respective pentaoxo-coordinate silicate species, which was fully characterized including SC-XRD analysis.

Experimental Section

General Information. All reaction were performed under argon atmosphere in heat-dried reaction vessels. Reactants for catalytic experiments 1,5-dimethoxypentane, diglyme, tetra- and poly-(ethylene-glycol) dimethyleher (TEG-DME, PEG-DME) were degassed and stored over molecular sieves (4 Å). 18-Crown-6 was dried in DCM-solution over molecular sieves (4 Å) prior to use. Solvents were distilled over elemental sodium/benzophenone (Et_2O) or calcium hydride (acetonitrile, chloroform) and stored over molecular sieves. The used Si(pin^F)$_2$·MeCN (**1**·MeCN) was synthesized according the literature.[13]

Synthesis of [**Et$_3$O**][**1**-OEt]. In a screwcap rection vessel 80.0 mg **1**·MeCN (109 µmol, 1.00 equiv.) were dissolved in 1.3 ml Et_2O (1.25 µmol, 11.5 equiv.). The reaction mixture was kept at room temperature for 24 h and afterwards stored at −30 °C for 5 days. A colorless precipitate was formed that was collected by filtration, washed three times with 1.0 ml hexane and dried in vacuum. A colorless solid was obtained in 44% yield.. **^{1}H-NMR** (500 MHz, acetonitrile-d_3) δ (ppm) = 4.65 (q, $^3J_{C-H}$ = 7.1 Hz, 6H, O(C*H*$_2$CH$_3$)$_3$), 3.71 (q, $^3J_{C-H}$ = 7.0 Hz, 2H, SiOC*H*$_2$CH$_3$), 1.51 (t, $^3J_{C-H}$ = 7.1 Hz, 9H, O(CH$_2$C*H*$_3$)$_3$), 1.05 (t, $^3J_{C-H}$ = 7.0 Hz, 3H, SiOCH$_2$C*H*$_3$). **^{13}C NMR** (126 MHz, acetonitrile-d$_3$) δ (ppm) = 122.82 (qm, $^1J_{C-F}$ = 293.1 Hz), 84.81 (s, O(CH$_2$CH$_3$)$_3$), 83.77 (br, OC(CF$_3$)$_2$), 59.64 (s, SiOCH$_2$CH$_3$), 17.92 (s, SiOCH$_2$CH$_3$), 12.56 (s, O(CH$_2$CH$_3$)$_3$). **^{19}F NMR** (471 MHz, acetonitrile-d$_3$) δ (ppm) = −69.69–−70.02 (m, 12F, CF$_3$), −70.18–−70.37 (m, 12F, CF$_3$). **^{29}Si NMR** (99 MHz, acetonitrile-d_3) δ (ppm) = −106.61(*Si*). **Elemental Analysis** calcd. [%] for $C_{20}H_{20}F_{24}O_4Si$: C

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(28.58), H (2.40), N (–), S (–); found (%): C (28,90), H (2.20), N (0.50), S (–). **m.p.**: 97.5–110.2 °C.

General procedure catalysis experiments. All C–O metathesis reactions were carried out in PTFE-sealed J-Young NMR tubes. The respective amount of reactant was dissolved in 0.4 ml $CDCl_3$ and 3.0 µl of mesitylene were added as an internal standard. A ^{1}H NMR analysis of that solution was performed as a zero-point measurement for yield determination. The reactions were started by the addition of the given amount of catalyst **1**·MeCN. The samples were then stored at various temperatures using an oil-bath. Reaction progress was monitored *via* ^{1}H NMR spectroscopy by the integration of the product signals with respect to the internal standard.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: C–O bond metathesis · Et_2O cleavage · Lewis acidic silanes · poly(ether) degradation · silicon catalysis

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[16] *7 mol% when referenced to the reaction product 1,4-dioxane..
[17] *10 mol% when referenced to the amount of reaction product.
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[22] Deposition Number 2241855 [MeCN Et][**1**-OEt] contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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