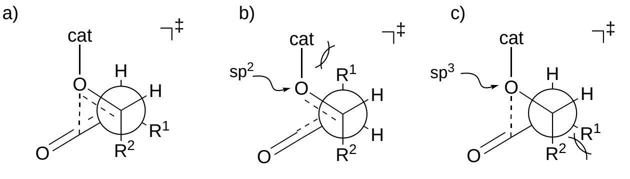

18 **19** **20**

Figure 3. Transition state models for rationalizing stereoselectivity in the [2+2] cycloaddition: a) Cossio's model[7c), l]), b) revised model leading to *trans* diastereomer with C–C bond formation as rate-limiting and selectivity-determining step, c) revised model leading to *cis* diastereomer with C–O bond formation as rate-limiting and selectivity-determining step.

oxygen atom is sp^2 hybridized and the Lewis acid is not free to rotate away from steric interactions with the silyl group. Alternatively, transition state structure **14** (Figure 2, cf. **20**, Figure 3c) is rate limiting for the formation of the *cis* product and in this case, the aldehydic oxygen atom is sp^3 hybridized and the Lewis acid can rotate away from steric interactions. Thus, catalyst bulk would have a greater inhibiting effect on formation of the *trans* product (i.e. greater cat./R^1 interaction) and lead to higher *cis* selectivity as observed. The observation by Yamamoto[3c] that bulky groups (R^1) on the ketene favor the *trans* product would be explained by an unfavorable steric interaction with the aldehydic substituent R^2 in **14** (Figure 2, cf. **20**, Figure 3c) which takes on added importance when one considers that C–C bond formation is rate limiting. This observation is not so readily understood from Cossio's model **20** (Figure 3a). Overall, one can conclude that R^1/R^2 interactions are most important during the formation of *cis*-β-lactone diastereomers since these impending eclipsed interactions have the greatest impact on the rate-limiting ring closure (C–O bond formation) following C–C bond rotation. On the other hand, catalyst/R^1 interactions predominate for the reaction pathway leading to the *trans* diastereomer.

More generally, the observations made in this study highlight that a broad range of factors must be pondered in order to understand and control stereoselectivity in a multistep reaction. Selectivity among competitive pathways may be determined by dissimilar transition states or divergent rate-limiting steps, and a strong energetic preference for one transition state over a stereoisomeric partner is not sufficient to guarantee high stereoselectivity. Rather, stereoselectivity must be controlled throughout a mechanism.

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[13] A comparison of the experimental and predicted KIEs provides ambiguous support for the calculated structures. The predicted ^{13}C KIEs for **9** are 1.034, 1.028, and 1.000 for C_β, C_α, and $C_{C=O}$, respectively, in qualitative agreement with the experimental values. The predicted ^{13}C KIEs for **14** are 1.017, 1.000, and 1.028 for C_β, C_α, and $C_{C=O}$, respectively. The qualitative discrepancy at C_α may mean that the KIEs for **4** are best interpreted as a concerted mechanism, or it may just reflect the difficulties of calculations on charged intermediates.

[14] Owing to a referee's concern over using an unbranched aldehyde as a theoretical model, we have repeated our calculations with isobutyraldehyde instead of acetaldehyde and the results are qualitatively identical (see Supporting Information). The energies for the isobutyl analogues of **9**–**14** (B3LYP/6-31G*/PCM//B3LYP/6-31G*/Onsager + zpe, versus starting materials) are 13.1, 11.0, 11.3, 12.5, 11.6, and 14.6 kcal mol^{-1}, respectively.

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Cyclotetrasilenide Ion: A Reversible Redox System of Cyclotetrasilenyl Cation, Radical, and Anion**

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Alkali metal derivatives of organosilicon compounds are useful not only in organosilicon chemistry, but also in organic synthesis. The synthesis, reactivity, and structural aspects of silyllithium compounds are the most studied of alkali metal derivatives.[1] Numerous anionic organosilicon compounds are

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known, however, knowledge of the chemistry of organosilicon compounds with an interaction between alkali metals and π electrons is very limited. To our knowledge, the only examples of such interactions are silole dianions $[\{Li(thf)_2\}\{Li(thf)_3\}\{\eta^1,\eta^5\text{-}C_4Ph_4Si\}]$, $[\{K[18]crown\text{-}6)\}_2\{\eta^5,\eta^5\text{-}C_4Me_4Si\}]$, and related compounds.[2]

Recently, we synthesized the cyclotetrasilenylium ion (1^+X^-),[3] which is a free silyl cation in the condensed phase, by the reaction of cyclotrisilene $[(tBu_2MeSi)_4Si_3]$[4] with $[Et_3Si(C_6H_6)]^+X^-$ (X^- = tetrakis(pentafluorophenyl)borate). We also reported the synthesis of the isolable cyclotetrasilenyl radical $1^\bullet$ by the one-electron reduction of 1^+X^-.[5] Therefore, it is reasonable to assume that the cyclotetrasilenide ion 1^- is formed by the two-electron reduction of 1^+ or one-electron reduction of $1^\bullet$. A recent report by Weidenbruch and coworkers, on an unexpected formation of a cyclotetragermenyllithium derivative by the reaction of tetrakis(2,4,6-triisopropylphenyl)digermene with lithium in dimethoxyethane,[6] prompts us to communicate our synthesis of the alkali metal derivatives of the cyclotetrasilenyl anion. We herein report the synthesis, characterization, and unique crystal structure of a cyclotetrasilenyllithium (1^-Li^+), which has a π-type structure with coordination of a lithium cation to a trisilaallyl moiety. We also report a unique, reversible chemical redox system of the cyclotetrasilenyl cation, radical, and anion (Scheme 1).

The reaction of $1^+\cdot X^-$ with an excess of lithium in oxygen-free, dry diethyl ether at room temperature lead to the immediate formation of a purplish red solution, caused by the formation of $1^\bullet$. After about 30 min, the color of the solution changed to green, caused by the formation of 4,4-di-*tert*-butyl-1,2,3-tris(di-*tert*-butyl(methyl)silyl)cyclotetrasilenide (1^-) by further reduction. After removal of the excess lithium and the solvent, hexane was added to give green crystals of 1^-Li^+, which contained one equivalent of Et_2O, in 85% yield (Scheme 2). Reduction of $1^\bullet$ with lithium in Et_2O at room temperature also produced 1^-Li^+ cleanly. Compound 1^+X^- also underwent two-electron reduction with sodium or potassium graphite (KC_8) in Et_2O, and the corresponding 1^-Na^+ and 1^-K^+ were obtained in 65% and 75% yields, respectively.

To determine the exact structure of 1^-Li^+ by X-ray crystallography, we performed a ligand exchange on the Li^+ ion, from Et_2O to tetrahydrofuran. A single crystal of 1^-Li^+, which contained one equivalent of THF, was obtained by recrystallization from a mixture of hexane and THF, the molecular structure was determined by X-ray crystallography (Figure 1).[7] The lithium cation is located over the four-membered ring, and is coordinated by the three silicon atoms (Si1, Si2, and Si3) in the four-membered ring, as well as by the oxygen atom of the THF molecule.

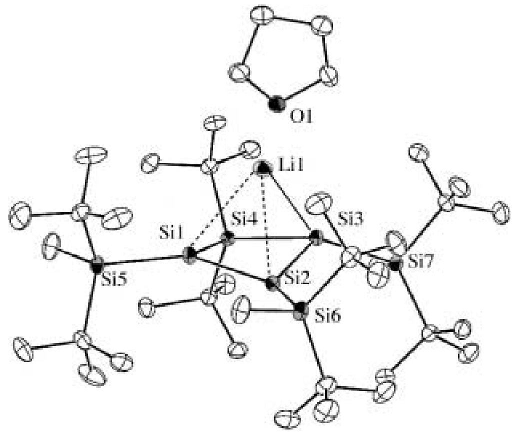
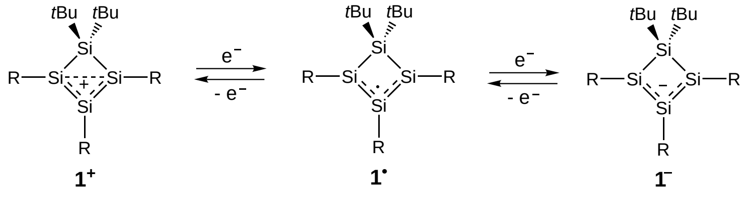


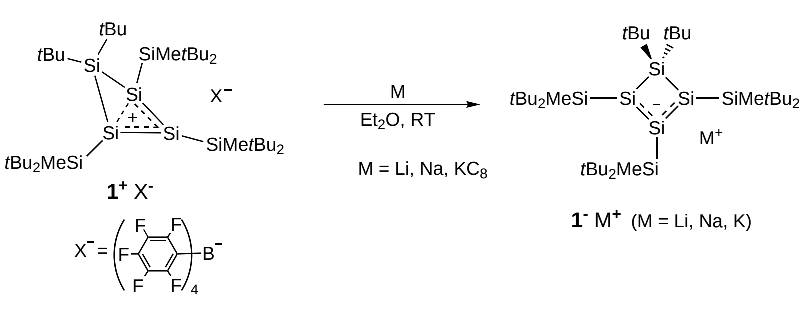
Figure 1. ORTEP representation of the structure of $1^-[Li(thf)]^+$ (hydrogen atoms are omitted for clarity; thermal ellipsoids set at the 30% level). Selected interatomic distances [Å] and angles [°]: Si1-Si2 2.2245(7), Si1-Si4 2.3692(7), Si1-Si5 2.3617(7), Si2-Si3 2.3153(7), Si2-Si6 2.4012(7), Si3-Si4 2.3955(7), Si3-Si7 2.3732(7), Si1-Li1 2.789(4), Si2-Li1 2.814(4), Si3-Li1 2.569(4); Si2-Si1-Si4 86.70(2), Si1-Si2-Si3 93.97(2), Si2-Si3-Si4 84.07(2), Si1-Si4-Si3 88.34(2).



1^+ $1^\bullet$ 1^-

R = SiMe*t*Bu$_2$

Scheme 1.



$1^+ X^-$

$1^- M^+$ (M = Li, Na, K)

Scheme 2. Reduction of 1^+X^- with alkali metals.

The four-membered ring deviates from planarity, as demonstrated by the dihedral angle of 27.3° between the Si2-Si3-Si4/Si2-Si1-Si4 planes. The bond length of Si3–Li1 (2.569(4) Å) lies within the range for typical η^1-type silyllithium compounds,[1] whereas the bond lengths of Si1–Li1 (2.789(4) Å) and Si2–Li1 (2.814(4) Å) are significantly longer than that of Si3–Li1 (2.569(4) Å). The bond length of Si1–Si2 is 2.2245(7) Å, which lies in the reported range for Si=Si double bonds (2.138–2.289 Å).[8] The bond lengths of Si2–Si3 (2.3153(7) Å) and Si1–Si4 (2.3692(7) Å) lie in the normal region for Si–Si single bonds (2.33–2.37 Å). These structural features suggest that 1^-Li^+ has a cyclotetrasilene structure with a Si=Si double bond in the ring, and that the lithium cation is bonded to the Si3 atom and also interacts with the double-bonded Si1 and Si2 atoms. Such an electrostatic interaction leads to elongation of the Si1–Si2 bond, which is intermediate between the Si=Si double bond (2.174(4) Å) and Si–Si single bond (2.349(4)–2.450(4) Å) in the four-membered ring of hexakis(*tert*-butyldimethylsilylcyclotetrasilene.[9, 10]

The NMR spectroscopic data of $\mathbf{1}^-\mathrm{Li}^+$ in [D$_8$]toluene indicate formation of a contact ion pair (CIP) with C_2 symmetry. The two *tert*-butyl groups that are attached to the Si4 atom show chemical shift nonequivalence, caused by coordination of the lithium cation (Figure 1). The two *tert*-butyl groups of *t*Bu$_2$MeSi that are attached to the Si1 and Si3 atoms are diastereotopic. Thus, the ^{1}H NMR spectrum of $\mathbf{1}^-\mathrm{Li}^+$ in [D$_8$]toluene reveals the presence of two methyl groups and five *tert*-butyl groups. The ^{13}C NMR spectrum also shows signals arising from two methyl carbons for *t*Bu*Me*Si, five methyl carbons for three *tBu$_2$*MeSi and two *t*Bu groups, and five signals for quaternary carbon atoms of *t*Bu groups. In the ^{29}Si NMR spectrum, five signals are observed at $\delta = -31.5$ (Si1 and Si3), 13.9 (Si6), 19.0 (Si5 and Si7), 26.0 (Si4), and 273.0 (Si2). The Si1 and Si3 atoms are equivalent, which indicates that the lithium cation is fluxional in solution, in accordance with an allylic-type anion. The signal appearing at $\delta = -31.5$ is assigned to the Si1 and Si3 atoms, which are shifted upfield because of the negative charge. Of particular interest is the highly deshielded signal at $\delta = 273.0$ arising from the Si2 atom, similar to the central carbon atom of allyllithium.[11]

However, the Li$^+$ ion can be separated from the anion to yield a solvent-separated ion pair (SSIP) in a solvating medium such as [D$_8$]THF. Consequently, the skeleton of $\mathbf{1}^-$ has the same environment above and below the ring; the two *t*Bu groups attached to the Si4 atom are equivalent.[12] The ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic data of $\mathbf{1}^-\mathrm{M}^+$ (M = Li, Na, and K) in [D$_8$]THF all indicate SSIP formation in the polar solvent, caused by solvation of the counter cations.

The anion $\mathbf{1}^-$ reacts readily with $[\mathrm{Et_3Si(C_6H_6)}]^+\mathrm{X}^-$ in benzene to regenerate $\mathbf{1}^\bullet$. The radical $\mathbf{1}^\bullet$ also undergoes one-electron oxidation to form $\mathbf{1}^+$ by the reaction of $\mathbf{1}^\bullet$ with $[\mathrm{Ph_3C^+}]\mathrm{X}^-$ in benzene.[5] Thus, we have prepared a reversible redox system of the cyclotetrasilenyl cation, radical, and anion.

Experimental Section

$\mathbf{1}^-\mathrm{Li}^+$: Crystals of $\mathbf{1}^+\mathrm{X}^-$ (65 mg, 0.047 mmol) and lithium (18 mg, 2.6 mmol) were placed in a sealed tube with a magnetic stirrer bar. After degassing the tube, dry oxygen-free Et$_2$O (2.5 mL) was introduced by vacuum transfer and stirred at room temperature to give a green solution of $\mathbf{1}^-$ within 1 h. After the solvent was removed in vacuo, degassed hexane was introduced by vacuum transfer. After the lithium and resulting X$^-$ salt had been removed from the tube, the solution was cooled to afford green crystals of $\mathbf{1}^-\mathrm{Li}[(\mathrm{Et_2O})]^+$ (31 mg, 85 %). ^{1}H NMR (300 MHz, [D$_8$]toluene, TMS): $\delta = 0.43$ (s, 6 H), 0.52 (s, 3 H), 1.03 (t, $J = 7.0$ Hz, 6 H), 1.21 (s, 18 H), 1.26 (s, 18 H), 1.28 (s, 18 H), 1.42 (s, 9 H), 1.75 (s, 9 H), 3.39 (q, $J = 7.0$ Hz, 4 H); ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]toluene, TMS): $\delta = -3.1$ (CH$_3$), -1.5 (CH$_3$), 15.1 (*C*H$_3$CH$_2$O), 22.0 (C), 22.4 (C), 22.6 (C), 23.4 (C), 25.1 (C), 30.4 (CH$_3$), 30.71 (CH$_3$), 30.74 (CH$_3$), 31.2 (CH$_3$), 34.8 (CH$_3$), 66.3 (CH$_3$*C*H$_2$O); ^{29}Si{^{1}H} NMR (79.5 MHz, [D$_8$]toluene, TMS) $\delta = -31.5$ (2*t*Bu$_2$MeSi*Si*), 13.9 (*t*Bu$_2$Me*Si*), 19.0 (2*t*Bu$_2$Me*Si*), 26.0 (*t*Bu$_2$*Si*), 273.0 (*t*Bu$_2$MeSi*Si*); ^{7}Li{^{1}H} NMR (116.6 MHz, [D$_8$]toluene, LiCl in MeOH, external standard): $\delta = 1.96$.

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[7] Crystal structure analysis of $\mathbf{1}^-[\mathrm{Li(thf)}]^+$: Diffraction data were collected at 120 K on a MacScience DIP2030 K Image Plate Diffractometer employing graphite-monochromated Mo–Kα radiation ($\lambda = 0.71070$ Å). Crystal data: $\mathrm{C_{39}H_{89}LiOSi_7}$, $M_r = 777.67$, monoclinic, space group $P2_1/n$, $a = 12.2510(3)$, $b = 21.7420(4)$, $c = 19.5840(5)$ Å, $\beta = 106.088(2)^\circ$, $V = 5012.1(2)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.031$ g cm^{-3}, GOF = 1.008. The final R factor was 0.0487 ($R_W = 0.1349$ for all data) for 12000 reflections with $I_o > 2\sigma(I_o)$. The structure was solved by the direct method and refined by the full-matrix least-squares method using the SHELXL-97 program. CCDC 174532 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

[8] a) M. Kaftory, M. Kapon, M. Botoshansky, *The Chemistry of Organic Silicon Compounds*, *Vol. 2 Part 1* (Eds.: Z. Rappoport, Y. Apeloig), Wi1ey, Chichester, **1998**, Chapter 5; b) T. A. Schmedake, M. Haaf, Y. Apeloig, T. Müller, S. Bukalov, R. West, *J. Am. Chem. Soc.* **1999**, *121*, 9479.

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[12] Spectral data of $\mathbf{1}^-\mathrm{Li}^+$ in [D$_8$]THF. ^{1}H NMR (300 MHz, [D$_8$]THF, TMS): $\delta = 0.12$ (s, 6 H), 0.33 (s, 3 H), 1.09 (s, 36 H), 1.15 (s, 18 H), 1.44 (s, 18 H); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_8$]THF, TMS): $\delta = -2.8$ (CH$_3$), -1.5 (CH$_3$), 22.0 (C), 23.1 (C), 25.2 (C), 31.3 (CH$_3$), 31.6 (CH$_3$), 33.6 (CH$_3$); ^{29}Si{^{1}H} NMR (59.6 MHz, [D$_8$]THF, TMS) $\delta = -24.7$ (2*t*Bu$_2$MeSi*Si*), 5.4 (*t*Bu$_2$Me*Si*), 7.4 (2*t*Bu$_2$Me*Si*), 77.1 (*t*Bu$_2$*Si*), 224.5 (*t*Bu$_2$MeSi*Si*); ^{7}Li{^{1}H} NMR (116.6 MHz, [D$_8$]THF, LiCl in MeOH, external standard): $\delta = 2.61$.