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Notes

Biphenylene Ring Expansion by a $(H_3C)_2Si$ Link from Silicone Grease As Proven by the Crystal Structures of [(Sodium$^+$[2.2.1]cryptand)(9,9-dimethylsilafluorene$^{\bullet -}$)] as Well as [Sodium$^+$(triglyme)$_2$(biphenylene$^{\bullet -}$)] and by Total-Reflection X-ray Fluorescence Spectrometry (TXRF)[1]

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Summary: Sodium metal mirror reduction of biphenylene in aprotic THF solution containing [2.2.1]cryptand yields as a structurally characterized product the 9,9-dimethylsilafluorene radical anion salt containing a $(H_3C)_2Si$ expanded cyclobutadiene ring. In addition, the Si content can be detected by total reflection X-ray (TXRF) analysis. When the use of any silicon grease was avoided for all glass fittings, the solvent-separated biphenylene radical anion contact pair crystallized from an aprotic diglyme solution.

Interest in the design, crystallization, and structural characterization of solvent-shared and solvent-separated contact ion pairs of π-hydrocarbon radical anions,[2] dianions,[3] radical trianions,[4] and even tetraanions[5] has stimulated the sodium metal mirror reduction of biphenylene in different ether solutions (Scheme 1; eqs 1 and 2).

Reaction 1 was carried out in a Schlenk apparatus under rigorous exclusion of air and moisture,[6] using polydimethylsiloxane grease for all the glass fittings. Dark violet crystals grew from the green solution, for which an X-ray crystallographic study at 150 K under a flow of cooled nitrogen revealed a monoclinic $P2_1/n$ unit cell with $Z = 4$ containing solvent-separated ion pairs (Figure 1A).[6] Expectedly, the [2.2.1]cryptand-solvated Na^+ cation was present, but much to our surprise, the counterion was the bare 9,9-dimethylsilafluorene radical anion (Figure 1B). The latter has been known so far only as a ligand in solvent-shared aggregates.[7−9]

The 9,9-dimethylsilafluorene radical anion (Figure 1A,B) exhibits almost planar five- and six-membered rings with a twist angle between their idealized planes of only about 4°. The strongest deviations from standard geometries are found in the central ring with C−C bond lengths between 1.43(1) and 1.45(1) Å and in the tetrahedrally distorted silicon center with Si−C bond lengths of 1.85(1) and 1.87(1) Å as well as angles between 92 and 118°. Compared to the known structures with 9,9-dimethylsilafluorene radical anion as contact ion ligands in chromium and tungsten carbonyl complexes,[7−9] their distortions are considerably smaller.

An extensive literature search reveals that the inclusion of one[10,11] and up to seven[12] $(H_3C)_2SiO$ subunits into organometallic compounds under reductive condi-

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[6] Preparation and crystal growth of [(sodium$^+$-[2.2.1]cryptand)-(9,9-dimethylsilafluorene$^{\bullet -}$)]: 38 mg (0.25 mmol) of biphenylene and 0.08 mL (0.28 mmol) of [2.2.1]cryptand in 10 mL of THF were added under argon to a mirror of 42 mg (1.83 mmol) of sodium. The blue solution soon turned green, and after 24 h, dark violet blocks crystallize. Crystal data: $C_{30}H_{46}SiN_2O_5Na$, dark violet, $M_r = 565.8$, monoclinic, $P2_1/n$, $a = 10.001(1)$ Å, $b = 14.876(1)$ Å, $c = 20.692(1)$ Å, $\beta = 95.886(5)°$, $V = 3062.3(3)$ Å^3, $Z = 4$, $T = 150$ K, $D_c = 1.229$ g cm^{-3}, $\mu_{\mathrm{Mo\,K\alpha}} = 0.13$ mm^{-1}, $F(000) = 1220$. The intensity data were collected on a Siemens P4 diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å), in the ω-scan mode. A total of 6495 reflections were measured in the range $3 \leq 2\theta \leq 48°$, containing 5892 unique reflections, 4788 of which with $I > 2\sigma(I)$ were used for refinement. Intensities were corrected for Lorentz−polarization effects. Absorption correction was applied by face indexing using XPREP 5.03: minimum transmission 0.960 37, maximum transmission 0.973 70. The structure was solved by direct methods and refined on F^2 using SHELXL 93: 376 parameters, $R = 0.0381$, wR2 = 0.0974 for $I < 2\sigma(I)$. Final difference maps showed no peaks >0.30 or <−0.22 e Å^{-3}; all Δ/ρ values <0.001. The H centers were placed at calculated positions. Atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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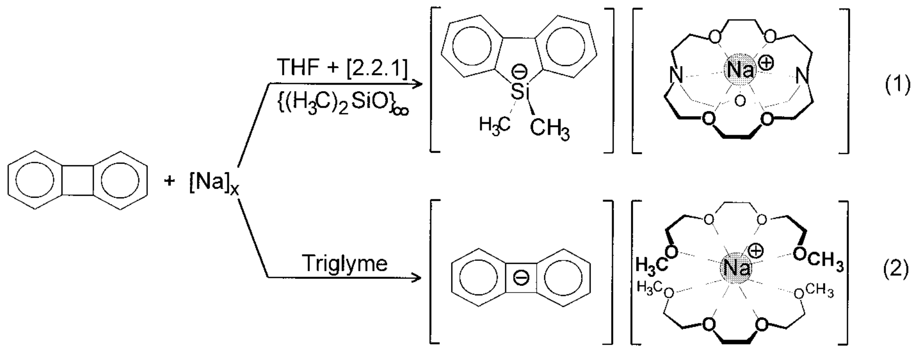
Scheme 1



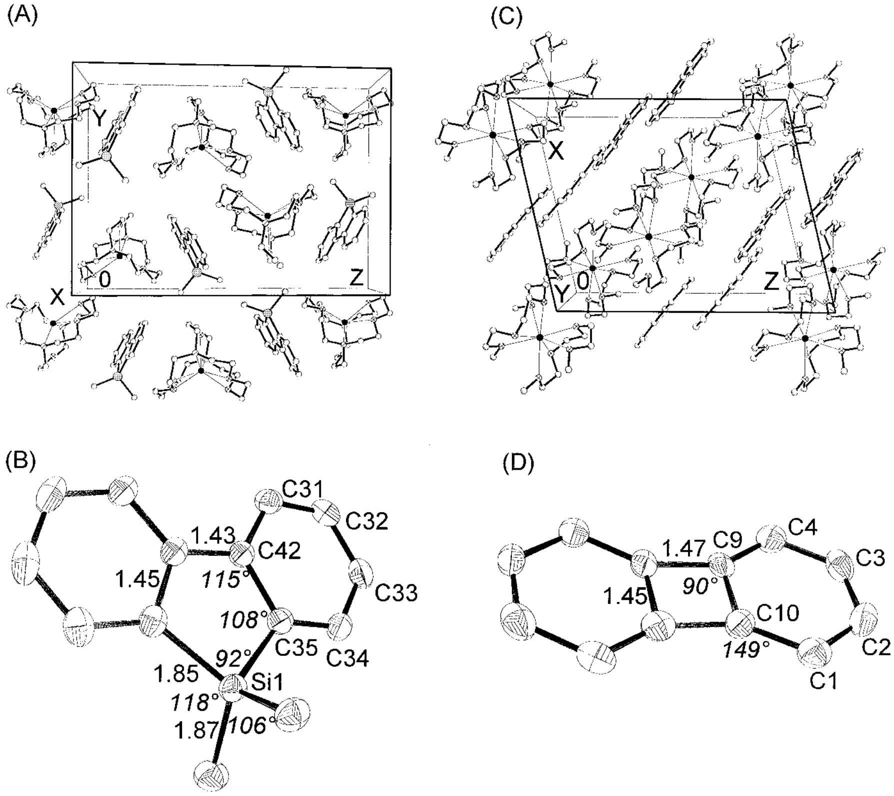


Figure 1. Single-crystal structures of [(sodium$^+$-[2.2.1]cryptand)(9,9-dimethylsilafluorene$^{\bullet-}$)] (I) and of [(sodium$^+$(triglyme)$_2$)-(biphenylene$^{\bullet-}$)] (II): (A/I) unit cell viewed along the *x* axis; (B/I) organosilicon radical anion (50% thermal ellipsoids) with numbering and selected structural data; (C/II) unit cell viewed along the *y* axis; (D/II) hydrocarbon radical anion (50% thermal ellipsoids) with numbering and selected structural data.

tions has been repeatedly reported, yielding, for example, an ytterbium pyrazole compound,[10] the hexameric lithium dimethylnaphthylsilanolate,[11] or an indium complex containing a K[OSi(CH$_3$)$_2$]$_7$ solvated cation.[12] In all these reports,[10-12] the silicon content has been assumed to result from the easily ether-soluble dimethylsiloxane grease used to seal the glass fittings.

To further substantiate the unexpected structural ring expansion of the four-membered biphenylene ring by an oxygen-free (H$_3$C)$_2$Si link (eq 1), the anisotropic displacement parameters have been used as first indicators only for silicon as the new center. A reasonable refinement resulted. The origin of the silicon could be traced by total-reflection X-ray fluorescence spectrometry (TXRF), a highly sensitive analysis method requiring only small samples which allows the detection of over 50 elements with a detection limit of <10 pg.[13] Despite the lower fluorescence yield of lighter elements, low Si concentrations can be qualitatively determined (Figure 2) without applying vacuum or excitation with synchrotron radiation.[14]

The TXRF spectra registered (Figure 2) clearly demonstrate that THF is not contaminated with detectable

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[10] Zhou, X.; Ma, H.; Huang, X.; You, X. *J. Chem. Soc., Chem. Commun.* **1995**, 2483.

[11] Bazhenova, T. A.; Lobkovskaya, R. N.; Shibaeva, R. P.; Shilov, A. E.; Shilova, A. K. *J. Organomet. Chem.* **1987**, *330*, 9.

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[14] TXRF spectra were measured using an EXTRA IIA spectrometer (Atomika Instruments, Oberschleissheim, Germany) equipped with excitation sources Mo Kα, W(L), and W(white), a Si(Li) solid-state detector, and a computer-controlled multichannel analyzer system. A 15 μL sample of each of the samples was pipetted onto a clean Perspex carrier and dried to a thin film, which was measured for 500 s with Mo Kα excitation.

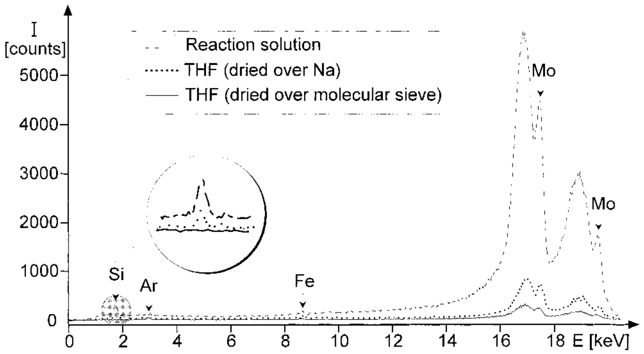

Figure 2. Total-reflection X-ray fluorescence spectra of the reaction solution containing 9,9-dimethylsilafluorene (- - -), of THF dried over Na (···), and of THF dried over molecular sieves (—) (the circle insert shows Si peaks).

amounts of Si by drying over molecular sieves (Figure 2, solid line). In contrast, the THF sample dried by refluxing over sodium metal for 2 days in a Schlenk-type apparatus, with silicone-greased glass fittings (Figure 2, dotted line) and especially the crystallization solution (Figure 2, dashed line) contained increasing amounts of silicon. These results suggest that the $(H_3C)_2Si$ group inserted into the four-membered ring of the presumably initially generated biphenylene radical anion (cf. Figure 1B) originates from trace silicone $[(H_3C)_2SiO]_n$ concentrations in the THF reaction mixture with the surplus oxygen removed at the sodium metal mirror surface. This is consistent with the previous literature assumptions.[10-12]

To avoid any unintended incorporation of silicon into the biphenylene molecule during its reduction, the experiment was repeated under similar conditions, but with rigorous replacement of any silicon grease by Teflon sleeves and with triglyme as an advantageous solvating ligand.[2] The structure[15] of the dark red crystals determined under a cooled N_2 flow at 150 K proved to be also monoclinic, $P2_1/n$, with four ion pairs in the unit cell (Figure 1C). The $Na^{\oplus}$ countercations are 8-fold O-coordinated by two triglyme molecules (Figure 1D) with distances Na···O between 2.46(1) and 2.63(1) Å. They separate the biphenylene radical anion layers along the *x*/*z* diagonal and the *y* axis (Figure 1C). The radical anion of biphenylene shows some significant differences relative to the neutral hydrocarbon,[16] predominantly in the four-membered ring: the bond lengths C9−C12 and C10−C11 are shortened by 0.04 Å from 1.51(1) to 1.47(1) Å (Figure 1B), and concomitantly the bonds C9−C10 and C11−C12 are lengthened slightly by 0.03 Å from 1.42(1) to 1.45(1) Å. In contrast to the planar hydrocarbon, the radical anion exhibits a twist angle between the six-membered rings of 4°.

In summation, our investigations prove that even with traces of a silicone compound such as poly(dimethylsiloxanes) from silicon grease, an incorporation of $(H_3C)_2Si$ centers (Figure 1A,B) is possible under reductive reaction conditions, especially when using alkali-metal mirrors (eq 1). The TXRF analyses (Figure 2) demonstrate convincingly that the use of silicon grease should be strictly avoided, and the successful crystallization of the desired biphenylene radical anion sodium salt (Figure 1C,D) shows how this difficulty can be circumvented.

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Supporting Information Available: Tables giving crystal data and refinement details, positional and thermal parameters, bond distances and angles, and torsional angles and figures giving additional views of the structure of I and II. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Preparation and crystal growth of $[(\text{sodium}^+(\text{triglyme})_2)(\text{biphenylene}^{\bullet-})]$: 38 mg (0.25 mmol) of biphenylene and 89 mg (0.5 mmol) of triglyme in 15 mL of THF were added under argon to a mirror of 45 mg (2.0 mmol) of sodium. From the dark red solution after 10 days dark red blocks crystallized. Crystal data: $C_{28}H_{44}O_8Na$, M_r = 531.6, monoclinic, $P2_1/n$, a = 12.996(1) Å, b = 13.405(1) Å, c = 16.484(2) Å, β = 103.27(1)°, V = 2795.1(7) Å^3, Z = 4, T = 150 K, D_c = 1.263 g cm^{-3}, μ(Mo Kα) = 0.10 mm^{-1}, $F(000)$ = 1148. The intensity data were collected on a Siemens P4 diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), in the ω-scan mode. A total of 2365 reflections were measured in the range $3 \leq 2\theta \leq 38°$, containing 2097 unique reflections, 1479 of which with $I > 2\sigma(I)$ were used for refinement. Intensities were corrected for Lorentz−polarization effects. Absorption correction was applied by face indexing using XPREP 5.03: minimum transmission 0.969 64, maximum transmission 0.980 95. The structure was solved by direct methods and refined on F^2 using SHELXL 93: 339 parameters, R = 0.0500, wR2 = 0.1358 for $I < 2\sigma(I)$. Final difference maps showed no peaks >0.34 or <−0.25 e Å^{-3}; all Δ/ρ values <0.001. The H centers were placed at calculated positions. Atomic coordinates, bond lengths, angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. On the recommendation of one reviewer, the crystal structure has been refined again with all centers isotropic and without a extinction variable to raise the data/parameter ratio: 153 parameters, R = 0.0773, wR2 = 0.1813 for $I < 2\sigma(I)$. Final difference maps showed no peaks >0.57 or <−0.33 e Å^{-3}; all Δ/ρ values <0.001. The H centers were placed at calculated positions.

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