Observation of Highly Stable Radical Anions of Ladder Oligosilanes

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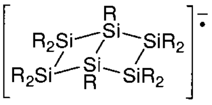
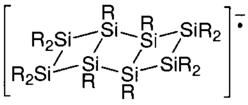
The radical anions of ladder oligosilanes were generated by the reduction with alkali metals and observed by UV–visible–NIR and ESR spectroscopies. The radical anions of the longer ladder oligosilanes are highly stable at room temperature.

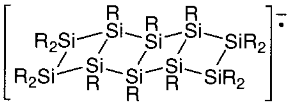
In recent years, polycyclic compounds of the group 14 elements have received considerable attention as interesting targets which provide access to the physical and chemical properties that are difficult to achieve with the corresponding carbon systems.[1,2] As part of the studies of the polycyclooligosilanes, we have reported the synthesis and reactions of the ladder oligosilanes.[3] The unique structures and properties of these ladder oligosilanes have prompted us to generate radical ions to gain further information about the intrinsic properties of the ladder molecules. This communication reports the reduction of the ladder oligosilanes with alkali metals which leads to novel radical anions $\mathbf{1}^{\bullet-}$–$\mathbf{4}^{\bullet-}$. Although many radical anions of the oligosilanes have been reported,[4,5] they are unstable species that can only be observed at low temperatures. We have found that the radical anion of the pentacyclic ladder oligosilane persists over several months at room temperature.



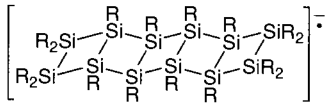
$\mathbf{1}^{\bullet-}$: R = *i*-Pr



$\mathbf{2}^{\bullet-}$: R = *i*-Pr



$\mathbf{3}^{\bullet-}$: R = *i*-Pr



$\mathbf{4}^{\bullet-}$: R = *i*-Pr

The radical anions $\mathbf{1}^{\bullet-}$–$\mathbf{4}^{\bullet-}$ were generated by the reduction of the corresponding ladder oligosilanes with K. When the ladder oligosilanes were treated with K in THF at ca. –70 °C, the solutions were immediately colored: $\mathbf{1}^{\bullet-}$, purple; $\mathbf{2}^{\bullet-}$, brown; $\mathbf{3}^{\bullet-}$, blue; and $\mathbf{4}^{\bullet-}$, black. In the UV–visible–NIR spectra, several absorption bands appeared (Figure 1). The absorption bands appeared during the initial stage of the reduction and grew in the same ratio of intensity as the reduction proceeded. In addition, ESR signals also grew as the reduction proceeded as shown below. Therefore, the absorption bands can be ascribed to radical anions. The intense absorption of $\mathbf{3}^{\bullet-}$ and $\mathbf{4}^{\bullet-}$ in the near-infrared region is noted because it has been reported that the absorption of the radical anions of the cyclic oligosilanes usually exists in the visible region and does not extend into the near-infrared region (e.g., $[(t\text{-Bu})\text{MeSi}]_4^{\bullet-}$, $\lambda_{\max}$ 410 nm[5h]; $(\text{Me}_2\text{Si})_5^{\bullet-}$, $\lambda_{\max}$ 645 nm[5b]; $(\text{Me}_2\text{Si})_6^{\bullet-}$, $\lambda_{\max}$ 425 nm[5b,6]). The absorption in the near-infrared region is probably due to the closely stacked molecular orbitals of the highly conjugated oligosilane systems.[7]

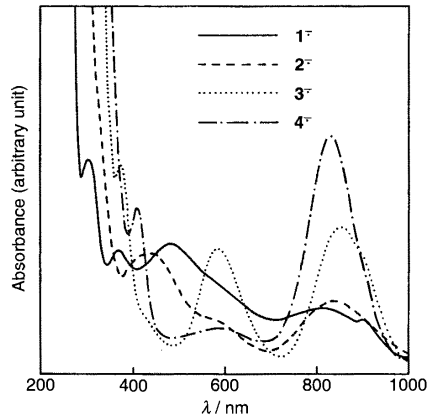


Figure 1. UV–visible–NIR spectra of $\mathbf{1}^{\bullet-}$–$\mathbf{4}^{\bullet-}$ in THF at –70 °C.

The ESR spectra of the radical anions of the ladder oligosilanes show a relatively broad signal with satellites (Figure 2). The satellites were analyzed by computer simulation and are summarized in Table 1. From the intensity, the satellites are attributed to the ^{13}C nuclei at the α-positions of the isopropyl groups rather than the ^{29}Si nuclei. The number of spin couplings is equal to the number of equivalent carbon atoms at the α-positions, indicating that the spin is highly delocalized. These results resemble those of the radical anions of other cyclooligosilanes observed by ESR[5] and can be explained by the model in which

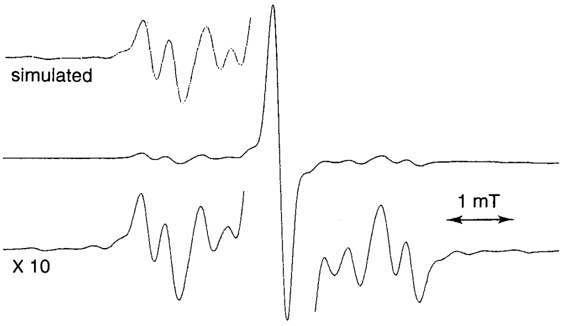


Figure 2. ESR spectrum of $\mathbf{4}^{\bullet-}$ in THF at room temperature with the simulated spectrum of satellites.

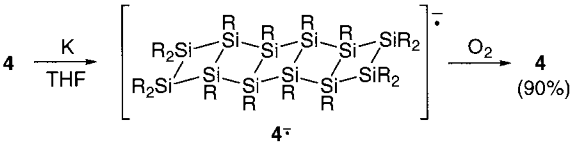
Table 1. ESR parameters for $\mathbf{1}^{\bullet-}$–$\mathbf{4}^{\bullet-}$ in THF

Radical anion	*T* / °C	*g*	$a(^{13}\text{C}(\alpha))$ / mT[a]
$\mathbf{1}^{\bullet-}$	−10	2.0046	2.12, 1.36 (1 : 4)
$\mathbf{2}^{\bullet-}$	−50	2.0044	3.08, 1.36 (1 : 2)
$\mathbf{3}^{\bullet-}$	rt	2.0046	4.15, 2.02, 1.02 (1 : 4 : 2)
$\mathbf{4}^{\bullet-}$	rt	2.0045	3.81, 3.16, 2.03, 1.40 (1 : 1 : 1 : 1)

[a] The value in parentheses is the intensity ratio of satellites.

the spin is delocalized to the substituent carbon atoms by the interaction between the Si–Si σ^* and Si–C σ^* orbitals in the singly occupied molecular orbital (SOMO).[5k,8] The *g*-values of **1**$^{\bullet-}$–**4**$^{\bullet-}$ range from 2.0044 to 2.0046 and are normal compared with those of the radical anions of other cyclooligosilanes.[5]

In order to confirm the structures of the radical anions, the following experiment was carried out. The reduction of the ladder oligosilanes was monitored by UV–visible–NIR spectroscopy. When the absorption of the ladder oligosilanes was completely replaced by the absorption of the radical anions, the sealed tube was opened. The radical anions were immediately oxidized, and the starting ladder oligosilanes were recovered in highly isolated yields. It is reasonable to consider that the radical anions of the ladder oligosilanes retain the ladder structure, and the Si–Si bond cleavage or skeletal rearrangement does not occur.



4$^{\bullet-}$

A remarkable feature of the radical anions is their stability. When the temperature of **1**$^{\bullet-}$ generated at –70 °C was raised above –10 °C, the ESR signals gradually decreased (Figure 3). However, the radical anions become more stable as the number of cyclotetrasilane rings progressively increases. In the case of **4**$^{\bullet-}$, the ESR signals do not decrease at all when the temperature is raised to room temperature. Furthermore, the ESR signals persist for several months at room temperature (Figure 3). The intensity loss after one month is 19%, and the half-life is too long to be measured. This stability is striking because almost all the radical anions of the cyclooligosilanes have been reported to be stable only below ca. –50 °C[5] except for $[(t\text{-Bu})\text{MeSi}]_4^{\bullet-}$, which persists for several days at room temperature.[5h] The unusual stability of **4**$^{\bullet-}$ is explained by the highly delocalized spin mentioned above.

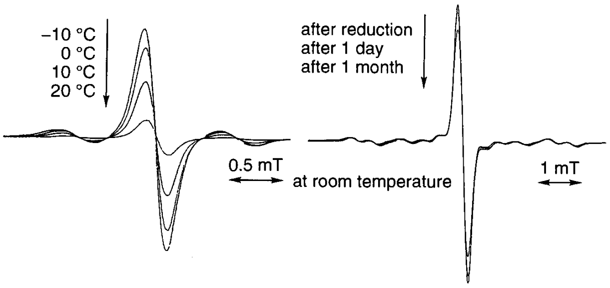


Figure 3. Decay of the ESR signals of **1**$^{\bullet-}$ (left) and **4**$^{\bullet-}$ (right) in THF.

Another notable point of **4**$^{\bullet-}$ is its generation with a weaker reducing agent, Li. Compound **4** can be reduced even with Li in THF at room temperature to produce **4**$^{\bullet-}$, although the reduction is far slower (ca. one day) than that with K. The radical anion **4**$^{\bullet-}$shows the identical UV–visible–NIR and ESR spectra as those in Figures 1 and 2, and is persistent at room temperature. Although many radical anions of oligosilanes have been generated by the reduction with K or the Na/K alloy,[5] no examples of the reduction with Li have been reported to our knowledge. The results show that the lowest unoccupied molecular orbital (LUMO) of **4** is significantly stabilized by the interaction between the Si–Si σ^* and Si–C σ^* orbitals extended over the molecule.

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