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Isolable 1,1-Disubstituted Silole Dianion: a Homogeneous Two-Electron-Transfer Reducing Reagent

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Supporting Information

ABSTRACT: The 1,1-disubstituted silole dianion **2** has been isolated and characterized by single-crystal X-ray analysis for the first time. **2** can be used as a two-electrontransfer reducing reagent for the reduction of organic compounds and inorganic salts with regeneration of the corresponding neutral silole in nearly quantitative yields, indicating that it is an excellent reducing reagent. Reduction of $(Mes)_2SiCl_2$ with **2** selectively yielded the cyclotrisilane $(Mes_2Si)_3$ in high yield, which has not been isolated in pure form with the existing methods.

T he development of homogeneous electron-transfer reagents has a great impact on synthetic chemistry. For example, Birch reduction, a naphthalene radical anion, and SmI_2 have been widely employed in synthetic chemistry.¹ These homogeneous reducing reagents have been proven to be superior to alkali metals in terms of their chemical selectivity and stereoselectivity.

Siloles (Chart 1) exhibit unique chemical and optical properties because of their low-lying lowest unoccupied



molecular orbital (LUMO) levels resulting from the orbital overlap between the π^* orbitals of the butadiene segment and the σ^* orbitals associated with the exocyclic σ bond on the silicon atom.² Because of their high electron affinity, it is possible to generate the corresponding silole dianions and radical anions by reduction. Although the reduction of boroles and alumoles yielded the isolable dianions or radical anions,³ chemical reduction of siloles has only been confined to NMR-scale reactions and the silole dianions (Chart 1, **A**) have not been isolated and structurally characterized so far.⁴ It is noted that the silole dianions with a divalent silicon atom (Chart 1, **B**) have been reported.^{2b,5a,6} Herein, we report the first isolation and X-ray crystal structure of a silole dianion of type **A** (Chart 1).

We envisioned that a 2,5-disilyl-substituted silole could be a suitable precursor to the corresponding 1,1-disubstituted silole dianion because the resulting carbanion could be stabilized by the α -silyl groups. Thus, the silyl-substituted silole 1 (Scheme 1) was prepared by the protocol developed by the Tamao group.⁷

Scheme 1. Synthesis of the Silole Alkali-Metal Salts 2-4



Reduction of 1 with 2 equiv of alkali metals (Li, Na, and K) was carried out in tetrahydrofuran (THF) at room temperature. The reaction with lithium for 2 h afforded the dilithium salt 2, $[Li^+(THF)]_2[1^{2-}]$, as orange crystals in 98% yield. Similarly, reduction of 1 with sodium and potassium yielded the sodium salt 3, $[Na^+(THF)]_2[1^{2-}]$, as purple powders in 95% yield and potassium salt 4, $[K^+(THF)]_2[1^{2-}]$, as blue powders in 95% yield, respectively. All of these alkali-metal salts have been characterized by ¹H, ¹³C, and ²⁹Si NMR spectroscopy. The molecular structure of 2 has been established by single-crystal X-ray analysis.

The ²⁹Si NMR spectra of 2-4 all exhibited two lines at -17.2and 8.8, -19.7 and 12.1, and -20.0 and 13.8 ppm, respectively. The negative values, assigned to the silicon atom in the silole ring, are upfield for 1 (ca. -10.4 ppm), while the chemical shifts for the SiMe₃ group are downfield from that for 1 (ca. 3.0 ppm).^{7b} The ⁷Li NMR spectrum of **2** exhibits a singlet at -2.43 ppm in C₆D₆, while two resonances at -0.36 and -2.31 ppm were observed in THF- d_{8} , indicating that the structure of the lithium salt in solution is solvent-dependent. X-ray crystallographic analysis of the lithium salt 2 revealed that there are four independent molecules in the asymmetric unit. Although some geometry variations among the four molecules cannot simply be ignored, their structural features as a whole are very similar. For simplicity, only one of the molecules is shown in Figure 1. The SiC₄ ring in 2 is not planar, and the silicon atom is ca. 15° above the C₄ plane. The two lithium atoms are located above and below the SiC₄ ring and coordinated to the silole ring in an η^5 fashion. This coordination mode is different from those of dilithium 2,3,4,5tetraphenylsilole and 3-n-butyl-2-phenyl-1-silaindene, in which one of the lithium atoms is η^1 -coordinated to the silicon atom while the other lithium is $\eta^{\text{5}}\text{-coordinated}$ to the silole ring. $^{\text{5c,d,j}}$ The Li1 atom in 2 is also coordinated to the N1 atom with a Li1-N1 bond distance of 2.132(5) Å, leading to the relatively short Li1-Si1 distance of 2.492(5) Å in comparison with a normal Li-

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Figure 1. Molecular structure of one of the four independent molecules of **2** in the asymmetric unit. Thermal ellipsoids were drawn at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Si–C1 1.839(3), Si–C4 1.843(3), Si–N1 1.812(2), Si–N2 1.741(2), C1–C2 1.497(3), C2–C3 1.399(4), C3–C4 1.492(3), Li1–Si1 2.492(5), Li2–Si1 2.628(5), Li1–C1 2.679(6), Li1–C2 2.360(5), Li1–C3 2.237(6), Li–C4 2.386(6), Li–N1 2.132(5), Li2–C1 2.223(6), Li2–C2 2.115(5), Li2–C3 2.101(5), Li2–C4 2.249(5); C1–Si1–C4 94.17(12), Si1–C1–C2 105.28(18), Si1–C4–C3 106.15(19); C4–Si1–C1–C2–15.98(18).

Si distance of 2.60 Å.^{2b,c,5c,6a} The C1–C2 [1.497(3) Å] and C3–C4 [1.492(3) Å] bond lengths are ca. 0.1 Å longer than that of C2–C3 [1.399(4) Å], indicating that electron delocalization in the C₄ unit is not significant. The nonplanar structure and C–C bond distances observed in the silole ring indicated that **2** does not possess noticeable aromaticity.

The molecular geometry predicted by DFT calculations on **2** at the RB3LYP/6-31G(d) basis set is in line with its X-ray crystal structural results. The calculated highest occupied molecular orbital (HOMO) and LUMO are given in Figure S1 in the Supporting Information (SI). The HOMO of **2** is mainly dominated by the π orbitals originating from the C=C double bond in the ring and the lone pairs on the silvl carbon atoms with small contributions from the three silicon σ orbitals. The HOMO of **2** displays a ring surface similar to that of the LUMOs of neutral 1,1-disubstituted siloles.⁸

The reaction chemistry of **2** has been investigated (Scheme 2). Solid **2**–**4** can be oxidized by oxygen to regenerate **1**; in toluene,

Scheme 2. Reduction of Diphenyl Ketone, 1,4-Benzoquinone, Dioxygen, MeI, and $Pd(PPh_3)_2Cl_2$ with the Silole Dianion 2



2 was cleanly oxidized by oxygen to give **1** in nearly quantitative yield. The reaction of **2** with diphenyl ketone and 1,4benzoquinone almost quantitatively yielded **1** with formation of the corresponding ketyl radical anion and dilithium hydroquinone (Scheme 2). These reactions are very similar to those reduced by alkali metals. The reaction of **2** with MeI exclusively yielded MeLi and **1**; reduction of Pd(PPh₃)₂Cl₂ yielded a palladium powder and **1**. In all of these reactions, **2** acted as a two-electron donor to the substrates and was converted to **1** in an almost quantitative yield. To the best our knowledge, rare carbanions could selectively exhibit electron-transfer reactivity toward a variety of substrates, except for the naphthalene radical anion and its derivatives.^{1b,9} It was found that the silole 1 could be reduced by lithium naphthalenide to form the lithium salt 2, but the reverse reduction reaction with 2 did not occur, indicating that 2 is a relatively mild reducing reagent, compared to lithium naphthalenide.

Alkali metals have been used for the synthesis of low-valent main-group and transition-metal complexes. However, over-reduction and other side reactions limited their wide applications.¹⁰ The silole dianion 2 possesses a number of unique features that make it an appealing alternative for reduction chemistry. For example, it is thermally stable and decomposed above 200 $^{\circ}$ C, it is soluble in a wide range of organic solvents, it can be easily prepared in nearly quantitative yield on gram scales, and it does not present any significant fire or toxicity hazards. Notably, the silole precursor 1 can be recovered in excellent yields.

To examine the reduction potential of **2** in synthetic chemistry, reduction of $(Mes)_2SiCl_2$ (Mes = 2,4,6-Me₃C₆H₂) with 2 has been investigated. Since the first disilene Mes₂Si=SiMes₂, a fascinating compound that stimulated great interest in maingroup multiple-bonding species,¹¹ was prepared via photolysis of $Mes_2Si(SiMe_3)_2$ by West et al. in 1981,¹² reduction of Mes_2SiCl_2 and Dmp_2SiCl_2 ($Dmp = 2,6-Me_2C_6H_3$) with alkali metals and lithium naphthalenide has been studied by several groups.^{13,14} In 2006, Napolitano and co-workers reported that reduction of Mes₂SiCl₂ with alkali metals yielded a mixture containing a number of products. Under optimized conditions with potassium graphite as the reductant, the cyclotrisilane (Mes₂Si)₃ was obtained as a major product containing other higher oligomers and has not been isolated in pure form.¹⁴ The problems might mainly lie in the stepwise electron-transfer process that may lead to a number of intermediates. The dianion 2 is a relatively mild reducing reagent and possesses two-electron-transfer capacity. Thus, it might be a good choice to avoid the formation of monohalide intermediates.

Reduction of Mes₂SiCl₂ with 1 equiv of **2** in THF at 0 °C proceeded completely in 4 h. Analysis of the crude product by the ¹H NMR spectrum (Figure S2 in the SI) indicated that the reaction is clean and yielded **1** and a new product (Scheme 3). The new product can be obtained as yellow-green crystals in 70% yield after crystallization from *n*-hexane, and the silole **1** can be recovered in 90% yield by column chromatography. The new product was identified as the cyclotrisilane **5** by ¹H, ¹³C, and ²⁹Si NMR spectra and elemental analysis. To the best our knowledge, **5** has not been reported to be isolated in pure form. Single-crystal

Scheme 3. Comparison of Reduction of Mes_2SiCl_2 with Different Reductants

Previous work in 1982 Dmp_2SiCl_2 \xrightarrow{LiNp} $(Dmp_2Si)_n$ in 2006 Mes_2SiCl_2 $\xrightarrow{KC_8}$ $(Mes_2Si)_n$ $-78 \ ^\circC, THF$ $(Mes_2Si)_n$ $n = 3,4,5 \ (83\% mixture)$ This work Mes_2SiCl_2 $\xrightarrow{2}$ $(Mes_2Si)_3$ $5 \ (70\% isolated)$ Dmn = 2.6 Ma C H. Mag = 2.4.6 Ma C H.

 $Dmp = 2,6-Me_2C_6H_3$, $Mes = 2,4,6-Me_3C_6H_2$

X-ray analysis of **5** further confirmed its cyclotrisilane skeleton, which is shown in Figure 2. The Si–Si bond lengths lie in a very



Figure 2. Molecular structure of **5**. Thermal ellipsoids were drawn at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Si1–Si2 2.4580(16), Si1–Si3 2.4278(15), Si2–Si3 2.4428(16); Si3–Si2–Si1 59.39(5), Si1–Si3–Si2 60.62(5), Si3–Si1–Si2 59.99(4).

narrow range from 2.4278(15) to 2.4580(16) Å. The three Si–Si–Si internal angles are very similar [from 59.39 to $60.62(5)^{\circ}$]. There are no noticeable structural differences between **5** and the other known cyclotrisilanes.¹⁵

In summary, we have isolated and structurally characterized a silole dianion with a four-coordinate silicon atom for the first time. The silole dianion 2 selectively underwent two-electron-transfer reactions with a number of substrates. 2 can be used as a selective and mild reductant, as demonstrated by reduction of Mes_2SiCl_2 . This work demonstrated that 2 is a promising electron-transfer reducing reagent. We are continuing to explore applications of 2 for the synthesis of low-valent main-group compounds and the electron-transfer properties of 2 toward organic substrates.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format and further details of the synthesis and characterization of compounds 1-5. This material is available free of charge via the Internet at http://pubs. acs.org.

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Notes

The authors declare no competing financial interest.

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