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Synthesis and NMR characterization of a spiro-silole tetra-anion: a homogeneous four-electron reductant

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Abstract: The development of highly selective homogeneous electron transfer reagents is highly desirable for synthetic chemistry. An isolable spiro-silole tetra-anion described in this paper has been proved to be a promising soluble electron transfer reagent. The reduction of octaphenyl-1,1'-spirobisilole (**1**) with lithium resulted in the formation of the isolable spiro-silole tetra-anion in good yield. The tetra-anion (**2**) has been characterized by nuclear magnetic resonance (NMR) and cleanly underwent electron transfer reactions with dioxygen, carbonyl groups, and transition metal halides to yield reduction products with the regeneration of **1**.

Keywords: anion; homogeneous; reductant; spiro-silole.

Introduction

Homogeneous reductants have played a great role on synthetic chemistry. For example, Birch reduction, naphthalene radical anion, and SmI_2 have been widely used in synthetic chemistry (Birch, 1947; Molander, 1992; Connelly and Geiger, 1996). These homogeneous reducing reagents have exhibited superior to traditional heterogeneous reductants owing to their high stereo and chemical selectivity. Hence, the development of new homogeneous reductants is very essential.

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

molecular orbital (LUMO) level due to the electronic interaction between the π^* orbital of the butadiene moiety and the σ^* orbital of the exocyclic Si-R bond (for reviews on siloles, see Yamaguchi and Tamao, 1996, 1998; Lee et al., 2000; Shirota and Kageyama, 2007; Zhan et al., 2009). They can be reduced by alkali metals to form the corresponding dianions. To date, the 'silole' dianions have been isolated and characterized completely (Saito and Yoshioka, 2005).

Spiro-siloles that contain a silicon center surrounded by four carbon atoms have attracted much attention because they may serve as starting materials for the preparation of macromolecules and polymers with interesting physical properties (Lee et al., 2005). On the other hand, there is a rare report on its anion compounds. Inspired by the generation of the 'silole' dianions (Janzen et al., 1967; O'Brien and Breeden, 1981; Hong, 2013; Han et al., 2014), here, we report the first isolation of a spiro-silole tetra-anion.

Considering octaphenyl-1,1'-spirobisilole (**1**) with the multiply phenyl groups, we selected compound **1** as the suitable precursor to the corresponding spiro-silole tetra-anion. Following published procedures, octaphenyl-1,1'-spirobisilole were synthesized by treatment of 1,4-dilithiotetraphenylbutadiene with 0.5 equivalent tetrachlorosilane with the reported low yield (4–10%; Timokhin et al., 2005). In order to improve the yield of compound **1**, we attempt the reaction (Scheme 1) in dimethoxyethane and precise stoichiometric ratio to afford the high yield (60%), which illustrated that strong cooperative oxy-solvent and precise stoichiometric ratio between diphenylacetylene and lithium were crucial in obtaining the spirobisilole (**1**).

Results and discussion

The choosing of the solvent is important for the isolation of the air- and moisture-sensitive anions. It is said that oxy-solvents like tetrahydrofuran (THF), diethyl ether, dimethoxyethane could contribute to the stabilization of the anions for its strong coordination to the metallic ions. We first select the THF and diethyl ether as solvent for the reduction of **2**. Unfortunately, they led to the formation of

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Chart 1: Chemical structures of silole, spiroisilole and silole dianion. **Scheme 1:** Synthesis of the octaphenyl-1,1'-spirobisilole.

a mixture that cannot be easily purified and isolated. The example inferred that the spiroisilole tetra-anion may be more reactive and needs the strong cooperative solvent. Dimethoxyethane contains two oxygen atoms in one molecule and exhibits the strong cooperation in the isolation of some reactive compounds. Therefore, the reduction of **1** was tried in dimethoxyethane (DME).

Treating **1** with four equivalents of lithium in DME at room temperature for 2 h afforded the tetra-anion **2** $[\text{Li}^+(\text{DME})]_4[1^{4-}]$ as air- and moisture-sensitive orange powders in 95% yield. The compound **2** had been characterized by ^1H , ^{13}C , and ^{29}Si NMR spectroscopy (Scheme 2).

Scheme 2: Synthesis of the spiroisilole tetra-anion **2**.

According to the ^1H NMR spectra, there are four DME molecules in one unit of tetra-anion **2**, indicating the DME was efficient to the stabilization of the **2**. The ^{29}Si NMR spectra of **2** exhibited at -13.7 ppm in C_6D_6 , are upfield for **1** (ca. -8.3 ppm), which attributed a four-coordinate silicon atom and was similar to the 1,1-disubstituted silole dianion (-15 – 20 ppm) reported by the Cui group (Han et al., 2014). The ^{13}C NMR spectra of **2** appears a peak at 78.6 ppm, which is obvious in the range of carbanions, belonged to the attribution of negative charge in the α -C atoms of the spiroisilole tetra-anion **2** and is upfield for **1** (128.4 ppm). The result indicates the change of the C-C bonds in the spiroisilole rings and is consistent with those of the reported silolenides with 2,5-carbodians $[\text{Ph}_4\text{C}_4\text{Si}(\text{R}_1)(\text{R}_2)]^{-2}$ (77.4 – 80 ppm; O'Brien and Breeden, 1981; Hong, 2013; Han et al., 2014). The ^{13}C NMR chemical shifts of two C_β , C_i , C_o , C_m , and C_p show at 127.7 ppm; 127.4 , 128.3 ppm; 129.5 , 131.6 ppm; 132.3 , 135.4 ppm; and 136.7 , 154.8 ppm for **2**, respectively (Table 1), which are similar to that of the related 2,5-carbanion silole dianions (O'Brien and Breeden, 1981; Hong, 2013; Han et al., 2014). In order to investigate the coordination behavior of the lithium in solution, the ^7Li NMR spectrum of **2** was determined and exhibits a single resonance at -8.5 ppm in C_6D_6 , which illustrated a single environment for the four lithium atoms in solution. Even though the ^7Li NMR resonance at -8.5 ppm means the possible aromaticity, the α -C atoms show obvious carbanions according to the ^{13}C NMR spectra of spiroisilole tetra-anion **2** (78.6 ppm). If the negative charge delocalizes in the ring of the spiroisilole, the ^{13}C NMR spectra of α -C atoms would appear at 120 – 130 ppm (Saito and Yoshioka, 2005). Cui and the coworkers have also reported a 2,5-carbanion silole dianions $[\text{Ph}_2(\text{SiMe})_2\text{C}_4\text{Si}(\text{NEt})_2]^{-2} \cdot 2[\text{Li}]^+$ (Han et al., 2014). The silole dianion also shows the negative ^7Li NMR resonance at -2.4 ppm, but the change of the C-C bond distances observed in the single-crystal X-ray analysis indicated that the silole dianions did not possess noticeable aromaticity. So it is hard to

Table 1: ^{13}C , ^{29}Si , and ^7Li NMR chemical shifts of reported 2,5-carbanion silole anions.

2,5-Carbanion silole anions	$[\text{Ph}_4\text{C}_4\text{Si}(\text{Me})_2]^{-2} \cdot 2[\text{Li}]^+$	$[\text{Ph}_4\text{C}_4\text{Si}(n\text{-Bu})_2]^{-2} \cdot 2[\text{Li}]^+$	$[\text{Ph}_2(\text{SiMe})_2\text{C}_4\text{Si}(\text{NEt})_2]^{-2} \cdot 2[\text{Li}]^+$	$[\text{Ph}_8\text{C}_8\text{Si}_2]^{-4} \cdot 4[\text{Li}]^+$
C_α	77.4	73.2	67.80	78.6
C_β	128.5	128.1	122.02	127.7
C_p	107.8, 120.5	108.5, 120.8	121.2	127.4, 128.3
C_m	123.3, 125.8	123.6, 126.6	125.3	129.5, 131.6
C_o	126.5, 132.4	132.9, 126.6	130.7	132.3, 135.4
C_i	150.6, 147.1	151.5, 147.7	145.5	136.7, 154.8
^{29}Si ring	3.2	-0.27	-17.2	-13.7
^7Li	—	—	-2.4	-8.5
Reference	O'Brien and Breeden (1981)	Hong (2013)	Han et al. (2014)	This work

demonstrate the spiroilole tetra-anion **2** shows obvious aromaticity.

As a contrast, a table with regard to ^{13}C , ^{29}Si , and ^7Li NMR chemical shifts of the related 2,5-carbanion silole anions has been built in Table 1. The NMR spectra of the tetra-anion **2** appear to be similar to those of the related silole dianions reported. All of these supply sufficient evidence to confirm the structure of tetra-anion **2** (Figure 1).

The molecular geometry predicted of **2** by DFT calculations at B3LYP/6-31G(d) basis set. The calculated highest occupied molecular orbital (HOMO) and LUMO are given in Figure 2 in the 'Experimental' section. The HOMO of **2** is mainly formed by the π orbitals originating from the C=C

Figure 1: X-ray photoelectron spectroscopy (XPS) spectra of Pd 3d .

Figure 2: Cyclic voltammograms of 1.0 mm of spiroilole **1** in CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. A Pt disk embedded in a glass tube was used as a working electrode (0.03 cm^2), a Pt wire as a counterelectrode, and an Ag wire as a quasi-reference electrode. The scan rate was at 0.1 V s^{-1} .

Scheme 3: Reaction of **2** with dioxygen.

double bond in the silole ring and the lone pairs on the α -carbon atoms with contribution from the silicon σ orbitals. The HOMO of **2** displays a ring surface similar to that of the LUMOs of neutral 1,1-disubstituted siloles.

Compound **2** is extremely air sensitive and can be slowly oxidized in sealed NMR tubes to generate **1**. Thus, the reaction of tetra-anion **2** with dioxygen has been investigated (Scheme 3). The reaction at room temperature cleanly generated **1** in nearly quantitative yield.

As a common oxidizing agent, 1,4-benzoquinone can reveal the reactivity of some reductants. Similarly, the reaction of tetra-anion **2** with 1,4-benzoquinone resulted in the quantitative regeneration of **1** with the formation of the corresponding dilithium benzoquinone (Scheme 4).

All these reactions indicated that tetra-anion **2** prefers electron transfer rather than nucleophilic addition to these substrates. The electron transfer property of tetra-anion **2** is further supported by its reaction with PdCl_2 . Reaction of **2** with PdCl_2 yielded a black precipitate and **1** (Scheme 5). In order to identify the black powder, we have done the X-ray photoelectron spectroscopy (XPS) to demonstrate the Pd 3d (335.1 and 340.9 eV).

All of these reactions converted **2** to **1** in an almost quantitative yield, and thus certified that the tetra-anion **2** acted as a homogeneous four-electron transfer reductant.

Figure 2 shows cyclic voltammograms (CV) of spiroilole **1** in dichloromethane solution containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. As the potential is scanned from 1.8 V to the negative region (-1.8 V), the reduction of spiroilole **1** showed four potential peaks (1.28, 0.85, -0.82 , and 1.27 V), indicating spiroilole **1** could get four electrons to form the corresponding spiroilole tetra-anion **2**.

Since tetra-anion **2** undergoes electron transfer reactions with most of electrophiles, we tried its reaction with dilute hydrochloric acid to further confirm the negative charge of alpha carbon atoms (Scheme 6), and got the 1,2,3,4,6,7,8,9-octaphenyl-5-silaspiro[4.4] nona-2,7-diene (**3**) as the hydrolyzed product. Compound **3** was characterized by ^1H , ^{13}C , and ^{29}Si NMR spectra and mass spectrum. The result illustrated that the alpha carbon atoms were

Scheme 4: Reaction of **2** with benzoquinone.

Scheme 5: Reaction of **2** with PdCl_2 .

Scheme 6: Reaction of **2** with dilute hydrochloric acid.

negatively charged and further confirm the structure of tetra-anion **2**.

To the best of our knowledge, rare carbanions could selectively display electron transfer reactivity with all of these substrates, except for naphthalene radical anion and its derivatives (Garst, 1971). We found that the spiro-silole **1** could be reduced by naphthalene lithium to form the tetra-anion **2**. But the reverse reaction did not occur, indicating that **2** is a relatively mild reducing reagent compared to naphthalene lithium.

It is well-known that alkali metals and lithium naphthalene as well as magnesium have been widely used as reductants for the synthesis of low-valent main group and transition metal complexes. The choice of the reductants is crucial to obtain the desired products due to over-reduction and the occurrence of other side reactions (Fischer and Power, 2010). In this respect, the spiro-silole tetra-anion **2** possesses a number of unique features that make it an appealing alternative to the above-mentioned reductants. For example, it is thermally stable and soluble in a wide range of organic solvents like THF, DME, and

toluene; it can be easily prepared in the nearly quantitative yield on gram scales; and it does not present any significant fire or toxic hazards. Most importantly, the silole precursor **1** can be recovered in excellent yields.

Conclusion

In summary, we have isolated and NMR characterized spiro-silole tetra-anions with a four-coordinate silicon atom for the first time. The silole tetra-anion **2** selectively underwent four-electron transfer reactions with a number of substrates and nucleophilic addition and substitution reactions that are common to carbanions have not been observed. This work demonstrated that **2** is a promising electron transfer reducing reagent that could be used in synthetic chemistry. We are continuing to explore the applications of tetra-anion **2** to the reduction of main group compounds and will report on this in due course.

Experimental

Materials and measurements

All operations were carried out under an atmosphere of dry argon by using modified Schlenk line and glovebox techniques. All solvents were freshly distilled from Na and degassed immediately prior to use. The ^1H , ^{13}C , and ^{29}Si NMR spectroscopic data were recorded on Varian Mercury Plus 400 MHz NMR spectrometers. Chemical shifts are referenced against external Me_4Si (^1H , ^{13}C , and ^{29}Si).

Synthesis of octaphenyl-1,1'-spirobisilole (1), tetra-anion (2)

Octaphenyl-1,1'-spirobisilole (1): To a solution of diphenylacetylene (7.0 g, 40.0 mmol) in dry DME (50 mL) was added clean lithium shavings (0.28 g, 40.0 mmol). The reaction mixture was stirred at room temperature for 12 h in a dry nitrogen atmosphere. The mixture was then followed by the addition of 1.7 g (10.0 mmol) silicon tetrachloride at room temperature. After refluxing for 5 h, the reaction mixture was cooled and filtered, and the filtrate was washed with water. The organic layer was extracted with toluene and dried over magnesium sulfate. The solvent was removed and the residue was recrystallized from ethanol gave a faintly greenish-yellow crystal in 60% yields (3.2 g). m.p. = 263°C. ^1H NMR (C_6D_6): δ = 6.93–7.26 (m, 40H, Ar). ^{13}C NMR (C_6D_6): δ = 124.8, 125.8, 126.2, 126.9, 127.3, 127.2, 127.5, 128.6, 130.2, 150.9. ^{29}Si NMR (C_6D_6): δ = -8.3. Analysis calculated for $\text{C}_{56}\text{H}_{40}\text{Si}$, C = 90.76%, H = 5.44%; found, C = 90.72%, H = 5.66%.

[Octaphenyl-1,1'-spirobisilole] $^{4-}$ [Li $^+$ (DME)] 4 (2): Lithium shavings (0.30 g, 44.0 mmol) was added to a DME solution (25 mL) of silole 1 (7.4 g, 10.0 mmol) at room temperature, and the mixture was stirred for 2 h. An excess of lithium was separated by filtration, and the filtrate was concentrated. The crude product was recrystallized from DME/*n*-hexane (2:1) to afford 2 as orange powders (11.3 g, 95%). ^1H NMR (C_6D_6): δ = 2.96 (24H, CH_2 -dme), 3.07 (36H, CH_3 -dme), 6.93–7.26 (m, 40H, Ar). ^{13}C NMR (C_6D_6): δ = 58.6 (CH_2 -dme), 71.0 (CH_3 -dme), 78.6 (C_α), 127.7 (C_β), 127.4 (C_γ), 128.3 (C_δ), 129.5 (C_m), 131.6 (C_n), 132.3 (C_o), 135.4 (C_p), 136.7 (C_i), 154.8 (C_j). ^{29}Si NMR (C_6D_6): δ = -13.7. ^7Li NMR (C_6D_6): δ = -8.5.

Reduction reactions of the tetra-anion 2

Reaction with dilute hydrochloric acid: An aqueous 5% HCl solution (10 mL) was slightly added to a solution of 2 (0.40 g, 0.25 mmol) in DME (10 mL) at room temperature, and the mixture became colorless. The solution was concentrated and toluene (25 mL) was added. The mixture was extracted with diethyl ether (3 $\times$ 25 mL). After its concentration to 10 mL under reduced pressure, the solution was stored in the freezer (-40°C) and 1,2,3,4,6,7,8,9-octaphenyl-5-silapropi[4.4] nona-2,7-diene (3) was afforded as a white powder (0.13 g, 67%). m.p. = 247°C. ^1H NMR (C_6D_6): δ = 7.30–7.33 (m, 4H, Ar), 7.82–7.11 (m, 36H, Ar), 2.87 (s, 4H, SiCH_2). ^{13}C NMR (C_6D_6): δ = 147.7 (C_j), 142.1 (C_i), 137.7 (C_o), 134.0 (C_p), 132.0 (C_m), 128.2 (C_n), 127.6 (C_p), 126.8 (C_p), 124.4 (C_p), 50.1 (C_α). ^{29}Si NMR (C_6D_6): δ = 11.9. MS(EI): m/z = 743.2 [M^+]. Analysis calculated for $\text{C}_{56}\text{H}_{40}\text{Si}$, C = 90.28%, H = 5.95%; found, C = 90.32%, H = 5.96%.

Reaction with dioxygen: The solid tetra-anion 2 (0.40 g, 0.25 mmol) was exposed to an excess of dioxygen at room temperature. It was stirred for 2 h until the color had become light yellow. To the solid was added toluene (25 mL) and the solution was filtered. The filtrate was concentrated to give the spiroisilole precursor 1 (0.18 g, 95% recovery).

Reaction of 2 with *p*-benzoquinone (1:2): A solution of *p*-benzoquinone (0.054 g, 0.5 mmol) in DME (10 mL) was added to a solution of 2 (0.40 g, 0.25 mmol) in DME (10 mL) at room temperature, and

Figure 3: The calculated HOMO and LUMO of 2.

the mixture became dark green immediately. The solution was concentrated and toluene (25 mL) was added. The mixture was filtered and the filtrate was concentrated to give the silole precursor 1 (0.16 g, 93% recovery). The residues were hydrolyzed with aqueous HCl. The resulting product was extracted with diethyl ether to afford dihydroquinone (0.04 g, 75%).

Reaction of 2 with dichloropalladium(II): To a mixture of 2 (0.40 g, 0.25 mmol) and dichloropalladium(II) (0.10 g, 0.50 mmol) was added DME (10 mL) at room temperature. After 2 h, the mixture became light yellow and the formation of dark powder was observed and demonstrated by XPS (340.9 eV for $\text{Pd}3d_{3/2}$ and 335.1 eV for $\text{Pd}3d_{5/2}$). The solution was concentrated and toluene (25 mL) was added. The mixture was filtered, and the filtrate was concentrated to give the spiroisilole precursor 1 (0.14 g, 90% recovery).

Computational details

All calculations were performed using the Gaussian 03 suite of programs, revision C. 02 (Frisch et al., 2004). The geometries and harmonic vibration frequency of 2 were optimized in DFT method with B3LYP method and 6-31+G(d) basis set. The calculated HOMO and LUMO for 2 are given in Figure 3.

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