

Dalton Transactions

An international journal of inorganic chemistry

rsc.li/dalton



ISSN 1477-9226










PAPER

Masaichi Saito *et al.*
Synthesis of a dilithiobutadiene bearing extremely bulky silyl
substituents and its reactivity toward functionalized silanes

PAPER

[View Article Online](#)
[View Journal](#) | [View Issue](#)Cite this: *Dalton Trans.*, 2025, **54**, 4030

Synthesis of a dilithiobutadiene bearing extremely bulky silyl substituents and its reactivity toward functionalized silanes†‡

Katharina Münster, ^a Shunsuke Kudo,^a Takuya Kuwabara, ^a Eriko Shimamura,^a Shunsuke Furukawa, ^a Yusuke Yoshida,^b Shintaro Ishida, ^b Takeaki Iwamoto, ^b Kazuki Tanifuji, ^c Yasuhiro Ohki, ^c Mao Minoura ^d and Masaichi Saito ^{*a}

The synthesis and full characterization of 1,4-dilithio-1,4-bis(triisopropylsilyl)-2,3-diphenylbuta-1,3-diene (**1b**) are reported. This molecule featuring extremely bulky silyl groups at the 1- and 4-positions serves as a precursor for the synthesis of 2,5-bis(triisopropylsilyl)-3,4-diphenyl-1-silacyclopenta-1,3-dienes (siloles) bearing various substituents at the silicon atom ($\text{SiR}_2 = \text{SiH}_2$ (**4**), SiH(OMe) (**5**), SiF_2 (**6**), SiBr_2 (**7**), SiBr(OMe) (**8**)). Importantly, compounds **6** and **7** reacted with lithium to afford 2,5-bis(triisopropylsilyl)-3,4-diphenyl-dilithiosilole (**9**). The solid-state molecular structure and solution NMR spectra reveal the formation of an aromatic ring system, as opposed to the precursors **6** and **7**, with two Li cations coordinated by the silacycle in η^5 -fashions. The sterically bulky dilithiosilole **9** can be applied as an important starting material in the pursuit of low-valent silicon species without donor stabilization.

Received 25th December 2024,
Accepted 2nd February 2025

DOI: 10.1039/d4dt03537b

rsc.li/dalton

Introduction

Silylenes, divalent silicon species, have long received considerable attention in terms of their electronic characteristics and reactivity,^{1–12} and many types of isolable silylenes stabilized by sterically demanding groups and/or by donor coordination have been reported.^{12–16} Among such intensively studied silylenes, a cyclic diaminosilylene reported by West is worthy of attention because its divalent silicon center is incorporated into a 6π -electron aromatic ring.^{17–19} On the other hand, a 1-silacyclopentadienylidene, where the divalent silicon center is situated within a butadiene skeleton, is of considerable interest because of its predicted planar structure featuring a potential 4π -electron system.^{20,21} Although a variety of 1-silacy-

clopenta-1,3-dienes (siloles) and derivatives thereof were reported,^{22,23} none of them emerged as a suitable precursor to obtain a donor-free silylene.¹⁶ Bulky substituents on the 1,4-positions should be necessary to sterically protect the reactive silylene center and avoid the necessity of stabilization by a Lewis base.¹⁶ To prepare such a silacyclopentadienylidene, 1,4-dilithio-1,3-butadienes²⁴ are reasonable precursors and they can be simply prepared by the reduction of phenylacetylenes with lithium.^{25,26} We have previously reported on the reactivity of 1,4-substituted dilithiobutadienes obtained by such reduction of phenylacetylenes bearing bulky silyl substituents SiR_3 ($\text{SiR}_3 = \text{tBuMe}_2$, Si^iBu_3 , Si^iPr_3) (Scheme 1).^{27,28} The reduction of phenyl(*tert*-butyldimethylsilyl)acetylene with lithium exclusively afforded dilithiobutadiene **1a**, whereas reduction of phenyl(*tri-tert*-butylsilyl)acetylene bearing the bulkiest silyl group among these compounds yielded only *tri-tert*-butylsilylacetylene (**3c**). In the reduction of phenyl(*triisopropylsilyl*)acetylene, highly crystalline dilithiodibenzopentadiene **2b** was isolated, even though dilithiobutadiene **1b** formed as the main product as evidenced by NMR spectroscopy. We now report the successful isolation and full characterization of dilithiobutadiene **1b**, which possesses thus far the bulkiest silyl groups on the 1,4-positions. Furthermore, we demonstrate the reaction of **1b** with functionalized silanes yielding siloles that serve as starting materials for the synthesis of a new dilithiosilole (**9**). This compound would act as a promising precursor in the pursuit of a silacyclopentadienylidene.

^aDepartment of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-okubo, Sakura-ku, Saitama-city, Saitama, 338-8570, Japan.
E-mail: masaichi@chem.saitama-u.ac.jp

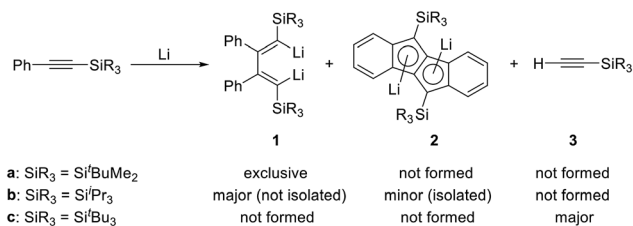
^bDepartment of Chemistry, Graduate School of Science, Tohoku University, Sendai, Miyagi, 980-8578, Japan

^cInstitute of Chemical Research, Kyoto University, Uji, Kyoto, 611-0011, Japan

^dDepartment of Chemistry, College of Science, Rikkyo University, Toshima-ku, Tokyo, 171-8501, Japan

†Electronic supplementary information (ESI) available. CCDC 2402953–2402955. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4dt03537b>

‡This work is dedicated to Professor Vadapalli Chandrasekhar on the occasion of his 65th birthday.

Scheme 1 Reduction of phenyl(SiR_3)acetylenes with lithium.

Results and discussion

Synthesis and characterization of 1,4-dilithio-1,4-bis(triisopropylsilyl)-2,3-diphenylbuta-1,3-diene (**1b**)

As described in the previous article,²⁷ the reduction of phenyl(triisopropylsilyl)acetylene leads to the simultaneous formation of dilithiobutadiene **1b** and dilithiodibenzopentalene **2b** (Scheme 2). Although **1b** was shown to be the major product in this reaction evidenced by NMR spectroscopy, the isolated yields of **1b** and **2b** are comparable because the isolation of **1b** is hampered by the facile crystallization of **2b** in the shape of orange crystals. Therefore, to isolate pure compound **1b**, repeated recrystallization from *n*-hexane or *n*-hexane/ Et_2O is necessary (Experimental section). By this method, **1b** contaminated by <2% of **2b** can be obtained in *ca.* 13% yield as a dark-red crystalline solid usually containing residual Et_2O and/or *n*-hexane. The compound is highly air- and moisture-sensitive, but can be stored over a prolonged period of time under inert conditions at ambient temperature without decomposition. In the solid state, decomposition is observed at a temperature of about 80 °C. In order to promote the crystallization of pure **1b**, other solvents for the recrystallization were attempted. However, although **1b** can be crystallized as a THF- or N,N,N',N' -tetramethylethane-1,2-diamine-coordinated (TMEDA) compound by using the respective coordinating solvent in combination with *n*-hexane at −30 °C, this method does not prevent **2b** from simultaneous crystallization. Furthermore, the higher polarity of THF and TMEDA in comparison to Et_2O makes it difficult to find a suitable concentration of the crystallization solution leading to the formation of isolable solid materials. As a result, in our experience the crystallization from Et_2O and *n*-hexane is the most convenient method to obtain **1b**. In this context, we would also like to note that coordinated Et_2O from the reaction is replaced by THF or TMEDA, respectively; but that the replacement or

removal of the latter solvents is very difficult. This should be taken into consideration for the following reactions where compound **1b** is planned to be used.

A characteristic feature of compound **1b** is its ^7Li NMR chemical shift of $\delta = 1.16$ ppm (C_6D_6), which lies in the range of resonances of vinylolithiums.^{29–33} Notably, ^7Li NMR spectra of **1b** sometimes exhibited additional resonances in the region between $\delta = 1$ –2 ppm, which disappeared upon addition of Et_2O to the NMR sample (refer to ESI† for details). Organolithium compounds are known to form aggregates in solution^{34,35} and therefore, we attribute these additional resonances not to impurities, but to structurally differing molecules of **1b** caused by the absence of sufficient coordinating solvent (Et_2O). In contrast to **1b**, the ^7Li NMR resonance of **2b** can be observed in the high-field region at $\delta \approx -8$ ppm,²⁷ characteristic of contact ion pairs in which the Li ion is coordinated to an aromatic ring system.^{32,36} Moreover, the ^{13}C NMR spectrum of dilithiobutadiene **1b** features a resonance at $\delta = 205.81$ ppm indicative of a lithiated vinyl carbon atom.²⁹ The solid-state structure of **1b** was determined by X-ray diffraction analysis of a single crystal obtained from a solution of **1b** in Et_2O and *n*-hexane at −30 °C (Fig. 1). The molecular structure reveals coordination of the Li atoms to the terminal carbon atoms of the butadiene framework. The Li–C bond distances lying in the range of 2.10–2.20 Å agree with those observed in analogous 1,4-disilyldilithiobutadienes ($\text{SiR}_3 = \text{SiMe}_3$, Si^tBuMe_2).^{27,29} Similar to the literature-reported 1,4-bis(trimethylsilyl)-substituted species containing two molecules of TMEDA,²⁹ in compound **1b** every Li atom is coordinated by one Et_2O molecule. In contrast, the Si^tBuMe_2 -functionalized version lacks a coordinating solvent leading to a dimeric structure with a Li_4 tetrahedron.²⁷ The C_4 chain in **1b** exhibits the expected alternation of bond lengths and a torsion angle of *ca.* 20°, which can be traced to the steric repulsion between the Ph and the silyl substituents. The latter effect is far less pronounced in the SiMe_3 derivative (2.4°) in line with the smaller steric hindrance of the substituents.²⁹

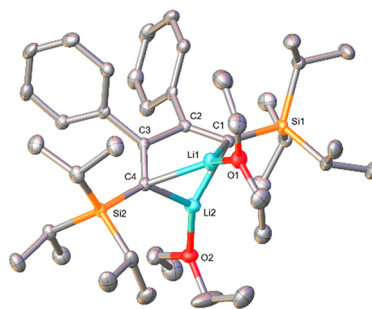
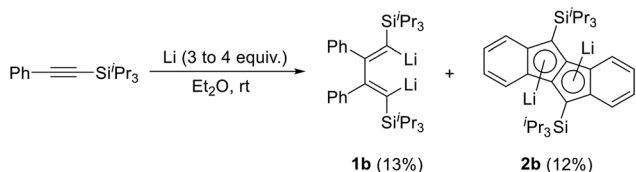


Fig. 1 The solid-state molecular structure of **1b**. The H atoms are omitted for clarity. Ellipsoids are depicted at the 50% probability level. Space group $P2_1/n$ (monoclinic). Selected bond distances (Å) and (torsion) angles (°): C1–C2 1.3604(19), C2–C3 1.5614(18), C3–C4 1.3552(19), Li1–C1 2.111(3), Li1–C4 2.184(3), Li2–C1 2.160(3), Li2–C4 2.109(3), C1–Si1 1.8635(13), C4–Si2 1.8647(13), Li1–O1 1.975(3), Li2–O2 1.948(3), Li1···Li2 2.579(4), Li1–C1–C2 86.67(11), Li1–C4–C3 80.15(10), Li2–C1–C2 85.34(11), Li2–C4–C3 91.85(11), C1–C2–C3–C4 2.4.

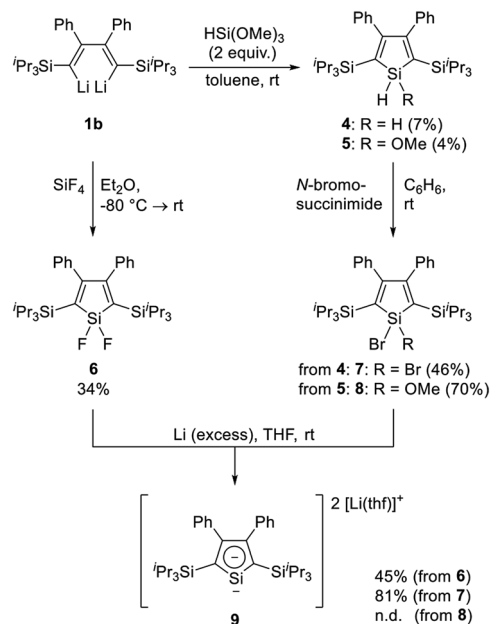
Scheme 2 Synthesis of dilithiobutadiene **1b** and dilithiodibenzopentalene **2b**.

Synthesis and characterization of 2,5-bis(triisopropylsilyl)-3,4-diphenylsiloles ($\text{SiR}_2 = \text{SiH}_2$ (**4**), SiH(OMe) (**5**), SiF_2 (**6**), SiBr_2 (**7**) and SiBr(OMe) (**8**))

Scheme 3 shows an overview over the synthetic route toward siloles **4–8** starting from dilithiobutadiene **1b**. Upon reaction with 2 equivalents of trimethoxysilane (HSi(OMe)_3), compounds **4** and **5** are formed simultaneously. In contrast to our expectation, methoxy-substituted silole **5** is obtained as a minor product (4%), whereas dihydrosilole **4** emerges as the main species (22%). The compounds are air- and moisture-stable and can be separated by column chromatography with subsequent recrystallization. Although the mechanism of this reaction was not investigated in more detail, we attribute this outcome to the ability of basic alkaline compounds such as **1b** to catalyze the disproportionation of alkoxy-silanes yielding SiH_4 among other species.³⁷ Similar behaviour was also observed upon synthesis of a silacyclopentane from a 1,4-dilithio-1,1,4,4-tetraarylbutane treated with an excess amount of HSi(OMe)_3 .³⁸ Variation of the reaction conditions (stoichiometry, solvent and temperature) did not alter the result shown here. In order to increase the efficiency in synthesizing **4** and **5**, and since pure **1b** was obtained in a low yield, a one-pot reaction starting from phenyl(triisopropylsilyl)acetylene (Scheme 2) was developed, in which the intermediately formed dilithiobutadiene was used for further reactions without prior isolation (for more details, refer to the Experimental section). Although a variety of compounds inherently formed in this reaction (e.g. hydrolyzed **2b**), purification by column chromatography afforded compounds **4** and **5**. In contrast, the synthesis of difluorosilole **6** was conducted using pure **1b**, since a column-chromatographic purification was expected to cause decomposition of the target compound. Instead, **6** was

obtained after recrystallization under inert conditions in 34% yield. To expand the library of halide-functionalized siloles, compounds **4** and **5** were treated with *N*-bromosuccinimide to afford the corresponding bromosiloles **7** and **8** in moderate to good yields. The siloles **4–8** are thermally stable compounds, which melt reversibly between 90 and 150 °C. Compounds **4** and **5** are insensitive to moisture and air, while compounds **6–8** do not decompose upon short exposure to atmospheric conditions; however, they should be handled under inert conditions to avoid hydrolysis. The purity of the compounds was confirmed by elemental and NMR spectroscopic analyses.

NMR spectra of siloles 4–8. Siloles **4–8** were fully characterized by the ^1H , ^{13}C , ^{19}F (**6**) and ^{29}Si solution NMR spectroscopy. The characteristic ^{29}Si NMR chemical shifts are summarized in Table 1. In all cases, the resonance for the triisopropylsilyl groups in 2,5-positions appears at a chemical shift close to $\delta = 0$ ppm as expected.^{22,39} In contrast, considerable differences are observed for the chemical shifts of the silicon atom incorporated into the five-membered ring (Si_{ring}). Herein, the dihydrosilole **4** shows the largest high-field shift with $\delta = -18.4$ ppm, while the methoxysilole **5** exhibits the most low-field shifted resonance ($\delta = 9.3$ ppm). The siloles **6**, **8** and **7** are found in between (in this order). Generally, the ^{29}Si NMR chemical shifts of silacyclopentadienes vary largely depending on the substituents,³⁹ but the values we observed are in good agreement with reported compounds.²² For example, the ^{29}Si nuclei of 1,2,3,4,5-pentamethylsilole, 1,1-difluoro-2,3,4,5-tetramethylsilole, 1-chloro-1-hydro-2,3,4,5-tetramethylsilole,⁴⁰ 1,1-dihydro-2,5-bis(trimethylsilyl)-3,4-diphenylsilole, 1,1-dimethoxy-2,5-bis(trimethylsilyl)-3,4-diphenylsilole,⁴¹ 1-bromo-1-tris(trimethylsilyl)silyl-2,3,4,5-tetramethylsilole,⁴² and 1,1-dibromo-2,5-bis(trimethylsilyl)-3,4-diphenylsilole⁴¹ resonate between $\delta = -38.1$ and 8.2 ppm. The Si–H coupling constants ($^1J \approx 200$ Hz) were observed in compounds **4** and **5**, and the presence of hydrogen atoms at the silicon atom incorporated into the five-membered ring was alternatively confirmed by non-proton-decoupled ^{29}Si NMR spectra.⁴⁰ The corresponding ^1H NMR resonances appear at $\delta = 4.78$ ppm (CDCl_3) and $\delta = 5.63$ ppm (C_6D_6), for **4** and **5**, respectively. For the difluorosilole **6**, an Si–F coupling constant of $^1J \approx 330$ Hz was recorded, in accordance with the analogous 1,1-difluoro-2,3,4,5-tetramethylsilole ($^1J = 320$ Hz).⁴⁰ In the ^{13}C NMR spectra (Table 1), a character-



Scheme 3 Synthesis of siloles **4–8** and dilithiosilole **9**.

Table 1 The ^{29}Si and selected ^{13}C NMR chemical shifts

Compound	Si_{ring}	Si_{ipr}	C_α	C_β
4 ^a	−18.4 $^1J_{\text{Si,H}} = 196$ Hz	0.8	135.85	172.71
5 ^b	9.3 $^1J_{\text{Si,H}} = 212$ Hz	0.7	135.04	171.80
6 ^b	−11.0 $^1J_{\text{Si,F}} = 332$ Hz	1.4	n. o.	173.85 $^3J_{\text{C,F}} = 7.2$ Hz
7 ^b	5.8	2.2	136.39	169.35
8 ^b	0.4	1.0	134.71	169.81
9 ^b	130.7	−0.1	139.72	142.66

^a (CDCl_3 , ppm) of compound **4** ^b (C_6D_6 , ppm) of compounds **5–9**.

istic resonance at $\delta \approx 170$ ppm was observed for all siloles 4–8 and corresponds to the β -C atoms of the silole ring. In contrast, the α -C atom bonded to the Si atom appears high-field-shifted at $\delta \approx 135$ ppm. This finding is in good agreement with the data reported on 2,5-bis(trialkylsilyl)-substituted siloles.^{43,44}

Solid-state molecular structure of dibromosilole 7. Single crystals suitable for X-ray diffraction analysis were obtained for the dibromosilole 7 (Fig. 2).

The X-ray diffraction analysis revealed the expected structure of a silacyclopentadiene with two bromide substituents at the 1-position. The bonding parameters are in good agreement with those of previously reported siloles whose solid-state molecular structures were established by X-ray diffraction analysis.^{41,42,45,46} The five-membered silacycle possesses almost ideal planarity with the angle between the planes formed by the atoms ($C_\alpha-C_\beta-C_\beta-C_\alpha$) and ($C_\alpha-Si1-C_\alpha$), respectively, being 2.0° . In addition, the three ring C–C distances alternate accounting for the presence of two double and one single bond, showing its diene character. The Si–C bond lengths within the silole ring were determined as 1.857(4) Å and 1.848(4) Å, respectively, being in the range of literature-reported values (1.85–1.88 Å).^{41,45,46} The silole silicon atom (Si1) features a distorted tetrahedral bonding sphere (angle $C_\alpha-Si1-C_\alpha$ $99.3(2)^\circ$).

Synthesis and characterization of 2,5-bis(triisopropylsilyl)-3,4-diphenyldilithiosilole (9)

Literature contains a number of studies on dianionic silacyclopentadienes with different substitution patterns and counter cations.^{42–44,47–55} Generally, the synthesis is accomplished by

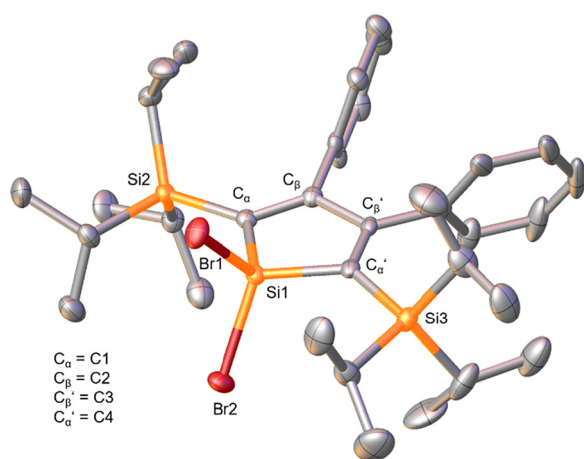


Fig. 2 The solid-state molecular structure of 7. One of the two independent molecules in the unit cell is shown. The H atoms and the second molecule in the asymmetric unit are omitted for clarity. Ellipsoids are depicted at the 50% probability level. Space group *I*121 (monoclinic). Selected bond distances (Å) and (torsion) angles ($^\circ$): $C_\alpha-C_\beta$ 1.351(6), $C_\beta-C_\beta'$ 1.537(6), $C_\beta'-C_\alpha'$ 1.350(6), $Si1-C_\alpha$ 1.857(4), $Si1-C_\alpha'$ 1.848(4), $Si1-Br1$ 2.208(2), $Si1-Br2$ 2.212(2), $C_\alpha-Si1-C_\alpha'$ $99.3(2)$, $Si1-C_\alpha-C_\beta$ $101.8(3)$, $C_\alpha-C_\beta-C_\beta'$ $118.3(4)$, $C_\beta'-C_\alpha'-Si1$ $102.0(3)$, $C_\alpha-C_\beta-C_\beta'-C_\alpha'$ $5.7(6)$, $Si2-C_\alpha-C_\alpha'-Si3$ 41.6 , angle between planes ($C_\alpha-C_\beta-C_\beta'-C_\alpha'$)–($C_\alpha-Si1-C_\alpha'$) 2.0 .

reaction of a 1,1-dihalide-substituted silole with an alkaline metal (Li, Na, K), and in one case even a 1-methyl-1-hydrosilole was used as the starting material.⁵³ Similarly, we obtained 2,5-disilyl-substituted dilithiosilole 9 by the reaction of either difluorosilole 6 or dibromosilole 7 with an excess amount of Li in THF at ambient temperature in moderate (45%) and good yield (81%), respectively. As evidenced by NMR spectroscopy, the methoxy-functionalized bromosilole 8 can also serve as the starting material indicated by a high-field resonance in the 7Li NMR spectrum; however, multiple other unidentified species were observed by 7Li NMR spectroscopy and the target compound could not be isolated in pure form (for details refer to ESI†). It is expected that the cleavage of the methoxy group is slow compared to halide cleavage, resulting in a longer reaction time,⁵³ accompanied by side-reactions, *e.g.* leading to the formation of 1-substituted monoanionic compounds or dimeric species.^{42,44,48,49}

Compound 9 was obtained as a dark-red crystalline solid after recrystallization from Et_2O and *n*-hexane. In the solid state, decomposition was observed above $150^\circ C$. The purity was confirmed by NMR spectroscopy (for selected NMR chemical shifts, refer to Table 1), since the high sensitivity against air and moisture prevented the collection of satisfying results in the elemental analysis. The 1H NMR spectrum shows well-resolved signals for the aryl protons between $\delta = 6.95$ and 7.12 ppm, slightly low-field shifted compared to those of dihalosiloles 6 and 7 ($\delta = 6.87$ – 6.73 and 6.84 – 6.67 ppm, for 6 and 7, respectively). The presence of two coordinated THF molecules is observed as broadened resonances at $\delta = 1.31$ and 3.58 ppm, differing from the chemical shifts of uncoordinated THF ($\delta = 1.40$, 3.57 ppm in C_6D_6).⁵⁶ In the ^{13}C NMR spectrum, all resonances appear at chemical shifts smaller than $\delta = 150$ ppm, which could indicate the introduction of two negative charges into the silole framework compared to the neutral precursor.⁴⁴ The latter exhibit characteristic ^{13}C NMR resonances at $\delta \approx 170$ and 135 ppm for the β - and α -C atoms, respectively, of the silacycle. Upon transformation to the dilithiosilole, the β -C resonance is shifted to higher field ($\delta \approx 142.7$ ppm; assigned by 2D NMR, see ESI†). Similar observations were made by the groups of Kovács and Müller upon investigation of 2,5-bis(trialkylsilyl)-substituted siloles,^{43,44} and can also be observed in alkyl- and aryl-substituted derivatives.^{42,52} In contrast, the resonance of the α -C atom shifts to lower field ($\delta = 139.72$ ppm), which is also observed in 2,3,4,5-tetraphenyldilithiosilole ($\delta = 129.71$ ppm).⁴⁸ The characteristic ^{29}Si NMR chemical shifts at $\delta = 130.7$ ppm for the ring Si atom and $\delta = -0.1$ ppm for the triisopropylsilyl group are in line with the formation of a dianionic silacycle and again agree with the reports cited before.^{43,44} In particular, the presence of silyl substituents in the 2,5-positions induces the pronounced low-field shift, probably due to the increase in a silylene character in 9, as it was observed in 2,5-silylated dilithiostannoles.^{28,44} On the other hand, the previous investigations on 2,5-alkyl- and 2,5-aryl-substituted silole derivatives found relatively high-field-shifted ^{29}Si NMR resonances,⁴² as for example 2,3,4,5-tetraphenyldilithiosilole ($\delta = 68.5$ ppm)^{47,48} and 2,3,4,5-tetramethyl-

dilithiosilole ($\delta = 29.8$ ppm).⁵⁵ Moreover, the ^7Li NMR shift of $\delta = -6.16$ ppm indicates the presence of two (on the NMR time scale) chemically equivalent Li atoms coordinated by an aromatic ring system.^{32,36} On the other hand, a previous report discussed the solution structure of tetraphenyldilithiosilole, which exhibits a ^7Li NMR resonance at $\delta = 0.23$ ppm, contrasting our findings for compound **9**.⁴⁷

The solid-state molecular structure (Fig. 3) confirmed the results of the NMR analysis. Single-crystals for the X-ray diffraction analysis were obtained from a solution of **9** in Et_2O , C_6H_6 and *n*-hexane at -30 °C. As indicated by the ^7Li NMR chemical shift, two Li atoms are found coordinated by the five-membered aromatic ring in η^5 fashions with an average distance of 2.23 Å between a carbon and a lithium atom, and each is additionally coordinated by one THF molecule. Similar to the dibromosilole discussed in the previous section, the silacycle is close to ideal planarity, as also observed for other derivatives.^{42,44,47} A pronounced difference compared to the silole **7** is found in the C–C bond distances within the five-membered ring. While in the neutral species values representing two double-bonds and one single-bond were found, the $\text{C}_\alpha\text{--C}_\beta$ and $\text{C}_\beta\text{--C}_\beta$ bond distances are now equal within the measurement uncertainty (*ca.* 1.45 Å). This suggests substantial delocalization of electrons within the ring and is diagnostic of the aromatic nature of this system.⁴⁴ The Si1--C_α bond distance is slightly elongated relative to those of the precursors

6 and **7** (*ca.* 0.03 Å), which is a result of elongation by silylene character and shortening by electronic delocalization to increase its double-bond character.⁵⁷ Upon comparison to the dipotassio-2,5-bis(trimethylsilyl)-3,4-diphenylsilole reported by Müller *et al.*, which forms a coordination polymer through the η^5 -coordination of K^+ ions to the aromatic ring and the ring Si atom ($\kappa\text{-Si}$),^{44,58} we conclude that in the present case of compound **9** the steric bulk of the triisopropylsilyl groups in 2,5-positions is sufficient to prevent the Si atom from such coordination. This is a promising structural feature with regard to the synthesis of a base-free silylene from this molecule.

Conclusions

We succeeded in the synthesis and full characterization of 1,4-dilithio-1,3-butadiene **1b** bearing extremely bulky triisopropylsilyl groups at its 1- and 4-positions. The triisopropylsilyl substituents in 1- and 4-positions feature the highest steric demanding among the 1,4-dilithio-1,4-disilyl-1,3-butadienes reported to date. We successfully employed this compound in the synthesis of various functionalized siloles bearing hydro, methoxy and halide substituents at the silole silicon atom. As a representative example, the solid-state molecular structure of dibromosilole **7** was successfully determined by X-ray diffraction analysis, showing its planar five-membered ring with a diene character. In the next step, the dihalide-functionalized siloles **6** and **7** were converted into dilithiosilole (**9**), which was fully characterized by NMR spectroscopic analysis and X-ray diffraction analysis. The high-fielded ^7Li NMR resonance indicates the coordination of Li ions by an aromatic ring system. This was confirmed by the solid-state molecular structure revealing a monomeric species containing a planar silacycle with delocalized bonds and two Li cations coordinated above and below the aromatic silole ring. We strongly believe the dilithiosilole bearing extremely bulky silyl groups will receive considerable attention as a promising precursor for an unconquered stable silacyclopentadienylidene.

Experimental

Materials and methods

If not otherwise stated, experiments were performed under an argon atmosphere in a glovebox or using standard Schlenk techniques. Hexane, benzene, diethyl ether, THF and deuterated benzene were purified by potassium mirror before use. Toluene and deuterated chloroform were stored over activated molecular sieves (3 Å). Phenyl(triisopropylsilyl)acetylene was synthesized according to a literature procedure.⁵⁹ *N*-Bromosuccinimide (FUJIFILM Wako Pure Chemical Corporation) was recrystallized from water and dried prior to use. Commercially purchased trimethoxysilane (Tokyo Chemical Industry Co., Ltd) was stored under argon and used as received. SiF_4 gas (Taiyo Nippon Sanso Corporation) was purchased and used without further purification. Lithium

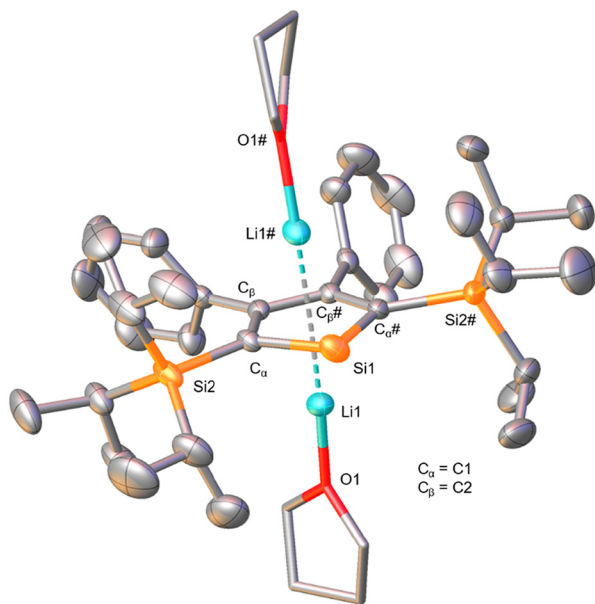


Fig. 3 The solid-state molecular structure of **9**. The H atoms and the minor part of the two-fold disordered THF molecule are omitted for clarity. Ellipsoids are depicted at the 50% probability level. The coordinated THF molecules are shown as sticks. Space group $C2$ (monoclinic). Selected bond distances (Å) and (torsion) angles (°): $\text{C}_\alpha\text{--C}_\beta$ $1.446(5)$, $\text{C}_\beta\text{--C}_\beta$ $1.438(6)$, Si1--C_α $1.881(4)$, Si2--C_α $1.875(3)$, Li1--silole plane 1.829 , Li1--O1 $1.875(6)$, $\text{C}_\alpha\text{--Si1--C}_\alpha$ $88.3(2)$, $\text{Si1--C}_\alpha\text{--C}_\beta$ $111.7(2)$, $\text{C}_\alpha\text{--C}_\beta\text{--C}_\beta$ $114.13(18)$, $\text{C}_\alpha\text{--C}_\beta\text{--C}_\beta\text{--C}_\alpha$ 1.0 , $\text{Si2--C}_\alpha\text{--C}_\alpha\text{--Si2}$ 11.8 , angle between planes $(\text{C}_\alpha\text{--C}_\beta\text{--C}_\beta\text{--C}_\alpha)\text{--}(\text{C}_\alpha\text{--Si1--C}_\alpha)$ 0.1 .

powder was prepared according to methods in the cited references from lithium lump (Kanto Chemical Co., Inc.).^{60–62} Column chromatography was performed using Kanto Silica Gel 60 (spherical, particle size 100–210 μm) and TLC silicagel 60 F₂₅₄ plates (Merck). The ^1H , ^{13}C , ^{19}F , ^7Li and ^{29}Si NMR spectra were recorded on Bruker AVANCE-300, Bruker AVANCE-400 Cryo, AVANCE-500 or AVANCE-500T spectrometers at 27 °C. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced against signals of residual protonated solvent.⁵⁶ The ^{19}F , ^7Li , ^{29}Si (non-decoupled) and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were calibrated externally. The chemical shifts (δ) are given in ppm, accompanied by coupling constants J in Hz and resonances classified as s (singlet), d (doublet), t (triplet), sept (septet), br (broad) and C_q (quaternary C atom). The intensity data for X-ray crystallographic analyses were collected under a cold N₂ stream on a Rigaku RA-Micro 7HFMR equipped with a Rigaku HyPix-6000HE detector at –150 °C for compound **7**, on a Bruker APEX2 for compound **1b**, and on a Bruker D8 QUEST ECO equipped with a Bruker PHOTON III detector at –123 °C for compound **9**, using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). For compound **7**: full data collection and reduction were performed using the CrysAlisPro program. The data sets were corrected for absorption using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The structures were solved by direct methods using the SHELXT program and refined by full-matrix least squares using the SHELXL program.^{63,64} For compounds **1b** and **9**: full data correction and reduction were performed using the APEX5 program software suite. The collected frames were integrated with the Bruker SAINT software. The absorption correction was performed by multi-scan method implemented in SADABS. The structure was solved and refined with the SHELXTL. Melting points were determined by a Yanaco macro melting point MP-S3 apparatus and were uncorrected. Elemental analysis was carried out at the Microanalytical Laboratory of Molecular Analysis and Life Science Center, Saitama University.

Synthetic procedures

1,4-Dilithio-1,4-bis(triisopropylsilyl)-2,3-diphenylbuta-1,3-diene (1b) and dilithiodibenzopentalene 2b. For the synthesis of compounds **1b** and **2b**, finely dispersed Li powder (0.455 g, 65.56 mmol, 3.1 equiv. (typically 3 to 4 equiv.)) was suspended in Et₂O (10 mL). Phenyl(triisopropylsilyl)acetylene (5.46 g, 21.12 mmol, 1 equiv.) was degassed in vacuum and added at room temperature while stirring. Et₂O (10 mL) was used to completely transfer the alkyne to the reaction mixture. After vigorous stirring for *ca.* 30 min to 2 h, a color change of the reaction mixture to yellow, later brown was observed. Vigorous stirring was continued for *ca.* 18 h to yield a dark red-brown solution and unreacted Li. The latter was removed by filtration, washed with Et₂O (30–50 mL) and the volatile substances were removed under reduced pressure for 2 h. The resulting oily or foamy dark-red residue was then suspended in *n*-hexane (8 mL) and stored at –30 °C overnight. The yellow/orange precipitate was separated by filtration over Celite®, the filtrate was

concentrated to *ca.* 7 mL and stored at –30 °C overnight. Recrystallization was continued by repeated decantation of the mother liquor, isolation of the solid (crystalline) material and storage of the mother liquor at –30 °C. The crystallization conditions varied case by case; however, a solution of low viscosity was necessary to promote crystallization. Therefore, the filtrate/mother liquor was sometimes diluted with *n*-hexane before further storage at –30 °C. Usually, the following observations were made during the recrystallization process:

1st vial: yellow/orange powder; mainly composed of dilithiodibenzopentalene **2b** with a trace amount of dilithiobutadiene **1b**.* (*In one case, large dark red crystals of **1b** were formed among orange powder of **2b**. They can be picked out by tweezers and further recrystallized.)

2nd vial: yellow/orange crystalline solid (+ powder); mainly composed of dilithiodibenzopentalene **2b**.

3rd vial: red crystalline solid or powder, sometimes sticky even after drying; mainly composed of **1b** (sometimes still contaminated with up to 20% of **2b**).

Usually from 4th vial: red crystalline solid, which becomes solid after drying (not sticky); composed of almost pure **1b** (<2% of **2b**).

The color of the mother liquor is generally very dark. However, after repetitive recrystallizations to remove **2b**, the color changes from orange-red (compound **2b**) to deep-red (compound **1b**).

Dilithiobutadiene 1b. Yield: red solid, 0.962 g (contains (Et₂O)_{2.5}, 1.344 mmol of **1b**, 13%). **Decomposition point:** *ca.* 80 °C. ^1H NMR (400 MHz, C₆D₆): δ = 7.12 (d, $^3J_{\text{H,H}}$ = 8.1 Hz, 4 H, *o*-Ph), 7.05–6.98 (m, 4 H, *m*-Ph-*H*), 6.85 (t, $^3J_{\text{H,H}}$ = 7.2 Hz, 2 H, *p*-Ph-*H*), 3.19 (q, $^3J_{\text{H,H}}$ = 7.4 Hz, 10 H, OCH₂), 1.25 (d, $^3J_{\text{H,H}}$ = 7.3 Hz, 36 H, $^i\text{Pr-CH}_3$ overlapped with 6H of CH(CH₃)₂), 1.06 (t, $^3J_{\text{H,H}}$ = 7.4 Hz, 15 H, OCH₂CH₃). The signal for the CH protons of the ^iPr groups was overlapped with the $^i\text{Pr-CH}_3$ signal, confirmed by HSQC measurement (see, ESI†). $^{13}\text{C}\{^1\text{H}\}$ (101 MHz, C₆D₆): δ = 205.81 (C_q, C α), 161.75 (C_q, C β), 153.17 (C_q, *i*-Ph), 129.02 (CH), 126.23 (CH), 123.67 (CH), 65.46 (CH₂, OCH₂), 20.33 (CH₃, $^i\text{Pr-CH}_3$), 14.26 (CH₃, OCH₂CH₃), 13.95 (CH, $^i\text{Pr-CH}$). ^7Li NMR (194 MHz, C₆D₆): δ = 1.16 (s). Because of the severe sensitivity towards air and moisture, satisfying results for the elemental analysis were not obtained.

Dilithiodibenzopentalene 2b. Yield: orange crystals, 0.328 g (0.620 mmol, 12%). Spectroscopic data were reported previously.²⁷

1,1-Dihydro-2,5-bis(triisopropylsilyl)-3,4-diphenylsilole (4) and 1-hydro-1-methoxy-2,5-bis(triisopropylsilyl)-3,4-diphenylsilole (5). Lithium (0.504 g, 72.62 mmol, 3.2 equiv.) was suspended in Et₂O (10 mL). A solution of phenyl(triisopropylsilyl)acetylene (5.90 g, 22.83 mmol, 1.0 equiv.) in Et₂O (10 mL) was added and the reaction mixture was stirred at room temperature for 18 h. The resulting dark-red reaction mixture was filtrated to remove unreacted Li metal and the filtrate was concentrated in vacuum for 3 h. The resulting dark-red foam was dissolved in toluene (50 mL) and cooled to 0 °C. To this solution was added HSi(OMe)₃ (2.9 mL, 22.83 mmol, 1.0 equiv.) dropwise while stirring. After the complete addition, stirring

was continued for 1 h at 0 °C and then for 20 h at room temperature resulting in an opaque orange reaction mixture. From this point on, all manipulations were conducted in air. The solvent was removed under reduced pressure. Hexane (30 mL) was added to the residue, sonicated for 10 min and the solvent was removed again in vacuum. Isolation of the target compounds was conducted by column chromatography. Typically, five fractions were obtained. Fractions 1 to 4 were eluted using *n*-hexane, while the last fraction was eluted by *n*-hexane/EtOAc 10 : 1. Compound **4** ($R_f \approx 0.55$ in *n*-hexane) was usually contained in the second fraction, while **5** was obtained from the last fraction ($R_f = 0.00$ in *n*-hexane). To obtain analytically pure compounds **4** and **5**, recrystallization from hexane was conducted. Other identified compounds obtained from the column-chromatographic purification include the starting material (phenyl(triisopropylsilyl)acetylene in fraction 1) and dibenzopentalene (deeply orange fraction following dihydrosilole **4**).

Dihydrosilole 4. **Yield:** light-yellow solid, 421 mg (0.770 mmol, 7%). **Melting point:** 89–95 °C. **Anal. calc. (%)** for $C_{34}H_{54}Si_3$ ($M = 547.06 \text{ g mol}^{-1}$) C 74.65, H 9.95; found C 74.06, H 10.17. $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 7.02\text{--}6.94$ (m, 6 H, *m*- and *p*-Ph-*H*), 6.91–6.83 (m, 4 H, *o*-Ph-*H*), 4.78 (s, 2 H, SiH_2), 1.00 (d, 36 H, $^3J_{\text{H,H}} = 7.4 \text{ Hz}$, $^1\text{Pr-CH}_3$), 0.84 (sept, 6 H, $^3J_{\text{H,H}} = 7.4 \text{ Hz}$, $^1\text{Pr-CH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): $\delta = 172.71$ (C_q , C_β), 143.21 (C_q , Ph-*C*), 135.85 (C_q , C_α), 129.12 (CH, *o*-Ph), 126.63 (CH, *m*-Ph), 126.35 (CH, *p*-Ph), 19.54 (CH_3 , $^1\text{Pr-CH}_3$), 13.43 (CH, $^1\text{Pr-CH}$). $^{29}\text{Si NMR}$ (99 MHz, CDCl_3): $\delta = 0.8$ (m, Si^iPr_3), -18.4 (t, $^1J_{\text{Si,H}} = 196.0 \text{ Hz}$, ring-*Si*).

Methoxysilole 5. **Yield:** yellow solid, 240 mg (0.416 mmol, 4%). **Melting point:** 112–113 °C. **Anal. calc. (%)** for $C_{35}H_{56}\text{OSi}_3$ ($M = 577.09 \text{ g mol}^{-1}$) C 72.85, H 9.78; found C 72.37, H 9.80. $^1\text{H NMR}$ (500 MHz, C_6D_6): $\delta = 6.98\text{--}6.73$ (m, 10 H, Ph-*CH*), 5.63 (s, 1 H, Si-*H*), 3.57 (s, 3 H, OCH_3), 1.16 (d, $^3J_{\text{H,H}} = 7.3 \text{ Hz}$, 36 H, $^1\text{Pr-CH}_3$), 1.06–0.97 (m, 6 H, $^1\text{Pr-CH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6): $\delta = 171.80$ (C_q , C_β), 143.10 (C_q , *i*-Ph), 135.04 (C_q , C_α), 129.54 (CH), 126.93 (CH), 126.69 (CH), 52.74 (CH_3 , OCH_3), 19.74 (CH_3 , $^1\text{Pr-CH}_3$), 13.67 (CH, $^1\text{Pr-CH}$). $^{29}\text{Si NMR}$ (99 MHz, C_6D_6): $\delta = 9.0$ (d, $^1J_{\text{Si,H}} = 210 \text{ Hz}$, ring-*Si*), 0.7 (m, Si^iPr_3).

1,1-Difluoro-2,5-bis(triisopropylsilyl)-3,4-diphenylsilole (6). Dilithiobutadiene **1b** (solvated with $(\text{Et}_2\text{O})_2$, 615 mg, 1.017 mmol) was dissolved in Et_2O (20 mL) and cooled to -80°C . Gaseous SiF_4 was passed into the reaction flask, leading to an immediate color change of the reaction mixture from dark red to yellow. Then, the flask was allowed to warm to room temperature resulting in the precipitation of a colorless solid. After the solvent was removed under reduced pressure, the residue was extracted with hexane (5 mL), filtrated and dried in vacuum. The pure compound was obtained after recrystallization from *n*-hexane at -30°C .

Yield: light-yellow solid, 204 mg (0.350 mmol, 34%). **Melting point:** 99 °C. **Anal. calc. (%)** for $C_{34}H_{52}\text{F}_2\text{Si}_3$ ($M = 583.04 \text{ g mol}^{-1}$) C 70.04, H 8.99; found C 69.96, H 9.17. $^1\text{H NMR}$ (400 MHz, C_6D_6): $\delta = 6.87\text{--}6.73$ (m, 10 H, Ph-*H*), 1.12 (d, $^3J_{\text{H,H}} = 7.0 \text{ Hz}$, 36 H, $^1\text{Pr-CH}_3$), 1.06–0.95 (m, 6 H, $^1\text{Pr-CH}$). ^{13}C

$\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): $\delta = 173.85$ (C_q , t, $^3J_{\text{C,F}} = 7.2 \text{ Hz}$, C_β), 141.88 (C_q , t, $^2J_{\text{C,F}} = 2.5 \text{ Hz}$, *i*-Ph), 128.78 (CH, Ph-*C*), 127.22 (CH, *p*-Ph-*C*), 127.06 (CH, Ph-*C*), 19.41 (CH_3 , $^1\text{Pr-CH}_3$), 13.38 (CH, $^1\text{Pr-CH}$). The resonance of the C_α atom was not observed and is probably covered by the signal of C_6D_6 . ^{19}F NMR (282 MHz, C_6D_6): $\delta = -141.1$ (s). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, C_6D_6): $\delta = 1.4$ (s, Si^iPr_3), -11.0 (t, $^1J_{\text{Si,F}} = 332 \text{ Hz}$, ring-*Si*).

1,1-Dibromo-2,5-bis(triisopropylsilyl)-3,4-diphenylsilole (7). Dihydrosilole **4** (464 mg, 0.848 mmol, 1.0 equiv.) and *N*-bromosuccinimide (453 mg, 2.55 mmol, 3.0 equiv.) were dissolved in C_6H_6 (9 mL) and stirred at room temperature for 15 h. The resulting light-yellow suspension was concentrated in vacuum, the residue was extracted with *n*-hexane ($3 \times 2 \text{ mL}$) and filtrated over Celite®. After removal of the solvent from the filtrate and recrystallization from *n*-hexane at -30°C , the product was obtained in a pure form.

Yield: yellow solid, 273 mg (0.387 mmol, 46%). **Melting point:** 101 °C. **Anal. calc. (%)** for $\text{C}_{34}\text{H}_{52}\text{Br}_2\text{Si}_3$ ($M = 704.8 \text{ g mol}^{-1}$) C 57.94, H 7.44; found C 55.75 (55.45), H 7.11 (7.23). Despite several attempts, a satisfying result could not be obtained, probably due to incomplete combustion even in the presence of a combustion additive. $^1\text{H NMR}$ (400 MHz, C_6D_6): $\delta = 6.84\text{--}6.67$ (m, 10 H, Ph-*CH*), 1.29–1.13 (m, 42 H, CH, CH_3 (^1Pr)). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): $\delta = 169.35$ (C_q , C_β), 141.00 (C_q , *i*-Ph), 136.39 (C_q , C_α), 129.20 (CH, Ph-*CH*), 127.26 (CH, Ph-*CH*), 127.02 (CH, Ph-*CH*), 20.18 (CH_3 , $^1\text{Pr-CH}_3$), 14.04 (CH, $^1\text{Pr-CH}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, C_6D_6): $\delta = 5.8$ (s, ring-*Si*), 2.2 (s, Si^iPr_3).

1-Bromo-1-methoxy-2,5-bis(triisopropylsilyl)-3,4-diphenylsilole (8). Methoxysilole **5** (335 mg, 0.580 mmol, 1.0 equiv.) and *N*-bromosuccinimide (114 mg, 0.639 mmol, 1.1 equiv.) were dissolved in C_6H_6 (6 mL) and stirred at room temperature for 14 h. The resulting orange suspension was concentrated in vacuum, the residue was extracted with *n*-hexane ($3 \times 2 \text{ mL}$) and filtrated over Celite®. After removal of the solvent from the filtrate and recrystallization from *n*-hexane at -30°C , the product was obtained in a pure form.

Yield: yellow solid, 292 mg (0.445 mmol, 70%). **Melting point:** 145–148 °C. **Anal. calc. (%)** for $\text{C}_{35}\text{H}_{55}\text{BrOSi}_3$ ($M = 655.98 \text{ g mol}^{-1}$) C 64.08, H 8.45; found C 63.85, H 8.53. $^1\text{H NMR}$ (400 MHz, C_6D_6): $\delta = 6.92\text{--}6.69$ (m, 10 H, Ph-*CH*), 3.63 (s, 3 H, OCH_3), 1.26–1.07 (m, 42 H, CH, CH_3 (^1Pr)). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): $\delta = 169.81$ (C_q , C_β), 142.04 (C_q , *i*-Ph), 134.71 (C_q , C_α), 129.23 (CH, Ph-*CH*), 129.16 (CH, Ph-*CH*), 127.02 (CH, Ph-*CH*), 126.93 (CH, Ph-*CH*), 126.84 (CH, Ph-*CH*), 52.76 (CH_3 , OCH_3), 20.10 (CH_3 , $^1\text{Pr-CH}_3$), 19.73 (CH_3 , $^1\text{Pr-CH}_3$), 13.99 (CH, $^1\text{Pr-CH}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (99 MHz, C_6D_6): $\delta = 1.0$ (s, Si^iPr_3), 0.4 (s, ring-*Si*).

2,5-Bis(triisopropylsilyl)-3,4-diphenyldilithiosilole (9)

Method A. Dibromosilole **7** (125 mg, 0.177 mmol, 1.0 equiv.) was dissolved in THF (1.5 mL) and Li powder (10 mg, 1.44 mmol, 8.1 equiv.) was added. The reaction mixture was stirred at room temperature for *ca.* 3 days yielding a dark-red solution and unreacted Li. After removal of the solvent in vacuum, the residue was extracted with C_6H_6 (3 mL) and insoluble components were removed by filtration over Celite®.

The filtrate was dried and recrystallized from Et₂O and hexane at −30 °C. **Yield:** dark-red crystalline solid, 67 mg (contains (thf)₂, 0.0953 mmol, 81%).

Method B. Difluorosilole **6** (166 mg, 0.285 mmol, 1.0 equiv.) was dissolved in THF (1.5 mL) and Li powder (20 mg, 2.85 mmol, 10.0 equiv.) was added. The reaction mixture was stirred at room temperature for *ca.* 3 days yielding a dark-red solution and unreacted Li. After removal of the solvent in vacuum, the residue was extracted with C₆H₆ (3 mL) and insoluble components were removed by filtration over Celite®. The filtrate was dried and recrystallized from Et₂O and hexane at −30 °C. **Yield:** dark-red crystalline solid, 91 mg (contains (thf)₂, 0.129 mmol, 45%).

Decomposition point. *ca.* 150 °C. ¹H NMR (400 MHz, C₆D₆): δ = 7.15–7.11 (m, 4 H, *m*-Ph), 7.09–7.03 (m (dd), 4 H, *o*-Ph), 6.99–6.92 (m, 4 H), 3.58 (br. s, 8 H, thf), 1.60–1.49 (m, 6 H, ¹Pr-CH), 1.35 (d, ³J_{H,H} = 7.4 Hz, 36 H, ¹Pr-CH₃), 1.31 (br. s, 8 H, thf). ¹³C{¹H}NMR (101 MHz, C₆D₆): δ = 146.57 (C_q, *i*-Ph), 142.66 (C_q, C_β), 139.72 (C_q, C_α), 131.96 (CH, Ph-C), 126.69 (CH, Ph-C), 125.00 (CH, Ph-C), 69.43 (CH₂, thf), 25.26 (CH₂, thf), 20.79 (CH, ¹Pr-CH), 14.36 (CH₃, ¹Pr-CH₃). ⁷Li NMR (117 MHz, C₆D₆): δ = 6.16 (s). ²⁹Si{¹H} NMR (99 MHz, C₆D₆): δ = 130.7 (s, ring-Si), −0.1 (s, Si³Pr₃). Because of the severe sensitivity towards air and moisture, a satisfying result for the elemental analysis was not obtained.

Author contributions

K. M. performed all the synthetic works and prepared the manuscript. S. K. and T. K. performed the preliminary synthetic works. E. S. performed the isolation of the dilithiobutadiene and its spectral analysis. S. F. contributed to preliminary discussion and helped experimental works. Y. Y., S. I. and T. I. contributed to the synthesis of the fluorosilole. K. T. and Y. O. performed the X-ray diffraction analysis of the bromosilole. M. M. performed preliminary X-ray diffraction analysis of siloles and contributed to the refinement of the structure of the dilithiosilole. M. S. conceived and directed the project, performed the X-ray diffraction analysis of the dilithiobutadiene and the dilithiosilole, and prepared the manuscript.

Data availability

The crystallographic data were deposited in the Cambridge Crystallographic Data Centre (CCDC): Dilithiobutadiene **1b** (2402955), dibromosilole **7** (2402953), dilithiosilole **9** (2402954).[†] ESI[†] include NMR charts of all compounds demonstrated in this work and crystallographic data.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was partially supported by a JSPS post-doctoral fellowship (K. M.), research grants from the Takahashi Industrial and Economic Research Foundation (M. S.) and the White Rock Foundation (M. S.), and the Grants-in-Aid for Scientific Research of 23H01974 for Y. O. and 22K05143 for K. T. from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors thank Professor Makoto Yamashita (Institute of Science Tokyo, Japan) for helping us to prepare lithium powder.

References

- 1 C. Shan, S. Yao and M. Driess, *Chem. Soc. Rev.*, 2020, **49**, 6733–6754.
- 2 N. J. Hill and R. West, *J. Organomet. Chem.*, 2004, **689**, 4165–4183.
- 3 P. P. Gaspar and R. West, in *The Chemistry of Organic Silicon Compounds*, 1998, pp. 2463–2568. DOI: [10.1002/0470857250.ch43](https://doi.org/10.1002/0470857250.ch43).
- 4 G. Frenking, R. Tonner, S. Klein, N. Takagi, T. Shimizu, A. Krapp, K. K. Pandey and P. Parameswaran, *Chem. Soc. Rev.*, 2014, **43**, 5106–5139.
- 5 R. S. Ghadwal, R. Azhakar and H. W. Roesky, *Acc. Chem. Res.*, 2013, **46**, 444–456.
- 6 S. Yao, Y. Xiong and M. Driess, *Organometallics*, 2011, **30**, 1748–1767.
- 7 M. Weidenbruch, *Coord. Chem. Rev.*, 1994, **130**, 275–300.
- 8 Y.-P. Zhou and M. Driess, *Angew. Chem., Int. Ed.*, 2019, **58**, 3715–3728.
- 9 S. Raoufmoghaddam, Y.-P. Zhou, Y. Wang and M. Driess, *J. Organomet. Chem.*, 2017, **829**, 2–10.
- 10 S. S. Sen, S. Khan, S. Nagendran and H. W. Roesky, *Acc. Chem. Res.*, 2012, **45**, 578–587.
- 11 L. Wang, Y. Li, Z. Li and M. Kira, *Coord. Chem. Rev.*, 2022, **457**, 214413.
- 12 B. Gehrhus and M. F. Lappert, *J. Organomet. Chem.*, 2001, **617–618**, 209–223.
- 13 M. Haaf, T. A. Schmedake and R. West, *Acc. Chem. Res.*, 2000, **33**, 704–714.
- 14 R. West and M. Denk, *Pure Appl. Chem.*, 1996, **68**, 785–788.
- 15 M. Kira, *Chem. Commun.*, 2010, **46**, 2893–2903.
- 16 Y. Gao, J. Zhang, H. Hu and C. Cui, *Organometallics*, 2010, **29**, 3063–3065.
- 17 L. A. Leites, S. S. Bukalov, A. V. Zabula, I. A. Garbuzova, D. F. Moser and R. West, *J. Am. Chem. Soc.*, 2004, **126**, 4114–4115.
- 18 L. A. Leites, S. S. Bukalov, M. Denk, R. West and M. Haaf, *J. Mol. Struct.*, 2000, **550–551**, 329–335.
- 19 M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, *J. Am. Chem. Soc.*, 1994, **116**, 2691–2692.
- 20 B. Goldfuss and P. V. R. Schleyer, *Organometallics*, 1997, **16**, 1543–1552.

- 21 E. Vessally, M. Nikoorazm, F. Esmaili and E. Fereyduni, *J. Organomet. Chem.*, 2011, **696**, 932–939.
- 22 J. Dubac, A. Laporterie and G. Manuel, *Chem. Rev.*, 1990, **90**, 215–263.
- 23 E. Colomer, R. J. P. Corriu and M. Lheureux, *Chem. Rev.*, 1990, **90**, 265–282.
- 24 Z. Xi, *Eur. J. Org. Chem.*, 2004, 2773–2781.
- 25 L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, 1941, **63**, 1184–1187.
- 26 A. G. Evans, J. C. Evans, P. J. Emes and T. J. Phelan, *J. Chem. Soc. B*, 1971, 315–318.
- 27 M. Saito, M. Nakamura, T. Tajima and M. Yoshioka, *Angew. Chem., Int. Ed.*, 2007, **46**, 1504–1507.
- 28 T. Kuwabara, J.-D. Guo, S. Nagase, M. Minoura, R. H. Herber and M. Saito, *Organometallics*, 2014, **33**, 2910–2913.
- 29 A. J. Ashe III, J. W. Kampf and P. M. Savla, *Organometallics*, 1993, **12**, 3350–3353.
- 30 P. A. Scherr, R. J. Hogan and J. P. Oliver, *J. Am. Chem. Soc.*, 1974, **96**, 6055–6059.
- 31 M. D. Rausch and L. P. Klemann, *J. Am. Chem. Soc.*, 1967, **89**, 5732–5733.
- 32 D. Schmid, A. Seyboldt, K. Eichele and D. Kunz, *Dalton Trans.*, 2017, **46**, 29–32.
- 33 R. H. Cox and H. W. Terry, *J. Magn. Reson.*, 1974, **14**, 317–322.
- 34 H. Oulyadi, *Synthesis*, 2018, 3603–3614.
- 35 V. H. Gessner, C. Däschlein and C. Strohmman, *Chem. – Eur. J.*, 2009, **15**, 3320–3334.
- 36 D. Johnels, A. Boman and U. Edlund, *Magn. Reson. Chem.*, 1998, **36**, S151–S156.
- 37 J. W. Ryan, *J. Am. Chem. Soc.*, 1962, **84**, 4730–4734.
- 38 R. Kobayashi, S. Ishida and T. Iwamoto, *Angew. Chem., Int. Ed.*, 2019, **58**, 9425–9428.
- 39 M. Bursch, T. Gasevic, J. B. Stückrath and S. Grimme, *Inorg. Chem.*, 2021, **60**, 272–285.
- 40 K.-I. Kanno and M. Kira, *Chem. Lett.*, 2003, **28**, 1127–1128.
- 41 J. Braddock-Wilking, Y. Zhang, J. Y. Corey and N. P. Rath, *J. Organomet. Chem.*, 2008, **693**, 1233–1242.
- 42 W. P. Freeman, T. D. Tilley, L. M. Liable-Sands and A. L. Rheingold, *J. Am. Chem. Soc.*, 1996, **118**, 10457–10468.
- 43 C. Fekete, L. Nyulászi and I. Kovács, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2014, **189**, 1076–1083.
- 44 Z. Dong, C. R. W. Reinhold, M. Schmidtman and T. Müller, *Organometallics*, 2018, **37**, 4736–4743.
- 45 L. Párkányi, *J. Organomet. Chem.*, 1981, **216**, 9–16.
- 46 G. Yu, S. Yin, Y. Liu, J. Chen, X. Xu, X. Sun, D. Ma, X. Zhan, Q. Peng, Z. Shuai, B. Tang, D. Zhu, W. Fang and Y. Luo, *J. Am. Chem. Soc.*, 2005, **127**, 6335–6346.
- 47 R. West, H. Sohn, U. Bankwitz, J. Calabrese, Y. Apeloig and T. Mueller, *J. Am. Chem. Soc.*, 1995, **117**, 11608–11609.
- 48 J.-H. Hong, P. Boudjouk and S. Castellino, *Organometallics*, 1994, **13**, 3387–3389.
- 49 J. H. Hong and P. Boudjouk, *J. Am. Chem. Soc.*, 1993, **115**, 5883–5884.
- 50 J.-H. Hong, *Molecules*, 2011, **16**, 8033–8040.
- 51 Z. Dong, L. Albers and T. Müller, *Acc. Chem. Res.*, 2020, **53**, 532–543.
- 52 W.-C. Joo, J.-H. Hong, S.-B. Choi, H.-E. Son and C. Hwan Kim, *J. Organomet. Chem.*, 1990, **391**, 27–36.
- 53 T. Wakahara and W. Ando, *Chem. Lett.*, 2005, **26**, 1179–1180.
- 54 M. S. Gordon, P. Boudjouk and F. Anwari, *J. Am. Chem. Soc.*, 1983, **105**, 4972–4976.
- 55 U. Bankwitz, H. Sohn, D. R. Powell and R. West, *J. Organomet. Chem.*, 1995, **499**, C7–C9.
- 56 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.
- 57 M. Saito, M. Sakaguchi, T. Tajima, K. Ishimura, S. Nagase and M. Hada, *Science*, 2010, **328**, 339–342.
- 58 M. Saito and M. Yoshioka, *Coord. Chem. Rev.*, 2005, **249**, 765–780.
- 59 T. He, Z.-W. Qu, H. F. T. Klare, S. Grimme and M. Oestreich, *Angew. Chem., Int. Ed.*, 2022, **61**, e202203347.
- 60 J. Belzner, U. Bunz, K. Semmler, G. Szeimies, K. Opitz and A.-D. Schlüter, *Chem. Ber.*, 1989, **122**, 397–398.
- 61 K. Nishihara, T. Kurogi and H. Yorimitsu, *ARKIVOC*, 2023, 202312017.
- 62 M. Yus, P. Martínez and D. Guijarro, *Tetrahedron*, 2001, **57**, 10119–10124.
- 63 G. M. Sheldrick, *SHELX*, Bruker AXS, 1997.
- 64 G. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.