Lithiated Compounds

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Reduction of Phenyl Silyl Acetylenes with Lithium: Unexpected Formation of a Dilithium Dibenzopentalenide**

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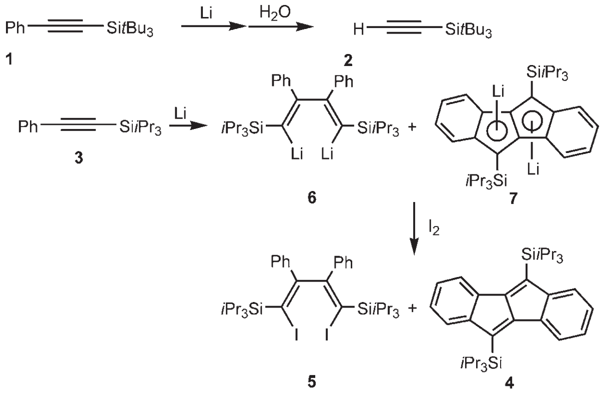
Dedicated to Professor Renji Okazaki on the occasion of his retirement

The 1,4-dilithio-1,3-butadiene that is obtained from phenylacetylene with lithium[1] is often employed as the starting compound for the synthesis of metal-containing carbocyclic π systems, for example, Group 14 metalloles.[2] X-ray crystal structure analyses of 1,4-dithio-1,3-butadienes have shown that these compounds are monomeric with two bridging lithium ions.[3] The pentalene dianion, on the other hand, has received considerable attention as a ligand of sandwich-type transition-metal complexes.[4,5] However, the dibenzopentalene dianion, which is π extended to a greater degree than the pentalene dianion, has received less attention in spite of its potential usefulness as a building block for ladder-type π-conjugated molecules of growing interest.[6–8]

During our studies on the synthesis of reactive species with a 1,3-butadiene skeleton,[9] the reduction of phenyl(trimethylsilyl)acetylene to give the corresponding 1,4-dilithio-1,3-butadiene[1b] prompted us to investigate the reduction of phenylacetylenes with a bulky silyl substituent. We report herein the reduction of phenyl(triisopropylsilyl)acetylene with lithium, which led to the unexpected formation of a dilithium dibenzopentalenide together with a 1,4-dilithio-1,3-butadiene, the normal reaction product. The first X-ray crystallographic characterization of a dilithium dibenzopentalenide, and a novel dimeric structure of a 1,4-dilithio-1,3-butadiene with an Li_4 tetrahedron, are also described.

In an attempt to synthesize the corresponding extremely encumbered 1,4-dilithio-1,3-butadiene, we first carried out a reduction of phenyl(tri-*tert*-butylsilyl)acetylene (**1**). The treatment of **1** with excess lithium, however, led to cleavage of the C–Ph bond, as evidenced by the formation of tri-*tert*-butylsilylacetylene (**2**; 92%)[10,11] when the reaction was quenched with H_2O (Scheme 1). Steric congestion apparently prevents dimerization of the radical intermediate derived from **1**. Next, the reduction of less bulky phenyl silyl acetylenes was investigated. The reaction of phenyl(triisopropylsilyl)acetylene (**3**)[12] with excess lithium gave a deep-red solution, which suggested the formation of an anionic species. Treatment of the resulting mixture with iodine afforded the unpredicted dibenzopentalene **4** (7%) as well as the *Z*,*Z* configured 1,4-diiodo-1,3-butadiene **5** (28%; Scheme 1), the structures of which were established by X-ray crystallographic analysis.[11,13] The C–C bonds in the six-membered rings of **4** are nearly equal in length, whereas remarkable bond alternation of the C–C bonds (1.357–1.512 Å) is found in the five-membered rings, as was observed in dibenzopentalenes described previously.[14]



Scheme 1. Reduction of phenyl silyl acetylenes **1** and **3**.

As the formation of a dibenzopentalene from a phenylacetylene is unprecedented, the reaction of **3** with excess lithium was monitored by NMR spectroscopy. The dark-red solution resulting from the reaction of **3** with lithium was placed in an NMR tube with C_6D_6 for NMR lock. In the ^{1}H NMR spectrum, the major signals could be assigned to 1,4-dilithio-1,3-butadiene **6**, although minor signals were observed in the aliphatic and aromatic regions. In the ^{13}C NMR spectrum, a low-field resonance was observed at $\delta = 205.95$ ppm, characteristic for lithiated vinyl carbon atoms of 1,4-dilithio-1,3-butadiene.[3a] After recrystallization of the reaction mixture from hexane in a glovebox at −30 °C, however, the dilithium dibenzopentalenide **7** was isolated in 8% yield. Compound **7** could be recrystallized easily from the crude product in spite of its low yield. The remarkable high-field resonance of the ^{7}Li nuclei at $\delta = -8.4$ ppm is caused by the strong shielding effect of the aromatic ring current.

The X-ray crystal structure analysis of **7** reveals that each lithium atom above or below each central five-membered ring is coordinated to the five-membered ring in an η^5 fashion and is also coordinated to one molecule of diethyl ether

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(Figure 1). The lengths of the C–C bonds in the five-membered rings are nearly equal (1.444–1.468 Å), whereas a slight bond alternation is found for the bonds in the six-membered ring (1.372–1.420 Å). The preference for aromatic delocalization in the five-membered ring over benzenoid delocalization has been found previously for some benzannulated anions.[15] Although a dibenzopentalene dianion has been synthesized by deprotonation of the parent dihydrodibenzopentalene or reduction of the parent dibenzopentalene,[16] the formation of a dibenzopentalene dianion from a phenylacetylene is unprecedented, and compound **7** is the first dibenzopentalene dianion to have been characterized by X-ray crystallography. The dilithium dibenzopentalenide **7** was oxidized by iodine to afford dibenzopentalene **4**.

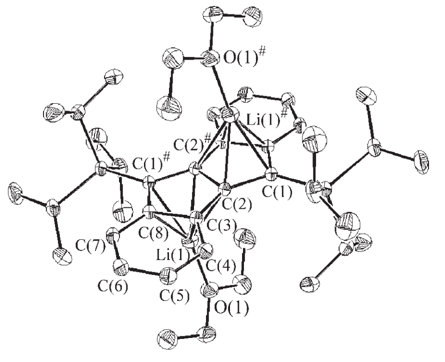
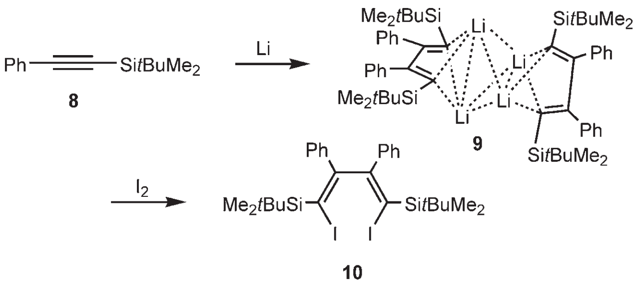


Figure 1. ORTEP drawing of the structure of **7** (thermal ellipsoids with 40% probability for non-hydrogen atoms). All hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C(1)–C(2) 1.4681(15), C(2)–C(3) 1.4434(16), C(3)–C(4) 1.4124(16), C(4)–C(5) 1.3765(17), C(5)–C(6) 1.4089(18), C(6)–C(7) 1.3715(18), C(7)–C(8) 1.4203(16), C(8)–C(1)# 1.4460(16), C(2)#–C(2) 1.451(2).

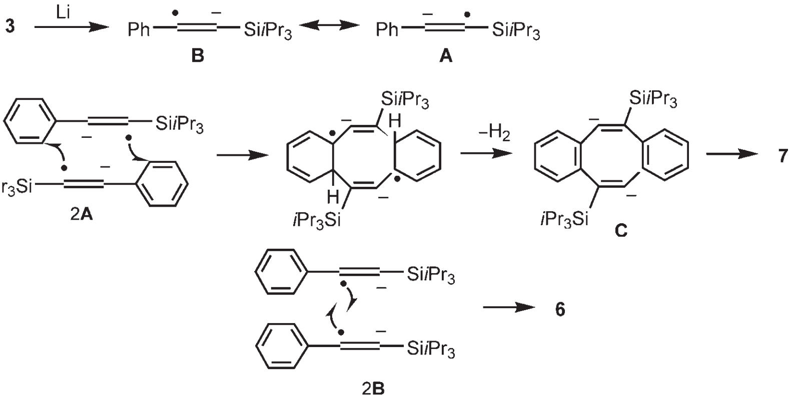
A tentative mechanism is proposed in Scheme 2, although attempts to trap intermediates with external reagents failed. The reaction route to **6** and **7** could involve the radical anion intermediate **A**/**B**, with **A** being the resonance form that leads to **7** through intermolecular cyclization followed by extrusion of dihydrogen to give the dianionic intermediate **C**, and **B** being the one that leads to **6**. The conversion of **6** into **7** at room temperature can be ruled out on the basis of evidence gained by monitoring the reaction by NMR spectroscopy. The isomerization of cyclooctatetraene to pentalene—similar to the proposed isomerization of **C** to **7**—has been reported previously.[17]

The reduction of less bulky phenyl(*tert*-butyldimethylsilyl)acetylene (**8**) was also examined.[18] In this case, however, 1,4-dilithio-1,3-butadiene **9** was generated as the main product without the formation of the corresponding dibenzopentalene dianion, as evidenced by the absence of any high-field ^{7}Li NMR signals characteristic of dilithium dibenzopentalenides ($\delta = -8.4$ ppm for **7**). The configuration of **9** was determined to be *Z*,*Z*, as *Z*,*Z* configured 1,4-diiodo-1,3-butadiene **10** was formed in 27% yield[11,13,19] when the reaction was quenched with iodine (Scheme 3). Recrystallization of the reaction mixture from hexane in a glovebox at −30 °C afforded **9** in 18% yield. In the ^{7}Li NMR spectrum, a single resonance was observed at $\delta = 1.1$ ppm, which suggests that **9** has a non-aromatic character. In the ^{13}C NMR spectrum, a signal assignable to the α carbon atom appeared at $\delta = 201.98$ ppm as a septet with a ^{13}C–^{7}Li coupling constant of 16 Hz. This coupling pattern suggests that the α carbon atom interacts strongly with two lithium atoms in solution; dilithium bridging was observed in the X-ray structures of *Z*,*Z* configured 1,4-dilithio-1,3-butadienes.[3]



Scheme 3. Reduction of the phenyl silyl acetylene **8**.

The X-ray structure analysis of **9** revealed a novel dimeric structure with an Li_4 tetrahedron, although the structure of the monomer unit is roughly similar to those of dilithium-bridged *Z*,*Z* configured 1,4-dilithio-1,3-butadienes.[3] The average length of the Li–Li bonds is 2.533 Å, which is comparable to bond lengths observed for some Li_4 tetrahedrons (2.56 Å for MeLi,[20] 2.55 Å for EtLi,[21] and 2.52 Å for 2-$Me_2NC_6H_4Li$).[22] Each lithium atom is coordinated by two butadiene moieties in different ways: through η^4 coordination (Li(2) and Li(4) in Figure 2) or η^2 coordination (Li(1) and Li(3) in Figure 2) by one butadiene moiety and η^1 coordination by a terminal carbon atom of the other butadiene moiety. Thus, each butadiene moiety is associated with an η^4-coordinated, an η^2-coordinated, and two η^1-coordinated lithium atoms. The average Li–C bond lengths in the case of η^4 and η^1 coordination are 2.22 and 2.26 Å, respectively. These values are also comparable to those observed for some Li_4 tetrahedrons (2.27 Å for MeLi,[20]



Scheme 2. Possible mechanism for the formation of **6** and **7**.

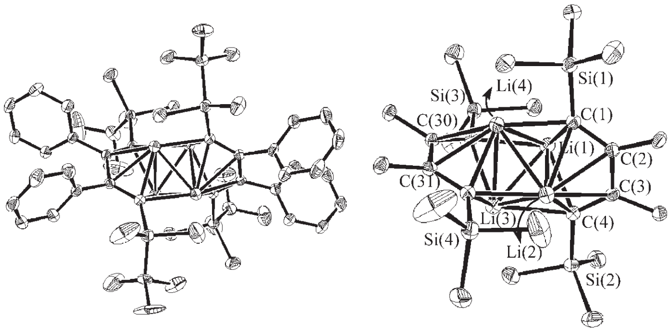


Figure 2. ORTEP drawing of the structure of **9** (thermal ellipsoids with 40% probability for non-hydrogen atoms). All hydrogen atoms and the atom positions of a disordered minor part are omitted for clarity. Selected bond lengths [Å]: C(1)–C(2) 1.366(3), C(2)–C(3) 1.548(3), C(3)–C(4) 1.369(3), C(1)–Li(2) 2.222(4), C(2)–Li(2) 2.299(4), C(3)–Li(2) 2.327(4), C(4)–Li(2) 2.124(4), C(1)–Li(1) 2.165(4), C(2)–Li(1) 2.602(4), C(3)-–Li(1) 2.558(4), C(4)–Li(1) 2.185(4).

2.25 Å for EtLi,[21] and 2.27 Å for 2-$Me_2NC_6H_4Li$).[22] The average Li–C bond length in the case of η^2 coordination is 2.18 Å, whereas the average distance between the η^2-coordinated lithium center and the C2 and C3 atoms is 2.62 Å, which is significantly longer than the other Li–C distances. Similar η^2 coordination of a lithium atom was also reported for other *Z*,*Z* configured 1,4-dilithio-1,3-butadienes.[3]

In summary, the reduction of phenyl(triisopropylsilyl)-acetylene (**3**) with lithium led to the unprecedented formation of the dilithium dibenzopentalenide **7** together with 1,4-dilithio-1,3-butadiene **6**, whereas the reduction of phenyl(*tert*-butyldimethylsilyl)acetylene (**8**) with lithium gave 1,4-dilithio-1,3-butadiene **9**. Thus, the bulkiness of the silyl substituent of the phenyl silyl acetylene strongly affects its reduction mode. Although the yield of the dilithium dibenzopentalenide is not high, its ready crystallization from the crude mixture will overcome the obstacle to further functionalization. X-ray crystallographic analysis revealed the unprecedented dimeric structure of **9**. Investigations on the synthesis of metal complexes derived from **7** are in progress.

Experimental Section

Isolation of **7**: A solution of **3** (4.010 g, 15.5 mmol) in diethyl ether (16 mL) was added to lithium (401 mg, 57.8 mmol) at room temperature, and the reaction mixture was stirred overnight. In a glovebox, insoluble material was removed by filtration and the filtrate was concentrated. Repeated recrystallization of the residue from hexane at −30 °C gave **7** (377 mg, 7%). ^{1}H NMR (400 MHz, diethyl ether/C_6D_6): $\delta = 1.18$ (d, $J = 8$ Hz, 36 H), 1.98 (sept, $J = 8$ Hz, 6 H), 6.59–6.65 (m, 2 H), 6.78–6.83 (m, 2 H), 7.81 (d, $J = 9$ Hz, 2 H), 8.12 ppm (d, $J = 8$ Hz, 2 H); ^{1}H NMR (400 MHz, C_6D_6): $\delta = -0.01$ (t, $J = 7$ Hz, 12 H), 1.45 (d, $J = 7$ Hz, 36 H), 2.24–2.32 (m, 14 H), 7.08–7.11 (m, 2 H), 7.24–7.28 (m, 2 H), 8.21 (d, $J = 9$ Hz, 2 H), 8.57 ppm (d, $J = 8$ Hz, 2 H); ^{13}C NMR (101 MHz, diethyl ether/C_6D_6): $\delta = 14.8$ (d), 20.1 (q), 112.8 (d), 117.6 (s), 119.6 (d), 121.8 (d), 122.8 (d), 141.7 ppm (s); ^{7}Li NMR(156 MHz, diethyl ether/C_6D_6): $\delta = -8.4$ ppm.

Isolation of **9**: A solution of **8** (931 mg, 4.30 mmol) in diethyl ether (4.3 mL) was added to lithium (92 mg, 13.3 mmol) at room temperature, and the reaction mixture was stirred for 6.5 h. In a glovebox, insoluble material was removed by filtration, and the filtrate was concentrated. Repeated recrystallization of the residue from hexane at −30 °C gave **9** (238 mg, 25%). ^{1}H NMR (400 MHz, diethyl ether/C_6D_6): $\delta = -0.52$ (s, 12 H), 0.93 (s, 18 H), 6.63–6.66 (m, 6 H), 6.74–6.77 ppm (m, 4 H); ^{13}C NMR (101 MHz, diethyl ether/C_6D_6): $\delta = -3.5$ (q), 18.3 (s), 28.2 (q), 123.5 (d), 126.6 (d), 129.1 (d), 152.3 (s), 163.6 (s), 202.0 ppm (sept, $J(^7\mathrm{Li},^{13}\mathrm{C}) = 16$ Hz); ^{7}Li NMR (156 MHz, diethyl ether/C_6D_6): $\delta = 1.1$ ppm.

Crystallographic data for **7**:[13] $C_{42}H_{70}Li_2O_2Si_2$, $M_r = 677.04$, $0.50 \times 0.25 \times 0.25$ mm^3, triclinic, $a = 9.7607(6)$, $b = 10.2083(6)$, $c = 11.5575(7)$ Å, $\alpha = 97.0870(10)$, $\beta = 105.3280(10)$, $\gamma = 105.0580(10)$°, $V = 1049.44(11)$ Å^3, $T = 153$ K, $\rho_{calcd} = 1.071$ g cm^{-3}, $Z = 2$, space group $P\bar{1}$, $R_1 = 0.042$ ($I > 2\sigma(I)$, 4315 reflections), $wR_2 = 0.126$ (for all reflections) for 4981 reflections and 225 parameters, GOF = 1.005.

Crystallographic data for **9**:[13] $C_{56}H_{80}Li_4Si_4$, $M_r = 893.32$, $0.35 \times 0.20 \times 0.20$ mm^3, monoclinic, $a = 11.7703(10)$, $b = 20.2245(16)$, $c = 23.4790(19)$ Å, $\beta = 96.203(2)$°, $V = 5556.4(8)$ Å^3, $T = 103$ K, $\rho_{calcd} = 1.068$ g cm^{-3}, $Z = 4$, space group $P2_1/n$, $R_1 = 0.048$ ($I > 2\sigma(I)$, 7294 reflections), $wR_2 = 0.133$ (for all reflections) for 9764 reflections and 681 parameters, GOF = 1.019. Disorder around one of the *tert*-butyl groups was found. The occupancies of the disordered *tert*-butyl groups were refined to be 0.59:0.41.

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