Persilylated Dimethylenecyclobutene Dianion Dilithium as the First 6C-8π Allyl Anion System

Akira Sekiguchi,* Tsukasa Matsuo, Keisuke Ebata,† and Hideki Sakurai*††
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305
†*NTT Basic Research Laboratories, Morinosato Wakamiya 3-1, Atsugi, Kanagawa 243-01*
††*Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278*

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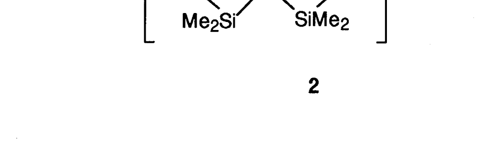
Reduction of persilylated dimethylenecyclobutene with lithium metal in 1,2-dimethoxyethane yields green crystals of persilylated dimethylenecyclobutene dianion dilithium as the first 6C-8π allyl anion system. The molecular structure, determined by X-ray crystallography, is discussed in comparison to that of the neutral starting molecule.

The introduction of a silyl group to a π-system causes remarkable steric and electronic perturbations.[1] In a proceeding paper, we reported preparations of various π-electron systems by the intramolecular oligomerization of macrocyclic polyacetylenes with $(\text{Me-Cp})\text{Mn(CO)}_3$ under photochemical conditions.[2]

Persilyl-substituted π-electron systems can be readily reduced by alkali metals to dianions. We previously reported successful preparations of dianion dilithium derivatives of silyl-substituted ethylenes[3] and benzenes[4] by two electron reduction. In the course of our dianion chemistry, we have reduced persilylated dimethylenecyclobutene (**1**) prepared by the intramolecular cyclotrimerization of dodecamethyl-3,5,8,10,13,15-hexasilacyclopentadeca-1,6,11-triyne,[2] producing unprecedented 6C-8π allyl anion system via cleavage of the central π-bond by two electron reduction. We wish to report herein the isolation, characterization, and molecular structure of persilylated dimethylenecyclobutene dianion dilithium as the first 6C-8π allyl anion system.

Reduction of persilylated dimethylenecyclobutene (**1**) with excess lithium metal in 1,2-dimethoxyethane (DME) at room temperature produced a solution of the dianion of **1** within 5 min. The solvent was removed in vacuo, and then dry degassed hexane was introduced by vacuum transfer. Crystallization from hexane at -20 °C afforded green crystals of the dimethylenecyclobutene dianion dilithium (**2**) containing two molecules of DME.[5]



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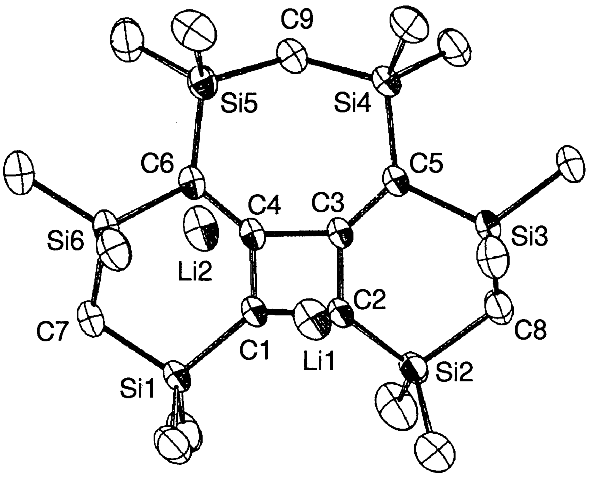

Figure 1. ORTEP drawing of **2** (DME is omitted for clarity). The selected bond distances (Å) and bond angles (deg.): C1-C2, 1.551(4); C1-C4, 1.414(4); C2-C3, 1.464(4); C3-C4, 1.573(4); C3-C5, 1.376(4); C4-C6, 1.436(4); C2-C1-C4, 92.6(2); C1-C2-C3, 88.3(2); C2-C3-C4, 89.8(2); C1-C4-C3, 89.2(2); C2-C3-C5, 132.5(2); C4-C3-C5, 137.6(2); C1-C4-C6, 132.4(2); C3-C4-C6, 138.4(2).

The structure of dianion dilithium **2** was determined by X-ray diffraction as shown in Figure 1.[6] Two lithium atoms are located up and below and one DME molecule is coordinated to each lithium atom. Thus, Li1 is above C1-C2 bond (C1-Li1, 2.323(7); C2-Li1, 2.084(7) Å) and Li2 is below C4-C6 bond (C4-Li2, 2.209(9); C6-Li2, 2.211(9) Å). Six carbons (C1, C2, C3, C4, C5, and C6) of π-skeleton are maintained nearly coplanar.

Comparison of the structural parameters of **1**[2] and **2** is quite interesting. The distance of C1-C2 of **2** is elongated by 0.18 Å relative to that of **1**. As well, the distances of C3-C5 and C4-C6 are stretched by 0.027 and 0.09 Å, respectively. By contrast, the distances of C1-C4 and C2-C3 of **2** are shortened by 0.079 and 0.037 Å, respectively. These structural features are reflected by the LUMO of **1**. Thus, C1-C4 and C2-C3 in **2** are bonding, whereas C1-C2, C3-C5, and C4-C6 are antibonding. The bond lengths of the Si-C bonds (C1-Si1, 1.828(2); C2-Si2, 1.805(2); C5-Si3, 1.870(2); C5-Si4, 1.835(2); C6-Si5, 1.824(4); C6-Si6, 1.851(4) Å) for **2** are remarkably shortened compared to **1** by pπ-σ^* conjugation.[7]

The structure of dianion dilithium **2** in solution was deduced on the basis of the NMR spectra. In ^{1}H NMR spectrum of **2** in toluene-d_8, three sets of methyl groups were observed at

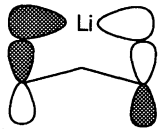

Figure 2. π-Bonding of allyllithium.

δ = 0.14, 0.29, and 0.38, and two sets of methylene groups at δ = -0.13 and 0.05, together with the signals due to DME. Three sets of ^{29}Si signals were found at δ = -30.1, -13.3 and -11.7, shifting to upper field relative to those of **1**.[2] This suggests that the negative charge is stabilized by the six silyl groups in **2**. The carbons assigned to the methyl groups were observed at δ = 3.6, 4.5, and 5.3, and methylene groups at δ = 2.8 and 11.5. ^{7}Li NMR spectrum of **2** yielded only one signal appearing at δ = 0.20.

The negative charge is largely delocalized on the four carbon atoms (C1, C2, C5, and C6) in the π-skeleton of **2** as evidenced by ^{13}C NMR spectral data. Thus, C1 and C2 carbons were observed at δ = 74.4, and C5 and C6 carbons were found at δ = 84.4. These carbons significantly shifted to upper field, about 100 ppm shift relative to those of **1**,[2] whereas the central carbons assigned C3 and C4 moved to lower field appearing at δ = 180.6. No scalar coupling between ^{7}Li and the anionic carbons (C1, C6 and C2, C5) was observed.

Allyllithium is a useful reagent for organic synthesis, however, the structural proof is still controversial.[8] Most NMR studies[9] and X-ray crystallographic investigations[10] favors the delocalized π-bonding. The X-ray crystallography and the NMR data presented here indicate that the structure of the dimethylenecyclobutene dianion dilithium (**2**) is evidently 6C-8π allyl anion system. Two negative charge is delocalized on C1, C6 and C2, C5. The structure is represented by the π-bonding of lithium with allyl anions (Figure 2). Thus, the dimethylenecyclobutene dianion dilithium (**2**) has allyl anion character stabilized by the silyl groups.

References and Notes

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5 Spectral data for **2**: dark green crystals; ^{1}H NMR (toluene-d_8) δ -0.13 (s, 4H), 0.05 (s, 2H), 0.14 (s, 12H), 0.29 (s, 12H), 0.38 (s, 12H), 2.94 (s, 8H, DME), 3.13 (s, 12H, DME); ^{13}C NMR (toluene-d_8) δ 2.8, 3.6, 4.5, 5.3, 11.5, 59.7, 70.7, 74.4, 84.4, 180.6; ^{29}Si NMR (toluene-d_8) δ -30.1, -13.3, -11.7; ^{7}Li NMR (toluene-d_8) δ 0.20.

6 A single crystal of **2** was sealed in a capillary glass tube for data collection. Diffraction data were collected on a Rigaku Denki AFC-5R diffractometer with a rotating anode (45 kV, 200 mA) with graphite-monochromatized Cu Kα radiation (λ = 1.541780 Å). Crystal data: MW = 657.20, MF = $C_{29}H_{62}Li_2O_4Si_6$, triclinic, a = 12.040(2), b = 16.367(2), c = 11.509(1) Å, α = 92.91(1), ß = 116.86(0), γ = 88.37(1)°, V = 2020.6(5) Å^3, space group = $P\bar{1}$, Z = 2, D_{calcd} = 1.081 g cm^{-3}. The final R factor was 0.0434 (R_w = 0.0431) for 5449 reflections with $F_o > 3\sigma (F_o)$.

7 The bond lengths of the Si-C bonds for **1** are as follows; (C1-Si1, 1.878(6); C2-Si2, 1.859(6); C5-Si3, 1.889(6); C5-Si4, 1.865(6); C6-Si5, 1.873(6); C6-Si6, 1.879(6) Å.

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