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Isolation and characterization of the monomeric and dimeric structures of tetrakis(trimethylsilyl)butatriene dianion dilithium†

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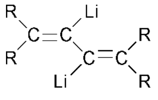
Tetrakis(trimethylsilyl)butatriene reacted with lithium metal in tetrahydrofuran to yield yellow crystals of the monomeric and dimeric molecules of the butatriene dianion dilithium with a lithium doubly bridged bisallylic structure.

The nature of the carbon–lithium bond has been a continuing subject of considerable attention in recent years.[1] Of particular interest is the degree of covalent or ionic character of the bond. The cumulated butatrienes with two sp^2 and two sp carbon atoms are highly reactive toward reduction. Alkyl-substituted butatriene reacts with lithium metal to yield the 2,3-dilithiobuta-1,3-diene derivative (**1**),[2] whereas phenyl-substituted butatriene affords the but-2-yne structure (**2**).[3,4]

According to theoretical calculations, the butatriene dianion dilithium prefers a lithium doubly bridged bisallylic structure (**3**).[5] However, the structure of the butatriene dianion dilithium is still open to dispute from both experimental and theoretical points of view.[5,6] We have studied a variety of silyl-substituted π-electron systems that readily undergo reduction with alkali metals to produce their alkali metal derivatives.[7] As a part of this study, we have examined the reaction of the persilyl-substituted butatriene **4** with lithium metal, and found an unexpected dimeric structure of the corresponding tetrasilylbutatriene dianion dilithium as well as a monomeric structure. We here report the isolation and characterization of the monomeric and dimeric structures of tetrasilylbutatriene dianion dilithium with a lithium doubly bridged bisallylic structure.



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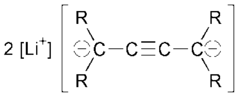

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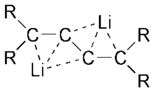

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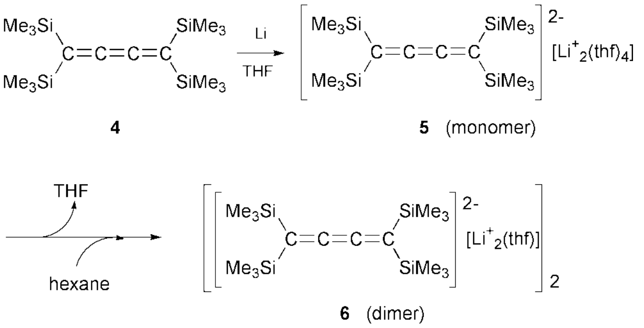
Reduction of tetrakis(trimethylsilyl)butatriene (**4**)[8] with lithium metal in dry, oxygen-free tetrahydrofuran (THF) at room temperature gave a yellow solution of the dianion of **4** within a few hours.[9] The resulting THF solution was cooled to afford air- and moisture-sensitive yellow crystals of the dilithium salt of tetrakis(trimethylsilyl)butatriene dianion (**5**) in a monomeric form (Scheme 1). Interestingly, after the THF solvent was removed *in vacuo*, crystallization from hexane at −30 °C led to an almost quantitative formation of a dimeric form (**6**).

Fig. 1 shows that the monomer **5** contains four molecules of THF in the crystals. The two lithium atoms (Li1 and Li2) are located above and below the π-skeleton and are bonded to the three carbon atoms, as in η^3-allyl lithium (C1, C2, C3 for Li1; C2, C3, C4 for Li2). In addition, the oxygen atoms of THF are coordinated to each lithium atom. The distances between the Li$^+$ ions and the carbon atoms range from 2.09(1) to 2.45(1) Å (av. 2.25 Å).



Scheme 1

The crystal structure of **5** containing THF molecules is close to that predicted by a theoretical calculation of the corresponding bisallylic structure (**3**).[5] The central C2–C3 distance [1.244(8) Å] is slightly longer than the typical carbon–carbon triple bond length (1.20 Å), whereas the C1–C2 [1.442(9) Å] and C3–C4 [1.446(9) Å] distances are intermediate between the carbon–carbon single and double bond lengths (1.54 Å and

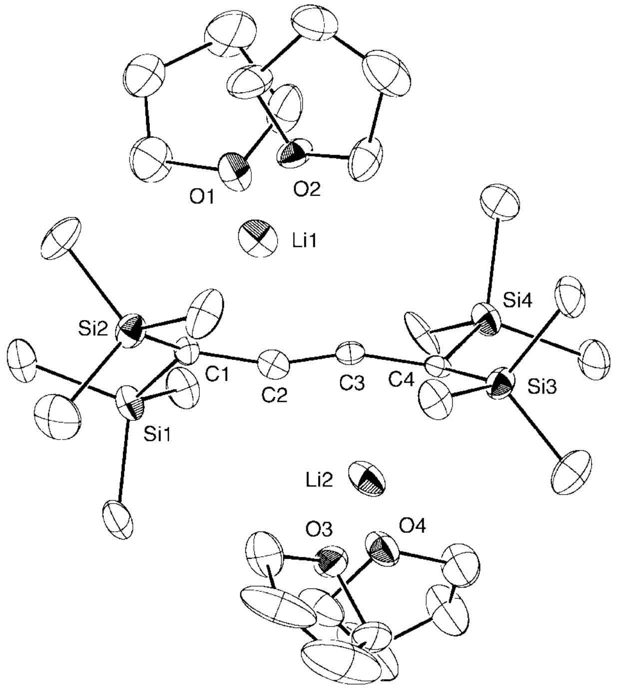


Fig. 1 Structure of **5** (THF and hydrogen atoms are omitted for clarity). Selected bond distances [Å] are: C1–C2 1.442(9), C2–C3 1.224(8), C3–C4 1.446(9), C1–Si1 1.829(7), C1–Si2 1.829 (7), C4–Si3 1.805(7), C4–Si4 1.844(7), C1–Li1 2.22(1), C2–Li1 2.12(1), C3–Li1 2.45(1), C2–Li2 2.43(1), C3–Li2 2.09(1), C4–Li2 2.21(1). Selected bond angles [°] are: C1–C2–C3 163.9(7), C2–C3–C4 164.3(6), C2–C1–Si1 114.6(5), C2–C1–Si2 119.8(5), Si1–C1–Si2 119.4(4), C3–C4–Si3 121.6(5), C3–C4–Si4 112.9(5), Si3–C4–Si4 120.9(4). CCDC 154554. See http://www.rsc.org/suppdata/cc/b0/b009337h/ for crystallographic files in .cif format.

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† Electronic supplementary information (ESI) available: experimental procedure and spectral and X-ray data of the products. See http://www.rsc.org/suppdata/cc/b0/b009337h/

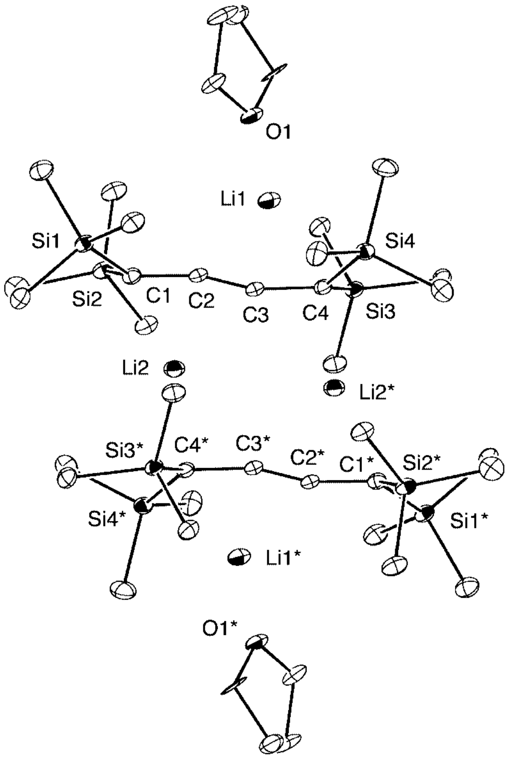

Fig. 2 Structure of **6** (THF and hydrogen atoms are omitted for clarity). Selected bond distances [Å] are: C1–C2 1.434(3), C2–C3 1.246(3), C3–C4 1.461(3), C1–Si1 1.841(2), C1–Si2 1.841(2), C4–Si3 1.844(2), C4–Si4 1.845(2), C2–Li1 2.301(4), C3–Li1 2.070(4), C4–Li1 2.298(4), C1–Li2 2.219(4), C2–Li2 2.094(4), C3–Li2 2.436(4), C4*–Li2 2.219(4). Selected bond angles [°] are: C1–C2–C3 165.3(2), C2–C3–C4 163.1(2), C2–C1–Si1 119.9(1), C2–C1–Si2 113.3(1), Si1–C1–Si2 118.9(1), C3–C4–Si3 113.5(1), C3–C4–Si4 118.3(1), Si3–C4–Si4 123.0(1). CCDC 154555. See http://www.rsc.org/suppdata/cc/b0/b009337h/ for crystallographic files in .cif format.

1.34 Å respectively). The π-skeleton exhibits a bent structure due to the π-coordination of the central acetylenic bond to the Li$^+$ ions; the bond angles are 163.9(7)° for C1–C2–C3 and 164.3(6)° for C2–C3–C4. The C1 and C4 atoms are slightly pyramidalyzed and the sum of the bond angles is 353.8° for Cl and 355.4° for C4. Thus, the negative charges are largely delocalized on the C1 and C4 atoms, which are stabilized by four silyl groups. The Si–C bond lengths of **5** (av. 1.827 Å) are shorter than those of the neutral starting molecule **4** (av. 1.881 Å).[8]

Fig. 2 shows the dimer molecule **6**, revealing that the four Li$^+$ ions are located in two different sites, and the outer site (Li1 and Li1*) and the inner site (Li2 and Li2*). In addition, one THF molecule is coordinated to the outer Li$^+$ ions. The outer Li1 is bonded to three carbon atoms (C2, C3 and C4), whereas the inner Li2 is bonded to four carbon atoms (C1, C2, C3 and C4*). The distances between the Li$^+$ ions and the carbon atoms range from 2.070(4) Å to 2.436(4) Å (av. 2.234 Å). The structural parameters of the π-skeleton are little affected by the aggregation state [C1–C2 1.434(3) Å, C2–C3 1.246(3) Å, C3–C4 1.461(3) Å, C1–C2–C3 165.3(2)°, C2–C3–C4 163.1(2)°]. The linear and planar π-skeleton of **6** makes it possible to produce a dimeric structure. As a result, the eight carbon atoms belonging to the two π-skeleton and the four Li$^+$ ions are arranged in almost the same plane.

Interestingly, in toluene-d_8 at 273 K, the dimer **6** shows two distinct ^{6}Li signals with equal intensities appearing at δ 1.72 and -0.53. At elevated temperature, these signals broaden and finally coalesce into one peak. Their dynamic behaviour is independent of the concentration (0.05 to 0.15 M). These observations strongly suggest that the two ^{6}Li signals are assigned to the two non-equivalent lithium sites, as found in the X-ray structure of **6**. From the Arrhenius and Eyring plots, the values E_a = 16.8 kcal mol^{-1}, $\Delta H^\ddagger$ = 16.2 kcal mol^{-1}, and $\Delta S^\ddagger$ = 6.7 cal mol^{-1} K^{-1} can be estimated for the Li$^+$ ion exchange reaction. The small positive $\Delta S^\ddagger$ value is a good indication of an intramolecular exchange of the Li$^+$ ions. No Li$^+$ ion exchange between monomer **5** and dimer **6** in toluene-d_8 was observed in the ^{6}Li NMR spectrum.

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