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

Tsukasa Matsuo, Masanobu Tanaka and Akira Sekiguchi∗
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki, 305-8571, Japan.
E-mail: sekiuch@staff.chem.tsukuba.ac.jp

Received (in Cambridge, UK) 21st November 2000, Accepted 6th February 2001
First published as an Advance Article on the web 20th February 2001

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 sp2 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-ynyl 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 family 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 tetrakis(trimethylsilyl)butatriene dianion dilithium with a lithium doubly bridged bisallylic structure.

Reduction of tetrakis(trimethylsilyl)butatriene (4)7 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.8 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 π-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).

† 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/

DOI: 10.1039/b009337h


503

This journal is © The Royal Society of Chemistry 2001

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 1.438(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-d8 at 273 K, the dimer 6 shows two distinct 6Li 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 6Li 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$^{-1}$, $\Delta H^\circ = 16.2$ kcal mol$^{-1}$, and $\Delta S^\circ = 6.7$ cal mol$^{-1}$ K$^{-1}$ can be estimated for the Li+ ion exchange reaction. The small positive $\Delta S^\circ$ 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-d8 was observed in the 6Li NMR spectrum.

This work was supported by Grants-in-Aid for Scientific Research (Nos. 10304051, 12020209, 12042213) from the Ministry of Education, Science and Culture of Japan, and TARA (Tsukuba Advanced Research Alliance) fund.

Notes and references


6. Ditriethylbenzylacetylenebistetraiodobut-2-ylene shows a 1,4-dilithiobut-2-yne structure in the crystal. Each lithium atom is bonded to a benzylcarbox and has further interactions with the phenyl ipso carbon and the aromatic π system. However, no structural parameters have been given see: W. N. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1985, 24, 390.


9. Radical anion of 4, which was prepared by the reaction of hexakis(trimethylsilyl)but-2-yne with a potassium mirror at 293 K in 1,2-dimethoxyethane, was investigated by Bock et al. using ESR see: W. Kaim and H. Bock, *J. Organomet. Chem.*, 1979, 164, 281.

Fig. 2 Structure of 6 (THF and hydrogen atoms are omitted for clarity). Selected bond distances [Å] are: C1–C2 1.438(3), C2–C3 1.246(3), C3–C4 1.461(3), C1–Si1 1.841(2), C1–Si2 1.844(2), C4–Si3 1.340(3), C2–Si4 1.246(3), C3–Si4 1.246(3), C4–Si4 1.183(3). 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 1.438(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-d8 at 273 K, the dimer 6 shows two distinct 6Li 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 6Li 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$^{-1}$, $\Delta H^\circ = 16.2$ kcal mol$^{-1}$, and $\Delta S^\circ = 6.7$ cal mol$^{-1}$ K$^{-1}$ can be estimated for the Li+ ion exchange reaction. The small positive $\Delta S^\circ$ 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-d8 was observed in the 6Li NMR spectrum.

This work was supported by Grants-in-Aid for Scientific Research (Nos. 10304051, 12020209, 12042213) from the Ministry of Education, Science and Culture of Japan, and TARA (Tsukuba Advanced Research Alliance) fund.

Notes and references


6. Ditriethylbenzylacetylenebistetraiodobut-2-ylene shows a 1,4-dilithiobut-2-yne structure in the crystal. Each lithium atom is bonded to a benzylcarbox and has further interactions with the phenyl ipso carbon and the aromatic π system. However, no structural parameters have been given see: W. N. Setzer and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1985, 24, 390.


9. Radical anion of 4, which was prepared by the reaction of hexakis(trimethylsilyl)but-2-yne with a potassium mirror at 293 K in 1,2-dimethoxyethane, was investigated by Bock et al. using ESR see: W. Kaim and H. Bock, *J. Organomet. Chem.*, 1979, 164, 281.