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1,4-Dilithio-1,2,3,4-tetraphenyl-butadiene – crystal structure of the 1,2-dimethoxyethane adduct

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Abstract

The crystal structure of $Li_2C_4Ph_4 \cdot 2DME$ (1, DME = 1,2-dimethoxyethane) is reported. In the solid state it is monomeric owing to the chelating properties of the bidentate donor solvent. The butadiene backbone exhibits *cis*-geometry with two essentially localized C–C double bonds, separated by a C–C single bond. The lithium ions coordinate on opposite sides of the C_4-backbone. They show short contacts to the terminal C-atoms of the butadiene moiety and significantly longer ones to the central C-atoms. No interactions between the Li^+ ions and the phenyl rings were observed. Crystal data (Mo–Kα radiation) at −120°C for $1 \cdot 0.5C_5H_{12}$: $a = 1036.5(4)$ pm, $b = 1084.0(5)$ pm, $c = 1709(1)$ pm, $\alpha = 105.11(4)°$, $\beta = 103.25(4)°$, $\gamma = 97.51(4)°$, triclinic, space group $P\bar{1}$, $R = 0.083$ for 3727 ($F > 6\sigma(F)$) data.

Key words: Crystal structure; X-ray diffraction; Alkene; Lithium; Group 1; Metallacycle

1. Introduction

Butadiene ligands are often employed in transition metal chemistry because of their ability to form stable π-complexes [1]. In order to enhance the steric bulk of this ligand, the hydrogen atoms of butadiene may be replaced by larger substituents such as phenyl groups. Different arrangements of the substituents may lead to different structures, as exemplified by two zirconium compounds. In the 1,4-diphenyl-butadienyl-dicyclopentadienyl-zirconium derivative [2], the butadienyl backbone has a *trans*-structure, whereas 2,3-diphenyl-butadienyl-dicyclopentadienyl-zirconium [3] adopts a *cis*-arrangement. In the σ-bonded $[C_4Ph_4]^{2-}$ complex $[AuCl(C_4Ph_4)(phen)]$ (phen = 1,10-phenanthroline) [4] there is a planar AuC_4 five-membered ring, which has a *cis*-arrangement of Ph substituents. The gold atom is bound to the carbons in the two- and five-positions. In addition, the dilithium derivative 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene has been employed as starting material for the formation of 1-chloro-1,2,3,4,5-pentaphenyl-1-germa-cyclopentadiene by reaction with phenyl-trichloro-germanium [5]. The substitution of the chlorine atom on germanium by hydrogen enables lithiation to afford an anionic five-membered ring, the aromatic properties of which have been investigated [6]. However, a crystal structure has not been reported to date.

The synthesis of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene was first reported in 1928 [7]. Smith and Hoehn reported the reaction of lithium metal with diphenylacetylene in diethyl ether in 1941 [8]. An excess of lithium has to be used to avoid the formation of dilithio-1-benzyl-2,3-diphenylindene. Under the experimental conditions described, the complete formation of the product was not achieved even after a reaction period of 36 h. A more extended reaction time results in the formation of the undesired by-product. In order to maximize yield, the preparation of the title compound was thus performed according to the conditions described by Braye *et al.* [9], who employed a larger scale preparation and a limited reaction time and obtained a yield of *ca.* 85%. The formation and steric arrangement of these and related compounds have often been the subject of theoretical calculations. Schleyer *et al.* have published the crystal structure and MNDO calculations of a 1,4-dilithio-1,4-diphenyl-2-

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butene [10a,b]. Because of a structural disorder at an inversion center, detailed structural parameters were not obtained. However, the data clearly show a *cis*-arrangement for the 2-butene backbone. Recently, the Et_2O adduct of bis(1,4-dilithio-1,4-diphenyl-2-butene) has been prepared and structurally characterized [11]. A dimeric structure was observed owing, perhaps, to the relatively weak donor characteristics of diethyl ether, which is incapable of preventing association, at least in this case. Two butadiene anions, which are positioned perpendicular to one another, are bridged by tetrahedral Li_4-core. The C_4-backbones of both monomeric units are planar (the mean deviation from the plane is less than 1 pm).

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$)

Atom	x	y	z	U_{eq} [a]
C(1)	5777(4)	2347(4)	6846(3)	30(2)
C(11)	5373(4)	2568(4)	6026(3)	29(2)
C(12)	6132(4)	3443(4)	5739(3)	33(2)
C(13)	5629(5)	3671(4)	4978(3)	40(2)
C(14)	4341(5)	3036(4)	4465(3)	41(2)
C(15)	3564(5)	2171(4)	4727(3)	39(2)
C(16)	4075(5)	1955(4)	5486(3)	34(2)
C(2)	7019(4)	2116(3)	7172(3)	26(2)
C(21)	8114(4)	2000(4)	6732(3)	28(2)
C(22)	9423(5)	2707(4)	7157(3)	37(2)
C(23)	10447(5)	2668(5)	6747(3)	47(2)
C(24)	10191(5)	1934(5)	5922(3)	46(2)
C(25)	8901(5)	1212(4)	5505(3)	41(2)
C(26)	7884(5)	1262(4)	5900(3)	32(2)
C(3)	7363(4)	1993(4)	8063(3)	27(2)
C(31)	8258(4)	1049(4)	8208(3)	30(2)
C(32)	8049(4)	−161(4)	7612(3)	38(2)
C(33)	8826(5)	−1069(5)	7756(3)	46(2)
C(34)	9843(5)	−779(5)	8497(4)	49(2)
C(35)	10074(5)	420(5)	9095(3)	46(2)
C(36)	9294(4)	1329(5)	8956(3)	38(2)
C(4)	6782(4)	2660(4)	8637(3)	32(2)
C(41)	6912(4)	2452(4)	9459(3)	34(2)
C(42)	7340(5)	3504(5)	10199(3)	45(2)
C(43)	7405(5)	3352(6)	10984(3)	56(2)
C(44)	7020(5)	2145(6)	11079(3)	53(3)
C(45)	6556(5)	1087(6)	10353(3)	52(2)
C(46)	6503(5)	1238(5)	9566(3)	42(2)
Li(1)	6349(8)	4059(7)	7992(5)	37(3)
C(51)	3954(5)	4975(5)	7093(3)	50(2)
O(1)	5093(3)	5289(3)	7813(2)	42(1)
C(52)	5842(5)	6585(4)	8024(3)	49(2)
C(53)	7076(5)	6744(4)	8722(3)	50(2)
O(2)	7743(3)	5727(3)	8435(2)	51(1)
C(54)	9019(5)	5835(5)	9004(4)	75(3)
Li(2)	4832(7)	1772(7)	7681(5)	36(3)
C(61)	3932(6)	−1082(5)	6669(3)	57(2)
O(3)	3758(3)	−74(3)	7350(2)	41(1)
C(62)	2380(5)	51(4)	7244(3)	46(2)
C(63)	2335(5)	1064(5)	8009(3)	49(2)
O(4)	3249(3)	2229(3)	8084(2)	40(1)
C(64)	3376(6)	3238(5)	8844(3)	64(3)
C(70)	9610(26)	5072(14)	5117(10)	108(13)
C(71)	9376(20)	4318(20)	4213(11)	152(23)
C(71′)	10587(13)	4287(27)	4299(13)	230(18)
C(72)	9872(13)	3967(9)	3444(9)	159(8)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

In this paper, the crystal structure of a monomeric dilithium salt of a 1,3-butadiene derivative is described [12*]. The structure of the title compound has a non-planar C_4 backbone in a *cis*-configuration with the Li^+ ions located on opposite sides of the central C_4 moiety.

2. Experimental details

All experiments were performed under anaerobic and anhydrous conditions. The compound **1** was synthesized according to the method described by Braye *et al.* [9]. 5 g (28 mmol) of diphenylacetylene were dissolved in diethyl ether (20 mL). 0.7 g of Li powder was added to the solution. After 2 h, a conversion of 85% of the diphenylacetylene was assumed. The excess lithium was removed by filtration and the diethyl ether was removed under reduced pressure. 20 mL of *n*-pentane and 2.88 g (32 mmol) of 1,2-dimethoxyethane were added, upon which the orange-brown precipitate dissolved, affording a green solution. After standing at a temperature of −35°C for 2 days, yellow-green crystals suitable for X-ray crystallography were obtained. Yield 3.6 g (38%), m.p. 40°C (decomp.).

2.1. X-ray structure determination of 1

The data collection for the structure determination of **1** was performed on a Syntex $P2_1$ four-circle diffractometer with monochromated Mo-Kα radiation (λ = 71.073 pm) at −120°C. The structure was solved by direct methods and refined by full-matrix least-squares methods, with all non-hydrogen atoms anisotropic [13]. The hydrogen atoms were positioned ideally and refined employing a riding model. Chemically equivalent hydrogen atoms were refined with the same isotropic displacement parameters. In the crystal, a disordered pentane molecule is located around a center of inversion (positional disorder of the carbon atoms in 2- and 3-positions). The central (3-position) carbon atom could only be refined with an s.o.f. of 0.5 (C70, C70a), whereas the two positions of the neighbouring carbon atom (in 2-position) were refined to s.o.f.'s of 0.33333 (C71) and 0.66667 (C7′). The terminal C atom in 1-position has been found not to be disordered (C72). Hydrogen atoms on C70, C71, C71′, and C72 were also positioned ideally and refined using a riding model, with the same s.o.f.'s as for the C atoms to which they are bound. Fractional coordinates for the non-hydrogen atoms are given in Table 1. Crystallographic data of **1** $\cdot 0.5C_5H_{12}$, empirical formula $C_{36}H_{46}Li_2O_4(\cdot 0.5C_5H_{12})$; formula weight 586.6; crystal dimensions (mm) 0.6 × 0.6 × 0.7; space group $P\bar{1}$; $a = 1036.5(4)$ pm, $b = 1084.0(5)$ pm, $c = 1709(1)$ pm, $\alpha = 105.11(4)°$, $\beta = 103.25(4)°$, $\gamma = 97.51(4)°$, cell volume 1.767(1) nm^{-3}, formula units $Z = 2$, calculated density 1.103 Mg m^{-3}, absorption coefficient μ 0.069 mm^{-1}, measured 2θ range 8–55°, number of measured reflections 8362, number of unique reflections 8075, number of observed reflections $(F > 3\sigma(F))$ 3727, $R = 0.083$, $Rw = 0.079$, goodness of fit 1.34, weighting scheme $(w^{-1} = \sigma^2(F) + 0.0008F^2)$, refined parameters 419, data-to-parameter ratio 8.9- : 1, largest differences peak 3.7 e $nm^{-3} \times 10^2$, largest difference hole 3.3 e $nm^{-3} \times 10^2$.

Further details of the crystal structure analysis can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-Technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the deposit number CSD-57180, the authors and the full title of the publication.

3. Results and discussion

The solid-state X-ray structure of the title compound **1** shows that there is a *cis*-arrangement of phenyl substituents on the butadiene backbone as illustrated in Fig. 1. The lithium ions are located on either side of the C1–C4 array. Both ions show short, slightly asymmetric contacts to the deprotonated C-atoms. Thus, the pair of contacts Li1–C4 (213(1) pm) and Li2–C1 (208(1) pm) are shorter than Li1–C1 (221.8(7) pm) and Li2–C4 (220.0(7) pm). The average Li–C distance is 216 pm. This is significantly shorter than Li–C distances observed in many related organolithium compounds [14] especially in view of the four-coordinate bridging nature of the Li^+ ion in **1** (*cf.* Li–C = *ca.* 228 pm) in $[Li(THF)_2\text{-}2,4,6\text{-}Me_3C_6H_2]_2$ [15] or *ca.* 233 pm in $[Li(Et_2O)Ph]_4$ [16]. The distances to the central carbon atoms C2 and C3, however, are considerably longer and are in the range 248.4(9) pm–262(1) pm. There are no interactions between the lithium ions and the phenyl rings.

Unlike the arrangement in the gold derivative [4] and in the dimeric 1,4-dilithio-1,4-diphenylbutadiene

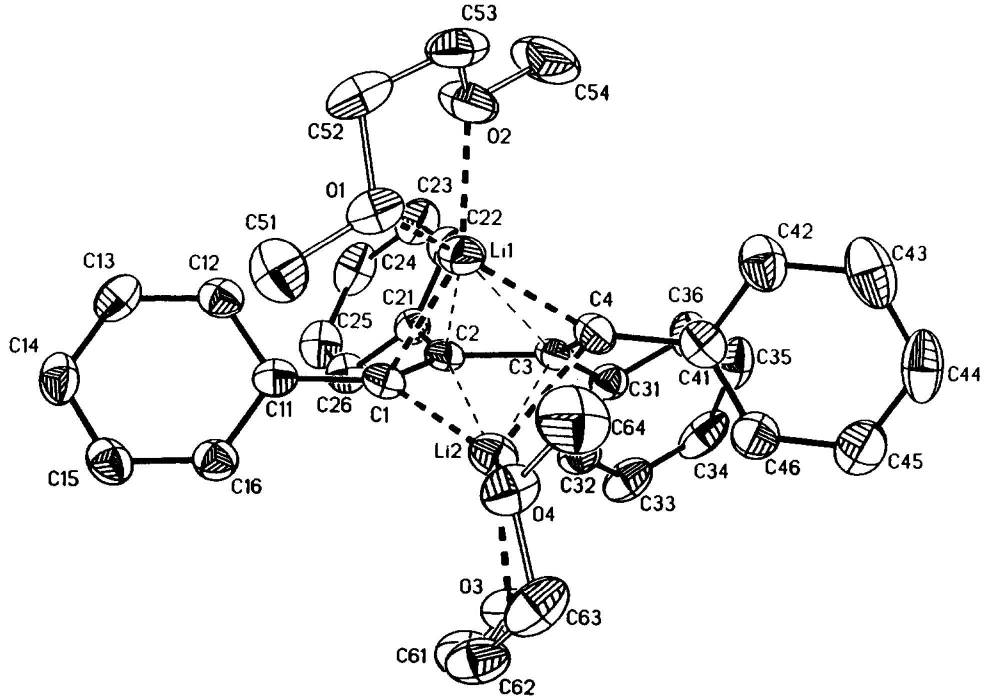

Fig. 1. The structure of **1** in the solid state; selected bond lengths (pm) and angles (°). C1–C2 136.3 (6); C2–C3 152.8(6); C3–C4 136.4(6); C1–Li1 221.8(7); C2–Li1 248.4 (9); C3–Li1 261.4(9); C4–Li1 213(1); C1–Li2 208(1); C2–Li2 262(1); C3–Li2 251.7(9); C4–Li2 220.0(7); Li1–O1 201.3(9); Li1–O2 200.8(7); Li2–O3 202.6(7); Li2–O4 199.1(9); C1–C2–C3 118.7(4); C2–C3–C4 119.1(4); C1–C2–C3–C4 29.7.

[11], the butadiene backbone in **1** is not planar but has a torsion angle (C1–C2–C3–C4) of 29.7°. The central C2–C3 bond is 152.8(6) pm long and thus significantly longer than the corresponding value in the underprotonated butadienes (146.3 pm) [17]. The C2–C3 distance is, however, consistent with a single bond. It is longer than the 148 pm predicted from the sum of the radii (74 pm) for sp^2 hybridized carbons [18]. The longer distance observed in **1** may be a consequence of the size of the substituents and increased negative charged density at the carbons. The peripheral C–C distances are also lengthened but within the range of double bonds (C1–C2–136.3(6) pm, C3–C4 136.4 (6) pm), which is close to the value of 134.2 pm in butadiene [17]. In the 1,4-dilithio-1,4-diphenylbutadiene there is no delocalization of the double bonds, either. Here, the central C–C bonds of the two independent butadiene moieties are 147.5(4) pm (av.) and the terminal C–C double bonds are 135.8(3) pm (av.) long. It may be noted that the structure of **1** is distinct from that observed for 1,4-dilithio-1,4-diphenyl-2-butene [10(b)], which is also monomeric owing to coordination by a bidentate donor molecule (TMEDA). Here, the peripheral C–C bonds are reported to be consistent with single C–C bonds, whereas the central C–C bond is essentially a double one. This result is supported by MNDO calculations, and is true for both the theoretical *cis* and the *trans* conformations.

4. Conclusion

The structural results for **1** that are presented here indicate the presence of localized negative charges at the carbon atoms in the 1,4-positions, localized peripheral double bonds (C1–C2 and C3–C4), a central single bond between C2 and C3, and a *cis*-arrangement for the C_4 backbone.

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12 After this paper had been submitted Prof. P. von Ragé Schleyer informed us that he and his coworkers had synthesized the compound $Li_2C_4Ph_4 \cdot 2TMEDA$, which has a similar structure to 1. For earlier work on related dilithiated arenes see in the following: M. Kranz, H. Dietrich, W. Mahdi, G. Muller, F. Hampel, T. Clark, R. Hacker, W. Neugebauer, A.J. Kos and P.v.R. Schleyer, *J. Am. Chem. Soc., 115* (1993) 4698.

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