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Reaction of an iron–lithium complex with tolane and the structure of dilithiumtetraphenylbutadiene formed [☆]

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Abstract

The crystal structure of 1,4-dilithiumbutadiene **2** obtained in the reaction of tolane with an iron(II) hydridolithium complex shows that **2** is a dimer with four lithium atoms, forming a distorted tetrahedron with short Li-Li and Li–C distances. Implication for the reaction of the iron–lithium complex with dinitrogen is discussed.

Keywords: Lithium; Iron

1. Introduction

Trans-dihydridotetralithiumtetraphenylferrate ([*trans*-$(H)_2Fe^{II}Ph_4]Li_4(Et_2O)_4$) forms a dinuclear iron(II) complex when dissolved in tetrahydrofuran (THF). The molecular structure of the dinuclear complex $[Fe_2H_3Ph_6]Li_5(THF)_5$ (**1**) reveals μ_2-Li and μ_2-H bridges and a short iron–iron bond distance (2.4 Å) [1,2]. As distinct from the parent coordinatively saturated *trans*-dihydrido complex, **1** and precursors of **1** formed in the process of its formation in THF react with unsaturated compounds, producing adducts with at least partial reduction of some substrates under the treatment of HCl. For example, ethylene forms a complex with **1**, producing ethane (70% yield) and ethylene (30%) when decomposed by HCl. Carbon monoxide forms a carbonyl complex (1 CO per 1 Fe) which liberates CO when reacting with HCl. The adduct with dinitrogen gives hydrazine (25–30% yield per iron atom) and N_2 (70–75%).

IR spectra of the complex of **1** with N_2 containing $^{14}N_2$, $^{15}N_2$ as well as ^7Li and ^6Li indicate that lithium ions participate in the interaction of **1** with N_2, apparently forming Li–N bonds and facilitating electron transfer to dinitrogen. Thus lithium ions play the role of acceptors similarly to acid protons in reducing N_2 in dinitrogen complexes [3].

After the treatment of the complex of **1** with N_2, iron turn out to be oxidized to iron(III), while only iron(II) is produced when **1** is treated with HCl under argon. Therefore iron atoms seem to be electron donors for N_2 reduction (and not Ph ligands as could be suggested alternatively; the yield of diphenyl both from **1** alone and from its adduct with N_2 is the same after treatment with HCl and amounts to about 17%).

Unfortunately so far no good crystals of the N_2 complex with **1** suitable for X-ray analysis have been obtained; therefore we tried to investigate crystalline products of reactions of **1** with other substrates. The reaction of **1** with tolane under similar conditions (i.e. in the process of **1** formation from the [*trans*-$(H)_2Fe^{II}Ph_4]Li_4(Et_2O)_4$) produced 1,4-dilithiumtetraphenylbutadiene (**2**) which was isolated in its complex with THF and forms suitable crystals for X-ray analysis. Previously **2** was prepared in reactions of tolane with lithium metal [4,5] and with *tert*-BuLi at 70°C[6] but no structural data for **2** have been published.

2. Experimental details

Crystals of [*trans*-$(H)_2Fe^{II}Ph_4]Li_4(Et_2O)_4$ [1] were dissolved in dry THF containing tolane (1:1 ratio to the iron complex) in an argon atmosphere. In the

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[☆] The paper is dedicated to Professor Fausto Calderazzo on the occasion of his 65th birthday.

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process of dissolving the complex the solution changed color from bright violet (λ_{max} = 515 nm) to dark brown. After standing for several hours at room temperature the solvent was evaporated in vacuum and the remainder was dissolved in a pentane–THF mixture (20:1 volume ratio) and filtered. On cooling the solution to −18°C and standing for about 24 h, formation of black well-formed crystals was observed. For X-ray analysis a crystal of **2** was sealed in a quartz capillary (diameter, 0.7 mm). The structure of **2** has been proven by the X-ray diffraction method (Siemens P3/PC diffractometer; Mo Kα radiation; graphite monochromator; θ–2θ scan; $2\theta < 50°$). Crystals of **2** are monoclinic, at 153 K: a = 22.871(10), b = 11.994(3), c = 23.081(7) Å; β = 114.20(3)°; V = 5775(6) Å^3; space group, $C2/c$; Z = 4; d_c = 1.332 g cm^3. Intensities of 6254 reflections were measured from the single crystal of **2** at a temperature of 153 K, and 4674 independent observable reflections with $I > 2.0\sigma(I)$ were used in structure solution and refinement.

The structure was solved by direct method and refined by least squares in the full-matrix anisotropic approximation. The positions of H atoms were calculated and these atoms were included in the refinement with the fixed coordinates and isotropic thermal factors U = 0.08 Å^2. The final refinement converged at R = 0.061, R_w = 0.056 and goodness of fit of 2.08. Important bond lengths and bond angles are given in Table 1. All calculations were performed using SHELXTL programs with an IBM/PC computer.

3. Results and discussion

The general view of the **2** is shown in Fig. 1. It corresponds to the dimer $[Li_4(THF)_4(C_4Ph_4)_2]$ with second-order symmetry axis. Lithium atoms form a strongly distorted tetrahedron with Li–Li bond distances of 2.440–3.011(5) Å and are coordinated to one THF molecule each (Li–O bond distances are 1.944(2) and 1.967(5) Å) as well as by carbon atoms of the butadiene chain C(1)–C(4) of dianions $[PhC^1{=}C^2(Ph){-}C^3(Ph){=}C^4(Ph)]^{2-}$. Each Li (1,2) is strongly coordinated by terminal carbon atoms C(1) and C(4) of butadiene chain of one C_4Ph_4 ligand and by one terminal carbon atom, C(1a,4a) of the second C_4Ph_4 (Li–C distances are 2.21–2.31 Å). Less strongly bonded to lithium atoms are internal carbon atoms C(2) and C(3). Li(1)–C(2,3) are 2.41 and 2.57 Å and Li(2)–C(2a,3a) are 2.40 and 2.58 Å. Therefore each lithium is bound to five carbon atoms of two butadiene molecules as well as to one oxygen from a THF molecule.

Table 1
Important bond lengths (Å) and angles (°) in the structure **2**

Bond lengths			
C(1)–C(2)	1.366(4)	Li(1)–C(1a)	2.293(5)
C(2)–C(3)	1.522(3)	Li(1)–O(1)	1.967(5)
C(3)–C(4)	1.356(3)	Li(1)–Li(2)	2.826(6)
C(1)–C(5)	1.484(3)	Li(1)–Li(1a)	2.440(4)
C(2)–C(11)	1.511(3)	Li(1)–Li(2a)	3.011(5)
C(3)–C(17)	1.508(4)	Li(2)–C(1a)	2.298(5)
C(4)–C(23)	1.489(3)	Li(2)–C(2a)	2.400(5)
Li(1)–C(1)	2.213(4)	Li(2)–C(3a)	2.581(5)
Li(1)–C(2)	2.570(4)	Li(2)–C(4a)	2.231(5)
Li(1)–C(3)	2.409(5)	Li(2)–C(4)	2.294(6)
Li(1)–C(4)	2.311(5)	Li(2)–O(2)	1.944(4)
Bond angles			
C(5)–C(1)–C(2)	115.7(2)	C(2)–C(3)–C(4)	121.9(2)
C(1)–C(2)–C(3)	122.2(2)	C(2)–C(3)–C(17)	112.3(2)
C(1)–C(2)–C(11)	123.2(2)	C(4)–C(3)–C(17)	125.8(2)
C(3)–C(2)–C(11)	114.5(2)	C(3)–C(4)–C(23)	118.5(2)

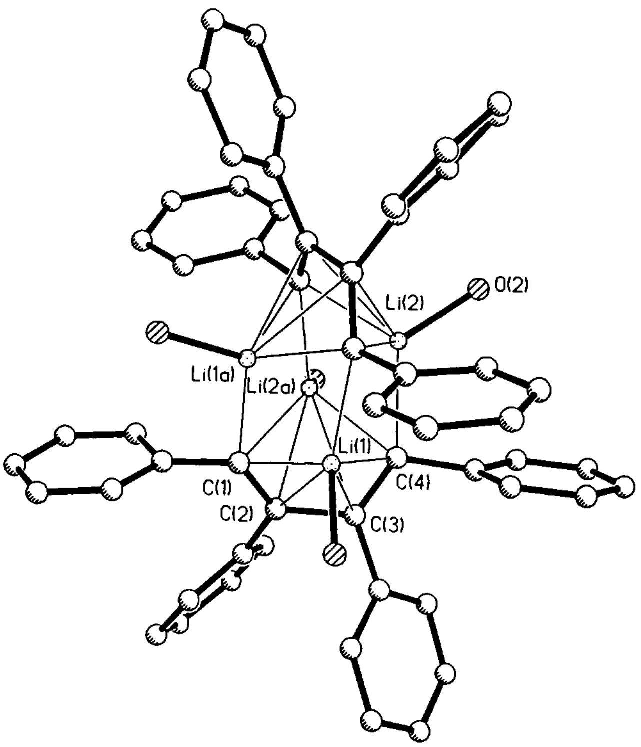

Fig. 1. The general view of the molecular structure of the 1,4-dilithiumbutadiene–THF complex.

The tetrahedral structure of the lithium cluster and polycenter bonding of lithium atoms with carbon atoms of unsaturated ligands is typical for lithium clusters (see the review in [7]). The geometrical parameters of **2** have expected values with cisoid conformation of the C_4Ph_4 ligand. The torsion angle C(1)–C(2)–C(3)–C(4) is −34.7°.

The bond distances of C(1)–C(2) and C(3)–C(4) correspond to essentially double bonds (1.366(4) and 1.356(3) Å whereas the central bond C(2)–C(3) is close to a single bond (1.522(3) Å). Compared with butadiene with 1.48 Å [8] for the central bond distance it is significantly longer in **2**, probably for steric reasons.

Li–Li bonds in the cluster are very short, shorter than in the Li_2 molecule (2.67 Å). Presumably this corresponds to a large positive charge on lithium cluster which can be considered as close to Li_4^{2+}. This is also confirmed by solvation of lithiums with THF. Stabilization of the cluster and shortening of the Li–Li bonds are due to the attraction of negatively charged ligands to lithium cations of the cluster, concentrating the charge and increasing the polarization effect.

The mechanism of **2** formation can be visualized as recombination of two Li–C(Ph)–C(Ph) fragments formed in the coordination sphere of one or two iron atoms after Li atom transfer to carbon atoms of the tolane ligand although, in the absence of kinetic data, the formation of these radicals outside the iron coordination sphere cannot be excluded.

The participation of lithium atoms in the reaction with tolane indirectly confirms the possibility of a similar reaction with dinitrogen. In the latter case instead of dimerization a disproportionation can proceed, forming N_2 and Li_2N_2 ligands. When treated with HCl the latter produces N_2H_2 which further disproportionates to form N_2H_4 and N_2 [9]. This double disproportionation is not necessarily the result of free N_2H_2 formed under treatment of HCl and may be the result of interaction of the iron complexes, inducing intermolecular electron transfer of the complexes with subsequent hydrazine and N_2 formation.

Supplementary materials

Tables of atom coordinates and temperature factors, bond distances and angles of all atoms, and a list of structure factors can be obtained from one of the authors (M.Yu. Antipin).

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