Journal of Organometallic Chemistry, 292 (1985) 319–324
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE UNEXPECTED FORMATION OF A LITHIUM-ENOLATE FROM BIS{2-[(DIMETHYLAMINO)METHYL]PHENYL}COPPER LITHIUM. X-RAY STRUCTURE OF $Li_4[OC(=CH_2)C_6H_4CH_2NMe_2\text{-}2]_4$ *

JOHANN T.B.H. JASTRZEBSKI, GERARD VAN KOTEN **

Anorganisch Chemisch Laboratorium, J.H. van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

MARTIN J.N. CHRISTOPHERSEN and CASPER H. STAM

Laboratorium voor Kristallografie, J.H. van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

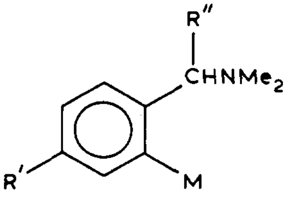
(Received February 11th, 1985)

Summary

Attempted crystallization of the bis(aryl)lithium cuprate, $Cu_2Li_2(C_6H_4CH_2\text{-}NMe_2\text{-}2)_4$, from diethyl ether/pentane afforded in one case colourless crystals which according to an X-ray diffraction analysis appeared to be the lithium enolate, $Li_4[OC(=CH_2)C_6H_4CH_2NMe_2\text{-}2]_4$. This consists of a central Li_4O_4 cube with intramolecular Li–N coordination of the CH_2NMe_2 substituent. This enolate, which has also been prepared via an independent route, is the first example of a structurally characterized lithium enolate and contains Li centres that are intramolecularly coordinated.

Introduction

We are currently investigating the structures of a series of aryl-lithium, -copper and -copperlithium compounds [1] in order to gain more insight in the structure/reactivity relationship of cuprates.



(R' = R'' = H;
1, M = Li(tetramer) [2];
2, M = Cu(tetramer) [3];
3, M = $\frac{1}{2}$CuLi(tetranuclear) [4,5])

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* Lithium 2-{2-[(dimethylamino)methyl]phenyl}-1-ethen-2-olate tetramer.

** To whom correspondence should be addressed.

0022-328X/85/$03.30

Our studies are mainly directed towards elucidation of the nature of the aryl–metal interaction. In the tetranuclear structures of species **1** (R′ = R″ = H) and **2** (R′ = Me, R″ = H) the aryl group bridges, via C(*ipso*), similar metal centres in a symmetrical fashion: i.e., three Li atoms via a four-centre, two-electron bond in **1**, and two Cu atoms via a three-centre, two-electron bond in **2**, respectively. In the cuprate **3** (R′ = R″ = H) the aryl group bridges between different metals, Cu and Li, and appears to be primarily bonded via C(*ipso*) to the Cu atom [5]. The interaction with the Li atom is weaker but still present, as can be concluded from the observation of a value for $^1J(^{13}C(ipso),^7Li)$ of 7.0 Hz [4]. Moreover, in the corresponding argentate, $Ag_2Li_2(C_6H_4CH_2NMe_2\text{-}2)_4$, a $^2J(^{107,109}Ag,^6Li)$ was observed of 1.46 Hz [1].

In the course of this study in one experiment we recrystallized the bis(aryl)lithium cuprate, **3**, from diethyl ether and carried out an X-ray structure analysis on the crystals obtained. Instead of the cuprate **3** the crystals proved to be the lithium enolate, $Li_4[OC(=CH_2)C_6H_4CH_2NMe_2\text{-}2]_4$, (**4**).

Much interest has been shown recently in diastereoselective reactions of alkali metal enolates [6]. Structures of only two lithium enolates have been reported; these consist of a central Li_4O_4-cube with each Li atom additionally coordinated via O by a THF molecule [7]. We now report the structure of **4**, which appears to be the first example of an enolate in which the Li centres are intramolecularly coordinated. An independent synthesis of **4** via a palladation reaction of *N,N*-dimethylbenzylamine is described.

Experimental

All reactions were carried out under dry oxygen-free nitrogen. ^1H NMR spectra were recorded on a Varian XL 100 spectrometer. ^{13}C NMR spectra were recorded on a Bruker WP 80 spectrometer. Bis{2-[(dimethylamino)methyl]phenyl}copperlithium was prepared by published methods [4]. 2-[(Dimethylamino)methyl]acetophenone was prepared by the procedure described by Holton and Natalie [8], see eq. 2. Overall yield 51%. ^1H NMR (in $CDCl_3$, δ ppm); NMe_2 2.15 (6H), $CH_3C{=}O$ 2.08 (3H), NCH_2 3.32 (2H), aromatic 7.10–7.30 (4H).

Synthesis of $Li_4[OC(=CH_2)C_6H_4CH_2NMe_2\text{-}2]_4$ *(4)*

A solution of 5 mmol of lithium dimethylamine was prepared from 5 mmol of diisopropylamine and 5 mmol of n-BuLi in diethyl ether (10 ml). The solution was cooled to −20°C and 5 mmol of 2-[(dimethylamino)methyl]acetophenone was added. The white precipitate of **4**, which formed immediately, was filtered off, washed with diethyl ether and n-pentane, and dried in vacuo. Yield 95%. According to its ^1H and ^{13}C NMR spectra this was pure **4**. ^1H NMR (in THF-d_8, δ ppm); NMe_2 2.15 (6H), NCH_2 3.40 (2H), $C{=}CH_2$ 3.50 (1H) and 3.70 (1H) (^2J(HH) 2 Hz), aromatic-H 7.0–7.4 (4H). ^{13}C NMR (in THF-d_8, δ ppm); NMe_2 45.8, NCH_2 64.0, $=CH_2$ 78.7, ArCO 171.0, aromatic resonances at 126.0, 127.7, 129.5, 132.5, 135.0 and 150.3.

Structure determination and refinement

Crystals of $Li_4[OC(=CH_2)C_6H_4CH_2NMe_2\text{-}2]_4$ (**4**) are tetragonal, space group $P4_2/n$, with 8 molecules in a unit cell of dimensions *a* 11.929(1) and *c* 15.179(1) Å. 1830 independent reflexions were measured on a NONIUS CAD4 diffractometer

TABLE 1

POSITIONAL PARAMETERS OF THE ATOMS OF $Li_4[OC(=CH_2)C_6H_4CH_2NMe_2\text{-}2]_4$, **4**, EXCLUDING HYDROGEN

Atoms	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$	Atoms	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$
O(1)	0.2840(4)	0.1346(4)	0.6819(4)	C(7)	0.6793(8)	−0.0171(8)	0.6457(7)
N(1)	0.4558(6)	0.2848(6)	0.5719(5)	C(8)	0.4953(8)	−0.0665(7)	0.7076(7)
C(2)	0.6121(8)	−0.0823(8)	0.7021(6)	C(9)	0.5102(7)	0.0832(7)	0.5981(6)
C(3)	0.4460(8)	0.0189(7)	0.6553(6)	C(10)	0.6265(8)	0.0628(8)	0.5934(6)
C(4)	0.3190(9)	0.0293(7)	0.6624(7)	C(11)	0.2515(8)	−0.0577(8)	0.6564(8)
C(5)	0.4602(7)	0.1681(7)	0.5351(6)	C(12)	0.3967(10)	0.3547(9)	0.5061(7)
C(6)	0.5711(8)	0.3295(8)	0.5849(7)	Li(1)	0.3541(14)	0.2792(13)	0.6849(13)

using graphite monochromated Cu-K_α-radiation; 718 were below the 3σ(I)-level and were treated as unobserved. No absorption correction was applied (μ 5.2 cm^{-1}; crystal dimensions 0.25 × 0.25 × 0.35 mm).

The structure was solved by means of the symbolic addition program set SIMPEL [9]. Refinement proceeded by block-diagonal least-squares calculations, anisotropic for Li, C, N and O and isotropic for H. The H atoms were located from a Fourier synthesis. The weighting scheme $w = 1/(4.7 + F_0 + 0.028F_0^2)$ was employed. The final R value was 0.047 for 1112 reflexions. Atomic coordinates are listed in Table 1. Lists of thermal parameters and structural factors can be obtained from the authors.

Results and discussions

In one of several crystallization experiments we attempted to prepare suitable single crystals of the bis(aryl)lithium cuprate **3** by vapour diffusion of pentane into a solution of **3** in diethyl ether. After two days a crop of suitable, colourless crystals was obtained which remained stable after isolation. A few yellow crystals were also present, and these were separated and identified by ^1H NMR spectroscopy as the known 2-[(dimethylamino)methyl]phenylcopper (**2**) [3].

One of the colourless crystals obtained from the experiment (and thought at that time to be **3**) was transferred to a glass capillary and X-ray data were collected. The results of the structure determination and refinement showed that these colourless crystals were the lithium enolate of 2-[(dimethylamino)methyl]acetophenone (**4**) and not the bis(aryl)lithium cuprate **3**. The ^1H NMR spectra of the remaining batch of colourless crystals confirmed this (vide infra).

Molecular geometry of the lithium enolate (4)

The molecule in the asymmetric unit gives rise to two $Li_4[OC(=CH_2)\text{-}C_6H_4CH_2NMe_2\text{-}2]_4$ tetramers around $\bar{4}$ axes. Intramolecular bond distances and angles are listed in Table 2.

The molecular structure consists of an almost regular Li_4 tetrahedron with two independent Li...Li distances of 2.594(7) and 2.678(8) Å (see Fig. 1). Each of the $2\text{-}Me_2NCH_2C_6H_4C(=CH_2)O^-$ ligands is bonded to an Li_3 face of this Li_4 tetrahedron via both the anionic oxygen atoms, with almost equal O–Li bond distances (1.97 Å mean, vide infra), and the neutral N donor site of the intramolecularly placed CH_2NMe_2 ligand, with a Li–N bond distance of 2.116(6) Å.

The four lithium and the four enolate O atoms in **4** together form a nearly regular

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°) IN **4** (excluding hydrogen)

Bond length			
O(1)–C(11)	1.333(4)	Li(1)–Li(2)	2.594(7)
O(1)–Li(2)	1.960(5)	C(1)–C(2)	1.410(4)
O(1)–Li(1)	1.920(5)	C(1)–C(6)	1.389(5)
O(1)–Li(3)	2.018(7)	C(1)–C(11)	1.501(5)
N(8)–C(7)	1.485(4)	C(2)–C(3)	1.397(4)
N(8)–C(10)	1.464(5)	C(2)–C(7)	1.511(5)
N(8)–Li(1)	2.116(6)	C(3)–C(4)	1.377(5)
N(8)–C(9)	1.472(5)	C(4)–C(5)	1.373(6)
		C(5)–C(6)	1.394(5)
		C(11)–C(12)	1.338(5)
Bond angles			
Li(1)–O(1)–C(11)	134.2(3)	O(1)–Li(1)–N(8)	104.4(3)
Li(2)–O(1)–C(11)	140.1(3)	O(1)–Li(2)–Li(1)	47.4(2)
Li(3)–O(1)–C(11)	106.4(3)	O(2)–C(1)–C(6)	118.8(3)
Li(1)–O(1)–Li(2)	83.9(2)	C(6)–C(1)–C(11)	118.4(3)
Li(1)–O(1)–Li(3)	85.7(3)	C(2)–C(1)–C(11)	122.8(3)
C(9)–N(8)–C(10)	108.3(3)	C(1)–C(2)–C(3)	118.6(3)
C(7)–N(8)–C(9)	111.2(3)	C(3)–C(2)–C(7)	119.0(3)
C(7)–N(8)–C(10)	108.0(3)	C(1)–C(2)–C(7)	122.2(3)
Li(1)–N(8)–C(9)	114.8(3)	C(2)–C(3)–C(4)	121.8(3)
Li(1)–N(8)–C(10)	107.6(3)	C(3)–C(4)–C(5)	119.6(3)
Li(1)–N(8)–C(7)	106.8(2)	C(4)–C(5)–C(6)	119.9(4)
O(2)–Li(1)–N(8)	116.2(3)	C(1)–C(6)–C(5)	121.2(4)
O(1)–Li(1)–O(2)	96.0(2)	N(8)–C(7)–C(2)	114.9(3)
O(1)–Li(1)–O(3)	95.1(3)	C(1)–C(11)–C(12)	120.8(3)
O(3)–Li(1)–N(8)	141.5(3)	O(1)–C(11)–C(1)	115.8(3)
N(8)–Li(1)–Li(2)	123.8(3)	O(1)–C(11)–C(12)	123.3(3)
O(1)–Li(1)–Li(2)	48.7(2)		

cube with edges averaging about 1.97 Å. This Li_4O_4 geometry is similar to that observed in lithium cyclopentenolate THF solvate and lithium 3,3-dimethyl-1-buten-2-olate THF solvate [7]; in the latter structures the tetrahedral geometry around each of the Li atoms is achieved by coordination of a THF molecule.

The C(11)–C(12) bond (1.338(5) Å) is almost in the plane defined by Li(1)CLi(2), being antiperiplanar to Li(2)–O (dihedral angle −15.8°). The dihedral angle with Li(3) is 85.8(4)°. This geometry contrasts with that observed in the two Li enolate THF solvates which have OC=CLi(1) (antiperiplanar) planes bisecting the Li(2)–O–Li(3) angle. This difference in orientation of the enolate moiety with respect to the OLi_3 terahedral array is probably due to the intramolecular coordination in **4**. This Li–N coordination results in a seven-membered chelate ring which is distinctly puckered. Striking structural features of this ring are (i) the small dihedral angle between the planes defined by the aryl ring and the enolate moiety, and (ii) the configuration around the C(2)–C(7) bond, with the NMe_2 group oriented out of the aryl plane (C(1)C(2)–C(7)–N(8) −77.1(4)°). The Li–N bond length (2.116(6) Å) is in the range expected for such bonding (cf. the Li–N distances in **1** 2.011(9) [2], and **3** 2.139(6) Å) [5].

We recently found that the intramolecular Li–N interactions in the tetranuclear structure of $Li_4(C_6H_4CH_2NMe_2\text{-}2)_4$ are not affected by weakly coordinating solvents

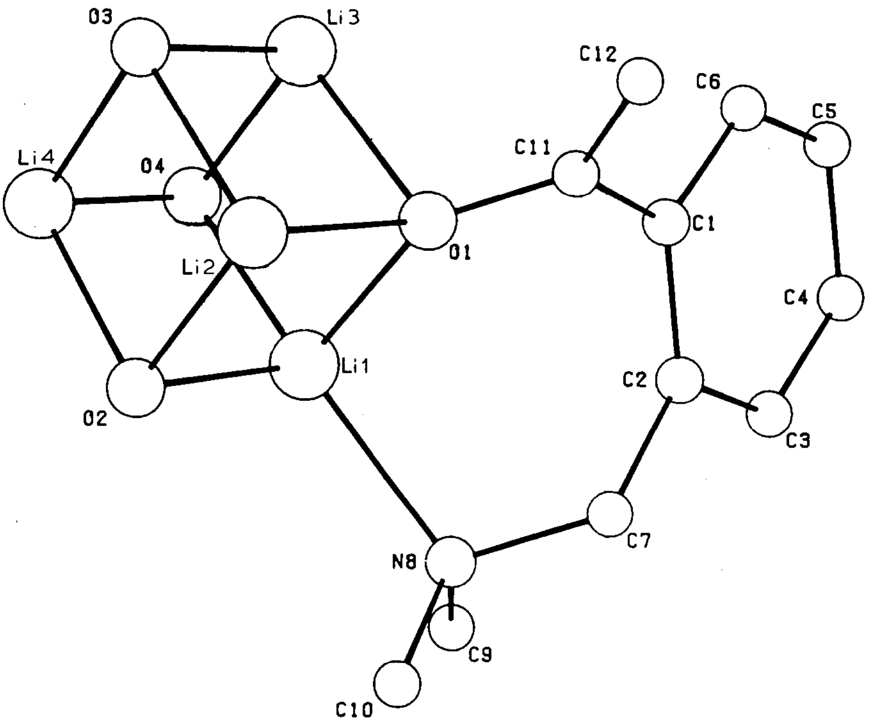


Fig. 1. Part of the molecular geometry of 4; the Li_4O_4 cube is shown together with one of the 1-ethen-2-olate groups; the other three 1-ethen-2-olate groups are ommited for clarity. Li(1), Li(2), Li(3) and Li(4) as well as O(1), O(2), O(3) and O(4) are symmetry related owing to a $\bar{4}$ axis.

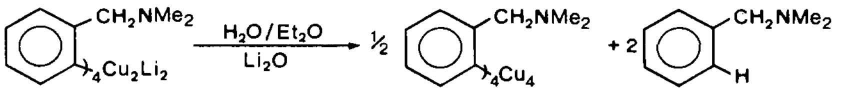
[2]. It is therefore unfortunate that the lithium enolate **4** is insoluble in both hydrocarbon solvents (e.g. benzene) and weakly coordinating solvents (e.g. diethyl ether), since this means no conclusions can be drawn about the retention of the structural features of **4**, e.g. the Li–N interaction, in solution.

Compound **4** dissolves readily in more strongly coordinating solvents. The ^1H and ^{13}C NMR data for **4** in THF-d_8 (see experimental part) strongly suggest that the coordinating NMe_2 groups are replaced by THF molecules. For example, the ^1H NMR spectrum shows a $\delta(NMe_2)$ of 2.15 ppm which is close to the chemical shift found for the uncoordinated NMe_2 group in $2\text{-}Me_2NCH_2C_6H_4C(CH_3){=}O$.

The present structure is a nice model for one of the intermediates suggested by Seebach et al. to be formed in reactions of lithium enolates with aldehydes or ketones [7]. It models the situation in which the C–C bonding between the enolate and electrophile already has been established and a subsequent switch of the positions of the neutral and anionic heteroatomic nuclei has occurred: i.e., **4** is an example of a lithium enolate having the negative O in "in" and the neutral N donor atom in "out" positions (cf. ref. 7).

Formation of the lithium enolate 4

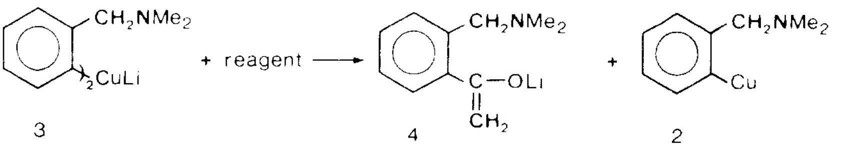
In an earlier study we showed that careful hydrolysis of the colourless cuprate **3** gave free *N,N*-dimethylbenzylamine and the yellow arylcopper **2**, according to eq. 1.



(1)

Although hydrolysis during crystallization of **3** would explain the formation of the arylcopper **2**, it can not account for the appearance of the lithium enolate **4**. It is obvious that the formation of **4** must be due to an impurity in the solvents used. Recrystallization of authentic samples of **3**, which were carried out various times, invariably gave only crystalline **3**. The single crystals formed in one such experiment were ultimately used for determination of the structure of **3** [5].

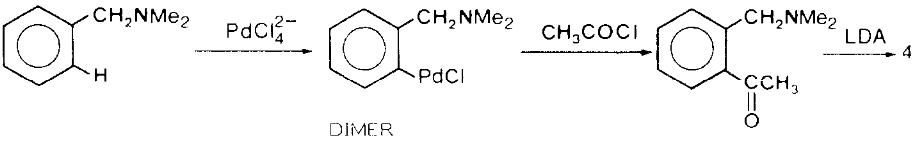
Comparison of the organic fragments present in **3** and **4** shows that the observed conversion formally comprises coupling of a "CH_2CO" fragment with the $C_6H_4CH_2NMe_2$-2 anion, see eq. 2.



(2)

At present the origin of the latter grouping is not clear. Attempted reactions of **3** with some acetylating reagents, acetyl chloride, acetic acid anhydride and acetic acid ethyl ester, neither gave **4** nor its most likely hydrolysis product 2-$Me_2NCH_2C_6H_4$-$C(=O)CH_3$.

In order to confirm the nature of the bulk of the crop of colourless crystals from which the single crystal was selected, **4** was also synthesized by the independent route outlined in eq. 3.



(3)

Further work is in progress to find what reagent was responsible for the observed conversion of the bis(aryl)lithium cuprate **3** into the enolate **4**.

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