Recl. Trav. Chim. Pays-Bas 107, 431-433 (1988)

Synthesis and structure of a bis-*ortho*-chelated aryllithium compound: 2,3,5,6-tetrakis[(dimethylamino)methyl]phenyllithium dimer

Adolphus A. H. van der Zeijden and Gerard van Koten*

Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands (Received December 17th, 1987)

Abstract. The reaction of 1,2,4,5-(Me₂NCH₂)₄C₆H₂ with one equivalent of *n*-butyllithium affords $Li_2[C_6H(CH_2NMe_2)_4-2,3,5,6]_2$ (1). The molecule consists of a dimeric unit containing three-centre, two-electron lithium-bonded aryl groups. The distorted tetrahedral coordination sphere of the lithium atoms is completed by two *N*-coordinating *ortho*-CH₂NMe₂ substituents. Complex 1 is the first dimeric aryllithium compound characterized in which the coordination around lithium is completed solely by intramolecular donating hetero atoms.

Introduction

Currently, interest is being shown in the structural aspects of organolithium compounds, both in solution and in the solid state¹. Organolithium compounds are usually aggregated through electron-deficient carbon-lithium bonds and show a great variety of structural forms, dependent upon steric factors and the presence (or absence) of inter- or intramolecular coordinating hetero atoms. There are two main types which can be categorized as having an organic group which is C-bonded either in a three-centre, twoelectron interaction to two lithium atoms, or one which has a four-centre, two-electron interaction to three lithium atoms. Examples of these types reported from our laborainclude the ortho-chelated compounds tory $Li_2[C_6H_3(CH_2NMe_2)_2-2,6]_2$ (2) and $Li_4[C_6H_4(CH_2NMe_2) -2]_4$ (3)². Both complexes are valuable precursors in the syntheses of other main-group or transition-metal complexes³. Occasionally, the reaction of these aryllithium compounds with transition-metal salts leads to an electrontransfer reaction and concomitant reduction of the transition-metal centre. For instance, the addition of CuBr to 3 affords, apart from $(ArCu)_4$, significant amounts of Ar_2 , ArH and metallic copper; the mixture of organic products pointing to a competing radical-decomposition pathway^{4a}. However, the reaction of 2 with either RhCl₃, VCl₃ or TaCl₅ leads to the exclusive formation of the biphenylic product [2,2',6,6'-(Me₂NCH₂)₄C₁₂H₆]^{4b}. This was explained as being a result of the special arrangement of the aryl moieties in the aryllithium complex: the dimeric nature, which implies three-centre, two-electron bonding suggests a short

C(aryl)-C'(aryl) distance, which could quench all possible intermolecular radical reactions after electron transfer and promote exclusive intramolecular C-C coupling. This view has been corroborated by an X-ray structure determination (for experimental details see ref. 6) of the related dimer $Li_2[C_6H(CH_2NMe_2)_4-2,3,5,6]_2$ (1), in which two of the four heteroatom substituents are suitably placed for intramolecular coordination. In this paper we wish to report details of the synthesis together with a discussion of the structural features of this aryllithium dimer.

Experimental

Synthesis of $Li_2[C_6H(CH_2NMe_2)_4-2,3,5,6]_2$, 1

(a) The reaction of 1,2,4,5-(BrCH₂)₄C₆H₂⁵ with a large excess of Me₂NH in dry benzene afforded 1,2,4,5-(Me₂NCH₂)₄C₆H₂ in 22% yield as white fluffy crystals. ¹H NMR (CDCl₃, δ , ppm) 2.20 (NMe, 24H), 3.47 (NCH₂, 8H), 7.17 (aryl H, 2H). ¹³C NMR (CDCl₃, δ , ppm) 45.4 (NMe), 60.9 (NCH₂), 132.3 (aryl CH), 136.3 (aryl C).

(b) A solution of 1,2,4,5-(Me₂NCH₂)₄C₆H₂ (383 mg, 1.05 mmol) in benzene (7 ml) and an equivalent amount of *n*-butyllithium (0.6 ml, 1.78 M in hexane) was stirred under nitrogen for 3 days at room temperature. The reaction mixture was then evaporated to dryness and extracted with hexane (15 ml). Concentrating the orange extract to 8 ml and subsequent cooling to -30° C for 3 days afforded large, faintly brown crystals of 1. ¹H NMR (+25°C, C₆D₆, δ , ppm) 2.10 (NMe, 12H), 2.26 (NMe, 12H), 3.48 (NCH₂, 4H), 3.86 (NCH₂, 4H), 6.87 (aryl CH, 1H). Details of X-ray data collection and structure determination of 1 are given in ref. 6. The compound is very air-sensitive; treatment with methanol-d₄ affords quantitatively the monodeuterated starting compound 1,2,4,5-(Me₂NCH₂)₄C₆HD. ¹H NMR as for its undeuterated analogue, see above; the signal at 7.17 ppm has half intensity.

^{*} To whom correspondence should be addressed at the Laboratory of Organic Chemistry, University of Utrecht, Dept. of Metal Mediated Synthesis, Padualaan 8, 3584 CH Utrecht, The Netherlands.



Results and discussion

The bis-ortho-chelated title compound 1 was synthesized by the reaction of 1,2,4,5-(Me₂NCH₂)₄C₆H₂ with one equivalent of BuLi in benzene, see eqn. 1.

It must be noted that ether was not required to induce formation of 1. It is argued that activation of the $(BuLi)_n$ aggregate is promoted by complexation of lithium to one of the CH_2NMe_2 groups of the tetramine ligand; this not only increases the nucleophilic character of the Bu group, but, through a repulsive interaction of the adjacent CH_2NMe_2 group, it also efficiently directs the activated BuLi into the neighbourhood of a C(aryl)-H bond and, hence, facilitates metallation.

The related organolithium compound 2 is a dimer, as was deduced from molecular-weight determinations in benzene and from the $^{7}\text{Li}-^{13}\text{C}$ coupling on C(aryl), which showed that two lithiums were attached to this carbon atom². A confirmative X-ray structure determination of 2 was not possible, since no suitable crystals could be obtained. However, since the coordination around lithium in 2 is likely to be very similar to that in 1, the structure of this latter compound should give a detailed insight into the structures of both of these organolithium dimers.

The molecular structure of 1 (see Fig. 1A) consists of a dimeric molecule located at the intersection of three perpendicular twofold axes. The two lithium atoms in 1 (Li and Li') are bridged by the two *ipso*-carbon atoms [C(1) and C(1")] of the aryl rings and thus 1 can be regarded as an aryllithium compound of the three-centre, two-electron bridged type. The coordination around each lithium atom is completed by the N atoms of the two *ortho*-CH₂NMe₂ substituents, one from each of the aryl rings; the remaining two *meta*-CH₂NMe₂ groups on each aryl ring are not coordinated. The resulting coordination of Li, comprising C(1), N(1), C(1") and N(1"), can be described as a distorted tetrahedral.

Fig. 1. (A) PLUTO drawing of $Li_2[C_6H(CH_2NMe_2)_4 -2,3,5,6/_2$, 1; the hydrogen atoms are omitted for clarity. Relevant bond lengths (Å): Li-Li' 2.401(6), C(1)-Li 2.209(3), $\begin{array}{l} N(1)-Li \ 2.109(3), \ C(1)-C(2) \ 1.411(2), \ C(2)-C(3) \ 1.397(3), \\ C(3)-C(4) \ 1.386(3); \ bond \ angles \ (^{\circ}): \ N(1)-Li-N(1'') \\ 114.1(2), \ N(1)-Li-C(1) \ 86.17(5), \ N(1)-Li-C(1'') \ 131.17(5), \end{array}$ C(1) - Li - C(1'') = 114.1(2),C(2) - C(1) - C(2')115.1(2), Li - C(1) - Li'65.9(2), C(2)-C(1)-Li102.2(1), C(5) - N(1) - Li100.1(2). (B) Projection of 1 along metanon-coordinated C(4) - C(1) - C(1'') - C(4'');the -CH₂NMe₂ substituents and the hydrogen atoms are omitted for clarity.





The high crystallographic symmetry of the molecule causes the four C-Li and N-Li bonds, respectively, to be equivalent. and it also leads to a straight C(4)-C(1)-C(1'')-C(4'') axis running through the aryl groups with a Li-Li' vector bisecting this axis. In this respect, the structure of 1 is more symmetrical than that of similar three-centre, two-electron bridged aryllithium compounds such as Li₂Ph₂(TMEDA)₂ (4)⁷, Li₂[8-(dimethylamino)-1-naphthyl]₂(Et_2O)₂ (5)⁸ and Li_2 (mesityl)₂(THF)₄ (6)⁹. Furthermore, 1 is the first dimeric aryllithium compound characterized in which the coordination around lithium is completed solely by intramolecularly donating hetero atoms.

Complex 1 has a lithium core which is shielded by the coordinating *ortho* substituents, and this probably explains its high solubility in alkanes. It also explains why reaction of the related bis-*ortho*-chelated lithium complex 2 with certain transition metal salts exclusively yields the C-C coupling product, since the two *ipso*-carbons in the dimers 1-2 are held in close proximity [C(1)...C'(1) = 3.708(4) Å in 1]. The strong intramolecular coordination of the amine substituents will further prevent an easy breakage of the dimeric structure, and thus hamper intermolecular decomposition reactions.

The implications of the intramolecular coordination around this lithium core, which leads to a five-membered Li-C(1)-C(2)-C(5)-N(1)(i) A small are: ring, N(1)-Li-C(1) bite angle of 86.17(5)° and a concurrent opening of the other angles around lithium, causing the distortion from perfect tetrahedral geometry. (ii) A C(1) – Li bond of 2.209(3) Å, which is short compared to those found in the unstrained, but also bis-ortho-substituted, aryllithium complex 6 [2.271(3) and 2.279(3) Å]. This bond length, however, has little influence on either the Li...Li' distance of 2.401(6) Å, which is comparable to that of 4 [2.490(6) Å], 5 [2.366(5) Å] and 6 [2.490(5) Å], or the acute Li-C-Li'angle of 65.9(2)° [compare 67.4(1)° in 4, 64.2(1)° in 5 and 66.4(1) in 6]. (iii) A consistently shorter N(1)-Li bond than in 4 [2.109(3) Å vs 2.177(4) and 2.208(4) Å for the TMEDA nitrogens]. (iv) An angle of 58.75(4)° between the aryl plane and the Li_2C_2 rhombus. This angle deviates substantially from the 90° expected for an electron-deficient aryl-metal bond (and that is indeed observed in the non-chelated complexes 4 and 6), but is similar to that found in the analogous C, N-chelated complex 5. (v) An angle of $59.01(4)^{\circ}$ between the Li_2C_2 and Li_2N_2 planes. (vi) An angle of 62.50(6)° between the symmetry-related aryl rings (cf. ca. 0° in 4, 5 and 6). Some of the effects of chelate binding are depicted in Fig. 1B, which shows a projection of the molecule along the C(4)-C(1)-C(1'')-C(4'') axis; the regular star-shaped appearance of this projection is due to the almost 60° angles described in points (v) and (vi).

The geometry of the aryl rings is distorted around the *ipso*-carbon C(1). These distortions, which include an elongated C(1)-C(2) bond of 1.411(2) Å and a small

C(2)-C(1)-C(2') angle of $115.1(2)^{\circ}$, seem to be a general feature of aryl-metal complexes bearing electropositive metals such as lithium and aluminium⁷. The non-coordinating *meta*-CH₂NMe₂ groups are bent away from the coordinating *ortho*-congeners, as is illustrated by the opposite torsion angles C(1)-C(2)-C(5)-N(1) and C(2)-C(3)-C(8)-N(2), which are 55.9(2) and $-64.4(3)^{\circ}$, respectively. These non-coordinating substituents are, in principle, suited for the stabilization of a further *para*-positioned metal-carbon bond, and in fact 1 can be used as precursor for binuclear compounds. Further research in this direction is in progress.

Acknowledgements

Dr. E. Wehman and Dr. D. M. Grove are thanked for their stimulating interest.

References

- ^{1a} E. Wehman, J. T. B. H. Jastrzebski, J. M. Ernsting and G. van Koten, J. Organomet. Chem., submitted for publication;
- ^b G. van Koten, J. T. B. H. Jastrzebski, C. H. Stam and C. Brevard in "Biological & Inorganic Copper Chemistry", K. D. Karlin and J. Zubieta, Eds., Adenine Press, 1985, Vol. 1, p. 267;
- ^c W. N. Setzer and P. von Rague Schleyer, Adv. Organomet. Chem. 24, 353 (1985);
- ^d G. W. Klumpp, Recl. Trav. Chim. Pays-Bas 105, 1 (1986);
- ^e D. Seebach, R. Haessig and J. Gabriel, Helv. Chim. Acta **66**, 308 (1983).
- ² J. T. B. H. Jastrzebski, G. van Koten, M. Konijn and C. H. Stam, J. Am. Chem. Soc. **104**, 5490 (1982).
- ^{3a} D. M. Grove, G. van Koten, J. N. Louwen, J. G. Noltes, A. L. Spek and H. J. C. Ubbels, J. Am. Chem. Soc. 104, 6609 (1982);
 ^b A. de Koster, J. A. Kanters, A. L. Spek, A. A. H. van der Zeijden,
- G. van Koten and K. Vrieze, Acta Crystallogr. Section C C41, 893 (1985); ^c A A H van der Zeijden and G van Koten Inorg Chem 25
- ^c A. A. H. van der Zeijden and G. van Koten, Inorg. Chem. 25, 4723 (1986);
- ^d A. L. Wayda and R. D. Rogers, Organometallics 4, 1440 (1985);
- ^e F. A. Cotton and G. N. Mott, Organometallics 1, 38 (1982);
- ^f L. E. Manzer, J. Am. Chem. Soc. 100, 8068 (1978).
- ^{4a} G. van Koten and J. G. Noltes, J. Organomet. Chem. 84, 419 (1975);
- ^bA. A. H. van der Zeijden, G. van Koten, R. Luijk, K. Vrieze, C. Slob, H. Krabbendam and A. L. Spek, Inorg. Chem. 27, 1014 (1988).
- ⁵ J. T. Stapler and J. Bornstein, J. Heterocycl. Chem. 10, 983 (1973).
- ⁶ W. J. J. Smeets, A. L. Spek, A. A. H. van der Zeijden and G. van Koten, Acta Crystallogr. Section C C47, 1429 (1987).
- ⁷ D. Thoennes and E. Weiss, Chem. Ber. 111, 3157 (1978).
- ⁸ J. T. B. H. Jastrzebski, G. van Koten, K. Goubitz, C. Arlen and M. Pfeffer, J. Organomet. Chem. 246, C75 (1983).
- ⁹ M. A. Beno, H. Hope, M. M. Olmstead and P. P. Power, Organometallics 4, 2117 (1985).