Notes

Crystal Structure of Trimeric (2,6-Di-tert-butoxyphenyl)lithium†

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Summary: The structure of (2,6-di-tert-butoxyphenyl)lithium has been determined by single-crystal X-ray diffraction. Crystal data: monoclinic; a = 42.365 (1), b = 9.934 (1), c = 21.768 (1) Å; β = 107.95 (1)°; V = 8715 (1) Å³; space group C2/c; (C₆H₄₂O₂Li)₃; Z = 8. The structure reveals a trimeric aggregate, which is rather unique in organolithium chemistry. The trimer is stabilized by intramolecular coordination bonds between lithium and the ortho-positioned t-BuO-substituents. Because of the bulky t-BuO substituents, the favored trigonal bonding geometry around the ether oxygen has been distorted to pyramidal for some of the oxygen atoms. The small but significant difference in Li-trigonal) and Li-pyramidal) bond distances has been evaluated by ab initio calculations and can be explained by using electrostatic arguments.

As part of our studies on the structure and reactivity of aryllithium compounds with an α- or β-heteroatom, we have determined their structures in the solid state. In the course of this study we became interested in the structure of (2,6-di-tert-butoxyphenyl)lithium because the rigidity of the anion in this compound gives rise to forced intramolecular O-Li coordination, which is expected to be distorted as a consequence of the bulkiness of the t-BuO substituents. This work reports the structure of (2,6-di-tert-butoxyphenyl)lithium in the crystalline solid state.

Results and Discussion

The crystal structure of (2,6-di-tert-butoxyphenyl)lithium reveals a trimeric aggregate (Figure 1). Fractional coordinates and isotropic thermal parameters, bond distances/angles, and the lithium coordination geometries are collected in Tables I–III, respectively. Trimeric organolithium aggregates are unique. Recently we published the structure of the first trimeric organolithium compound, (2,6-bis(dimethylamino)phenyl)lithium, which shows a remarkable similarity with the present structure. Both trimeric organolithium aggregates consist of a nearly planar six-membered ring of alternating C(ipso) and Li atoms (maximum deviation of least-squares plane
The averaged Li-Li distance in dimeric and tetrameric aggregates varies from 2.55 Å, whereas Li-C-Li angles in the trimers vary from 87.3 (3)° to 90.5 (3)° (average 89.7 (3)°). The formation of trimers is most likely due to the rigidity of the bridging 2,6-bis(dimethylamino)phenyl and 2,6-di-tert-butoxyphenyl anion. For these systems, intramolecular N-Li (or O-Li) coordination proceeds most efficiently with long Li-Li distances and concomitant wide Li-C-Li angles. In addition, the bulkiness of the ortho substituent plays a role, since (2,6-dimethoxyphenyl)lithium forms a tetrameric aggregate that has been shown to consist of two distinct dimeric units. A further discussion on the formation of trimers is given in the paper on the structure of (2,6-bis(dimethylamino)phenyl)lithium.2*

In the present structure, the geometry of the bridging di-tert-butoxyphenyl anions needs further attention. At first sight the aggregate displays C₃ symmetry, but there are differences in the conformations of the di-tert-butoxyphenyl anions. The crystal structure shows three conformations for these anions; i.e. one with both t-BuO- substituents oriented parallel to the aryl ring plane (in-plane), one with both t-BuO- substituents perpendicular (out-of-plane), and one with a parallel and a perpendicular substituent. Since each Li atom interacts with t-BuO-substituents of both the in-plane and out-of-plane type, the occurrence of both t-BuO orientations is most likely due to the steric crowding around Li. The orientation of the t-BuO substituents affects the bonding geometry around O. A Cambridge Structural Database search3 on the directional preferences of ether O atoms toward Li atoms leads to the conclusion that the Li atoms lie close to the bisector of the ether grouping, i.e. along the direction of the trigonal sp² lone pair. Distortion from this trigonal bonding geometry can be subdivided in T-shape distortion (i.e. bending of the Li-O axis in the C-O-C plane) or pyramidal distortion (i.e. bending of the Li-O axis per...
The Li-O bond distances in the Li2O3 molecule are 1.984(6) and 2.000(5) Å, and the Li-O(pyramidal) bond is 2.074(6) Å. The Li-O coordinate geometry is characterized by the planar conformation (C6) with a small T-shape distortion (or combination of (i) and (ii)). The high increase of energy involved with T-shape distortion is in agreement with the small occurrence of this type of distortion. Both types of distortion result in an elongation of the Li-O bond.

The mixed dimer of (2,6-di-hydroxyphenyl)lithium and lithium hydride has been chosen as a model to study the intramolecular H-O-Li interaction observed in the crystal structure of (2,6-di-hydroxyphenyl)lithium. In order to stress the importance of the intramolecular O-Li interaction, calculations are compared to the mixed dimer of phenyllithium with lithium hydride. Two conformations of this mixed dimer are studied: a planar conformation (1) and a perpendicular conformation (2). The perpendicular conformation is 5.8 kcal/mol more stable than the planar conformation (this result contrasts with lower level MNDO calculations on the phenyllithium dimer for which the planar geometry is favored by 5.9 kcal/mol). Solvation of each Li by one H2O molecule does not change the preference for the perpendicular conformation (ΔE(3→4) = +7.1 kcal/mol). However, for (2,6-dihydroxyphenyl)lithium the planar structure (6) is calculated to be 26.1 kcal/mol more stable than the perpendicular one (5). This reversal is obviously due to strong intramolecular solvation in the planar conformation, which is shut off in the perpendicular conformation. The strong HO-Li interaction results in widening of the Li-C-Li’ angle, a concomitant increase of the Li-Li’ distance, and a decrease of the C1-C2-O angle (Table IV). These distortions are caused by the rigidity of the 2,6-dihydroxyphenyl anion: the Li-Li’ distance increases in order to minimize the T-shape distortion at O, but some T-shape distortion remains (29.8°). Rotation of the OH substituents on the C-O axis results in an increase of pyramidal distortion and a decrease of T-shape distortion. The extent to which both types of distortions are changed determines the energy involved with such a process. A 45° rotation of both OH substituents around the C-O axis is endothermic by 1.9 kcal/mol, and a 90° rotation is endothermic by 12.1 kcal/mol. A 90° rotation of both OH substituents in 1,3-dihydroxybenzene (9), resulting in 10, needs only 6.0 kcal/mol. Enlargement of the rotation barrier in the theoretical evidence for the nonplanarity of H*–OH2 (C6) in which bonding is expected to be less ionic. Ab initio calculations (RHF/SV 6-31G*) on the model system HLi–OH2 are performed to study the geometry of Li–ether interactions. The structure with minimal energy is characterized by the planar conformation (C6) with the trigonal-surrounded O atom. The ideal planar geometry may be distorted in two distinctive ways (Figure 3): (i) pyramidal distortion or (ii) T-shape distortion (or combination of (i) and (ii)). The high increase of energy involved with T-shape distortion is in agreement with the small occurrence of this type of distortion. Both types of distortion result in an elongation of the Li-O bond.
Table IV. Calculated Distances (Å) and Angles (deg) for the Molecules Shown in Figure 4*

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energy (SV -244.21332 -244.20408 -395.48296 -395.47165 -393.11771 -393.15933 -393.16262 -393.14003 -378.30145 -378.29353 -3-21G)

*The numbering is shown in formula 1 of Figure 4.

lithiated species must be mainly due to a less favorable Li-0H interaction in species 7 and 8 compared to 6. The C-Li bond distance does not show a large variance in the series 6, 7, and 8, but the Li-C-Li' angle and the O-Li distance vary considerably. A smaller T-shape distortion in 7 and 8 compared to 6 results in smaller Li-C-Li' angles, shorter Li-Li' distances and larger C1-C2-O angles. In agreement with the features observed in the structure of (2,6-di-tert-butoxyphenyl)lithium, the O-Li bond distances increase by rotation of the OH substituents: 1.961 Å (69º) → 1.985 Å (45º) → 2.085 Å (96º).

The O-Li bonding is mainly ionic, these differences in O-Li bond distances may be explained on the basis of electrostatic arguments. The polar Li+O- bond tends to lie in the R4+-O-R4- plane along the sp2 lone pair in order to minimize repulsive Li+-R4+ interactions. A distortion from this ideal position results in increase of the Li-O bond distances.

Experimental Section

Syntheses. (2,6-Di-tert-butoxyphenyl)lithium was prepared by heating a mixture of 1,3-di-tert-butoxybenzene (3.0 g; 13.5 mmol) and an equimolar amount of butyllithium (8.5 mL; 1.6 M BuLi in hexane) under reflux for 2 h. The hexane was removed in vacuo, and recrystallization from diethyl ether afforded the product in 50% yield. The low yield is ascribed to the high solubility of the lithium compound in diethyl ether as well as in hydrocarbons. 1H NMR (25 °C, benzene-d6): δ = 1.30 (s, 18 H, t-BuO), 6.82 (d, J = 7.5 Hz, 2 H, H4), 7.13 (t, J = 7.5 Hz, 1 H, H3). 13C{1H} NMR (35 °C, toluene-d8): δ = 29.0, 77.3 (t-BuO-), 156.3 (q, J{13C, 1H} = 6.7 Hz, 113.3, 128.4, 164.5 (aromatic signals).

1,3-Di-tert-butoxybenzene was prepared by reaction of the di-Germain derivative of 1,3-dibromobenzene and tert-butoxyperbenzoate analogously to the method described in ref 8. Yield: 40%. 1H NMR (benzene-d6): δ = 1.21 (s, 18 H, t-BuO), 6.74 (dd, J = 8.2 and 2.0 Hz, 2 H, H3), 6.83 (t, J = 2.0 Hz, 1 H, H2), 7.01 (dd, J = 8.0 and 8.4 Hz, 2 H, H6). 13C{1H} NMR (benzene-d6): δ = 29.0, 78.0, 119.2, 120.4, 128.7, 156.8.

X-ray Data Collection and Structure Determination. Single crystals were obtained by recrystallization from diethyl ether. A suitable colorless single crystal with dimensions 1.5 × 0.4 × 0.3 mm³ was sealed under nitrogen in a Lindemann glass capillary and mounted on an Enraf-Nomius CAD4 diffractometer.

Figure 4. Ab initio calculations (RHF, SV 3-21G). Symmetry restrictions: C3v for 1–6 and 9; C2 for 7, 8, and 10 (lithium atoms in 7 and 8 restricted in the aryl plane). Information on the geometries is gathered in Table IV.

(λCu Kα) = 1.54154 Å. The cell constants were determined by refining the setting angles of 25 reflections with 4 in the range 19–25º. Crystal data: monoclinic, a = 42.356 (1), b = 9.934 (1), c = 51.756 (1) Å, β = 107.95 (1)º, V = 8716.4 (1) Å³, space group C2/c; (CuH3O2Li): Z = 8; D(calcd) = 1.044 g/cm³. A total of 8239 unique reflections were collected at T = 20 °C within the Cu sphere of 4 to 70º (0 ≤ k ≤ 51, 0 ≤ l ≤ 26) of which 4068 reflections with 4 ≥ 2.5σ were considered to be observed. Standard reflections (221, 820, and 802) were measured.
Carbon Monoxide Induced Allyl Coupling from $\text{Mo}_2(\mu_2^+\eta^3-\text{allyl})_2(\eta^3-\text{allyl})_2$
Yielding the Labile Complex $\text{Mo(}\text{CO})_4(\eta^5-1,5$-hexadiene)

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Summary: Carbon monoxide induces the reductive elimination of two pairs of allylic ligands from $\text{Mo}_2(\mu_2^+\eta^3-\text{allyl})_2(\eta^3-\text{allyl})_2$ with the accompanying cleavage of the Mo-Mo quadruple bond. $\text{Mo(}\eta^5-1,5$-hexadiene)$$(\text{CO})_4$ is obtained from the reaction of 8 equiv of CO with $\text{Mo}_2(\mu_2^+\eta^3-\text{allyl})_2(\eta^3-\text{allyl})_2$. Structural data for and the reactivity of $\text{Mo(}\eta^5-1,5$-hexadiene)$$(\text{CO})_4$ suggest that 1.5-hexadiene is bound very weakly to molybdenum.

Since its discovery, tetraallyldimolybdenum, $\text{Mo}_2(\mu_2^+\eta^3-\text{allyl})_2(\eta^3-\text{allyl})_2$, has been utilized as a precursor to heterogeneous catalysts. It is a Mo(II) dimer containing a quadruple metal-metal bond. It is considerably more reactive than most Mo(II) dimers due partially to the reactivity of its pendent allylic ligands. It is unique in that its four allylic ligands are coordinated through two different bonding modes: two $\pi$-allyls are bridging the Mo-Mo quadruple bond with each $\pi$-allyl in the remaining pair binding to a single molybdenum atom. Exchange of allyls between bridging and terminal positions is not observed even at 80 °C.

A goal of our research is to investigate the reactivity pathways of this molybdenum dimer and related multiply bonded metal dimers bridged by $\eta^3$-allylic ligands. Of special interest is the synergic relationship between the bridging allyls and the multiple metal-metal bond. We report here the reaction of tetraallyldimolybdenum with carbon monoxide.

Results and Discussion

Reaction of $\text{Mo}_2(\mu_2^+\eta^3-\text{allyl})_2(\eta^3-\text{allyl})_2$ with Carbon Monoxide. $\text{Mo}_2(\mu_2^+\eta^3-\text{allyl})_2(\eta^3-\text{allyl})_2$ reacts completely with an excess of carbon monoxide within 10–15 min at ambient temperature to form Mo(CO)₅ and 1,5-hexadiene: $\text{Mo}_2(\mu_2^+\eta^3-\text{C}_3\text{H}_5)_2(\eta^3-\text{C}_3\text{H}_5)_2 + 12\text{CO} \rightarrow 2\text{C}_2\text{H}_6 + 2\text{Mo(CO)}_5$ (1)

Carbon monoxide induces the reductive elimination of two pairs of allylic ligands with the accompanying cleavage of the Mo-Mo quadruple bond. The cleavage of multiple metal-metal bonds induced by $\pi$-acceptor ligands such as CO, NO, and CNR has been widely reported. Such reac-