Notes

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

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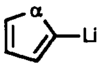
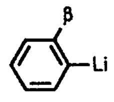
Summary: The structure of (2,6-di-*tert*-butoxyphenyl)lithium has been determined by single-crystal X-ray diffraction. Crystal data: monoclinic; a = 42.365 (1), b = 9.934 (1), c = 21.768 (1) Å; β = 107.95 (1)°; V = 8715 (1) Å^3; space group $C2/c$; $(C_{14}H_{21}O_2Li)_3$; Z = 8. The structure reveals a trimeric aggregate, which is rather unique in organolithium chemistry. The trimer is stabilized by intramolcular 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–O(trigonal) and Li–O(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.[1]





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.

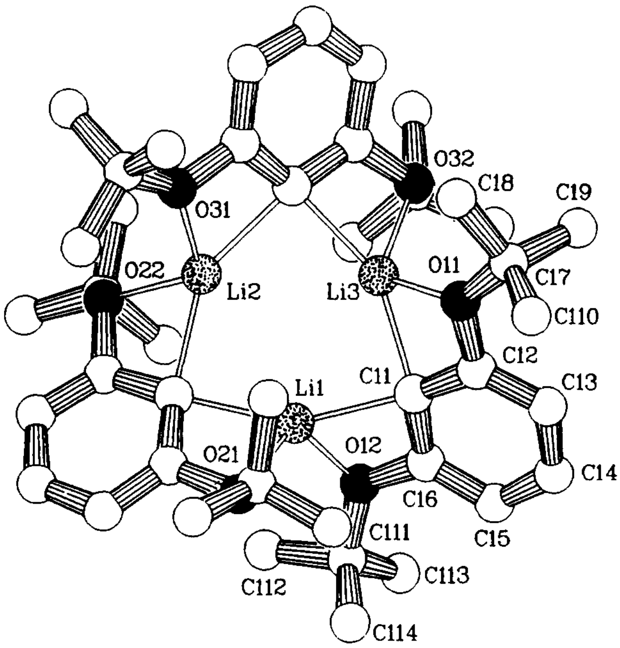


Figure 1. Crystal structure of (2,6-di-*tert*-butoxyphenyl)lithium (oxygen atoms black and lithium atoms speckled). The atom numbering is shown for molecule 1; the first digit gives the molecule number, and the second, the atom number.

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,[1f] 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

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† Dedicated to the 61st birthyear of Prof. Dr. Paul von Ragué Schleyer.

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Table I. Final Coordinates and Equivalent Isotropic Thermal Parameters for (2,6-Di-*tert*-butoxyphenyl)lithium

atom	*x*	*y*	*z*	*U*(eq), Å^2
O(11)	0.06907 (5)	0.3302 (2)	0.12678 (9)	0.0827 (9)
O(12)	0.06673 (4)	0.1105 (2)	−0.06149 (9)	0.0724 (8)
O(21)	0.10653 (4)	0.4000 (2)	−0.07320 (9)	0.0636 (7)
O(22)	0.20234 (4)	0.1480 (2)	0.03995 (8)	0.0623 (7)
O(31)	0.19846 (5)	0.3484 (2)	0.16161 (9)	0.0777 (8)
O(32)	0.11480 (4)	0.0729 (2)	0.19359 (9)	0.0676 (8)
Li(1)	0.1035 (1)	0.2376 (6)	−0.0154 (2)	0.068 (2)
Li(2)	0.1712 (1)	0.2366 (5)	0.0879 (2)	0.065 (2)
Li(3)	0.1061 (1)	0.2130 (6)	0.1216 (2)	0.075 (2)
C(11)	0.06632 (6)	0.2197 (3)	0.0320 (1)	0.059 (1)
C(12)	0.04816 (7)	0.2736 (3)	0.0691 (1)	0.067 (1)
C(13)	0.01384 (7)	0.2707 (4)	0.0531 (2)	0.087 (1)
C(14)	−0.00322 (8)	0.2129 (4)	−0.0053 (2)	0.102 (2)
C(15)	0.01254 (7)	0.1583 (4)	−0.0460 (2)	0.087 (1)
C(16)	0.04702 (6)	0.1631 (3)	−0.0257 (1)	0.064 (1)
C(17)	0.05931 (8)	0.4067 (4)	0.1740 (2)	0.078 (1)
C(18)	0.09239 (8)	0.4540 (4)	0.2192 (2)	0.113 (2)
C(19)	0.0424 (1)	0.3169 (5)	0.2096 (2)	0.135 (2)
C(110)	0.0382 (1)	0.5252 (4)	0.1441 (2)	0.143 (2)
C(111)	0.05534 (8)	0.0690 (4)	−0.1287 (1)	0.073 (1)
C(112)	0.08784 (8)	0.0351 (4)	−0.1412 (2)	0.093 (1)
C(113)	0.03350 (9)	−0.0544 (4)	−0.1390 (2)	0.116 (2)
C(114)	0.03876 (9)	0.1861 (4)	−0.1710 (2)	0.114 (2)
C(21)	0.15380 (6)	0.2721 (3)	−0.0150 (1)	0.0528 (9)
C(22)	0.13928 (6)	0.3563 (3)	−0.0668 (1)	0.058 (1)
C(23)	0.15270 (8)	0.3881 (4)	−0.1156 (2)	0.080 (1)
C(24)	0.18383 (8)	0.3402 (4)	−0.1108 (2)	0.091 (1)
C(25)	0.20050 (7)	0.2595 (3)	−0.0600 (1)	0.075 (1)
C(26)	0.18482 (6)	0.2252 (3)	−0.0150 (1)	0.057 (1)
C(27)	0.10126 (8)	0.5343 (4)	−0.0508 (2)	0.080 (2)
C(28)	0.1159 (1)	0.5423 (4)	0.0220 (2)	0.121 (2)
C(29)	0.06367 (8)	0.5468 (4)	−0.0698 (2)	0.122 (2)
C(210)	0.1161 (1)	0.6430 (4)	−0.0827 (2)	0.131 (2)
C(211)	0.20573 (7)	0.0022 (3)	0.0340 (2)	0.069 (1)
C(212)	0.21914 (9)	−0.0425 (4)	0.1031 (2)	0.111 (2)
C(213)	0.17213 (8)	−0.0599 (3)	−0.0004 (2)	0.100 (2)
C(214)	0.22988 (9)	−0.0299 (4)	−0.0026 (2)	0.115 (2)
C(31)	0.15810 (6)	0.2069 (3)	0.1766 (1)	0.054 (1)
C(32)	0.18602 (6)	0.2837 (3)	0.2067 (1)	0.059 (1)
C(33)	0.20081 (7)	0.2925 (3)	0.2729 (1)	0.076 (1)
C(34)	0.18622 (8)	0.2232 (4)	0.3125 (1)	0.084 (1)
C(35)	0.15844 (7)	0.1467 (3)	0.2865 (1)	0.073 (1)
C(36)	0.14571 (6)	0.1395 (3)	0.2197 (1)	0.058 (1)
C(37)	0.22101 (7)	0.4618 (3)	0.1732 (2)	0.070 (1)
C(38)	0.21947 (8)	0.5050 (4)	0.1057 (2)	0.097 (2)
C(39)	0.25578 (8)	0.4153 (5)	0.2092 (2)	0.120 (2)
C(310)	0.2095 (1)	0.5721 (4)	0.2076 (2)	0.133 (2)
C(311)	0.11354 (9)	−0.0707 (4)	0.1780 (2)	0.084 (2)
C(312)	0.1337 (1)	−0.1521 (4)	0.2354 (2)	0.125 (2)
C(313)	0.07711 (9)	−0.1029 (5)	0.1614 (2)	0.136 (2)
C(314)	0.1258 (1)	−0.0915 (4)	0.1207 (2)	0.154 (3)

Table II. Bond Distances (Å) and Angles (deg) for (2,6-Di-*tert*-butoxyphenyl)lithium

	X = 1	*X* = 2	*X* = 3
C*X*1–C*X*2	1.384 (4)	1.385 (4)	1.390 (4)
C*X*2–C*X*3	1.387 (4)	1.388 (4)	1.386 (4)
C*X*3–C*X*4	1.379 (5)	1.375 (5)	1.389 (5)
C*X*4–C*X*5	1.374 (5)	1.372 (5)	1.368 (5)
C*X*5–C*X*6	1.390 (4)	1.385 (4)	1.387 (4)
C*X*6–C*X*1	1.389 (4)	1.394 (4)	1.381 (4)
C*X*2–O*X*1	1.411 (4)	1.419 (3)	1.405 (3)
C*X*6–O*X*2	1.406 (3)	1.422 (3)	1.420 (3)
O*X*1–C*X*7	1.438 (4)	1.461 (4)	1.448 (4)
O*X*2–C*X*11	1.452 (4)	1.465 (4)	1.464 (4)
C*X*7–C*X*8	1.517 (5)	1.516 (5)	1.513 (5)
C*X*7–C*X*9	1.500 (6)	1.522 (5)	1.512 (5)
C*X*7–C*X*10	1.500 (6)	1.520 (6)	1.492 (5)
C*X*11–C*X*12	1.522 (5)	1.502 (5)	1.522 (5)
C*X*11–C*X*13	1.510 (6)	1.520 (5)	1.510 (6)
C*X*11–C*X*14	1.515 (5)	1.511 (5)	1.515 (5)
C*X*6–C*X*1–C*X*2	114.0 (2)	112.6 (2)	113.1 (2)
C*X*1–C*X*2–C*X*3	125.0 (3)	125.2 (3)	124.8 (3)
C*X*2–C*X*3–C*X*4	116.8 (3)	118.2 (3)	118.0 (3)
C*X*3–C*X*4–C*X*5	122.5 (3)	120.5 (3)	120.6 (3)
C*X*4–C*X*5–C*X*6	117.0 (3)	118.3 (3)	118.0 (3)
C*X*5–C*X*6–C*X*1	124.7 (3)	125.1 (3)	125.5 (3)
C*X*2–O*X*1–C*X*7	127.4 (2)	119.5 (2)	127.1 (2)
C*X*6–O*X*2–C*X*11	126.4 (2)	119.9 (2)	120.7 (2)
O*X*1–C*X*7–C*X*8	102.5 (3)	109.9 (3)	102.9 (2)
O*X*1–C*X*7–C*X*9	110.1 (3)	103.8 (3)	109.7 (3)
O*X*1–C*X*7–C*X*10	111.6 (3)	111.7 (3)	111.0 (3)
O*X*2–C*X*11–C*X*12	101.9 (2)	102.7 (2)	111.0 (3)
O*X*2–C*X*11–C*X*14	110.0 (3)	110.9 (3)	109.2 (3)

Table III. Li Coordination Geometries (Å and deg)

Li1–C11	2.139 (5)	Li2–O31	2.000 (5)
Li1–C21	2.156 (6)	Li2–Li3	3.074 (6)
Li1–O12	2.016 (6)	Li3–C11	2.150 (5)
Li1–O21	2.074 (6)	Li3–C31	2.160 (6)
Li1–Li2	3.051 (5)	Li3–O11	1.984 (6)
Li2–C21	2.161 (5)	Li3–O32	2.043 (5)
Li2–C31	2.188 (5)	Li3–Li1	2.962 (4)
Li2–O22	2.111 (5)		
C11–Li1–C21	152.3 (2)	Li2–C31–Li3	90.0 (3)
C11–Li1–O12	67.5 (2)	C11–Li3–C31	152.1 (3)
Li1–C21–Li2	89.9 (3)	C11–Li3–O11	67.8 (2)
C21–Li2–C31	147.1 (3)	Li3–C11–Li1	87.3 (3)
C21–Li2–O22	67.7 (2)		

is 0.08 (1) Å). The aryl planes make angles with this six-membered ring varying from 33.5 (2) to 35.4 (2)° and give the aggregate a "propeller-like" appearance. The most striking feature of both trimeric structures is the long Li···Li distance and the concomitant large Li–C–Li angle. The averaged Li···Li distance in dimeric and tetrameric aggregates is circa 2.55 Å, whereas Li···Li distances in both trimers range from 2.962 (4) to 3.113 (7) Å (average 3.055 (5) Å). The averaged Li–C–Li angle in dimeric and tetrameric aggregates is circa 65°, 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.[1f]

In the present structure, the geometry of the bridging di-*tert*-butoxyphenyl anions needs further attention. At first sight the aggregate displays C_3 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 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 search[2] 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 sp^2 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-

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(2) Chakrabarti, P.; Dunitz, J. D. *Helv. Chim. Acta* **1982**, *65*, 1482.

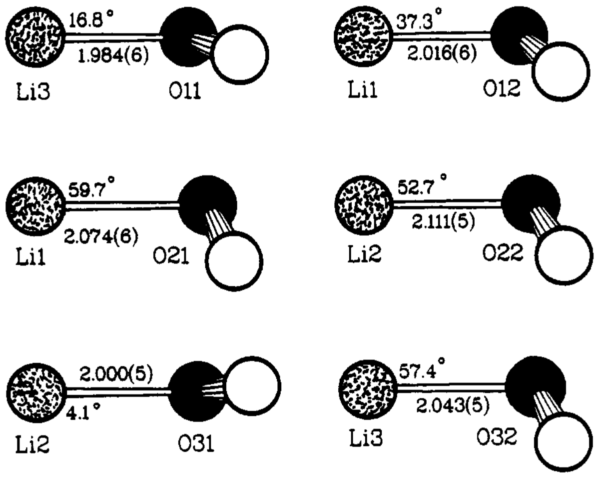

Figure 2. Plots of the COC···Li units viewed along the C···C vector, showing the Li–O bond distance (Å) and the angle between the Li–O vector and the COC plane (degrees).

pendicular on the C–O–C plane). This database search[2] shows that distortion from a trigonal to a pyramidal bonding geometry is common, but extreme distortion to a T-shape geometry around O seldom occurs, apparently because it is a higher energy state. The bonding geometries of the O atoms in trimeric (2,6-di-*tert*-butoxyphenyl)lithium are illustrated in Figure 2, which shows the COC···Li units viewed along the C···C vector. The small T-shape distortion of the oxygen coordination geometry, which cannot be seen from Figure 2, varies from 15.7 to 24.8°. This type of distortion is a consequence of the rigid structure of the anion. Apart from this T-shape distortion, the bonding geometries for O(11) and O(31) are nearly trigonal. The geometry around O(12) is distorted from trigonal, whereas the geometries of O(21), O(22), and O(32) are strongly distorted to pyramidal. These distortions are accompanied by small but significant changes in the Li–O bond distances. The Li–O(trigonal) bond distances are 1.984 (6) and 2.000 (5) Å (average 1.992 (6) Å) whereas the Li–O(pyramidal) bond distances are 2.043 (6), 2.074 (6), and 2.111 (5) Å (average 2.076 (6) Å). A comparison of bond lengths is normally complicated by the fact that these are based on X-ray structures of different compounds. In the present case, the different types of Li–O bonding are found in the structure of one molecule and in nearly identical structural units (the Li coordination geometry is broadly the same for all Li atoms). The differences in the bond distances of both types are therefore hardly affected by other factors. Accordingly, this structure can be used as an internal calibration of Li–O(trigonal) and Li–O(pyramidal) distances.

The difference in bond lengths between a Li–O(trigonal) and Li–O(pyramidal) bond has been evaluated by ab initio calculations.

Ab initio calculations have shown O–Li interactions to be primarily electrostatic:[3,4] a large electrostatic component (Coulomb and ion–dipole attraction) is involved and a small polarization component (ion-induced dipole) is expected, but negligible charge transfer from O to Li is observed. The essentially electrostatic interaction results theoretically in a planar minimum energy structure (C_{2v}) for RLi–OR$_2$ and Li$^+$–OR$_2$.[5] This is in contrast with

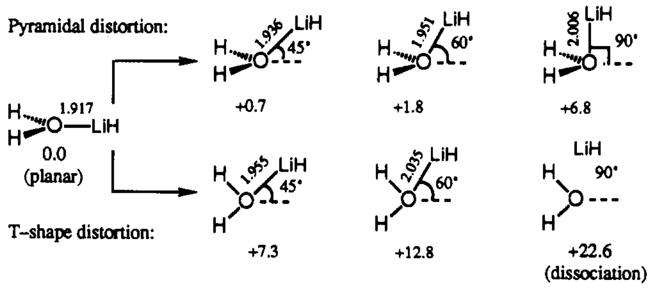

Figure 3. Calculated energies (in kcal/mol; RHF, SV 6-31G*) involved in pyramidal and T-shape distortion of the oxygen bonding geometry in a H$_2$O–LiH complex. The Li–O bond distances are given in Å.

theoretical evidence[6] for the nonplanarity of H$^+$–OH$_2$ (C_{3v}) in which bonding is expected to be less ionic. Ab initio calculations (RHF/SV 6-31G*) on the model system HLi···OH$_2$ are performed to study the geometry of Li··· ether interactions. The structure with minimal energy is characterized by the planar conformation (C_{2v}) 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 seldom 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-dihydroxyphenyl)lithium and lithium hydride has been chosen as a model to study the intramolecular R$_2$O···Li interaction observed in the crystal structure of (2,6-di-*tert*-butoxyphenyl)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[7] on the phenyllithium dimer for which the planar geometry is favored by 5.9 kcal/mol). Solvation of each Li by one H$_2$O molecule does not change the preference for the perpendicular conformation ($\Delta E(\mathbf{3} \rightarrow \mathbf{4}) = +7.1$ 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 5.0 kcal/mol. Enlargement of the rotation barrier in the

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Table IV. Calculated Distances (Å) and Angles (deg) for the Molecules Shown in Figure 4[a]

	formula									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
C1–C2	1.412	1.409	1.412	1.412	1.388	1.373	1.374	1.378	1.379	1.380
C2–C3	1.387	1.386	1.388	1.386	1.388	1.382	1.380	1.378	1.386	1.381
C3–C4	1.384	1.383	1.385	1.383	1.383	1.389	1.389	1.389	1.381	1.383
C–O					1.397	1.426	1.438	1.451	1.372	1.395
C–Li	2.141	2.122	2.186	2.204	2.129	2.141	2.134	2.133		
H–Li	1.813	1.806	1.845	1.837	1.810	1.865	1.861	1.834		
Li⋯Li	2.328	2.271	2.362	2.317	2.294	2.503	2.480	2.421		
O–Li			2.000	2.000	3.185	1.961	1.988	2.088		
C2–C1–C2′	115.0	114.5	114.5	113.6	115.4	115.5	115.4	115.2	119.9	120.0
C1–C2–C3	122.7	123.1	123.0	123.6	123.5	124.2	124.2	124.2	120.4	120.2
C2–C3–C4	119.9	119.9	120.0	120.1	118.4	117.5	117.7	117.9	119.2	119.5
C3–C4–C3′	119.7	119.4	119.3	119.0	120.7	121.1	120.8	120.6	121.0	120.5
C1–C2–O					115.7	112.1	113.2	115.7	116.9	119.7
C2–O–Li						92.5	90.8	87.6		
C2–O–H					112.6	115.5	113.4	110.0	113.0	111.9
Li–C1–Li′	65.9	64.7	65.4	63.4	65.2	71.3	71.2	69.5		
Li–H–Li′	79.9	77.9	79.6	78.2	78.6	84.0	83.7	83.1		
C1–Li–OH_2			119.6	131.2						
energy (SV 3-21G)	−244.21332	−244.20408	−395.48296	−395.47165	−393.11771	−393.15933	−393.15626	−393.14003	−378.30145	−378.29353

[a] The numbering is shown in formula 1 of Figure 4.

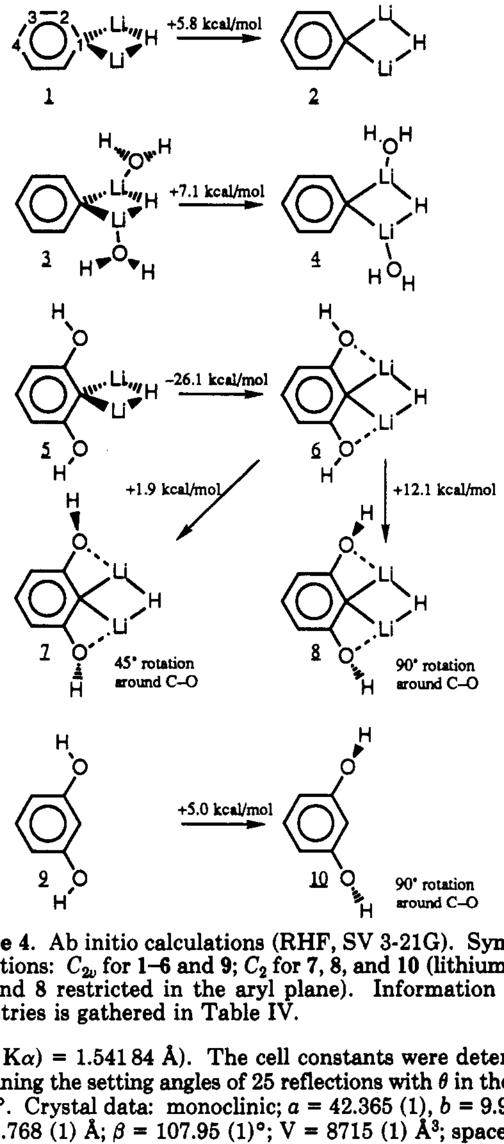

Figure 4. Ab initio calculations (RHF, SV 3-21G). Symmetry restrictions: C_{2v} for **1**–**6** and **9**; C_2 for **7**, **8**, and **10** (lithium atoms in **7** and **8** restricted in the aryl plane). Information on the geometries is gathered in Table IV.

lithiated species must be mainly due to a less favorable Li⋯OH 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 (0°) → 1.988 Å (45°) → 2.088 Å (90°).

Since 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 $Li^+–O^{\delta-}$ bond tends to lie in the $R^{\delta+}–O^{\delta-}–R^{\delta+}$ plane along the sp^2 lone pair in order to minimize repulsive $Li^+\cdots R^{\delta+}$ 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-d_6): δ = 1.30 (s, 18 H, *t*-BuO), 6.82 (d, J = 7.5 Hz, 2 H, H_{ar}), 7.13 (t, J = 7.5 Hz, 1 H, H_{ar}). $^{13}C\{^1H\}$ NMR (−35 °C, toluene-d_8): δ = 29.0, 77.3 (*t*-BuO–), 156.3 (q, $^1J(^{13}C, ^6Li)$ = 6.7 Hz), 113.3, 128.4, 164.5 (aromatic signals).

1,3-Di-*tert*-butoxybenzene was prepared by reaction of the di-Grignard derivative of 1,3-dibromobenzene and *tert*-butoxyperbenzoate analogous to the method described in ref 8. Yield: 40%. ^1H NMR (benzene-d_6): δ = 1.21 (s, 18 H, *t*-BuO), 6.74 (dd, J = 8.2 and 2.0 Hz, 2 H, H_{ar}), 6.83 (t, J = 2.0 Hz, 1 H, H_{ar}), 7.01 (dd, J = 8.0 and 8.4 Hz, 2 H, H_{ar}). $^{13}C\{^1H\}$ NMR (benzene-d_6): 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 mm^3 was sealed under nitrogen in a Lindemann glass capillary and mounted on an Enraf-Nonius CAD4 diffractometer (λ(Cu Kα) = 1.54184 Å). The cell constants were determined by refining the setting angles of 25 reflections with θ in the range 19–25°. Crystal data: monoclinic; a = 42.365 (1), b = 9.934 (1), c = 21.768 (1) Å; β = 107.95 (1)°; V = 8715 (1) $Å^3$; space group $C2/c$; $(C_{14}H_{21}O_2Li)_3$; Z = 8; D(calcd) = 1.044 g/cm^3. A total of 8239 unique reflections were collected at T = 20 °C within the Cu sphere of θ to 70° ($-51 \leq h \leq 51$, $0 \leq k \leq 12$, $0 \leq l \leq 26$) of which 4058 reflections with $I \geq 2.5\sigma$ were considered to be observed. Standard reflections (221, 820, and $\bar{8}0\bar{2}$) were measured

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every 50 reflections. Correction for Lorentz–polarization effects and linear decay were applied.

On the basis of regular extinctions, the space group was determined as $C2/c$. The structure was determined by direct methods (SHELXS-86). Full-matrix least-squares refinement with SHELX-76 (non-hydrogen atoms with anisotropic temperature factors; hydrogen atoms on calculated positions and refined with a riding model; correction for extinction with the SHELX-76 method) converged to $R(F) = 0.054$ and $R(wF) = 0.059$ with $w = 1/\sigma^2(F)$ and 470 refined parameters. Neutral-atom scattering factors[9] were used for all atoms. Anomalous dispersion factors were taken from Cromer and Liberman.[10] Calculations were performed on a MicroVax-II computer using the programs SHELXS-86,[11] SHELX-76,[12] and the EUCLID package[13] (geometric calculations and graphics).

Ab Initio Calculations. Ab initio calculations were performed on a Cyber 205 and a Convex C120 computer using the program GAMESS.[14] Geometries were located by spin-restricted Hartree–Fock (RHF) optimization with use of the SV 3-21G or SV 6-31G* basis set. The H_2O molecules in 3 and 4 (Figure 4) were placed at a distance of 2.0 Å from Li, and their geometries were fixed at the minimum energy structure for H_2O in an SV 3-21G basis: O–H = 0.967 Å and H–O–H = 107.7°. Average and maximum gradients of 0.0005 and 0.000 75, respectively, were taken as the convergence criteria.

Acknowledgment. Part of the ab initio calculations were performed on a Cyber 205 computer of SARA (Amsterdam). We thank the Dutch Supercomputing Working Group (WGS) for an allowance of computer time.

Supplementary Material Available: Tables of bond distances and angles, torsion angles, anisotropic thermal parameters, and hydrogen positional and thermal parameters (8 pages); a table of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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Carbon Monoxide Induced Allyl Coupling from $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ Yielding the Labile Complex $Mo(CO)_4(\eta^4\text{-1,5-hexadiene})$

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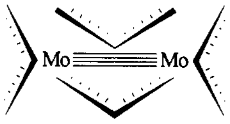
Summary: Carbon monoxide induces the reductive elimination of two pairs of allylic ligands from $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ with the accompanying cleavage of the Mo–Mo quadruple bond. $Mo(\eta^4\text{-1,5-hexadiene})(CO)_4$ is obtained from the reaction of 8 equiv of CO with $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$. Structural data for and the reactivity of $Mo(\eta^4\text{-1,5-hexadiene})(CO)_4$ suggest that 1,5-hexadiene is bound very weakly to molybdenum.

Since its discovery,[1] tetraallyldimolybdenum, $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$, has been utilized as a precursor to heterogeneous catalysts.[2,3] 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 π-allyls are bridging the Mo–Mo quadruple bond with each π-allyl in the remaining pair binding to a single molybdenum atom.[4] Exchange of allyls between bridging and terminal positions is not observed even at 80 °C.[5]



$Mo_2(endo\text{-}\mu_2\text{-}\eta^3\text{-allyl})(exo\text{-}\mu_2\text{-}\eta^3\text{-allyl})(endo\text{-}\eta^3\text{-allyl})_2$

A goal of our research is to investigate the reactivity pathways of this molybdenum dimer and related multiply bonded metal dimers bridged by η^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 tetraalylldimolybdenum with carbon monoxide.

Results and Discussion

Reaction of $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ with Carbon Monoxide. $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ reacts completely with an excess of carbon monoxide within 10–15 min at ambient temperature to form $Mo(CO)_6$ and 1,5-hexadiene:

$$Mo_2(\mu_2\text{-}\eta^3\text{-}C_3H_5)_2(\eta^3\text{-}C_3H_5)_2 + 12CO \rightarrow 2C_6H_{10} + 2Mo(CO)_6 \quad (1)$$

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 π-acceptor ligands such as CO, NO, and CNR has been widely reported. Such reac-

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