Synthesis and X-ray Crystal Structure Determination of Tetrahydrofuran Adducts of Two Terphenyllithium Compounds†

Gerd W. Rabe,*,‡ Roger D. Sommer,§ and Arnold L. Rheingold§

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstrasse 4, 85747 Garching, Germany, and Department of Chemistry, University of Delaware, Newark, Delaware 19716

Received August 8, 2000

*Summary: The molecular structures of two terphenyllithium derivatives, namely dimeric [DppLi]$_2$(THF) (**1**) and monomeric DnpLi(THF)$_2$ (**2**) (Dpp = 2,6-diphenylphenyl; Dnp = 2,6-di(1-naphthyl)phenyl) are reported, which feature differently aggregated structures in the solid state. The main features of both molecular structures are the different coordination environments for the two lithium atoms in dimeric **1** and a trigonal-planar coordination geometry around the three-coordinate lithium atom in monomeric **2**.*

Introduction

Sterically demanding terphenyl substituents are useful for stabilizing main-group,[1] transition-metal,[1] and lanthanide complexes.[2,3] Structural determinations of complexes with terphenyl ligands revealed that such ligands are capable of stabilizing a variety of complexes in unusual coordination geometries and bonding situations which are not readily accessible with less bulky ligands.[1] Lithium derivatives are typically employed as transfer reagents. A number of solid-state structures of hydrocarbon-soluble, unsolvated terphenyllithium compounds as well as of their Lewis base adducts were reported earlier.[4,5] However, there are only few reported structure determinations of aryllithium solvates of monodentate ethers.[5] We report here the synthesis and X-ray crystal structure determination of two low-coordinate THF adducts of terphenyllithium compounds, namely [DppLi]$_2$(THF) (**1**) and DnpLi(THF)$_2$ (**2**). These exhibit different arrangements in their solid-state structures as well as an unprecedented structural motif in aryllithium chemistry in the case of complex **1**.

Experimental Section

The compounds described below were handled under nitrogen using Schlenk double-manifold, high-vacuum, and glovebox (M. Braun, Labmaster 130) techniques. Solvents were dried, and physical measurements were obtained following typical laboratory procedures. DppI and DnpI were prepared by following the general synthetic route for the preparation of terphenyl iodides reported by Hart et al.[6,7] We failed to obtain reasonable combustion analysis data (C, H) for the obtained terphenyllithium derivatives DppLi and DnpLi. This observation can most likely be attributed to the fact that both DppLi and DnpLi are contaminated with small amounts of lithium iodide. Iodine analyses of the obtained hexane- and toluene-washed DppLi and DnpLi, respectively, demonstrated that both lithium compounds contain iodine-containing byproducts as impurities (approximately 6−7% iodine content in the case of **1** and 4−5% in the case of **2**). This observation indicates that presumably a competing coupling reaction producing lithium iodide plus *n*-Bu-Dpp and *n*-Bu-Dnp, respectively, is mainly but not completely suppressed in the cases of DppLi and DnpLi by their insolubility in hydrocarbons. Thus, they are removed from the equilibrium by precipitation. On the other hand, we had no problems obtaining reasonable combustion analysis data from single-crystal material of both THF adducts **1** and **2**. NMR spectra were recorded on a JMN-GX 400 instrument. The ^{13}C NMR spectra, recorded in THF-d_8, were referenced to the two solvent signals (67.4 and 25.2 ppm, respectively).

[DppLi]$_2$(THF) (1). To a colorless suspension of DppI (3.0 g, 8.4 mmol) in 100 mL of hexanes was added 5.3 mL of a 1.6 M solution of *n*-BuLi (8.5 mmol) in hexanes slowly via syringe. After the mixture was stirred overnight, filtration of the resulting white suspension, followed by washing with hexanes and toluene and drying under vacuum, gave DppLi as a fine white powder (1.6 g, 80%). DppLi is insoluble in hexanes and aromatic solvents but easily soluble in THF. Yellow solutions of DppLi in THF were found to decompose slowly at room temperature (forming brownish solutions within a few hours) but remained unchanged over long time periods at −30 °C. [DppLi]$_2$(THF) (**1**) crystallizes almost quantitatively from freshly prepared centrifuged solutions of DppLi in toluene/THF (100:1) at −30 °C, forming colorless crystals. **1** does not lose coordinated THF upon drying under vacuum (0.01 mbar at room temperature). **1** is insoluble in hexanes and only sparingly soluble in arene solvents but is readily soluble in THF. Anal. Calcd for $C_{40}H_{34}Li_2O$: C, 88.24; H, 6.29. Found: C, 88.02; H, 6.04. ^{13}C NMR (C_4D_8O, 100.4 MHz, 25 °C): δ 195.6 (*ipso*-C), 153.6, 152.8, 128.3, 128.1, 124.7, 123.5, 122.4. Mp: >110 °C dec.

DnpLi(THF)$_2$ (2). To a colorless suspension of finely powdered DnpI (2.0 g, 4.4 mmol) in 100 mL of hexanes was added 2.8 mL of a 1.6 M solution of *n*-BuLi (4.4 mmol) in hexanes slowly via syringe. After the mixture was stirred for 2 days, filtration of the obtained colorless suspension followed by washing with hexanes and toluene and drying under

† Dedicated to Prof. Dr. Dr. h. c. mult. Herbert W. Roesky on the occasion of his 65th birthday.

‡ Technische Universität München.

§ University of Delaware.

(1) Twamley, B.; Haubrich, S. T.; Power, P. P. *Adv. Organomet. Chem.* **1999**, *44*, 1 and references therein.

(2) Rabe, G. W.; Strissel, C. S.; Liable-Sands, L. M.; Concolino, T. E.; Rheingold, A. L. *Inorg. Chem.* **1999**, *38*, 3446.

(3) Heckmann, G.; Niemeyer, M. *J. Am. Chem. Soc.* **2000**, *122*, 4227.

(4) Ruhlandt-Senge, K.; Ellison, J.; Wehmschulte, R. J.; Pauer, F.; Power, P. P. *J. Am. Chem. Soc.* **1993**, *115*, 11353.

(5) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 2847 and references therein.

(6) Du, C.-J. F.; Hart, H.; Ng, K.-K. D. *J. Org. Chem.* **1986**, *51*, 3162.

(7) Saednya, A.; Hart, H. *Synthesis* **1996**, 1455.

10.1021/om0006864 CCC: $19.00
Publication on Web 11/11/2000

Table 1. Crystallographic Data for [DppLi]$_2$(THF) (1) and DnpLi(THF)$_2$ (2)[a]

	1	2
formula	$C_{40}H_{34}Li_2O$	$C_{34}H_{33}LiO_2$
fw	544.45	480.54
space group	*C*2/*c*	$P2_1/c$
a, Å	12.3391(10)	7.7747(7)
b, Å	15.5925(13)	20.330(2)
c, Å	16.5319(14)	16.8532(17)
β, deg	101.176(2)	97.085(2)
V, Å^3	3120.4(4)	2643.5(4)
Z	4	4
D_{calcd}, g cm^{-3}	1.159	1.207
temp, °C	−100(2)	−100(2)
radiation	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
μ(Mo Kα), cm^{-1}	6.6	7.2
R1, %	5.52	9.53
wR2, %	13.24	21.14

[a] The quantity minimized was as follows: wR2 = $\sum[w(F_o^2 - F_c^2)^2/\sum(wF_o^2)^2]^{1/2}$; R1 = $\sum\Delta/\sum(F_o)$, $\Delta = |(F_o - F_c)|$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + \mathrm{Max}(F_o,0)]/3$.

vacuum gave DnpLi as a fine white powder (1.2 g, 80%). DnpLi is insoluble in hexanes and aromatic solvents but is readily soluble in THF. Yellow solutions of DppLi in THF were found to decompose rapidly at room temperature (forming brownish solutions) but remained unchanged over long time periods at −30 °C. DnpLi(THF)$_2$ (**2**) crystallizes almost quantitatively from freshly prepared and instantly cooled centrifuged solutions of DnpLi in toluene/THF (100:1) at −30 °C, forming yellow crystals. **2** does not lose coordinated THF upon drying under vacuum (0.01 mbar at room temperature). **2** is insoluble in hexanes and only sparingly soluble in arene solvents but is readily soluble in THF. Anal. Calcd for $C_{34}H_{33}LiO_2$: C, 84.98; H, 6.92. Found: C, 84.79; H, 6.70. ^{13}C NMR (C_4D_8O, 100.4 MHz, −30 °C): δ 201 (br, *ipso*-C), 151.9, 151.7, 151.6, 151.2, 135.2, 135.1, 133.7, 128.5, 127.0, 126.2, 125.3, 123.4, 122.0. Mp: >90 °C dec.

General Aspects of X-ray Data Collection, Structure Determination, and Refinement for Complexes 1 and 2. Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals for single-crystal X-ray diffraction were selected and mounted in nitrogen-flushed, thin-walled glass capillaries. The data were collected on a Siemens P4 diffractometer equipped with a SMART CCD detector.

The systematic absences in the diffraction data of **1** and **2** are uniquely consistent for the reported space group for **2** and for the *C*-centered monoclinic space groups *Cc* and *C*2/*c* for **1**. *E*-statistics suggested the centrosymmetric option. A solution by direct methods presented the framework of the molecules. The non-hydrogen framework of the structure was completed by subsequent difference Fourier syntheses and refined by full-matrix, least-squares procedures. Hydrogen atoms were placed at calculated positions and treated as idealized contributions with thermal parameters of 1.2 or 1.5 times that of the parent ion.

The *R* factor of **2** is relatively high. The diffraction pattern from the sample was diffuse, due to the small size and low quality of the crystal. Data above 50° (2θ) was omitted to remove weak reflections and inconsistent equivalents in the high-angle data. The lack of disorder and the well-behaved thermal ellipsoids both suggest a well-behaved structure of only modest resolution.

All software sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. M. Sheldrick, Siemens XRD, Madison, WI).

Results and Discussion

[DppLi]$_2$(THF) (1). DppI reacts with an equimolar amount of *n*-BuLi in hexanes at room temperature to give colorless DppLi in good yield. In contrast to hexane-soluble DmpLi,[4] DppLi is found to be insoluble in aliphatic and aromatic hydrocarbons, but it is soluble in THF. Colorless crystals of **1** suitable for an X-ray diffraction study were obtained from a toluene/THF (100:1) solution of DppLi at −30 °C.

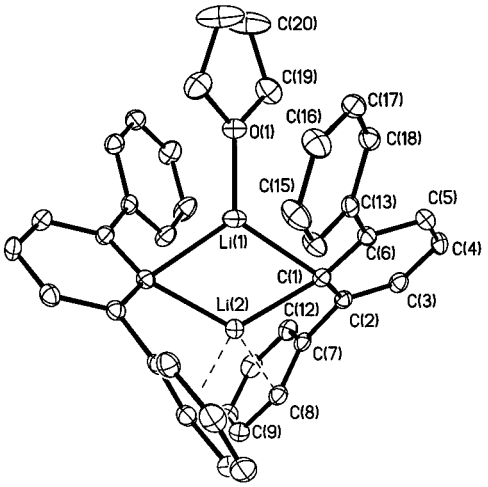

Figure 1. ORTEP diagram of [DppLi]$_2$(THF) (**1**), showing the atom-labeling scheme. Thermal ellipsoids are shown at 30% probability, and the hydrogen atoms are omitted for clarity. Selected interatomic separations (Å) and angles (deg): Li(1)−C(1) = 2.225(4), Li(1)···C(6) = 2.755(3), Li(1)−O(1) = 1.857(6), Li(1)···Li(2) = 2.284(8), Li(2)−C(1) = 2.124(4), Li(2)···C(8) = 2.431(4), Li(2)···H(8) = 2.19(2), Li(2)···C(7) = 2.752(2); O(1)−Li(1)−C(1) = 123.81(13), Li(1)−C(1)−Li(2) = 63.31(19), C(1)−Li(1)−C(1A) = 112.4(3), C(1)−Li(2)−C(1A) = 121.0(3), C(1)−C(2)−C(7) = 117.5(2), C(1)−C(6)−C(13) = 119.0(2).

The molecular structure of complex **1** (Figure 1) shows a rather peculiar asymmetric dimeric arrangement of two DppLi moieties, which differs from the dimeric arrangement found in the solid-state structure of unsolvated [DmpLi]$_2$[4] (crystals of which were obtained from hexane in the absence of THF) and also from the solid-state structures of previously reported dimeric [MesLi(THF)$_2$]$_2$[8] and [TripLi(Et$_2$O)]$_2$ (Trip = 2,4,6-triisopropylphenyl).[9] The observed asymmetric structural motif in **1** has, to our knowledge, not been observed before for any other aryllithium species. It is, however, somewhat reminiscent of the asymmetric lithium thiolate dimer [DmpSLi]$_2$(Et$_2$O)$_2$, in which only one of the lithium cations is solvated by ethers, the other being "solvated" by mesityl rings.[10] In the molecular structure of complex **1**, coordination of only one THF molecule to one of the two lithium cations, namely Li(1), is found. In contrast, Li(2) appears to be formally two-coordinate. However, closer examination of the molecular structure of **1** reveals the presence of an additional π interaction through the *ortho* carbon atoms of two neighboring phenyl groups of different Dpp ligands (C(8) and C(8a), respectively) with Li(2) (Li(2)···C(8) = 2.431(4) Å). These interatomic separations are, as one would expect, considerably longer than the Li(2)−C(1) distance (2.124(4) Å) and also the Li(1)−C(1) distance (2.225(4) Å). The

(8) Beno, M. A.; Hope, H.; Olmstead, M. M.; Power, P. P. *Organometallics* **1985**, *4*, 2117.
(9) Bartlett, R. A.; Dias, H. V. R.; Power, P. P. *J. Organomet. Chem.* **1988**, *341*, 1.
(10) Ellison, J. J.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 4231.

proton attached to C(8) was located from a difference map with a Li(2)···H distance of 2.19(2) Å. In addition, the C(1)−C(2)−C(7) angle (117.5(2)°) deviates considerably from the ideal 120°, while the C(1)−C(6)−C(13) angle is 119.0(2)°. There is no π interaction between Li(1) and the phenyl groups in the 2,6-positions. In addition to the Li(1)−C(1) distance (2.225(4) Å), Li(1) has a secondary contact only with the *ortho* carbon atom C(6) (2.755(3) Å), while Li(2) interacts weakly with the *ipso* carbon atom C(7) (2.752(2) Å). Therefore, the asymmetric structure of **1** differs from that of the molecular structure of dimeric $[DmpLi]_2$[4] in that the lithium atoms in the latter interact with the *ipso* carbon atoms of the phenyl groups and display, in addition, significantly weaker interactions with the mesityl *ipso* carbon atoms, but not with any of the *ortho* carbon atoms. As one would expect, the Li(1)−O(1) distance (1.857(6) Å) in **1** is significantly shorter than the Li−O distances in four-coordinate $[MesLi(THF)_2]_2$ (2.036(3) and 2.044(3) Å, respectively),[8] while the two Li−C distances in the latter (2.271(3) and 2.279(3) Å, respectively) are found to be only slightly longer than the Li(1)−C(1) distance (2.225(4) Å) in **1**. Further comparisons of the Li(1)−O(1) as well as the Li(1)−C(1) distance in **1** can be made, for example, with the three-coordinate lithium atoms in dimeric $[TripLi(Et_2O)]_2$ (Li−C = 2.249(3) and 2.203(3) Å, respectively; Li−O = 1.930(3) Å)[9] and in monomeric $DppLi(Et_2O)_2$ (Li−C = 2.106(9); Li−O = 1.943(5) Å).[11] The torsion angle relating the two central, lithiated aromatic rings in **1** is 80.3°. More details on interatomic separations and angles of complex **1** can be derived from the figure caption of Figure 1.

$DnpLi(THF)_2$ (2). DnpI reacts with an equimolar amount of *n*-BuLi in hexanes at room temperature to give colorless DnpLi in good yield. DnpLi is, similar to DppLi, insoluble in aliphatic and aromatic hydrocarbons but soluble in THF. Yellow crystals of **2** suitable for an X-ray diffraction study were obtained from a toluene/THF (100:1) solution of DnpLi at −30 °C.

The molecular structure of complex **2** (Figure 2) features a monomeric terphenyllithium moiety with a formally three-coordinate lithium atom. The Li(1)−C(1) distance of 2.085(8) Å in **2** is slightly shorter than the Li(2)−C(1) distance (2.124(4) Å) and significantly shorter than the Li(1)−C(1) distance (2.225(4) Å) in complex **1**, while the Li(1)−O(1) distance (1.887(8) Å) and the Li(1)−O(2) distance (1.908(7) Å) in **2** are, within the error limits of the determinations, in good agreement with the value observed for the Li(1)−O(1) distance (1.857(6) Å) in **1**. The Li−C as well as the Li−O distances in **2** can furthermore be favorably compared with the corresponding distances found in monomeric $DppLi(Et_2O)_2$[11] and $(2,4,6\text{-}Ph_3C_6H_2)Li(Et_2O)_2$.[12,13] The coordination environment of the lithium atom in **2** is trigonal planar (sum of angles around the lithium atom 359.9°). As can be seen from Figures 2 and 3, the two naphthyl substituents are arranged in a way that two of the carbon atoms, namely atoms C(15) and C(25), point toward the lithium cation with Li···C distances

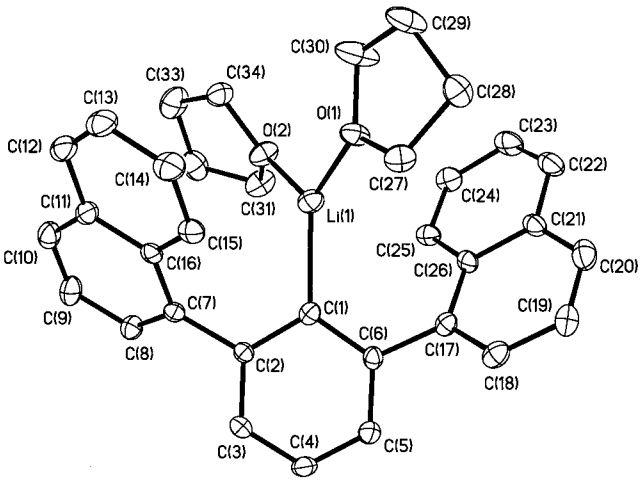

Figure 2. ORTEP diagram of $DnpLi(THF)_2$ (**2**), showing the atom-labeling scheme. Thermal ellipsoids are shown at 30% probability, and hydrogen atoms are omitted for clarity. Selected interatomic separations (Å) and angles (deg): Li(1)−O(1) = 1.887(8), Li(1)−O(2) = 1.908(7), Li(1)−C(1) = 2.085(8), Li···C(15) = 2.828(8), Li···H(15) = 2.66(2), Li···C(25) = 2.809(8), Li···H(25) = 2.58(2); O(1)−Li(1)−O(2) = 112.4(4), O(1)−Li(1)−C(1) = 125.9(4), O(2)−Li(1)−C(1) = 121.6(4), C(1)−C(2)−C(7) = 119.5(3), C(1)−C(6)−C(17) = 119.2(4).

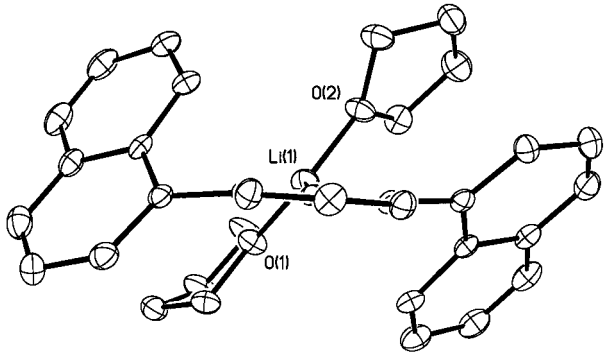

Figure 3. Molecular structure of complex **2** viewed along the C(4)···C(1)···Li(1) vector.

of 2.828(8) Å (C(15)) and 2.809(8) Å (C(25)). The protons attached to these two carbon atoms were located from a difference map (Li(1)···H(15) = 2.66(2) Å, Li(1)···H(25) = 2.58(2) Å). The dihedral angles between the central phenyl ring and the mean plane of the two 1-naphthyl substituents are +46.9 and −50.9°, and the dihedral angle between the central phenyl ring and the O(1)−Li(1)−O(2) triangle is 54.7°. Further details on interatomic separations and angles of complex **2** can be derived from the figure caption of Figure 2.

NMR Spectroscopic Investigations. Solution NMR spectroscopic investigations of **1** and **2** as well as comparisons with other terphenyllithium species, e.g., hexane-soluble, dimeric $[DmpLi]_2$, were hampered by the fact that both **1** and **2** are only sparingly soluble in arene solvents. Another problem was the limited stability of THF solutions of both **1** and **2** at room temperature, with the latter being even less stable in THF at room temperature than solutions of **1** in the same solvent. A ^{13}C NMR study of both **1** and **2** in THF-d_8 was undertaken. A good-quality ^{13}C NMR spectrum of a saturated solution of **1** at ambient temperature could be obtained (no decomposition of a freshly prepared

(11) Crittendon, R. C.; Beck, B. C.; Su, J. S.; Li, X.-W.; Robinson, G. H. *Organometallics* **1999**, *18*, 156.
(12) Girolami, G. S.; Riehl, M. E.; Suslick, K. S.; Wilson, S. R. *Organometallics* **1992**, *11*, 3907.
(13) Olmstead, M. M.; Power, P. P. *J. Organomet. Chem.* **1991**, *408*, 1.

THF-d_8 solution over a 30−60 min period). However, a ^{13}C NMR spectrum of **2** in the same solvent at room temperature could not be obtained because of rapid decomposition of the sample. Therefore, a low-temperature study (−30 °C) of a precooled THF-d_8 solution was undertaken in the case of **2**.

A strong low-field shift for the *ipso* carbon atom signal (a narrow signal at 195.6 ppm) was observed in the ^{13}C NMR spectrum of a THF-d_8 solution of **1**, while the low-temperature ^{13}C NMR spectrum of **2** showed a broad and poorly resolved signal at 201 ppm for the *ipso* carbon atom. It was previously shown[5] that ^{13}C chemical shifts of *ipso* carbon atoms of both monomeric and dimeric solvated lithium aryls are in the range 180−200 ppm. We note that the solution structures of **1** and **2** are not clear. However, our ^{13}C solution NMR spectroscopic investigations indicate that the asymmetric arrangement found in the solid-state structure of complex **1**, exhibiting different coordination modes for the two lithium atoms, is not retained in THF solution.

Conclusion

Our results provide more insight into the solid-state structures of two differently aggregated terphenyllithium complexes and demonstrate that the arrangement found in the solid-state structure of THF adducts of terphenyllithium compounds is mostly determined by the nature of the sterically demanding terphenyl ligand. Lower aggregation numbers can be induced by increased crowding at the aryl group, resulting in formation of monomeric aryllithium species: e.g., complex **2**. Our work also allows a detailed comparison of the structural data of **1** and **2** with previously reported solvated and unsolvated terphenyllithium salts.

Acknowledgment. We are grateful for financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Leonhard−Lorenz Foundation. Generous support from Professor H. Schmidbaur is gratefully acknowledged. The University of Delaware acknowledges the National Science Foundation for their support of the purchase of the CCD-based diffractometer (Grant No. CHE-9628768).

Supporting Information Available: X-ray crystallographic files in CIF format for the structures of $[DppLi]_2(THF)$ (**1**) and $DnpLi(THF)_2$ (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

OM0006864

Additions and Corrections

2000, Volume 19

Sung-Joon Kim, Namkeun Yang, Dae-Hyun Kim, Sang Ook Kang, and Jaejung Ko*: New Types of Base-Stabilized Alkyl Aluminum, Gallium, and Indium Complexes.

Page 4042. The Acknowledgment should read as follows: "The authors wish to acknowledge the financial support of the Korea Research Foundation made in the program year of 1998 (1998-001-D00439)."

OM000869Q

10.1021/om000869q
Published on Web 11/10/2000