Lithium Lithiates

DOI: 10.1002/anie.201406320

Characterization of a Multicomponent Lithium Lithiate from a Combined X-Ray Diffraction, NMR Spectroscopy, and Computational Approach**

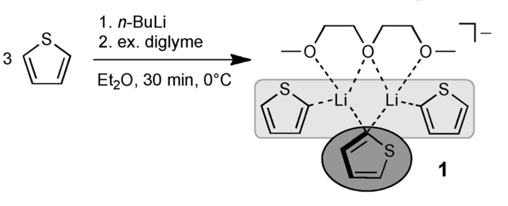
*Ann-Christin Pöppler, Markus Granitzka, Regine Herbst-Irmer, Yu-Sheng Chen, Bo B. Iversen, Michael John, Ricardo A. Mata, and Dietmar Stalke**

Abstract: *An unusual lithium lithiate [Li(diglyme)$_2$]-[(diglyme)Li$_2$(C$_4$H$_3$S)$_3$], made up from three carbanions, two lithium cations, and a single donor base molecule in the anion and a single lithium cation, coordinated by two donor base molecules, is investigated in a combined study including X-ray diffraction, NMR spectroscopy and computational approaches in solution and the solid state. While the multicomponent lithiate is the only species present in the solid state, solution NMR spectroscopy and computational methods were employed to identify a second species in solution. The dimer [(diglyme)Li(C$_4$H$_3$S)]$_2$ coexists with the lithiate in solution in a 1:1 ratio, the more the higher the polarity of the solvent is. Only the combination of this multitude of methods provides a firm picture of the whole.*

Addressing structure–reactivity relations is an important area of organolithium research. In solid state and solution, these compounds exist as diverse aggregates and coordination motifs based on the complex interplay of solvation effects, Lewis–basic additives, and the carbanion itself.[1] While in nonpolar media larger aggregates and contact ion pairs (CIP) dominate, they are progressively converted to smaller arrangements and solvent separated ion pairs (SSIP) when solvents with higher dielectric constants are employed. The presence of such charged species was already proposed in 1933 on the basis of conductivity measurements[2] and confirmed for phenyllithium by Wittig et al. in the early 1950s.[3] Lithium lithiates [Li(donor)$_n$]$^+$[LiR$_2$]$^-$ containing an anionic triple ion are rare in organolithium chemistry. However, it is known that steric bulk[4] and polydentate ligands,[5] especially crown ethers[6] and hexamethylphosphoramide,[7] promote their formation. Triple ions may be formed with localized sp^2- and sp^3-centered carbanions, yet also delocalized lithium π-complexes such as cyclopentadienyl lithiums or carbamides could be characterized.[8]

The most frequently used methods for structure elucidation of organolithium species have been single-crystal structure analysis and high-resolution as well as solid-state NMR spectroscopy.[9] In many mechanistic studies the reactivity or selectivity was found to strongly depend on the aggregates,[10] which in the case of lithiumamides and organolithiums are assumed to be mainly monomers, dimers, open dimers, and SSIPs.[11] This underlines the importance of accurate structure elucidation to adequately tune reaction conditions and thereby also reaction pathways. In the course of our studies on lithiated thiophenes[12] we were able to synthesize an unprecedented carbon-centered lithium lithiate that further broadens the territory of known organolithium species. The structure and aggregation were characterized by means of X-ray diffraction and NMR spectroscopy combined with electronic structure calculations.

The reaction of thiophene with *n*BuLi in Et$_2$O followed by addition of an excess of diglyme and subsequent storage at −19 °C reproducibly yields very temperature sensitive crystals that easily decompose upon removal from the solvent. The crystalline material could be characterized as [Li(diglyme)$_2$]-



(1)

Scheme 1. Reaction of thiophene and *n*BuLi in the presence of an excess of diglyme reproducibly yields crystals containing the solvent separated ion pair **1**. Dark gray indicates an arrangement resembling dimeric structures, while light gray represents a monomeric motif.

---

[*] Dr. A.-C. Pöppler, Dr. M. Granitzka, Dr. R. Herbst-Irmer, Dr. M. John, Prof. Dr. D. Stalke
Institut für Anorganische Chemie der Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)
E-mail: dstalke@chemie.uni-goettingen.de

Dr. R. A. Mata
Institut für Physikalische Chemie der Universität Göttingen
Tammannstrasse 6, 37077 Göttingen (Germany)

Dr. Y.-S. Chen
University of Chicago
9700 S. Cass Avenue, Argonne, IL 60539 (USA)

Prof. Dr. B. B. Iversen
Center for Materials Crystallography, Department of Chemistry and iNano, Aarhus University
Langelandsgade 140, DK-8000 Aarhus C (Denmark)

[**] We are grateful to the DNRF funded Centre of Materials Crystallography (DNRF93). ChemMatCARS Sector 15 is principally supported by the National Science Foundation/Department of Energy under Grand NSF/CHE-1346572. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science and the Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. We appreciate chemical donations from Rockwood Lithium.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201406320.

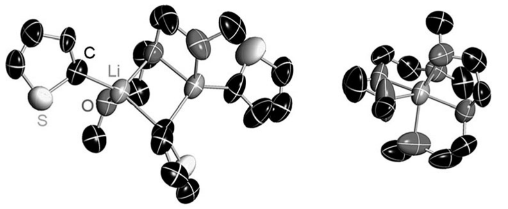


Figure 1. Molecular structure of $[Li(diglyme)_2][(diglyme)Li_2(C_4H_3S)_3]$ (**1**).[29] Ellipsoids are set at 50% probability; only the major domain is depicted, and hydrogen atoms are omitted for clarity.

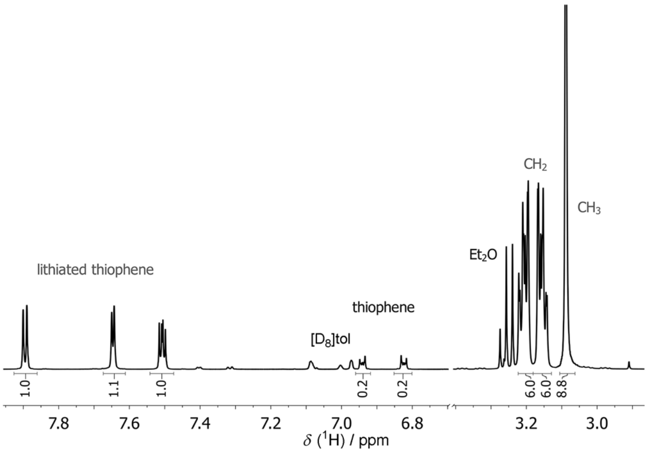


Figure 2. ^1H NMR spectrum of **1** in $[D_8]$toluene at 25 °C. The corresponding integrals as well as existing impurities and solvents are marked. Owing to fast exchange at room temperature, only one set of signals is observed for the diglyme molecules.

$[(diglyme)Li_2(C_4H_3S)_3]$ **1** (Scheme 1, Eq. (1)), which crystallizes in the orthorhombic space group *Pbca*, containing one complete SSIP in the asymmetric unit (Figure 1). Although the detailed discussion of bond lengths and angles is impeded by a high amount of disorder in the crystal (see also the Supporting Information), the structural motif can unambiguously be derived: the complex anion is composed of five charged moieties, namely two lithium cations and three carbanions. One μ-bridging thienyl moiety (dark gray) is coordinated to both lithium cations resembling the arrangement in dimeric R_2Li_2 aggregates, whereas the environment of the other two residues (light gray) resembles a monomeric motif with only one $Li{-}C_\alpha$ contact. The coordination sphere is completed by μ-coordination of diglyme. The counter ion $[Li(diglyme)_2]^+$ is a prominent cation present in many other solid-state structures.[13]

To the best of our knowledge, this multicomponent lithium lithiate is unprecedented in homometallic organolithium chemistry, although the assembly of five (two positively and three negatively) charged moieties is frequently found in heterobimetallic "ate" complexes (particularly in magnesiate and zincate compounds).[14] In this case, the charges add to zero, yielding predominantly neutral complexes both in the solid state and in solution.

To enable a thorough analysis of the behavior in solution, selected crystals of **1** from the mother liquor were directly transferred into NMR tubes, dissolved in $[D_8]$toluene, and sealed. Drying of the crystals as well as handling at ambient temperature for more than a few minutes led to decomposition, while the solution stayed stable for several days. The prepared sample was subjected to various ^1H, ^7Li, and ^{13}C NMR experiments both at room temperature and below. In accord to the assumption of a fast equilibrium exchange of the digylme molecules in the anion and the cation, only one set of signals can be observed in all spectra obtained at room temperature.

In the ^1H NMR spectrum, 2-thienyllithium can straightforwardly be identified alongside an excess of diglyme, thiophene, and Et_2O from the mother liquor (Figure 2). The ^{13}C chemical shift of the quaternary carbon atom directly attached to the lithium was already used as an indicator for the degree of aggregation in 2-thienyllithium derivatives before.[12] With a value of 172.5 ppm (for full spectrum, see the Supporting Information), it is in the range of dimeric structures previously observed in the presence of the Lewis bases dimethoxyethane (DME) or *N*,*N*,*N*′,*N*′-tetramethylethylene-1,2-diamine (TMEDA). By means of COSY as well as HSQC and HMBC experiments (see Supporting Information), a complete peak assignment was accomplished at room temperature.

To distinguish between the different lithium sites in a possible SSIP, low-temperature NMR experiments at 0, −25, −50, and −80 °C were conducted. Over this whole temperature range, only one broadening set of signals could be observed in the ^1H NMR spectrum. In contrast, a splitting of the initial ^7Li singlet into at least three distinct signals with significantly dissimilar line widths is observed at −80 °C (Figure 3). As a result of the SSIP structure, two distinct lithium environments are justifiable, just as the observation of broad lines for the complex anion owing to its lower symmetry.[4b] Therefore, the presence of three or more signals promotes the assumption of additional and interconverting species in solution. Comparable rearrangements both in the solid state and in solution are known.[9a,b,15]

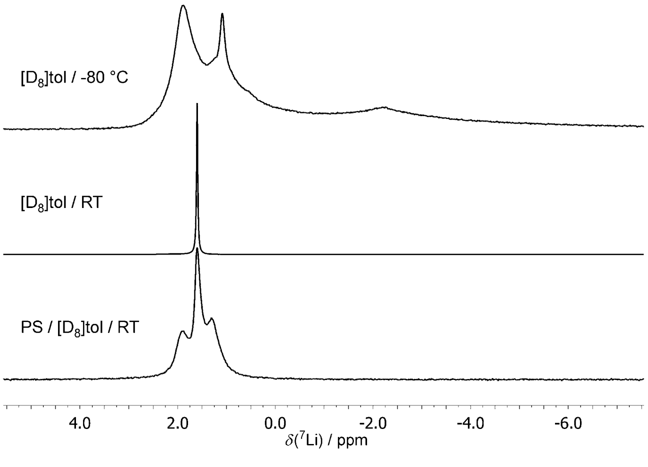


Figure 3. Low-temperature ^7Li NMR spectrum of **1** in $[D_8]$toluene at −80 °C (top), and the corresponding isotropic (center) and anisotropic (bottom) NMR spectra at room temperature.

More elaborated NMR experiments, such as diffusion or Heteronuclear Overhauser Effect (HOE) experiments at low temperature, were hampered by the immense line broadening observed at lower temperatures (see the Supporting Information). It has to be concluded at this point that there are more than two species involved in an equilibrium that is still fast at temperatures as low as −80 °C, impeding an unambiguous structural assignment. Therefore, further experiments were solely carried out at room temperature.

^{1}H- and ^{7}Li-DOSY spectra were then recorded at room temperature. The diffusion coefficient for the thienyl moiety ($D=8.5\times10^{-}10\,\mathrm{m^2\,s^{-1}}$) matches the one extracted from the ^{7}Li DOSY experiment. This indicates all lithium atoms either to be bound tightly to thienyl moieties or at least be incorporated in species with the same diffusion coefficient. The diglyme fragment shows a different diffusion coefficient ($D=1.2\times10^{-9}\,\mathrm{m^2\,s^{-1}}$) that is due to the excess present in solution, leading to an averaged value between coordinated and free molecules. As the build-up of the ^{1}H,^{7}Li HOE could successfully promote the characterization of aggregates in solution before, ^{1}H,^{7}Li HOESY spectra with varying mixing times (0.01–0.8 s) were recorded. A representative ^{1}H,^{7}Li HOESY spectrum is depicted in Figure 4 a.

In the ^{1}H,^{7}Li-HOESY spectrum, cross-peaks to the thienyl proton as well as to the CH_2 and CH_3 groups of the coordinating diglyme molecules are easily observed. The hitherto obtained absolute integrals are plotted as a function of the mixing time, which results in a typical HOE build-up (see the Supporting Information). Subsequently, the slope of the build-up at low mixing times is extracted and comparison with the H—Li distances from a geometry optimization of the SSIP yields the correlation represented by the black squares in Figure 4 b. Therein, the methyl contacts appear to be overrepresented by the distances derived from the geometry optimization. This further supports the hypothesis that the aggregation of **1** in solution cannot be described by one single structure alone for example, a SSIP. Dissociation of one sidearm or an additional species, such as a dimer with a bidentate coordination of both diglyme moieties, seem feasible expansions.

To obtain complementary information on the solution structure and to judge on possible aggregates, an anisotropic sample was prepared by letting a polystyrene stick (0.2 vol % DVB) swell one week in a solution of **1** in [D$_8$]toluene. As this lithium lithiate is very sensitive and easily decomposes, swelling was carried out at 4 °C, which could be identified as reasonable swelling condition in an earlier investigation.[16] A room-temperature ^{7}Li ($I=3/2$) NMR spectrum (Figure 3, bottom) was recorded, which displays a clear quadrupolar triplet with a splitting of $\Delta\nu_Q=48$ Hz in the anisotropic environment. This is in accordance with a low-symmetry aggregate (less than T_d).[17]

To better understand the NMR experiments, electronic structure calculations were conducted as a complementary source of information. In a first step, the lithium lithiate (**1a**) as well as dimeric (**1b**), monomeric (**1c**), and trimeric (**1d**) arrangements, all with a 1:1:1 ratio of thiophene, lithium, and diglyme, were identified as conceivable structural motifs, while tetramers and higher aggregates were not considered.

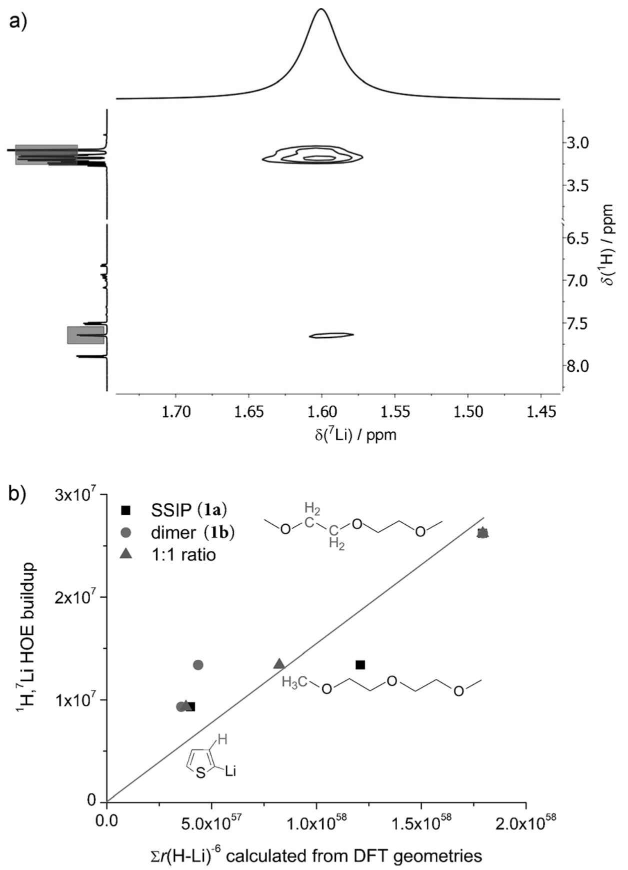


Figure 4. a) Representative ^{1}H,^{7}Li HOESY spectrum of **1** in [D$_8$]toluene recorded at 25 °C (top) with the mixing time 0.5 s. Cross-peaks could be observed to the neighboring thienyl proton along with the CH_2 and CH_3 groups of diglyme. b) Comparison of the slope of the build-up with calculated $\Sigma r(\mathrm{H}\cdots\mathrm{Li})^{-6}$ from the geometry-optimized SSIP **1 a** (squares), dimer **1 b** (dots), and a 1:1 mixture of both (triangles).

The possible disorder of the thienyl rings was accounted for by sampling different orientations of the ring and a separate optimization was carried out for the two ionic species that form the crystal structure. Furthermore, the formation of another “ate” species, commonly referred to as a triple ion, is not feasible owing to the low steric demand of the thienyl moieties. Preliminary structural studies of **1a–d** were carried out, confirming stable minima for structures only of the type **1a–1c** (Figure 5 a), whereas the trimeric arrangement only yielded dimers and was not considered for further calculations.

The structures obtained in our preliminary calculations were then re-optimized at the B3LYP-D3/def2-TZVP level of theory[18] (Figure 5 a, see the Supporting Information for Cartesian coordinates and further computational details) and Gibbs formation energies were calculated including solvent effects through the COSMO model.[19] We included both toluene ($\varepsilon=2.4$, NMR solvent) and Et$_2$O ($\varepsilon=4.3$, solvent for synthesis). Local coupled cluster calculations were also used to further refine the electronic energies (LCCSD(T0)).[20] The basis set applied in the latter calculations was cc-pVTZ[21] (cc-pCVTZ[22] for Li, correlating the 1s electrons). DFT calcu-

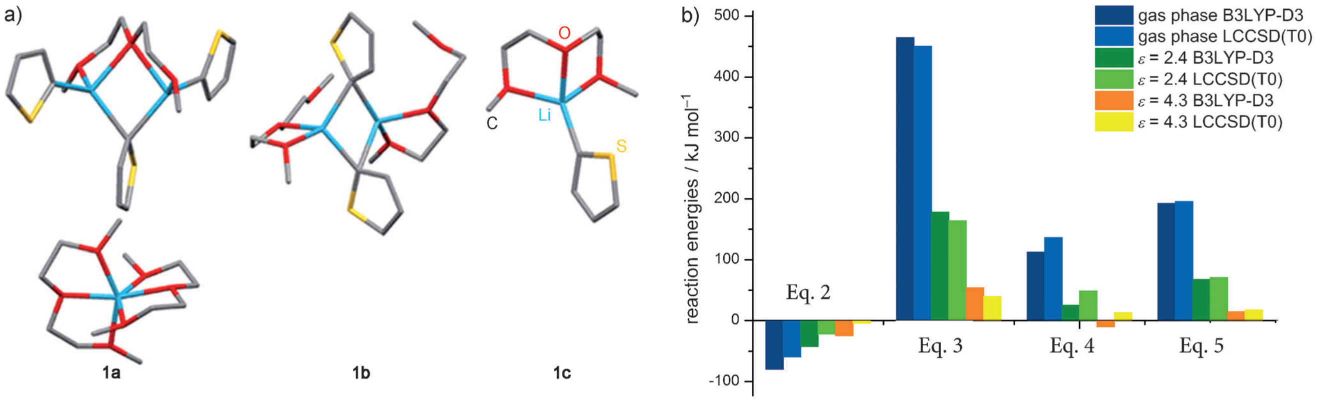
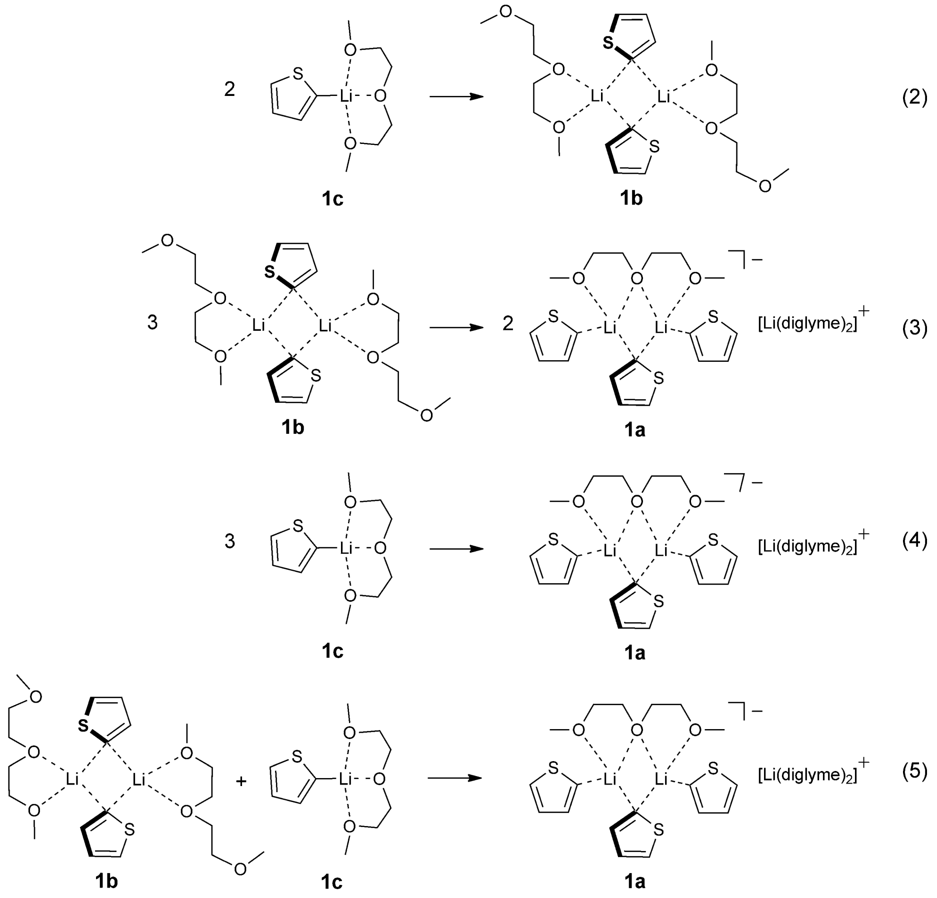


Figure 5. a) Final structure refinement for minimum energy structures at the B3LYP-D3/def2-TZVP level of theory (**1a** SSIP, **1b** dimer, **1c** monomer; see also Scheme 2). The two species of the SSIP **1a** were optimized separately, and hydrogen atoms are omitted for clarity. b) Reaction energies of possible interconversions. B3LYP-D3 and local coupled-cluster theory with single and double excitations including non-iterative perturbative triples (LCCSD(T0)) approaches were combined with COSMO corrections for the solvents environments $\varepsilon = 2.4$ (toluene) and $\varepsilon = 4.3$ (Et_2O).



Scheme 2. Calculated interconversion reactions of **1** (see also Figure 5).

lations were performed with the ORCA program package,[23] wave function calculations with Molpro2010.1.[24]

To judge the thermodynamic stability of the aggregates, the free energies were used to calculate free reaction energies for different interconversions (for example, two monomers **1c** can interconvert to one dimer **1b**; Eq. (2) in Scheme 2). A comparison of the latter values is depicted in Figure 5b. Considering the general trend of the energies upon going from the gas phase to a solvent description, the formation of a dimer is thermodynamically favored yet destabilized upon introducing the solvent environment. This trend is sustained with increasing solvent polarity, while the charged (ion pair) crystal structure is stabilized at the same time. This observation agrees very precisely with both the solid state structure and the NMR analysis. The presence of Et_2O from which the crystals were obtained considerably favors charged species, yet only to a small extent still outnumbered by the energy gain of crystal formation. The presence of polar components (excess diglyme, Et_2O) in the NMR sample supports the coexistence of dimers and charged species, which could be further supported by a fitting of the $^1H,^7Li$ HOE data to a 1:1 mixture of the solvent separated ion pair **1a** and the dimer **1b** (cicles and triangles in Figure 4b) and is in good agreement with residual dipolar coupling (RDC) data, which does not fit one structure alone despite modeling of the inner flexibility of this type of compounds.

In summary, we could show that a combination of X-ray diffraction experiments with NMR spectroscopic studies and electronic structure calculations allows a first deeper insight into the formation of this unprecedented type of lithium lithiate. It underlines the diversity of lithium species still to be investigated. Owing to the complex behavior of **1** in solution, which depends significantly on the polarity of the solvent and Lewis base additives, more investigations will have to be conducted to get a complete in depth picture of the analyzed compound, which at this point is most reliably described by computational methods. Starting from these data, this would require chemical shift calculations, additional in situ studies, NMR titrations, (low-temperature) NMR experiments in $[D_{10}]$-diethyl ether as well as the comparison with other compounds and the extraction of reaction rates to judge the reactivity and selectivity of the new lithium species presented herein.

Experimental Section

For NMR measurements, crystals of **1** were taken from the mother liquor at low temperature, dissolved in $[D_8]$toluene, and the tube was sealed. ^{1}H NMR (400.13 MHz, $[D_8]$toluene, 25 °C): $\delta = 7.89$ (d, $^3J_{HH} = 4.1$ Hz, 3H, H_5), 7.65 (d, $^3J_{HH} = 2.8$ Hz, 3H, H_3), 7.51 (dd, $^3J_{HH} = 4.1$, 2.8 Hz, 3H, H_4), 3.21 (m, 12H, $H_{1'}$), 3.16 (m, 12H, $H_{2'}$), 3.09 ppm (s, 18H, CH_3); ^{13}C NMR (100.61 MHz, $[D_8]$toluene, 25 °C): $\delta = 172.5$ (C_2), 136.3 (C_3), 130.0 (C_5), 127.1 (C_4), 71.2 ($C_{2'}$), 69.6 ($C_{1'}$), 58.3 ppm ($C_{3'}$); ^{7}Li-NMR (155.51 MHz, $[D_8]$toluene, 25 °C): $\delta = 1.60$ ppm (s).

Single crystals of **1** were mounted in inert oil under argon atmosphere by applying cryo-application techniques.[25] The X-ray data set was collected at 100(0.2) K on an INCOATEC microfocus source[26] with mirror-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) and equipped with a Bruker Smart Apex II detector. The data were semi-empirical absorption corrected (SADABS).[27] The structure was solved by direct methods with SHELXS and refined by full-matrix least squares on F^2 for all data with SHELXL within the SHELXle GUI.[28] Distance restraints and ADP restraints were applied to stabilize refinement of the considerably disordered model (for the refinement and data, see the Supporting Information). Along with the data presented herein, we collected data from on-sight prepared crystals at various temperatures and wavelengths at the APS. However, none of them was any better in quality than the presented data.

1: $Li_3C_{30}H_{51}O_9S_3$, $M = 672.71$ g mol^{-1}, orthorhombic, space group *Pbca*, $a = 16.158(3)$, $b = 14.931(3)$, $c = 31.134(6)$ Å, $V = 7511(3)$ Å^3, $Z = 8$, μ(Mo-K_α) = 0.242 mm^{-1}, $T = 100(0.2)$ K, 172 801 reflections measured, 5410 unique reflections, $R_{int} = 0.1626$, 854 parameters refined, $R1\ [I > 2\sigma(I)] = 0.1167$, $wR_2[I > 2\sigma(I)] = 0.3639$, GOF = 1.560, largest diff. peak and hole 0.878 and -0.489 e Å^{-3}.

Received: June 17, 2014

Keywords: aggregation · computational chemistry · lithium · NMR spectroscopy · X-ray diffraction

---

[1] a) E. Carl, D. Stalke in *Lithium Compounds in Organic Synthesis* (Eds.: R. Luisi, V. Capriati), Wiley-VCH, Weinheim, **2014**, pp. 1–32; b) H. J. Reich, *Chem. Rev.* **2013**, *113*, 7130–7178; c) V. H. Gessner, C. Däschlein, C. Strohmann, *Chem. Eur. J.* **2009**, *15*, 3320–3334; d) D. B. Collum, A. J. McNeil, A. Ramirez, *Angew. Chem. Int. Ed.* **2007**, *46*, 3002–3017; *Angew. Chem.* **2007**, *119*, 3060–3077; e) T. Stey, D. Stalke in *The Chemistry of Organolithium Compounds* (Eds.: Z. Rappoport, I. Marek), Wiley, Chichester, **2004**, pp. 47–120; f) M. C. Whisler, S. MacNeil, V. Snieckus, P. Beak, *Angew. Chem. Int. Ed.* **2004**, *43*, 2206–2225; *Angew. Chem.* **2004**, *116*, 2256–2276; g) B. Lucht, D. B. Collum, *Acc. Chem. Res.* **1999**, *32*, 1035–1042.

[2] R. M. Fuoss, C. A. Kraus, *J. Am. Chem. Soc.* **1933**, *55*, 2387–2399.

[3] a) G. Wittig, F. J. Meyer, G. Lange, *Justus Liebigs Ann. Chem.* **1951**, *571*, 167–201; b) G. Wittig, *Angew. Chem.* **1958**, *70*, 65–71.

[4] a) C. Eaborn, P. B. Hitchcock, J. D. Smith, A. C. Sullivan, *J. Chem. Soc. Chem. Commun.* **1983**, 827–828; b) U. J. Bildmann, G. Müller, *Organometallics* **2001**, *20*, 1689–1691.

[5] a) B. L. Lucht, M. A. Bernstein, J. F. Remenar, D. B. Collum, *J. Am. Chem. Soc.* **1996**, *118*, 10707–10718; b) J. Arnold, *J. Chem. Soc. Chem. Commun.* **1990**, 976–978; c) N. H. Buttrus, C. Eaborn, P. B. Hitchcock, J. D. Smith, J. G. Stamper, A. C. Sullivan, *J. Chem. Soc. Chem. Commun.* **1986**, 969–970.

[6] a) H. Gornitzka, D. Stalke, *Organometallics* **1994**, *13*, 4398–4405; b) P. P. Power, *Acc. Chem. Res.* **1988**, *21*, 147–153; c) M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1985**, *107*, 2174–2175; d) P. P. Power, X. Xiaojie, *J. Chem. Soc. Chem. Commun.* **1984**, 358–359.

[7] a) H. J. Reich, W. H. Sikorski, B. Ö. Gudmundsson, R. R. Dykstra, *J. Am. Chem. Soc.* **1998**, *120*, 4035–4036; b) F. E. Romesberg, D. B. Collum, *J. Am. Chem. Soc.* **1994**, *116*, 9198–9202; c) F. E. Romesberg, D. B. Collum, *J. Am. Chem. Soc.* **1992**, *114*, 2112–2121; d) L. M. Jackman, L. M. Scarmoutzos, W. Porter, *J. Am. Chem. Soc.* **1987**, *109*, 6524–6525.

[8] For examples, see: a) L. A. Paquette, W. Bauer, M. R. Sivik, M. Bühl, M. Feigel, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 8776–8789; b) S. Harder, M. H. Prosenc, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1744–1766; *Angew. Chem.* **1994**, *106*, 1830–1832; c) J. Wessel, E. Lork, R. Mews, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2376–2378; *Angew. Chem.* **1995**, *107*, 2565–2567; d) R. Michel, R. Herbst-Irmer, D. Stalke, *Organometallics* **2011**, *30*, 4379–4386; e) D. Stalke, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2168–2171; *Angew. Chem.* **1994**, *106*, 2256–2259; f) L. M. Jackman, L. M. Scarmoutzos, B. D. Smith, P. G. Williard, *J. Am. Chem. Soc.* **1988**, *110*, 6058–6063.

[9] a) H. Gornitzka, D. Stalke, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 693–695; *Angew. Chem.* **1994**, *106*, 695–698; b) F. Pauer, J. Rocha, D. Stalke, *J. Chem. Soc. Chem. Commun.* **1991**, 1477–1479; c) D. Barr, W. Clegg, R. E. Mulvey, R. Snaith, *J. Chem. Soc. Chem. Commun.* **1984**, 226–227; d) A. G. Avent, C. Eaborn, P. B. Hitchcock, G. A. Lawless, P. D. Lickiss, M. Mallien, J. D. Smith, A. D. Webb, B. Wrackmeyer, *J. Chem. Soc. Dalton Trans.* **1993**, 3259–3264; e) R. H. Cox, H. W. J. Terry, *J. Magn. Reson.* **1974**, *14*, 317–322; f) G. Fraenkel, M. P. Hallden-Abberton, *J. Am. Chem. Soc.* **1981**, *103*, 5657–5664.

[10] H. J. Reich, W. H. Sikorski, *J. Org. Chem.* **1999**, *64*, 14–15.

[11] a) A. C. Hoepker, D. B. Collum, *J. Org. Chem.* **2011**, *76*, 7985–7993; b) X. Sun, D. B. Collum, *J. Am. Chem. Soc.* **2000**, *122*, 2452–2458; c) J. F. Remenar, D. B. Collum, *J. Am. Chem. Soc.* **1998**, *120*, 4081–4086; d) A. C. Jones, A. W. Sanders, W. H. Sikorski, K. L. Jansen, H. J. Reich, *J. Am. Chem. Soc.* **2008**, *130*, 6060–6061; e) H. J. Reich, W. H. Sikorski, A. W. Sanders, A. C. Jones, K. N. Plessel, *J. Org. Chem.* **2009**, *74*, 719–729; f) F. E. Romesberg, D. B. Collum, *J. Am. Chem. Soc.* **1995**, *117*, 2166–2178.

[12] M. Granitzka, A.-C. Pöppler, E. K. Schwarze, D. Stern, T. Schulz, M. John, R. Herbst-Irmer, S. K. Pandey, D. Stalke, *J. Am. Chem. Soc.* **2012**, *134*, 1344–1351.

[13] Cambridge Structural Database, v5.34 (November 2012), Cambridge Crystallographic Data Centre, Cambridge, **2012**.

[14] a) R. E. Mulvey, *Acc. Chem. Res.* **2009**, *42*, 743–755; b) R. E. Mulvey, F. Mongin, M. Uchiyama, Y. Kondo, *Angew. Chem. Int. Ed.* **2007**, *46*, 3802–3824; *Angew. Chem.* **2007**, *119*, 3876–3899; c) D. R. Armstrong, W. Clegg, S. H. Dale, E. Hevia, L. M. Hogg, G. W. Honeyman, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2006**, *45*, 3775–3778; *Angew. Chem.* **2006**, *118*, 3859–3862; d) V. L. Blair,

A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, *Chem. Eur. J.* **2010**, *16*, 8600 – 8604.
[15] S. Freitag, W. Kolodziejski, F. Pauer, D. Stalke, *J. Chem. Soc. Dalton Trans.* **1993**, 3479 – 3488.
[16] A.-C. Pöppler, S. Frischkorn, D. Stalke, M. John, *ChemPhysChem* **2013**, *14*, 3103 – 3107.
[17] A.-C. Pöppler, H. Keil, D. Stalke, M. John, *Angew. Chem. Int. Ed.* **2012**, *51*, 7843 – 7846; *Angew. Chem.* **2012**, *124*, 7963 – 7967.
[18] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098 – 3100; b) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104 – 154119; c) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297 – 3305.
[19] A. Klamt, G. J. Schüürman, *J. Chem. Soc. Perkin Trans. 2* **1993**, 799 – 805.
[20] H.-J. Werner, M. Schütz, *J. Chem. Phys.* **2011**, *135*, 144116 – 144115.
[21] T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007 – 1023.
[22] B. Prascher, D. Woon, K. Peterson, T. Dunning, Jr., A. Wilson, *Theor. Chem. Acc.* **2011**, *128*, 69 – 82.
[23] ORCA, v. 2.8, F. Neese, U. Becker, D. Ganiouchine, S. Koßmann, T. Petrenko, C. Riplinger, F. Wennmohs, University of Bonn (Germany), **2010**.
[24] H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby and M. Schütz, et al., MOLPRO, version 2010.1, a package of ab initio programs, **2010**, see http://www.molpro.net.
[25] a) D. Stalke, *Chem. Soc. Rev.* **1998**, *27*, 171 – 178; b) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615 – 619; c) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1996**, *29*, 465 – 468.
[26] T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* **2009**, *42*, 885 – 891.
[27] G. M. Sheldrick, *SADABS*, 2008/2; Universität Göttingen, **2008**.
[28] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467 – 473; b) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112 – 122; c) P. Müller, R. Herbst-Irmer, A. L. Spek, T. R. Schneider, M. R. Sawaya in *Crystal Structure Refinement-A Crystallographer's Guide to SHELXL, IUCr Texts on Crystallography, Vol. 8* (Ed.: P. Müller), Oxford University Press, Oxford, UK, **2006**; d) C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281 – 1284.
[29] CCDC 1008655 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.