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The Crystal Structure of the THF Adduct of Monolithioferrocene

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Abstract. Single crystals of $[Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)]_2Li_2(thf)_4$ (**1**) were obtained from a tetrahydrofuran solution containing monolithioferrocene. The title compound crystallizes in the monoclinic space group $P2_1$ with a = 9.6589(5) Å, b = 17.4285(9) Å, c = 30.3116(15) Å, β = 91.911(2)° and V = 5099.8(5) Å^3 with three independent molecules of **1**. All individual molecules feature a non- symmetric almost planar Li_2C_2 four-membered ring with two shorter (2.118–2.215 Å) and two longer Li–C distances (2.257–2.309 Å). The lithium cations are each coordinated by two carbanionic atoms of two ferrocenyl substituents and two tetrahydrofuran molecules in a distorted tetrahedral fashion. All ferrocenyl moieties display an eclipsed conformation of the C_5 rings.

Introduction

Substituted ferrocenes have found widespread interest in a variety of applications ranging from fundamental research to biology, catalysis and materials science.[1–3] The selective monofunctionalization of ferrocene is one of the most important reactions of organometallic chemistry.[1] Standard organic transformations such as Friedel–Crafts or Mannich reactions are quite often employed while the most versatile reaction is probably the lithiation of ferrocene giving access to e.g. B, C, Si, Sn, N, P, O, S and halide substituted ferrocenes after quenching with suitable electrophiles.[1] The most convenient method to monolithioferrocene is probably the metallation of ferrocene with *t*BuLi/KO*t*Bu in tetrahydrofuran according to *Mueller-Westerhoff*'s[4] optimized *Kagan* procedure.[5] To access highly pure and donor base-free monolithioferrocene lithium-halogen exchange is feasible from FcI or FcBr with *n*BuLi in ethyl ether at low temperatures[6] while FcCl yields a mixture of ferrocene, chloroferrocene, *n*-butylferrocene and biferrocene.[7]

The base-free monolithioferrocene LiFc is poorly soluble in non-coordinating solvents and is presumably a polymeric material, possibly similar to $[LiCp]_\infty$,[8] but its structure in the solid state is at present unknown. With coordinating solvents the polymeric structure is certainly disrupted giving soluble and solvated $[LiFc]_n(solv)_m$ which can be characterized by NMR spectroscopy.[9] In spite of its tremendous utility and its extensive application in organometallic synthesis the solid-state structures of base-free and donor-base coordinated LiFc have not been reported. However, a few solid-state structures of *ortho*-substituted monolithiated ferrocenes have been described in the literature by the groups of *Edelmann*, *Jacob*, *Erker* and *Strohmann*.[10–13] The basic structural motif is the well-known Li_2C_2 four-membered ring.[14] Typically, the lithium cation is three or four coordinate by the chelating amine side arm, sometimes assisted by a solvent molecule such as diethyl ether. The solid-state structures of the tmeda and pmdta adducts of 1,1'-dilithiated ferrocene (tmeda = *N*,*N*,*N'*,*N'*-tetramethylethane-1,2-diamine,[15a] pmdta = *N*,*N*,*N'*,*N'*,*N''*-pentamethyldiethylenetriamine[15b]) have been reported as well. The tetrahydrofuran adduct $[Fe(\eta^5\text{-}C_5H_4)_2]_2Li_4(thf)_6$ has been prepared and structurally characterized by *Wagner*.[16] Basically, all 1,1'-dilithiated ferrocenes display a central Li_2C_2 four-membered ring and two terminal base-coordinated lithium cations. The substituted dilithio derivative $[(\eta^5\text{-}C_5H_4Li)Fe(\eta^5\text{-}1,2\text{-}C_5H_3Li(CHMeNMe_2))]_4(LiOEt)_2(tmeda)_2$ features a more complicated structure due to the presence of several different donor ligands.[17] A 1,1',3,3'-tetrametallated ferrocene $[\{Fe(\eta^5\text{-}C_5H_3)_2\}Na_4Mg_4\{iPr_2N\}_8$ has been reported by *Mulvey* displaying a crown of sodium and magnesium amide units.[18] To the best of our knowledge solid-state structures of simple monolithio ferrocenes are unknown up to now.

Results and Discussion

Monolithioferrocene has been prepared from ferrocene and the super base *t*BuLi/KO*t*Bu at low temperature according to *Mueller-Westerhoff*.[4] Quenching with iodine gave the pure iodoferrocene.[19] The latter was lithiated by *n*BuLi in petroleum ether (b.p. 40–60 °C) at room temperature.[6,7] The precipitated LiFc was thoroughly washed with petroleum ether (b.p. 40–60 °C).

Solid LiFc easily dissolved in THF and was fully characterized by multinuclear and two-dimensional NMR spectroscopy (Exp. Section, Supporting Information). After a few days, orange crystals precipitated from the solution at room

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temperature. The tetrahydrofuran adduct of LiFc crystallized in the chiral monoclinic space group $P2_1$ as a racemic twin with three independent molecular entities $[Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)]_2Li_2(thf)_4$ (**1**) in the unit cell (Figure 1).

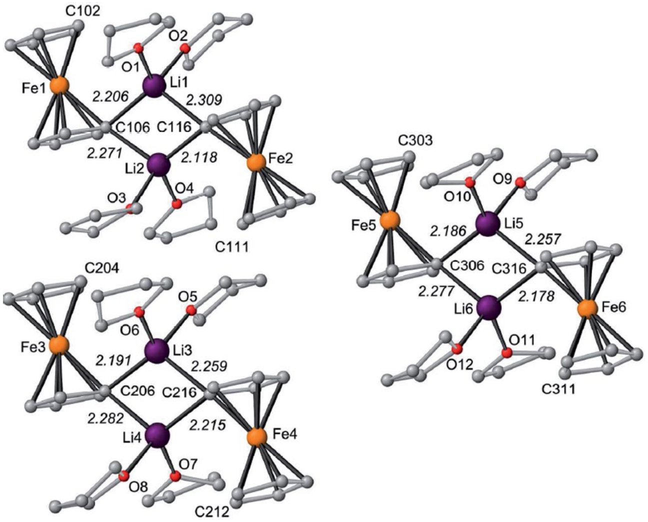

Figure 1. Molecular structures of the three independent molecules of **1** in the solid state.

The three independent molecules differ only slightly in their metrical data (Figure 1, Table 1). All display a non-symmetric almost planar Li_2C_2 four-membered ring similar to the structures of $((thf)_2LiMes)_2$,[20] $((tmeda)LiPh)_2$,[21a] and $(((–)\text{-sparteine})LiPh)_2$[21b] and different to the tetrameric assembly of phenyllithium etherate $((Et_2O)LiPh)_4$.[21c] Possibly the steric bulk of the ferrocenyl carbanion assists in reducing the cluster size to a dimeric structure. In contrast to $((thf)_2LiMes)_2$,[20] $((tmeda)LiPh)_2$,[21a] and $(((–)\text{-sparteine})LiPh)_2$,[21b] the Li_2C_2 rings of **1** are not C_2 or C_i symmetric but feature a pair of longer (2.257–2.309 Å) and a pair of shorter Li–C distances (2.118–2.215 Å). The lithium cations are approximately tetrahedrally surrounded with a κ^2O κ^2C coordination. All ferrocenyl moieties display an essentially eclipsed conformation of the co-planar C_5 rings (Figure 1, Table 1). No further unusual intermolecular contacts are observed. The solid state ^{7}Li NMR spectrum[22] reveals a broad resonance at around $\delta = 3.5$ ppm probably enclosing several close-lying resonances of the lithium ions in slightly different chemical environments in crystalline **1**.

DFT (B3LYP, LANL2DZ, IEFPCM THF) calculations[23] on **1** reveal a similar geometry as found in the solid state with an essentially centrosymmetric Li_2C_2 ring with a longer and a shorter Li-C distance (Table 2). The C_5 rings of the ferrocenyl moieties are eclipsed and co-planar. A hypothetical monomeric species $(thf)_3LiFc$ (**2**) has been calculated as well (Table 2). Apart from the lone pairs of the oxygen atoms of the thf molecules significant accessible electron density is found on top of the C_5H_4 and C_5H_5 rings (Figure 2). Hence, one can speculate that upon removal of the coordinating thf ligands the lithium cation of the unsaturated LiFc fragment will attach to the C_5H_4 or C_5H_5 ring of a neighbouring molecule. This bridging $(\eta^5\text{-}C_5H_4)/(\eta^5\text{-}C_5H_5)$ and $(\eta^1\text{-}C_5H_4)$ coordination of the lithium ion could give rise to a polymeric one-dimensional structure $[LiFc]_\infty$ **3** similar to cyclopentadienyllithium $[LiCp]_\infty$.[8] However, the experimental verification of this hypothesis must await the structure determination of donor base-free **3**.

Table 1. Selected bond lengths /Å and angles /° of **1** from XRD data.

Fe1/Fe2		Fe3/Fe4		Fe5/Fe6	
Li1···Li2	2.4876 (0.0289)	Li3···Li4	2.5355 (0.0223)	Li5···Li6	2.5236 (0.0225)
Li1–C106	2.2064 (0.0217)	Li3–C206	2.1909 (0.0202)	Li5–C306	2.1857 (0.0194)
Li1–C116	2.3092 (0.0297)	Li3–C216	2.2589 (0.0191)	Li5–C316	2.2570 (0.0202)
Li2–C106	2.2708 (0.0225)	Li4–C206	2.2817 (0.0228)	Li6–C306	2.2766 (0.0234)
Li2–C116	2.1184 (0.0219)	Li4–C216	2.2150 (0.0214)	Li6–C316	2.1784 (0.0210)
Li1–O1	1.9752 (0.0228)	Li3–O5	1.9884 (0.0208)	Li5–O9	2.0012 (0.0216)
Li1–O2	1.9784 (0.0216)	Li3–O6	1.9541 (0.0197)	Li5–O10	1.9974 (0.0195)
Li2–O3	2.0188 (0.0201)	Li4–O7	2.0120 (0.0217)	Li6–O11	2.0357 (0.0211)
Li2–O4	2.0484 (0.0229)	Li4–O8	1.9478 (0.0221)	Li6–O12	1.9560 (0.0252)
Li1···Fe1	3.4568 (0.0200)	Li3···Fe3	3.4808 (0.0172)	Li5···Fe5	3.5010 (0.0173)
Li2···Fe2	3.5258 (0.0197)	Li4···Fe4	3.5242 (0.0192)	Li6···Fe6	3.5311 (0.0194)
Fe1–X1[a)]	1.634	Fe3–X1[a)]	1.656	Fe5–X1[a)]	1.650
Fe1–X2[b)]	1.657	Fe3–X2[b)]	1.669	Fe5–X2[b)]	1.664
Fe2–X1[a)]	1.652	Fe4–X1[a)]	1.648	Fe6–X1[a)]	1.643
Fe2–X2[b)]	1.647	Fe4–X2[b)]	1.647	Fe6–X2[b)]	1.658
C106-Li1–C116	109.74 (1.16)	C206-Li3–C216	111.82 (0.86)	C306-Li5–C316	111.08 (0.86)
C106-Li2–C116	114.56 (0.98)	C206-Li4–C216	110.07 (0.98)	C306-Li6–C316	110.61 (1.01)
Li1–C106-Li2	67.49 (0.88)	Li3–C206-Li4	69.03 (0.68)	Li5–C306-Li6	68.85 (0.68)
Li1–C116-Li2	68.21 (0.77)	Li3–C216-Li4	69.04 (0.70)	Li5–C316-Li6	69.33 (0.73)
ω(Fe1)[c)]	–3.2	ω(Fe3)[e)]	1.3	ω(Fe5)[g)]	0.4
ω(Fe2)[d)]	–0.7	ω(Fe4)[f)]	–0.8	ω(Fe6)[h)]	–0.2
τ(Fe1)[i)]	178.6	τ(Fe3)[i)]	179.6	τ(Fe5)[i)]	179.0
τ(Fe2)[i)]	179.5	τ(Fe4)[i)]	178.0	τ(Fe6)[i)]	178.0

a) X1 = centroid of the coordinated C_5H_5 ring. b) X2 = centroid of the coordinated C_5H_4 ring. c) ω(Fe1) = C106-X2–X1–C102.[a,b)] d) ω(Fe2) = C116–X2–X1–C111.[a,b)] e) ω(Fe3) = C206–X2–X1–C204.[a,b)] f) ω(Fe4) = C216–X2–X1–C212.[a,b)] g) ω(Fe5) = C306–X2–X1–C303.[a,b)] h) ω(Fe6) = C316–X2–X1–C311.[a,b)] i) τ(Fe) = X2–Fe–X1.[a,b)].

Table 2. Selected bond lengths /Å and angles /° of **1** and **2** from DFT calculations.

1		2	
Li1···Li2	2.565		
Li1–C106	2.189	Li1–C106	2.134
Li1–C116	2.375		
Li2–C106	2.190		
Li2–C116	2.376		
Li1–O1	1.998	Li1–O1	2.027
Li1–O2	1.993	Li1–O2	1.989
Li2–O3	1.998	Li1–O3	2.009
Li2–O4	1.993		
Li1···Fe1	3.644	Li1···Fe1	4.000
Li2···Fe2	3.637		
Fe1–X1[a)]	1.741	Fe1–X1[a)]	1.740
Fe1–X2[b)]	1.734	Fe1–X2[b)]	1.734
Fe2–X1[a)]	1.741		
Fe2–X2[b)]	1.734		
C106-Li1–C116	111.4		
C106-Li2–C116	111.4		
Li1–C106-Li2	68.2		
Li1–C116-Li2	68.2		
ω(Fe1)[c)]	1.5	ω(Fe1)[c)]	–0.01
ω(Fe2)[d)]	1.8		
τ(Fe1)[e)]	179.9	τ(Fe1)[e)]	179.3
τ(Fe2)[e)]	179.9		

a) X1 = centroid of the coordinated C_5H_5 ring. b) X2 = centroid of the coordinated C_5H_4 ring. c) ω(Fe1) = C6–X2–X1–C1.[a,b)] d) ω(Fe2) = C16–X2–X1–C11.[a,b)] e) τ(Fe) = X2–Fe–X1.[a,b)]

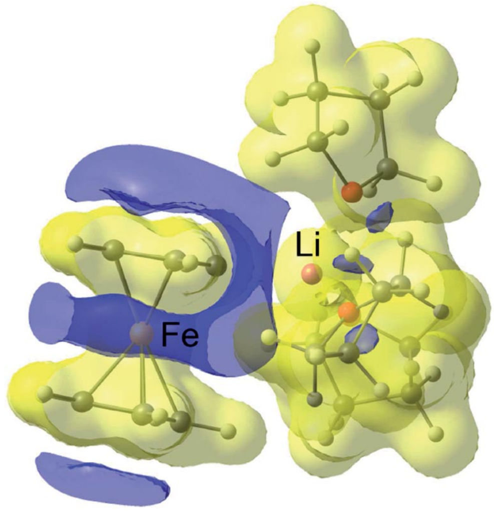

Figure 2. Electrostatic potential of **2** calculated by DFT (contour value 0.07 a.u.; negative = blue, positive = yellow).

Conclusions

The thf adduct of monolithioferrocene crystallizes as $[Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)]_2Li_2(thf)_4$ in the monoclinic space group $P2_1$ featuring Li_2C_2 four-membered rings. Together with the solid-state structure of the thf adduct of dilithiated ferrocene $[Fe(\eta^5\text{-}C_5H_4)_2]_2Li_4(thf)_6$ reported by *Wagner*[16] the two probably most often employed lithiated ferrocenes are now structurally characterized.

Experimental Section

Solution NMR spectra were recorded with a Bruker Avance DRX 400 spectrometer at 400.31 MHz (^{1}H), 100.657 MHz (^{13}C) and 155.575 MHz (^{7}Li). All resonances are reported in ppm vs. the solvent signal as internal standard [THF (^{1}H: δ = 1.73, 3.58 ppm; ^{13}C: δ = 25.37, 67.57 ppm)]. Solid state NMR measurements were conducted using a 400 MHz Bruker Avance spectrometer at a frequency of 155.40 MHz and 8 kHz spinning at the magic angle for ^{7}Li. 5 µs pulse length for the 90° single pulse excitation experiment and recycle delays of 120 s were used in all cases. 8 transients were averaged when acquiring the ^{7}Li NMR signal. A commercial 3-channels Bruker 4 mm probe-head, capable of fast MAS was used for all measurements. The spectra were referenced to external aqueous 3 M LiCl solution.

X-ray diffraction data were collected with a Bruker AXS Smart 1000 CCD diffractometer with an APEX II detector and an Oxford cooling system and corrected for absorption and other effects using Mo-K_α radiation (λ = 0.71073 Å) at 173(2) K. The diffraction frames were integrated using the SAINT package, and most were corrected for absorption with MULABS.[24,25] The structure was solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXTL software package.[26,27] All non-hydrogen atoms were refined anisotropically, while the positions of carbon bonded hydrogen atoms were generated with appropriate geometric constraints and allowed to ride on their respective parent atoms with fixed isotropic thermal parameters. For the refinement of the structure SADI, SAME, RIGU and SIMU restraints have been used. Split models were applied for disordered tetrahydrofuran molecules. The occupancies of the disordered atom sites were as follows: C121 (0.65), C21A (0.35); C128 (0.50), C28A (0.50); C129 (0.50), C29A (0.50); C135 (0.65), C035 (0.35); C232 (0.70), C32A (0.30); C235 (0.80), C35B (0.20); C328 (0.55), C08A (0.45); O12···C336 (0.70); O12A···C36A (0.30). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-1035257. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: +44-1223-336-033; E-mail deposit@ccdc.cam.ac.uk).

DFT calculations were carried out with the Gaussian09/DFT[28] series of programs. The B3LYP formulation of DFT was used employing the LANL2DZ basis set. No symmetry constraints were imposed on the molecules. The presence of energy minima was checked by analytical frequency calculations. The integral-equation-formalism polarizable continuum model (IEFPCM, THF) was employed for solvent modeling.

Crystallographic data of **1**: $C_{36}H_{50}Fe_2Li_2O_4$ (672.34); monoclinic; $P2_1$; a = 9.6589(5) Å, b = 17.4285(9) Å, c = 30.3116(15) Å, β = 91.911(2)°, V = 5099.8(5) Å^3; Z = 6; density, calcd. = 1.314 g cm^{-3}, μ = 0.889 mm^{-1}; F(000) = 2136; crystal size 0.28 × 0.24 × 0.14 mm; θ = 1.34 to 26.48 deg.; $-12 \le h \le 12$, $-20 \le k \le 21$, $-38 \le l \le 38$; rfln collected = 52804; rfln unique = 18772 [R(int) = 0.0997]; completeness to θ = 26.48 = 99.7 %; semi-empirical absorption correction from equivalents; max. and min. transmission 0.883 and 0.780; data 18762; restraints 1218, parameters 1244; goodness-of-fit on F^2 = 0.922; final R indices [$I > 2\sigma(I)$] R_1 = 0.0676, wR_2 = 0.1444; R indices (all data) R_1 = 0.1408, wR_2 = 0.1696; largest diff. peak and hole 1.02 and –1.26 e·Å^{-3}; absolute structure parameter 0.55(6).

Synthesis of 1: Solid LiFc[4] prepared from FcI[19] and nBuLi (2.5 M in hexane) was dissolved in THF. For NMR spectroscopic measurements

$[D_8]$THF was used. Crystals of **1** suitable for X-ray diffraction studies precipitated from the solution upon standing at –28 °C.

^{1}H NMR ($[D_8]$THF): $\delta = 3.73$ (s, 2 H, H^3), 3.79 (s, 5 H, H^4), 4.02 (s, 2 H, H^2) ppm. **^{13}C{^{1}H} NMR** ($[D_8]$THF): $\delta = 66.6$ (C^4), 69.9 (C^2), 80.5 (C^3), 96.0 (C^1) ppm. **^{7}Li{^{1}H} NMR** ($[D_8]$THF): $\delta = 1.89$ ppm. **MAS ^{7}Li NMR:** $\delta = 3.5$ (br) ppm.

Supporting Information (see footnote on the first page of this article): selected NMR spectra of **1**; Cartesian coordinates of optimized geometries of **1** and **2**.

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References

[1] a) *Ferrocenes: Homogenous Catalysis, Organic Synthesis Materials Science* (Eds.: A. Togni, T. Hayashi), VCH Weinheim, **1995**; b) *Ferrocenes – Ligands, Materials, Biomolecules* (Ed.: P. Štěpnička), John Wiley & Sons Ltd, Chichester, **2008**.
[2] Special issue of *J. Organomet. Chem.* marking the 50th anniversary of the first reports of ferrocene: R. D. Adams, *J. Organomet. Chem.* **2001**, *637–639*, 1.
[3] Special issue of, *Organometallics* highlighting modern ferrocene chemistry: K. Heinze, H. Lang, *Organometallics* **2013**, *32*, 5623–5625.
[4] R. Sanders, U. T. Mueller-Westerhoff, *J. Organomet. Chem.* **1996**, *512*, 219–224.
[5] a) F. Rebiere, O. Samuel, H. B. Kagan, *Tetrahedron Lett.* **1990**, *31*, 3121–3124; b) D. Guillaneux, H. B. Kagan, *J. Org. Chem.* **1995**, *60*, 2502–2505.
[6] a) F. L. Hedbern, H. Rosenberg, *Tetrahedron Lett.* **1969**, *46*, 4011–4012; b) M. D. Rausch, G. A. Moser, C. F. Meade, *J. Organomet. Chem.* **1973**, *51*, 1–11.
[7] J. W. Huffman, L. H. Keith, R. L. Asbury, *J. Org. Chem.* **1965**, *30*, 1600–1604.
[8] R. E. Dinnebier, U. Behrens, F. Olbrich, *Organometallics* **1997**, *16*, 3855–3858.
[9] No NMR spectroscopic data of LiFc have been reported so far.
[10] K. Jacob, M. Schiller, A. Steiner, G. M. Sheldrick, F. T. Edelmann, *J. Organomet. Chem.* **1995**, *487*, C18–C20.
[11] F. Voigt, A. Fischer, C. Pietzsch, K. Jacob, *Z. Anorg. Allg. Chem.* **2001**, *627*, 2337–2343.
[12] C. Chen, R. Fröhlich, G. Kehr, G. Erker, *Organometallics* **2008**, *27*, 3248–3253.
[13] P. Steffen, C. Unkelbach, M. Christmann, W. Hiller, C. Strohmann, *Angew. Chem.* **2013**, *125*, 10019–10023; *Angew. Chem. Int. Ed.* **2013**, *52*, 9836–9840.
[14] a) T. Stey, D. Stalke, in: *The Chemistry of Organolithium Compounds, Part 1* (Eds.: Z. Rappoport, I. Marek), Wiley-VCH, Weinheim, **2004**, pp. 47–120; b) V. H. Gessner, C. Däschlein, C. Strohmann, *Chem. Eur. J.* **2009**, *15*, 3320–3334; c) K. Gregory, P. v. Ragué Schleyer, R. Snaith, *Adv. Inorg. Chem.* **1991**, *37*, 47–142; d) R. E. Mulvey, *Chem. Soc. Rev.* **1991**, *20*, 167–209.
[15] a) I. R. Butler, W. R. Cullen, J. Ni, S. J. Rettig, *Organometallics* **1985**, *4*, 2196–2201; b) M. Walczak, K. Walczak, R. Mink, M. D. Rausch, G. Stucky, *J. Am. Chem. Soc.* **1978**, *100*, 6382–6388.
[16] A. S. Perucha, J. Heilmann-Brohl, M. Bolte, H.-W. Lerner, M. Wagner, *Organometallics* **2008**, *27*, 6170–6177.
[17] I. R. Butler, W. R. Cullen, J. Reglinski, S. J. Rettig, *J. Organomet. Chem.* **1983**, *249*, 183–194.
[18] W. Clegg, K. W. Henderson, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, R. B. Rowlings, D. M. Tooke, *Angew. Chem.* **2001**, *113*, 4020–4023; *Angew. Chem. Int. Ed.* **2001**, *40*, 3902–3905.
[19] B. Bildstein, M. Malaun, H. Kopacka, K. Wurst, M. Mitterböck, K.-H. Ongania, G. Opromolla, P. Zanello, *Organometallics* **1999**, *18*, 4325–4336.
[20] M. A. Beno, H. Hope, M. M. Olmstead, P. P. Power, *Organometallics* **1985**, *4*, 2117–2121.
[21] a) D. Thoennes, E. Weiss, *Chem. Ber.* **1978**, *111*, 3157–3161; b) C. Strohmann, S. Dilsky, K. Strohfeldt, *Organometallics* **2006**, *25*, 41–44; c) H. Hope, P. P. Power, *J. Am. Chem. Soc.* **1983**, *105*, 5320–5324.
[22] D. Johnels, H. Günther, in: *The Chemistry of Organolithium Compounds, Part 1* (Eds.: Z. Rappoport, I. Marek), Wiley-VCH, Weinheim, **2004**, pp. 47–120.
[23] For a combined experimental and DFT study on LiMe see: K. Götz, V. H. Gessner, C. Unkelbach, M. Kaupp, C. Strohmann, *Z. Anorg. Allg. Chem.* **2013**, *639*, 2077–2085.
[24] *SMART Data Collection and SAINT-Plus Data Processing Software for the SMART System*, various versions; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, USA, **2000**.
[25] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.
[26] a) G. M. Sheldrick, *SHELXTL*, version 5.1, Bruker AXS, Madison, WI, USA, **1998**; b) C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.
[27] a) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1997**; b) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[28] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, Revision A.02, Gaussian, Inc., Wallingford CT, USA, **2009**.

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