Electronic Supplementary Material (ESI) for Chemical Communications.

SUPPORTING INFORMATION

The Structure-defining Incorporation of Chloride in Methyllithium Dimers

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Content:

A. General Procedures

All experiments were performed under an atmosphere of argon using standard Schlenk techniques. Diethylether and *n*-pentane were dried by refluxing over sodium and distilled under an atmosphere of argon prior to use. All reagents were used as commercial products without further purification.

B. Experimental Details

Crystallization of Coordination Polymer 4

A solution of 0.21 mL (1 mmol, 1 eq.) *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (pmdta) in 3 mL dry *n*-pentane was cooled to −78 °C. At this temperature, 3.75 mL (6 mmol, 6 eq.) of a 1.6 M solution of methyllithium in diethylether was added. The mixture was slowly warmed to room temperature and subsequently stored at 4 °C. After one day, colorless crystals of coordination polymer **4** were obtained which were subjected to single crystal x-ray analysis.

Crystallization of Coordination Polymer 5

A solution of 0.21 mL (1 mmol, 1 eq.) *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (pmdta) in 3 mL dry *n*-pentane was cooled to −78 °C. At this temperature, 2.50 mL (4 mmol, 4 eq.) of a 1.6 M solution of methyllithium in diethylether was added. The mixture was slowly warmed to room temperature and subsequently stored at 4 °C. After one day, colorless crystals of coordination polymer **5** were obtained which were subjected to single crystal x-ray analysis.

Crystallization of (MeLi · (*R*,*R*)-TMCDA)$_2$ (6)

A solution of 0.170 g (1 mmol, 1 eq.) (*R*,*R*)-*N*,*N*,*N*',*N*'-tetramethylcyclohexyldiamine in 3 mL dry *n*-pentane was cooled to −78 °C. At this temperature, 0.63 mL (1 mmol, 1 eq.) of a 1.6 M solution of methyllithium in diethylether was added. The mixture was slowly warmed to room temperature and subsequently stored at −30 °C. After two days, colorless crystals of (MeLi · (*R*,*R*)-TMCDA)$_2$ (**6**) were obtained which were subjected to single crystal X-ray analysis. The structure is shown below.

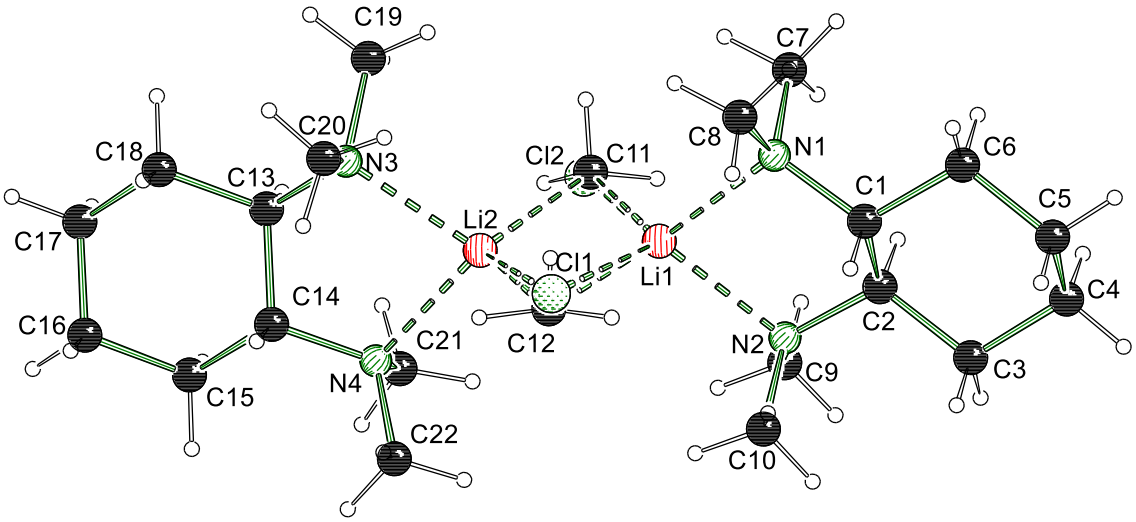

Figure S1: Molecular structure of (MeLi · (*R*,*R*)-TMCDA)$_2$ (**6**) in the crystal. Selected bond lengths [Å] and angles [°]: Li1-C11 2.181(14), Li1-C12 2.209(15), Li1-Cl1 2.27(4), Li1-Cl2 2.38(3), Li2-C11 2.215(18), Li2-C12 2.199(13), Li2-Cl1 2.35(3), Li2-Cl22.28(4).

Crystallization of (LiCl · 2 thf)$_2$ (7)

To a solution of 0.21 mL (1 mmol, 1 eq.) *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (pmdta) in 3 mL dry *n*-pentane, 3.75 mL (6 mmol, 6 eq.) of a 1.6 M solution of methyllithium in diethylether was added at 0 °C. After warming to room temperature, several amounts of LiCl (see Table S1) were added. To achieve solution of the salt, 2 mL of thf were added each. Since no crystallization appeared upon cooling to 4 °C and storing for 48 h, the mixtures were stored at –80 °C. After three days, colorless crystals of (LiCl · 2 thf)$_2$ (**7**) were obtained, the structure of which is shown below.

Table S1: Amounts of LiCl added to pmdta-stabilized methyllithium.

Entry	m_{LiCl} [g]	n_{LiCl} [mmol]	eq_{LiCl}
1	0.021	0.5	0.5
2	0.042	1.0	1.0
3	0.127	3.0	3.0
4	0.254	6.0	6.0

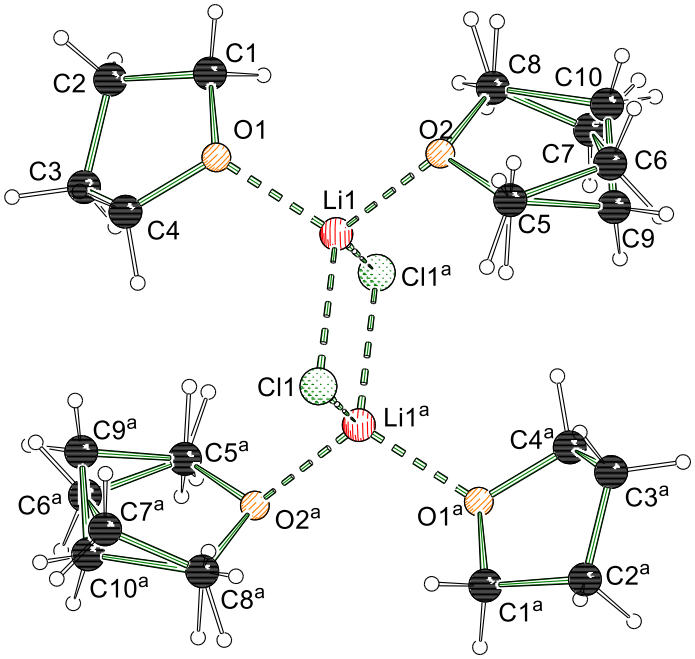

Figure S2: Molecular structure of $(LiCl \cdot 2\ thf)_2$ (**7**) in the crystal; symmetry code [a]= 1–x,1–y,1–z. Selected bond lengths [Å] and angles [°]: Li1-Cl1 2.313(4), Li1-Cl1[a] 2.345(4), Li1-O1 1.939(4), Li1-O2 1.959(4), Li1-Cl1-Li1[a] 77.17(16), Cl1-Li1-Cl1[a] 102.83(16), O1-Li1-O2 107.3(2).

C. X-Ray Crystallographic Analyses

Data collection was conducted on a Bruker *D8 Venture* four-circle diffractometer by *Bruker AXS GmbH* using a *PHOTON100* CMOS area detector by *Bruker AXS GmbH*. X-ray radiation was generated by microfocus source *IμS* Mo and Cu, respectively, by *Incoatec GmbH* with *HELIOS* mirror optics and a single-hole collimator by *Bruker AXS GmbH*.

For data collection, the programs *Apex 3 Suite* (v.2017.3-0) with the integrated programs *SAINT* (integration) and *SADABS* (absorption correction) by *Bruker AXS GmbH* were used. Using *Olex²*,[§1] the structures were solved with the *ShelXT*[§2] structure solution program using Intrinsic Phasing and refined with the *XL*[§3] refinement package using Least Squares minimization.

Crystallographic data have been deposited at the CCDC (Cambridge Crystallographic Data Centre). These data can be obtained free of charge from the CCDC at www: http://www.ccsc.cam.ac.uk. CCDC deposition numbers are 2021306 (**4**), 2021308 (**5**), 2033358 (**6**), 2021310 (**7**).

Table S2: Crystal data and structure refinement for compounds **4**–**7**.

Compound	**4**	**5**	**6**	**7**
CCDC	2021306	2021308	2033358	2021310
Empirical formula	$C_{27.72}H_{73.16}Cl_{0.28}Li_6N_6O$	$C_{11.88}H_{31.63}Cl_{0.12}Li_3N_3$	$C_{10.9}H_{24.7}Cl_{0.1}LiN_2$	$C_{16}H_{32}Cl_2Li_2O_4$
Formula weight	558.61	241.72	194.16	373.19
Temperature/K	100	100	100	100
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*	$P2_1/n$	$P2_1/n$
a/Å	37.719(2)	19.9942(6)	8.3118(6)	9.4887(17)
b/Å	9.9975(6)	11.0399(3)	14.2665(9)	11.075(3)
c/Å	27.5561(14)	17.1245(5)	11.2840(8)	9.7615(19)
α/°	90	90	90	90
β/°	129.9150(10)	110.5060(10)	106.848(2)	95.203(10)
γ/°	90	90	90	90
Volume/Å^3	7970.1(8)	3540.44(18)	1280.63(15)	1021.6(4)
Z	8	8	4	2
ρ_{calc}g/cm^3	0.931	0.907	1.007	1.213
μ/mm^{-1}	0.072	0.540	0.077	0.332
F(000)	2498.0	1080.0	435.0	400.0
Crystal size/mm^3	0.206 x 0.167 x 0.087	0.273 x 0.127 x 0.085	0.286 x 0.271 x 0.110	0.508 × 0.703 × 0.874
Radiation	MoKα (λ = 0.71073 Å)	CuKα (λ = 1.54178 Å)	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073 Å)
2Θ range for data collection/°	4.31 to 52	9.30 to 158.46	4.73 to 56	5.576 to 56
Index ranges	–46 ≤ h ≤ 46 –12 ≤ k ≤ 12 –33 ≤ l ≤ 33	–24 ≤ h ≤ 25 –13 ≤ k ≤ 9 –21 ≤ l ≤ 20	–10 ≤ h ≤ 10 –18 ≤ k ≤ 18 –14 ≤ l ≤ 14	–12 ≤ h ≤ 12 –14 ≤ k ≤ 14 –12 ≤ l ≤ 11
Reflections collected	32960	13246	26849	9271
Independent reflections	7820 [R_{int} = 0.0405, R_{sigma} = 0.0414]	3667 [R_{int} = 0.0373, R_{sigma} = 0.0346]	6141 [R_{int} = 0.0243, R_{sigma} = 0.0228]	2470 [R_{int} = 0.0275, R_{sigma} = 0.0284]
Data/restraints/parameters	7820/0/486	3667/0/227	6141/19/299	2470/0/128
Goodness-of-fit on F^2	1.068	1.042	1.060	1.111
Final R indexes [I≥2σ (I)]	R_1 = 0.0596 wR_2 = 0.1457	R_1 = 0.0424 wR_2 = 0.1108	R_1 = 0.0400 wR_2 = 0.1077	R_1 = 0.0381 wR_2 = 0.0836
Final R indexes [all data]	R_1 = 0.0946 wR_2 = 0.1668	R_1 = 0.0517 wR_2 = 0.1175	R_1 = 0.0414 wR_2 = 0.1087	R_1 = 0.0477 wR_2 = 0.0879
Largest diff. peak/hole / e Å^{-3}	0.62/–0.21	0.20/–0.14	0.21/–0.23	0.22/–0.28
Flack Parameter	-	-	–0.01(5)	-

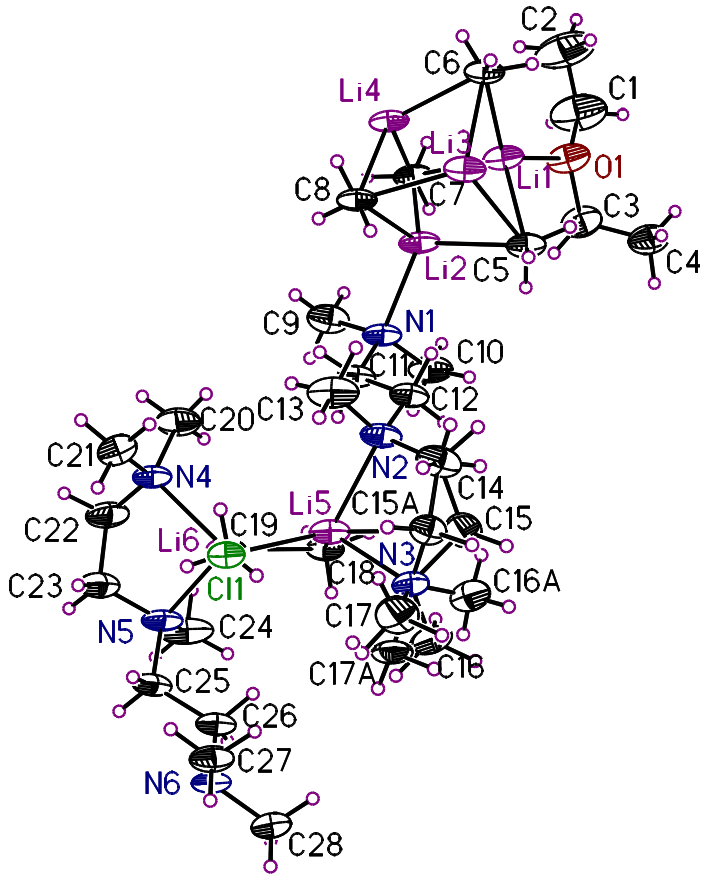

Figure S3: Ortep[§4] plot and numbering scheme of compound **4**. Selected bond lengths [Å] and angles [°]: Li1-O1 2.031(4), Li2-N1 2.128(3), Li5-N2 2.210(4), Li5-N3 2.100(4), C18-Li5 2.188(4), C18-Li6 2.195(5), C19-Li5 2.21(3), C19-Li6 2.21(2), Cl1-Li5 2.317(17), Cl1-Li6 2.341(14), N2-Li5-N3 85.81(15), N4-Li6-N5 84.94(15).

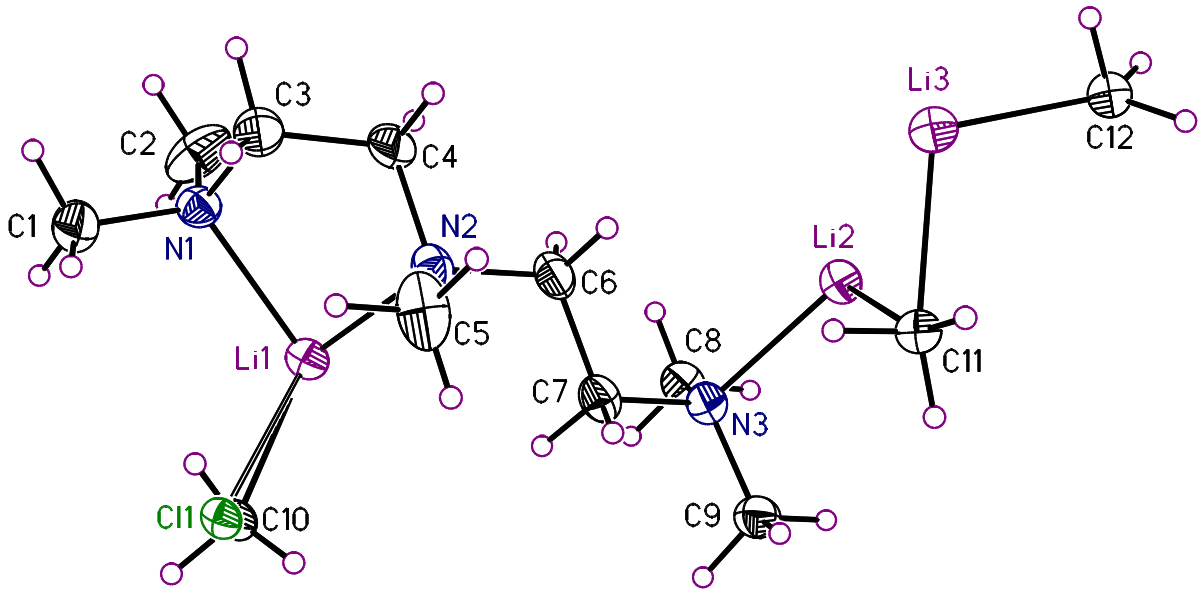

Figure S4: Ortep[§4] plot and numbering scheme of compound **5**. Selected bond lengths [Å] and angles [°]: N1-Li1 2.186(2), N2-Li1 2.180(2), C10-Li1 2.183(14), Cl1-Li1 2.26(3), N3-Li2 2.166(2), C11-Li2 2.231(2), C11-Li3 2.259(2), C12-Li3 2.243(2), Li2-Li3 2.530(3), N1-Li1-N2 84.57(7), Li2-C11-Li3 68.60(7).

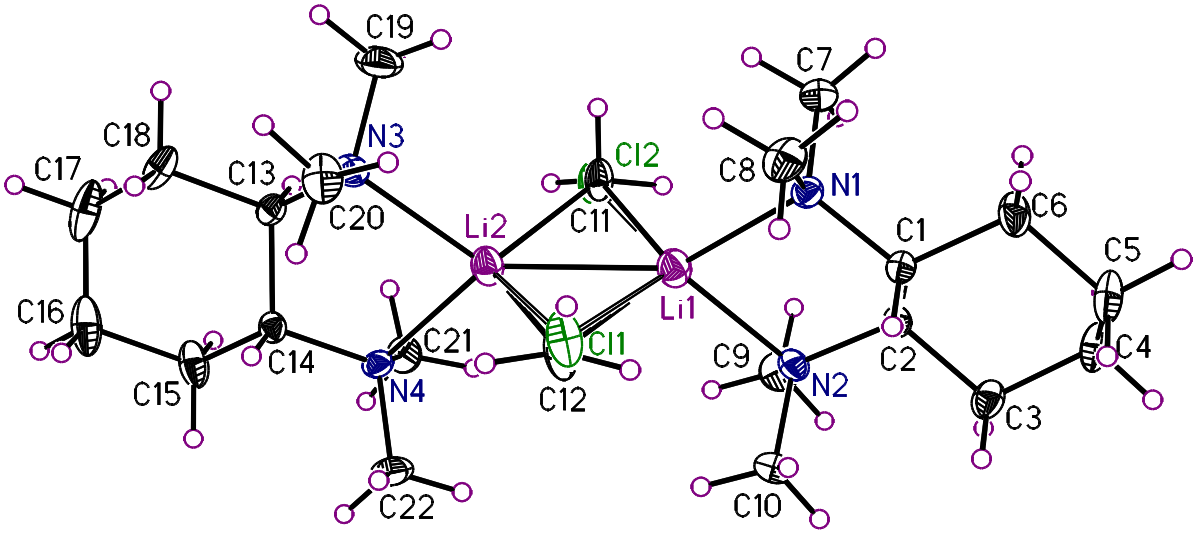

Figure S4: Ortep[§4] plot and numbering scheme of compound **6**. Selected bond lengths [Å] and angles [°]: Li1-C11 2.181(14), Li1-C12 2.209(15), Li1-Cl1 2.27(4), Li1-Cl2 2.38(3), Li2-C11 2.215(18), Li2-C12 2.199(13), Li2-Cl1 2.35(3), Li2-Cl22.28(4).

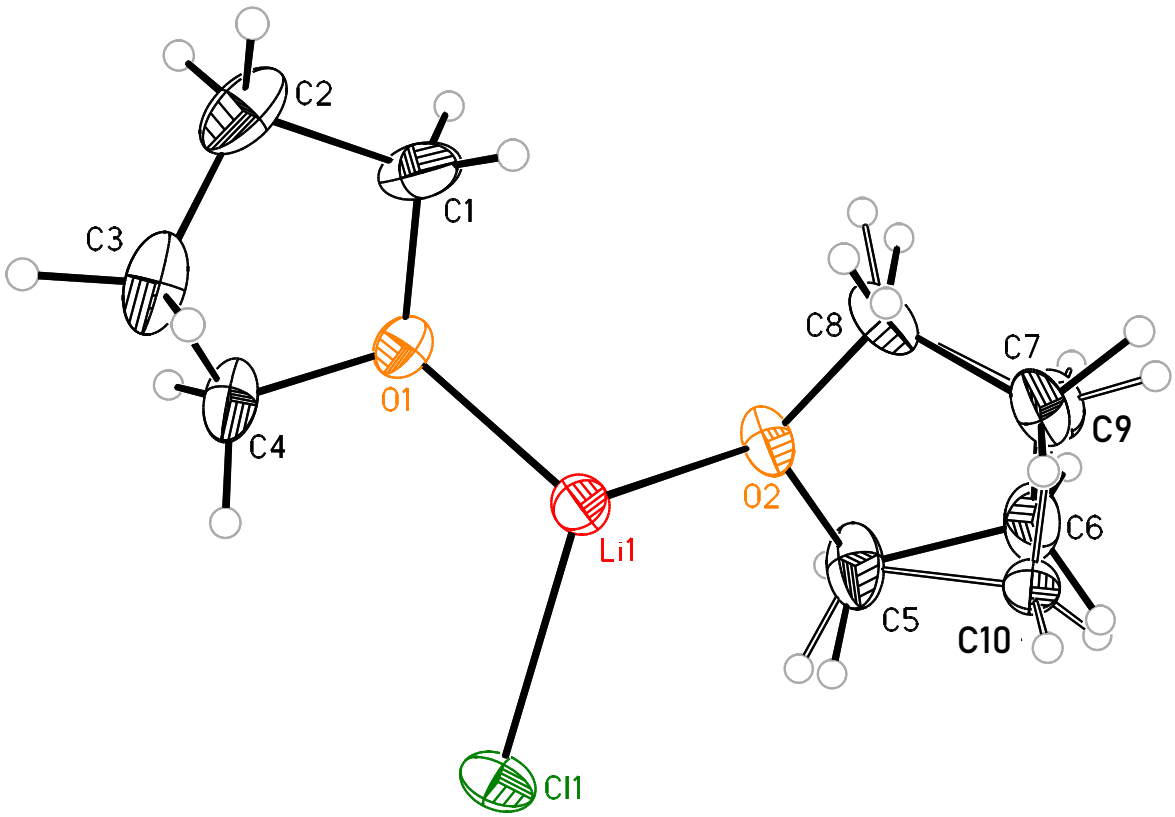

Figure S5: Ortep[§4] plot and numbering scheme of compound **7**. Selected bond lengths [Å] and angles [°]: Li1-Cl1 2.313(3), Li1-O1 1.941(3), Li1-O2 1.959(3), O1-Li1-O2 107.28(13), O1-Li1-Cl1 112.60(12), O2-Li1-Cl1 114.12(12).

D. Quantum chemical calculations

Optimization and additional harmonic vibrational frequency analysis were performed with the software package Gaussian 16.[§5] The GJF input files were created with the program GaussView 5.0. The ground state structures were optimized without symmetry restrictions. The vibrational frequency analyses showed no imaginary frequency in the harmonical approximation for the ground state. The calculated standard orientations of the optimized structures can be found in Tables S3 and S4. The visualization of the optimized structures was performed with the program Molekel V. 4.3[§6] (Figures S6 and S7).

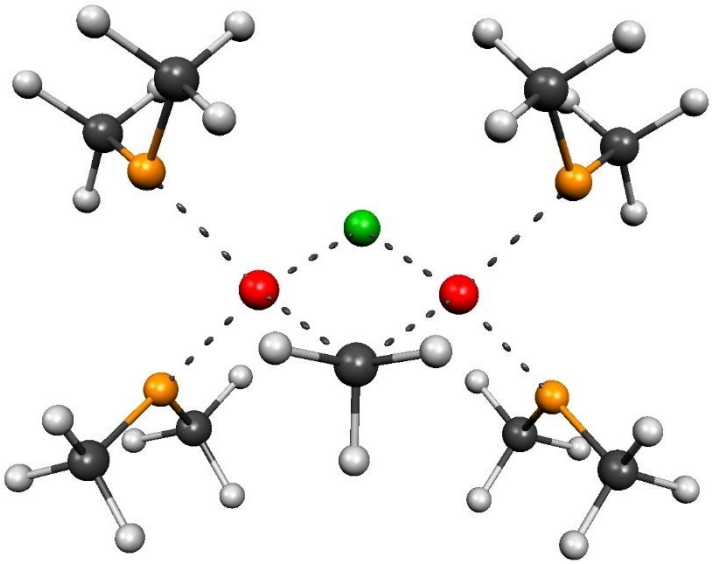

Figure S6: Molekel[§6] plot of the fictive mixed dimer [B3LYP/6-31+G(d)].

Table S3: Standard orientation of the fictive mixed dimer [B3LYP/6-31+G(d)].

Atomic symbol	x	y	z
O	-2.596170	1.529700	0.257904
O	-2.591215	-1.516257	0.080671
C	-2.106277	2.777129	0.737255
H	-1.518966	2.565505	1.632634
H	-2.942070	3.446043	0.989535
C	-2.326065	-2.592289	-0.815842
H	-1.747004	-2.176596	-1.642255
H	-3.268451	-3.020955	-1.186757
C	-3.301420	-1.918553	1.246175
H	-4.273107	-2.355813	0.973741
H	-3.459336	-1.023673	1.851460
C	-3.365689	1.664047	-0.936147
H	-4.230950	2.319237	-0.758905
H	-3.708336	0.663608	-1.205163
Li	-1.264316	0.001878	0.234409
O	2.592587	-1.514509	0.081382

O	2.594344	1.531980	0.258660
C	2.330416	-2.589789	-0.816889
H	1.751228	-2.174098	-1.643218
H	3.273987	-3.016021	-1.187600
C	2.101388	2.778815	0.736470
H	1.513469	2.566702	1.631328
H	2.935563	3.449584	0.989180
C	3.364903	1.666975	-0.934635
H	4.228597	2.324116	-0.756973
H	3.709971	0.667044	-1.202463
C	3.302595	-1.916947	1.246953
H	4.275533	-2.351587	0.974795
H	3.457875	-1.022640	1.853762
Li	1.264527	0.002367	0.234644
H	2.722549	-2.651956	1.822422
H	1.749644	-3.378302	-0.316415
H	2.748096	2.069126	-1.748699
H	1.463881	3.259065	-0.019204
H	-1.744132	-3.378906	-0.313737
H	-2.720255	-2.651360	1.823317
H	-1.468868	3.259280	-0.017297
H	-2.748821	2.068146	-1.749197
C	-0.000083	-0.161665	1.982048
H	0.000968	-1.224770	2.296661
H	0.867017	0.279521	2.514933
H	-0.868143	0.277724	2.514856
Cl	0.000261	0.159153	-1.742892

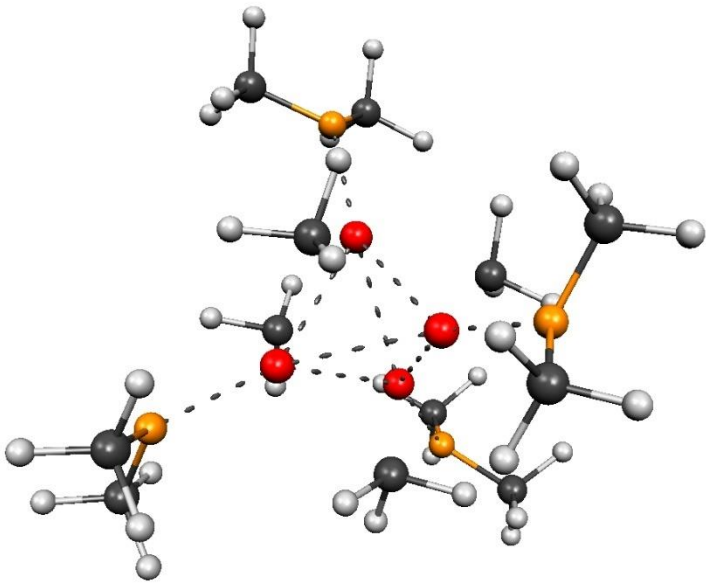

Figure S7: Molekel[§6] plot of the fictive dme-stabilized methyllithium tetramer [B3LYP/6-31+G(d)].

Table S4: Standard orientation of the fictive dme-stabilized methyllithium tetramer [B3LYP/6-31+G(d)].

Atomic symbol	x	y	z
C	1.7383813	0.543318	1.297500
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C	0.543318	-1.738313	-1.297500
C	-0.543318	1.738313	-1.297500
H	2.454954	-0.271599	1.526346
H	1.450874	0.926603	2.296856
H	2.379999	1.348530	0.888317
H	-2.379999	-1.348530	0.888317
H	-2.454954	0.271599	1.526346
H	-1.450874	-0.926603	2.296856
H	1.348530	-2.379999	-0.888317
H	0.926603	-1.450874	-2.296856
H	-0.271599	-2.454954	-1.526346
H	-0.926603	1.450874	-2.296856
H	0.271599	2.454954	-1.526346
H	-1.348530	2.379999	-0.888317
C	2.604558	1.065845	-3.402035
H	1.650949	1.585575	-3.514664
H	3.418352	1.704560	-3.774343
H	2.585593	0.128716	-3.976916
C	3.995874	0.131315	-1.717502
H	4.854138	0.735090	-2.045359
H	4.033025	0.000000	-0.634515
H	4.028595	-0.850317	-2.210864
C	-1.065845	2.604558	3.402035
H	-0.128716	2.585593	3.976916
H	-1.704560	3.418352	3.774343
H	-1.585575	1.650949	3.514664
C	-0.131315	3.995874	1.717502
H	0.850317	4.028595	2.210864
H	0.000000	4.033025	0.634515
H	-0.735090	4.854138	2.045359
C	-3.995874	-0.131315	-1.717502
H	-4.028595	0.850317	-2.210864
H	-4.854138	-0.735090	-2.045359
H	-4.033025	0.000000	-0.634515
C	-2.604558	-1.065845	-3.402035
H	-2.585593	-0.128716	-3.976916
H	-1.650949	-1.585575	-3.514664
H	-3.418352	-1.704560	-3.774343
C	0.131315	-3.995874	1.717502
H	0.735090	-4.854138	2.045359
H	-0.850317	-4.028595	2.210864
H	0.000000	-4.033025	0.634515
C	1.065845	-2.604558	3.402035
H	1.704560	-3.418352	3.774343
H	1.585575	-1.650949	3.514664
H	0.128716	-2.585593	3.976916
Li	-1.174037	-0.408316	-0.863568
Li	-0.408316	1.174037	0.863568

Li	1.174037	0.408316	-0.863568
Li	0.408316	-1.174037	0.863568
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O	-0.803671	2.775318	2.013717
O	2.775318	0.803671	-2.013717

E. References

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[§5] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[§6] a) P. Flükiger, H. P. Lüthi, S. Portmann, J. Weber, Swiss Center for Scientific Computing, Molekel 4.3, Manno (Switzerland), *2000–2002*; b) S. Portmann, H. P. Lüthi, *CHIMIA*, 2000, **54**, 766.