Supplementary Material (ESI) for Chemical Communications

Supporting Information: *iso-Propyllithium Diamine Adducts: From a Non Symmetric Aggregate to Monomeric i-PrLi·(1R,2R)-N,N,N',N'-Tetraethylcyclohexane-1,2-diamine*

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Experimental Details

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried over sodium and distilled prior to use. *N,N,N',N'*-Tetramethylethylenediamine (**1**) and *N,N,N',N'*-tetraethylethylenediamine (**2**) were obtained from Aldrich, (1*R*,2*R*)-*N,N,N',N'*-tetraethylcyclohexan-1,2-diamine [(*R,R*)-TECDA, (**3**)] was synthesized starting from a cis/trans mixture of cyclohexan-1,2-diamine (Aldrich), which was first resolved as the tartrate salt according to *E. N. Jacobsen,*[1] enantiomericall pure (1*R*,2*R*)-cyclohexane-1,2-diamine released with KOH and then transformed into compound **3**:[2]

Synthesis of (1*R*,2*R*)-*N*,*N*,*N'*,*N'*-tetraethylcyclohexan-1,2-diamine (3)

5.25 g (46.0 mmol) (1*R*,2*R*)-Cyclohexane-1,2-diamine was solved in 240 ml toluene and wurden 16.1 g (0.67 mol) NaH (60 % solution of NaH in oil) therin suspended. After carefull addition of 50 ml (42.4 g, 0.28 mol) diethylsulfat, the mixture was stirred for 16 h under reflux and two days at room temperature. The reaction was then quenched with 80 ml methanol, 23 ml 25 %-iger NH_3 and 400 ml 2M NaOH and afterwards extracted with diethylether (5 x 500 ml). After drying the combined organic fractions over Na_2SO_4, the solvent was removed and the oily residue distilled in vacuo to give 9.46 g (43.4 mmol; 94 %) a colourless liquid (65°C, $6 \cdot 10^{-2}$ bar).

^{1}H-NMR: (500.1 MHz, $CDCl_3$, CD Cl_3): δ = 0.99 (t, 12H; $^3J_{HH}$ = 7.1 Hz C*H*$_3$), 1.02-1.11 (m, 4H; *CH*$_2$), 1.64-1.66 (m, 2H; C*H*$_2$CH$_2$CHN), 1.77-1.80 (m, 2H; C*H*$_2$CHN), 2.40-2.47 (m, 4H; C*H*$_2$N), 2.56-2.60 (m, 2H; C*H*N), 2.58-2.65 (m, 4H; C*H*$_2$N).

{^{1}H}^{13}C-NMR (125.8 MHz, $CDCl_3$, $CDCl_3$): δ = 14.9 (*C*H$_3$), 26.3 (*C*H$_2$CH$_2$CHN), 27.6 (*C*H$_2$CH$_2$N), 43.8 (*C*H$_2$N), 60.5 (*C*HN).

HCN analysis: found: C 73.68 H 13.22 N 12.56
calculated: C 74.27 H 13.36 N 12.37

GC-MS t_R = 6.108 min [80 °C (2 min) – 10 °C·min^{-1} – 280 °C (5min)]; m/z (%): 226 (20) (M^+), 197 (15) (M^+ – C_2H_5), 112 (62) {[$(C_6H_8(NH_2)_2]^+$}, 86 (100) {[$N(C_2H_5)_2CH_2]^+$}, 58 (50) {[$HN(C_2H_5)CH_2]^+$}, 29 (45) [$(C_2H_5)^+$].

Synthesis of (*i*-PrLi·TMEDA)$_2$ (4)

120 mg (1.03 mmol) TMEDA were dissolved in 5 ml *n*-pentane and cooled to –70 °C. At this temperature 1.5 ml (1.05 mmol) *i*-PrLi (0.7 M in *n*-pentane) were carefully added. Cooling to –78 °C gave (*i*-PrLi·TMEDA)$_2$ as colourless needles after 4 hours. At higher temperatures decomposition of the ligand was observed.

Synthesis of [(*i*-PrLi)$_3$·(TEEDA)$_2$] (5)

170 mg (1.0 mmol) *N*,*N*,*N'*,*N'*-Tetraethylethylenediamine (TEEDA) were dissolved in 3 ml *n*-pentane and the mixture was carefully covered with 1.43 ml (1.0 mmol) *i*-PrLi (0.7 M Lösung in *n*-pentane) at

–50 °C. Cooling to –78 °C yielded colourless crystals of [(*i*-PrLi)$_3$·(TEEDA)$_2$] after ten days, which were characterised by cryo-x-ray analysis. At higher temperatures decomposition of the ligand was observed.

Synthesis of *i*-PrLi·(*R,R*)- TECDA (6)

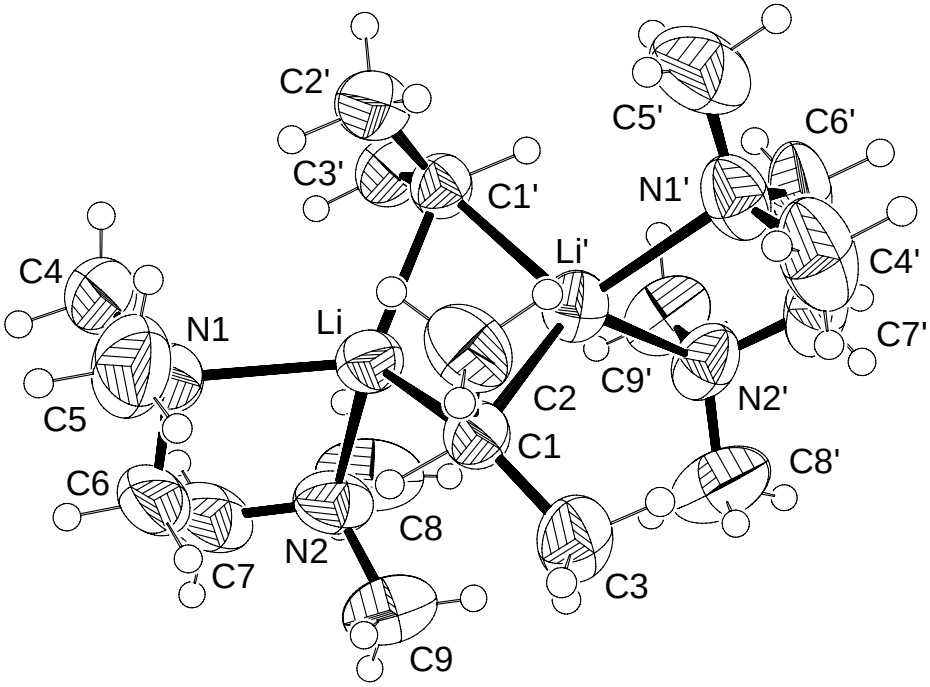
180 mg (0.80 mmol) (*R,R*)-TECDA were dissolved in 4 ml *n*-pentane, the reaction mixture cooled to –65 °C and at this temperature 1.1 ml (0.77 mmol) *i*-PrLi (0.7 M in *n*-pentan) carefully added. Cooling to –78 °C yielded colorless crystals of the monomeric compound, which was characterised by cryo-x-ray analysis. At higher temperatures decomposition of the ligand was observed.

Crystal Structure Determination of Compounds 4, 5 and 6

Data collection of all compounds was conducted with a Bruker APEX-CCD (D8 three-circle goniometer) (Bruker AXS), cell determination and –refinement with Smart version 5.622 (Bruker AXS, 2001), integration with SaintPlus version 6.02 (Bruker AXS, 1999); empirical absorption correction with Sadabs version 2.01 (Bruker AXS, 1999).

The crystals of all three compounds were mounted in an inert oil (perfluoropolyalkylether) at –60 °C (N_2 stream), using the X-TEMP 2 device (Kottke, T.; Stalke, D. *J. Appl. Cryst.* **1993**, *26*, 615. Kottke, T.; Lagow, R. J.; Stalke, D. *J. Appl. Cryst.* **1996**, *29*, 615. Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171.), the crystal structure determinations were effected at and at –100 °C (type of radiation: Mo-Kα, λ = 0.71073 Å). The structures were solved applying direct and fourier methods, using SHELXS-90 (G. M. Sheldrick, University of Göttingen 1990) and SHELXL-97 (G. M. Sheldrick, SHELXL97, University of Göttingen 1997). Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 681928 [compound **4**], CCDC CCDC 681929 [compound **5**] and CCDC 681930 [compound **6**]. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

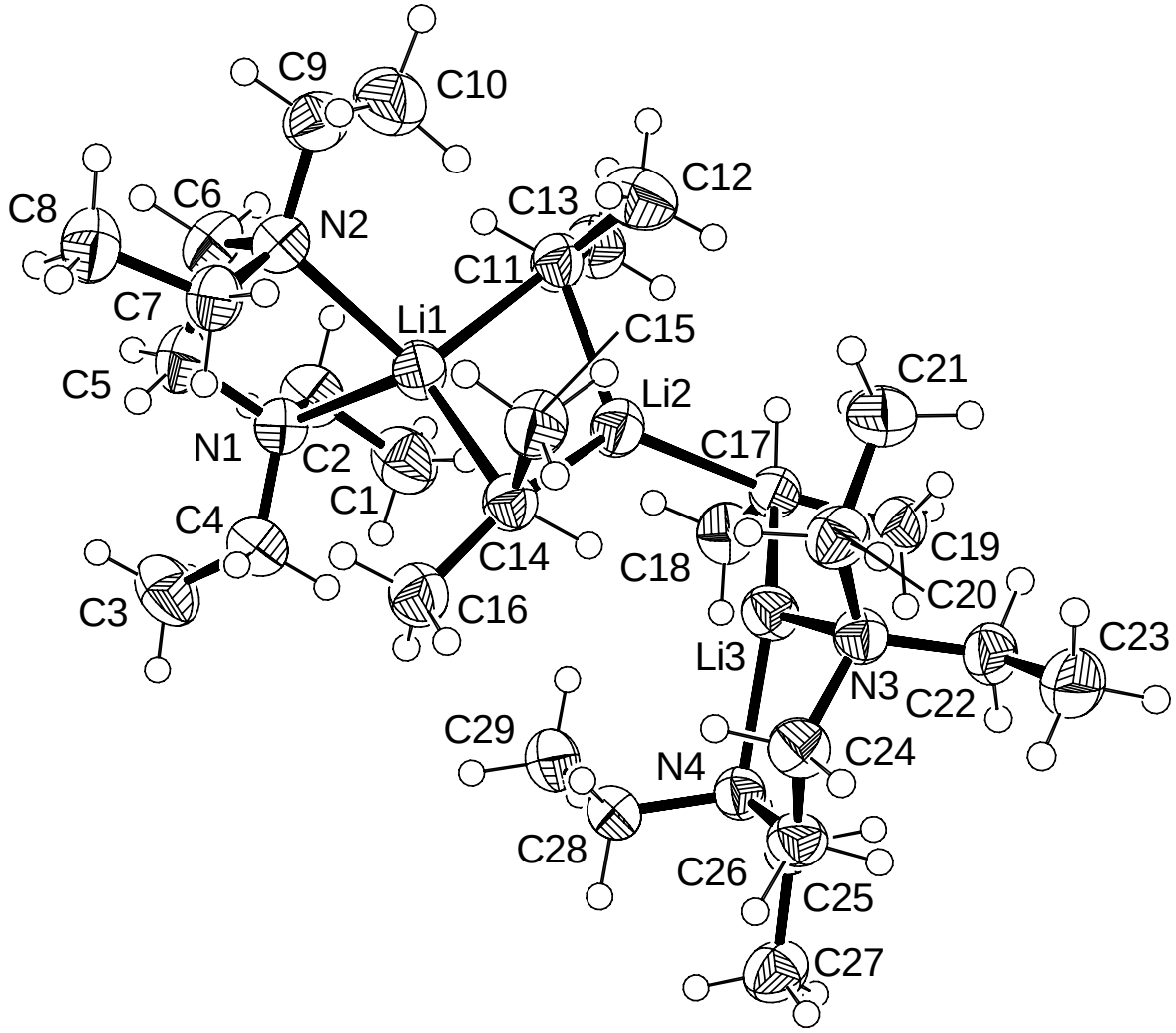
Crystallographic data for compound 4 (colorless, from *n*-pentane, 0.40 × 0.40 × 0.10 mm^3): $C_9H_{23}LiN_2$, M = 166.23, orthorhombic, space group $Fdd2$ (no. 43), a = 16.652(18), b = 33.27(3), c = 8.570(8), V = 4748 (8) $Å^3$, Z = 8, D_c = 0.930 $Mg·m^{-3}$, μ = 0.054 mm^{-1}. 6084 reflections measured with 2θ in the range 2.45-24.99°, 1119 unique reflections; 903 with $I > 2\sigma(I)$; refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-97); anisotropic thermal parameters for all non-H atoms in the final cycles; the H atoms were refined on a riding model in their ideal geometric positions, except for H(1), which was refined independently; $R1$ = 0.0664 [$I > 2\sigma(I)$], $wR2(F_o^2)$ = 0.1695 (all data).



ORTEP plot of **4** at 50 % probability level.

Crystallographic data for compound 5 (colorless needles from *n*-pentane, 0.40 × 0.20 × 0.20 mm^3): $C_{29}H_{69}L_3N_4$, M = 494.7, monoclinic, space group $P2_1/n$ (no. 14), a = 9.986 (4), b = 15.741(6), c = 21.549(9) Å, β = 95.459(7)° V = 3372(2) $Å^3$, Z = 4, D_c = 0.974 $Mg·m^{-3}$, μ = 0.055 mm^{-1}. 38982 reflections measured with 2θ in the range 1.60-25.00°, 5938 unique reflections; 4307 with $I > 2\sigma(I)$; refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-97); anisotropic thermal parameters for all non-H atoms in the final cycles; the H atoms were refined on a riding model in their

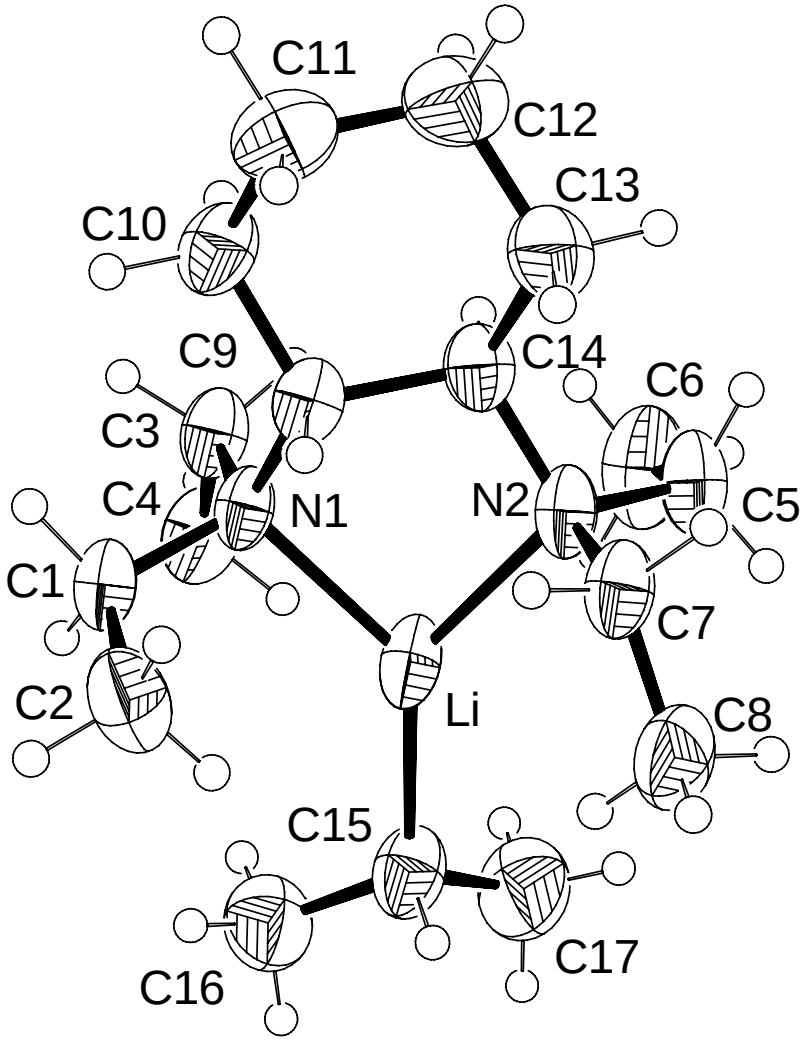
ideal geometric positions, except for H(11), H(14), and H(17), which were refined independently; $R1$ = 0.0662 [$I > 2\sigma(I)$], $wR2(F_o^2)$ = 0.1668 (all data).



ORTEP plot of **5** at 50 % probability level.

Crystallographic data for compound 6 (colorless needles from *n*-pentane, 0.40 × 0.20 × 0.20 mm^3): $C_{17}H_{37}LiN_2$, M = 276.43, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 7.798(3), b = 14.839(6), c = 16.313(6) Å, V = 1887.7(12) Å^3, Z = 4, D_c = 0.973 Mg·m^{-3}, μ = 0.055 mm^{-1}. 14886 reflections measured with 2θ in the range 1.86-25.00°, 1923 unique reflections; 1556 with $I > 2\sigma(I)$; refinement by full-matrix least-squares methods (based on F_o^2, SHELXL-97); anisotropic thermal parameters for all non-H atoms in the final cycles; the H atoms were refined on a riding model in their ideal geometric positions,

except for H(15), which was refined independently; $R1 = 0.0525$ [$I > 2\sigma(I)$], $wR2(F_o^2) = 0.1216$ (all data), absolute structure (Flack-) parameter 3(4). The refinement of the correct stereoisomer is unambiguous due to the fixed absolute configuration at C(9), and C(14) of the (*R*,*R*)-TECDA (Flack parameter not significant).



ORTEP plot of **6** at 50 % probability level.

Computational Studies

All calculations were done without symmetry restrictions [except of (*i*-PrLi)$_6$]and modelled after the molecular structures in the crystal. Starting coordinates were obtained with Chem3DUltra 10.0, optimization was performed with Gaussian 03 Revision B.04 at the B3LYP/6-31+G(d) level.[4] Harmonic vibrational frequency analyses showed no imaginary frequencies for all stationary points. Table 1 lists the total (SCF) and zero-point energies (ZPE) of all compounds.

Table 1 Results from Theoretical Studies.

Compound	method/basis	Min./TS	SCF [Hartree]	ZPE [Hartree]
(*i*-PrLi)$_6$	B3LYP/6-31+G(d)	Global Min.	–756.439578	–755.876686
TEEDA (**2**)	B3LYP/6-1+G(d)	Global Min.	–505,012394	–504.674652
[(*i*-PrLi)$_3$·(TEEDA)$_2$] (**5**)	B3LYP/6-31+G(d)	Global Min.	–1388.253929	–1387.294923
(*i*-PrLi·TEEDA)$_2$	B3LYP/6-31+G(d)	Global Min.	–1262.175089	–1261.309030
i-PrLi·TEEDA	B3LYP/6-31+G(d)	Global Min.	–631.084356	–630.652840
i-PrLi·(*R,R*)-TECDA	B3LYP/6-31+G(d)	Global Min.	–826.442215	–825.888121

For polar compounds entropy is crucially influenced by solvent effects. Additionaly calculated Gibbs free energies seem in such large systems to be less reliable due to very low frequencies, where the harmonic oscillator model produces significant deviations.[3] Thus, enthalpy values are discussed. Corrections for basis set superposition errors (BSSE) are not included.

Table 2 Standard Orientation of (*i*-PrLi)$_6$ [global minimum, B3LYP/6-31+G(d)].

Atomic symbol	x	y	z
H	-0.1630230135	-0.0254107751	0.0407116569
H	-0.1739806097	0.1713745157	2.4824244906
H	1.3178526867	0.0745756811	-0.9232380462
C	0.9078389318	-0.295648141	0.026996067
H	0.9042580905	-1.4008402969	-0.0381892497
H	1.5636773109	1.3462618897	1.1717109746
C	0.8878927047	-0.1316431147	2.5324204085
H	3.0460293989	2.3090368804	-1.2054648597

C	1.6822112192	0.2445348113	1.2566904812
H	0.8812537217	-1.2173328831	2.7133523749
H	1.2884926832	0.3405804239	3.4431132076
H	3.9874565901	3.8061609186	-1.2640725362
H	3.2199317571	3.3325716104	0.2275153197
C	3.7657207066	2.9202710889	-0.642713602
H	3.6796776416	-0.1208425314	-2.5576115304
H	2.547111554	2.3806948014	3.4472490192
H	1.7013998168	-3.1239304769	1.4950353984
H	4.2239635417	-1.5465833364	-3.4536426339
H	3.2140684275	-2.1831303734	-1.2869936801
Li	2.9502480677	-1.3516662063	0.4803120165
Li	3.52769596	1.4521551797	1.1733579079
H	3.7675642318	3.3477285221	2.610104622
C	4.3899768264	-0.9593721431	-2.5329816226
C	3.6218203808	2.6172748919	3.4214721801
C	2.6869651173	-3.5808929431	1.6765219865
H	3.8310129632	3.16723028	4.3573042937
H	3.0199468484	-4.0086475542	0.7186685619
H	2.4974112057	-4.4431444256	2.3416291617
C	4.2591612622	-1.807990323	-1.2428583576
C	5.0365312142	2.1253606532	-0.2472819812
Li	3.4054363534	-0.427705679	2.6234086022
H	5.3989271921	-0.5252842329	-2.6704571946
H	5.4682491067	1.8266315946	-1.2267221259
H	3.3560608599	0.0662142528	4.6856649545
H	3.2867389453	-2.2857015747	3.2419298858
H	6.2575768463	3.9840744455	-0.3264214019
H	4.9239750888	-3.6263002601	-2.3420965338
H	5.7350412036	3.5495775741	1.296539198
C	3.7184568378	-2.5844306333	2.2624897411
Li	5.3495516985	-0.0313643011	-0.6082008423
C	4.4958267898	1.3489203429	3.2580661175
C	6.0680229347	3.121822963	0.3386857734
C	5.1331676712	-3.076344872	-1.4062644202
C	4.3650112256	0.500302163	4.5481893825
H	4.9874238202	-3.8067985022	-0.5948968621
H	4.5310245103	1.0875133563	5.4688503938
H	5.5409196245	1.7240603933	3.30220144
Li	5.227292092	-1.9112251599	0.841849852
Li	5.8047399843	0.8925962262	1.5348957434
H	7.0535882352	2.6648604968	0.5201723615
H	6.2078764979	-2.8397647815	-1.4320412593
H	5.0753104103	-0.3382274487	4.5728192902
C	4.9892673454	-3.379341069	2.6579213619

H	4.7675314618	-4.2652308987	3.2792802961
H	5.5350562949	-3.7916415905	1.7876924402
H	7.4664953688	-0.799650404	-1.4279054477
H	7.8737343303	0.758262903	-0.698144615
H	5.7089586531	-2.7681068605	3.2206726196
C	7.0727768328	-0.7036047914	0.7585172787
C	7.8670953473	-0.3274268654	-0.5172126486
H	7.1913107411	-1.8053318699	0.8434967853
H	7.8507299615	0.9417703168	2.0533970096
H	7.4371353653	-0.5336456612	2.9384458061
C	7.8471491201	-0.1634218392	1.9882116929
H	8.9289686616	-0.6304444958	-0.4672167307
H	8.9180110654	-0.433659205	1.974496103

Table 3 Standard Orientation of TEEDA (**2**) [global minimum, B3LYP/6-31+G(d)].

Atomic Symbol	x	y	z
C	2.7513506749	0.7278695562	0.7037699901
N	1.5196476154	0.1547526985	0.1546534773
C	3.5956771967	1.4908726138	-0.3196927657
C	1.7173238697	-0.7908495405	-0.9515372952
H	3.3817309858	-0.0374442239	1.2016847113
H	2.4482223057	1.4277351588	1.4933534992
C	0.6541409042	-0.3321544365	1.2260407967
C	2.478996119	-2.0916624128	-0.632405148
H	2.2403367683	-0.2568818587	-1.7526596349
H	0.5127986341	0.4999008465	1.9272848936
H	1.1284858477	-1.1402674028	1.8213558977
C	-0.718550399	-0.8738325614	0.7922119131
H	-0.5911492226	-1.8570776422	0.3218839221
N	-1.4636014374	-0.0418869259	-0.1489035725
H	-1.2769008885	-1.0564593481	1.7337048657
H	0.7266477989	-1.0256464761	-1.3525590987
C	-2.6297563756	-0.7373260115	-0.7060714209
C	-3.8057752682	-1.0254258311	0.2481357868
H	-2.2661497469	-1.6865786929	-1.1217309829
H	-2.9960476768	-0.1552542026	-1.5590538615
H	-4.2392593751	-0.1028707033	0.6521861982
H	-3.5056163146	-1.6544071469	1.0943040065
H	-4.6003154442	-1.5547139045	-0.2927815408
H	2.9839253982	2.2268905267	-0.8542314773
H	4.0601413174	0.8293637882	-1.0594101382
H	4.4054456593	2.0227723035	0.1940880749

H	1.9748572875	-2.6869039258	0.1384830067
H	3.5011975237	-1.8961865882	-0.2869681164
H	2.5482687472	-2.7113039118	-1.5353886517
C	-1.7233065575	1.3101848046	0.3506016002
H	-0.7563604411	1.7333417301	0.6369423067
H	-2.3519022507	1.3001331346	1.2651049957
C	-2.3530953061	2.2419086686	-0.6879632971
H	-3.3863061709	1.9704315333	-0.9324000727
H	-1.7666713786	2.2372585614	-1.6140625062
H	-2.3697317591	3.2665989403	-0.2979205911

Table 4 Standard Orientation of [(*i*-PrLi)$_3$·(TEEDA)$_2$] (**5**) [global minimum, B3LYP/6-31+G(d)].

Atomic symbol	x	y	z
C	-0.0977698051	-0.1399915086	0.0805351329
C	-0.0622717651	1.3845386142	-0.0135450778
C	-5.9156310945	-3.1898670686	0.0039027048
C	1.1239646226	1.9207606151	2.8272080896
C	-3.4351732772	0.5415244956	-1.8922495008
C	-6.3602592413	-3.0197558376	1.455605497
C	-0.3389902843	1.6655183773	2.4277126238
C	-9.1323258801	-4.4261543427	1.3811383504
C	-3.4979152164	-0.7495748567	2.0655338057
C	-3.6700066922	1.9189114841	-1.2289102384
C	-0.5975208687	3.5524914482	0.8496384503
C	-8.7752023571	-3.0039017592	0.921183984
N	-7.6597293036	-2.318568838	1.6236632271
C	-4.2927317404	2.8543085	-2.2832845524
Li	-3.1283362263	2.0557929206	0.9633044378
C	-4.3431350097	0.5349741527	2.1605494264
Li	-5.1895512104	1.1308368046	0.1277903334
C	-7.915815196	-2.1103303851	3.0657341527
C	-8.3593931139	-0.0889324311	-1.2894242751
C	-1.3517195732	4.4469883777	1.8343142556
C	-4.3217960745	1.0123442737	3.6221642184
C	-7.2735888822	0.8522972447	-0.7194698358
Li	-7.6271888983	-0.2433905579	1.0350938843
N	-2.820287119	4.301721412	1.770053509
C	-9.1037200857	-1.1849740782	3.3445380532
C	-3.3718860527	5.1959109048	0.7240048003
C	-7.8328103792	2.2894711622	-0.729503619
N	-8.9315873881	0.1608248519	2.7469395374
C	-3.4438384675	4.5076958605	3.0973711921

C	-4.8888484732	5.1269335174	0.5708095556
C	-8.2044993231	1.0480123884	3.6924336553
C	-10.2247158696	0.730287304	2.2884755014
C	-3.3130284331	5.9080021835	3.719110362
C	-7.8849520366	2.4336248341	3.1356514493
C	-11.2752031204	1.0296443786	3.3681133119
H	0.2881442027	-0.5611176709	-0.8549014437
H	0.5244485113	-0.5287108637	0.8945033142
H	-1.1178916692	-0.5087050202	0.2184057988
H	0.989345459	1.7197211671	-0.079317341
H	-0.5472343392	1.6916726979	-0.9462336515
H	-4.8858764776	-3.5636607524	-0.0110841565
H	-6.5311293616	-3.908114154	-0.5490028489
H	-5.9324724164	-2.2339634519	-0.5307017046
H	1.8301363392	1.4272992149	2.149798382
H	1.2982441546	1.5203984992	3.8333392493
H	1.3727647687	2.9878957377	2.8513424805
H	-2.8705755297	0.5945434943	-2.8484020675
H	-2.8875129432	-0.1562556123	-1.2415714125
H	-4.3861888716	0.0441188198	-2.1491711844
H	-6.3848461603	-4.0030924351	1.9563805306
H	-5.6136889881	-2.4202123712	1.982422142
H	-0.5514178027	0.596206461	2.4993745801
H	-1.0026501965	2.1396923246	3.1575157626
H	-8.2908511736	-5.1189468318	1.2736568871
H	-9.9529542068	-4.8065690879	0.7614889266
H	-9.4667054044	-4.4601410369	2.4241657816
H	-3.5567696946	-1.2256190865	1.0755601499
H	-2.4326921421	-0.5404392505	2.2427642113
H	-3.7643960311	-1.5284935153	2.8165666734
H	-2.6503811493	2.3291823159	-1.0566215187
H	0.4687897631	3.8436719375	0.8754735672
H	-0.9432930418	3.755274565	-0.1705015148
H	-8.5219876831	-3.0188972444	-0.1416396013
H	-9.6620152147	-2.3669422516	0.9996056005
H	-3.7262527025	2.8803881413	-3.239327742
H	-5.3151381762	2.5469815759	-2.5508126994
H	-4.3664991253	3.8939501201	-1.9342303778
H	-5.3999306272	0.2093597852	1.9828706157
H	-8.0785164875	-3.0633884629	3.5977648027
H	-7.0049368094	-1.6740621434	3.4915111502
H	-7.9651020064	-1.0865139801	-1.5305126951
H	-8.8263117998	0.2988303242	-2.2169491811
H	-9.2137441126	-0.2449011168	-0.5994645117
H	-1.0250132978	4.2272599897	2.8553757969

H	-1.0460781606	5.4895354993	1.6372862414
H	-3.314022659	1.3402032283	3.9252575427
H	-4.602268598	0.2250849632	4.3599680904
H	-4.9896986658	1.8665914923	3.7984696619
H	-6.4757684583	0.8288199447	-1.4830932116
H	-10.0219150265	-1.6274793849	2.9453653068
H	-9.2427651222	-1.1236285715	4.4361901991
H	-2.9120240858	4.9030371955	-0.2251313295
H	-3.0651013186	6.2411447497	0.9137328219
H	-7.0781870743	3.0399078342	-0.4563059576
H	-8.2338373931	2.5955897068	-1.7174889864
H	-8.6639297492	2.4137559434	-0.0163747067
H	-3.0022066534	3.7679978175	3.7733330323
H	-4.5001574797	4.2388578766	3.0127724013
H	-5.2144995037	4.0946682692	0.4107456202
H	-5.1911053215	5.7102874467	-0.305867795
H	-5.4192653447	5.5378043865	1.4369847314
H	-7.2644998598	0.5467004146	3.9447788329
H	-8.7718190926	1.1436344332	4.6343675659
H	-10.6425276023	0.0213477735	1.5637712954
H	-10.0045089264	1.6412568226	1.7253791511
H	-2.2653721333	6.2068848429	3.8432520661
H	-3.8138151698	6.6775243248	3.1209905217
H	-3.7766088243	5.909891256	4.7132665298
H	-7.339255237	2.3646782981	2.1894219003
H	-7.2544341816	2.9690189816	3.8538287697
H	-8.7830552206	3.03888513	2.972050232
H	-11.5348669847	0.1375971816	3.9502685251
H	-10.9429062116	1.8051625516	4.0665766065
H	-12.1931793029	1.390961754	2.8895907232
N	-0.7649543587	2.103402564	1.0781864648

Table 5 Standard Orientation of (*i*-PrLi·TEEDA)$_2$ [global minimum, B3LYP/6-31+G(d)].

Atomic symbol	x	y	z
C	-3.4433851887	2.5378666648	-3.6992898746
C	-4.3092140573	1.3885817881	-3.1856996183
C	2.4170579106	1.5371307987	-3.5189129747
C	-5.7383390679	3.11995084	-1.0009222769
C	-1.1029480959	-0.5148831416	-3.8620762385
C	2.9439010536	0.9648888716	-2.2038243059

C	-4.3939705429	2.3770852808	-0.9178442718
C	4.1248688686	-1.6287943992	-3.5158883611
N	-4.2415865207	1.1418450457	-1.722720804
C	-0.3744962938	2.397052073	-0.9499682036
C	-1.3508329669	-1.3791475414	-2.6057118676
C	-5.249123908	0.1143326422	-1.3965169122
C	2.6909098872	-1.3553564836	-3.0305018075
N	2.51783016	-0.4232975272	-1.8906057807
C	-1.0266653534	-2.8381518194	-2.9861743789
Li	-2.2126290439	-0.0148293581	-0.9536028453
C	-0.5918759485	1.1944208754	-0.0051516602
Li	0.1615281297	-0.6481540645	-1.127774707
C	3.2568885339	-0.849992905	-0.6865321829
C	-5.2051650972	-0.3966632759	0.044389051
C	-1.1649650659	1.749167179	1.3145841201
N	-4.000401064	-1.1873650851	0.3565349533
C	2.8307617129	-2.1992892722	-0.1057932994
C	-4.1814807151	-2.5778785124	-0.1193159174
N	1.4958949944	-2.1868864775	0.5167468753
C	-3.6541514063	-1.1042011211	1.7943554115
C	-2.9976208984	-3.4974579169	0.1611925827
C	1.5852294998	-1.6056460041	1.8748124543
C	0.8771597211	-3.5313489026	0.4967660086
C	-4.6639923499	-1.6924537505	2.7936180569
C	0.2602533157	-1.5502803501	2.6289056738
C	1.5876339245	-4.6442159946	1.2858779677
H	-3.4256927166	2.5045032419	-4.7946827237
H	-3.8335139725	3.5194516897	-3.4083244296
H	-2.411893139	2.4588427488	-3.3444290735
H	-5.3562263552	1.5659409113	-3.4950913394
H	-3.994277523	0.4579802689	-3.6709136778
H	2.6443916403	2.6088693126	-3.5531001003
H	2.8870396693	1.0751690938	-4.394044226
H	1.3332656431	1.4207326159	-3.6086654849
H	-5.9888670085	3.4151779175	-2.0262802373
H	-5.6788709046	4.0351317707	-0.3994863171
H	-6.5723835446	2.5262666893	-0.6094778084
H	-1.6701159405	-0.8494401958	-4.7584938957
H	-1.3458955529	0.5457310526	-3.7112730566
H	-0.0445052129	-0.5448660846	-4.161973023
H	4.0479333343	1.0343902831	-2.2039503217
H	2.593635392	1.5899950819	-1.3745647753
H	-3.5869106946	3.0521170035	-1.2108019316
H	-4.1879971311	2.121655184	0.1253440758
H	4.651937939	-0.7098279363	-3.7968956608

H	4.0850402304	-2.2710666631	-4.4039534528
H	4.7326244906	-2.1476989868	-2.7658465246
H	0.0853861599	2.1153595744	-1.9071275959
H	-1.3297951612	2.8817289941	-1.2036301215
H	0.2576168171	3.2023150418	-0.5153667988
H	-2.4593672567	-1.3756513073	-2.4694648527
H	-6.2720645099	0.4808787423	-1.598167844
H	-5.088507081	-0.7213367307	-2.086495037
H	2.0968108724	-0.9626908238	-3.8578903081
H	2.2145855474	-2.302386943	-2.7611079059
H	-1.5360937786	-3.1797063097	-3.9139748248
H	0.0496656726	-2.9767179737	-3.1791394697
H	-1.2958855978	-3.5573055608	-2.2009214406
H	0.4347954783	0.8513389457	0.2680676573
H	4.3433764661	-0.8927064449	-0.8843262639
H	3.1211884249	-0.0663919826	0.0666854577
H	-5.2547173345	0.4466031681	0.739875135
H	-6.1231428108	-0.9872191317	0.2156587395
H	-2.1824256852	2.1508155051	1.1783522633
H	-0.5743156466	2.5908602955	1.7378271035
H	-1.2353449973	0.9904264253	2.1055605485
H	2.8365028259	-2.9602800355	-0.8922047064
H	3.6050199988	-2.5053186308	0.6214575166
H	-4.3354011049	-2.5332340924	-1.2019734677
H	-5.1024879069	-3.0145354943	0.3100900868
H	-3.4904927876	-0.0452567631	2.0189146829
H	-2.6858007206	-1.59197145	1.9298737003
H	-2.0719770946	-3.0465561997	-0.2053114111
H	-3.1422784387	-4.4484892982	-0.3639299539
H	-2.8873979392	-3.7235834036	1.2275661675
H	1.9612937515	-0.5837292448	1.766128303
H	2.3344006388	-2.150978017	2.479673027
H	0.7925162433	-3.8261229756	-0.5551725536
H	-0.1465377263	-3.4286979203	0.8637245858
H	-5.6448945004	-1.2080556156	2.7243632801
H	-4.8079507767	-2.76942346	2.6508182617
H	-4.2926727522	-1.5420044371	3.8146904648
H	-0.5064416625	-1.070618693	2.015542932
H	0.3855634716	-0.9550391704	3.5407029524
H	-0.0930225838	-2.5427102909	2.9301874352
H	2.6073170877	-4.8221924979	0.9253170826
H	1.642886752	-4.4217349548	2.3576465602
H	1.0294608751	-5.5816479942	1.1725757298

Table 6 Standard Orientation of *i*-PrLi·TEEDA [global minimum, B3LYP/6-31+G(d)].

Atomic symbol	x	y	z
C	-3.286447574	1.0434236131	0.982444975
C	-1.9802379682	1.8372590092	1.0130120841
C	-1.9923234973	2.7744220115	-1.9282974019
C	-1.5021128292	1.422922923	-1.3848863654
N	-0.9827581113	1.3995499221	0.0058803718
C	0.2844296173	2.1373252306	0.1702671499
C	-2.1415738616	-2.6784131059	-0.855407114
C	-1.4083630695	-2.3986173059	0.471863047
Li	-0.3697071968	-0.6206985409	0.3083579498
C	1.4848905925	1.4158997625	-0.4599461657
C	-0.611893115	-3.6545231872	0.8653475148
N	1.6535680482	0.0396142994	0.0523172598
C	2.34694315	0.0426415759	1.3629715471
C	2.2772855201	-0.8627790261	-0.9469819547
C	2.4493616124	-1.3340822053	2.0205312327
C	3.7282919946	-0.5565429202	-1.3467235252
H	-3.8885440489	1.3107463877	1.8585712077
H	-3.8900913472	1.2622700169	0.0949216204
H	-3.0905359039	-0.0339110451	1.0139827317
H	-2.1906103288	2.9171033874	0.9164607465
H	-1.5093209467	1.7003894213	1.9940637468
H	-2.8375514108	3.1671867967	-1.3528612094
H	-2.3312901365	2.6436605709	-2.9627152054
H	-1.2047490566	3.5365462217	-1.935520786
H	-2.3116952076	0.6895549454	-1.4396471196
H	-0.7114228538	1.0384113295	-2.0385576316
H	0.234179432	3.1606716451	-0.2388732443
H	0.4537260747	2.2515216221	1.2464486759
H	-2.8347559079	-1.8673986988	-1.1355489444
H	-2.7464169059	-3.6135972412	-0.8476544801
H	-1.4378077135	-2.7924552559	-1.6988576868
H	-2.1988386953	-2.2848769008	1.2426181199
H	1.3527694546	1.3587913091	-1.5455896385
H	2.3857447227	2.0305600787	-0.2902524686
H	-0.187733838	-3.5795130157	1.8791605044
H	-1.2134203473	-4.5916618734	0.8475198581
H	0.2369569462	-3.8378730271	0.1828526962
H	1.7787146452	0.7058267473	2.0249843865
H	3.3512947746	0.4917092501	1.267642394
H	1.640269671	-0.8322142857	-1.8392826752

H	2.2027572121	-1.8833328911	-0.5609379885
H	1.4753812333	-1.834353632	2.0533761165
H	2.8125175763	-1.2176266013	3.0481440725
H	3.1514046266	-1.993303819	1.499238559
H	3.8370488608	0.4522176565	-1.7625844631
H	4.4199148419	-0.6512424421	-0.5021673745
H	4.051274057	-1.2679987806	-2.1158905749

Table 7 Standard Orientation of *i*-PrLi·(*R*,*R*)-TECDA [global minimum, B3LYP/6-31+G(d)].

Atomic symbol	x	y	z
C	-2.1343180568	-3.1873182986	-1.0804056608
C	-1.7931316947	1.4756969329	-1.0293345421
C	2.0203021549	-0.5224329824	-0.9664865241
C	-2.3924870594	-1.8066449522	-0.4619997463
C	-0.9612327483	-3.8792622759	-0.378903371
C	-1.1472623365	-0.8839628121	-0.514633295
C	0.2869686505	-2.9879991042	-0.4230891023
N	-1.3642412724	0.4984893992	0.0038163072
C	0.0466209728	-1.5915802987	0.198869918
Li	0.5519371527	1.2588665563	0.4463160372
N	1.2567651068	-0.728052851	0.2963603461
C	-2.1603204146	0.5522664633	1.2523652636
C	2.1066692699	-1.0857592311	1.4556453751
C	1.4083759045	3.1474911447	0.6094642063
C	2.6964479658	3.3117082432	-0.220756767
C	0.4769057467	4.3293150734	0.2824193339
C	-3.2153760541	1.3650627685	-1.6027168155
C	3.1203478477	-1.5296879972	-1.3503778856
C	-2.128486464	1.9122431641	1.9550525524
C	3.1583935555	-0.029650504	1.8041411723
H	-1.9093309854	-3.0805657351	-2.1524704618
H	-3.0430389055	-3.7992544444	-1.0119696927
H	-1.0692947407	1.4055232256	-1.8506817895
H	-1.6552253846	2.4730270671	-0.6025919619
H	1.2895079962	-0.4634196262	-1.7805619591
H	2.4821157128	0.4705712216	-0.9064887118
H	-3.234434252	-1.3202328394	-0.9640960333
H	-2.6951252101	-1.9508027153	0.5838418035
H	-0.7446008523	-4.8481936592	-0.8469703888
H	-1.2320925503	-4.0898891376	0.6667290107
H	-0.877274011	-0.7620405805	-1.5725289969

H	0.5882471713	-2.8695317773	-1.4726096228
H	1.1209111304	-3.4777708613	0.0935809334
H	-0.2632982005	-1.752880491	1.2406152938
H	-3.2087158512	0.2637628633	1.0783411777
H	-1.7427558425	-0.2009223248	1.9307163419
H	1.4338723517	-1.2010193306	2.3138856702
H	1.7092215676	3.2836248796	1.6704588704
H	3.1706812262	4.313990857	-0.1204665026
H	2.5058685173	3.1849851752	-1.3011914321
H	3.473426657	2.578490985	0.0494528183
H	0.9639079934	5.3250511837	0.3838306403
H	-0.4158809498	4.3580035928	0.9272301309
H	0.1120498601	4.2879512911	-0.7592101738
H	-3.9805169936	1.3868108603	-0.8183886927
H	-3.3596095031	0.4563988747	-2.1967411232
H	-3.3993879184	2.2213415583	-2.26302093
H	2.746938686	-2.5458882249	-1.5009499721
H	3.9194193263	-1.5706679217	-0.6033300392
H	3.5766474315	-1.1978325049	-2.2910853156
H	-2.6773922522	2.6798591783	1.4002589502
H	-1.1041160408	2.2746458671	2.0989987419
H	-2.6033964571	1.817692598	2.9387993018
H	2.7012117069	0.9549800482	1.950508815
H	3.9246524943	0.0716994581	1.0292263033
H	3.6656598044	-0.3210978538	2.7316448355
H	2.5971655308	-2.0629682654	1.3115248056

[1] J. F. Larrox, E. N. Jacobsen, *J. Org. Chem.* 1994, **59**, 1939.

[2] A. P. Cole, V. Mahadevan, L. M. Mirica, X. Ottenwaelder, T. D. P. Stack, *Inorg. Chem.* 2005, **44**, 7345.

[3] Würthwein, E.-U.; Hoppe, D. *J. Org. Chem.* 2005, **70**, 4443

[4] Gaussian 03 (Revision B.04), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W.

Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 2003.