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Note

# Lithiation of Diamine Ligands to Chiral Building Blocks: Syntheses, Selectivities, and Lithiated Intermediates

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*Summary: The direct deprotonation of the chiral nitrogen ligands (R,R)-TECDA (**2**) and (R,R)-TEMCDA (**6**) with tert-butyllithium to highly reactive building blocks is reported. The regioselectivity of the lithiation reactions can be explained by the isolated precoordinated intermediates such as tBuLi·(R,R)-TECDA in combination with computational studies.*

## Introduction

The application of chiral nitrogen ligands in combination with organolithium compounds is among the most important methodologies in asymmetric synthesis, which has been pioneered by Hoppe and Beak.[1] However, recent investigations have shown that the ligand systems used are not always inert under the reaction conditions and undergo decomposition reactions with the lithium base. α-Lithiation and β-deprotonation reactions of tertiary methyl and ethyl amines, respectively, have been reported resulting in side products and the loss of Lewis base.[2] Besides this disfavored decomposition of the ligand, these reactions can also be employed synthetically such as for the preparation of nitrogen ligands or amino-functionalized organometallics. This was proven by means of chiral α-lithiated (1*R*,2*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-diamine [(*R*,*R*)-TMCDA, **1**] and a series of further di- and triamines (Chart 1).[3]

Preliminary studies in our group have proven that these reactions proceed via precoordinated intermediates of the Lewis base and the organolithium reagent. This precoordination and the involved proximity of the relevant groups are necessary for the viability of the reaction and give way to regioselective lithiations.[4] Thereby, the isolation and structure elucidation of crucial intermediates is a powerful tool to gain insight into the reaction mechanism. As such, it could be explained why *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (TEEDA) is deprotonated in β-position to the nitrogen, whereas TMEDA undergoes α-lithiation.[5] This selective β-lithiation attracted our interest, as this methodology provides access to unsymmetrical lithium amides and their corresponding amines. Starting from a chiral ethyl-substituted amine even chiral secondary amines should be accessible, which bear synthetic potential above all as chiral auxiliaries in organocatalysis.[6] To evaluate this pathway, the symmetric diamine (1*R*,2*R*)-*N*,*N*,*N*′,*N*′-tetraethylcyclohexane-1,2-diamine [(*R*,*R*)-TECDA, **2**] (Chart 1) seemed to be a suitable starting system.

## Results and Discussion

The diamine (*R*,*R*)-TECDA was synthesized by ethylation of the (1*R*,2*R*)-cyclohexane-1,2-diamine with ethyl sulfate.[7] The free amine can easily be obtained by racemic resolution of a mixture of all isomers with L-tartaric acid and subsequent release with KOH.[8] To clarify the reactivity of **2** toward deprotonation reactions with alkyllithiums, a solution of the amine in pentane was treated with an equimolar amount of *tert*-butyllithium at −78 °C and warmed to room temperature. Upon warming, gas formation was observed at around 0 °C. Subsequent cooling of the reaction mixture to −78 °C gave crystals of chiral lithium amide **4** in 79% yield as result of the abstraction of the β-hydrogen atom and following elimination of ethene. The same reactivity was observed with *s*BuLi and *i*PrLi.[3,4,9]

Lithium amide $\mathbf{4_3}$ crystallizes in the trigonal crystal system, space group *R*3 (Figure 1). The highly symmetric molecule

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(1) For asymmetric synthesis with chiral organolithium bases, see: (a) Hoppe, D.; Hintze, F.; Tebben, P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1422. (b) Kerrick, S. T.; Beak, P. *J. Am. Chem. Soc.* **1991**, *113*, 9708. (c) Whisler, M. C.; Beak, P. *J. Org. Chem.* **2003**, *68*, 1207. (d) Coldham, I.; Copley, R. C. B.; Haxell, T. F. N.; Howard, S. *Org. Biomol. Chem.* **2003**, *1*, 1532. (e) Metallinos, C.; Szillat, H.; Taylor, N. J.; Snieckus, V. *Adv. Synth. Catal.* **2003**, *345*, 370. (f) Würthwein, E.-U.; Behrens, K.; Hoppe, D. *Chem.—Eur. J.* **1999**, *5*, 3459.

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(5) Gessner, V. H.; Strohmann, C. *J. Am. Chem. Soc.* **2008**, *130*, 14412.

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(9) The formation of **4** via α-lithiation is very unlikely, as no carbenoid behavior has ever been observed for analogous α-lithiated compounds: (a) Boche, G.; Marsch, M.; Harbach, J.; Harms, K.; Ledig, B.; Schubert, F.; Lohrenz, J. C. W.; Ahlbrecht, H. *Chem. Ber.* **1993**, *126*, 1887. (b) Strohmann, C.; Abele, B. C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2378.

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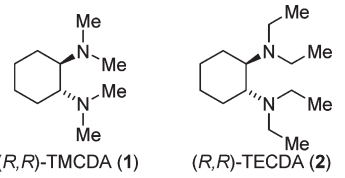
**Chart 1**




forms a trimeric structure with a central Li−N six-membered ring, which adopts a chair conformation. The Li−N distances vary between 1.972(7) and 2.146(7) Å and are thus comparable to those of known lithium amides.[10] Due to the high symmetry of the molecule ($C_3$), the lithium atoms form a equilateral $Li_3$-triangle with lateral lengths of 3.013(12) Å. The $\beta$-lithiation can be employed synthetically (Scheme 1) such as for the preparation of unsymmetrical chiral ligands. Lithium amide **4** can be hydrolyzed to amine **5** in 84% isolated yield, which can afterward be transferred via Eschweiler−Clarke methylation in 91% yield to (1*R*,2*R*)-*N*′,*N*′,*N*″-triethyl-*N*″-methylcyclohexane-1,2-diamine [(*R*,*R*)-TEMCDA (**6**)] (Scheme 1). Contrary to (*R*,*R*)-TMCDA (**1**), which undergoes selective α-lithiation of its methyl group, **2** is a rare example of a tertiary amine, which shows direct $\beta$-deprotonation.[5]

To clarify this reactivity, the intermediate *tert*-butyllithium adduct was isolated at −78 °C without previous warming to prevent the decomposition to the lithium amide **4**. *t*BuLi·(*R*,*R*)-TECDA (**3**) crystallizes out of pentane as monomeric alkyllithium species in the orthorhombic crystal system, space group $P2_12_12_1$, with two molecules in the asymmetric unit (one of them depicted in Figure 2). Both molecules show shortened Li−C [2.138(4) and 2.140(4) Å] and Li−N distances [2.087(4) to 2.124(4) Å] typical for monomeric alkyllithiums.[11] Such a monomer has also been observed with isopropyllithium as lithium reagent.[11c] Both, *i*PrLi·(*R*,*R*)-TECDA and *t*BuLi·(*R*,*R*)-TECDA represent possible intermediates of the deprotonation reaction of **2**. In these adducts, the ethyl groups are arranged toward the alkyllithium, bringing the $\beta$-hydrogen atoms proximate to the carbanionic center. This precoordination according to

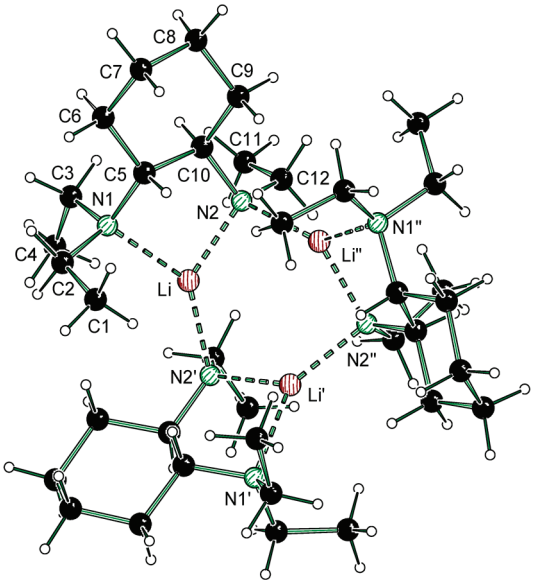
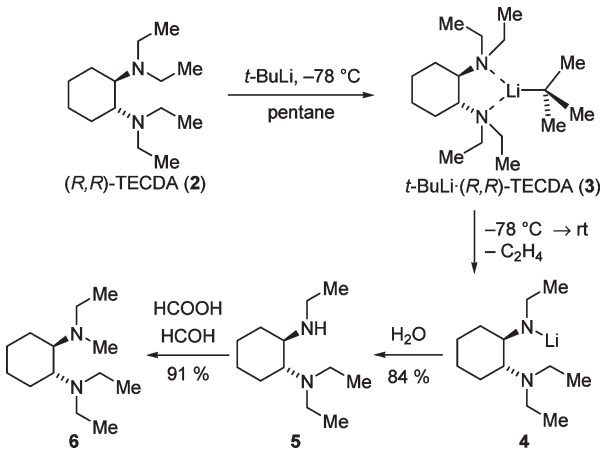



**Figure 1.** Molecular structure of chiral lithium amide $\mathbf{4}_3$. Selected bond lengths [Å] and angles [deg]: Li−N(2) 1.972(7), Li−N(2)″ 2.022(7), Li−N(1) 2.146(7), Li−Li′ 3.013(12); N(2)−Li−N(2)″ 131.7(4), N(2)−Li−N(1) 88.6(3), N(2)″−Li−N(1) 139.6(4), Li−N(2)−Li′ 97.9(4), Li″−Li−Li′ 60.0. Symmetry operations: ′: $-x+y$, $-x+1$, $z$; ″: $-y+1$, $x-y+1$, $z$.

**Scheme 1**




the complex-induced proximity effect (CIPE) results in the selective abstraction of the $\beta$-hydrogen atom to **4** (Scheme 1).[12]

To evaluate the energetic difference between the observed selective $\beta$-lithiation and a potential competing α-deprotonation of **2**, DFT studies at the B3LYP/6-31+G(d) level were performed. Starting from *t*BuLi·(*R*,*R*)-TECDA (**3**) the reaction barriers for all possible transition states were calculated. Due to the chirality of the molecule, two transition states for the $\beta$-lithiation of the ethyl group and two for the α-lithiaton of the methylene units are possible (Figure 3). The $\beta$-lithiation possesses the lowest reaction barrier, being preferred by 9 kJ·mol$^{-1}$ compared to the α-deprotonation. The most favored transition state shows a barrier of only 92 kJ·mol$^{-1}$, which confirms the viability of the reaction at temperatures below room temperature. Interestingly, the trimerization of the product via this transition state would

(10) For lithium amide structures, see: (a) Sun, C.; Williard, P. G. *J. Am. Chem. Soc.* **2000**, *122*, 7829. (b) Neculai, D.; Roesky, H. W.; Neculai, A. M.; Magull, J.; Herbst-Irmer, R.; Walfort, B.; Stalke, D. *Organometallics* **2003**, *22*, 2279. (c) Arnold, P. L.; Mungur, S. A.; Blake, A. J.; Wilson, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 4981. (d) Lappert, M. F.; Slade, M. J.; Singh, A.; Atwood, J. L.; Rogers, R. D.; Shakir, R. *J. Am. Chem. Soc.* **1983**, *105*, 302. (e) Wanat, R. A.; Collum, D. B.; Van Duyne, G.; Clardy, J.; DePue, R. T. *J. Am. Chem. Soc.* **1986**, *108*, 3416. (f) Bernstein, M. P.; Romesberg, F. E.; Fuller, D. J.; Harrison, A. T.; Collum, D. B.; Liu, Q. Y.; Williard, P. G. *J. Am. Chem. Soc.* **1992**, *114*, 5100. (g) Sakuma, K.; Gilchrist, J. H.; Romesberg, F. E.; CajthamL, C. E.; Collum, D. B. *Tetrahedron Lett.* **1993**, *34*, 5213.

(11) For organolithium structures, see: (a) Nichols, M. A., Williard, P. G. *J. Am. Chem. Soc.* **1993**, *115*, 1568. (b) Strohmann, C.; Strohfeldt, K.; Schildbach, D. *J. Am. Chem. Soc.* **2003**, *125*, 13672. (c) Strohmann, C.; Strohfeldt, K.; Schildbach, D.; McGrath, M. J.; O'Brien, P. *Organometallics* **2004**, *23*, 5389. (d) Strohmann, C.; Dilsky, S.; Strohfeldt, K. *Organometallics* **2006**, *25*, 41. (e) Strohmann, C.; Gessner, V. H. *J. Am. Chem. Soc.* **2007**, *129*, 5982. (f) Gessner, V. H.; Däschlein, C.; Strohmann, C. *Chem.—Eur. J.* **2009**, *15*, 3320. (g) Kottke, T.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 580. (h) Strohmann, C.; Gessner, V. H.; Damme, A. *Chem. Commun.* **2008**, 3381. (i) Strohmann, C.; Seibel, T.; Strohfeldt, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 4531.

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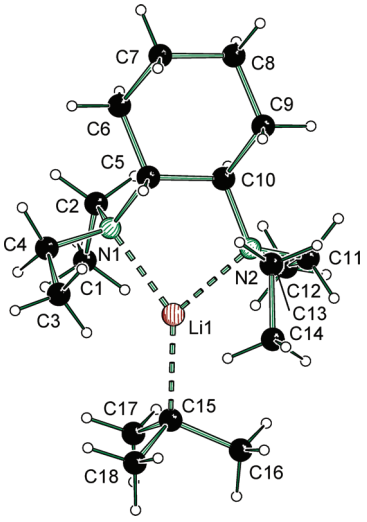



**Figure 2.** Molecular structure of *t*BuLi·(*R,R*)-TECDA (**3**). Selected bond lengths [Å]: C(33)−Li(2) 2.140(4), C(15)−Li(1) 2.138(4), Li(1)−N(2) 2.096(4), Li(1)−N(1) 2.124(4), Li(2)−N(3) 2.087(4), Li(2)−N(4) 2.0963(4).

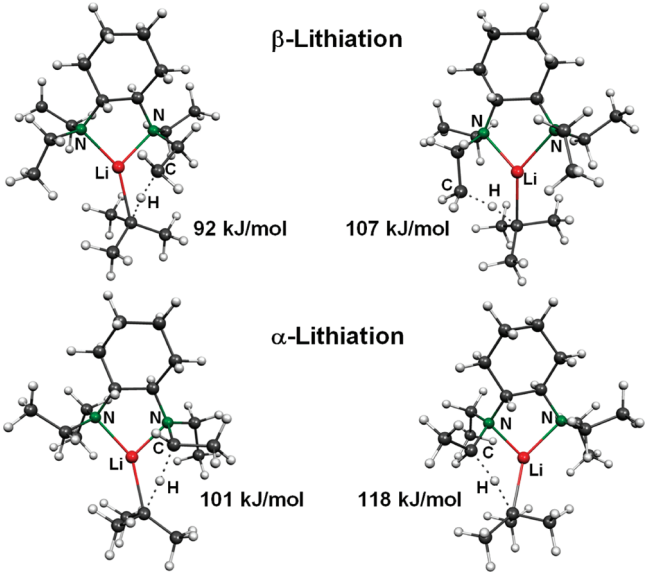
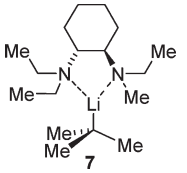



**Figure 3.** Optimized transition states and reaction barriers of the α- and *β*-deprotonation of **2**; [B3LYP/6-31+G(d)].

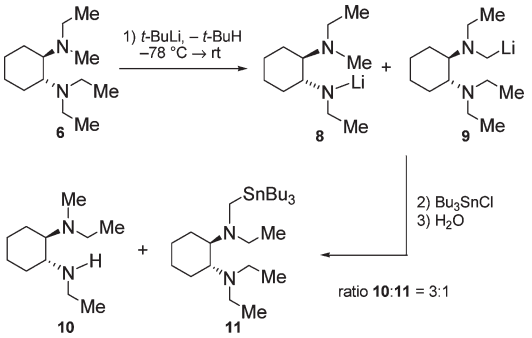
yield the configuration at the lithiated nitrogen observed in the molecular structure of lithium amide $\mathbf{4}_3$.



**7**

Regarding amine **6**, α- and *β*-deprotonation of a methyl group are possible. Again we mainly observed *β*-deprotonation of the diethyl-substituted amino function ($NEt_2$), however, with the α-lithiation of the methyl group as a side-reaction. Lithiation of the (*R,R*)-TEMCDA (**7**) ligand (same reaction conditions as for **2**) and subsequent trapping with tributyltin chloride resulted in a 3:1 mixture of amine **10** (formed by aqueous workup of the interim formed stannazane) and the

**Scheme 2**




α-stannylated amine **11** (Scheme 2). Only traces of the unlithiated amine **6** and the secondary amine resulting from lithiation/elimination of the N(Me)Et group could be detected (see Supporting Information (SI)). This suggests the formation of the lithiated intermediates **8** and **9** during the reaction sequence. For insight into this reaction step the intermediate *tert*-butyllithium adduct, *t*BuLi·(*R,R*)-TEMCDA (**7**), was isolated. This monomer is isomorphous to the presented TECDA adduct **3** due to disorder of the methyl group in the molecule. Yet, this disorder prevented the formation of crystals of sufficient quality (see SI). It has to be noted that upon precoordination of the alkyllithium to the diamine, the nitrogen atom with the methyl substituent becomes stereogenic. The disorder indicates no specific preference of one configuration at the stereogenic nitrogen atom. Computational studies [B3LYP/6-31+G(d)] of the two diastereomers show an energetic difference of only 4 $kJ \cdot mol^{-1}$.

To obtain further information about the observed selectivities of the deprotonation, calculations of the possible transition states of the α- and the *β*-deprotonation were performed with *t*BuLi·(*R,R*)-TEMCDA (**7**) as starting point. Due to the unsymmetrical substitution pattern and the chirality of the molecule, a total of eight α- and six *β*-lithiations as well as several conformers have to be considered (see SI).[13] Contrary to (*R,R*)-TECDA, four of these transition states are in the range of only 8 $kJ \cdot mol^{-1}$. Thereby, in contradiction to experiment the most favored transition state is that of the *β*-deprotonation of the N(Me)Et moiety, which has been observed only in traces. However, the experimentally observed main product **8** exhibits two transition states of suitable energies disfavored by only 1 and 8 $kJ \cdot mol^{-1}$. The competing α-lithiation of the methyl group to **9** possesses an 8 $kJ \cdot mol^{-1}$ higher reaction barrier. Overall, considering the statistical favoritism of the *β*-lithiation of the $NEt_2$ over the N(Me)Et moiety, the calculations reflect the formation of the product mixture. Comparable to the deprotonation of (*R,R*)-TECDA, the barrier of 97 $kJ \cdot mol^{-1}$ confirms the viability of the reaction.

In conclusion we have described a simple synthetic procedure to an unsymmetrical chiral amine by direct deprotonations of tertiary amines. While (1*R*,2*R*)-*N,N,N′,N′*-tetraethylcyclohexane-1,2-diamine [(*R,R*)-TECDA, **2**] shows selective *β*-lithiation to the corresponding lithium amide **4**, (1*R*,2*R*)-*N′,N′,N″*-triethyl-*N″*-methylcyclohexane-1,2-diamine [(*R,R*)-TEMCDA (**6**)] undergoes *β*-lithiation but also α-lithiation of its methyl group. We are currently investigating the control of regioselectivity by variation of the employed deprotonation reagent and the substitution pattern of the diamine.

(13) Additional calculations were performed on the MP2/6-31G level, giving the same results as the DFT studies with a barrier of 98 kJ/mol (for further information, see the Supporting Information).

## Experimental Section

**General Methods.** 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. *tert*-Butyllithium was titrated against diphenylacetic acid before use. $^{1}H$, $^{13}C$, and $^{119}Sn$ NMR spectra were recorded on Bruker Avance-500 or Avance-400 spectrometers at 22 °C if not stated otherwise. Assignment of the signals was supported by additional DEPT-135 and C,H COSY experiments. All values of the chemical shift are in ppm regarding the $\delta$-scale. GC/MS analysis were performed on a ThermoQuest TRIO-1000 (EI = 70 eV); Zebron capillary GC column ZB-1.

**Synthesis of *t*BuLi·(*R,R*)-TECDA (3).** (*R,R*)-TECDA (**2**) (180 mg, 0.80 mmol) was dissolved in 3 mL of *n*-pentane and the reaction mixture cooled to −65 °C. At this temperature 0.6 mL (1.02 mmol) of *t*BuLi (1.69 M in *n*-pentane) was added and cooled to −78 °C, giving colorless needles of the monomeric compound. NMR studies of *t*BuLi·(*R,R*)-TECDA were not possible due to the decomposition of the ligand and the solvent as well as the low solubility of the compound at low temperatures.

**Synthesis of Lithium Amide $4_3$.** (*R,R*)-TECDA (**2**) (180 mg, 0.80 mmol) was dissolved in 3 mL of *n*-pentane and the reaction mixture cooled to −65 °C. At this temperature 0.6 mL (1.02 mmol) of *t*-BuLi (1.69 M in *n*-pentane) was added, and the mixture warmed to room temperature and stirred for 4 h. Subsequent cooling to −78 °C gave colorless plates of the lithium amide after 12 h. Removal of the remaining solution and washing the crystals with cooled pentane gave lithium amide $\mathbf{5_3}$ in 79% yield. The lithiation was also achieved with *sec*-butyllithium and isopropyllithium.

**Synthesis of 5.** (*R,R*)-TECDA (3.80 g, 16.8 mmol) was dissolved in 15 mL of *n*-pentane, and at −30 °C 20.0 mL (34.0 mmol) of *t*BuLi (1.69 M in *n*-pentane) was added. Upon warming to room temperature, the formed precipitate of adduct **3** dissolved with gas evolution at around 0 °C. After stirring for 4 days at room temperature the reaction mixture was trapped with $H_2O$ and subsequently extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over $Na_2SO_4$, the solvent was removed, and the residue was purified by Kugelrohr distillation (oven temperature: 80 °C, $9 \times 10^{-2}$ mbar), giving amine **5** as a colorless oil (yield: 2.79 g, 14.1 mmol; 84%). $^{1}H$ NMR (500.1 MHz, $CDCl_3$): $\delta$ 0.97 [t, $^{3}J_{HH}$ = 7.10 Hz, 6H; $N(CH_2CH_3)_2$], 1.09 (t, $^{3}J_{HH}$ = 7.12 Hz, 3H; $HNCH_2CH_3$), 1.01−1.23 (m, 4H; $CH_2$), 1.62−1.65 (m, 1H; $CH_2$), 1.70−1.76 (m, 2H; $CH_2$), 2.02−2.06 (m, 1H; $CH_2$), 2.22−2.33 [m, 4H; $N(CH_2CH_3)_2$ + CHN], 2.40 + 2.42 [dq, $^{3}J_{HH}$ = 7.08 Hz, $^{2}J_{HH}$ = 11.20 Hz, 1H; $N(H)CH_2CH_3$], 2.52 + 2.55 [dq, $^{3}J_{HH}$ = 7.34 Hz, $^{2}J_{HH}$ = 12.90 Hz, 2H; $N(CH_2CH_3)_2$], 2.42−2.65 (br, 1H; NH), 2.71+ 2.73 [dq, $^{3}J_{HH}$ = 7.23 Hz, $^{2}J_{HH}$ = 11.27 Hz, 1H; $N(H)CH_2CH_3$]. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$): $\delta$ 15.0 [$(N(CH_2CH_3)_2$], 15.4 [$(H)NCH_2CH_3$], 23.1 + 24.8 + 25.9 + 32.2 ($CH_2$), 41.7 [$(H)NCH_2CH_3$], 43.3 [$N(CH_2CH_3)_2$], 58.6 [$CHN(H)CH_2CH_3$], 63.2 [$(CHN(CH_2CH_3)_2$]. $[\alpha]^{20}_{D}$ = −140.2 (cyclohexane, 0.375 g/100 mL). Anal. Obsd: C 73.68, H 13.22, N 12.56. Calcd: C 72.66, H 13.21, N 14.12. GC-MS: $t_R$ = 6.918 min [80 °C (2 min)−10 °C·min$^{-1}$−280 °C (5 min)]; *m/z* (%): 198 (9) ($M^+$), 126 (25) {$[(C_6H_8(NH_2)NHCH_3]^+$}, 112 (44) {$[(C_6H_8(NH_2)_2]^+$}, 86 (100) {$[N(C_2H_5)_2CH_2]^+$}.

**Synthesis of 6.** (1*R*,2*R*)-*N,N,N′*-Triethylcyclohexane-1,2-diamine [(*R,R*)-**5**] (2.97 g, 15.0 mmol) was suspended in 6 mL of formic acid, and in portions 7 mL of formaldehyde (40% aquous solution) was added. Subsequently the reacction mixture was refluxed for 6 h and stirred for an additional 3 h at rt. After addition of 2 M $NaOH_{aq}$ to pH 11 the mixture was extracted with diethyl ether (3 × 150 mL), and the combined organic layers were washed with water (2 × 200 mL) and dried over $Na_2SO_4$. After removal of the solvent the residue was purified by Kugelrohr distillation (oven temperature: 55−60 °C, $6 \times 10^{-3}$ mbar), giving product (*R,R*)-**6** as a colorless oil (2.89 g, 13.6 mmol; 91%). $^{1}H$ NMR (500.1 MHz, $CDCl_3$): $\delta$ 0.98 [t, $^{3}J_{HH}$ = 7.10 Hz, 3H; $N(CH_2CH_3)_2$], 0.99 [t, $^{3}J_{HH}$ = 7.10 Hz, 6H; $N(CH_2CH_3)_2$], 1.03−1.18 (m, 4H; $CH_2$), 1.61−1.65 (m, 2H; $CH_2$), 1.70−1.77 (m, 2H; $CH_2$), 2.23 (s, 3H; $NCH_3$), 2.31−3.64 (m, 8H; CHN + $NCH_2CH_3$). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ 14.0 ($NCH_2CH_3$), 14.4 [$(N(CH_2CH_3)_2$], 25.9 + 26.0 + 26.8 + 27.1 ($CH_2$), 36.5 ($NCH_3$), 43.4 [$N(CH_2CH_3)_2$], 47.8 [$(CH_3)NCH_2CH_3$], 60.2 [$CHN(H)CH_2CH_3$], 62.9 [$(CHN(CH_2CH_3)_2$]. GC-MS: $t_R$ = 4.734 min [80 °C (2 min)−10 °C·min$^{-1}$−280 °C (5 min)]; *m/z* (%): 212 (90) ($M^+$), 183 (25) [$(M - Me)^+$], 112 (100) {$[(C_6H_8(NH_2)_2]^+$}, 86 (83) {$[N(C_2H_5)_2CH_2]^+$}.

**Synthesis of *t*BuLi·(*R,R*)-TEMCDA (7).** TEMCDA (100 mg, 0.47 mmol) was dissolved in 3 mL of *n*-pentane and cooled to −50 °C. At this temperaure 0.4 mL (0.53 mmol) of *t*BuLi (1.32 M solution in *n*-pentane) was added and cooled to −78 °C, giving colorless crystals of the monomeric compound. NMR studies of *t*BuLi·(*R,R*)-TECDA were not possible due to the decomposition of the ligand and the solvent as well as the low solubility of the compound at low temperatures. For X-ray crystallography, see SI.

**Lithiation and Trapping to 10 and 11.** TEMCDA (100 mg, 0.47 mmol) was dissolved in 3 mL of *n*-pentane, and at −78 °C 0.4 mL (0.53 mmol) of *t*BuLi (1.32 M solution in *n*-pentane) was added, resulting in the formation of the *t*BuLi adduct. The reaction mixture was warmed to room temperature, upon which the formed solid dissolved. After 3 days stirring at rt the mixture was trapped with 195 mg (0.60 mmol) of tributyltin chloride at −20 °C and stirred for 1 h at rt. After addition of 20 mL of 2.5 M $HCl_{aq}$ and 20 mL of diethyl ether the mixture was extracted three times with 2.5 M $HCl_{aq}$. The combined aqueous layers were afterward set to pH = 11 and extracted with diethyl ether (3 × 30 mL). The combined organic layers were dried over $Na_2SO_4$, and the solvent was removed under reduced pressure. The crude product was investigated by NMR spectroscopy, showing a 3:1 mixture of amine **10** and the stannylated compound **11**. Amine **10**: $^{1}H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ 0.98 [t, $^{3}J_{HH}$ = 7.15 Hz, 3H; $N(CH_2CH_3)_2$], 1.08 [t, $^{3}J_{HH}$ = 7.10 Hz, 3H; $N(CH_2CH_3)_2$], 1.03−1.18 (m, 4H; $CH_2$), 1.68−1.87 (m, 3H; $CH_2$), 2.03−2.08 (m, 1H; $CH_2$), 2.15 (s, 3H; $NCH_3$), 2.21−2.23 (m, 3H; CHN + $NCH_2CH_3$), 2.40−2.46 (m, 2H; $NCH_2CH_3$), 2.69−2.75 (m, 1H; CHNH), 3.15 (bs, 1H; NH). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ 13.6 + 15.3 ($NCH_2CH_3$), 21.6 + 24.6 + 25.5 + 31.8 ($CH_2$), 36.1 ($NCH_3$), 41.4 + 46.9 [$N(CH_2CH_3)$], 58.2 + 66.0 (CHN). GC-MS: $t_R$ = 4.329 min [80 °C (2 min)−10 °C·min$^{-1}$−280 °C (5 min)]; *m/z* (%): 184 (45) ($M^+$), 155 (13) [$(M - C_2H_5)^+$], 126 (55) [$(M - 2\ C_2H_5)^+$], 112 (22) {$[(C_6H_8(NH_2)_2]^+$}, 98 (72) [$NC_6H_{12})^+$], 72 (100) [$C_4H_{10}N)^+$]. α-Stannylated amine (**11**): $^{1}H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ 0.80−0.91 (m, 6H; $SnCH_2$), 0.84 (t, $^{3}J_{HH}$ = 7.30 Hz, 9H; $SnCH_2CH_2CH_2CH_3$), 0.87 [t, $^{3}J_{HH}$ = 7.45 Hz, 3H; $N(CH_2CH_3)$], 0.99 [t, $^{3}J_{HH}$ = 7.10 Hz, 6H; $N(CH_2CH_3)_2$], 1.03−1.18 (m, 4H; $CH_2$), 1.22−1.29 (m, 6H; $CH_2$), 1.40−1.47 (m, 6H; $CH_2$), 1.59−1.82 (m, 4H; $CH_2$), 2.26−3.61 (m, 10H; CHN + $NCH_2$). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta$ 6.6 ($SnCH_2$, $^{1}J_{117Sn-C}$ = 145.2 Hz, $^{1}J_{119Sn-C}$ = 152.7 Hz), 13.5 [$(NCH_2CH_3)_2$], 14.0 ($SnCH_2CH_2CH_2CH_3$), 14.7 ($NCH_2CH_3$), 24.8 + 26.24 + 26.9 + 27.8 ($CH_2$), 27.4 ($SnCH_2CH_2$, $^{2}J_{117Sn-C}$ = 26.4 Hz, $^{2}J_{119Sn-C}$ = 27.6 Hz), 29.2 ($SnCH_2CH_2CH_2$, $^{3}J_{SnC}$ = 9.85 Hz), 36.7 ($NCH_2Sn$), 43.6 [$N(CH_2CH_3)_2$], 47.9 [$N(CH_2CH_3)$], 60.3 + 61.7 (CHN). $^{119}Sn$ NMR (111.9 MHz, $CDCl_3$, $CDCl_3$): $\delta$ −29.3.

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**Supporting Information Available:** Crystallographic data as a CIF file, ORTEP plots, and crystallographic, computational, and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.