Stereoselective Reactions. XXVII.[1] Solution Structures of a Chiral Tridentate Lithium Amide in Relation to Enantioselective Deprotonation of 4-*tert*-Butylcyclohexanone

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Received March 12, 1997; accepted May 19, 1997

^{6}Li- and ^{15}N-NMR spectroscopic studies on the solution structures of a chiral tridentate lithium amide have revealed that it exists as a chelated monomer in which the lithium is tri-coordinated, as a chelated dimer in which the lithium is tetra-coordinated, or as a mixture of these two species depending upon the solvent used. It is concluded that lower Lewis acidity of the tri- and tetra-coordinated lithium compared to the di-coordinated lithium makes tridentate lithium amides inferior to bidentate lithium amides as bases in enantioselective deprotonation reaction.

Key words chiral lithium amide; solution structure; tri-coordinated lithium; tetra-coordinated lithium; enantioselective deprotonation

Enantioselective deprotonation of prochiral cyclic ketones by chiral lithium amides to give the corresponding chiral lithium enolates has become one of the useful methods for asymmetric synthesis.[2] We have previously reported enantioselective deprotonation of prochiral 4-*tert*-butylcyclohexanone (**1**) using a chiral bidentate lithium amide ((*R*)-**2a**) in the presence of excess trimethylsilyl chloride (TMSCl) to isolate the corresponding lithium enolate ((*R*)-**4**) as its trimethylsilyl enol ether ((*R*)-**5**).[1,3] As shown in Table 1, the reaction was found to be highly dependent on the solvent used. The chemical and optical yields of the products ((*R*)-**5**) are higher in tetrahydrofuran (THF) (run 1), lower in toluene (run 2), and higher in THF and in toluene containing 2 eq of hexamethylphosphoric triamide (HMPA) (runs 7,8).

By means of ^{6}Li- and ^{15}N-NMR spectroscopic studies on [^{6}Li, $^{15}N_2$]-(*R*)-**2a**, it has been shown that (*R*)-**2a** exists as a chelated monomer ((*R*)-**6**) in THF, as a chelated dimer ((*R*)-**7**) in toluene, and as a chelated monomer ((*R*)-**6**) in THF and in toluene containing 2 eq of HMPA.[1,3a] Thus, (*R*)-**6** is a superior species to (*R*)-**7** for the present deprotonation reaction of **1** to give (*R*)-**5** in higher chemical and optical yields.

Based on model studies, we supposed that a chiral tridentate lithium amide ((*R*)-**2b**) might be superior to the chiral bidentate lithium amide ((*R*)-**2a**) for the present deprotonation reaction, since (*R*)-**2b**, which has a dimethylamino group as an additional internal ligation site for the lithium instead of one of the methyl groups in (*R*)-**2a**, may form the corresponding bicyclo[3.3.0]octane-type chelated monomer. It is known that *cis*-bicyclo[3.3.0]octane is much more stable than the corresponding

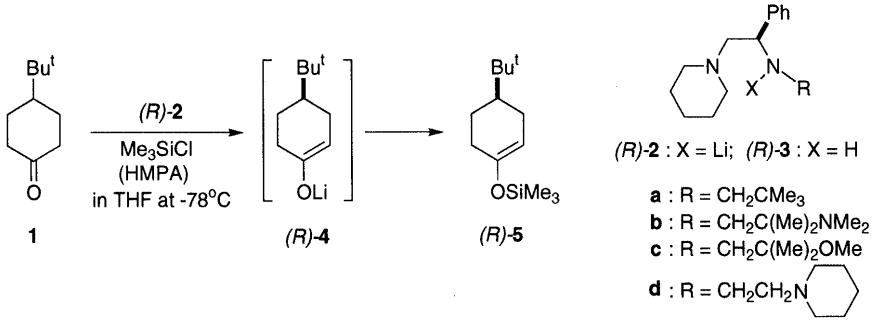

Chart 1

Table 1. Deprotonation of **1** in the Absence and the Presence of HMPA to Give **5**[a]

Lithium amide (**2**)	Solvent	Run	In the absence of HMPA		Run	In the presence of HMPA	
			Chem. y. (%)	e.e. (%) (Confign.)		Chem. y. (%)	e.e. (%) (Confign.)
(*R*)-**2a**	THF	1	86	84 (*R*)	7	82	82 (*R*)
(*R*)-**2a**	Toluene	2	12	58 (*R*)	8	87	82 (*R*)
(*R*)-**2b**	THF	3	14	50 (*R*)	9	28	58 (*R*)
(*R*)-**2b**	Toluene	4	2	26 (*R*)	10	34	57 (*R*)
(*R*)-**2c**	THF	5	3	56 (*R*)	11	33	77 (*R*)
(*R*)-**2d**	THF	6	11	15 (*R*)	12	35	68 (*R*)

a) Data using (*R*)-**2a** are taken from ref. 3*a*.

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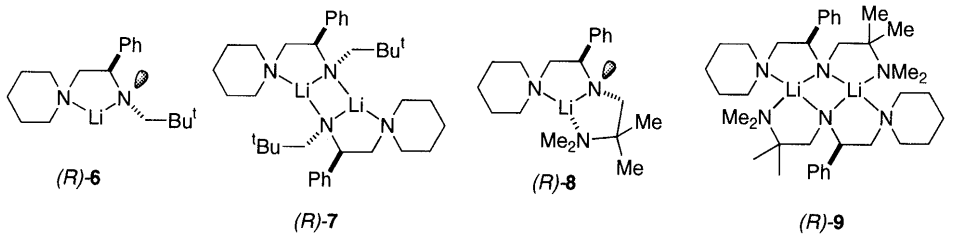

Chart 2

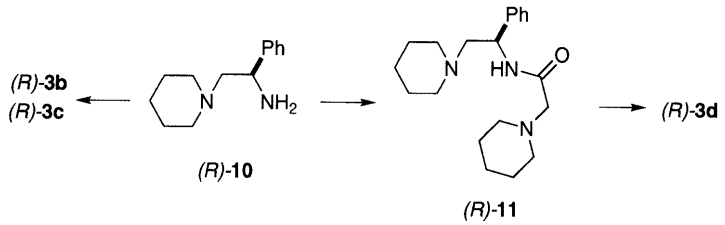

Chart 3

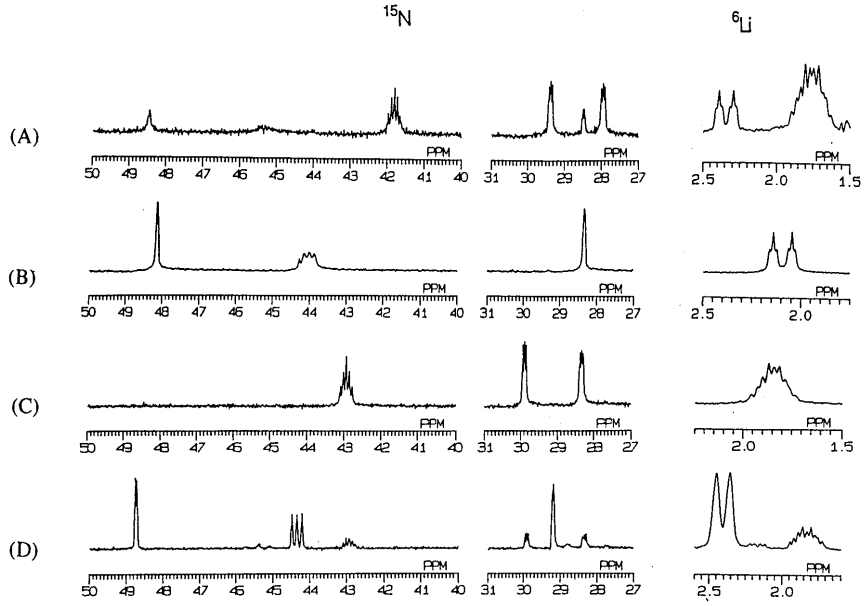

Fig. 1. ^{6}Li- and ^{15}N-NMR Spectra of a 0.07 M Solution of [^{6}Li,$^{15}N_3$]-(*R*)-**2b** Recorded at −80 °C
(A), in THF-d_8; (B), in THF-d_8 with 2 eq of HMPA-d_{18}; (C), in toluene-d_8; (D), in toluene-d_8 with 2 eq of HMPA-d_{18}.

trans-isomer,[4] so the chelated monomer of (*R*)-**2b** should be *cis*-fused, as shown in (*R*)-**8**. The formation of (*R*)-**8** in solution means that the amide nitrogen is chiral and the lone pair on the amide nitrogen is fixed *cis* to the phenyl group, and also *cis* to the vacant orbital of the lithium. Assuming that the deprotonation process proceeds *via* synchronous proton transfer (from carbon to nitrogen) and lithium ion transfer (from nitrogen to oxygen) in an eight-membered[5] or a six-membered[6] transition state, (*R*)-**8** seems to be an excellent species. Although (*R*)-**8** may aggregate depending upon the solvent used, the degree of aggregation may be controllable by addition of HMPA.[3] We therefore prepared chiral tridentate amines having a dimethylamino group ((*R*)-**3b**), a methoxy group ((*R*)-**3c**), or a 1-piperidino group ((*R*)-**3d**) as shown in Chart 3. Deprotonation reactions of **1** using (*R*)-**2b**—**d** were carried out under the same conditions, and the results were compared with those using (*R*)-**2a**, as summarized in Table 1.

When (*R*)-**2b** was used as a chiral lithium amide, chemical and optical yields of the products ((*R*)-**5**) were lower in THF (run 3) and in toluene (run 4), compared with those using (*R*)-**2a** (runs 1, 2). Addition of 2 eq of HMPA at the start of the reactions increases these yields to some extent (runs 9, 10), but they are still far below those obtained using (*R*)-**2a** (runs 7, 8). Similarly, with (*R*)-**2c** and (*R*)-**2d**, chemical and optical yields of the products are lower in THF (runs 5, 6), compared with those using (*R*)-**2a** (run 1). Addition of 2 eq of HMPA at the start of the reaction gives the products in moderate chemical and optical yields (runs 11, 12). It is now clear that chiral tridentate lithium amides ((*R*)-**2b**—**d**) are inferior to the chiral bidentate lithium amide ((*R*)-**2a**) as bases for the present enantioselective deprotonation reaction.

To understand the above phenomenon, we prepared [^{6}Li,$^{15}N_3$]-(*R*)-**2b**, and examined its solution structures by ^{6}Li- and ^{15}N-NMR spectroscopy in THF-d_8 and in

toluene-d_8 in the absence and in the presence of 2 eq of HMPA-d_{18} at $-80\,^{\circ}C$. The spectra are shown in Fig. 1.

In THF-d_8 in the presence of 2 eq of HMPA-d_{18} (Fig. 1B), the ^{6}Li-NMR spectrum shows a doublet of triplets, indicating that the ^{6}Li couples to three neighboring ^{15}N nuclei (^{15}N: spin 1/2). The corresponding ^{15}N spectrum is analyzed as three sets of triplets (1 : 1 : 1), indicating that each ^{15}N couples to one neighboring ^{6}Li nucleus (^{6}Li: spin 1). These observations suggest that (*R*)-**2b** exists almost entirely as a chelated monomeric form ((*R*)-**8**) in THF in the presence of 2 eq of HMPA. In toluene-d_8 (Fig. 1C), the ^{15}N-NMR spectrum shows a quintet and two sets of triplets, indicating that one ^{15}N couples to two neighboring ^{6}Li nuclei with the same coupling constants, while each of the remaining two ^{15}N couples to one neighboring ^{6}Li nucleus. The corresponding ^{6}Li spectrum is expected to be a doublet of doublets of triplets, and is actually a complex multiplet. These observations suggest that (*R*)-**2b** exists almost entirely as a chelated dimeric form ((*R*)-**9**) in toluene. In THF-d_8 (Fig. 1A) and in toluene-d_8 in the presence of 2 eq of HMPA-d_{18} (Fig. 1D), the spectra show the existence of the above two species ((*R*)-**8**, (*R*)-**9**). The ratio of these two species ((*R*)-**8**/(*R*)-**9**) is roughly estimated to be 3/7 in THF, and 8/2 in toluene in the presence of 2 eq of HMPA. Thus, HMPA acts as a reagent to deaggregate a chelated dimer ((*R*)-**9**) to a chelated monomer ((*R*)-**8**), but does not open the internally chelated structure.

It is clear that (*R*)-**2b** exists as a chelated monomer ((*R*)-**8**) in which the lithium is tri-coordinated, as a chelated dimer ((*R*)-**9**) in which the lithium is tetra-coordinated, or as a mixture of these two species depending on the solvent used. The Lewis acidity of the lithium is considered to be decreased as the internal coordination to the lithium increases. Evaluating the importance of the carbonyl oxygen in coordinating to the lithium for **1** to be deprotonated by lithium amides, it is concluded that the low chemical yields observed by using (*R*)-**2b**—**d** as bases (runs 3—6, 9—12) can be rationalized in terms of the decrease in the Lewis acidity of the lithiums of these tridentate lithium amides compared with the lithium of (*R*)-**2a** in runs 1, 7, and 8. The same explanation may be applied to explain the low chemical yield in the deprotonation reaction of **1** by (*R*)-**2a** in toluene (run 2).

It is thus shown that the structure of the lithium amide for the deprotonation of carbonyl compounds should be such that its lithium in solution is mono-coordinated or di-coordinated (other than the coordination by the solvent) to get the deprotonated product in high yield.

Experimental

All melting and boiling points are uncorrected. IR spectra were recorded on a JASCO IRQ-1 or a JASCO DS-402G spectrometer. ^{1}H-NMR spectra were recorded on a JEOL JNM-EX 270 or a JEOL GSX-400 spectrometer, operating at 270 or 400 MHz, respectively. The chemical shifts are given in δ (ppm) values using tetramethylsilane as an internal standard. ^{6}Li- and ^{15}N-NMR spectra were recorded on a JEOL GSX-500 spectrometer operating at 73.45 and 50.55 MHz, respectively. The ^{6}Li chemical shifts are given in δ (ppm) using ^{6}LiCl in MeOH ($\delta = 0.0$) as an external standard. The ^{15}N chemical shifts are given in δ (ppm) using [^{15}N]aniline in THF ($\delta = 52.0$) as an external standard. Coupling constants (J) are given in hertz. The following abbreviations are used: br = broad, s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, t = triplet, q = quartet, quint = quintet, m = multiplet. Mass spectra (MS) were recorded on a JEOL JMS-01 SG-Z or a JEOL JMX-DX-300 spectrometer. THF, toluene, THF-d_8, and toluene-d_8 were distilled from sodium/benzophenone ketyl under an argon atmosphere. HMPA, HMPA-d_8, and TMSCl were distilled from CaH_2 under an argon atmosphere.

[$^{15}N_3$]-(*R*)-2-Dimethylamino-2-methyl-*N*-[1-phenyl-2-(1-piperidino)ethyl)]propylamine ([$^{15}N_3$]-(*R*)-3b) Under an argon atmosphere, dimethyl sulfonide (DMSO) (1.48 ml, 19.3 mmol) was added to a solution of oxalyl chloride (0.79 ml, 8.92 mmol) in dichloromethane (5 ml) at $-60\,^{\circ}C$, and the whole was stirred for 5 min. A solution of [^{15}N]-2-dimethylamino-2-methyl-1-propanol (0.88 g, 7.43 mmol) in dichloromethane (2 ml) was added, and the whole was stirred for 30 min. Triethylamine (7.5 ml) was added, and the whole was warmed to room temperature. Colorless precipitates were filtered off, washed with benzene (30 ml) and toluene (20 ml), and the filtrate and the washings were combined. [$^{15}N_2$]-(*R*)-**10**[7,8] (0.85 g, 4.13 mmol) and *p*-toluenesulfonic acid (200 mg) were added to this solution, and the solvent was evaporated under ordinary pressure at 30—95 °C. The residue was dissolved in a mixture of benzene (50 ml) and ether (20 ml), and the whole was washed with saturated aqueous $NaHCO_3$ (30 ml) and brine (30 ml), and dried over anhydrous K_2CO_3. Evaporation of the solvent *in vacuo* gave a brown oil (1.71 g), which was dissolved in EtOH (100 ml). Under ice-cooling, $NaBH_4$ (0.45 g, 11.8 mmol) was added, and the whole was stirred at room temperature for 1 h. Evaporation of the solvent *in vacuo* gave a residue, which was mixed with saturated aqueous $NaHCO_3$ (30 ml), and the whole was extracted with hexane. The organic extracts were combined and evaporated to dryness *in vacuo* to give a pale yellow oil, which was converted to the picrate in the usual manner. Recrystallization from EtOH gave [$^{15}N_3$]-(*R*)-**3b**·di-picric acid salt (2.56 g, 81%) as a yellow powder of mp 204—205 °C. *Anal.* Calcd for $C_{19}H_{33}{}^{15}N_3 \cdot 2C_6H_3N_3O_7$: C, 48.88; H, 5.14; N, 16.88. Found: C, 48.85; H, 5.09; N, 16.50. The free amine ([$^{15}N_3$]-(*R*)-**3b**) was obtained in a usual manner and was purified by bulb-to-bulb distillation as a colorless oil of bp 200 °C (bath temperature) (0.5 mmHg). ^{1}NMR (in $CDCl_3$): 0.94 (3H, s), 1.08 (3H, s), 1.1—1.6 (6H, m), 2.22 (6H, s), 2.0—2.5 (8H, m), 3.65 (1H, dd, $J = 6.3$, 12), 7.2—7.4 (5H, m). $[\alpha]_D^{25}$ $-90.0°$ ($c = 1.11$, MeOH). MS m/z: 307 ($M^+ + 1$).

The corresponding non-labeled amine ((*R*)-**3b**) was prepared by the same procedure.

(*R*)-2-Methoxy-2-methyl-*N*-[1-phenyl-2-(1-piperidino)ethyl]propylamine ((*R*)-3c) Under an argon atmosphere, DMSO (1.91 ml, 26.9 mmol) was added to a solution of oxalyl chloride (1.01 ml, 11.5 mmol) in dichloromethane (10 ml) at $-60\,^{\circ}C$, and the whole was stirred for 5 min. A solution of 2-methoxy-2-methyl-1-propanol (1.0 g, 9.6 mmol) in dichloromethane (3 ml) was added during 3 min, and the whole was stirred for 15 min. Triethylamine (9.6 ml) was added, and the whole was warmed to room temperature. Colorless precipitates were filtered off, and washed with benzene (30 ml) and toluene (20 ml). The filtrate and washings were combined. (*R*)-**10**[7,8] (1.63 g, 7.7 mmol) was added and the resulting solution was concentrated under ordinary pressure at 30—100 °C. The residue was dissolved in benzene (50 ml), and the whole was washed with saturated aqueous $NaHCO_3$ (30 ml) and brine (30 ml), and dried over anhydrous K_2CO_3. Evaporation of the solvent *in vacuo* gave a yellow oil, which was dissolved in EtOH (50 ml). Under ice-cooling, $NaBH_4$ (0.60 g, 16.8 mmol) was added, and the whole was stirred at room temperature for 1 h. Evaporation of the solvent *in vacuo* gave a residue, which was mixed with saturated aqueous $NaHCO_3$ (30 ml), and the whole was extracted with hexane. The organic extracts were combined and evaporated to dryness *in vacuo* to give a pale yellow oil, which was converted to the picrate in the usual manner. Recrystallization from EtOH gave (*R*)-**3c**·di-picric acid salt (4.98 g, 86%) as yellow needles of mp 171.5—172.5 °C (dec.). *Anal.* Calcd for $C_{18}H_{30}N_2O \cdot 2C_6H_3N_3O_7$: C, 48.41; H, 4.88; N, 14.68. Found: C, 48.13; H, 4.84; N, 14.96. The free amine ((*R*)-**3c**) was obtained in the usual manner and was purified by bulb-to-bulb distillation as a colorless oil of bp 200 °C (bath temperature) (0.5 mmHg). ^{1}N-NMR (in $CDCl_3$): 1.12 (3H, s), 1.23 (3H, s), 1.4—1.65 (6H, m), 2.2—2.6 (9H, m), 3.19 (3H, s), 3.71 (1H, dd, $J = 4$, 12), 7.2—7.4 (5H, m). $[\alpha]_D^{25}$ $-88.0°$ ($c = 1.14$, MeOH).

(*R*)-*N*-[1-Phenyl-2-(1-piperidino)ethyl]-1-piperidineacetamide ((*R*)-11) Triethylamine (3.29 g, 22.4 mmol) was added under ice-cooling to a solution of (*R*)-**10**[7,8] (2.20 g, 10.8 mmol), 1-piperidineacetic acid hydrobromide (2.66 g, 11.2 mmol), and diethylphosphorocyanidate (DEPC)[9] (90%, 2.39 ml, 13.2 mmol) in dimethylformamide (DMF) (15 ml), and the reaction mixture was stirred at room temperature for 3 h. After

addition of water (50 ml) and saturated aqueous $NaHCO_3$ (50 ml), the whole was extracted with ethyl acetate (200 ml). The organic layer was washed with water (100 ml) six times, and with brine (50 ml) twice, then dried over anhydrous K_2CO_3. Evaporation of the solvent gave a colorless solid, which was recrystallized from aqueous EtOH to give (*R*)-**11** (3.20 g, 90%) as colorless needles of mp 75—76 °C. IR (KBr) cm^{-1}: 3370, 1650. MS *m/z*: 330 ($M^+ + 1$). *Anal.* Calcd for $C_{20}H_{31}N_3O$: C, 72.91; H, 9.48: N, 12.75. Found: C, 72.87; H, 9.56; N, 12.48.

(*R*)-2-(1-Piperidino)-*N*-[2-(1-piperidino)ethyl]-1-phenylethylamine ((*R*)-3d) (*R*)-**11** (4.3 g, 13 mmol) was added portionwise to a suspension of $LiAlH_4$ (1.58 g, 36 mmol) in THF (200 ml), and the whole was heated under reflux for 2 d. Under ice-cooling, water (3.2 ml), 10% aqueous NaOH (1.6 ml) and water (3.2 ml) were added successively, and the whole was filtered. The filtrate and THF washings were combined, dried over anhydrous K_2CO_3, and evaporated to dryness *in vacuo*. The residue was purified by bulb-to-bulb distillation to give a colorless oil, which solidified on standing. Recrystallization from pentane gave (*R*)-**3d** (3.1 g, 75%) as colorless needles of mp 50—50.5 °C. ^{1}H-NMR (in $CDCl_3$): 1.35—1.75 (12H, m), 1.8—2.9 (15H, m), 3.74 (1H, dd, *J*=3, 5), 7.2—7.4 (5H, m). $[\alpha]_D^{18}$ −64.8° (*c*=0.90, $CHCl_3$). *Anal.* Calcd for $C_{20}H_{33}N_3$: C, 76.14; H, 10.54; N, 13.32. Found: C, 76.36; H, 10.62; N, 13.29.

Deprotonation of 1 by (*R*)-2b in Toluene in the Absence of HMPA (Run 4) Under an argon atmosphere, a solution of BuLi in hexane (1.66 N, 1.11 ml, 1.84 mmol) was added to a solution of (*R*)-**3b** (608.2 mg, 1.94 mmol) in toluene (30 ml) at −78 °C. The whole was warmed to room temperature, stirred for 5 min, cooled to −78 °C, and stirred for 5 min. A solution of **1** (237.0 mg, 1.53 mmol) and TMSCl (0.97 ml, 7.65 mmol) in toluene (2 ml) was added dropwise during 90 s, and the whole was stirred at −78 °C for 10 min. After addition of triethylamine (2 ml) and saturated aqueous $NaHCO_3$ (5 ml), the reaction mixture was warmed to room temperature, and extracted with hexane (200 ml). The organic extract was washed with 0.1 N aqueous citric acid (50 ml) several times until the pH of the aqueous washings was nearly 4, then with water (20 ml), saturated aqueous $NaHCO_3$ (20 ml) and brine (20 ml), and dried over anhydrous Na_2SO_4. Evaporation of the solvent *in vacuo* gave a pale yellow oil, which was purified by column chromatography (silica gel, hexane) followed by bulb-to-bulb distillation to give **5** (7.7 mg, 2%) as a colorless oil of bp 180 °C (10 mmHg), $[\alpha]_{365}^{25}$ +60.9° (*c*=0.39, benzene), corresponding to 26% ee (*R*).[10]

Deprotonation of 1 by (*R*)-2b in THF in the Presence of HMPA (Run 9) Under an argon atmosphere, a solution of BuLi in hexane (1.66 N, 0.90 ml, 1.50 mmol) was added to a solution of (*R*)-**3b** (493.4 mg, 1.57 mmol) in THF (25 ml) at −78 °C. The whole was warmed to room temperature, and stirred for 5 min. After addition of HMPA (0.52 ml, 3.00 mmol) and stirring for 5 min, the whole was cooled to −78 °C, and stirred for 5 min. A solution of **1** (190.6 mg, 1.25 mmol) and TMSCl (0.79 ml, 6.26 mmol) in THF (3 ml) was added dropwise during 90 s, and the whole was stirred at −78 °C for 10 min. After addition of triethylamine (2 ml) and saturated aqueous $NaHCO_3$ (4 ml), the reaction mixture was warmed to room temperature, and extracted with hexane (200 ml). The organic extract was washed with 0.1 N aqueous citric acid (50 ml) several times until the pH of the aqueous washings was nearly 4, then with water (20 ml), saturated aqueous $NaHCO_3$ (20 ml) and brine (20 ml), and dried over anhydrous Na_2SO_4. Evaporation of the solvent *in vacuo* gave a pale yellow oil, which was purified by column chromatography (silica gel, hexane) followed by bulb-to-bulb distillation to give **5** (76.8 mg, 28%) as a colorless oil of bp 180 °C (bath temperature) (10 mmHg), $[\alpha]_{365}^{25}$ +136.6° (*c*=1.04, benzene), corresponding to 58% ee (*R*).[10]

Rotational Values Obtained in the Deprotonation Reactions All deprotonation reactions were carried out and the products (**5**) were isolated and purified as described above. Chemical yields and ee's of **5** are given in Table 1. Rotational values[10] of **5** obtained were as follows. Run 3: $[\alpha]_{365}^{25}$ +117.2° (*c*=1.13, benzene); run 5: $[\alpha]_{365}^{25}$ +131.7° (*c*=0.48, benzene); run 6: $[\alpha]_{365}^{25}$ +35.2° (*c*=0.82, benzene); run 10: $[\alpha]_{365}^{25}$ +134.7° (*c*=1.05, benzene); run 11: $[\alpha]_{365}^{25}$ +182.8° (*c*=1.03, benzene); run 12: $[\alpha]_{365}^{25}$ +161.0° (*c*=1.04, benzene).

Typical Procedure for Preparing a Sample of [^{6}Li,$^{15}N_3$]-(*R*)-2b in THF-d_8 in the Presence of HMPA (2 eq) for the Measurement of ^{6}Li- and ^{15}N-NMR Spectra (Fig. 1B) [$^{15}N_2$]-(*R*)-**3b** (56.1 mg, 0.18 mmol) was placed in a dried NMR sample tube. The tube was placed under a septum, and the inside of the tube was flushed with argon. THF-d_8 (0.5 ml) was charged *via* a syringe to dissolve [$^{15}N_2$]-(*R*)-**3b**. A solution of Bu^{6}Li in hexane (5.5 N, 33 μl, 0.18 mmol) was added using a micro-syringe, and the solution adhering to the inside wall of the tube was washed down with THF-d_8 (0.5 ml). HMPA-d_{18} (60 μl, 0.35 mmol) was added using a micro-syringe, and the HMPA-d_{18} on the inside wall of the tube was washed down with THF-d_8 (1.2 ml). The tube was then dipped in a dry ice–acetone bath, and sealed with a flame. This sample was used for the measurement of NMR spectra.

All other samples of [^{6}Li,$^{15}N_3$]-(*R*)-**2b** for the measurements of NMR spectra were prepared in a similar way.

^{6}Li- and ^{15}N-NMR Spectral Data for [^{6}Li,$^{15}N_3$]-(*R*)-2b (a) In THF-d_8 (Fig. 1A). Major species: ^{6}Li-NMR: 1.8 (m); ^{15}N-NMR: 28.0 (t, *J*=2.4), 29.4 (t, *J*=2.4), 41.8 (quint, *J*=4.0). Minor species: ^{6}Li-NMR: 2.4 (dt, *J*=7.3, 1.5, 1.5); ^{15}N-NMR: 28.5, 45.4, 48.5. (b) In THF-d_8 with 2 eq of HMPA-d_{18} (Fig. 1B). ^{6}Li-NMR: 2.1 (dt, *J*=7.2, 1.2, 1.2). ^{15}N-NMR: 28.4, 44.0 (t, *J*=7.0), 48.2. (c) In toluene-d_8 (Fig. 1C). ^{6}Li-NMR: 1.85 (m); ^{15}N-NMR: 28.4 (t, *J*=2.1), 29.9 (t, *J*=2.4), 43.0 (quint, *J*=4.1). (d) In toluene-d_8 with 2 eq of HMPA-d_{18} (Fig. 1D). Major species: ^{6}Li-NMR: 2.4 (br d, *J*=7.0); ^{15}N-NMR: 29.2, 44.4 (t, *J*=7.0), 48.8. Minor species: ^{6}Li-NMR: 1.8 (m); ^{15}N-NMR: 28.4 (t, *J*=2.8), 29.9 (t, *J*=2.4), 42.9 (quint, *J*=4.0).

Acknowledgments Financial support from the Ministry of Education, Science, Sports and Culture of the Japanese Government, Ciba-Geigy Foundation for the Promotion of Science, and Japan Research Foundation for Optically Active Compounds is gratefully acknowledged.

References and Notes

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