Solution Structure of a Dilithiumamide/Diethylzinc Heterocomplex that Catalyzes Asymmetric Alkylation Reactions

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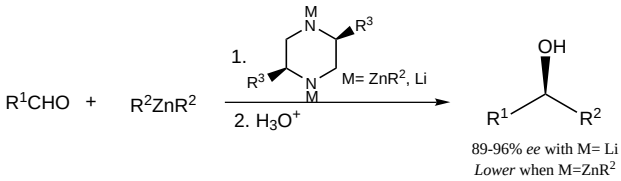
Abstract: The catalytic complex between diethylzinc and the lithium salt of the chiral piperazine, (2*S*,5*S*)-2-isobutyl-5-isopropylpiperazine (**1**) in THF was investigated by NMR spectroscopy. The lithium salt of **1** was found to undergo fast chair–twisted boat–chair conformational exchange. However, upon addition of one equivalent of diethylzinc this process was found to slow down on the NMR timescale. The piperazine ring in **1** adopts a boat conformation in which the zinc bridges the two amide nitrogens in **1**. Small additions of a substrate, for example benzaldehyde, resulted in a dramatic increase of the chair–twisted boat–chair conformational exchange, as seen in the NMR spectra.

Keywords: aldehydes · asymmetric synthesis · conformation analysis · lithium · NMR spectroscopy · zinc

Introduction

The asymmetric alkylation of aldehydes is one of the most important and fundamental asymmetric reactions. The optically active secondary alcohols thus produced find wide use as starting materials and intermediates in the synthesis of naturally occurring compounds and pharmaceuticals.[1] Traditionally, Grignard and alkyllithium reagents have been used together with chiral ligands, for example, [1,*n*]-substituted diamines and aminoalcohols, in stochiometric amounts to obtain high enantioselectivity in the above addition reaction.[2] However, dialkylzinc reagents are currently the most widely used reagents for this reaction. The low reactivity of dialkylzinc reagents towards aldehydes in the absence of ligands that contain Lewis acidic functionalities makes these reagents ideal for the catalytic and enantioselective alkylation of aldehydes. The most effective ligands for the asymmetric addition of dialkylzinc reagents to aldehydes are chiral [1,*n*]-substituted diamines and aminoalcohols.[3] Soai and co-workers have described the use of C_2-symmetrical piperazines in the catalytic enantioselective addition of dialkylzinc reagents to aldehydes (Scheme 1).[4] Interestingly, they obtained higher enantioselectivities with dilithiated piperazines, that is lithium piperazides, than with the unlithiated analogues.

Despite the extended use of reagent–ligand complexes of this type in preparative organic chemistry, very little is known about their structure and dynamics in solution.[5] Furthermore, the control of the enantioselectivity in the addition reaction of alkylgroups to ketones with an organometallic reagent is still meager.[6, 10] Our interest in lithium organic chemistry and asymmetric synthesis led us to investigate the chiral piperazines and their dilithium piperazide analogues used in the catalytic asymmetric addition of diethylzinc to benzaldehyde. The intention of this investigation was to obtain structural information about possible initial solution-state structures for the piperazine/dilithium piperazide–diethylzinc complexes, to be used as starting points for the elucidation of the reaction mechanism. Information about structure, dynamics, and reaction mechanism will provide us with the necessary tools to understand and control stereoselectivity in these reactions. This would also be beneficial for the development of new chiral ligands to be used in the catalytic asymmetric addition of organometallic reagents to ketones.



Scheme 1. The use of C_2-symmetrical piperazines in the catalytic enantioselective addition of dialkylzinc reagents to aldehydes.

Results and Discussion

In order to simplify the NMR investigations of the complexes formed between diethylzinc and the piperazine or the

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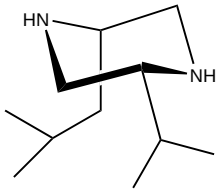
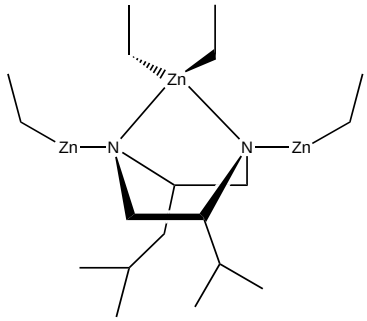


1

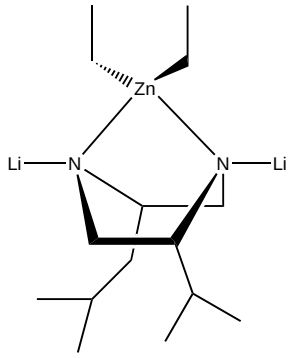
dilithiumpiperazide, we prepared the unsymmetrically substituted chiral piperazine, (2*S*,5*S*)-2-isobutyl-5-isopropylpiperazine (**1**).

A solution of **1** (60 μL) in [D_8]toluene (640 μL) was titrated with diethylzinc (2 M in [D_8]toluene). The ^{1}H and ^{13}C NMR spectra showed broad and unresolved signals at all additions below 3 equivalents of diethylzinc. However, after the addition of ≥3 equivalents of diethylzinc the NMR signals narrowed. Raising the temperature to 40 °C and application of a shifted sine-bell weighting of the FID facilitated the measurement of ring ^{1}H,^{1}H coupling constants. These coupling constants were found to be ≈11 Hz. This observation indicates that the catalytic complex between diethylzinc and **1** adopts a boat conformation (**2**).



2

The ^{1}H,^{1}H-NOESY spectra showed correlations between the ethylzinc moieties and all the ring protons in **2**. This is apparently caused by the coordination of two ethylzinc moieties to the two amine nitrogens in conjunction with the coordination of a diethylzinc molecule that bridges the two amine ring nitrogens in **2**. This arrangement will result in NOE correlations to both faces of the piperazine ring in **2** by the ethylzinc moieties.



3

The dilithiated piperazide was prepared by addition of two equivalents of *n*Bu^{6}Li (70 μL, 10 M) to a solution of **1** (70 μL) in [D_8]toluene (630 μL). The ^{6}Li, ^{1}H, and ^{13}C NMR of the resulting gelatinous solution showed very broad NMR signals at all temperatures used (−90 to 60 °C). The broad ^{6}Li, ^{13}C, and ^{1}H NMR signals for the dilithium piperazide salt **3** indicate that fast dynamic processes take place in solution on the NMR timescale. The dynamics of **3** originate from either fast interaggregate or conformational exchange. The energy barrier for the interconversion of the different species involved in the exchange is low, as shown by the variable-temperature study.[7]

A new solution of **3** was prepared in [D_8]THF. The NMR spectra of this solution were similar to the spectra obtained in [D_8]toluene above. The ^{1}H, ^{13}C, and ^{6}Li NMR signals were all broad after the addition of 2 equivalents of *n*BuLi. However, upon titration with diethylzinc, there was a significant sharpening of the signals in the ^{6}Li NMR spectra. In addition, two new signals began to appear at $\delta = 1.2$ and -0.4. After a total addition of 1 equivalent of diethylzinc, the two signals at $\delta = 1.2$ and -0.4 dominated the ^{6}Li NMR spectra. The integral ratio for the two signals was 1:1; however, there were large differences in linewidths (0.9, 1.9 Hz) between the signals (Figure 1).

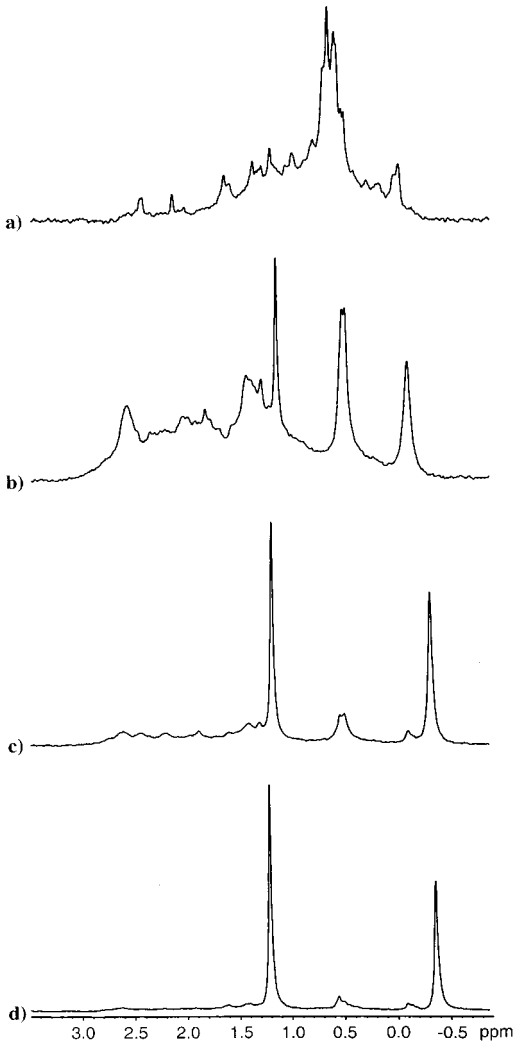


Figure 1. ^{6}Li NMR spectra of the dilithiated **1** in [D_8]THF at −70 °C with different amounts of added Et_2Zn: a) 0 equiv, b) 0.20 equiv, c) 0.60 equiv, and d) 1.0 equiv.

Large differences in ^{6}Li NMR linewidths for lithium atoms present in the same aggregate have previously been observed by us for chiral lithium amide dimers.[8] This difference originates from different environments around the lithium atoms, especially with respect to differences in the solvation

numbers of lithium. Narrow NMR signals were also observed in the ^{1}H and ^{13}C NMR spectra upon addition of diethylzinc (Figure 2a). Variable-temperature studies and the ^{1}H and ^{13}C NMR spectra indicated that only one major species was present in solution. The assignment of the ^{13}C NMR spectra from the complex between **3** and $ZnEt_2$ is shown in Figure 3.

The ^{1}H NMR of the above solution showed ^{1}H,^{1}H couplings of 6–14 Hz for the ring protons. This is in sharp contrast to the ^{1}H,^{1}H couplings of 4–5 Hz observed for **1** in the absence of diethylzinc. The magnitude of the coupling constants (6–14 Hz) shows that the piperazine ring adopts a boat conformation. Furthermore, the ^{1}H,^{1}H NOESY of **3** with added diethylzinc showed NOE correlations between the diethylzinc protons and the protons from only one face of **3** (Figure 4). These results suggest that the addition of diethylzinc forces the piperazide ring in **3** to adopt a boat conformation in which the zinc atom bridges the two amide nitrogens in **3**.

The complexation of diethylzinc favors a boat conformation for the piperazide ring and thereby affects the barrier for chair–twisted boat–chair conformational exchange. However, we hasten to add that the diethylzinc addition may also affect the rate of interaggregate exchange.

The addition of an aldehydic substrate, namely benzaldehyde, to the above complex at $-70\,^\circ$C resulted in severe broadening of the linewidths in the ^{6}Li, ^{1}H, and ^{13}C NMR spectra. No signal from the aldehyde proton was observed in the ^{1}H NMR spectra, even if 1 equivalent of benzaldehyde was added. Accordingly, no carbonyl carbon signal was observed in the ^{13}C NMR spectrum. Furthermore, the ^{13}C and ^{1}H signals from the phenyl ring in benzaldehyde were broad. After the addition of $\approx$3 equivalents of benzaldehyde the ^{6}Li NMR spectrum showed a large resemblance to that obtained of **3** prior to the addition of diethylzinc (Figure 5).

The above results are likely to be caused by the coordination of the carbonyl oxygen in benzaldehyde to one of the lithium atoms in **3**. One of the two bonds between zinc and nitrogen is then lost, and a fast chair–twisted boat–chair conformational exchange, as previously observed for **3** with no added diethylzinc, is again facilitated. These dynamics also result in broad NMR signals from the coordinated benzaldehyde. In this context, it is interesting to note that the ^{6}Li NMR signal at $\delta = 1.2$, caused by the lithium with the higher coordination number, disappears very rapidly. This is in agreement with the expected lower energy barrier for coordination at this lithium center. The mechanism for the addition reaction has been suggested to involve a possible six-center reactive complex (Figure 6; page 2360).[9]

The carbonyl oxygen of benzaldehyde coordinates to one of the two lithium atoms in the boat conformation of **3**. This is an important feature in the transition-state structure as the metal–carbonyl oxygen interaction will activate the carbonyl carbon

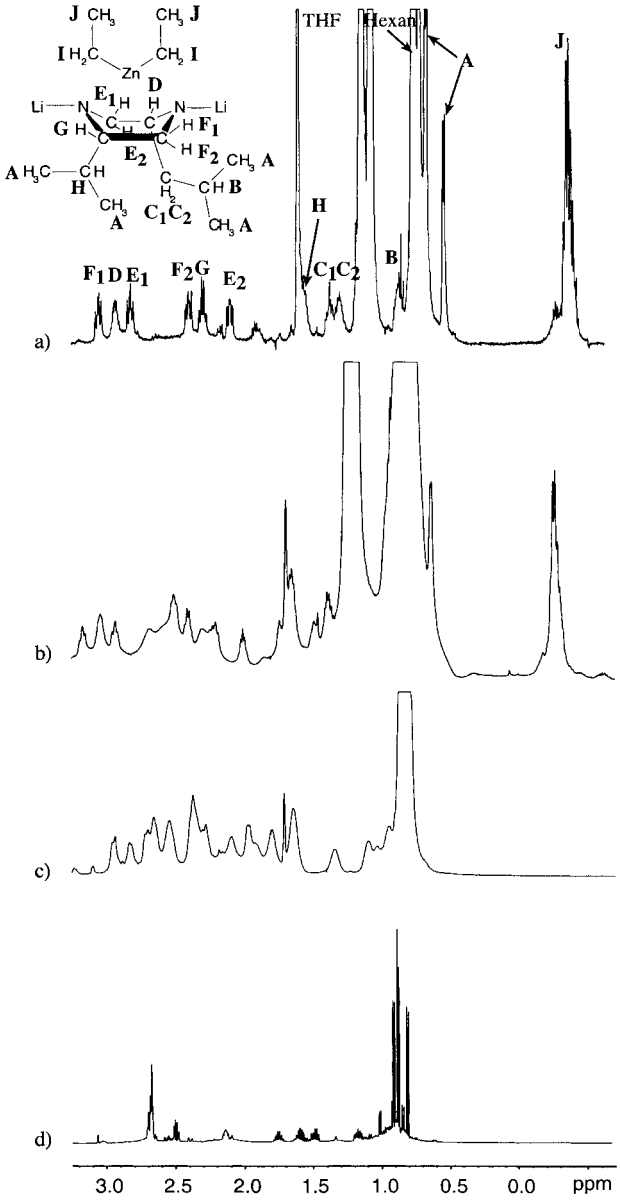


Figure 2. ^{1}H NMR spectra of a) **1** with *n*BuLi (2.0 equiv) and Et_2Zn (1.0 equiv) in [D_8]THF at $-70\,^\circ$C; b) **1** with *n*BuLi (2.0 equiv) and Et_2Zn (0.40 equiv) in [D_8]THF at $-70\,^\circ$C; c) **1** with *n*BuLi (2.0 equiv) in [D_8]THF at $-70\,^\circ$C; d) **1** in [D_8]THF at 25 °C.

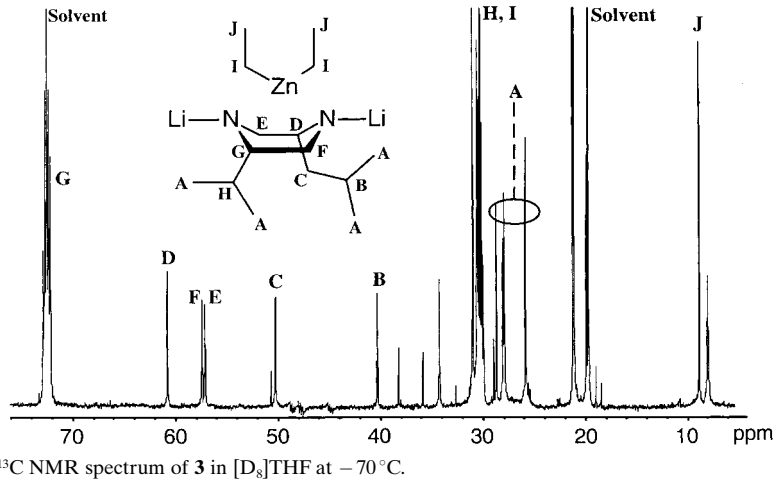


Figure 3. ^{13}C NMR spectrum of **3** in [D_8]THF at $-70\,^\circ$C.

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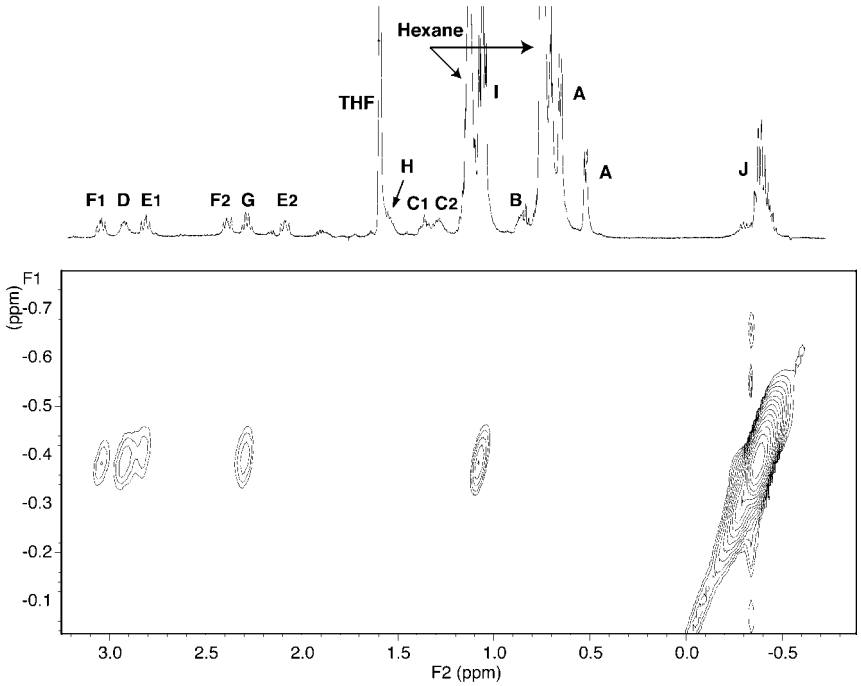

Figure 4. $^{1}H,^{1}H$-NOESY of **3** in [D_8]THF at $-70\,^{\circ}C$.

for nucleophilic attack. The importance of the above activation has recently been shown in the reaction of dialkylzinc with ketones.[10] The next step involves an interaction between one of the diethylzinc methylene carbons and the carbonyl carbon atom in the benzaldehyde, which results in the formation of a six-center transition state. Our NMR results strongly suggest that the initial state for the reaction is a chair and *not* a boat conformation. The coordination of benzaldehyde results in an opening of the nitrogen-zinc-nitrogen coordination in the boat conformation; this facilitates a fast chair – twisted boat – chair conformational exchange.

The alkylation of benzaldehyde with diethylzinc has been performed in the presence of the modified piperazine **1**. The enantiomeric excess (*ee*) of the product (*S*)-1-phenyl-1-propanol obtained with nonlithiated **1** and diethylzinc was 74%. The use of both monolithiated or dilithiated **1** gave the product in lower enantiomeric excess, 40% and 1 – 3%, respectively. The last result contradicts the expected increase in the product *ee* as previously observed when the dilithiated analogues of the symmetrically substituted piperazines in Scheme 1 were used as alkylation catalysts. This unexpected result might be attributable to the increased number of possible transition states available for the C_1-symmetrical complexes between benzaldehyde and **2** or **3**, compared with the C_2-symmetrical complex formed between benzaldehyde and the symmetrically substituted piperazines in Scheme 1.

Conclusions

Multinuclear and multidimensional NMR spectroscopy have been used to clarify the solution-state structure of the catalytic complexes between diethylzinc and piperazines, and diethylzinc and dilithium piperazides. The reagent complexes were shown to adopt a boat conformation which, upon coordination with an aldehyde substrate, for example, benzaldehyde, changed into a chair conformation and exhibited fast chair – twisted boat – chair conformational exchange. Furthermore, it appears that C_2-symmetry of the ligand is essential in order to obtain a good *ee* in this diethylzinc ethylation of benzaldehyde.

Experimental Section

General: All glassware used for the syntheses was dried overnight in a oven at 120 °C. Glassware and syringes used for the NMR studies and alkyla-

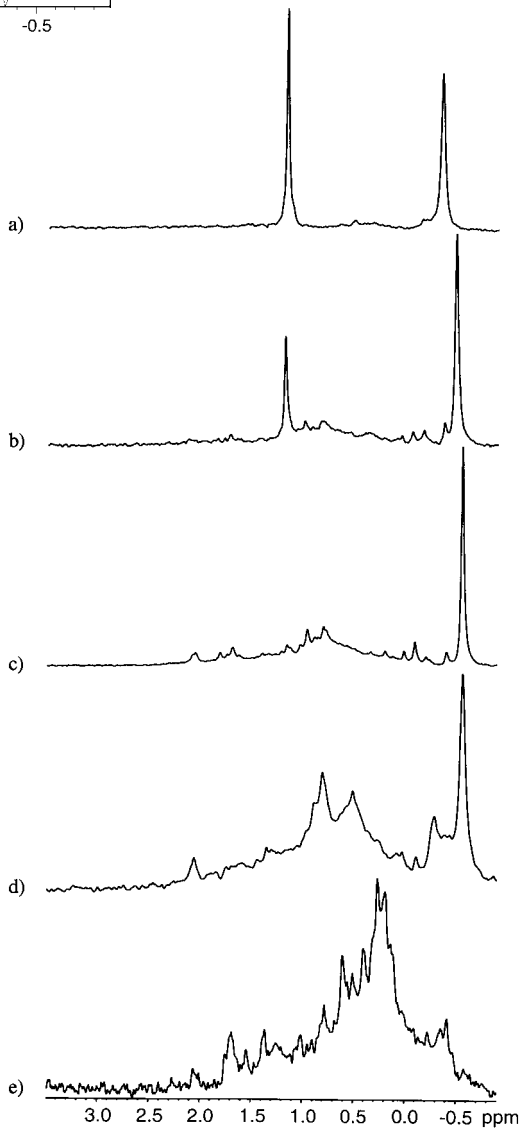

Figure 5. ^{6}Li NMR spectra of **3** in [D_8]THF at $-70\,^{\circ}C$ with different amounts of added benzaldehyde: a) 0 equiv, b) 0.40 equiv, c) 0.68 equiv, d) 1.22 equiv, and e) 3.50 equiv.

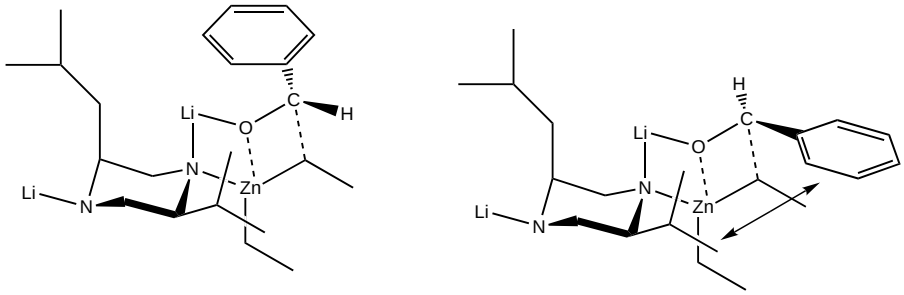

Figure 6. The six-center reactive complex that is suggested to be involved in the addition reaction.

tion reactions were dried at 50 °C in a vacuum oven before transfer into a glove box (Mecaplex GB 80 equipped with a gas-purification system to remove oxygen and moisture) containing a nitrogen atmosphere. Typical moisture content was < 0.5 ppm. Ethereal solvents, distilled from sodium and benzophenone under nitrogen, were kept over 4 Å molecular sieves in a septum-sealed flask inside the glove box. The concentration of the commercially available *n*BuLi solution (*n*BuLi, 2.5 M solution in hexanes, Aldrich) was determined by titration with biphenylmethanol.[11] Routine 1D ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 400 MHz instrument. Chromatographic analyses were carried out on a Varian Star 3400 CX gas chromatograph. All GC analyses were run on a chiral stationary phase column (CP-Chirasil-DEX CB, 25 m, 0.32 mm) from Chrompack. All analyses were performed at 115 °C (injector: 225 °C; detector: 250 °C) with He (2 mL min^{-1}) as the carrier gas.

NMR spectroscopy: All NMR spectra were recorded on a Varian Unity 500 spectrometer equipped with three channels and a 5 mm ^{1}H, ^{13}C, ^{6}Li, ^{15}N quad-resonance probe head, custom built by Nalorac. Measuring frequencies were 500 MHz (^{1}H) and 74 MHz (^{6}Li). The ^{1}H and ^{13}C spectra were referenced to the solvent signals: [D$_8$]THF $\delta = 3.58$. Lithium spectra were referenced to external [^{6}Li]Cl in [D$_4$]MeOH (0.3 M; $\delta = 0.0$). A typical 90° ^{6}Li pulse was 12 μs.

Preparation of (2*S*,5*S*)-2-isobutyl-5-isopropylpiperazine (1)

Boc-Val-Leu-OMe: Boc-(L)-Val-OH (12.67 g, 58.3 mmol) and H-(L)-Leu-OMe (9.83 g, 58.6 mmol) was dissolved in dichloromethane (180 mL). Triethylamine (8.5 mL, 61.0 mmol) was added, and the reaction mixture cooled to 0 °C. *N*,*N*′-dicyclohexylcarbodiimide (DCC; 12.53 g, 60.7 mmol) was added. The reaction mixture was stirred at 0 °C. After 4 h the mixture was heated to room temperature and stirred overnight. The solid was filtered off by suction, and the filtrate was evaporated. The residue was dissolved in ethyl acetate and washed with 2% HCl (3 × 100 mL), 4% $NaHCO_3$ (3 × 100 mL), and finally brine (3 × 100 mL). The organic layer was dried over anhydrous $MgSO_4$, filtrated, and evaporated. The residue was recrystallized from ethyl acetate/diethyl ether. Yield 12.72 g (67%); ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.99$ (dd, 12H), 1.48 (d, 9H), 1.60 (q, 1H), 1.69 (m, 3H), 2.15 (m, 1H), 3.76 (s, 3H), 3.93 (dd, 1H), 4.66 (dt, 1H), 5.09 (d, 1H), 6.26 (s, 1H).

(2S,5S)-2-isobutyl-5-isopropyldiketopiperazine: The *t*Boc-protected diamino acid (38.7 mmol) prepared above was deprotected in formic acid (100 mL). After the solution was stirred at room temperature for 2 h, the reaction mixture was evaporated under reduced pressure at a temperature below 30 °C. The residue was dissolved in methanol and was evaporated under reduced pressure at a temperature below 30 °C. One-third of the residue was then dissolved in *s*-butanol (130 mL) and toluene (80 mL). The solvent was distilled off and fresh *s*-butanol was added continuously. The distillation was interrupted after 2 h and the reaction mixture was allowed to cool to room temperature. The crystals formed were filtered off, and the filtrate was evaporated. A second crop of crystals was obtained by evaporating the filtrate, redissolving the precipitate in methanol, and precipitating by addition of DEE. The precipitate was filtered off and pooled together with the first crop of crystals. Yield (based on the *t*boc-diamino acid): 3.53 g (46%); ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.96$ (d, 3H), 1.01 (d, 3H), 1.06 (d, 3H), 1.56 (m, 2H), 1.63 (ddd, 1H), 1.78 (m, 1H), 1.92 (ddd, 1H), 2.45 (m, 1H), 3.92 (s, 1H), 4.03 (d, 1H), 5.89 (s, 1H), 6.04 (s, 1H).

*(2S,5S)-2-isobutyl-5-isopropylpiperazine (**1**)*: The diketopiperazine crystals (0.91 g, 0.46 mmol) were suspended in dry dimethoxyethane (DME, 40 mL) and then sonicated to finely divide the crystals. $TiCl_4$ (1.5 mL, 13.7 mmol) was added to a mixture of $NaBH_4$ (1.09 g, 29.0 mmol) in dry DME (20 mL) at 0 °C.[12] The diketopiperazine slurry was added to the flask at 0 °C. DME (10 mL) was then added, and the reaction mixture was stirred at room temperature overnight and then quenched with water. The precipitate which had formed was filtered off, and the filtrate was made alkaline with 25% NH_3. The alkaline solution was extracted with dichloromethane (3 × 75 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated. The residue was dissolved in methanol (50 mL) and HCl (6 M, 30 mL) and stirred over night to hydrolyze the titanium complexes formed. Methanol was evaporated, and the remaining solution was made alkaline with NaOH (1 M). The solution was extracted with CH_2Cl_2 (3 × 75 mL) and the combined organic layers were dried over anhydrous $MgSO_4$ and evaporated. Yield 0.84 g (70%); ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.90$ (m, 12H), 1.23 (m, 1H), 1.47 (m, 1H), 1.63 (m, 1H), 1.67 (m, 2H), 1.88 (m, 1H), 2.25 (m, 1H), 2.64 (m, 1H), 2.81 (m, 4H).

Enantioselective alkylation of benzaldehyde: Compound **1** (8 μL, ≈0.04 mmol) was dissolved in toluene (3 mL) and cooled to 0 °C. *n*BuLi (38 μL, 0.09 mmol, 2.4 M in hexane) was added and stirred for 10 min at 0 °C. Pure Et_2Zn (160 μL, 1.56 mmol, 9.76 M) was added to the ice-cooled mixture, and the resulting solution was stirred for 30 min. Benzaldehyde (78 μL, 0.76 mmol) was added and the reaction mixture was stirred at 20 °C for 20 h. The reaction was monitored by withdrawing 20 μL samples, which were quenched in diethylether (1 mL) and HCl (0.5 mL, 1 M). The layers were separated, and the organic phase was washed with saturated NaCl and dried over anhydrous Na_2S. The same procedure was followed for the mono- and nonlithiated piperazine reactions; however, the amount of *n*BuLi was altered.

Acknowledgments

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