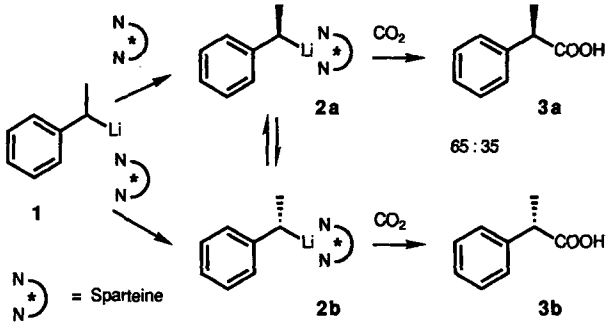
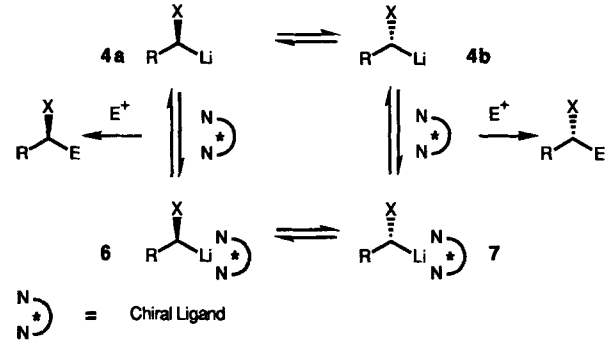
Stereoselective Transformations with Configurationally Labile α-Phenylselenoalkyllithium Compounds**

Abstract: Complexation of the configurationally labile α-phenylselenoalkyllithium compound **8** with 1,2-bisdimethylaminocyclohexane **15** led to two diastereomeric complexes **13** and **14** in a 7:3 ratio. Owing to ligand acceleration the complexes **13** and **14** added more rapidly to benzaldehyde than the uncomplexed organolithium compound **8**. Trapping of complexes **13** and **14** by benzaldehyde was shown to occur more rapidly than their equilibration. This corresponds to non-Curtin–Hammett kinetics, in which enantiomeric enrichment in the products reflects the equilibrium ratio of the complexes **13** and **14**.

Keywords
asymmetric alkylations · chiral auxiliaries · kinetics · organolithium compounds · stereoselective syntheses

From the viewpoint of a synthetic organic chemist chiral organolithium compounds with allyl,[2] benzyl,[3] α-seleno,[4, 5, 6] and α-thio[5, 6, 7] substituents are configurationally labile, since they racemize rapidly at low temperatures (e.g., at −78 °C). These synthons can nevertheless be utilized in stereoselective synthesis, as demonstrated many years ago by Nozaki and Noyori.[8] They showed that the complexation of α-methylbenzyllithium (**1**) with sparteine generates two diastereomeric complexes **2**, which give enantiomerically enriched hydratropic acid **3** on treatment with carbon dioxide (Scheme 1). This method of complexing configurationally labile organolithium reagents **4** with a chiral ligand and subsequently trapping the resulting diastereomeric complexes **6** and **7** with electrophiles has since been used to synthesize **5** with varying degrees of enantiomeric enrichment (Scheme 2).[9, 10]





Although the sequential addition of a chiral ligand and an electrophile to an organolithium compound is operationally simple, the stereochemical outcome of such experiments depends on a complex mixture of factors. To understand these processes the following questions need to be addressed: Is the rate at which the organolithium species are trapped by the electrophile sufficiently accelerated by the ligand? In other words, are the products **5** formed from complexes **6** and **7**, and not from the uncomplexed species **4**? If this is the case, the next point to be considered is whether the rate of trapping of complexes **6** and **7** by the electrophile is faster than their equilibration. If so, the enantiomeric enrichment in product **5** would reflect the diastereomeric ratio of the complexes **6** and **7** (the non-Curtin–Hammett case; cf. the dotted curves in Fig. 1). If the answer is no, a Curtin–Hammett situation prevails (cf. the solid lines in Fig. 1). The enantiomeric enrichment in the product then depends on the relative rates at which the two diastereomeric complexes **6** and **7** react with the electrophile, that is, the result is determined by kinetic resolution.

We describe here a series of experiments designed to answer the questions outlined above. The system studied was the addition of α-phenylselenoalkyllithium compound **8** to benzaldehyde in the presence of chiral diamine **15**. Some aspects of these experiments have been communicated in preliminary form.[11]

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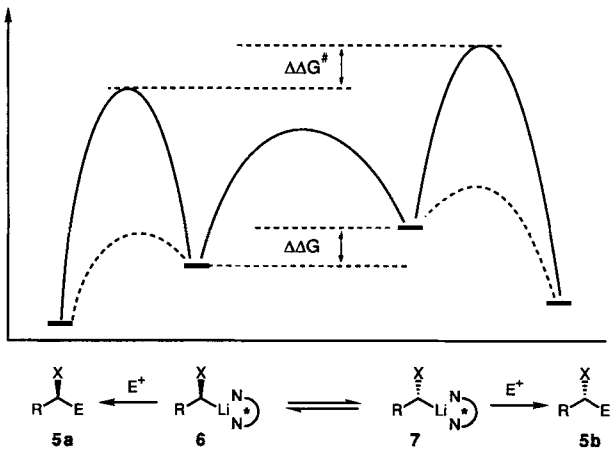
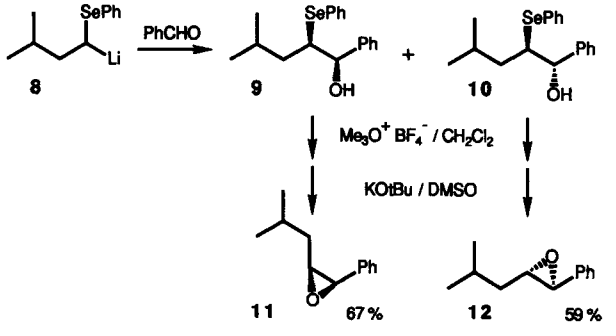


Fig. 1. Reaction of the complexes **6** and **7** with electrophiles: Curtin–Hammett (solid line) versus non-Curtin–Hammett (dotted line) behavior.

Results

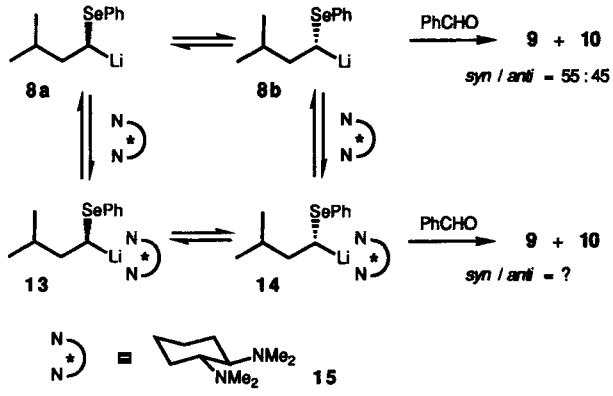
Addition of the complexed organolithium species 13 and 14 to benzaldehyde: Initially, the reaction of the uncomplexed lithium compound **8**[12] was studied. It was generated[13] in diethyl ether from the selenoacetal in a two-compartment low-temperature reaction vessel[14] and was added at −60 °C to a precooled solution of benzaldehyde (2 equiv) in ether. The *syn* and *anti* adducts **9** and **10** were isolated from the reaction in 80% yield. The two diastereomers were separated by MPLC and individually converted into the epoxides **11** and **12** as indicated in Scheme 3.



Scheme 3.

In the ^{13}C NMR spectra, the signals corresponding to the epoxide carbons of **11** are at higher field ($\delta = 57.3$ and 58.7) than those of **12** ($\delta = 58.7$ and 62.0). Epoxide **11** was therefore assigned the *cis* and epoxide **12** the *trans* structure. Assuming that epoxide formation proceeds with inversion at the selenium-bearing stereocenter, the relative configuration of the epoxides **11** and **12** allows the assignment of **9** as the *syn* and **10** as the *anti* adduct. The *syn*/*anti* ratio was determined by reversed phase HPLC on the crude reaction mixture to be 55:45. This number can be used to identify the reaction of the uncomplexed organolithium species.[15]

On addition of the diamine **15** to an ethereal solution of **8** the diastereomeric complexes **13** and **14** were formed (Scheme 4) in a 70:30 ratio with complexation constants of $>800\ L\,mol^{-1}$ and $>300\ L\,mol^{-1}$, respectively, as detailed elsewhere.[12] When an ethereal solution of **8** was first treated with 1.82 equiv of the diamine **15** and the solution of the resulting complexes



Scheme 4.

was added to benzaldehyde at −60 °C as described above, the *syn* and *anti* adducts **9** and **10** were obtained in 81% yield with a 72:28 ratio. The change in the *syn*/*anti* ratio (compared to the reaction of the uncomplexed organolithium species **8**) shows that at least some of the products **9** and **10** must be derived from the reaction of complexes **13** and **14**, since these species are expected to react with different *syn*/*anti* selectivities than **8**.

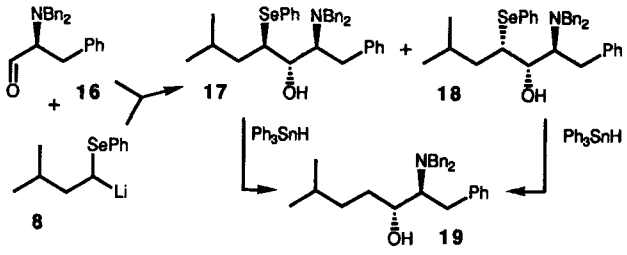
In order to estimate what proportion of the reaction proceeds via the complexes **13** and **14**, competition experiments were carried out: the uncomplexed organolithium compound **8** and the complexes **13** and **14** were allowed to compete for an inadequate supply of benzaldehyde. The *syn*/*anti* ratio was then determined. Thus, 0.2–0.96 equiv of the diamine **15** was added to 1.0 equiv of the lithium compound **8**, and a solution of 0.1 equiv of benzaldehyde was then added at −60 °C. After workup the *syn*/*anti* ratio of **9** and **10** was determined by HPLC. The results obtained are given in Table 1.

Table 1. Dependence of the *syn*/*anti* ratio of the products (**9**:**10**) on the amount of diamine **15** added.

Equiv. **15**	(**13**,**14**):**8**	**9**:**10**	% *ee* **9**	% *ee* **10**
0.2	1:4	74:26	38	46
0.75	3:1	71:29	42	46
0.96	24:1	70:30	40	48

Since the complexation constant for the formation of **13** and **14** is greater than 100, it may be assumed that all of the ligand is complexed so long as there is an excess of lithium compound **8**. The ratio of the complexed to the uncomplexed organolithium compound was therefore varied between 1:4 and 24:1. In all experiments essentially the same *syn*/*anti* ratio of approximately 70:30 was recorded. This invariance is consistent with the complexes **13** and **14** reacting with benzaldehyde in all experiments. We therefore conclude that the complexes **13** and **14** react significantly faster with benzaldehyde than the uncomplexed organolithium species **8**, and that the *syn*/*anti* ratio of 72:28 represents the average *syn*/*anti* selectivity of the two complexes **13** and **14**. If complexes **13** and **14** had reacted with benzaldehyde at a similar rate to the uncomplexed species **8**, a gradual change in the *syn*/*anti* ratio would have been expected from the characteristic value for the reaction of the uncomplexed species **8** (55:45) to that for the reaction of the complexes **13** and **14** (72:28). We therefore conclude that, in the system studied here, the rate of addition to benzaldehyde is substantial accelerated by the ligand. This is an essential prerequisite if enantiomeric enrichment in the products is to be attained.

Relative rates of equilibration and trapping of 13/14: The next question to be examined is whether or not the complexes **13** and **14** equilibrate more rapidly than they are trapped by benzaldehyde. Although the rate of equilibration of the complexes **13** and **14** is known,[12] the rate of addition to benzaldehyde at −60 °C is too fast to be measured macroscopically. Indirect methods therefore have to be used to answer the above question. We have previously developed a test[16] based on kinetic resolution, which allows us to differentiate between Curtin–Hammett and non-Curtin–Hammett situations. The application of this test to a simple α-phenylselenoalkyllithium compound in THF showed that trapping by aldehyde **16** is barely faster than enantiomerization of the lithium compound.[17] We decided to repeat this test with the organolithium compound **8** in diethyl ether (Scheme 5), the solvent of interest here.



Scheme 5.

Addition of the organolithium compound **8** to a precooled solution of aldehyde **16** at −60 °C led to two diastereomeric adducts **17** and **18**. Their structures were assigned by comparison of their ^1H and ^{13}C NMR spectra with those of the adducts of known structure from the reaction of α-phenylselenopentyllithium and aldehyde **16**.[17] Moreover, a mixture of **17** and **18** was reduced with triphenyltin hydride to furnish a single diastereomer (75%) of the amino alcohol **19**. This established that **17** and **18** differed only in the relative configurations at the selenium-bearing stereocenter, as postulated.

The product ratios of **17** and **18** were determined by reversed phase HPLC. The ratio of 71:29 for the reaction of racemic **8** with racemic aldehyde **16** indicates that there is kinetic resolution between the two reactants (Table 2), a prerequisite for the test. Reaction of the organolithium compound **8** with the enantiomerically pure aldehyde **16** led to a different diastereomeric ratio, 54:46 (approaching a 50:50 ratio; Table 2). This is characteristic[16] for a situation in which enantiomeric equilibration of **8** is slower than trapping by the aldehyde **16**, that is, the non-Curtin–Hammett case.

Table 2. Dependence of the **17**:**18** product ratio on the amount of diamine **15** added.

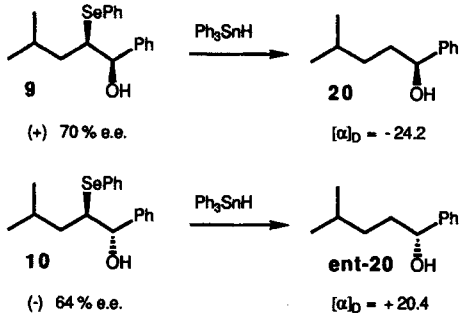
Equiv. **15**	Equiv. (*S*)-**16**	Yield **17**+**18** (%)	**17**:**18**
none	1.20 [a]	79	71:29
none	1.16	80	54:46
1.7	0.10	89	78:22
1.4	1.24	92	71:29

[a] *rac*-**16** used.

While this statement pertains to the uncomplexed organolithium species **8**, it is the behavior of the complexes **13** and **14** that is of actual interest here. This was established by a slight modification of our test: The complexes **13** and **14** were generated by addition of 1.7 equiv of diamine **15** to the lithium compound **8**, and 0.1 equiv of the enantiomerically pure aldehyde **16** were then added at −60 °C. This resulted in the formation of the two diastereomeric adducts **17** and **18** in a 78:22 ratio (Table 2). In interpreting this ratio we should bear in mind that 1) the diastereomeric complexes **13** and **14** were present in a 70:30 ratio,[12] 2) the absolute configuration of the complexes at the selenium-bearing stereocenter is known (see below), and 3) the absolute configuration of the products **17** and **18** at the selenium-bearing stereocenter is also known.[17] Thus, the reaction of aldehyde **16** with seven parts **13** and three parts **14** led to **17** and **18** in a 78:22 ratio. This means that **13** is (78:22/70:30 =) 1.5 times more reactive than **14** towards the aldehyde **16**. Thus, kinetic resolution occurs in the reaction of complexes **13** and **14** with aldehyde **16**. In a second experiment the solution of **13** and **14** was added to an excess of the enantiomerically pure aldehyde **16** at −60 °C. This time, the two adducts were formed in a 71:29 ratio (Table 2). The difference between 78:22 and 71:29 is significant. The 71:29 ratio corresponds to the initial ratio of 70:30 for the complexes **13** and **14**.[12] Despite kinetic resolution, the products **17** and **18** were therefore formed in the same ratio as was present in the starting materials **13** and **14**. This means that trapping of **13** and **14** is faster than the equilibration.

We have just described the behavior of complexes **13** and **14** towards the chiral aldehyde **16**; however, the actual information sought is their behavior towards benzaldehyde. Thus, the final link is an experiment to define the relative reactivities of benzaldehyde and aldehyde **16** towards the complexes **13** and **14**. To this end, the complexes **13** and **14** were allowed to react with a mixture of 2.6 equiv of benzaldehyde and 1.9 equiv of **16**. MPLC separation and isolation of the products indicated that benzaldehyde is around 2.2 times more reactive than **16**. Since benzaldehyde reacts faster than aldehyde **16** with the complexes **13** and **14** and since aldehyde **16** reacts faster with the complexes **13** and **14** than they equilibrate, the latter must also be true of benzaldehyde. We have thus finally established that the system under consideration (**13**/**14** + benzaldehyde) has a non-Curtin–Hammett behavior.

Enantiomeric enrichment in the products: The non-Curtin–Hammett behavior of the **8**/**15**/PhCHO system implies that the enantiomeric enrichment in the products **9** and **10** directly reflects the diastereomeric ratio of the complexes **13** and **14**. In order to determine their enantiomeric purity, the *syn* and *anti* adducts **9** and **10** were separately esterified with enantiomerically pure triaminophosphine **21**.[18] The resulting alkoxydiazaphospholidines **22** showed baseline-separated ^{31}P NMR signals. The enantiomeric purities could be determined to an accuracy of ±1% by the intergration of these signals. In order to establish the absolute configuration of **9** and **10**, dextrorotatory **9** with an *ee* of 70% was reduced with triphenyltin hydride to give levorotatory alcohol **20** (Scheme 6). Likewise, levorotatory **10** with an



Scheme 6.

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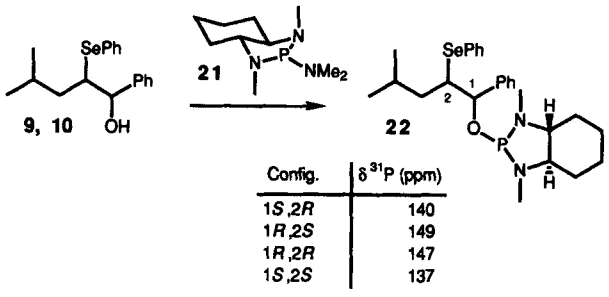
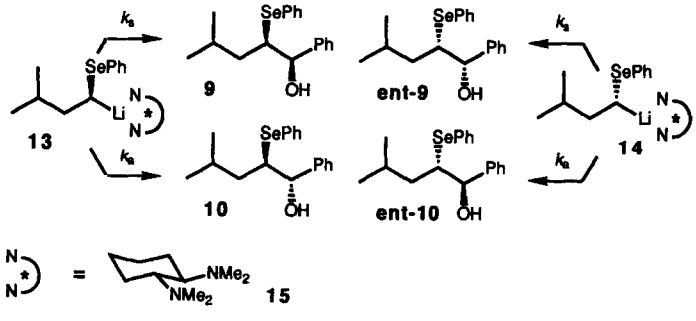
ee 64% gave the dextrorotatory alcohol **20**. Since (*R*)-phenylalkylcarbinols are dextrorotatory,[19] we conclude that the absolute configurations of the adducts **9** and **10** are as shown in Schemes 3 and 6. With this information the ^{31}P NMR signals of **22** can be assigned as shown in Scheme 7.



Config.	$\delta^{31}P$ (ppm)
1*S*,2*R*	140
1*R*,2*S*	149
1*R*,2*R*	147
1*S*,2*S*	137

Scheme 7.

The enantiomeric enrichment in the adducts obtained from the reaction of **8** in the presence of 1.8 equiv of the diamine **15** was found to be 40% *ee* for the *syn* diastereomer **9** and 44% *ee* for the *anti* diastereomer **10**. The average *ee* of 42% is equivalent to an enantiomeric ratio of 71:29, which closely corresponds to the 70:30 equilibrium ratio for the diastereomeric complexes **13** and **14** as determined by ^{77}Se NMR spectroscopy.[12] Similar enantiomeric excesses were obtained for the experiments in which complexes **13** and **14** and uncomplexed **8** competed for a limited amount of benzaldehyde (Table 1). It is initially surprising that the *ee* values for the *syn* and *anti* adducts **9** and **10** differ, although closer examination reveals that this is in fact to be expected. The complexes **13** and **14** are diastereomers and therefore distinct chemical entities. It is not to be expected that the *syn*/*anti* selectivity k_s/k_a for the two diastereomeric complexes **13** and **14** should be identical (Scheme 8). The *ee* values for *syn* **9** and *anti* **10** are thus expected

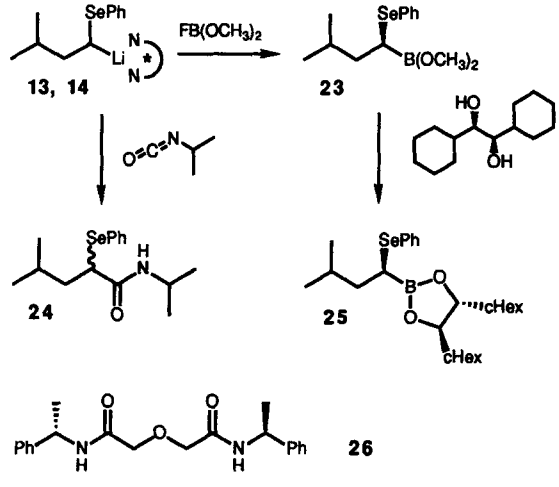


Scheme 8.

to differ, lying on either side of the value defined by the ratio of the two diastereomeric complexes **13** and **14**. The data obtained correspond to a *syn*/*anti* selectivity of 69:31 for **9** and 72:28 for **10**. Thus, the enantiomeric ratio in the products obtained is fully consistent with the non-Curtin–Hammett situation, where a 70:30 mixture of the diastereomeric complexes **13** and **14** is trapped by benzaldehyde much faster than the complexes equilibrate.

The 70:30 enantiomeric enrichment in the product should be independent of the electrophile, as long as the electrophiles used trap the complexes **13** and **14** more rapidly than the latter equilibrate. If, on the other hand, equilibration of the complexes were faster than trapping, the enantiomeric enrichment in the products would depend on the electrophile.[10] To clarify this point, we tested two other electrophiles, fluorodimethoxyborane and isopropylisocyanate.

Reaction of the complexes **13** and **14** at −80 °C with fluorodimethoxyborane led to α-phenylselenoalkylboronate **23**, which was transesterified with (*R*,*R*)-dicyclohexylethanediol[20] to give a mixture of the diastereomeric esters **25** (Scheme 9). These diastereomers showed different chemical shifts for three of their ^{13}C NMR signals. This allowed the diastereomeric ratio to be estimated at approximately 80:20. In view of the uncertainties in the derivatization step and the NMR analysis, we consider this ratio not to differ significantly from the expected 70:30 ratio.



Scheme 9.

Complexes **13** and **14** were also allowed to react with an excess of isopropylisocyanate at −60 °C. This led to formation of amide **24** in 89% yield. Its enantiomeric composition was determined by the use of the chiral solvating reagent **26**,[21] under the influence of which one methyl signal of **24** was doubled, as verified with racemic **24**. The enantiomeric enrichment of **24** was thus estimated to be 70:30, which is in line with the result expected from the above-mentioned arguments.

Other ligands: The enantiomeric enrichment in the products obtained from systems showing non-Curtin–Hammett behavior depends on the ratio of the diastereomeric complexes **6** and **7**, which is critically influenced by the nature of the diamine used. The diamine **15** was chosen because it allowed a maximum of information to be obtained about this system, and not because it led to maximum enantiomeric enrichment. As detailed elsewhere[12] we tested a number of diamines and other ligands with respect to their ability to influence the diastereomeric ratio of the complexes **6** and **7**. Most of the diamines tested in conjunction with lithium compound **8** and benzaldehyde gave unexceptional results.[22] Diamines **27** and **28** did, however, show notable features, and we would therefore like to describe their reactions here.

The highest ratio of diastereomeric complexes **6** and **7** (9:1) measured to date was induced by diaminocyclopentane **27**.[12] This was reflected in an average enantiomeric enrichment of

80% *ee* in the products **9** and **10** obtained on addition to benzaldehyde. Since (−)-diamine **27** induces the same configuration in the adducts **9** and **10** as did the (*R,R*)-diamine **15**, we assume that the it is the (*R,R*) enantiomer, by analogy with the rotation of (−)-(*R,R*)-diamine **15**. The complexation constant for diamine **27** with organolithium compound **8** is $>1000\ L\,mol^{-1}$,[12] as for diamine **15**. But differences to the behavior of the diamine **15** became apparent when less than one equivalent of diamine **27** was used (Table 3).

Table 3. Dependence of the *syn/anti* ratio of the products (**9**:**10**) on the nature and amount of diamines added.

Diamine (equiv)	(6+7):8	Yield 9+10 (%)	9:10	%*ee* 9	%*ee* 10
–	–	80	55:45	–	–
27 (0.5) [a]	1:1	95	62:38	44	46
27 (2)	>25:1	83	68:32	74	86
28 (1.4)	>10:1	97	56:44	16	−12

[a] 0.15 equiv of benzaldehyde.

In the presence of an excess of diamine **27** (i.e., when only the complexes **6** and **7** are present), it is clear that the average enantiomeric enrichment in the products (80% *ee*) corresponds to the diastereomeric ratio (9:1) of the complexes **6** and **7**. The *syn/anti* ratio of 68:32 should then approximate the average *syn/anti* selectivity of the complexes **6** and **7**. However, when benzaldehyde was given a choice of reacting with either the complexes **6** and **7** or the uncomplexed lithio compound **8** (i.e., when 0.5 equiv of **27** relative to **8** was used), a lower *syn/anti* ratio and a lower *ee* in the products were obtained; this indicates that complexes **6** and **7** and uncomplexed **8** have similar reactivities. The ligand no longer accelerates the addition to benzaldehyde!

Another interesting result was recorded with the diamine **28** for which ^{77}Se NMR spectra indicated the formation of the complexes **6** and **7** in a 3:1 ratio.[12] This should lead to an average of a 50% *ee* in the products. The much lower *ee* values found (cf. Table 3) indicated that only a small fraction of the products **9** and **10** was derived from the complexes **6** and **7**. Most of the adducts must have been formed from addition of the uncomplexed organolithium species **8**. The *syn/anti* ratio of 56:44 found is consistent with this conclusion. Given the fact that **8** is completely transformed into complexes **6** and **7** in solution (^{77}Se NMR), diamine **28** must decelerate the addition to benzaldehyde. There is a hidden twist in this interpretation: The complexes **6** and **7** (present in a 3:1 ratio) were added into an excess of an ethereal benzaldehyde solution. Under these conditions (approximately) racemic products could only arise if the uncomplexed organolithium compound racemized more rapidly than it was trapped by benzaldehyde—a Curtin–Hammett situation! This might, in fact, be possible, because the organolithium compound was completely present as the complexes **6** and **7**. Assuming a complexation constant of over $10^3\ L\,mol^{-1}$, the concentration of the free organolithium compound **8** would be lowered by a factor of 10^{-3}, as is the case for the actual rate of addition to benzaldehyde. We have previously shown that, at the 0.1 M concentration of **8** usually used, the rate at which **8** is trapped by benzaldehyde is barely faster than the rate of enantiomerization (a non-Curtin–Hammett situation).[17] Lowering the concentration of the organolithium compound by a factor of 10^{-3} could well shift the situation to one in which bimolecular trapping by benzaldehyde is slower than monomolecular[6] enantiomerization!

Conclusion

The detailed study reported here emphazises that the operationally simple procedure involving the reaction of a configurationally labile organolithium compound **8** complexed to a chiral diamine with an electrophile may—but does not always—lead to significant enantiomeric enrichment in the products. We have defined the conditions that have to be fulfilled in order to achieve enantiomeric enrichment in the products and have described experiments by which the situation in any given case may be analyzed.

Experimental Section

All temperatures quoted are not corrected. ^{1}H, ^{13}C, and ^{31}P NMR: Bruker AC-300, WH-400, and AMX-500. Boiling range of petroleum ether: 40–60 °C; pH 7 buffer: 56.2 g $NaH_2PO_4\cdot 2H_2O$ and 213.16 g $Na_2HPO_4\cdot 2H_2O$ in 1.0 L of water; flash chromatography: silica gel Si 60, E. Merck, Darmstadt, 40–63 μm; MPLC: 30 × 2 cm column with silica gel Si 60, E. Merck, Darmstadt, 15–25 μm, 10 bar, detection by differential refractometry (Knaur); HPLC: Merck-Hitachi, L-4000, UV detection, L-6200 intelligent pump; D-2500 chromato-integrator, RP-18 column with nucleosil 120-5 C-18 of CS Chromatography Service. All reactions with organolithium reagents were carried out under an atmosphere of dry nitrogen or argon.

4-Methyl-1-phenyl-2-phenylseleno-1-pentanol (9 and 10): Normal addition mode: A solution of 3-methyl-1,1-diphenylselenobutane (380 mg, 1 mmol) in anhydrous ether (10 mL) was placed in the lower compartment of a two-compartment reaction vessel [14]. The required amount of the diamine **15** was added, and the reactor cooled to −60 °C. The upper compartment was filled with a solution of benzaldehyde (ca. 200 μL) in anhydrous ether (10 mL). A solution of freshly sublimed *t*BuLi (1 mmol) in hexane was injected into the lower chamber, and the contents of the reactor were stirred magnetically for 15 min. The solution in the top compartment was added dropwise over 30 min to the lower compartment. After stirring for 15 min, methanol (2 mL) and saturated aqueous NH_4Cl solution (10 mL) were added. The mixture was allowed to reach room temperature before the phases were separated and the aqueous phase extracted with ether (3 × 10 mL). The combined organic phases were washed with water (10 mL) and brine (10 mL), dried with Na_2SO_4, and concentrated. The product was isolated by MPLC by using 4% ethyl acetate in petroleum ether as the eluent.

Inverse addition mode: A solution of benzaldehyde (200 μL) in dry ether (10 mL) was placed into the lower compartment of the reactor. A previously prepared solution of the organolithium compound **8** or of the complexes **13** and **14** in ether (10 mL) was transferred into the upper compartment via a canula. The reactor was maintained at −60 °C for 20 min before the solution of the lithium compound was added dropwise over a 30 min period to the aldehyde solution. Workup as described above furnished **9** and **10** (265 mg, 80% yield).

(1*R,2*R**)-9**: m.p. 64–65 °C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.65$ (d, $J = 6.5$ Hz, 3H), 0.77 (d, $J = 6.9$ Hz, 3H), 1.02 (ddd, $J = 14.4$, 9.7, 3.8 Hz, 1H), 1.30 (ddd, $J = 14.4$, 11.0, 3.9 Hz, 1H), 1.97 (m, 1H), 3.27 (ddd, $J = 11.0$, 8.1, 3.8 Hz, 1H), 3.38 (d, $J = 2.4$ Hz, 1H, OH), 4.34 (dd, $J = 8.2$, 2.3 Hz, 1H), 7.20–7.51 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 23.2, 26.0, 40.3, 46.0, 75.8, 127.0, 127.9, 128.1, 128.3, 129.0, 135.9, 141.3. $C_{18}H_{22}OSe$ (333.3): calcd. C 64.86, H 6.65; found C 64.89, H 6.91. (1*R*,2*R*) enantiomer with 70% *ee*: $[\alpha]_D^{20} = +42.7$ ($c = 1.17$, methanol).

(1*S,2*R**)-10:** ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.79$ (d, $J = 6.5$ Hz 3H), 0.82 (d, $J = 6.7$ Hz, 3H), 1.25 (ddd, $J = 14.7$, 9.9, 3.6 Hz, 1H), 1.46 (ddd, $J = 14.7$, 10.9, 4.1 Hz, 1H), 1.76 (m, 1H), 2.81 (brs, 1H, OH), 3.52 (ddd, $J = 10.9$, 3.3, 3.3 Hz, 1H), 4.77 (m, 1H), 7.21–7.62 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.9$, 23.4, 26.3, 36.8, 54.1, 74.1, 126.0, 127.2, 127.8, 128.0, 129.0, 129.2, 134.8, 140.9. $C_{18}H_{22}OSe$ (333.3): calcd. C 64.86, H 6.65; found C 64.92, H 6.83. (1*S*,2*R*) enantiomer with 64% *ee*: $[\alpha]_D^{20} = -8.4$ ($c = 1.00$, methanol).

The diastereomeric ratio **9**/**10** was determined by HPLC with methanol/water 70:30 (v/v) as eluent. The UV-detector response at 254 nm was calibrated by means of defined mixtures of **9** and **10**. The *ee* of **9** and **10** was determined in the following manner: **9** or **10** (ca. 10 mg, 0.03 mmol) was placed in an NMR tube, which was closed with a septum. The tube was evacuated and filled with dry nitrogen. This operation was repeated 3–4 times, before a solution of (*R,R*)-**21** [18] (1.5 equiv) in deuterobenzene was added. The mixture was allowed to stand for 12 h, and the total volume was brought up to ca. 0.8 mL by addition of dry toluene. The enantiomeric ratio was determined by 162 MHz ^{31}P NMR spectroscopy. The peak ratios for the diasteromeric products **22** were calibrated with racemic **9** and **10**.

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(1*R,2*S**)-2-(2-Methylpropyl)-1-phenyloxirane (11)**: To a suspension of trimethyloxonium tetrafluoroborate (378.9 mg, 2.6 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added a solution of **9** (568 mg, 1.70 mmol) in the same solvent (20 mL). After the reaction mixture had been stirred for 12 h, the solvent was removed in vacuo and the residue taken up in dry dimethyl sulfoxide (10 mL). Potassium *tert*-butoxide (390 mg, 3.5 mmol) was added, and the mixture stirred for 12 h at room temperature. Water was then added (30 mL), the phases separated, and the aqueous phase extracted with ether (3 × 10 mL). The combined organic phases were washed with saturated aqueous NH_4Cl solution, water, and brine (10 mL each), dried with Na_2SO_4, and concentrated. The remaining mixture of methylphenylselenide and **11** was separated by MPLC with ethyl acetate (1%) in petroleum ether as eluent. This furnished **11** (201 mg, 67%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (d, J = 6.7 Hz, 3H), 0.87 (d, J = 6.7 Hz, 3H), 1.11 (ddd, J = 14.0, 7.5, 5.6 Hz, 1H), 1.24 (ddd, J = 14.1, 6.5, 6.5 Hz, 1H), 1.71 (m, 1H), 3.21 (ddd, J = 6.5, 5.7, 4.3 Hz, 1H), 4.03 (d, J = 4.3 Hz, 1H), 7.22–7.34 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.5, 22.9, 26.5, 35.4, 57.3, 58.7, 126.6, 127.5, 128.0, 135.0. $C_{12}H_{16}O$ (176.3): calcd. C 81.77, H 9.15; found C 81.56, H 8.92.

(1*R,2*R**)-2-(2-Methylpropyl)-1-phenyloxirane (12)**: Trimethyloxonium tetrafluoroborate (154.6 mg, 1.05 mmol), **10** (289 mg, 0.87 mmol), and potassium *tert*-butoxide (200 mg, 1.78 mmol) were allowed to react as described for compound **11**. MPLC furnished **12** (90.5 mg, 59%) as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 (d, J = 6.6 Hz, 3H), 0.97 (d, J = 6.6 Hz, 3H), 1.47 (m, 1H), 1.62 (m, 1H), 1.83 (m, 1H), 2.92 (ddd, J = 5.9, 5.9, 2.2 Hz, 1H), 3.54 (d, J = 2.1 Hz, 1H), 7.18–7.40 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.3, 22.9, 26.2, 41.3, 58.7, 62.0, 125.3, 127.8, 128.3, 137.8. $C_{12}H_{16}O$ (176.3): calcd. C 81.77, H 9.15; found C 81.64, H 9.27.

4-Methyl-1-phenyl-1-pentanol (20): A solution of **9** with a 70% *ee* (156.1 mg, 0.47 mmol) and triphenyltin hydride (300 mg, 0.86 mmol) in degassed toluene (5 mL) was refluxed for 12 h. Ether (20 mL) and water (10 mL) were then added. The phases were separated, and the organic phase was washed with brine (10 mL), dried with Na_2SO_4, and concentrated. The product was purified by MPLC with ethyl acetate (8%) in petroleum ether to furnish **20** (61 mg, 73%). $[\alpha]_D^{20}$ = −24.2 (c = 1.13, benzene). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.71 (2 d, J = 6.5, 6.6 Hz, 6H), 0.96–1.60 (m, 6H), 4.26 (m, 1H), 6.79–7.16 (m, 5H). ^{13}C NMR (75 MHz, C_6D_6): δ = 22.6, 22.7, 28.3, 35.2, 37.7, 74.8, 125.8, 127.4, 128.3, 144.9.

ent-**20**: Similarly, **10** (48.4 mg, 0,15 mmol) with 64% *ee* and triphenyltin hydride (201 mg, 0.57 mmol) led to *ent*-**20** (16.4 mg, 62%) as a colorless liquid. $[\alpha]_D^{20}$ = +20.4 (c = 1.40, C_6H_6). $C_{12}H_{18}O$ (178.3): calcd. C 80.85, H 10.18; found C 80.75, H 10.06.

2-(*N*,*N*-Dibenzylamino)-6-methyl-1-phenyl-4-phenylseleno-3-heptanol (17, 18): The reaction between organolithium compound **8** and aldehyde **16** [23] was carried out as described for **9** and **10** (inverse addition mode). The reaction products were separated by MPLC with ether (5%) in petroleum ether to furnish the diastereomeric adducts **17** and **18**.

(2*S*,3*S*,4*R*)-Diastereomer 17: m.p. 87 °C. $[\alpha]_D^{20}$ = +30.1 (c = 1.39, methanol). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.79 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.5 Hz, 3H), 0.90 (ddd, J = 14.2, 10.6, 3.4 Hz, 1H), 1.34 (ddd, J = 14.5, 12.2, 3.8 Hz, 1H), 1.76 (m, 1H), 2.26 (d, J = 3.7 Hz, 1H, OH), 2.90 (dd, J = 14.1, 4.8 Hz, 1H), 3.04 (dd, J = 14.1, 6.7 Hz, 1H), 3.09 (ddd, J = 6.7, 6.6, 5.0 Hz, 1H), 3.43 (d, J = 14.0 Hz, 2H), 3.51 (d, J = 13.9 Hz, 2H), 3.62 (ddd, J = 12.0, 3.1, 3.1 Hz, 1H), 3.91 (ddd, J = 6.5, 3.2, 3.2 Hz, 1H), 7.08–7.41 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.5, 23.7, 26.7, 33.1, 35.4, 52.2, 54.0, 60.7, 74.1, 125.8, 126.9, 127.7, 128.2, 128.3, 128.9, 129.0, 129.1, 129.3, 129.7, 135.0, 139.5, 141.8. $C_{34}H_{39}NOSe$ (556.7): calcd. C 73.36, H 7.06, N 2.52; found C 73.62, H 7.15, N 2.43.

(2*S*,3*S*,4*S*)-Diastereomer 18: m.p. 77–79 °C. $[\alpha]_D^{20}$ = −6.4 (c = 1.19, methanol). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.49 (d, J = 6.5 Hz, 3H), 0.73 (d, J = 6.7 Hz, 3H), 0.82 (ddd, J = 14.7, 10.0, 3.2 Hz, 1H), 1.19 (ddd, J = 14.7, 11.2, 3.6 Hz, 1H), 1.87 (m, 1H), 2.90 (m, 2H), 2.96 (d, J = 2.8 Hz, 1H, OH), 3.04 (dd, J = 13.9, 7.4 Hz, 1H), 3.14 (ddd, J = 7.2, 7.2, 2.0 Hz, 1H), 3.64 (d, J = 14.1 Hz, 2H), 3.70 (ddd, J = 8.8, 2.6, 2.6 Hz, 1H), 3.78 (d, J = 14.1, Hz, 2H), 7.06–7.45 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.0, 23.4, 26.2, 31.5, 40.9, 54.4, 54.5, 60.7, 73.2, 125.8, 126.8, 127.2, 128.0, 128.2, 128.8, 129.1, 129.8, 135.6, 140.2, 141.0. $C_{34}H_{39}NOSe$ (556.7): calcd. C 73.36, H 7.06, N 2.52; found C 73.43, H 7.15, N 2.62.

The diastereomeric ratio was determined by HPLC with methanol/water (90:10 v/v) as eluent. The detector response at 254 nm was calibrated with defined mixtures of **17** and **18**.

(2*S,3*R**)-2-(*N*,*N*-Dibenzylamino)-6-methyl-1-phenyl-3-heptanol (19)**: A mixture of **17** and **18** (200 mg, 0.36 mmol) was reduced with triphenyltin hydride (200 mg, 0.52 mmol) as described for compound **20**. MPLC with ethyl acetate (8%) in petroleum ether furnished **19** (108 mg, 75%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (d, J = 6.6 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H), 1.02–1.70 (m, 5H), 1.64 (brs, 1H, OH), 2.81 (dd, J = 12.7, 5.7 Hz, 1H), 2.99–3.12 (m, 2H), 3.66 (m, 3H), 3.78 (d, J = 13.8 Hz, 2H), 6.97–7.30 (m, 15H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.5, 22.7, 28.0, 32.0, 32.7, 35.6, 55.1, 63.3, 72.2, 126.0, 127.6, 128.3, 128.4, 129.4, 139.9, 140.7. $C_{28}H_{35}NO$ (401.6): calcd. C 83.74, H 8.78, N 3.49; found C 83.84, H 8.81, N 3.53.

Competition between benzaldehyde and aldehyde 16 for the complexes 13 and 14: The lithium compound **8** (0.84 mmol), the racemic diamine **15** (248 mg, 1.45 mmol), benzaldehyde (161 mg, 2.23 mmol), and racemic aldehyde **16** (525 mg, 1.60 mmol) were allowed to react as described for **9** and **10** (inverse addition mode). Separation of the products by MPLC with ethyl acetate (2%) in petroleum ether furnished **18** (43.0 mg), **17** (77.0 mg), **10** (71.8 mg), and **9** (146.1 mg). The ratio for the diastereomeric products was determined by HPLC on the crude reaction mixture (methanol/water 9:1, **17**:**18** = 64:36; methanol/water = 7:3, **9**:**10** = 67:33).

(4*R*,5*R*)-4,4-Dicyclohexyl-2-(1′-phenylseleno-4′-methylbutyl)-1,3,2-dioxaborolane (25): A 1.5 M solution of *t*BuLi in pentane (0.40 mL, 0.60 mmol) was added at −80 °C to a solution of 3-methyl-1,1-diphenylselenobutane (182 mg, 0.475 mmol) and (1*R*,2*R*)-*N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminocyclohexane (**15**) (128 mg, 0.753 mmol) in ether (10 mL). After the mixture had been stirred for 15 min, a solution of dimethoxyfluoroborane (100 μL) in anhydrous ether (2 mL) was added dropwise. After 1 h of stirring at −80 °C the mixture was allowed to reach room temperature. Saturated aqueous NH_4Cl solution (10 mL) was added, the phases separated, and the organic phase washed with water and brine (10 mL each). The solution was dried with Na_2SO_4 and concentrated in vacuo to give crude **23** (202 mg). Chloroform (10 mL), (1*R*,2*R*)-1,2-dicyclohexyl-1,2-ethanediol (200 mg) [20], and $MgSO_4$ (1 g) were added. The mixture was stirred for 12 h at room temperature. Water was added (10 mL), the phases separated, and the aqueous phase extracted with chloroform (2 × 10 mL). The combined organic phases were washed with saturated aqeuous NH_4Cl solution, water, and brine (10 mL each), dried with $MgSO_4$ and concentrated. The diastereomeric ratio was determined with an aliquot of the crude reaction product by ^{13}C NMR. The crude product was purified by MPLC with ethyl acetate (10%) in petroleum ether to give a mixture (278 mg) of *tert*-butylphenylselenide and product **25**, with an 87% yield of **25**. The spectral data were taken from the mixture: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–1.71 (m, 31H), 2.89 (m, 1H), 3.80 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.1, 22.2, 22.3, 22.5, 25.8, 25.9, 26.0, 26.4, 26.5, 27.3, 27.5, 28.1, 28.3, 28.4, 28.4, 28.5, (40.8, 41.1), (42.9, 43.0), (83.7, 83.9). The latter three pairs of signals were found in a 1:1 ratio when starting from racemic **8** in the absence of **15**.

4-Methyl-(*N*-isopropyl)-2-phenylselenopentanoic amide (24): 3-Methyl-1,1-diphenylselenobutane (221 mg, 0.58 mmol), **15** (239.0 mg, 1.40 mmol), a 1.5 M solution of *t*BuLi in pentane (0.50 mL, 0.75 mmol), and isopropylisocyanate (60 mg, 0.71 mmol) were allowed to react as described for **9** and **10** (normal addition mode). The reaction was quenched by stirring it into an aqueous pH 7 buffer (50 mL), the phases were separated, and the aqueous phase was extracted with ether (3 × 50 mL). The combined organic phases were washed with water and brine (10 mL each), dried with Na_2SO_4, and concentrated in vacuo. The crude product was purified by MPLC with ethyl acetate (15%) in petroleum ether to give **24** (161 mg, 89%) as a colorless solid. M.p. 84 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (2d, J = 6.3, 6.5 Hz, 6H), 0.93 (2d, J = 6.5, 6.6 Hz, 6H), 1.55 (m, 1H), 1.75 (m, 2H), 3.57 (dd, J = 7.4, 7.4 Hz, 1H), 3.89 (dqq, J = 7.8, 6.6, 6.6 Hz, 1H), 5.58 (d, J = 7.0 Hz, 1H, NH), 7.20–7.50 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.3, 22.5, 22.6, 22.7, 27.0, 41.2, 41.6, 46.0, 128.2, 128.8, 129.3, 134.7, 171.0. $C_{15}H_{23}NOSe$ (312.3): Calcd. C 57.68, H 7.42, N 4.48; found C 57.90, H 7.66, N 4.50.

Determination of the enantiomeric excess: To **24** (5 mg) was added a 1 M solution of (*S*,*S*)-(−)-2,2′-oxybis[*N*-(1-phenylethyl)-acetamide] (**26**) (0.6 mL). The solution was analysed by 500 MHz ^{1}H NMR spectroscopy. When using racemic **24**, one signal was shifted from δ = 0.93 to 1.04 and was doubled. This was used to determine the enantiomeric ratio of nonracemic **24**.

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