Asymmetric Synthesis of Planar Chiral (Arene)tricarbonylchromium Complexes *via* Enantioselective Deprotonation by Conformationally Constrained Chiral Lithium-Amide Bases

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Dedicated to Professor *Albert Eschenmoser* on the occasion of his 75th birthday

Enantioselective lithiation/electrophile addition reactions with eight chiral Li-amide bases, **1**–**8**, and five [Cr(arene)$(CO)_3$] complexes, **9**–**13**, were investigated. Restriction of conformational freedom in the chiral Li-amide base Li-**1**, in general, did not result in an increase in asymmetric induction. A new route to enantiomerically enriched (75–92%) planar chiral *ortho*-substituted benzaldehyde complexes *via* enantioselective lithiation of benzaldimine complexes **16** and **17** is reported. Within the (1*S*)-enantiomer series of *o*-substituted benzaldehyde complexes **18a**–**d**, the sign of the specific rotation, $[\alpha]_D^{20}$, is found to be positive, except for the trimethylstannyl derivative **18b**. This is interpreted in terms of a reversed conformation of the aldehyde group.

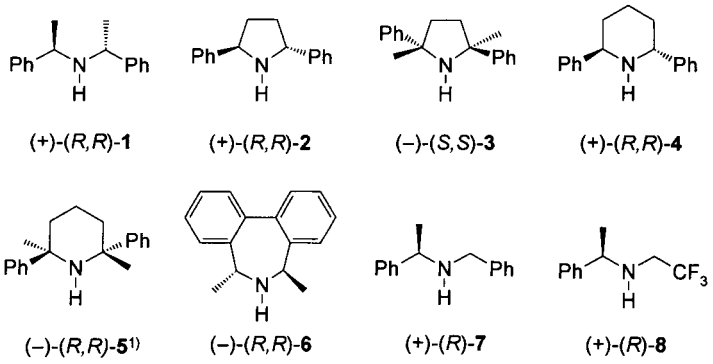
Introduction. – Temporary complexation of an arene to the electrophilic $Cr(CO)_3$ group results in a considerable extension of the scope of synthetically useful transformations of arenes. [Cr(Arene)$(CO)_3$] Complexes are accessible in high yield and, while the metal–arene bond is stable under a variety of reaction conditions, it is efficiently cleaved by mild oxidation. The role of the $Cr(CO)_3$ group is twofold: it activates the arene and thus makes reactions possible that are not viable with the free arene; secondly, it blocks one arene face and thus acts as an efficient stereocontrol unit. In the complex, benzylic cations and anions are stabilized, ring substitution *via* lithiation or nucleophilic addition is readily realized, and mild pathways exist for the regio- and stereocontrolled transformation of arenes into substituted alicyclic molecules. These characteristics have led to widerspread use of this class of compounds in organic synthesis [1].

Complexes of *ortho*-disubstituted arenes with different substituents are chiral, and reactions at the ring (*e.g.*, nucleophilic addition) and at side-chain positions often take place with high diastereoselectivity [2][3]. In addition, planar chiral *ortho*-disubstituted [Cr(arene)$(CO)_3$] complexes are also finding use as chiral ligands in asymmetric catalysis [4]. Stimulated by these successful applications, attention has been directed to efficient access of enantiomerically pure and enantiomerically enriched complexes. Resolution procedures can be applied successfully to complexes of *ortho*-substituted benzaldehydes [5]. Other methods include diastereoselective complexation of chiral arenes [3c][5c][6], diastereoselective or enantioselective nucleophilic addition/hy-

dride abstraction [7], deprotonation of chirally modified complexes, followed by an electrophilic quenching [8] and enantioselective *ortho*-lithiation/electrophile addition reactions [9].

The last procedure is based on the successful and widely used directed *ortho*-metalation procedure [10]. Because of the increased acidity of ring H-atoms in the complex, deprotonation occurs readily with *sec*-Li-amides. A number of chiral amines have been used successfully in these reactions, and the methodology is applicable to substrates for which other methods fail (*e.g.*, phenol derivatives). Moreover, it allows introduction of a broad range of *ortho*-substituents, and, as the chiral information is carried by an external reagent rather than the complex itself, it avoids the two steps required for attachment and cleavage of a chiral auxiliary. This makes the recycling of the chiral agent easier and has the potential to lead to a catalytic process.

The structure of the chiral base is crucial for success in these reactions. Our knowledge of the transition state of enantioselective arene deprotonation is in its infancy, and often even the sense of asymmetric induction cannot be predicted. This situation parallels that found in other enantioselective deprotonation reactions [11]. In view of this, an extension of the structural variety of reported bases and an extension of this chemistry to arene complexes that have not received previous attention is important. These issues are the focus of this paper. We have synthesized five-, six-, and seven-membered enantiomerically pure cyclic amines, and they, together with other chiral Li-amide bases, have been screened for their efficiency in regio- and in enantioselective lithiation reactions of mono-substituted complexes with different functionality. The bases used in this study are obtained by deprotonation of the chiral amines **1**–**8** with BuLi.

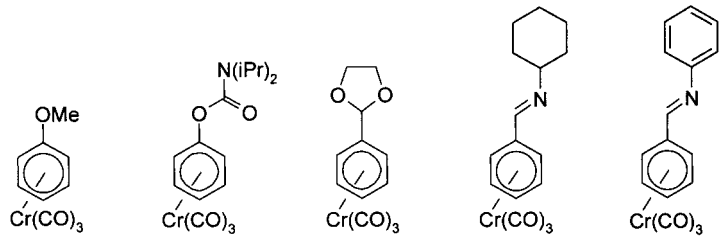


The Li-amide derived from **1** [12] has previously been used successfully in the enantioselective lithiation of the anisole complex **9** [9a,b,e–h]. The cyclic amines **2**, **4**, and **6** were chosen to probe the effect of reducing conformational freedom. For **2** and **4**, the ring structure replaces the benzylic Me groups, whilst the chiral dibenzo[*c*,*e*]azepine **6** is the cyclic analogue of **1** bearing an aryl–aryl bond. In addition to the ring structure, amines **3** and **5**[1]) incorporate tertiary benzylic centers. Finally, the non-C_2-symmetric

[1]) The assignment of the (*R*,*R*) absolute configuration to (–)-**5** is tentative. It is based on the analogy of CD spectra of (+)-(*R*,*R*)-**4** and (–)-**5**, and the sense of asymmetric induction in products **10**, **12**, and **14**.

amines **7** and **8** were selected for their efficiency in the enantioselective deprotonation of ketones [13–15].

Enantioselective lithiation/electrophile addition was investigated with five [Cr(arene)$(CO)_3$] complexes. Two are phenol derivatives: the anisole complex **9** and the aryl carbamate complex **11**. The other three are benzaldehyde derivatives: the acetal complex **13** and the 'benzaldimine' (benzylideneamine) complexes **16** and **17**. The phenol derivatives were chosen because there are no reported efficient alternative methods of access to this class of non-racemic *ortho*-substituted complexes. The situation is different for benzaldehyde complexes, but their widespread use in synthesis makes the search for new approaches desirable. All five complexes possess functional groups capable of interaction with the Li-atom of the chiral base; therefore, *ortho*-regioselectivity in lithiation can be expected. Complex **13** has a benzylic H-atom and competitive deprotonation at this site is recognized as a potential problem. Enantioselective lithiation of complexes **9**, **11**, and **13** has been investigated previously [9a,b], but benzaldimine complexes **16** and **17** have not received prior attention in this reaction sequence.



9 **11** **13** **16** **17**

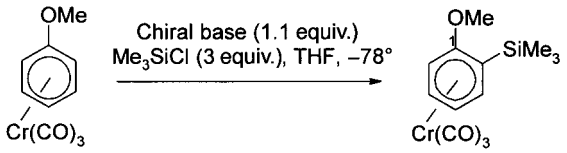
Results and Discussion. – 1. *Chiral Amines.* Chiral amines **1**–**3** and **5**–**7** were prepared according to literature methods (see *Exper. Part*). The *trans*-2,6-diphenylpiperidine **4** was synthesized from 1,5-diphenylpentane-1,5-dione according to the same procedure as described for the pyrrolidine **2** [16]. Amine **8** was prepared by borane reduction of the amide obtained by reaction of enantiomerically pure sodium methylbenzylamide with CF_3COOEt.

The enantiomeric purity of the amines was confirmed prior to use either by HPLC (for **1** and **3**), or by derivatization with *Mosher*'s acid and integration of the ^{1}H-NMR signals assigned to benzylic protons or benzylic Me groups. In all cases, only one enantiomer respectively one diastereoisomer was detected.

2. *Enantioselective Lithiation/Electrophile Addition*. The reactions were carried out in THF at $-78°$ with the bases derived from **1**–**8** and trapping of the lithiated arene complexes by *in situ* quenching (ISQ) with an excess of Me_3SiCl. The ISQ procedure was chosen because it was shown by *Simpkins* and co-workers that the lithiated anisole complex (Li-**9**) racemizes rapidly by H-exchange with the starting material [9b]. Our own experience in the reaction of the carbamate complex **11** with base Li-**1** also indicated a similar problem [9c]. Furthermore, in preliminary experiments involving the acetal complex **13**, ISQ was found to reduce competing benzylic deprotonation and to give higher enantioselectivity.

The sense of induction observed in the reactions with complex **9** correlates with the absolute configuration of the chiral bases, *i.e.*, the bases with (*R*)-configuration all gave (1*S*,2*R*)-**10** as the major product (*Scheme 1*), and *Entries 3* and *5* in *Table 1* show the reaction to be stereospecific. In terms of the degree of induction, the best result by far was achieved when Li-**1** was employed as base, as first reported by *Simpkins* and co-workers [9a]. The inductions obtained with the other bases are poor-to-moderate, and yields also drop considerably. We note a large increase in induction upon introduction of a second substituent in α-position to the N-atom in the pyrrolidine bases (*Entry 3 vs. Entry 2*). To a much minor extent, this is also observed for the six-membered ring bases (*Entry 5 vs. Entry 4*). Remarkable also is the sharp drop in induction when one of the stereogenic centers in **1** is removed (bases derived from **7** and **8**; *Entries 7* and *8*).

Scheme 1



9 (+)-(1*S*)-**10**

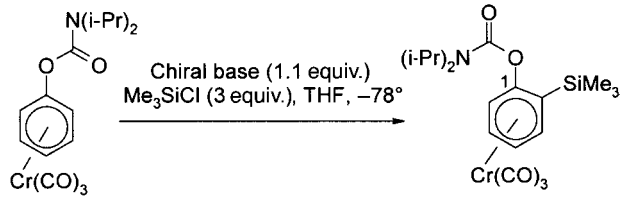
Table 1. *Enantioselective Lithiation/Me$_3$SiCl Quenching with Complex* **9**

Entry	Base	Yield [%][a])	ee [%][b])	Product[c])
1	Li-(+)-(*R*,*R*)-**1**	90[d]	90[d])	(+)-(1*S*)-**10**
2	Li-(+)-(*R*,*R*)-**2**	69	0	*rac*-**10**
3	Li-(+)-(*S*,*S*)-**3**	72	73	(−)-(1*R*)-**10**
4	Li-(+)-(*R*,*R*)-**4**	67	9	(+)-(1*S*)-**10**
5	Li-(+)-(*S*,*S*)-**5**	40	22	(−)-(1*R*)-**10**
6	Li-(−)-(*R*,*R*)-**6**	43	14	(+)-(1*S*)-**10**
7	Li-(+)-(*R*)-**7**	93	48	(+)-(1*S*)-**10**
8	Li-(+)-(*R*)-**8**	81	13	(+)-(1*S*)-**10**

[a]) Yields of isolated products after flash chromatography. [b]) The enantiomeric excess (ee) of **10** was determined by chiral HPLC (*Chiracel OD-H* column, hexane/i-PrOH). [c]) The absolute configuration of **10** was determined by correlation of the sign of optical rotation with that given in the literature [9g]. [d]) Previous literature reports: [9a,g]: 83% yield, 84% ee; [9e]: 95% yield, 88% ee.

Chelation of the Li-amide by the carbamate complex **11** occurs at the γ-position (carbonyl O-atom), whereas, in the anisole complex, it involved the α-position of the side chain (*Scheme 2*). The sense of asymmetric induction in the lithiation step is the same for **11** as that found for the anisole complex **9**. Base Li-**1** provided only low induction (*Entry 1* in *Table 2*). The five- and six-membered Li-amides, and the bases **7** and **8** were even less efficient. Of the series tested here, the best result was achieved with the chiral dibenzo[*c*,*e*]azepine **6**. The 62% ee achieved for (1*S*)-**12**, albeit with a modest yield of 48% (*Entry 6*), is close to that obtained earlier with the base Li-**19** (64% ee under ISQ conditions) [9h].

Scheme 2

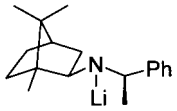


11 (+)-(*1S*)-**12**

Table 2. *Enantioselective Lithiation/Me_3SiCl Quenching with Complex* **11**

Entry	Base	Yield [%][a])	ee [%][b])	Product[c])
1	Li-(+)-(*R*,*R*)-**1**	56	39	(+)-(1*S*)-**12**
2	Li-(+)-(*R*,*R*)-**2**	51	0	*rac*-**12**
3	Li-(+)-(*R*,*R*)-**3**	97	27	(+)-(1*S*)-**12**
4	Li-(+)-(*R*,*R*)-**4**	65	29	(+)-(1*S*)-**12**
5	Li-(+)-(*S*,*S*)-**5**	72	24	(−)-(1*R*)-**12**
6	Li-(−)-(*R*,*R*)-**6**	48	62	(+)-(1*S*)-**12**
7	Li-(+)-(*R*)-**7**	49	13	(+)-(1*S*)-**12**
8	Li-(+)-(*R*)-**8**	88	0	*rac*-**12**

[a]) Yields of isolated products after flash chromatography. [b]) Enantiomeric excess (ee) of **12** determined by chiral HPLC (*Chiracel OD* column, hexane/i-PrOH). [c]) Configuration of **12** determined by correlation of the sign of optical rotation with that given in the literature [9c,h].



Li-**19**

As anticipated, the problem with the benzaldehyde acetal complex **13** is that Li-amides competitively deprotonate at the ring and at benzylic positions[2]). The data show that the ratio of products **14** and **15** is sensitive to both the base strength and steric effects (*Scheme 3* and *Table 3*). Notable is the complete change in regioselectivity of deprotonation with the two pyrrolidine bases Li-**2** and Li-**3**. The highest ee value in product **15** was realized with Li-**1**, but the formation of product mixtures renders this approach of little synthetic value.

We have previously shown that benzaldimine complex **16** reacts with alkyllithium reagents by 1,4-addition to give, after oxidation, *ortho*-substituted benzaldehydes [17]. $Cr(CO)_3$ Complexation can be conserved if the intermediate anionic cyclohexadienyl complex is treated with a trityl salt to effect an *endo*-hydride abstraction. This procedure has been developed into an enantioselective route to $Cr(CO)_3$ complexes of *ortho*-substituted benzaldehydes (**18**) [7]. Enantioselective lithiation would be an

[2]) More reactive bases give higher ratios of ring *vs.* benzylic deprotonation. Alkyllithium reagents react selectively at ring positions, and this has been used successfully with chiral reagents [9f].

Scheme 3

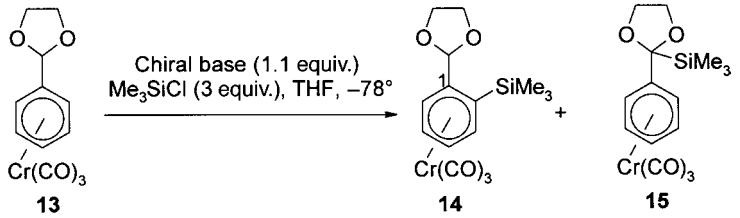


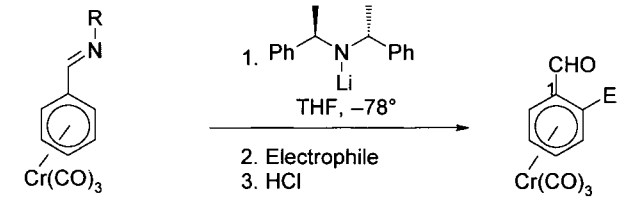
Table 3. *Enantioselective Lithiation/Me_3SiCl Quenching with Complex* **13**

Entry	Base	Product ratio [%][a])		ee [%][b])	Configuration[c])
		14	**15**		
1	Li-(+)-(*R*,*R*)-**1**	48	52	81	(+)-(1*S*)-**14**
2	Li-(+)-(*R*,*R*)-**2**	0	100[d])	–	–
3	Li-(−)-(*S*,*S*)-**3**	100	0[e])	51	(−)-(1*R*)-**14**
4	Li-(+)-(*R*,*R*)-**4**	30	70	5	(+)-(1*S*)-**14**
5	Li-(−)-(*R*,*R*)-**5**	57	43	4	(+)-(1*S*)-**14**
6	Li-(−)-(*R*,*R*)-**6**	57	43	11	(+)-(1*S*)-**14**
7	Li-(+)-(*R*)-**7**	0	100[f])	–	(+)-(1*S*)-**14**
8	Li-(+)-(*R*)-**8**	–	–[g])	–	–

[a]) Product ratio **14**/**15** determined by HPLC. [b]) Enantiomeric excess (ee) of **14** determined by chiral HPLC (*Chiracel OD* column, hexane/i-PrOH). [c]) Configuration of **14** determined by correlation of the sign of optical rotation with reported literature data [9c]. [d]) Ratio **13**/**15** 1:1 by ^{1}H-NMR of the crude mixture, 46% isolated yield of **15**. [e]) 40% of conversion. [f]) Ratio **13**/**15** 2:1 determined by ^{1}H-NMR of the crude mixture. [g]) Only **13** was detected in ^{1}H-NMR of the crude mixture.

attractive alternative and complementary pathway since the *ortho*-substituent would be introduced as an electrophile rather than as a nucleophile. We show here that this can be successfully realized. Enantioselective deprotonation of the benzaldimine complexes with several bases led to poor conversion, and we suspect that some of the Li-amides undergo 1,2-nucleophilic addition to the imine function. The base Li-**1** deprotonates complexes **16** and **17** with high enantioselectivity, however, and these results are shown in *Scheme 4* and *Table 4*. Mild hydrolysis affords enantiomerically enriched arylaldehyde complexes. Enantiomer ratios are between 87:13 (for **18c**) and 96:4 (for **18a**).

Scheme 4



16 R = Cyclohexyl
17 R = Ph

18

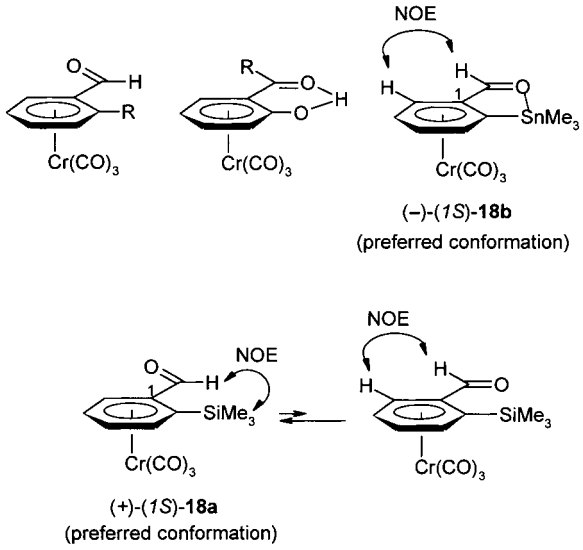
Table 4. *Enantioselective Lithiation/External Quenching (EQ) with Complexes* **16** *and* **17**

Entry	Starting complex	Reaction conditions	Electrophile	Yield [%]	ee [%][a])	Product[b])
1	**16**	ISQ	Me_3SiCl	84	84	(+)-(1*S*)-**18a**
2	**16**	EQ	Me_3SiCl	82	78	(+)-(1*S*)-**18a**
3	**16**	EQ	Me_3SnCl	67	78	(−)-(1*S*)-**18b**
4	**16**	EQ	MeI	62	72	(+)-(1*S*)-**18c**
5	**16**	EQ	$ClCO_2Me$	66	74	(+)-(1*S*)-**18d**
6	**17**	ISQ	Me_3SiCl	76	88	(+)-(1*S*)-**18a**
7	**17**	EQ	Me_3SiCl	67	92	(+)-(1*S*)-**18a**
8	**17**	EQ	Me_3SnCl	65	89	(−)-(1*S*)-**18b**
9	**17**	EQ	$ClCO_2Me$	68	90	(+)-(1*S*)-**18d**

[a]) Determined by chiral HPLC for **18a**, **18b**, and **18d**; and with chiral SFC (*Chiracel OD-H* column, 10% MeOH) for **18c**. The formation of the chiral aminal with (*R*,*R*)-cyclohexane-1,2-diamine and (+)-**18c** confirmed both the configuration and the enantioselectivity [5c]. [b]) Absolute configuration assigned based on CD spectroscopy.

An aspect that surprised us initially was the finding that the enantiomerically enriched complex (1*S*)-**18b** (E = $SnMe_3$) has the opposite sign of rotation of polarized light when compared to (1*S*)-**18a** (E = $SiMe_3$) (*Scheme 5*). An interpretation of opposite sense of chirality appears unlikely since this would require that the intermediate aryl-lithium complex rapidly undergoes equilibration, and that the reaction with the electrophiles Me_3SiCl and Me_3SnCl, under the influence of the chiral amine, leads to opposite dynamic resolution. The finding of very similar induction in both *in situ* quenching (ISQ) and external quenching (EQ) is an argument for configurational stability. A more likely explanation, therefore, is that the absolute configuration is the same in both **18a** and **18b**.

Scheme 5



The sign of $[\alpha]$ in this class of compounds is determined by the orientation of the C=O group with respect to the *ortho*-substituent. In the majority of cases, an *anti*-conformation is preferred in order to reduce $A^{1,3}$-strain [2a][18]. Phenol complexes are exceptions because of the establishment of intramolecular H-bridging to the *ortho*-carbonyl group. We reason that the *Lewis* acidity of the Me_3Sn group, enhanced by the arene coordinated to the electrophilic $Cr(CO)_3$ group, may bring about a *syn*-aldehyde orientation in this case. This then accounts for the change in sign of the first *Cotton* effect in the two complexes (*Fig.*).

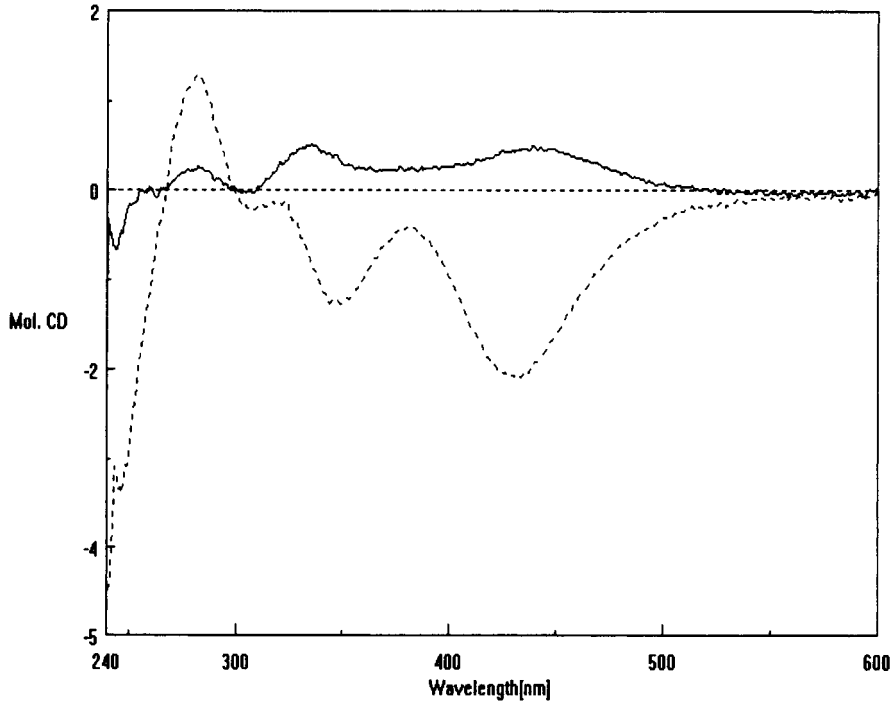
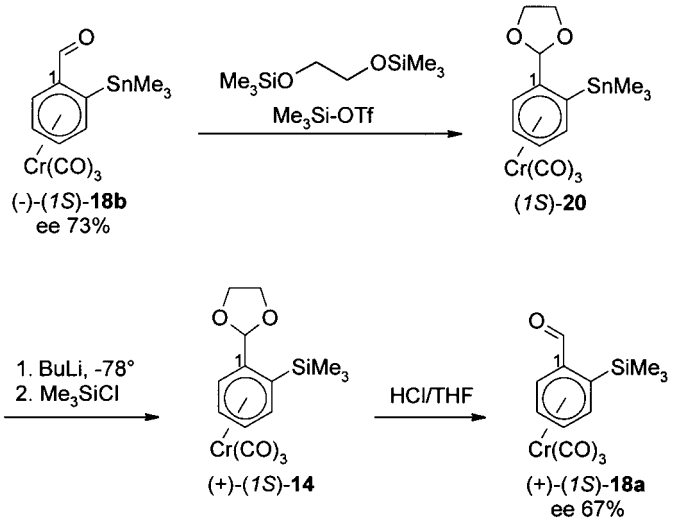


Figure. *CD Spectra of* ortho-*(trimethylsilyl)- and* ortho-*(trimethyltin)benzaldehyde* $Cr(CO)_3$ *complexes in* $CHCl_3$ (—: (+)-(1*S*)-**18a**; – – : (−)-(1*S*)-**18b**)

The above argument is supported by both spectral (NMR) and chemical data. The NOESY spectra of **18a** and **18b** in C_6D_6 show the NOE effects indicated in *Scheme 5*. This is in keeping with an equilibrium between *anti*- and *syn*-aldehyde conformation in **18a**, whereas the *syn*-aldehyde conformation is dominant in **18b**. Confirmation of the same absolute configuration of the two compounds was established by the interconversion of enantiomerically enriched (−)-**18b** into (+)-**18a** *via* the route shown in *Scheme 6*.

Conclusions. – The restriction of conformational freedom in the chiral Li-amide base in general does not result in an increase in asymmetric induction [11c]. The only example where a cyclic amide base significantly outperformed the base Li-**1** is in the case of the carbamate complex **11**. The chiral dibenzo[*c*,*e*]azepine **6** adopts a preferred

Scheme 6



conformation in which the Me groups at the stereogenic center are pseudoequatorial. Thus, the Me groups, the benzylic C-atoms, and the N-atom are close to lying in a plane, an arrangement that is also observed in acyclic dibenzylic amines [19]. It remains to be seen if forcing the benzylic Me groups into pseudoaxial positions, *e.g.*, by introducing Me groups in the *ortho*-positions of aryl leads to increased selectivity with this base. The non-C_2-symmetric amines **7** and **8**, selected for their efficiency in the enantioselective deprotonation of ketones, performed poorly in this reaction sequence [13–15]. We were pleased to find, in the course of these studies, a new, highly enantioselective route to *ortho*-substituted benzaldehyde complexes, a class of compounds that have been most widely used in synthesis. Thus, for both anisole and benzaldehyde complexes simple procedures are now available that afford *ortho*-substituted complexes with enantioselectivities in the range of 75–92%. The hypothesis that different C=O conformations are adopted in the Me_3Sn-substituted benzaldehyde complex and in the corresponding Me_3Si complex has obvious stereochemical implications in diastereoselective reactions. This is presently under investigation.

Experimental Part

1. *General*. See [9h]. Optically enriched secondary amines **1** [19b], **2** [16], **3** [20], **5** [21], and **6** [22], as well as Cr complexes **9** [23], **11** [9h], **13** [24], and **16** [17], were synthesized following literature procedures. (+)-(*R*)-Benzyl(1-phenylethyl)amine (**7**; ee 99%, GC) was obtained from *Fluka*.

2. *Synthesis of Chiral Amines. (+)-(*R,R*)-2,6-Diphenylpiperidine* (**4**)[3]. Under N_2, 100 ml of dry THF were added slowly to a mixture of 5.000 g (19.8 mmol) of 1,5-diphenylpentane-1,5-dione and 13.315 g (41.5 mmol, 2.1 equiv.) of (–)-Ipc_2BCl (Ipc = isopinocampheyl). The resulting suspension was stirred at –78° for 2 h, then brought slowly to r.t. and stirred for 15 h (progressive dissolution of solids). THF was removed under vacuum, and the oily residue was warmed to 40° at 5 mbar pressure during 24 h to remove pinene. Bis(2-hydroxyethyl)-

[3]) For literature precedent of a synthesis *via* a different route, see [25].

amine (4.800 g, 45.5 mmol, 2.3 equiv.) in 100 ml of dry Et_2O was added dropwise to the residue at 0°. After complete addition, the mixture was stirred for 45 min. The ice bath was removed, and the stirring was continued overnight at r.t. (formation of a white precipitate). The solid was eliminated by filtration over *Celite*. The solvent was removed by evaporation, and the oily orange residue was purified by CC (silca gel; hexane/Et_2O 1:1 to 1:3), to give 4.285 g (16.7 mmol, 84%) of (−)-(*S*,*S*)-1,5-Diphenylpentane-1,5-diol as a white solid. M.p. 95°. $[\alpha]_D^{20} = -19.7$ ($c = 1.065$, MeOH). IR (CH_2Cl_2): 3597, 3063, 2954, 1948, 1883, 1812, 1485, 1447, 1419, 1382, 1305, 1191, 1060, 1022, 919, 896, 847, 624. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.42–1.52 (*quint.*, $J = 7.6$, 2 H); 1.68–1.92 (*m*, 4 H); 1.89 (br. *s*, 2 H); 4.67 (*dd*, $J = 7.8$, 5.4, 2 H); 7.26–7.37 (*m*, 10 H). ^{13}C-NMR (100.5 MHz, $CDCl_3$): 22.3 (CH_2); 38.8 (CH_2); 74.5 (CH); 125.8 (CH); 127.6 (CH); 128.5 (CH); 144.8 (C). MS: 239 (1, $[M - H_2O]^+$), 238 (5), 147 (2), 133 (6), 132 (16), 120 (20), 117 (5), 107 (36), 105 (19), 104 (100), 91 (8), 79 (26), 77 (17). HR-MS: 238.1348 ($[M - H_2O]^+$, $C_{17}H_{18}O^+$; calc. 238.1358).

A soln. of 2.4 ml (30.8 mmol, 2.5 equiv.) of MsCl in 100 ml of dry CH_2Cl_2 was cooled to −20° and then treated dropwise with a soln. of 3.000 g (12.5 mmol, 1 equiv.) of (−)-(*S*,*S*)-1,5-Diphenylpentane-1,5-diol and 5.2 ml of Et_3N in 100 ml of dry CH_2Cl_2. After complete addition, the mixture was stirred for 2.5 h at −20°. Allylamine (89 ml, 118 mmol, 9.5 equiv.) was then added, and the resulting soln. was stirred at r.t. overnight. Volatile products were removed under vacuum, and the residue was diluted with 350 ml of Et_2O. The org. phase was washed with 2 × 75 ml of an aq. $NaHCO_3$ soln. and 75 ml of brine. The aq. phases were combined and extracted with 2 portions of Et_2O. The combined org. phases were dried ($MgSO_4$). After filtration and evaporation of solvents, the residue was purified by CC (silica gel; hexane/Et_2O 30:1) to give 2.303 g (8.4 mmol, 67%) of (*R*,*R*)-1-allyl-2,6-diphenylpiperidine as a colorless oil. IR (CH_2Cl_2): 3074, 3019, 2932, 2867, 1948, 1887, 1807, 1638, 1594, 1491, 1447, 1365, 1256, 1223, 1125, 1028, 918. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.65–2.10 (*m*, 6 H); 2.89 (*dd*, $J = 14.4$, 6.2, 1 H); 3.14 (*dd*, $J = 14.4$, 6.2, 1 H); 4.21 (*dd*, $J = 6.4$, 4.8, 2 H); 4.95 (*s*, 1 H); 4.98 (*d*, $J = 8.8$, 1 H); 5.64–5.75 (*m*, 1 H); 7.22–7.52 (*m*, 10 H). ^{13}C-NMR (100.5 MHz, $CDCl_3$): 19.8 (CH_2); 27.9 (CH_2); 51.0 (CH_2); 58.7 (CH); 115.8 (CH_2); 126.4 (CH); 128.0 (CH); 128.1 (CH); 137.5 (CH); 144.4 (C). MS: 277 (36, M^+), 276 (12), 236 (9), 201 (16), 200 (100), 146 (21), 144 (44), 118 (13), 117 (65), 115 (12), 104 (56), 91 (43), 77 (13). HR-MS: 277.1828 (M^+, $C_{20}H_{23}N^+$; calc. 277.1830).

(*R*,*R*)-1-Allyl-2,6-diphenylpiperidine (2.303 g, 8.3 mmol) and 0.369 g (0.43 mmol, 5 mol%) of $RhCl(PPh_3)_3$ were placed in a three-neck round-bottomed flask equipped with a N_2 inlet, a dropping funnel, and a *Claisen* bridge. MeCN/H_2O 84:16 (250 ml) was added, and the resulting soln. was heated to boiling point. The solvent level was maintained by continuous addition of solvents. After 3.5 h, the mixture was cooled to r.t. and diluted with Et_2O (400 ml). H_2O (100 ml) was added, and the phases were separated. The org. phase was washed with 2 × 200 ml of brine, and aq. phases were back-extracted with 2 × 100 ml of Et_2O. The org. phases were combined, dried ($MgSO_4$), and filtered over *Celite*. Evaporation of solvents left an oily residue, which was purified by FC (silica gel; hexane/Et_2O 1:1) to afford 1.411 g (5.95 mmol, 72%) of **4**. Yellow oil. $[\alpha]_D^{20} = +70.0$ ($c = 1.205$, $CHCl_3$). IR (CH_2Cl_2): 3086, 3028, 2937, 2862, 1951, 1887, 1812, 1600, 1494, 1447, 1326, 1210. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.63–1.78 (*m*, 2 H); 1.85–2.10 (*m*, 4 H); 2.10–2.20 (br. *s*, 1 H); 4.10–4.18 (*m*, 2 H); 7.20–7.50 (*m*, 10 H). ^{13}C-NMR (100.5 MHz, $CDCl_3$): 20.8 (CH_2); 31.4 (CH_2); 54.8 (CH); 126.6 (CH); 126.7 (CH); 128.5 (CH); 144.3 (C). MS: 237 (61, M^+), 236 (19), 194 (17), 160 (15), 133 (21), 132 (41), 120 (46), 117 (37), 106 (30), 105 (17), 104 (100), 103 (13), 91 (35), 78 (11), 77 (13). HR-MS: 237.1508 (M^+, $C_{17}H_{19}N^+$; calc. 237.1518).

*(+)-(*R*)-(1-Phenylethyl)(2,2,2-trifluoroethyl)amine* (**8**). NaH (2.2 g, 55 mmol; 55–65% in mineral oil) was placed in a two-neck 250-ml round-bottomed flask. Dry Et_2O (150 ml) was added under N_2, and the resulting suspension was cooled to 0°. (+)-(*R*)-1-Phenylethylamine (6.36 ml, 50 mmol) was added, and the mixture was first left 20 min at 0°, and then 2 h at r.t. After cooling to 0°, 7.16 ml (60 mmol) of CF_3COOEt were added, and the mixture was stirred for 1 h at this temp. and then overnight at r.t. A white precipitate formed, and the starting material was no longer visible by TLC. The reaction was quenched by careful addition of 1M HCl (60 ml). The resulting phases were separated, and the aq. phase extracted with 2 × 30 ml of Et_2O. The combined org. phases were dried ($MgSO_4$), and the solvent was evaporated to give 10.844 g (49.9 mmol, 100%) of (+)-(*R*)-2,2,2-Trifluoro-*N*-(1-phenylethyl)acetamide as a white solid. The crude product was used without purification in the next step. M.p. 88°. $[\alpha]_D^{20} = +115.3$ ($c = 1.24$,CH_2Cl_2). IR (CH_2Cl_2): 3420, 2932, 1713, 1523, 1447, 1207, 1164. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.60 (*d*, $J = 7.0$, 3 H); 5.16 (*q*, $J = 7.0$, 1 H); 6.50 (br. *s*, 1 H); 7.27–7.42 (*m*, 5 H). ^{13}C-NMR (100.5 MHz, $CDCl_3$): 21.0 (Me); 49.8 (CH); 116.0 (*d*, CF_3); 126.2 (CH); 128.2 (CH); 129.1 (CH); 140.9 (C); 157.0 (*q*, C=O). MS: 217 (100, M^+), 216 (71), 215 (10), 203 (9), 202 (91), 148 (10), 132 (11), 107 (26), 105 (61), 104 (42), 103 (31), 96 (12), 79 (53), 78 (18), 77 (39), 69 (37), 51 (26), 50 (11). HR-MS: 217.0700 (M^+, $C_{10}H_{10}F_3NO^+$; calc. 217.0714).

The amide (4.366 g, 20 mmol) was placed in a 250-ml round-bottomed flask; 40 ml of a 1M $BH_3 \cdot THF$ soln. were added, followed by 40 ml of THF. The resulting soln. was stirred at 40° for 60 h (the reaction was monitored

by IR; disappearance of the amide band). The reaction was then quenched with conc. HCl, the solvent was removed, and the resulting aq. phase was neutralized by addition of solid NaOH and extracted with 4 portions of Et_2O. The combined org. phases were dried ($MgSO_4$), and the solvent was evaporated. The yellow oil, which was purified by bulb-to-bulb distillation (60°/0.8 mbar), afforded 3.355 g (16.5 mmol, 82%) of **8**. Colorless liquid. $[\alpha]_D^{20} = +46.7$ ($c = 1.305$, CH_2Cl_2). IR (CH_2Cl_2): 3028, 2965, 2869, 1493, 1451, 1402, 1373, 1278, 1252, 1215, 1146, 1097, 971, 822. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.56 (*d*, $J = 6.6$, 3 H); 3.02–3.21 (*m*, 2 H); 5.16 (*q*, $J = 6.6$, 1 H); 7.25–7.48 (*m*, 5 H). ^{13}C-NMR (100.5 MHz, $CDCl_3$): 23.0 (Me); 47.3 (*m*, CH_2); 58.2 (CH); 127.1 (CH); 128.7 (C); 129.1 (CH); 129.3 (CH). MS: 203 (1, M^+), 202 (4), 189 (14), 188 (100), 126 (21), 110 (24), 106 (15), 105 (38), 91 (9), 77 (16). HR-MS: 203.0894 (M^+, $C_{10}H_{12}NF_3^+$; calc. 203.0922).

(−)-2,6-Dimethyl-2,6-diphenylpiperidine (**5**). Compound **5** was prepared according to the procedure reported by one of us (*J. E.*) [21]. Colorless oil. $[\alpha]_D^{20} = -44$ ($c = 1.5$, AcOEt). IR ($CHCl_3$): 3318, 3154, 2938, 2864, 2252, 1793, 1732, 1600, 1493, 1444, 1370, 1078. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.12 (*s*, 6 H); 1.56 (br. *s*, 1 H); 1.68–1.82 (*m*, 2 H); 1.88–2.20 (*m*, 2 H); 2.17–2.31 (*m*, 2 H); 7.24–7.33 (*m*, 2 H); 7.36–7.48 (*m*, 4 H); 7.71–7.79 (*m*, 4 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 19.3 (CH_2); 33.7 (Me); 37.0 (CH_2); 55.6 (C); 126.2 (CH); 126.8 (CH); 128.5 (CH); 151.1 (C). MS: 265 (3, M^+), 264 (1), 252 (2), 251 (20), 250 (100), 188 (11), 146 (7), 132 (23), 131 (76), 120 (22), 118 (32), 103 (10), 91 (22), 77 (11). HR-MS: 265.1835 (M^+, $C_{19}H_{23}N^+$; calc. 265.1830).

3. *Determination of Enantiomeric Excess of Chiral Amines* **1**–**6**. *(+)-(*R,R*)-Bis(1-phenylethyl)amine* (**1**). The trifluoroacetamide derivative was formed, and the two enantiomers were separated by chiral HPLC. *Chiracel OD-H*, hexane/i-PrOH 99.5 : 0.5, flow: 1 ml/min, UV detection: 254 nm, t_R ((*R*,*R*)) 5.6 min, t_R ((*S*,*S*)) 7.7 min, ee > 98% (only one enantiomer detected).

*(+)-(*R,R*)-2,5-Diphenylpyrrolidine* (**2**). The amide derivative was formed with (−)-(*S*)-3,3,3-Trifluoro-2-methoxy-2-phenylpropanoic acid (*Mosher*'s acid) [26], and de value was determined by integration of the H-atoms at the stereogenic centers (500 MHz, $CDCl_3$). With *rac*-**2**: δ 4.55 and 4.85 (*t*, $J = 7.6$). With (+)-(*R*,*R*)-**2**: $\delta = 4.83$, de > 96% (only one diastereoisomer detected).

*(−)-(*S,S*)-2,5-Dimethyl-2,5-diphenylpyrrolidine* (**3**). Determination of the ee *via* chiral HPLC of the nitroxide derivative [20].

*(+)-(*R,R*)-2,6-Diphenylpiperidine* (**4**). The amide derivative was formed with (−)-(*S*)-3,3,3-Trifluoro-2-methoxy-2-phenylpropanoic acid (*Mosher*'s acid) [26], and the de value was determined by integration of the H-atoms at the stereogenic centers of the piperidine (500 MHz, $CDCl_3$). With *rac*-**4**: δ 4.26 and 4.32 (*dd*, $J = 7.0$, 3.9). With (+)-(*R*,*R*)-**4**: δ 4.22, de > 96% (only one diastereoisomer detected).

*(+)-(*S,S*)-2,6-Dimethyl-2,6-diphenylpiperidine* (**5**). The amide derivative was formed using (−)-(*S*)-3,3,3-Trifluoro-2-methoxy-2-phenylpropanoic acid (*Mosher*'s acid) [26], and the de value was determined by integration of *singlets* associated with the Me groups of the piperidine ring (500 MHz, CD_3OD). With *rac*-**5**: δ 1.24 and 1.68. With (+)-(*S*,*S*)-**5**: δ 1.20, de > 96% (only one diastereoisomer detected).

*(−)-(*R,R*)-5,7-Dimethyl-6,7-dihydro-5*H*-dibenzo[*c,e*]azepine* (**6**). A salt was formed with (−)-(*R*)-mandelic acid, and the de value was determined by integration of *doublets* associated with the benzylic Me groups (400 MHz, C_6D_6). With *rac*-**6**: δ 1.42 and 1.49 (*d*, $J = 7.0$). With (−)-(*R*,*R*)-**6**: δ 1.42, de > 96% (only one diastereoisomer detected).

4. *Synthesis of Tricarbonyl[(1,2,3,4,5,6-η-benzylidene)phenylamine]chromium* (**17**). (η^6-Benzaldehyde)tricarbonyl chromium (4.840 g, 20 mmol) [17] was dissolved in 100 ml of Et_2O. Aniline (2.2 ml, 24 mmol, 1.2 equiv.) and 6.2 g of 4-Å molecular sieves were added, and the mixture was stirred at r.t. during 8 h. After filtration over *Celite* and concentration of the soln., the product was precipitated with hexane and dried under vacuum, affording 6.397 g (20 mmol, 100%) of **17**. Red solid. M.p. 110°. ^{1}H-NMR (200 MHz, C_6D_6): 0.44 (*s*, 1 H); 4.30–4.48 (*m*, 3 H); 5.27–5.34 (*m*, 2 H); 7.00–7.20 (*m*, 5 H). ^{13}C-NMR (50.3 MHz, C_6D_6): 91.6 (CH); 93.7 (CH); 93.8 (CH); 100.2 (C); 121.7 (CH); 127.1 (CH); 128.6 (C); 129.9 (CH); 156.8 (CH); 232.8 (C). MS: 317 (3, M^+), 289 (1), 261 (16), 234 (26), 233 (100), 181 (24), 180 (28), 77 (27). HR-MS: 317.0131 (M^+, $C_{16}H_{11}NO_3Cr^+$; calc. 317.0144).

5. *Lithiation According to the ISQ Method: General Procedure.* A 0.02M soln. of the chiral base was prepared by adding 1.1 equiv. of BuLi (*ca.* 1.6M in hexane) to 1.1 equiv. of the chiral amine in THF at −78°. After 1 h, 3 equiv. of Me_3SiCl were added, immediately followed by the complex (in solid form, or dissolved in a minimum of THF). After complete reaction (TLC), THF was evaporated, the residue was diluted in 15 ml of Et_2O and 15 ml of 1M HCl. The phases were separated, and the aq. phase was extracted twice with 10 ml of Et_2O. The combined org. phases were dried ($MgSO_4$), the solvent was evaporated, and the residue was purified by FC (silica gel) or analyzed directly by chiral HPLC. The chiral base was recovered by basification of the aq. phase with 1M NaOH, extraction with 3 portions of Et_2O, drying ($MgSO_4$), and evaporation of solvent.

*Chiral Base Li-(+)-(*R,R*)-***1**/*Complex* **9**. The reaction was carried out with 1.480 g (6.07 mmol) of **9**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 95:5) to yield 1.725 g (5.46 mmol, 90%) of (+)-(1*S*)-**10**, ee 90%.

*Chiral Base Li-(−)-(*S,S*)-***2**/*Complex* **9**. The reaction was carried out with 165 mg (0.68 mmol) of **9**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 20:1), affording 133 mg (0.47 mmol, 69%) of *rac*-**10**.

*Chiral Base Li-(−)-(*S,S*)-***3**/*Complex* **9**. The reaction was carried out with 142 mg (0.57 mmol) of **9**. The yellow residue was purified by FC (silica gel; hexane/AcOEt 98:2), affording 131 mg (0.41 mmol, 72%) of (−)-(1*R*)-**10**, ee 73%.

*Chiral Base Li-(+)-(*R,R*)-***4**/*Complex* **9**. The reaction was carried out with 209 mg (0.86 mmol) of **9**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 20:1), affording 183 mg (0.58 mmol, 67%) of (+)-(1*S*)-**10**, ee 9%.

*Chiral Base Li-(+)-(*S,S*)-***5**/*Complex* **9**. The reaction was carried out with 134 mg (0.55 mmol) of **9**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 20:1), affording 68 mg (0.22 mmol, 40%) of (−)-(1*R*)-**10**, ee 22%.

*Chiral Base Li-(−)-(*R,R*)-***6**/*Complex* **9**. The reaction was carried out with 106 mg (0.44 mmol) of **9**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 20:1), affording 60 mg (0.19 mmol, 43%) of (+)-(1*S*)-**10**, ee 14%.

*Chiral Base Li-(+)-(*R*)-***7**/*Complex* **9**. The reaction was carried out with 210 mg (0.86 mmol) of **9**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 20:1), affording 252 mg (0.80 mmol, 93%) of (+)-(1*S*)-**10**, ee 48%.

*Chiral Base Li-(+)-(*R*)-***8**/*Complex* **9**. The reaction was carried out with 290 mg (1.18 mmol) of **9**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 20:1), affording 301 mg (0.95 mmol, 81%) of (+)-(1*S*)-**10**, ee 13%.

*Tricarbonyl[(1*R,*2*S*)-[(1,2,3,4,5,6-η-2-Methoxyphenyl)trimethylsilane]chromium*) (**10**)[4]) ((+)-(1*S*)-**10**): Yellow solid. M.p. 128°. $[\alpha]_D^{20} = +220$ ($c = 0.62$, $CHCl_3$). IR (hexane): 2930, 2846, 1974, 1904, 1565, 1472, 1451. ^{1}H-NMR (200 MHz, C_6D_6): 0.30 (*s*, 9 H); 2.91 (*s*, 3 H); 3.98 (*dm*, $J = 7.1$, 1 H); 4.02 (*tm*, $J = 7.1$, 1 H); 4.86 (*tm*, $J = 7.1$, 1 H); 5.12 (*dd*, $J = 6.1, 1.5$, 1 H). ^{13}C-NMR (50.3 MHz, C_6D_6): 0.2 (Me); 55.2 (Me); 73.8 (CH); 85.6 (CH); 88.6 (C); 96.2 (CH); 102.0 (CH); 147.9 (C); 234.6 (C). MS: 316 (14, M^+), 260 (6), 233 (27), 232 (100), 217 (5), 202 (6), 201 (7), 187 (8), 165 (16), 135 (44), 91 (6), 52 (32). HR-MS: 316.0252 (M^+, $C_{13}H_{16}O_4SiCr^+$; calc. 316.0223). Chiral HPLC: *Chiracel OD*, hexane/i-PrOH 90:10, flow: 0.5 ml/min, UV detection: 254 nm, t_R ((−)) 13.3 min, t_R ((+)) 18.0 min.

*Chiral Base Li-(+)-(*R,R*)-***1**/*Tricarbonyl(1,2,3,4,5,6-η-phenyl* N,N-*diisopropylcarbamate)chromium* (**11**). The reaction was carried out with 204 mg (0.57 mmol) of **11**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 7:3), affording 136 mg (0.32 mmol, 56%) of (+)-(1*S*)-**12**, ee 39%.

*Chiral Base Li-(+)-(*R,R*)-***2**/*Complex* **11**. The reaction was carried out with 211 mg (0.59 mmol) of **11**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 7:3), affording 129 mg (0.30 mmol, 51%) of *rac*-**12**.

*Chiral Base Li-(+)-(*R,R*)-***3**/*Complex* **11**. The reaction was carried out with 275 mg (0.77 mmol) of **11**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 7:3), affording 322 mg (0.75 mmol, 97%) of (+)-(1*S*)-**12**, ee 27%.

*Chiral Base Li-(+)-(*R,R*)-***4**/*Complex* **11**. The reaction was carried out with 306 mg (0.86 mmol) of **11**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 7:3), affording 202 mg (0.56 mmol, 65%) of (+)-(1*S*)-**12**, ee 29%.

*Chiral Base Li-(+)-(*S,S*)-***5**/*Complex* **11**. The reaction was carried out with 214 mg (0.60 mmol) of **11**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 7:3), affording 185 mg (0.43 mmol, 72%) of (−)-(1*R*)-**12**, ee 24%.

*Chiral Base Li-(−)-(*R,R*)-***6**/*Complex* **11**. The reaction was carried out with 150 mg (0.42 mmol) of **11**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 7:3), affording 85 mg (0.20 mmol, 48%) of (+)-(1*S*)-**12**, ee 62%.

*Chiral Base Li-(+)-(*R*)-***7**/*Complex* **11**. The reaction was carried out with 307 mg (0.86 mmol) of **11**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 7:3), affording 181 mg (0.42 mmol, 49%) of (+)-(1*S*)-**12**, ee 13%.

*Chiral Base Li-(+)-(*R*)-***8**/*Complex* **11**. The reaction was carried out with 448 mg (1.25 mmol) of **11**. The yellow residue was purified by FC (silica gel; hexane/Et_2O 7:3), affording 476 mg (1.11 mmol, 88%) of *rac*-**12**.

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[4]) The numbering of the benzene moiety differs from that used in the text.

*Tricarbonyl[(1*R*,2*S*)-(1,2,3,4,5,6-η-2-(trimethylsilyl)phenyl* N,N-*diisopropylcarbamate]chromium* ((−)-(1*R*)-**12**). Yellow solid. M.p. 122°. $[\alpha]_D^{20} = -104.4$ ($c = 0.20$, CH_2Cl_2). IR (CH_2Cl_2): 2973, 1968, 1892, 1721, 1427, 1405, 1372, 1313, 1274, 1191, 1152, 1039, 979, 842. ^{1}H-NMR (200 MHz, C_6D_6): 0.29 (*s*, 9 H); 0.92–1.02 (*m*, 6 H_A); 1.20–1.30 (*m*, 6 H_B); 3.22 (*quint.*, $J = 13.3$, 1 H_A); 4.34 (*quint.*, $J = 13.3$, 1 H_B); 3.96–4.04 (*m*, 1 H); 4.75–4.86 (*m*, 2 H); 4.98–5.03 (*dm*, $J = 5.5$, 1 H). ^{13}C-NMR (50.3 MHz, C_6D_6): 0.0 (Me); 21.0 (Me); 46.4 (CH); 48.3 (CH); 87.3 (CH); 88.3 (CH); 92.4 (C); 96.3 (CH); 100.2 (CH); 138.5 (C); 152.1 (C); 234.3 (C). MS: 429 (3, M^+), 373 (12), 345 (100), 187 (15), 128 (26), 86 (38), 52 (18). HR-MS: 429.1111 (M^+, $C_{19}H_{27}NO_5SiCr^+$; calc. 429.1064). Chiral HPLC: *Chiracel OD*, hexane/i-PrOH 99:1, flow: 0.6 ml/min, UV detection: 254 nm, t_R ((−)) 19 min, t_R ((+)) 24 min.

*Chiral Base Li-(+)-(*R,R*)-***1***/Tricarbonyl[1,2,3,4,5,6-η-1-(1,3-dioxolan-2-yl)phenyl]chromium* **13**. The reaction was carried out with 230 mg (0.80 mmol) of **13**. The yellow residue was analyzed by ^{1}H-NMR, showing a **14**/**15** ratio of 48:52. Separation by FC (silica gel, hexane/Et_2O 7:3) afforded 149 mg (0.42 mmol) of **15** and 115 mg (0.32 mmol, 40%) of (+)-(1*S*)-**14**, ee 81%.

*Chiral Base Li-(+)-(*R,R*)-***2***/Complex* (**13**). The reaction was carried out with 217 mg (0.76 mmol) of **13**. The yellow residue was analyzed by ^{1}H-NMR, showing a **13**/**15** ratio of 1:1. Complex **15** could be separated from unreacted **13** by FC (silica gel; hexane/Et_2O 10:1), affording 124 mg (0.26 mmol, 46%) of **15**.

*Chiral Base Li-(−)-(*S,S*)-***3***/Complex* **13**. The reaction was carried out with 139 mg (0.49 mmol) of **13**. The yellow residue was not purified, but analyzed by ^{1}H-NMR to determine the conversion (40%), and by chiral HPLC to determine the enantiomeric excess ((−)-(1*R*)-**14**, 51% ee).

*Chiral Base Li-(+)-(*R,R*)-***4***/Complex* **13**. The reaction was carried out with 263 mg (0.92 mmol) of **13**. The yellow residue (298 mg) was not purified, but analyzed by ^{1}H-NMR (ratio **14**/**15** 30:70). The chiral HPLC showed an ee of 5% ((+)-(1*S*)-**14**).

*Chiral Base Li-(−)-(*R,R*)-***5***/Complex* **13**. The reaction was carried out with 267 mg (0.93 mmol) of **13**. The yellow residue was not purified, but analyzed by ^{1}H-NMR (ratio **14**/**15** 57:43). The chiral HPLC showed an ee of 4% ((+)-(1*S*)-**14**).

*Chiral Base Li-(−)-(*R,R*)-***6***/Complex* **13**. The reaction was carried out with 159 mg (0.55 mmol) of **13**. The yellow residue was not purified, but analyzed by ^{1}H-NMR (ratio **14**/**15** 57:43). The chiral HPLC showed an ee of 11% ((+)-(1*S*)-**14**).

*Chiral Base Li-(+)-(R)-***7***/Complex* **13**. The reaction was carried out with 246 mg (0.86 mmol) of **13**. The yellow residue (253 mg) was not purified, but analyzed by ^{1}H-NMR, showing unreacted **13** and substitution in benzylic position (**15**) in a 2:1 ratio.

*Chiral Base Li-(+)-(*R*)-***8***/Complex* **13**. The reaction was carried out with 333 mg (1.16 mmol) of **13**. The yellow residue was not purified, but analyzed by ^{1}H-NMR, showing only unreacted **13**.

*Tricarbonyl{(1*S*)-[1,2,3,4,5,6-η-2-(1,3-dioxolan-2-yl)phenyl]trimethylsilane]chromium*)[4] ((+)-(1*S*)-**14**). Yellow solid. M.p. 68°. $[\alpha]_D^{20} = +24.8$ ($c = 0.25$, $CHCl_3$). IR ($CHCl_3$): 3000, 2931, 2886, 2354, 1970, 1888, 1098, 848. ^{1}H-NMR (200 MHz, C_6D_6): 0.32 (*s*, 9 H); 3.25–4.02 (*m*, 4 H); 4.36 (*t*, $J = 6.3$, 1 H); 4.79 (*t*, $J = 6.3$, 1 H); 4.96 (*d*, $J = 6.3$, 1 H); 5.12 (*d*, $J = 6.3$, 1 H); 5.67 (*s*, 1 H). ^{13}C-NMR (50.3 MHz, C_6D_6): 1.0 (Me); 65.6 (CH_2); 65.9 (CH_2); 88.9 (CH); 91.1 (CH); 94.7 (CH); 98.8 (C); 100.1 (CH); 101.8 (CH); 114.3 (C); 233.8 (C). MS: 358 (37, M^+), 302 (6), 274 (100), 231 (39), 212 (44), 163 (73), 126 (39), 96 (10), 73 (10). Anal. calc. for $C_{15}H_{18}O_5CrSi$: C 50.27, H 5.06; found: C 50.29, H 5.01. Chiral HPLC: *Chiracel OD*, hexane/i-PrOH 99.5:0.5, flow: 0.8 ml/min, UV detection: 254 nm, t_R ((−)) 22 min, t_R ((+)) 24 min.

*Tricarbonyl{1,2,3,4,5,6-*η*$^{-1}$-[2-(trimethylsilyl)-1,3-dioxolan-2-yl]phenylchromium*} (**15**). Yellow solid. M.p. 147°. IR ($CHCl_3$): 3023, 2953, 2872, 1970, 1883, 837, 662. ^{1}H-NMR (200 MHz, C_6D_6): −0.08 (*s*, 9 H); 3.44 (*t*, $J =$ 7.6, 2 H); 4.10–4.28 (*m*, 4 H); 4.56 (*t*, $J = 7.6$, 1 H); 5.21 (*d*, $J = 7.6$, 2 H). ^{13}C-NMR (100.5 MHz, C_6D_6): −4.41 (CH_3); 65.9 (CH_2); 88.1 (CH); 93.0 (CH); 95.2 (CH); 122.6 (C); 126.6 (C); 233.6 (C). MS: 358 (13, M^+), 302 (8), 274 (25), 149 (100), 126 (40), 105 (37), 73 (26). Anal. calc. for $C_{15}H_{18}O_5CrSi$: C 50.27, H 5.06; found: C 50.34, H 5.05.

*Chiral Base Li-(+)-(*R,R*)-***1***/Tricarbonyl[1,2,3,4,5,6-η-(cyclohexylimino)benzyl]chromium* (**16**). The reaction was carried out with 358 mg (1.1 mmol) of **16**. The red residue was purified by FC (silica gel; cyclohexane/Et_2O 10:1), affording 260 mg (0.92 mol, 84%) of (+)-(1*S*)-**18a**, ee 84%.

*Chiral Base Li-(+)-(*R,R*)-***1***/Tricarbonyl[1,2,3,4,5,6-η-(phenylimino)benzyl]chromium* (**17**). The reaction was carried out with 317 mg (1 mmol) of **17**. The red residue was purified by FC (silica gel; cyclohexane/Et_2O 10:1), affording 213 mg (0.76 mmol, 76%) of (+)-(1*S*)-**18a**, ee 88%.

*Tricarbonyl(1*S*)-[1,2,3,4,5,6-η-2-(trimethylsilyl)benzaldehyde]chromium* (**18a**) ((+)-(1*S*)-**18a**). Red oil. $[\alpha]_D^{20} = +104.3$ ($c = 0.12$, $CHCl_3$). IR ($CHCl_3$): 3019, 1982, 1915, 1695, 1198, 847, 780. ^{1}H-NMR (200 MHz, C_6D_6): 0.24 (*s*, 9 H); 4.38–4.52 (*m*, 2 H); 4.75–4.84 (*m*, 2 H); 9.13 (*s*, 1 H). ^{13}C-NMR (100.5 MHz, C_6D_6):

– 0.02 (Me); 92.2 (CH); 92.4 (CH); 94.2 (CH); 97.7 (CH); 100.7 (C); 101.0 (C); 190.6 (CH); 231.3 (C). MS: 314 (16, M^+), 258 (5), 243 (4), 231 (16), 230 (58), 215 (10), 164 (15), 163 (100), 126 (27), 96 (8), 52 (69). HR-MS: 314.0054 (M^+, $C_{13}H_{14}O_4CrSi^+$; calc. 314.0067). Chiral HPLC: *Chiracel OD-H*, hexane/i-PrOH 98 : 2, flow: 1 ml/min, UV detection: 254 nm, t_R ((–)) 10.7 min, t_R ((+)) 12.2 min.

6. *Lithiation According to the EQ Method: General Procedure.* The chiral Li-amide base was prepared by adding 1.1 equiv. of BuLi (*ca.* 1.6M in hexane) to 1.1 equiv. of the chiral amine (+)-(*R*,*R*)-**1** in 10–20 ml of THF at – 78°. After 1 h at – 78°, 1 equiv. of imine complex **16** or **17** was added as a solid. After 2 h at – 78°, 3 equiv. of electrophile were added. After 1 h at – 78°, the mixture was quenched with 1 ml of HCl (2M) and stirred at r.t. for 1 h. THF was evaporated, and the residue was extracted with 15 ml of Et_2O and 15 ml of 1M HCl. The phases were separated, and the aq. phase was extracted twice with 10 ml of Et_2O. The combined org. phases were dried ($MgSO_4$), concentrated, and the residue was purified by FC (silica gel).

Complex **16**/*Me_3SiCl*. The reaction was carried out with 660 mg (2.04 mmol) of **16**. The red residue was purified by FC (silica gel; cyclohexane/Et_2O 10 : 1), affording 473 mg (1.68 mmol, 82%) of (+)-(1*S*)-**18a**, ee 78%.

Complex **17**/*Me_3SiCl*. The reaction was carried out with 330 mg (1.04 mmol) of **17**. The red residue was purified by FC (silica gel; cyclohexane/Et_2O 10 : 1), affording 197 mg (0.70 mmol, 67%) of (+)-(1*S*)-**18a**, ee 92%.

Complex **16**/*Me_3SnCl*. The reaction was carried out with 199 mg (0.62 mmol) of **16**. The red residue was purified by FC (silica gel; pentane/Et_2O 9 : 1), affording 168 mg (0.41 mmol, 67%) of (–)-(1*S*)-**18b**, ee 78%.

Complex **17**/*Me_3SnCl*. The reaction was carried out with 317 mg (1 mmol) of **17**. The red residue was purified by FC (silica gel; pentane/Et_2O 7 : 1), affording 263 mg (0.65 mmol, 65%) of (–)-(1*S*)-**18b**, ee 89%.

*Tricarbonyl[(*R*)-1,2,3,4,5,6-η-2-(trimethylstannanyl)benzaldehyde]chromium* (**18b**) ((–)-(1*S*)-**18b**). Red oil. $[\alpha]_D^{20} = -354$ ($c = 0.185$, $CHCl_3$). IR (CH_2Cl_2): 1978, 1909, 1698, 1260, 1196. ^{1}H-NMR (200 MHz, C_6D_6): 0.35 (*s*, 9 H); 4.37 (*t*, *J* = 6.3, 1 H); 4.51–4.62 (*m*, 2 H); 4.86 (*d*, *J* = 6.2, 1 H); 9.73 (*s*, 1 H). ^{13}C-NMR (100.5 MHz, C_6D_6): – 7.1 (Me); 91.1 (CH); 95.2 (CH); 97.8 (CH); 98.1 (CH); 99.6 (C); 101.6 (C); 128.3 (CH); 231.6 (C). MS: 410 (1), 408 (1), 406 (7), 405 (3), 404 (5), 403 (3), 402 (3), 391 (3), 322 (21), 320 (16), 318 (10), 255 (18), 253 (14), 225 (13), 223 (10), 172 (33), 158 (20), 157 (100), 52 (57). HR-MS: 403.9481 (M^+, $C_{13}H_{14}O_4{}^{118}CrSn^+$; calc. 403.9313), 405.9492 (M^+, $C_{13}H_{14}O_4{}^{120}CrSn^+$; calc. 405.9319). Chiral HPLC: *Chiracel OD*, hexane/i-PrOH 98 : 2, flow: 0.5 ml/min, UV detection: 254 nm, t_R ((+)) 15.8 min, t_R ((–)) 17.7 min.

Complex **16**/*MeI*. The reaction was carried out with 162 mg (0.5 mmol) of **16**. The red residue was purified by FC (silica gel; pentane/Et_2O 9 : 1), affording 79 mg (0.31 mmol, 62%) of (+)-(1*S*)-**18c**, ee 72%.

*Tricarbonyl[(*R*)-1,2,3,4,5,6-η-2-methylbenzaldehyde]chromium* (**18c**) ((+)-(1*S*)-**18c**). Red oil. $[\alpha]_D^{20} = +464$ ($CHCl_3$, $c = 0.125$). IR (CH_2Cl_2): 1982, 1913, 1694, 1268, 1203. ^{1}H-NMR (400 MHz, C_6D_6): 1.88 (*s*, 3 H); 3.99 (*d*, *J* = 6.4, 1 H); 4.21 (*t*, *J* = 6.4, 1 H); 4.72 (*t*, *J* = 6.2, 1 H); 5.49 (*d*, *J* = 6.5, 1 H); 9.28 (*s*, 1 H). ^{13}C-NMR (100.5 MHz, C_6D_6): 17.3 (Me); 87.5 (CH); 91.2 (CH); 94.6 (CH); 93.8 (C); 95.0 (CH); 116.7 (C); 186.7 (CH); 230.9 (C). MS: 256 (13, M^+), 200 (4), 173 (8), 172 (42), 53 (12), 52 (100). HR-MS: 255.9834 (M^+, $C_{11}H_8CrO_4^+$; calc. 255.9828). Chiral SFC: *Chiracel OD-H*, 10% MeOH, flow: 2 ml/min, UV detection: 220 nm, t_R ((–)) 21.4 min, t_R ((+)) 23.3 min, ee 72%. Formation of the chiral aminal with (*R*,*R*)-cyclohexane-1,2-diamine and analysis by ^{1}H-NMR showed a de > 70% and confirmed the absolute configuration [5c].

Complex **16**/*$ClCO_2Me$*. The reaction was carried out with 162 mg (0.5 mmol) of **16**. The dark-red residue was purified by FC (silica gel; pentane/Et_2O 4 : 1), affording 99 mg (0.33 mmol, 66%) of (+)-(1*S*)-**18d**, ee 74%.

Complex **17**/*$ClCO_2Me$*. The reaction was carried out with 317 mg (1.0 mmol) of **17**. The dark-red residue was purified by FC (silica gel; pentane/Et_2O 4 : 1), affording 205 mg (0.68 mmol, 68%) of (+)-(1*S*)-**18d**, ee 90%.

*Tricarbonyl[methyl (*S*)-1,2,3,4,5,6-η)-2-formylbenzoate]chromium* (**18d**)[4] ((+)-(1*S*)-**18d**). Dark-red solid. $[\alpha]_D^{20} = +432$ ($CHCl_3$, $c = 0.053$). IR (CH_2Cl_2): 1997, 1937, 1725, 1689, 1602, 1272.^{1}H-NMR (200 MHz, C_6D_6): 3.27 (*s*, 3 H); 4.26 (*t*, *J* = 6.3, 1 H); 4.40 (*t*, *J* = 6.4, 1 H); 5.11 (*d*, *J* = 6.6, 1 H); 5.51 (*d*, *J* = 6.6, 1 H); 10.32 (*s*, 1 H). ^{13}C-NMR (100.5 MHz, C_6D_6): 52.4 (Me); 90.7 (CH); 90.8 (CH); 91.8 (CH); 91.9 (CH); 94.8 (C); 97.2 (C); 165.8 (CH); 188.2 (CH); 229.8 (C). MS: 300 (7, M^+), 244 (4), 216 (24), 188 (14), 158 (25), 53 (13), 52 (100). HR-MS: 299.9729 (M^+, $C_{12}H_8CrO_6^+$; calc. 299.9726). Chiral HPLC: *Chiracel OD*, hexane/i-PrOH 90 : 10, flow: 0.3 ml/min, UV detection: 245 nm, t_R ((–)) 60.3 min, t_R ((+)) 66.8 min.

7. *Transformation of (–)-(1*S*)-***18b*** into (+)-(1*S*)-***18a***. Tricarbonyl[[1,2,3,4,5,6-η-2-(1,3-dioxolan-2-yl)phenyl]trimethylstannane]chromium* (**20**)[4] ((1*S*)-**20**). Complex (–)-(1*S*)-**18b** (73% ee) (258 mg, 0.64 mmol) was dissolved in 2 ml of THF. Bis(trimethylsilyl)ethylene glycol (1.1 equiv.) was added, followed by 10 mol-% of Me_3SiOTf [27]. After 1 h, the mixture was diluted with Et_2O and filtered through a plug of silica, affording 236 mg (0.52 mmol, 81%) of (1*S*)-**20** as an orange oil. IR ($CHCl_3$): 2977, 2872, 1965, 1888, 1108. ^{1}H-NMR (200 MHz, C_6D_6): 0.32 (*s*, 9 H); 3.15–3.43 (*m*, 4 H); 4.40 (*td*, *J* = 6.2, 1.1, 1 H); 4.71 (*td*, *J* = 6.5, 1.1, 1 H); 4.97 (*dd*, *J* = 6.2, 1.1, 1 H); 5.20 (*dd*, *J* = 6.6, 1.0, 1 H); 10.32 (*s*, 1 H). ^{13}C-NMR (50.3 MHz, C_6D_6): – 6.3 (Me); 65.4

(CH_2); 65.7 (CH_2); 91.1 (CH); 92.4 (CH); 94.0 (CH); 100.7 (CH); 102.5 (CH); 115.8 (C), 108.2 (C), 234.1 (C). MS: 452 (2), 451 (2), 450 (9), 449 (4), 448 (7), 447 (3), 446 (4), 406 (4), 366 (14), 364 (11), 338 (11), 320 (12), 307 (11), 306 (14), 305 (11), 304 (12), 291 (10), 225 (16), 253 (13), 225 (15), 223 (12), 188 (10), 186 (10), 172 (21), 158 (22), 157 (100), 53 (12), 52 (98). HR-MS: 447.9622 (M^+, $C_{15}H_{18}O_5Cr^{118}Sn^+$; calc. 447.9576) and 449.9615 (M^+, $C_{15}H_{18}O_5Cr^{120}Sn^+$; calc. 449.958 (1).

Complex (1*S*)-**20** (205 mg, 0.46 mmol) was dissolved in 5 ml of THF. The soln. was cooled to $-78°$, and 1 equiv. of BuLi was added. After 1 h, 3 equiv. of Me_3SiCl were added. The mixture was left 30 min at $-78°$, quenched with 1 ml of sat. $NaHCO_3$ soln. and filtered through a plug of silica, affording 149 mg (0.42 mmol, 91%) of (+)-(1*S*)-**14**.

Complex (+)-(1*S*)-**14** (120 mg, 0.34 mmol) was dissolved in 5 ml of THF, and 1 ml of conc. HCl was added. After 2 h, the reaction was complete (followed by TLC). The mixture was put directly on a column and purified by FC (silica gel; pentane/Et_2O 9:1 to 4:1), affording 91 mg (0.32 mmol, 96%) of (+)-(1*S*)-**18a**, $[\alpha]_D^{20} = +76$ ($c = 0.185$, $CHCl_3$), ee 67% (by chiral HPLC).

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