Enantioselective Deprotonation/Electrophile Addition Reactions of Tricarbonyl(phenyl carbamate)chromium Complexes

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Sequential reaction of the tricarbonyl[(η^6-phenyl) carbamate]chromium complex **3** with chiral amide bases (see **4** and **5**) and electrophiles yielded planar chiral *ortho*-substituted complexes **6** with up to 70% enantiomeric excess (ee) (*Scheme 2*, *Table 1* and *2*). The enantiomer purity could be increased to >90% ee by fractional crystallization. In all but one case the racemate crystallized selectively, leaving the enantiomerically enriched complex in solution. X-Ray crystal-structure analyses of *rac*-**6a** and (1*R*)-**6a** suggest that this can be ascribed to a more favorable packing of enantiomers of opposite configuration in the solid state than that of the enantiomerically pure solid. Increasing the temperature of the intermediate *ortho*-lithiated aryl carbamate complex induced an anionic *ortho-Fries* rearrangement: The 1,3-transposition of the carbamoyl group yielded the *ortho*-substituted (η^6-benzamide)tricarbonylchromium complexes **10** in 65% yield, after exposure to the electrophile (*Scheme 6*), and the use of a chiral amide base **5** in the deprotonation step afforded the product with an ee of 54%.

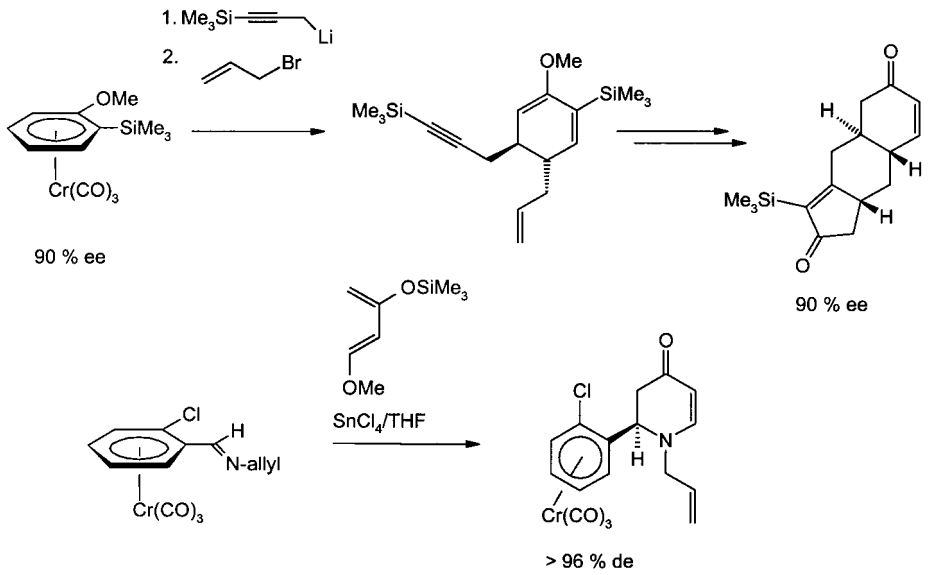
Introduction. – Planar chiral transition-metal π-complexes of *ortho*-disubstituted arenes have emerged as useful starting materials in organic synthesis because the metal coordination enhances arene reactivity, and the planar chirality enables new stereogenic centers to be formed highly diastereoselectively [1] [2]. Recent examples from this laboratory include diastereoselective cycloaddition, dearomatization, and intramolecular *Heck* reactions [3]. Two examples are shown in *Scheme 1.*

Stimulated by the success of planar-chiral arene complexes in asymmetric synthesis, attention has been directed to improve routes of access to enantiomerically pure and enantiomerically enriched complexes. Efficient resolution methods exist only for *o*-substituted benzaldehyde complexes [4]. Diastereoselective methods include complexation of chiral arenes [4a] [5], deprotonation of chirally modified complexes followed by electrophile addition [6], and a diastereoselective nucleophile addition/hydride abstraction sequence with chiral (arenecarbaldehyde hydrazone) complexes [7]. An enantioselective version of the last method, with extension to dihydrophenyloxazole and benzenemethanimine complexes was published recently [8].

In parallel and independent studies, three groups published preliminary data on the use of chiral bases to enantioselectively deprotonate the monosubstituted arene ligand of [Cr(arene)$(CO)_3$] complexes in 1994 in short succession [9]. Further results of enantioselective ring C–H deprotonations [10] and benzylic C–H deprotonations [11] in [Cr(arene)$(CO)_3$] complexes followed shortly – attesting to both the interest in this approach and its versatility.

An attractive feature of enantioselective lithiation is that it is applicable to products for which efficient resolution methods are not readily available. A good example in this

Scheme 1



respect are phenol derivatives that are of interest for further, highly diastereoselective transformations, *e.g.*, to enantiomerically enriched cyclohexenone derivatives [3c] [12] as depicted in *Scheme 1*.

We here report details of our study of the phenyl carbamate complex **3**. The carbamate function was chosen for its numerous synthetic possibilities [13] and its strong *ortho*-directing ability that was expected to control the regioselectivity of the lithiation and help in enantioselection when treated with a chiral base.

Results and Discussion. – *Enantioselective Deprotonation/Electrophile Addition.* Complex **3** was synthesized in high yield from phenyl carbamate **1** *via* arene exchange in $[Cr(CO_3)(\eta^6\text{-naphthalene})]$ (**2**) (*Scheme 2*). Lithium amides **4** and **5**, chosen for their efficiency in other asymmetric deprotonations [14], were used as chiral bases in this study. Regioselectivity was as expected: both bases selectively removed a proton in the *ortho*-position of the phenyl group of complex **3**. Quenching with electrophiles furnished products **6**. Initial studies focused on Me_3SiCl as electrophile since this allowed an evaluation of both sequential addition of base and electrophile (external quench) as well as enantioselective deprotonation in the presence of the electrophile (*in situ* quench). The results are shown in *Table 1*.

Addition of 1.15 equiv. of base **4** followed by Me_3SiCl afforded complex **6a** (R = Me_3Si) in good yield but as racemic mixture (2% ee[1]), *Table 1*, *Entry 1*). Excess of base **4** produced **6a** with *ca.* 66% ee[1]) (*Entries 2* and *3*), but at the expense of yield as the *o*-disubstituted product **7** (R = Me_3Si) was also formed. The major enantiomer of **6a**

[1]) The enantiomeric excess (ee) of the resulting *ortho*-substituted complex **6** was determined by HPLC on a chiral column (*Chiralcel OD* column, hexane/i-PrOH). Determination of the major enantiomer's absolute configuration will be discussed below.

Scheme 2

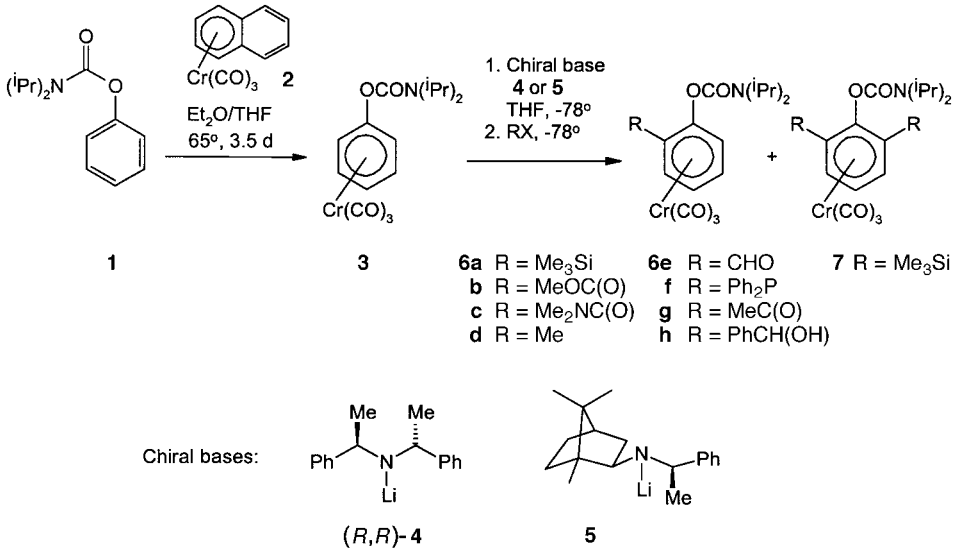


Table 1. *Enantioselective Deprotonation/Me_3SiCl Quench with Complex* **3**

Entry	Base/Conditions	Product ratio [%][a])		ee [%][b])	Configuration[c])	Yield [%][d])
		6a	**7**			
1	**4** (1.15 equiv.)/external quench[e])	100	0	2	–	83
2	**4** (1.53 equiv.)/external quench[e])	62	38	66	(1*R*)	88
3	**4** (1.73 equiv.)/external quench[e])	50	50	67	(1*R*)	90
4	**4** (1.15 equiv.)/*in situ* quench[f])	92	8	39	(1*S*)	60[g])
5	**5** (1.15 equiv.)/*in situ* quench[f])	92	8	64	(1*R*)	85[h])
6	**5** (1.15 equiv.)/external quench[e])	100	0	67	(1*R*)	83
7	**5** (1.15 equiv.)/external quench[e]) + LiCl	100	0	31	(*1R*)	90

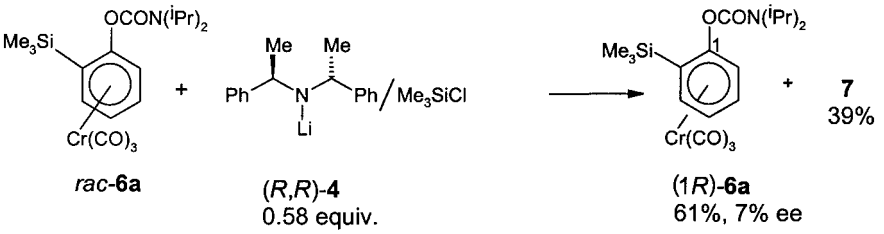
[a]) Product ratio **6a**/**7** (R = Me_3Si) determined by ^{1}H-NMR of the crude mixture. [b]) Enantiomeric excess (ee) of **6a** determined by HPLC (*Chiralcel OD* column, hexane/i-PrOH). [c]) The absolute configuration refers to the major enantiomer of **6a** and was deduced from the X-ray analysis of the hydrazonechromium complex obtained from **6e** (R = CHO; (1*R*)) and SAMP (see below); (1*R*) and (1*S*) refer to the chiral center bearing the carbamate substituent. [d]) Yields of isolated products after flash chromatography. [e]) External quench: Me_3SiCl (3 equiv.) was added after stirring the −78° reaction mixture for 2.5 h. [f]) *in situ* Quench: complex **3** in THF was added to a solution of **4** and Me_3SiCl in THF. [g]) 18% of **3** recovered. [h]) 9% of **3** recovered.

formed in this reaction had the configuration (1*R*). When base **4** was used in the presence of Me_3SiCl (*in situ* quench conditions; *Table 1*, *Entry 4*), **6a** was obtained in 56% yield and 39% ee[1]) along with minor amounts (4%) of the disilylated product **7** and some unreacted starting material **3** (18%). In contrast to the reactions in *Entries 2* and *3*, the major enantiomer of **6a**, formed under *in situ* quench conditions, had the opposite configuration (1*S*).

Several hypotheses can be formulated to explain the correlation between observed enantioselectivity and the amount of base used under external-quench conditions. Referring to *Entries 1* and *2*, a first premise is that asymmetric metallation of **3** under

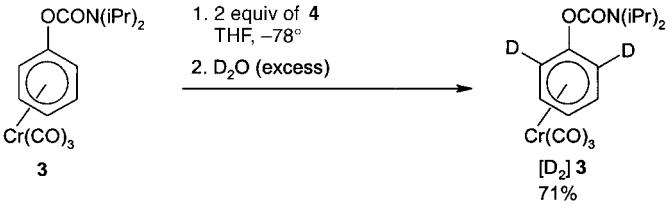
external-quench conditions was undermined by a rapid racemization process involving proton transfer between **3** and (**3**-H)Li [9b]. Therefore, in the presence of excess base, the first equivalent would react under rapid racemization of the lithiated complex before the addition of the electrophile and would yield *rac*-**6a** (*Entry 1*). After this first silylation, the excess chiral base would react under the *in situ* quench conditions on the *ortho*-sililated complex *rac*-**6a** with enantiomer discrimination to give the result shown in *Entry 2*. This hypothesis was put to the test by reacting *rac*-**6a** with 0.58 equiv. of base **4** under *in situ* quench conditions (*Scheme 3*): the result differs from that in *Entry 2* so that the intermediacy of *rac*-**6a** could be discarded.

Scheme 3



A second possible mechanism consists in the formation of a dilithiated intermediate in the presence of excess base. This supposition was checked out – and the hypothesis confirmed – by the deuteration experiment shown in *Scheme 4*, *i.e.*, by reaction of **3** with 2 equiv. of **4** at $-78°$ followed by quenching with excess D_2O which yielded 71% of D_2-**3**.

Scheme 4



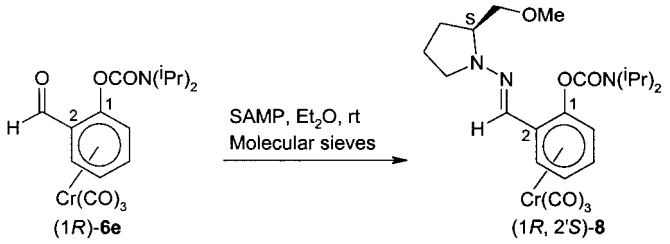
The dilithiation of **3** by the base **4** being confirmed, the results in *Entries 1–3* of *Table 1* can be explained. Thus, enantioselective lithiation of **3** by **4** gives at first preferentially the (1*S*)-monolithiated complex (1*S*)-(**3**-H)Li. In the absence of Me_3SiCl trapping, the (1*S*)-(**3**-H)Li deprotonates starting material resulting in racemization, even at $-78°$. In the presence of excess base (*Entries 2* and *3*, and *Scheme 4*), the racemic *o*-lithiated complex (**3**-H)Li undergoes then a second lithiation with the (1*S*)-enantiomer (1*S*)-(**3**-H)Li reacting more rapidly than the (1*R*)-enantiomer. Electrophile quench then yields the achiral complex **7** and the enantiomerically enriched complex (1*R*)-**6a**.

Base **5** behaved differently. Under *in situ* quench conditions with Me_3SiCl (*Table 1*, *Entry 5*), complex (1*R*)-**6a** was obtained in 78% yield and 64% ee, along with minor amounts (7%) of the disilylated product **7** and some unreacted starting material **3**. External quenching with Me_3SiCl gave selectively (1*R*)-**6a** in 83% yield and 67% ee. We conclude that deprotonation of **3** with base **5** was more rapid than with the lithiated

complex, forestalling the racemization *via* the mechanism operative when base **4** was used. The result also shows that the mono-lithiated complex is configurationally stable. The presence of LiCl under external-quench conditions (*Entry 7*), presumably by changing the aggregation state of base **5**, resulted in a significant decrease of the ee. Independent of the nature of the reaction conditions (*in situ* quench, external quench, or external quench + LiCl), the major enantiomer obtained was (1*R*)-**6a**. Analogous reactions in toluene proved sluggish and gave no improvement of enantioselectivities.

The configurational stability of the lithiated complex obtained with base **5** and its rapid formation allowed variation of the quenching electrophile RX. These reactions led to the enantiomerically enriched planar chiral complexes **6b–h** with a similar level of selectivity as in the case of **6a** and with yields of 70–93% (*Table 2*). The reactions were carried out either by direct reaction of the aryllithium intermediate with the electrophile or, in the case of acetyl chloride, after a transmetallation step, *via* an arylcopper intermediate[2]) [15]. The reaction with benzaldehyde (*Entry 8*), carried out at $-100°$ to optimize the diastereoselectivity of this transformation, gave a 3:1 mixture of diastereoisomers[3]). Attempts to use this chiral (η^6-arene)tricarbonylchromium anion in an asymmetric S_N2' reaction with 3-methylbut-2-enyl bromide were not successful, mostly due to the lack of selectivity of the S_N2' vs. S_N2 pathway [17]. The enantiomeric excesses of **6** were determined by HPLC on a chiral column (*Chiralcel OD* column, hexane/i-PrOH), except for **6e** (*Entry 5*) whose enantiomers could not be separated. Thus **6e** was derivatized with SAMP ((*S*)-2-(methoxymethyl)pyrrolidin-1-amine) (*Scheme 5*) and the diastereoisomer ratio (d.r.) of the resulting hydrazone derivative **8** determined by ^{1}H-NMR. Recrystallization of **8** afforded crystals of the major (1*R*,2′*S*)-diastereoisomer that were suitable for X-ray analysis. The assignment of the absolute configuration of the major (1*R*)-enantiomer of **6a–h** in *Table 2* is based on the X-ray structure of (1*R*,2′*S*)-**8** (*Fig. 1*).

Scheme 5



A single recrystallization allowed enantiomeric enrichment of compounds **6a–h** (*Table 2*). The major (1*R*)-enantiomer of **6f** crystallized selectively with 98% ee (*Entry 6*). In all of the other cases, the racemic product crystallized first, leaving in solution the enantiomerically enriched (1*R*)-complex. An X-ray analysis of the

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[2]) Direct reaction of the aryllithium intermediate with MeC(O)Cl resulted in an intractable mixture of products.

[3]) Diastereoselectivity of reactions of *ortho*-lithiated arene complexes with aldehydes is generally poor, but good selectivities have been achieved in cases where the *ortho*-substituent is able to form a rigid transition state [9a] [16].

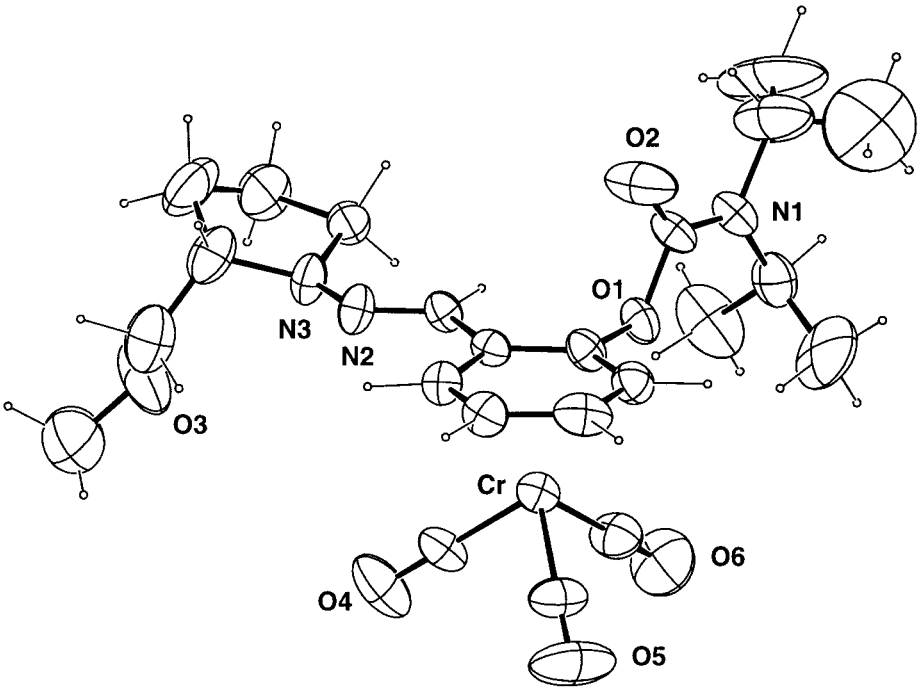

Fig. 1. *Perspective view of the absolute structure of (1*R,*2′*S*)*-**8**. Ellipsoids are represented with 40% probability.

Table 2. *Enantioselective Deprotonation of Complex* **3** *with Base* **5**/*Electrophile Addition*

Entry	RX	R		Product[a]) **6**	Recrystallization of **6**
				yield [%][a]) (ee [%][b])	yield [%][c]) (ee [%])
1	Me_3SiCl	Me_3Si	**6a**	86 (67)	44 (93)[d])
2	MeOC(O)Cl	MeOC(O)	**6b**	71 (72)[e])	41 (91)[d])
3	$Me_2NC(O)Cl$	$Me_2NC(O)$	**6c**	85 (68)	
4	MeI	Me	**6d**	93 (64)	46 (87)[d])
5	1) DMF; 2) H_2O	CHO	**6e**	93 (69)[f])	47 (95)[d])[f])
6	Ph_2PCl	Ph_2P	**6f**	81 (74)	56 (98)[g])
7	1) $CuI \cdot SMe_2$; 2) MeC(O)Cl[i])	MeC(O)	**6g**	70 (67)[h])	40 (92)
8	PhCHO[j])	PhCH(OH)	**6h**	85 (78)[k])	

[a]) Yields of **6** correspond to the isolated products after flash chromatography (FC). [b]) Enantiomeric-excess (ee) determination by HPLC (*Chiralcel OD* column, hexane/i-PrOH); the major enantiomer of **6** has (1*R*)-configuration, assigned by comparison with complex (1*R*,*2′S*)-**8**; obtained from **6e** (1*R*) and SAMP; (1*R*) refers to the chiral center bearing the carbamate substituent; [c]) Yield based on FC-purified **6**. [d]) ee of product **6** (1*R*) isolated from the mother liquor after a single crystallization from Et_2O/hexane of the less soluble racemic complex. [e]) 17% of **3** recovered. [f]) Determined by ^{1}H-NMR of the hydrazonechromium complex **8** .[g]) The major (1*R*)-enantiomer crystallized selectively. [h]) 22% of **3** recovered. [i]) The temperature was increased to $-20°$ after addition of the copper salt, then to room temperature after addition of MeC(O)Cl. [j]) Reaction performed at $-100°$. [k]) The diastereoisomer ratio of the corresponding alcohol was determined by ^{1}H-NMR (d.r. 3:1).

complexes *rac*-**6a** and (1*R*)-**6a** shows that stacking interactions occurring in the packing of *rac*-**6a** are the likely cause for this facility of enantiomer enrichment[4]) (*Fig. 2*).

The complexes *rac*-**6a** are associated in pairs through an inversion center. Thus, their aromatic rings are parallel, and the interplane distance of 3.4 Å is typical for a π-

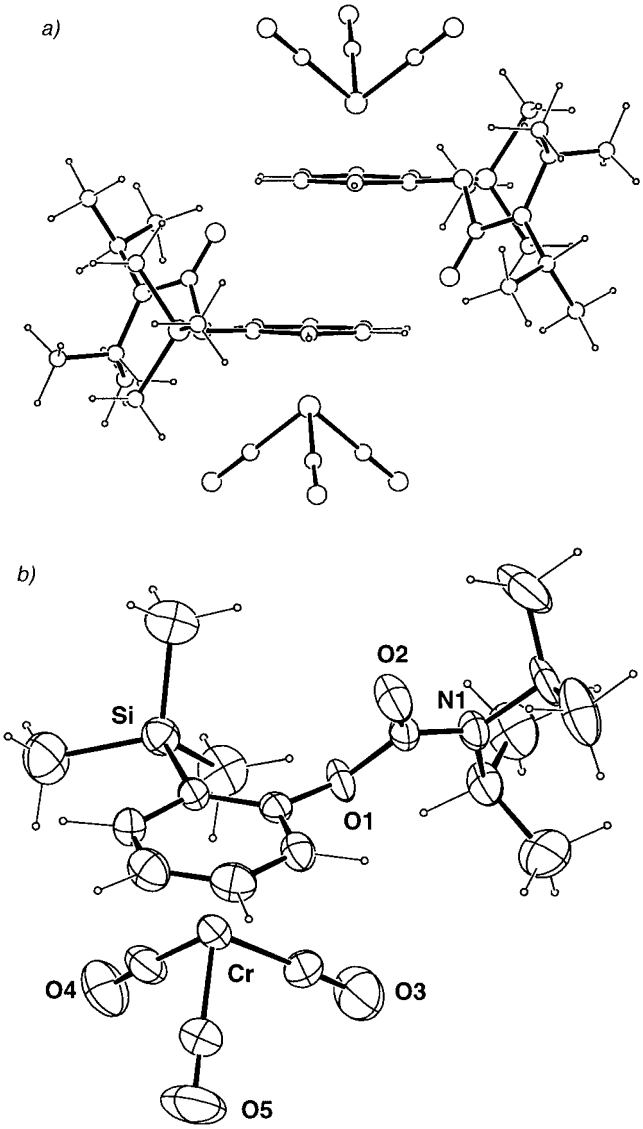

Fig. 2. *View of* a) *the crystal structure of* rac-**6a** *showing the stacking interactions of the molecules through a center of inversion*, b) *the absolute structure of (1*R*)-***6a***.* Ellipsoids represented with 40% probability.

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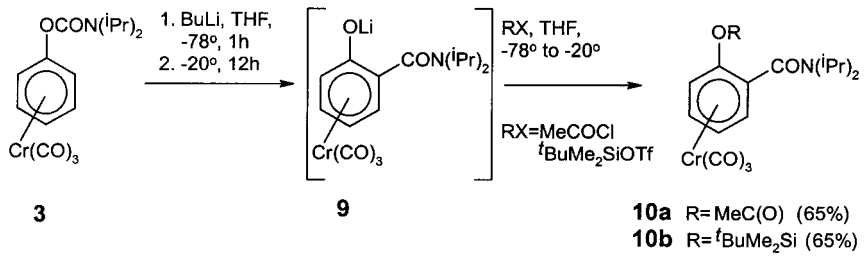
[4]) For a discussion of the density and stability of racemic crystals as compared with their chiral counterparts, see [18].

stacking interaction (*Fig. 2*). In the enantiomerically pure compound (1*R*)-**6a**, this stacking interaction does not occur, and the compound crystallizes less readily. As mentioned above, a converse sequence of selective crystallization was found for **6f**, and we note that both the size of the aryl substituent Ph_2P and the polarization in this complex differ from the other examples.

Anionic ortho-Fries *Rearrangement*. All of the reactions described above were carried out by adding the electrophile to the lithiated complex at low temperature. Raising the temperature after the lithiation step gave access to a different reaction pathway. Literature precedent in uncomplexed phenyl carbamates shows that *ortho*-lithiated aryl carbamates, on warming to room temperature, undergo an anionic *ortho-Fries* rearrangement [13] [19]. This 1,3-transposition of the carbamoyl group also occurred in complex **3** on warming the Li-intermediate (**3**-H)Li to $-20°$ (*Scheme 6*). Since tricarbonyl(η^6-phenol)chromium complexes are labile [20], and to prevent decomposition, the intermediate anionic phenolate **9** formed from **3** under these conditions was reacted directly with the reactive electrophiles acetyl chloride or (*tert*-butyl)dimethylsilyl triflate to give complexes **10a** and **10b**, respectively. In both cases, the compounds were isolated in 65% yield.

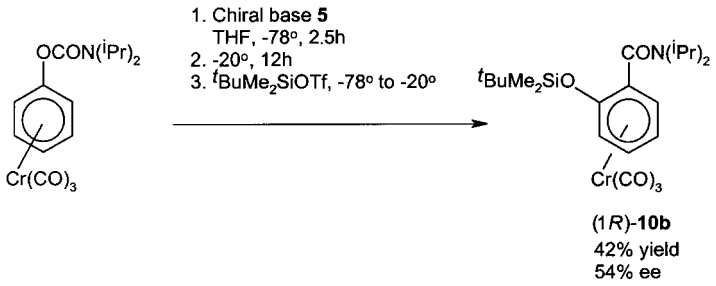
Scheme 6



An asymmetric approach of this transformation consists in carrying out the lithiation step with the chiral base **5** (*Scheme 7*). Following enantioselective lithiation, the reaction mixture was kept at $-20°$ for 12 h before adding (*t*-Bu)Me_2SiOTf which afforded **10b** in 42% yield and 54% ee. The lower enantioselectivity of the reaction leading to **10b** as compared with that of the examples shown in *Table 2* may be ascribed to the reaction conditions. The long reaction time (12 h) at $-20°$ may result in partial racemization before completion of the 1,3-carbamoyl transposition.

Conclusions. – The results reported here attest to the viability of the concept of a kinetically controlled enantioselective *ortho*-deprotonation of a tricarbonyl(phenyl carbamate)chromium complex to yield enantiomerically enriched complexes with planar chirality. The choice of the chiral amide base and the 'precoordination' of the base to the carbamate moiety are crucial for enantioselection and regiochemistry. Of particular significance is the finding that a single recrystallization allows the isolation of enantiomerically highly enriched products. The possibility of carrying out enantioselective anionic *ortho-Fries* rearrangements with this class of compounds is also demonstrated for the first time. In synthesis, planar-chiral complexes have already been

Scheme 7



demonstrated to transfer chirality very efficiently, and more examples of applications of this methodology will be forthcoming.

Experimental Part

1. *General*. Optically enriched secondary amines **4** and **5** were synthesized following literature procedures [23]. THF and Et_2O were dried and distilled from Na/benzophenone ketyl under N_2 before use, CH_2Cl_2 was freshly distilled from CaH_2 under N_2, and hexane was distilled before use. BuLi (*Fluka*, 1.6M) was titrated before use [24]. All other chemicals were purchased from *Aldrich* or *Fluka* and purified following standard literature procedures [25].

Reactions and manipulations involving organometallic compounds were carried out under purified N_2 using an inert gas/vacuum double manifold and standard *Schlenk* techniques [21]. Flash column chromatography (FC) [22]: in air; silica gel *Merck 60*. M.p.: *Büchi-510* apparatus; not corrected. IR Spectra: in NaCl cells; *Perkin-Elmer 1650* FT-IR spectrometer; in cm^{-1}. NMR Spectra: ^1H at 200 or 400 MHz and ^{13}C at 50.3 or 100.5 MHz; at r.t. *Varian-XL-200* or *Bruker-400-MHz* spectrometer as indicated; chemical shifts δ in ppm rel. to $SiMe_4$ (= 0 ppm) as internal standard and referenced to the proton signal of the residual solvent (C_6D_6; δ(H) 7.15 and δ(C) 128.0); *J* in Hz. Mass spectra: *Varian-CH4* or -SM1 spectrometer; *m/z* rel. (%). High-resolution (HR) mass spectra: *VG* anal. *7070E* instrument (data system 11250, resolution 7000). Elemental analyses were performed by *H. Eder*, Service de Microchimie, Institut de Chimie Pharmaceutique, Université de Genève.

2. *Tricarbonyl[diisopropylcarbamic Acid (η^6-Phenyl) Ester]chromium* (**3**). NaH (1.310 g, 55–65% in oil) was washed with hexane, dried *in vacuo*, and then suspended in THF (25 ml). The stirred mixture was cooled to $-10°$, and a soln. of phenol (2.562 g, 27.23 mmol) in THF (17 ml) was added dropwise. Stirring was continued at rt for 30 min, followed by cooling to $-10°$, treatment with diisopropylcarbamic chloride (5.548 g, 33.9 mmol), and heating to reflux for 16 h. After cooling to 0°, H_2O was added until the inorg. salts dissolved. The soln. was extracted with Et_2O (3×15 ml), the combined org. layer dried ($MgSO_4$) and evaporated, the yellow oil bulb-to-bulb distilled (110°/0.25 Torr) and the distillate crystallized in hexane at $-30°$: 5.458 g (95%) of *phenyl diisopropylcarbamate* (**1**) [26]. Colorless oily solid. IR ($CHCl_3$): 3009, 2974, 2936, 1697, 1439, 1370, 1320, 1300, 1201, 1152. ^1H-NMR ($CDCl_3$, 200 MHz): 7.41–7.07 (*m*, 5 arom. H); 4.25–3.75 (br. *s*, 2 H), 1.31 (br. *d*, $J = 6.6$, 4 Me). MS: 221 (2, M^+) (2), 206(1), 164(1), 128(77), 94(100), 86(100), 77(14). HR-MS: 221.1416 (M^+, $C_{13}H_{19}O_2N^+$; calc. 221.1416).

A soln. of **1** (4.810 g, 22.8 mmol) and tricarbonyl(η^6-naphthalene)chromium (**2**; 3.000 g, 11.4 mmol) in Et_2O (40 ml) and THF (4 ml) was degassed by three freeze/pump/thaw cycles and then heated in a *Carius* tube to 65° for 84 h [27]. Volatiles were removed *in vacuo* and purification by FC (silica gel, hexane/Et_2O 4:1) afforded 3.660 g (10.25 mmol, 90%) of **3**. Yellow solid. M.p. 114–116°. IR ($CHCl_3$): 3020, 2975, 1975, 1901, 1712, 1435, 1317, 1150, 1040. ^1H-NMR (C_6D_6, 200 MHz): 4.81 (*d*, $J = 6.4$, 2 H_o); 4.45 (*t*, $J = 6.4$, 2 H_m); 3.86 (*t*, $J = 6.4$, H_p); 3.82–3.60 (*m*, 2 H), 1.06 (br. *d*, $J = 6.8$, 4 Me). MS: 357 (2, M^+), 301(20), 273(100), 145(36), 128(69), 94(33), 86(100), 52(72). Anal. calc. for $C_{16}H_{19}CrNO_5$ (357.33): C 53.78, H 5.36; found: C 53.45, H 5.40.

3. *General Procedure for Lithiation/Electrophilic Addition to* **3**. Complex **3** (0.5–1 mmol) was added at $-78°$ to a THF soln. (7 ml) of chiral base (1.15 equiv.), freshly prepared from the chiral secondary amine and

BuLi (−78 → −10°, 1 h) [17]. The mixture was stirred at −78° for 2.5 h, then treated with the electrophile (3 equiv.), and kept at −78° until starting material was no longer detected (TLC). Volatiles were removed and the composition of the crude mixture was determined by ^{1}H-NMR. Product purification was by FC (silica gel, hexane/Et_2O).

Lithiation with **4** (1.15 equiv.), *Addition of Me_3SiCl.* According to the *General Procedure*, **3** (0.232 g, 0.649 mmol) was added to the soln. of **4** (0.746 mmol, 1.15 equiv.) and stirred at −78° for 2.5 h. Addition of Me_3SiCl (1.95 mmol, 3 equiv.) resulted within minutes in complete reaction and afforded a crude product in which only **6a** (R = Me_3Si) could be detected by ^{1}H-NMR. FC (SiO_2, hexane/Et_2O 7:3) afforded 0.231 g (83%) of **6a**. HPLC (*Chiralcel OD*, hexane/i-PrOH 99:1; 0.6 ml/min, t_R 19 and 24 min) indicated an ee of 2%.

Lithiation with **4** (1.73 equiv.), *Addition of Me_3SiCl.* An analoguous reaction with **3** (0.171 g, 0.479 mmol), **4** (0.829 mmol, 1.73 equiv.), and Me_3SiCl (1.44 mmol, 3 equiv.) gave crude **6a**/**7** 1:1 (^{1}H-NMR). FC afforded 90 mg (44%) of **6a** and 110 mg (46%) of **7**. The isolated **6a** had an ee of 67% (HPLC; major enantiomer (1*R*)-**6a**).

4. *Lithiation with* **4** *using* in situ *Quench Conditions.* A soln. of **3** (0.204 g, 0.571 mmol) in THF (2 ml), cooled to −78° was added to a soln. of **4** (0.657 mmol, 1.15 equiv.) and Me_3SiCl (1.71 mmol, 3 equiv.) in THF (7 ml). The mixture was stirred at −78° for 1 h and then evaporated while warming up: crude **6a**/**7** 92:8 (^{1}H-NMR). FC afforded 0.136 g (56%) of **6a** and 11.5 mg (4%) of **7**; some **3** (36.7 mg, 18%) was also recovered. An ee of 39% was determined for **6a** (HPLC, major enantiomer (1*S*)-**6a**).

5. *Lithiation of* rac-**6a** *with* **4** (0.58 equiv.) *Using* in situ *Quench Conditions.* Complex *rac*-**6a** (0.209 g, 0.487 mmol) was added at −78° to a soln. of **4** (0.282 mmol, 0.58 equiv.) and Me_3SiCl (1.46 mmol, 3 equiv.) in THF (7 ml). The mixture was stirred at −78° for 1 h and then evaporated while warming up: crude **6a**/**7** 61:39 (^{1}H-NMR). FC afforded 0.115 g (55%) of **6a** and 86.1 mg (35%) of **7**. An ee of 7% was determined for **6a** (HPLC; major enantiomer (1*R*)-**6a**).

6. *Lithiation with* **4** (2.3 equiv.), *Addition of D_2O.* According to the *General Procedure*, **3** (0.270 g, 0.756 mmol) was added to the soln. of **4** (1.74 mmol, 2.3 equiv.) and stirred at −78° for 2.5 h. Treatment with D_2O (2.27 mmol, 3 equiv.) for 30 min gave a crude mixture containing 71% (by ^{1}H-NMR) of *tricarbonyl*[*diisopropylcarbamic acid (η^6-[2,6-D_2]phenyl) ester]chromium* (D_2-**3**). ^{1}H-NMR (C_6D_6, 200 MHz): 4.81 (*d*, *J* = 6.4, 0.58 H, 2 H_o (29%)); 4.45 (*m*, 2 H, 2 H_m (100%)); 3.86 (*t*, *J* = 6.4, 1 H, H_p (100%)); 3.82–3.6 (*m*, 2 H), 1.06 (br. *d*, *J* = 6.8, 12 H, 4 Me). MS: 303 (16, $[M-2\ CO]^+$ 302(9), 301(2), 275(84), 274(48), 273(13), 147(22), 146(11), 145(3), 128(27), 86(100), 52(53).

7. *Lithiation with* **5** (1.15 equiv.), *Addition of Me_3SiCl.* According to the *General Procedure*, with **3** (0.164 g, 0.460 mmol), THF soln. of **5** (0.529 mmol, 1.15 equiv.), and Me_3SiCl (1.38 mmol, 3 equiv.; 10 min): crude **6a** only (^{1}H-NMR). FC (hexane/Et_2O 7:3) afforded 0.164 g (83%) of **6a**. An ee of 67% was determined for **6a** (HPLC; major enantiomer (1*R*)-**6a**). Crystallization from Et_2O/hexane gave 29% (based on **3**) of **6a** with an ee of 3%. From the mother liquor, 44% (based on **3**) of (1*R*)-**6a** with an ee of 93% were isolated.

Lithiation with **5** *Using* in situ *Quench Conditions.* Complex **3** (0.157 g, 0.440 mmol) was added at −78° to a soln. of **5** (0.506 mmol, 1.15 equiv.) and Me_3SiCl (1.32 mmol, 3 equiv.) in THF (7 ml). The mixture was stirred at −78° for 1 h and then evaporated while warming up: crude **6a**/**7** 92:8. FC yielded 0.147 g (78%) of **6a** and 16.0 mg (7%) of **7**; some starting material **3** (15.0 mg, 9%) was also recovered. An ee of 64% was determined for **6a** (HPLC; major enantiomer (1*R*)-**6a**).

*Tricarbonyl[(1*R*,2*S*)-diisopropylcarbamic Acid (1,2,3,4,5,6-η)-2-(trimethylsilyl)phenyl Ester]chromium* ((1*R*)-**6a**): 93% ee. M.p. 122–123°. $[\alpha]_D^{20} = -104$ (CH_2Cl_2, *c* = 0.20). IR ($CHCl_3$): 3053, 2973, 1969, 1892, 1722, 1314, 1274, 1189, 845. ^{1}H-NMR (C_6D_6, 200 MHz): 5.65 (*t*, *J* = 6.5, 1 arom. H); 5.54 (*d*, *J* = 6.5, 1 arom. H); 5.26 (*d*, *J* = 6.5, 1 arom. H); 4.88 (*t*, *J* = 6.5, 1 arom. H); 4.48–4.26 (*m*, 1 H); 3.77–3.50 (*m*, 1 H); 1.42–1.13 (*m*, 4 Me); 0.34 (*s*, Me_3Si). MS: 429 (3, M^+), 373(12), 345(100), 187(15), 128(26), 86(38), 52(18). Anal. calc. for $C_{19}H_{27}CrNO_5Si$ (429.51): C 53.13, H 6.34; found: C 52.39, H 6.51.

Tricarbonyl[diisopropylcarbamic Acid (1,2,3,4,5,6-η)-2,6-bis(trimethylsilyl)phenyl Ester]chromium (**7**): M.p. 189–190°. IR (CH_2Cl_2): 3054, 2971, 2899, 1966, 1892, 1715, 1433, 1372, 1293, 1252, 1172, 1128, 1040. ^{1}H-NMR (C_6D_6, 200 MHz): 5.22 (*d*, *J* = 6.2, 2 arom. H); 4.63–4.47 (*m*, 1 H); 4.14 (*t*, *J* = 6.2, 1 arom. H); 3.05–2.90 (*m*, 1 H); 1.31 (*d*, *J* = 6.7, 2 Me); 0.90 (*d*, *J* = 6.7, 2 Me); 0.35 (*s*, 2 $SiMe_3$). MS: 445 (1, $[M-2\ CO]^+$), 417(14), 289(2), 151(5), 128(58), 86(100), 73(19), 52(73).

8. *Lithiation with* **5** (1.15 equiv.), *Addition of MeOC(O)Cl.* According to the *General Procedure*, with **6** (0.714 g, 2.0 mmol), **5** (2.3 mmol, 1.15 equiv.), and MeOC(O)Cl (6.0 mmol, 3 equiv.; 15 min). FC (hexane/Et_2O 1:1) yielded **6b** (0.593 g, 71%) and 25 mg of an unidentified product mixture. The isolated **6b** had 72% ee (HPLC, *Chiralcel OD*, hexane/i-PrOH 95:5, flow rate 0.8 ml/min): t_R 40 (minor enantiomer (1*S*)-**6b**) and 45.5 min (major enantiomer (1*R*)-**6b**). Crystallization from Et_2O/hexane gave 25% (based on **3**) of **6b** of 15% ee. From the mother liquor, *tricarbonyl[(1*S*,2*R*)-(1,2,3,4,5,6-η)-[(diisopropylcarbamoyl)oxy]benzoic acid*

methyl ester}chromium[5]) (1*R*)-**6b**. 0.347 g, 41% based on **3** with an ee of 91% was isolated. M.p. 113–115°. $[\alpha]_D^{20} = +82$ (CH_2Cl_2, $c = 0.20$). IR ($CHCl_3$): 3032, 2975, 2878, 1959, 1918, 1720, 1433, 1376, 1319, 1196. ^{1}H-NMR (C_6D_6, 200 MHz): 5.74 (*dd*, *J* = 1.3, 6.6, 1 arom. H); 4.64–4.49 (*m*, 2 arom. H); 4.17–4.0 (*m*, 1 H); 3.89 (*ddd*, *J* = 1.4, 5.5, 6.6, 1 arom. H); 3.74–3.57 (*m*, 1 H); 3.32 (*s*, Me); 1.27–1.1 (*m*, 4 Me). MS: 387 (1, $[M-CO]^+$); 359(13), 331(34), 273(4), 203(26), 173(42), 151(74), 128(25), 105(6), 86(91), 70(10), 52(100). Anal. calc. for $C_{18}H_{21}CrNO_7$ (415.36): C 52.05, H 5.10, N 3.37; found: C 52.06, H 5.14, N 3.52.

9. *Lithiation with* **5** (1.15 equiv.), *Addition of Me2NC(O)Cl*. The *General Procedure* was applied (0.57 mmol of **3**) with addition of $Me_2NC(O)Cl$ (3 equiv.) after the enantioselecive lithiation: **6c** (0.207 g, 85%). The ee was 68% (HPLC, *Chiralcel OD*, hexane/i-PrOH 9:1, flow rate 0.8 ml/min): t_R 27 (minor enantiomer (1*S*)-**6c**) and 33.5 min (major enantiomer (1*R*)-**6c**). Crystallization from Et_2O/hexane gave **6c** (70% based on **3**) of 54% ee. From the mother liquor *tricarbonyl[(1*R,2S*)-diisopropylcarbamic acid (1,2,3,4,5,6-η)-2-(dimethylcarbamoyl)-phenyl ester]chromium* ((1*R*)-**6c**) with an ee of 80% was isolated. M.p. 128° (dec.). $[\alpha]_D^{20} = -9.6$ (CH_2Cl_2, $c = 0.22$). IR ($CHCl_3$): 3036, 2969, 2932, 2878, 1982, 1913, 1715, 1649, 1394, 1317, 1242, 1198, 1149. ^{1}H-NMR (C_6D_6, 200 MHz): 4.92 (*d*, *J* = 5.9, 1 arom. H); 4.78 (*d*, *J* = 5.9, 1 arom. H); 4.46–4.58 (br. *t*, *J* = 5.9, 1 arom. H); 3.99–4.15 (*m*, 1 H); 3.86–3.98 (*m*, 1 arom. H); 3.44–3.60 (*m*, 1 H); 2.45–2.8 (*m*, 6 H); 1.04–1.21 (*m*, 4 Me). MS: 372 (14, $[M-2\,CO]^+$), 344(46), 314(10), 273(19), 216(25), 201(57), 173(55), 128(30), 86(71), 52(100). Anal. calc. for $C_{19}H_{24}CrN_2O_6$ (428.40): C 53.27, H 5.65; found: C 53.07, H 5.71.

10. *Lithiation with* **5** (1.15 equiv.), *Addition of MeI*. According to the *General Procedure* with 0.481 mmol of **3**. Treatment of the lithium intermediate with MeI (1.44 mmol, 3 equiv.) gave **6d** (0.166 g, 93%). The ee was 64% (HPLC, *Chiralcel OD*, hexane/i-PrOH 97:3, flow rate 0.8 ml/min): t_R 35 (minor enantiomer (1*S*)-**6d**) and 42 min (major enantiomer (1*R*)-**6d**). Two crystallizations from Et_2O/hexane yielded, from the mother liquor; *tricarbonyl[(1*R,2S*)-diisopropylcarbamic acid (1,2,3,4,5,6-η)-2-methylphenyl ester]chromium* ((1*R*)-**6d**; 46% based on **3**) with 87% ee. M.p. 101–102°. $[\alpha]_D^{20} = -40$ (CH_2Cl_2, $c = 0.23$). IR ($CHCl_3$): 3037, 2975, 2932, 2878, 1970, 1894, 1711, 1437, 1377, 1317, 1231, 1149, 1040. ^{1}H-NMR (C_6D_6, 200 MHz): 4.93 (*d*, *J* = 6.3, 1 arom. H); 4.55 (*d*, *J* = 6.3, 1 arom. H); 4.43 (*t*, *J* = 6.3, 1 arom. H); 4.15 (*t*, *J* = 6.3, 1 arom. H); 3.88–3.62 (*m*, 2 H); 1.9 (*s*, 3 H); 1.2–0.9 (*m*, 4 Me). MS: 371 (3, M^+), 315(14), 287(100), 159(25), 128(18), 108(12), 86(56), 52(67). Anal. calc. for $C_{17}H_{21}CrNO_5$ (371.35): C 54.98, H 5.70; found: C 54.96, H 5.67.

11. *Lithiation with* **5** (1.15 equiv.), *Addition of Ph2PCl*. According to the *General Procedure*, with **3** (0.50 mmol, and Ph_2PCl (1.50 mmol): **6f** (0.220 g, 81%) with an ee of 74% (HPLC (*Chiralcel OD*, hexane/i-PrOH 97:3; flow rate1 ml/min): t_R 15 (minor enantiomer (1*S*)-**6f**) and 39 min (major enantiomer (1*R*)-**6f**)). Crystallization from Et_2O/hexane gave *tricarbonyl[(1*R,2S*)-diisopropylcarbamic acid (1,2,3,4,5,6-η)-2-(diphenylphosphino)phenyl ester]chromium* ((1*R*)-**6f**; 56% based on **3**) with an ee of 98%. M.p. 126–127°. $[\alpha]_D^{20} = +83$ (CH_2Cl_2, $c = 0.22$). IR ($CHCl_3$): 2953, 2930, 2344, 1974, 1904, 1720, 1314, 1215, 1186. ^{1}H-NMR (C_6D_6, 200 MHz): 7.65–7.5 (*m*, 2 H); 7.42–7.25 (*m*, 2 H); 7.25–7.0 (*m*, 6 H); 5.15 (*dd*, *J* = 3.2, 6.2, 1 arom. H); 4.7–4.6 (*m*, 2 arom. H); 4.23 (*m*, 1 H); 3.82 (*t*, *J* = 6.2, 1 arom. H); 3.18 (*m*, 1 H); 1.2–0.75 (*m*, 4 Me). MS: 485 (15, M^+), 457(92), 405(55), 305(37), 278(45), 128(43), 86(100), 52(30). HR-MS: 457.1277 ($[M-3\,CO]^+$, $C_{25}H_{28}CrNO_2P^+$; calc. 457.1263).

12. *Lithiation with* **5** (1.15 equiv.), *Addition of MeC(O)Cl*. According to *General Procedure*, **3** (0.176 g, 0.50 mmol) was lithiated with **5** followed by addition of $CuBr \cdot SMe_2$ (0.120 g, 0.584 mmol). The mixture was warmed to −20°, stirred for 1 h, and then treated with MeC(O)Cl (1.50 mmol, 3 equiv.). Warming up to r.t. overnight and workup gave **6g** (0.140 g, 70%) and recovered **3** (40 mg, 22%). The ee of **6g** was 67% (HPLC (*Chiralcel OD*, hexane/i-PrOH 95:5 1 ml/min): t_R 23 (minor enantiomer (1*S*)-**6g**) and 27 min (major enantiomer (1*R*)-**6g**). Crystallization from Et_2O/hexane gave **6g** (50 mg, 25% based on **3**) with an ee of 20%. From the mother liquor, *tricarbonyl[(1*R,2S*)-diisopropylcarbamic acid (1,2,3,4,5,6-η)-2-acetylphenyl ester]chromium* ((1*R*)-**6g**; 80 mg, 40% based on **3**) with an ee of 92% was isolated. M.p. 114–115°. $[\alpha]_D^{20} = +136$ (CH_2Cl_2, $c = 0.22$). IR ($CHCl_3$): 2960, 2919, 2872, 1986, 1919, 1723, 1687, 1316, 1270, 1185. ^{1}H-NMR (C_6D_6, 200 MHz): 5.41 (*dd*, *J* = 1.3, 6.6, 1 arom. H); 4.64 (*dt*, *J* = 1.3, 6.6, 1 arom. H); 4.52 (*dd*, *J* = 1.1, 6.6, 1 arom H); 4.06 (*m*, 1 H); 3.90 (*dt*, *J* = 1.1, 6.6, 1 arom. H); 3.50 (*m*, 1 H), 2.11 (*s*, 3 H); 1.3–1.0 (*m*, 4 Me). MS: 343 (28, $[M-2\,CO]^+$), 315(100), 272(13), 187(70), 151(86), 86(71), 52(75). HR-MS: 315.0903 ($[M-3\,CO]^+$, $C_{15}H_{21}O_3CrN^+$; calc. 315.0926).

13. *Lithiation with* **5** (1.15 equiv.), *Addition of PhCHO*. According to *General Procedure*, **3** (0.176 g, 0.50 mmol) was lithiated (−100°, 2.5 h) and then treated with PhCHO (1.50 mmol, 3 equiv.): **6h** as a 3:1

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[5]) The numbering of the benzene moiety differs from to the one used in the text.

diastereoisomer mixture. FC yielded 50 mg (21%) of the minor diastereoisomer of **6h** and 150 mg (64%) of the major diastereoisomer of **6h**.

An ee of 78% was determined for both diastereoisomers of **6h** by HPLC (*Chiralcel OD*, hexane/i-PrOH 95:5; flow rate 1 ml/min); t_R(minor diastereoisomer) 16 (minor (1*S*)-enantiomer) and 22 min (major (1*R*)-enantiomer); t_R(major diastereoisomer) 15 (minor (1*S*)-enantiomer) and 37 min (major (1*R*)-enantiomer).

*Tricarbonyl[(1*R*,2*S*)-diisopropylcarbamic Acid (η-1,2,3,4,5,6)-2-[Hydroxy(phenyl)methyl]phenyl Ester]-chromium* ((1*R*)-**6h**; minor diastereoisomer): 78% ee. M.p. 113–115° (dec). $[\alpha]_D^{20} = -81$ (CH_2Cl_2, $c = 0.18$). IR ($CHCl_3$): 3697, 3029, 2974, 2907, 1973, 1901, 1724, 1432, 1372, 1315, 1210, 1148. ^{1}H-NMR (C_6D_6, 400 MHz): 7.32 (*d*, *J* = 7.2, 2 H); 7.12 (*t*, *J* = 7.2, 2 H); 7.03 (*t*, *J* = 7.2, 1 H); 5.68 (br. *d*, *J* = 4.4, PhC*H*(OH)); 5.59 (*d*, *J* = 6.4, 1 arom. H); 4.92 (*d*, *J* = 6.4, 1 arom. H); 4.59 (*t*, *J* = 6.4, 1 arom. H), 4.08 (*t*, *J* = 6.4, 1 arom. H); 3.86 (*m*, 1 H); 3.42 (*m*, 1 H); 2.10 (br. *s*, OH); 1.2–0.8 (*m*, 4 Me). MS: 407 (12, $[M-2\,CO]^+$), 379 (84), 234 (51), 181 (39), 165 (22), 151 (31), 128 (46), 86 (100), 52 (70). HR-MS: 379.1224 ($[M-3\,CO]^+$, $C_{20}H_{25}CrNO_3^+$; calc. 379.1239).

*Major Diastereoisomer of (1*R*)-***6h***:* 78% ee. M.p. 133–135° (dec.). $[\alpha]_D^{20} = +77$ (CH_2Cl_2, $c = 0.19$). IR ($CHCl_3$): 3444, 3018, 2965, 2918, 1978, 1908, 1695, 1434, 1373, 1297, 1220, 1150. ^{1}H-NMR (C_6D_6, 200 MHz): 7.86 (*d*, *J* = 7.2, 2 H); 7.31 (*t*, *J* = 7.2, 2 H); 7.25–7.15 (*m*, 1 H), 5.93 (br. *s*, 1 H); 4.94 (*d*, *J* = 6.5, 1 arom. H); 4.6–4.42 (*m*, 3 H); 3.9–3.55 (*m*, 3 H); 1.2–0.8 (*m*, 4 Me). MS: 407 (7, $[M-2\,CO]^+$), 379 (56), 234 (27), 181 (70), 165 (14), 151 (15), 128 (84), 86 (100), 52 (36). HR-MS: 379.1224 ($[M-3CO]^+$, $C_{20}H_{25}CrNO_3^+$; calc. 379.1239).

14. *Lithiation with* **5** (1.15 equiv.), *Addition of DMF* ($CH(O)NMe_2$). According to the *General Procedure*, **3** (0.207 g, 0.579 mmol) was lithiated and then treated with DMF (1.74 mmol, 3 equiv.) and, after 30 min, with N_2-sat. H_2O (5 ml). After evaporation, the residue was dissolved in Et_2O (7 ml) and the soln. washed with H_2O (5 ml) and evaporated. FC (hexane/Et_2O 1:1) afforded **6e** (0.208 g, 93%). An ee of 69% was determined for **6e** by derivatization with (*S*)-2-(methoxymethyl)pyrrolidin-1-amine (SAMP) yielding **8** (*vide infra*). The major enantiomer corresponded to (1*R*)-**6e**. Crystallization from Et_2O/hexane gave **6e** (46% based on **3**) of 38% ee. From the mother liquor, *tricarbonyl[(1*R*,2*S*)-diisopropylcarbamic acid (1,2,3,4,5,6-η)-2-formylphenyl ester]-chromium* ((1*R*)-**6e**; 47% based on **3**) with an ee of 95% was isolated. M.p. 103–104°. $[\alpha]_D^{20} = +497$ (CH_2Cl_2, $c = 0.21$). IR ($CHCl_3$): 3039, 2975, 2932, 2932, 2878, 1991, 1926, 1719, 1520, 1424, 1374, 1313, 1253, 1229, 1147, 1039. ^{1}H-NMR (C_6D_6, 400 MHz): 9.67 (*s*, CHO); 5.56 (*d*, *J* = 6.4, 1 H); 4.52–4.65 (*m*, 2 H); 3.71–3.9 (*m*, 2 H); 3.48–3.66 (*m*, 1 H); 0.9–1.25 (*m*, 4 Me). MS: 329 (9, $[M-2\,CO]^+$), 301 (22), 258 (2), 242 (3), 173 (54), 151 (48), 128 (66), 86 (90), 52 (100). Anal. calc. for $C_{17}H_{19}CrNO_6$ (385.34): C 52.99, H 4.97; found: C 52.94, H 5.01.

15. *Derivatization of (1*R*)-***6e*** with (*S*)-2-(Methoxymethyl)pyrrolidin-1-amine* (SAMP). A soln. of (1*R*)-**6e** (84.7 mg, 0.220 mmol) and SAMP (0.045 ml, 0.338 mmol, 1.5 equiv.) in Et_2O (5 ml) was stirred overnight at r.t. in a sealed tube over 4-Å molecular sieves. The soln. was diluted with Et_2O, filtered over *Celite*, and evaporated. (^{1}H-NMR: complete conversion). The diastereoisomer ratio of the obtained crude hydrazone **8** was determined by the ^{1}H-NMR (C_6D_6) integral ratio of the N–N = C*H*–C(2) signals of the two diastereoisomers (*s* at 6.87 and 6.75 ppm): d.r. 84.5 : 15.5. FC (silica gel, hexane/Et_2O 1:1) afforded **8** (0.089 g, 82%) as diastereoisomer mixture. The major diastereoisomer *tricarbonyl[(1*R*,2*S*)-diisopropylcarbamic acid (1,2,3,4,5,6-η)-2-{[[(2*S*)-2-(methoxymethyl)pyrrolidin-1-yl]imino]methyl}phenyl ester]chromium* ((1*R*,2′*S*)-**8**) was then obtained by recrystallization from hexane/Et_2O: d.r. ≥ 96%. The crystals were used for X-ray analysis (see below). M.p. 125–127° (dec.). $[\alpha]_D^{20} = +676$ (CH_2Cl_2, $c = 0.16$). IR (CH_2Cl_2): 3054, 2975, 2932, 2834, 1965, 1980, 1714, 1556, 1414, 1314, 1203, 1148, 1040. ^{1}H-NMR (C_6D_6, 400 MHz): 6.79 (*s*, N–N = C*H*–C(2)); 6.27 (*d*, *J* = 6.1, 1 H); 5.03 (*d*, *J* = 6.1, 1 H); 4.57 (*t*, *J* = 6.1, 1 H); 4.36 (*t*, *J* = 6.1, 1 H); 3.93–3.82 (*m*, 1 H); 3.82–3.73 (*m*, 1 H); 3.73–3.67 (*m*, 1 H); 3.63 (*dd*, *J* = 3.3, 9.2, 1 H); 3.47 (*dd*, *J* = 6.6, 9.2, 1 H); 3.23 (*s*, MeO); 3.05–2.97 (*m*, 1 H); 2.7–2.6 (*m*, 1 H); 1.8–1.6 (*m*, 3 H); 1.45–1.35 (*m*, 1 H); 1.25–1.05 (*m*, 4 Me). MS: 413 (8, $[M-3\,CO]^+$), 361 (5), 316 (29), 189 (15), 128 (47), 86 (100), 70 (67). HR-MS: 413.1776 ($[M-3\,CO]^+$, $C_{20}H_{31}CrN_3O_3^+$; calc. 413.1771).

16. *X-Ray Structure Analyses.* Yellow crystals of (1*R*,2′*S*)-**8**, *rac*-**6a** and (1*R*)-**6a** suitable for X-ray diffraction were obtained by crystallization from Et_2O/ether solns. Cell dimensions and intensities were measured at r.t. on a *Nonius-CAD4* diffractometer with graphite-monochromated CuK_α radiation (λ 1.5418 Å), ω-2θ scans, scan width 1.2° + 0.25 tg θ, and scan speed 0.02–0.14°/s. Reference reflections measured every 100 reflections showed no variation. Data were corrected for *Lorentz* and polarization effects and for absorption by anal. integration [28]. The structures were solved by direct methods using MULTAN 87 [29], all other calculations used XTAL [30] system and ORTEP [31] programs. The absolute structure parameter *x* [32] was refined for (1*R*,2′*S*)-**8** and (1*R*)-**6a**. All coordinates of the H-atoms were calculated. For (1*R*,2′*S*)-**8**, the Me groups of one isopropyl substituent showed large atomic displacement parameters, and all attempts to split the

atomic sites failed. In (1*R*)-**6a**, both molecules of the asymmetric unit showed the same configuration and slightly differed in the Me_3Si and $(i\text{-}Pr)_2$ substituent orientations. Relevant crystal data, intensity measurements, and structure refinements are given in *Table 3*. Crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallographic Data Base* (deposition No. 103235, 103236, and 103237 for (1*R*,2′*S*)-**8**, (1*R*)-**6a**, and *rac*-**6a**, resp.). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. + 44 (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 3. *Crystal Data, Intensity Measurement, and Structure Refinement for (1*R,*2*′S*)*-**8**, rac-**6a**, *and (1*R*)*-**6a***

	(1*R*,2′*S*)-**8**	*rac*-**6a**	(1*R*)-**6a**
Formula	$[Cr(C_{20}H_{31}N_3O_3)(CO)_3]$	$[Cr(C_{16}H_{27}NO_2Si)(CO)_3]$	$[Cr(C_{16}H_{27}NO_2Si)(CO)_3]$
M_r	497.5	429.5	429.5
Crystal system	othorhombic	monoclinic	monoclinic
Space group	$P\,2_12_12$	$P\,2_1/c$	$P\,2_1$
a [Å]	19.7375(7)	11.868(3)	11.485(3)
b [Å]	20.358(1)	16.081(2)	12.855(7)
c [Å]	6.4054(4)	13.224(1)	15.350(5)
β [°]	90	116.029(7)	94.03(1)
V [Å^3]	2573.8(2)	2267.8(7)	2261(2)
Z	4	4	4
$F(000)$	1048	904	904
D_c [gr·cm^{-3}]	1.284	1.258[a])	1.262[a)]
β(Cu$K\alpha$) [mm^{-1}]	3.999	4.834	4.899
Transmission coeff.	0.4652 – 0.7053	0.3056 – 0.5737	0.1954 – 0.5635
$((\sin\theta)/\lambda)_{max}$ [Å^{-1}]	0.56	0.54	0.54
Temperature [K]	298	298	298
hkl	$+h, +k, +l$[b])	$\pm h, +k, +l$	$\pm h, +k, +l$[b)]
No. measured refl.	4507	3328	6628
No. observed refl.	3172	2247	5297
Criterion for observed	$\lvert F_o\rvert > 4\sigma(F_o)$	$\lvert F_o\rvert > 4\sigma(F_o)$	$\lvert F_o\rvert > 4\sigma(F_o)$
Refinement (on F)	Full-matrix	Full-matrix	Full-matrix
No. parameters	295	263	489
Weighting scheme	$\omega = 1/\sigma^2(F_o)$	$\omega = 1/\sigma^2(F_o)$	$\omega = 1/[\sigma^2(F_o) + 10^{-4}(F_o)^2]$
Max. and average Δ/σ	$0.14\cdot10^{-3}$, $0.14\cdot10^{-4}$	$0.12\cdot10^{-3}$, $0.14\cdot10^{-4}$	$0.14\cdot10^{-3}$, $0.14\cdot10^{-4}$
Max. and min. $\Delta\varrho$ (e·Å^{-3})	0.44, −0.47	0.57, −0.59	0.27, −0.28
Absolute structure x [32]	0.00(1)	–	0.00(1)
R[c]), ωR[d])	0.064, 0.038	0.078, 0.045	0.045, 0.042

[a]) It should be noted that for **6a**, *Wallach*'s rule fails ($D_{(1R)\text{-}6a} > D_{rac\text{-}6a}$) and Δ (%) = −0.3 [18]. [b]) And all *anti*-reflections. [c]) $R = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$. [d]) $\omega R = [\Sigma\,(\omega|F_o| - |F_c|)^2/\Sigma\,\omega|Fo|^2]^{1/2}$.

17. *Anionic* ortho-Fries *Rearrangement Applied to* **3:** *General Procedure* [13]. BuLi in hexane (1.6M 1.1 equiv.) was added dropwise at −78° to a soln. of **3** (0.5–1 mmol) in THF (7 ml). The mixture was stirred at −78° for 1 h, then warmed to −20° within 2 h, and stirred at −20° for an additional 12 h. The soln. was cooled to −78° and the electrophile (1.5 equiv.) added. The mixture was warmed to −20° within 3 h, stirred at −20° for an additional 2 h, and then evaporated while warming up. The crude product was purified by FC (silica gel, hexane/Et_2O).

Anionic ortho-Fries *Rearrangement/Acetyl-Chloride Addition*. According to the *General Procedure*, with **3** (0.370 g, 1.04 mmol) and then MeC(O)Cl (1.56 mmol, 1.5 equiv.). FC (hexane/Et_2O 6:4) yielded *[acetic acid (1,2,3,4,5,6-η)-2-(diisopropylcarbamoyl)phenyl ester]tricarbonylchromium* (**10a**; 0.270 g, 65%). M.p. 110–112°. IR ($CHCl_3$): 3019, 2971, 2921, 1985, 1915, 1771, 1640, 1438, 1372, 1331, 1206. ^{1}H-NMR (C_6D_6, 200 MHz): 4.95 (*dd*, *J* = 1.1, 6.0, 1 arom. H); 4.63 (*dd*, *J* = 1.1, 6.0, 1 arom. H); 4.46 (*dt*, *J* = 1.1, 6.0, 1 arom. H); 3.93 (*dt*, *J* = 1.1, 6.0, 1 arom. H); 4.05–3.6 (*m*, 1 H); 3.15–2.75 (*m*, 1 H); 1.65 (*s*, Me); 1.5–1.25 (*m*, 2 Me); 1.0–0.6 (*m*, 2

Me). MS: 343 (10, $[M-2\ CO]^+$), 315 (16), 272 (21), 258 (13), 210 (19), 173 (26), 144 (52), 111 (20), 104 (43), 71 (20), 52 (100). HR-MS: 343.0873 ($[M-2\ CO]^+$, $C_{16}H_{21}CrNO_4^+$; calc. 343.0875).

Anionic ortho-Fries *Rearrangement/*(tert-*Butyl)dimethylsilyl-Triflate Addition*. According to the *General Procedure*, with **3** (0.179 g, 0.5 mmol) and (*tert*-butyl)dimethylsilyl triflate (0.75 mmol, 1.5 equiv.) afforded **11b** (0.154 g, 0.326 mmol, 65%).

This reaction was repeated (same scale) by using **5** (1.15 equiv.): *{(1,2,3,4,5,6-η)-2-{[(*tert-*butyl)dimethylsilyl]oxy}-N,N-diisopropylbenzamide}tricarbonylchromium* (**11b**; 0.100 g, 42%) with an ee of 56% (HPLC (*Chiralcel OD*, hexane/i-PrOH 99:1; flow 1 ml/min)): t_R 16 (minor enantiomer (1*S*)-**11b**) and 24 min (major enantiomer (1*R*)-**11b**). M.p. 90–92°. $[\alpha]_D^{20} = +30$ ($CHCl_3$, $c = 0.16$). IR ($CHCl_3$): 2964, 2930, 2849, 1973, 1899, 1644, 1458, 1331, 1278. ^{1}H-NMR (C_6D_6, 400 MHz, 60°): 5.12 (*d*, $J = 6.1$, 1 arom. H); 4.77 (br. *s*, 1 arom. H); 4.58 (*d*, $J = 6.1$, 1 arom. H); 4.05 (*t*, $J = 6.1$, 1 arom. H); 3.85–3.45 (*m*, 1 H), 3.3–2.9 (*m*, 1 H); 1.5–1.1 (*m*, 4 Me); 0.96 (*s*, 3 Me); 0.19 (*s*, 2 Me). MS: 415 (11, $[M-2\ CO]^+$), 387 (100), 330 (7), 278 (49), 236 (17), 194 (11), 176 (10), 86 (9), 75 (19), 52 (100). HR-MS: 387.1669 ($[M-3\ CO]^+$, $C_{19}H_{33}CrNO_2Si^+$; calc. 387.1686).

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