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Absolute Asymmetric Synthesis of Stereochemically Labile Aldehyde Helicates and Subsequent Chirality Transfer Reactions

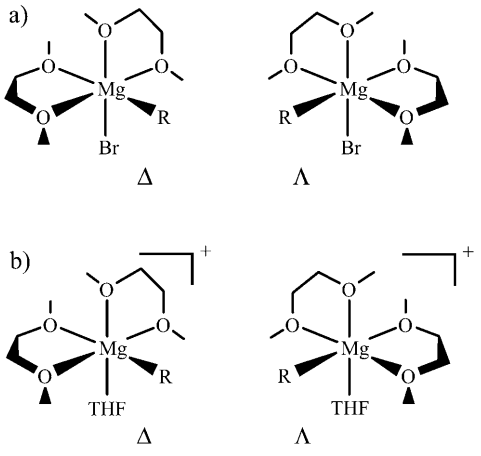
Anna Johansson and Mikael Håkansson*[a]

Abstract: Helical complexes formed between aluminum tris(2,6-diphenylphenoxide) (ATPH) and five different aldehydes have been prepared and structurally characterized by X-ray diffraction. It was found that [Al($OC_6H_3Ph_2$)$_3$PhCHO] (**2**), [Al($OC_6H_3Ph_2$)$_3$(4-$CH_3C_6H_4CHO$)] (**3**), [Al($OC_6H_3Ph_2$)$_3$(4-*t*BuC_6H_4CHO)] (**4**), and [Al($OC_6H_3Ph_2$)$_3$(*p*-$CH_3OC_6H_4$-CHO)] (**5**) all crystallize as conglomerates, while crystals of [Al($OC_6H_3Ph_2$)$_3$(*o*-$CH_3OC_6H_4CHO$)] (**6**) are racemic. Supramolecular CH/π interactions between molecules in crystals of **2**–**5** that enable stereochemical information to be mediated in three dimensions have been identified and explain the high frequency of conglomerate formation among ATPH helicates. Since **2**–**5** are stereochemically labile and thus enantiomerize rapidly in solution, the conglomerates can be resolved by crystallization-induced asymmetric transformation. The determination of the enantiomeric excess (*ee*) in solid samples of stereochemically labile molecules is not trivial, but solid-state CD spectroscopic data, anomalous dispersion data, and the *ee* values in alkylation reactions all indicate that preferential crystallization of **2**–**5** yields an essentially enantiopure product. Thus the preparation of **2**–**5** constitute new examples of absolute asymmetric synthesis. The helical chirality can be transferred (and thus trapped) to alcohols (with *ee* values of up to 16%) in crystal-to-crystal reactions with achiral organometallic reagents.

Keywords: asymmetric synthesis · chiral resolution · helical structures · total spontaneous resolution

Introduction

Reactions that form an enantiomerically enriched product from achiral precursors (without the participation of preformed optical activity) constitute examples of absolute asymmetric synthesis.[1–6] Such reactions may have been responsible for the formation of a homochiral pool of molecules on prebiotic Earth, and may thus be related to the origin of biomolecular homochirality. True examples of absolute asymmetric syntheses are rare (especially if reactions using circularly polarized light are excluded) and usually involve the transformation of an achiral substrate in a chiral crystal.[7] Although these reactions frequently give products with high *ee*, they are limited to special (but very interesting) cases. We recently reported on a different approach;[8–10] chiral-at-metal Grignard reagents (of the [$RMgX(LL)_2$] type, see Scheme 1) can be subjected to total spontaneous resolution since they are stereochemically labile in solution. The resulting reagents were obtained in high yield and *ee*, and although they racemize quickly in solution, the chirality can be transferred (and thus trapped) to carbon (with an *ee*



Scheme 1. *cis*-Octahedral Grignard reagents [$RMgX(LL)_2$] (a) X = Br, LL = $CH_3OCH_2CH_2OCH_3$; b) X = THF, LL = $CH_3OCH_2CH_2OCH_3$) are chiral-at-magnesium and enantiomerize rapidly in solution.

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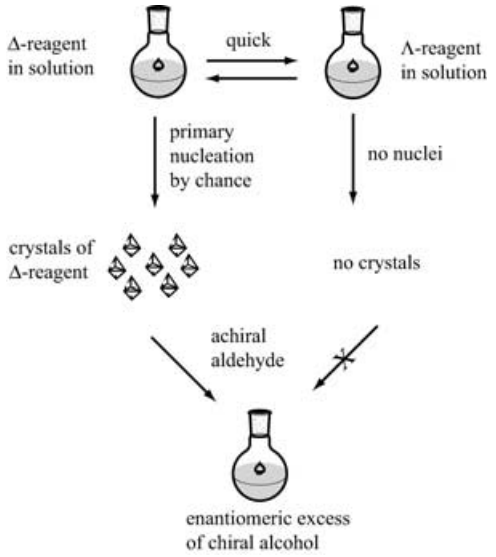


Figure 1. Absolute asymmetric synthesis using a chiral and stereochemically labile organometallic reagent.

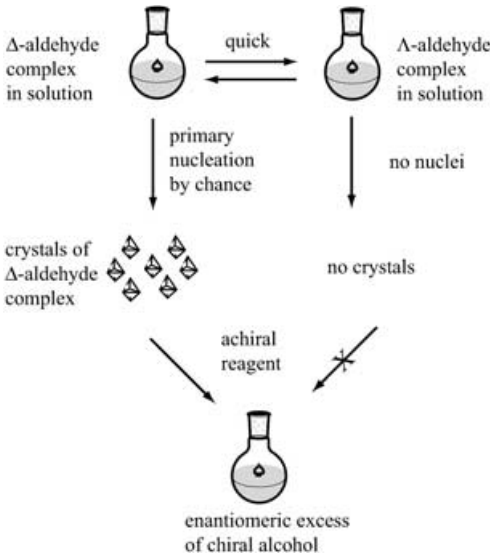
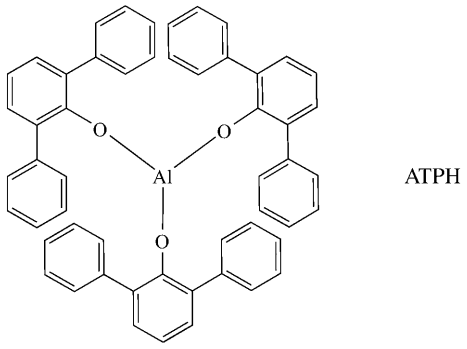


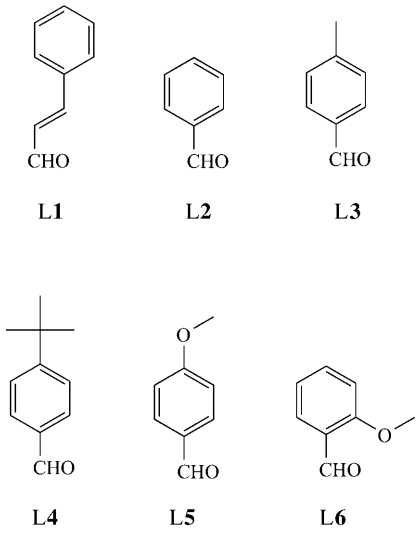
Figure 2. Absolute asymmetric synthesis using a chiral and stereochemically labile substrate complex.

of 22%) during either heterogeneous or solid–solid alkylation of aldehydes (Figure 1). This strategy is different from previous examples of absolute asymmetric syntheses in one important sense: since the reaction proceeds on the surface of a general reagent and not inside a crystal, many different external substrates can be used. As a result of the well-known versatility of Grignard reagents, a wide variety of reactions and products can thus be envisioned from the absolute asymmetric synthesis of a single reagent. As a logical extension of this approach we set out to prepare chiral (but stereochemically labile) complexes that can coordinate common substrates. If such a complex would form a conglomerate, then total spontaneous resolution could give one enantiomer in 100% yield and *ee*. Subsequent surface reaction with an achiral reagent completes the absolute asymmetric synthesis (Figure 2).

The design and preparation of a chiral and labile substrate complex is not an insurmountable task; carbonyl groups can, for example, be coordinated by Zn^{II} or Ni^{0} centers.[11,12] However, identifying a conglomerate of such a complex could be a very time-consuming enterprise since our understanding of the factors that determine whether a conglomerate or a racemic phase will form is still rudimentary. It is estimated that less than 10% of all chiral compounds form conglomerates,[13] however, these statistics are largely based on organic compounds, and the numbers could be very different for stereochemically labile coordination compounds. We were therefore very pleased to find (after a search in the Cambridge Structural Database) that aluminum tris(2,6-diphenylphenoxide) (ATPH, Scheme 2) forms conglomerates with both cinnamaldehyde[14] and benzaldehyde.[15] Yamamoto and co-workers have reported remarkable regio- and stereoselective reactions of ATPH complexes in solution,[16–22] and we were intrigued to learn that ATPH has a chiral pocket because the phenoxide ligands are wrapped



Scheme 2. Aluminium tris(2,6-diphenylphenoxide), ATPH, can coordinate a fourth, neutral ligand.



Scheme 3. The neutral aldehyde ligands (L) in ATPH complexes **1–6**.

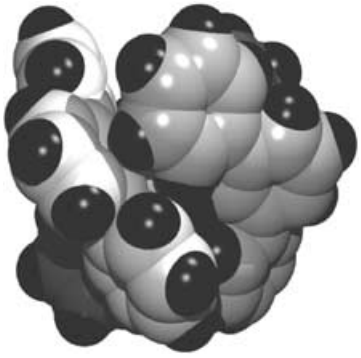


Figure 3. The left-handed Λ-helicate of ATPH.

Figure 4. The right-handed Δ-helicate of ATPH with the chiral cavity (empty) at the top.

around the metal, much like in a helicate (Figure 3 and Figure 4). Moreover, these complexes should be stereochemically labile, which would set the stage for total spontaneous resolution and (thereafter) enantioselective alkylation. However, on closer inspection it became evident that some ATPH complexes could be less suitable for this purpose than others since the substrate can adopt several different orientations in the chiral pocket. The asymmetric unit in $[Al(OC_6H_3Ph_2)_3PhCH{=}CHCHO]$ (**1**) (Scheme 3) consists of three molecules, each with a different orientation of the cinnamaldehyde ligand. Hence the preparation of new ATPH–aldehyde complexes was a logical starting point in the search for a conglomerate with an ordered substrate ligand.

Results and Discussion

Isolation of new conglomerates: The crystal structure of $[Al(OC_6H_3Ph_2)_3PhCHO]$ (**2**), which has previously been deposited with the Cambridge Structural Database,[15] is based on a conglomerate that crystallizes in the $P2_1$ space group. This crystal structure was determined by using $Mo_{K\alpha}$ radiation, and the asymmetric unit contains one molecule with the following unit cell dimensions: $a=10.731$, $b=20.441$, $c=10.908$ Å, $\beta=99.75°$. We decided to collect new diffraction data for a single crystal of **2** by using $Cu_{K\alpha}$ radiation to determine the absolute configuration and to relate it to the solid-state CD spectrum. Surprisingly, we obtained a phase (also crystallizing in the $P2_1$ space group) that had a unit cell with dimensions of $a=10.874(1)$, $b=20.344(2)$, $c=21.216(3)$ Å, and $\beta=99.28(1)°$. While the dimensions along the *a* and *b* axes are similar to those of the CSD structure, the length of the *c* axis is approximately doubled and the asymmetric unit now exhibits two independent molecules. The crystals are still enantiopure with regard to the orientation of the phenoxy ligands since both molecules in the asymmetric unit have the same helical handedness. However, as shown in Figure 5, the benzaldehyde ligands are oriented differently in the two molecules of the asymmetric unit. Since the benzaldehyde ligand in the CSD structure shows signs of disorder (e.g. irregular aryl bond lengths), it

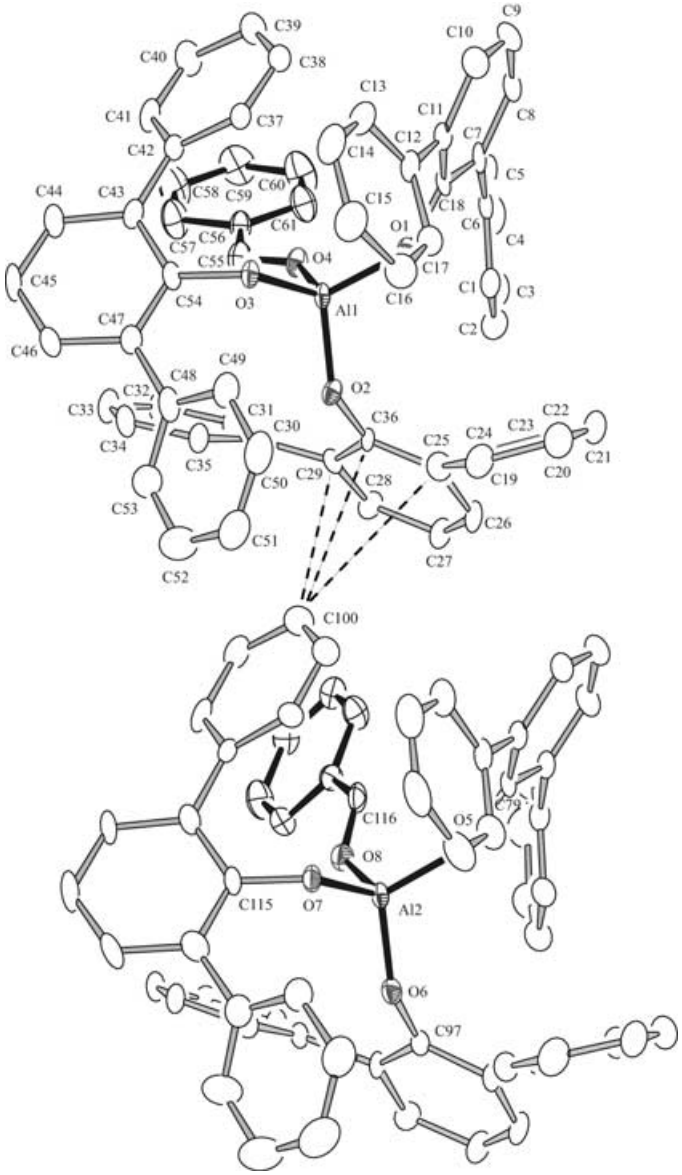


Figure 5. ORTEP drawing of Δ-**2** (the ATPH complex with benzaldehyde). Two molecules exist in the asymmetric unit which differ in the orientation of the neutral benzaldehyde ligand. Supramolecular CH/π vertex-to-face interactions are indicated by dashed lines.

is likely that the two phases are identical. Benzaldehyde ligands exhibiting more than one orientation in the ATPH pocket resembles the situation in the cinnamaldehyde–ATPH crystals and a continued search for new conglomerates with ordered substrate ligands was necessary. Four more ATPH complexes containing 4-tolualdehyde (**3**), 4-*tert*-butylbenzaldehyde (**4**), 4-methoxybenzaldehyde (**5**), and 2-methoxyaldehyde (**6**) were prepared and characterized by single-crystal X-ray diffraction (Table 1 and Scheme 3). All the complexes **1–6** have similar molecular structures; the aluminum center exhibits a tetrahedral coordination geometry, being surrounded by four oxygen donors. Selected Al–O bond lengths and O-Al-O bond angles in complexes **2–6** are presented in Table 2 and in the Supporting Information.

Table 1. Crystallographic data for complexes **2–6**.

Compound	Δ-**2**	Λ-**3**	Δ-**4**	Λ-**5**	**6**
formula	$C_{61}H_{45}AlO_4$	$C_{62}H_{47}AlO_4$	$C_{65}H_{53}AlO_4$	$C_{62}H_{47}AlO_5$	$C_{63.5}H_{50}AlCl_3O_5$
formula weight	868.95	882.98	925.05	898.98	1026.36
T [K]	153(2)	193(2)	143(2)	123(2)	123(2)
λ [Å]	1.54178	1.54178	1.54178	1.54178	1.54178
crystal system	monoclinic	orthorhombic	trigonal	monoclinic	monoclinic
space group	$P2_1$	$P2_12_12_1$	$R3$	$P2_1$	Pc
a [Å]	10.874(1)	18.221(2)	15.963(3)	10.545(3)	10.528(2)
b [Å]	20.344(2)	25.834(3)	15.963(3)	19.408(6)	36.853(7)
c [Å]	21.216(3)	10.2664(16)	16.803(9)	23.460(8)	13.472(5)
α [°]	90	90	90	90	90
β[°]	99.28(1)	90	90	90.48(2)	91.49(2)
γ[°]	90	90	120	90	90
V [Å^3]	4632(1)	4833(1)	3708(2)	4801(3)	5225(2)
Z	4	4	3	4	4
δ_{calcd} [g cm^{-3}]	1.246	1.214	1.243	1.244	1.305
μ [mm^{-1}]	0.773	0.748	0.754	0.779	2.159
size [mm^3]	0.5×0.4×0.4	0.5×0.4×0.3	0.5×0.4×0.4	0.4×0.3×0.3	0.4×0.4×0.2
color	yellow	yellow	yellow	yellow	yellow
θ range [°]	2.11–60.00	2.97–60.03	4.14–60.06	2.95–60.02	3.49–60.00
reflns collected	14727	26136	1323	7635	8073
indep. reflns	13455	7159	1268	7195	8073
parameters	1189	604	210	1225	1306
R_1 [$I>2\sigma(I)$]	0.065	0.051	0.043	0.043	0.051
wR_2 [$I>2\sigma(I)$]	0.165	0.071	0.101	0.099	0.127
wR_2 [all data]	0.200	0.093	0.129	0.129	0.168
Flack parameter	0.01(6)	0.04(5)	0.00(14)	0.05(7)	0.00(2)
max peak [e Å^{-3}]	0.36	0.14	0.19	0.24	0.69
max hole [e Å^{-3}]	−0.30	−0.20	−0.23	−0.27	−0.40

Figure 6 illustrates how the tolualdehyde ligand in Λ-[Al(OC$_6$H$_3$Ph$_2$)$_3$(4-CH$_3$C$_6$H$_4$CHO)] (Λ-**3**) sits in the chiral cavity that is formed by the helical arrangement of the aryloxy ligands. There is only one molecule in the asymmetric unit and the space group ($P2_12_12_1$) lacks both an inversion center and a mirror (or glide) plane, so all complexes in crystals of **3** exhibit the same handedness. Since no sign of disorder can be discerned in the tolualdehyde ligand, crystals of **3** should be ideal candidates for use in enantioselective alkylation reactions. Figure 7 shows the structure of Δ-[Al(OC$_6$H$_3$Ph$_2$)$_3$(4-*t*BuC$_6$H$_4$CHO)] (Δ-**4**). Unfortunately, the *tert*-butylbenzaldehyde ligand shows disorder at three sites, which corresponds to three different orientations of the substrate (Figure 8). The plane of the ligand's aryl group is rotated by 120° in each orientation since a crystallographic threefold axis runs through the ligand. Thus, although the substrate occupies the chiral cavity of ATPH (and crystallizes as a conglomerate), it is not a good candidate for enantioselective alkylation reactions. [Al(OC$_6$H$_3$Ph$_2$)$_3$(*p*-CH$_3$OC$_6$H$_4$CHO)] (**5**)) also crystallizes as a conglomerate. However, it is apparent from Figure 9 that crystals of **5** have two different molecules in the asymmetric unit. The helical arrangement of the aryloxy ligands is similar in the two complexes, but the 4-methoxybenzaldehyde ligand (in the chiral cavity) exhibits two different orientations. Finally, the 2-methoxybenzaldehyde ligand yields the first ATPH–aldehyde complex that is not a conglomerate. Figure 10 shows that in [Al(OC$_6$H$_3$Ph$_2$)$_3$(*o*-CH$_3$OC$_6$H$_4$-CHO)] (**6**), the aluminum center coordinates the aldehyde ligand in the usual chiral cavity. However, since **6** crystallizes in a *Pc* space group, both enantiomers (Δ and Λ) exist in equal amounts in the crystal. In conclusion, while complexes **1–5** all form conglomerates, **3** is best suited for enantioselective reactions since the tolualdehyde ligand exhibits a single orientation in the chiral pocket.

Table 2. Selected bond lengths [Å] and angles [°] in **3**.

Al1–O1	1.707(3)	Al1–O2	1.713(3)
Al1–O3	1.703(3)	Al1–O4	1.855(3)
O1–C18	1.349(5)	O2–C36	1.350(4)
O3–C54	1.352(4)	O4–C55	1.243(5)
O1-Al1-O2	112.47(14)	O2-Al1-O3	111.31(14)
O1-Al1-O3	118.96(14)	O2-Al1-O4	105.24(13)
O1-Al1-O4	106.30(14)	O3-Al1-O4	100.78(14)

Total spontaneous resolution: A conglomerate can be resolved by preferential crystallization of one enantiomer. Moreover, if the chiral complex has a low enantiomerization barrier, the solution will stay racemic despite the fact that one enantiomer has been preferentially crystallized. This process is known as crystallization-induced asymmetric transformation or total spontaneous resolution. Kondepudi and co-workers[23,24] have shown that stirred sodium chlorate solutions will give enantiopure crystal batches, and McBride and Carter[25] have demonstrated (even in a video recording) how stirring spawns and distributes secondary nuclei. We

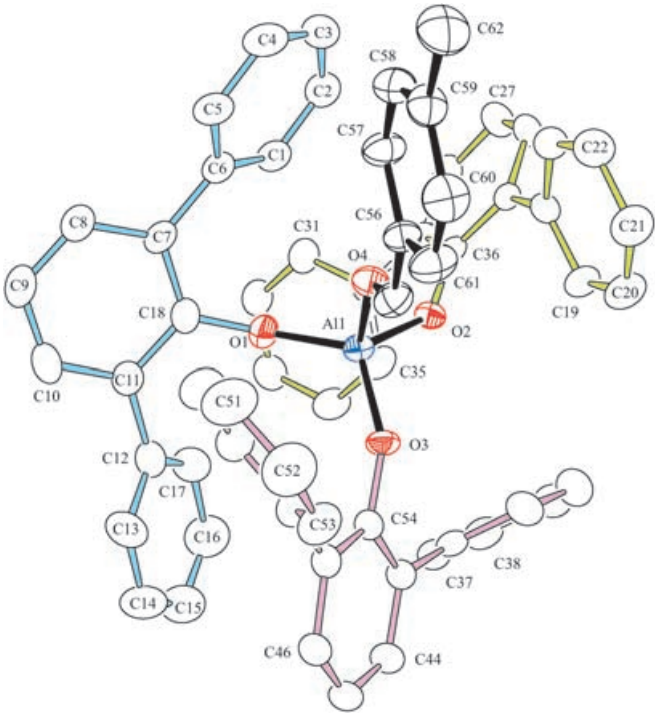


Figure 6. ORTEP drawing of Λ-**3** (the ATPH complex with *p*-tolualdehyde). All tolualdehyde ligands in Λ-**3** have identical conformations in the unique chiral cavity. The carbonyl carbon (C55) is shielded on one side by the C48–C53 aryl ring (cf. Figure 14) resulting in an excess of the (*S*)-alcohol after alkylation.

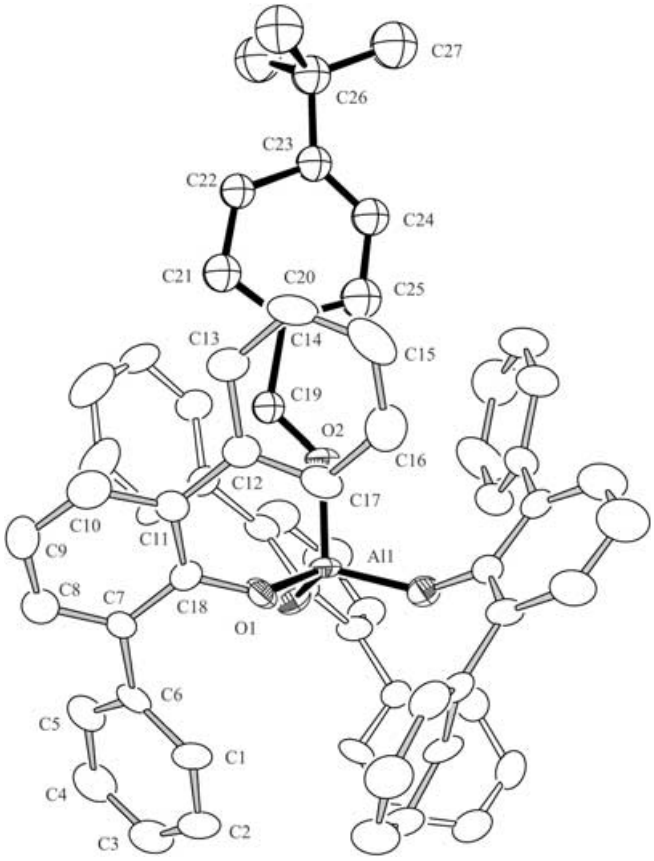


Figure 7. ORTEP drawing of **4** (the ATPH complex with *tert*-butylbenzaldehyde) showing the disordered aldehyde ligand in one out of three possible orientations.

have reported several examples of racemic solutions of stereochemically labile molecules[8,9,26–28] that yield enantiopure crystal batches without stirring. In these cases preferential crystallization is achieved by single-colony growth, a mechanism that also depends on secondary nucleation. We therefore added aldehyde ligands (corresponding to **1**–**5**) to solutions of ATPH in dichloromethane and allowed the solutions to crystallize slowly without stirring when large single crystals were the main objective (e.g., to create a CD calibration line and for X-ray diffraction). Indeed, cubic crystals of **1**–**5** (up to 10 mm) were deposited in high yields (up to 92%). When a microcrystalline product is acceptable, for example, for use in subsequent reactivity studies, stirring is beneficial as a result of the reduced time of crystallization.

Solid-state CD spectroscopy: To estimate the optical purity and determine the absolute configuration of the bulk samples to be used in reactions, CD spectra of **1**–**3** were recorded. Solutions of enantiopure samples of **1**–**3** are CD silent owing to rapid racemization in solution, but solid-state CD spectroscopy is a viable option.[27–29] Indeed, by grinding a single crystal of Λ-**3** with KBr and pressing a thin disk (the disk preparation is similar to IR spectroscopy, but much less sample is needed and thorough grinding is essential) it is possible to record the CD spectrum of the Λ enantiomer. The absolute configuration of the crystal was known since diffraction data (including Friedel pairs) could be collected

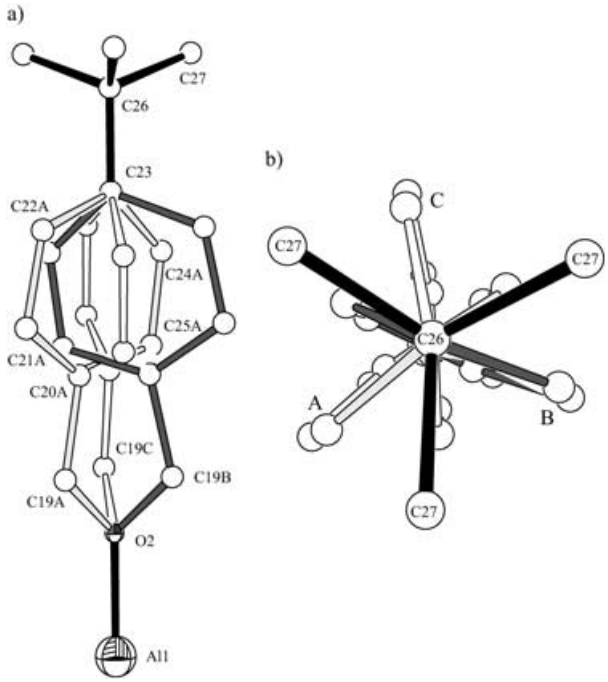


Figure 8. a) Side view of the disordered aryl rings of the aldehyde ligand in **4**. b) Top view.

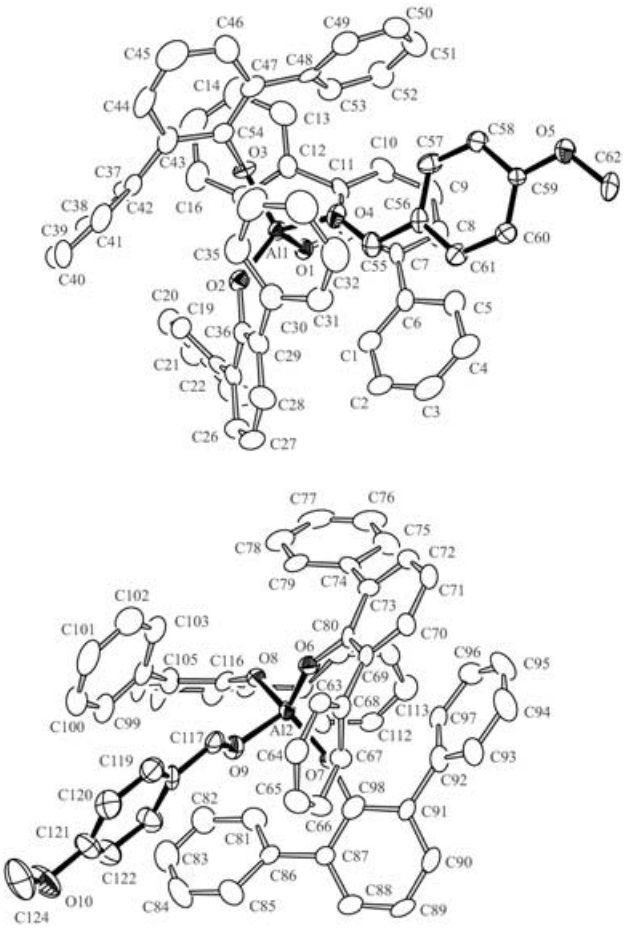


Figure 9. ORTEP drawing of **5** (the ATPH complex with *p*-anisaldehyde) which exhibits two independent molecules in the asymmetric unit. Short CH/π interactions include C77–H23 (2.84 Å) and C17*–H45 (2.65 Å).

by using the very same crystal before grinding. All the helicates in this crystal were unambiguously determined to be left-handed (i.e., Λ-**3**) from the Flack parameter[30,31] (0.01) and its estimated standard deviation (0.05), and there was no indication of racemic twinning. A crystal with right-handed helicates (i.e. Δ-**3**) was isolated from another batch and it was found to exhibit the anticipated mirror-image CD spectrum. Both spectra are displayed in Figure 11. By following similar procedures the CD spectra of Λ- and Δ-**1** (Figure 12) as well as Λ- and Δ-**2** (Figure 13) were obtained. Rewardingly, all crystals from the same batch exhibited identical CD spectra. Also, by mixing all crystals in a batch and extracting a representative sample of the same mass as the single crystal, CD spectra exhibiting similar amplitudes were obtained. In other words, all batches were essentially enantiopure showing that preferential crystallization had been successful. In contrast to recently published results concerning total spontaneous resolution of a copper(I) coordination helix,[28] a stochastic distribution of Λ and Δ crystal batches of **1**–**3** was found.

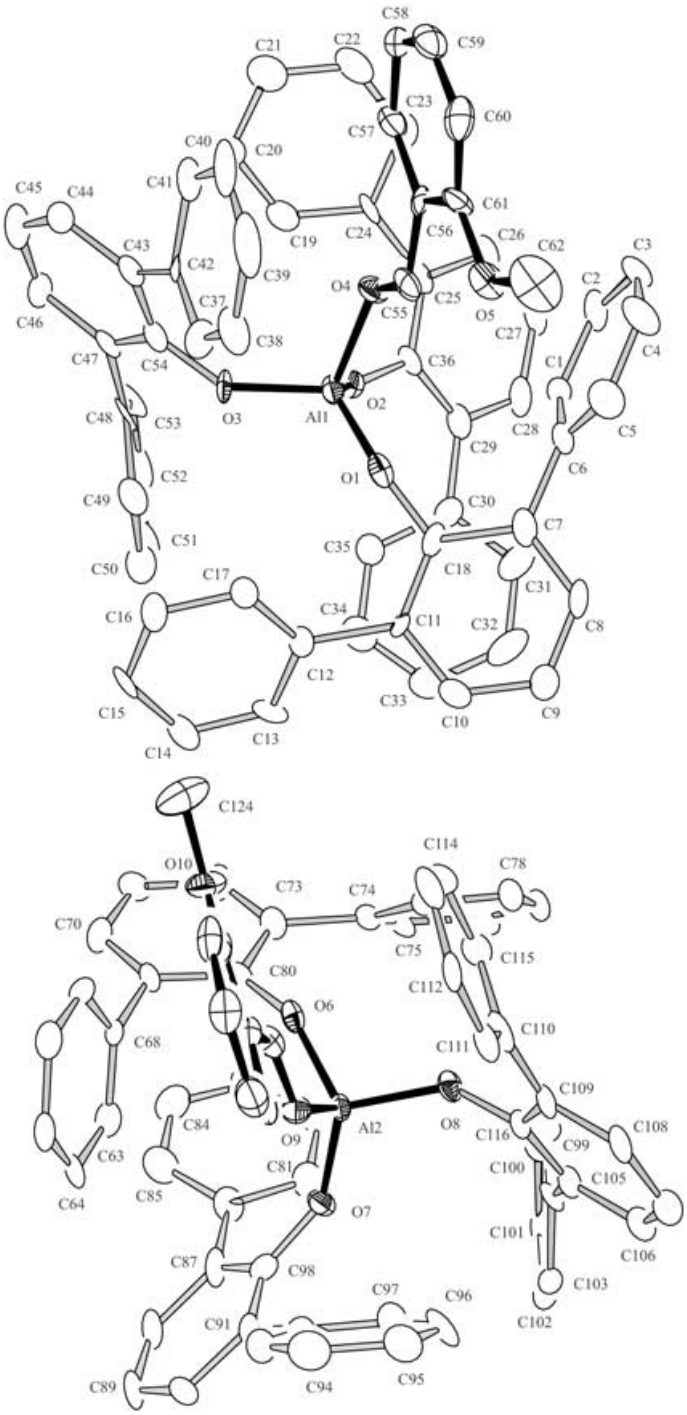


Figure 10. ORTEP drawing of **6** (the ATPH complex with *o*-anisaldehyde), which contains co-crystallized dichloromethane solvent molecules (omitted for clarity). The shortest intermolecular interactions involve solvent CH/π bonds, which prohibit direct transfer of stereochemical information from helicate to helicate.

Transfer reactions: To avoid racemization of the enantiopure substrate complexes in solution, reactions with organometallic nucleophilic reagents were performed in the absence of solvent. Solvent-free reactions have several advantages (including the environmental aspects),[32] but enantio-

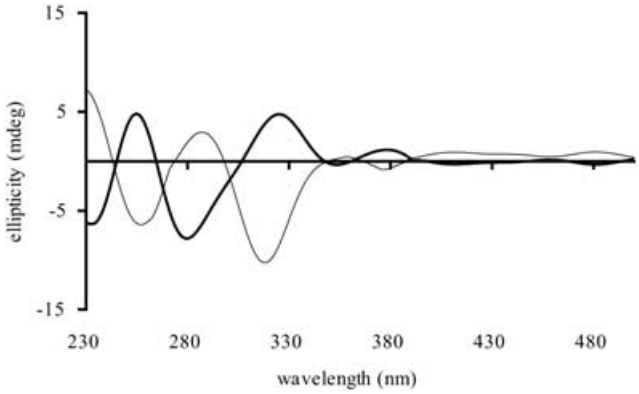


Figure 11. Solid-state CD spectra of Δ-**3** (bold) and Λ-**3**.

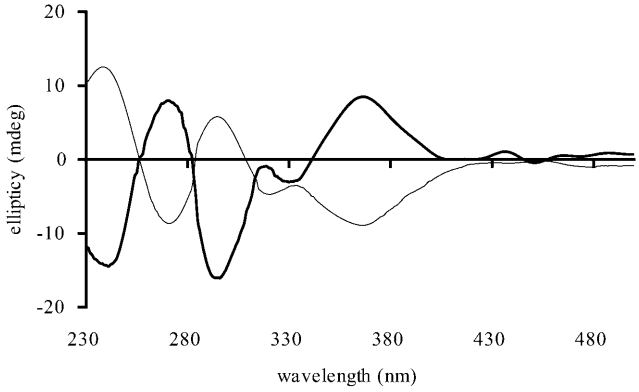


Figure 12. Solid-state CD spectra of Δ-**1** (bold) and Λ-**1**.

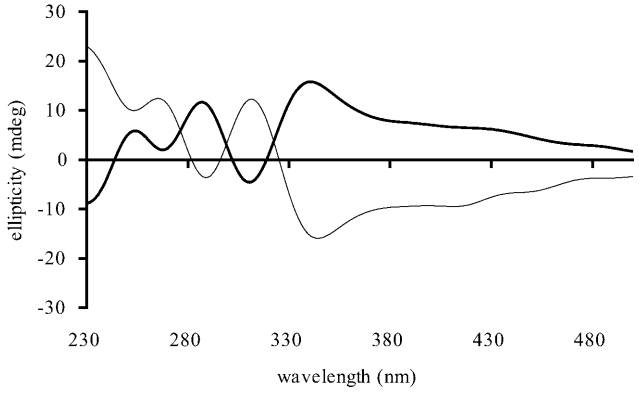
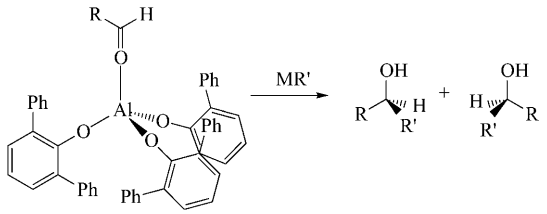


Figure 13. Solid-state CD spectra of Δ-**2** (bold) and Λ-**2**.

selective strategies using chiral substrate crystals have so far focused on reactions that occur within a chiral crystal (intracrystal) and not on the surface (intercrystal).[7,33] In this work, we attempted to transfer the Δ,Λ chirality of the stereochemically labile ATPH–aldehyde complexes to the *R*,*S* chirality of the corresponding alkylated adduct. This means that both the reagent and the substrate should be in the solid state and that the surface and contact areas need to be maximized by mixing and grinding. The ATPH–aldehyde complexes **1**–**5** were treated with a number of different solid organometallic reagents (Scheme 4). Table 3 shows that all complexes **1**–**5** yielded an optically active product when al-



Scheme 4. Alkylation of ATPH complexes with solid reagents (see Table 3).

kylated. The highest *ee* (16%, entry 12) was achieved by using the ATPH–tolualdehyde complex (**3**), as expected. Entries 8 and 9 in Table 3 confirm that when the Λ enantiomer of an ATPH complex gives the (*S*)-alcohol, then the Δ enantiomer gives the (*R*)-alcohol. Further verification of the enantiopurity of batches of **1**–**3** has now been obtained since alkylation of a single crystal of **1**–**3** gave similar *ee* values to the alkylation of a batch sample of **1**–**3**. Actually, solid-state reactions could provide an alternative method (to solid-state CD spectroscopy)[27] by which to determine the *ee* of stereochemically labile samples.[34] It is evident from entries 3 and 10 in Table 3 that the use of suspensions of ATPH complexes in hexane at low temperature is indeed detrimental to the enantioselectivity. Alkylation of the cinnamaldehyde substrate in **1** led to two different products (corresponding to 1,2- or 1,4-addition). While Yamamoto et al.[22] achieved virtually complete blocking of the carbonyl group in reactions with Grignard reagents in solution (90–99%, 1,4-adduct), entry 2 in Table 3 shows an excess of the 1,2-adduct from the solid-state reaction. One explanation for this could be that uncomplexed cinnamaldehyde has been liberated as a result of the partial decomposition of crystalline **1** during the reaction. This would mean that the enantioselectivity of the actual solid-state 1,2-addition reaction has to be much higher than 10%. Alternatively one could simply acknowledge the fact that solid-state selectivity may drastically differ from that in solution.[32]

Since the absolute configuration of both the ATPH–tolualdehyde complex (**3**) and the alkylated alcohol is known, information concerning the reaction mechanism can be deduced. The crystal structure of Λ-**3** shows that the tolualdehyde ligand sitting in the chiral pocket of the left-handed helicate (Figure 14) is more shielded on one side. This shielding is confirmed by the fact that the shortest intramolecular $C_{(carbonyl)}$–$C_{(aryl)}$ interaction is 3.30 Å on the shielded side and 3.74 Å on the "open side" of the carbonyl group. Moreover, the carbonyl hydrogen atom is engaged in several short CH/π interactions (2.9–3.2 Å) with the shielding aryl group of one of the phenoxy ligands. Attack by an alkylating reagent from the open side, as indicated by the arrow in Figure 14, would result in an alcohol with an *S* configura-

Table 3. Chirality transfer reaction data.

Entry	Complex	Reagent	Temp. [°C]	Time [h]	Conv.[a]	*ee*[a] [%]	Configuration [%]
1	Δ-**1**	$[LiMe(dee)_x]_{(s)}$[b]	20	24	29/40[c]	6.6/7.5[c]	n.d.[d]
2	Δ-**1**	$[Mg(Et)_2(dioxane)]_{(s)}$[e]	20	24	19/55[c]	8.3/9.7[c]	n.d.[d]
3	Δ-**1**	BuLi in hexane[f]	−78	1	3.0/4.1[c]	2.6/2.4[c]	n.d.[d]
4	Δ-**2**	$[LiMe(dee)_x]_{(s)}$[b]	20	24	29	7.3	*R*
5	Δ-**2**	$[LiMe(dee)_x]_{(s)}$[b]	20	96	97	7.2	*R*
6	Δ-**2**	$[LiMe(dee)_x]_{(s)}$[b]	20	168	100	7.4	*R*
7	Λ-**2**	$[Mg(Et)_2(dioxane)]_{(s)}$[e]	−78	72	5.0	9.3	*S*
8	Λ-**2**	$[Mg(Et)_2(dioxane)]_{(s)}$[e]	20	72	44	7.3	*S*
9	Δ-**2**	$[Mg(Et)_2(dioxane)]_{(s)}$[e]	20	72	68	8.5	*R*
10	Δ-**2**	BuLi in hexane[f]	−78	1	11	0.6	*R*
11	Λ-**3**	$[LiMe(dee)_x]_{(s)}$[b]	20	24	84	14	*S*
12	Λ-**3**	$[Mg(Et)_2(dioxane)]_{(s)}$[e]	20	72	96	16	*S*
13	Λ-**4**	$[LiMe(dee)_x]_{(s)}$[b]	20	24	47	2.9	n.d.[d]
14	Λ-**5**	$[LiMe(dee)_x]_{(s)}$[b]	20	24	79	1.8	n.d.[d]

[a] Determined by GC. [b] 1.6 M MeLi in diethyl ether was evaporated to dryness under nitrogen (pyrophoric!). [c] 1,4-Adduct/1,2-adduct. [d] Not determined. [e] See the Experimental Section for details of preparation. [f] 1.6 M.

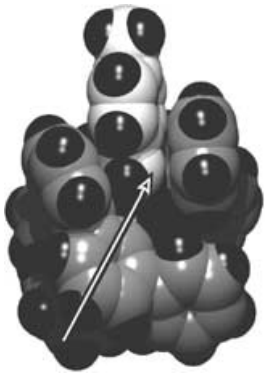


Figure 14. The carbonyl carbon of the tolualdehyde ligand (shown in white) is less shielded and thus open to nucleophilic attack on one side. The figure shows the left-handed Λ-helicate, which gives an enantiomeric excess of the (*S*)-alcohol when treated with solid methyllithium or diethylmagnesium.

tion. Indeed, as the data in Table 3 show, this is also observed experimentally. Although the absolute configurations are also known in the reactions of the other complexes (**1**, **2**, **4**, and **5**), an analogous analysis of the modes of attack is considerably more intricate since the aldehyde ligands can adopt several different conformations in these crystals.

Supramolecular transfer of stereochemical information: It is remarkable that out of the six structurally characterized ATPH–aldehyde complexes, five crystallize as conglomerates. The marked deviation from the common estimate of 5–10% conglomeration[13] calls for a closer analysis of how stereochemical information is transferred between ATPH complexes in the solid state. Since the carbonyl groups of the substrates are involved in solely intramolecular coordination, one might anticipate that the most important intermolecular contacts would be π–π stacking, considering the multitude of aryl groups present in the ATPH crystals. However, in complexes **2**–**6**, it seems that the dominating intermolecular contacts are various CH/π interactions, as exemplified in Figure 15, Figure 16, and Figure 17. Although such vertex-to-face interactions are weak, they are known to be able to play a significant role in the assembly of crystalline compounds.[35] In both **2** and **4**, the shortest contacts are of the type illustrated in Figure 15; these distances are 2.65 Å (complex **2**; CH100–C36 in Figure 5) and

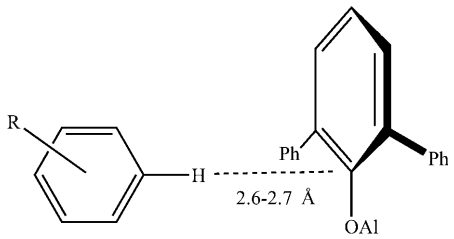


Figure 15. Short vertex-to-face CH/π interactions in **2** and **4** can transfer stereochemical information from helicate to helicate.

2.75 Å (complex **4**; CH15–C18* in Figure 7) with C–H–π angles of 168.7° (**2**) and 158.6° (**4**). The molecules in **5** interact in a similar manner, the main difference being that the donor π ring is now a terminal ring. Also, the C–H bond (C45–H45) interacts primarily with two of the carbon atoms (C12 and C17) in the aryl ring, as shown in Figure 16. The CH/π distance from H45 to the midpoint of the C12–C17 bond in **5** is only 2.57 Å with a C–H–π angle of 154.5°. A different set of CH/π interactions seem to dominate in **3** (Figure 17). The pairwise interactions between the C4 and C38 hydrogen atoms form a new motif in these structures and is complemented by CH5–π interactions. Finally, the fact that **6** is the only ATPH complex not to crystallize as a conglomerate needs consideration. Are the supramolecular interactions in **6** perhaps different from those in the conglomerates **1**–**5**? Crystals of **6** contain co-crystallized dichloromethane molecules which participate in several CH/π interactions, the shortest being 2.66 Å. There are also a few CH/π interactions involving the 2-methoxybenzaldehyde substrate. But there are no short helicate–helicate interactions in **6** and consequently there is no possibility of direct transfer of stereochemical information. It is therefore not surprising that a conglomerate is not formed.

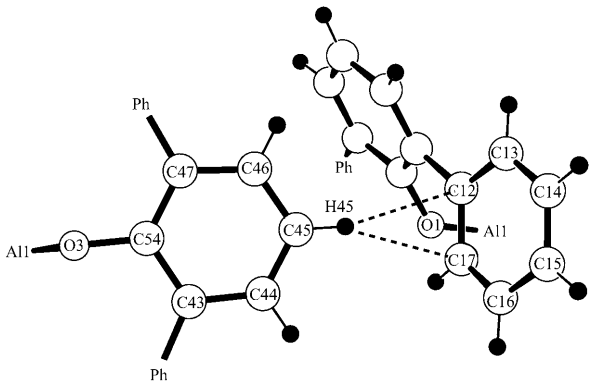


Figure 16. Short vertex-to-face CH/π interactions in **5** involve the terminal rings of the phenoxy ligands.

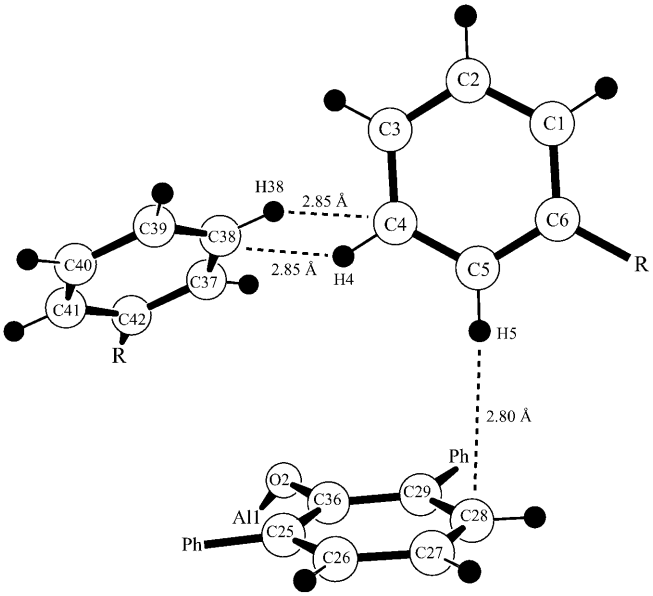
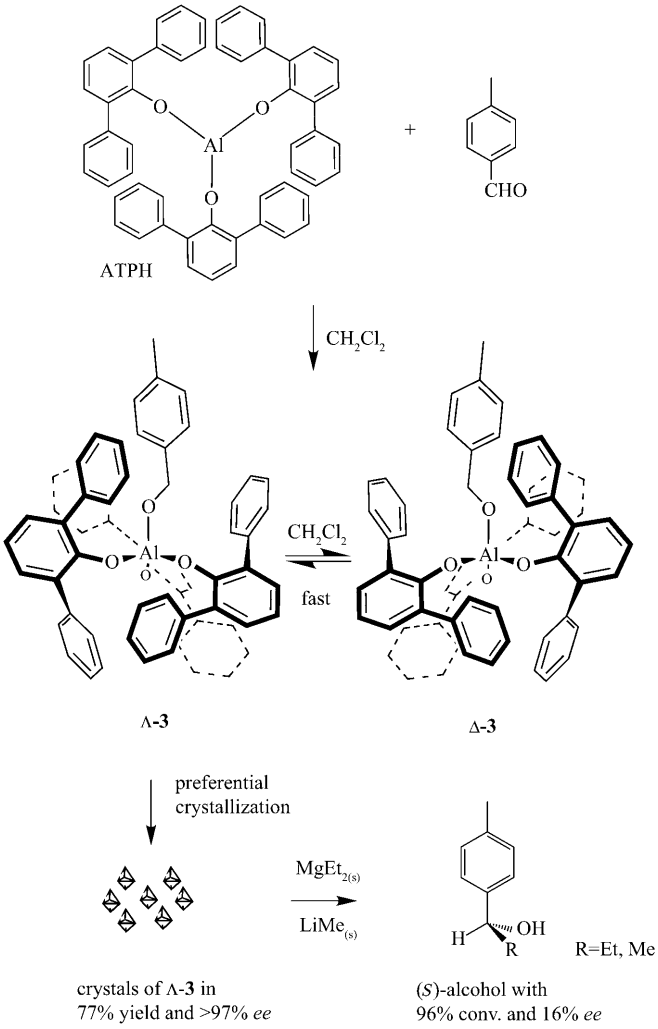


Figure 17. Short CH/π interactions in **3**. The pairwise CH4–CH38 interaction is unique among ATPH conglomerates.



Scheme 5. Absolute asymmetric synthesis of stereochemically labile aldehyde helicates and subsequent chirality transfer reactions.

Conclusions

Absolute asymmetric synthesis of chiral alcohols has been successful and the synthetic route is illustrated in Scheme 5. The actual symmetry-breaking occurs during the crystallization-induced asymmetric transformation step, which results in essentially enantiopure crystal batches of the ATPH complex. Preferential crystallization by single-colony growth was achieved without stirring the solution. Solid-state CD spectroscopy is a powerful method by which to determine the *ee* (and indirectly, the absolute configuration) of batches of stereochemically labile molecules.[27] Information concerning the mechanism of the solid-state reaction of the ATPH–tolualdehyde complex (**3**) with organometallic reagents has been obtained since the absolute configuration of both the substrate complex and the product are known. Although still at a moderate level of enantioselectivity, it is apparent that stereochemical information can be transferred in "crystal-to-crystal" organometallic reactions (using stereochemically labile complexes). Whether the moderate enantioselectivity is caused by decomposition of the crystal surfaces or is an inherent deficiency of the reaction is still unclear. An unusually high number of the ATPH complexes have been found to form conglomerates, which can be explained by the transfer of stereochemical information through a variety of supramolecular CH/π interactions between helicate molecules in the crystal. The conglomerates each exhibit unique interaction patterns indicating that homochiral packing is indeed favored among ATPH helicates.

Experimental Section

General: Reactions were carried out under nitrogen using Schlenk or low-temperature techniques.[36] Dichloromethane was distilled from calcium hydride and stored over 4 Å molecular sieves. Toluene, tetrahydrofuran (THF), diethyl ether (DEE), 1,2-dimethoxyethane (DME), 1,4-diox-

ane, and hexane were distilled from sodium/benzophenone shortly prior to use. Commercial methyllithium (1.6 M in DEE, Acros), butyllithium (1.6 M in hexane, Acros), and trimethylaluminum (2 M in toluene, Fluka) were used as delivered. All NMR spectra were recorded using a Varian Unity 400 MHz spectrometer. CD spectra were recorded with a Jasco J-175 spectropolarimeter. Chromatographic analyses were carried out with a Varian Star 3400 CX gas chromatograph. All GC analyses were run on a chiral stationary phase column (CP-Chirasil-DEX CB, 25 m, 0.32 mm) from Chrompack. Analyses were performed isothermally at 90–115 °C depending on the alcohol resolved (injector: 225 °C; detector: 250 °C) and with helium as the carrier gas. The retention times for the chiral adducts are given in the Supporting Information.

Preparation of [Al(OC$_6$H$_3$Ph$_2$)$_3$(C$_6$H$_5$CH=CHCHO)] (1): A 2.0 M solution of trimethylaluminum in toluene (0.25 mL, 0.50 mmol) was added dropwise to a stirred solution of 2,6-diphenylphenol (0.370 g, 1.50 mmol) in dry dichloromethane (2 mL) at ambient temperature, and the resulting mixture was stirred for 30 min. Cinnamaldehyde (60 μL, 0.5 mmol) was added slowly and after 13 h red single crystals of X-ray quality were deposited. Yield: 0.41 g, 92 %. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ = 7.42 (d, $J_{H,H}$ = 8.40 Hz, 3H, Ph), 7.40 (t, $J_{H,H}$ = 7.30 Hz, 3H, Ph), 7.33 (t, $J_{H,H}$ = 7.92 Hz, 2H, Ph), 7.20–7.17 (m, 5H, Ph), 7.08–7.0 (m, 13H, Ph), 6.95–6.89 (m, 10H, Ph), 6.87 (t, $J_{H,H}$ = 7.30 Hz, 7H, Ph), 6.77 (d, $J_{H,H}$ = 14.80 Hz, 1H, CHPh), 6.52 (d, $J_{H,H}$ = 8.40 Hz, 1H, OCCH), 6.20 ppm (d, $J_{H,H}$ = 8.40 Hz, 1H, OCH); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K): δ = 140.44, 137.85, 132.47, 129.86, 129.44, 129.33, 129.02, 128.83, 127.74, 126.87, 125.40, 117.97, 21.45 ppm. Solid-state CD (KBr) for Δ-**1**: λ = 365 (max), 330 (min), 316 (max), 294 (min), 269 (max), 239 nm (min); for Λ-**1**: λ = 365 (min), 330 (max), 316 (min), 294 (max), 269 (min), 239 nm (max).

Preparation of [Al(OC$_6$H$_3$Ph$_2$)$_3$(C$_6$H$_5$CHO)] (2): A 2.0 M solution of trimethylaluminum in toluene (0.25 mL, 0.50 mmol) was added dropwise to a stirred solution of 2,6-diphenylphenol (0.370 g, 1.50 mmol) in dry toluene (2 mL) at ambient temperature, and the resulting mixture was stirred for 30 min. Benzaldehyde (53.1 mg, 0.50 mmol) was added slowly and crystals started to deposit after a few minutes. When no more crystals formed, the solvent was removed by syringe and toluene (5 mL) was added. The mixture was heated to reflux and another portion of toluene (approximately 4 mL) was added until no solid material was present. The solution was allowed to cool to ambient temperature very slowly and yellow single crystals of X-ray quality started to form at about 30 °C. Yield: 0.37 g, 85 %. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ = 7.79 (d, $J_{H,H}$ = 7.28 Hz, 3H, Ph), 7.61 (t, $J_{H,H}$ = 7.27 Hz, 3H, Ph), 7.49 (t, $J_{H,H}$ = 7.27 Hz, 2H, Ph), 7.39–7.22 (m, 5H, Ph), 7.13–7.04 (m, 17H, Ph), 6.90–6.81 (m, 13H, Ph), 5.32 ppm (s, 1H, CH); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K): δ = 151.66, 140.17, 132.40, 129.93, 129.60, 129.49, 129.33, 129.02, 128.83, 128.21, 127.61, 125.94, 118.87 ppm; solid-state CD (KBr) for Δ-**2**: λ = 338 (br max), 309 (min), 285 (max), 265 (min), 252 nm (max); for Λ-**2**: λ = 338 (br min), 309 (max), 285 (min), 265 (max), 252 nm (min).

Preparation of [Al(OC$_6$H$_3$Ph$_2$)$_3$(4-CH$_3$C$_6$H$_4$CHO)] (3): A 2.0 M solution of trimethylaluminum in toluene (0.25 mL, 0.50 mmol) was added dropwise to a stirred solution of 2,6-diphenylphenol (0.370 g, 1.50 mmol) in dry dichloromethane (1 mL) at ambient temperature. The resulting mixture was stirred for 30 min after which 4-tolualdehyde (60 mg, 0.5 mmol) was added slowly. Crystals started to form after a few minutes. The solvent was removed by a syringe and toluene (5 mL) was added, after which the suspension was heated to reflux and more toluene was added until no solid material was present. The solution was allowed to reach ambient temperature very slowly and yellow single crystals of X-ray quality started to form at approximately 30 °C. Yield: 0.34 g, 77 %. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ = 7.48 (d, $J_{H,H}$ = 8.44 Hz, 3H, Ph), 7.40 (t, $J_{H,H}$ = 7.32 Hz, 3H, Ph), 7.33–7.22 (m, 2H, Ph), 7.21–7.17 (m, 5H, Ph), 7.10–7.00 (m, 13H, Ph), 6.9–6.8 (m, 17H, Ph), 5.33 (s, 1H, CH), 2.40 ppm (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K): δ = 151.65, 140.18, 132.39, 129.92, 129.49, 129.33, 129.02, 128.83, 128.21, 127.63, 125.94, 125.28, 53.41, 22.68 ppm; solid-state CD (KBr) for Δ-**3**: λ = 376 (max), 352 (min), 323 (max), 279 (min), 253 (max), 232 nm (min); for Λ-**3**: λ = 376 (min), 352 (max), 323 (min), 279 (max), 253 (min), 232 nm (max).

Preparation of [Al(OC$_6$H$_3$Ph$_2$)$_3$(4-*t*BuC$_6$H$_4$CHO)] (4): Complex **4** was synthesized by following the procedure used for the preparation of [Al(OC$_6$H$_3$Ph$_2$)$_3$(*p*-CH$_3$C$_6$H$_4$CHO)] (**3**), but by using 4-*tert*-butylbenzaldehyde (81.1 mg, 0.50 mmol) instead of 4-tolualdehyde. Yellow single crystals of X-ray quality were deposited. Yield: 0.31 g, 67 %. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ = 7.49 (d, $J_{H,H}$ = 7.32 Hz, 3H, Ph), 7.41 (t, $J_{H,H}$ = 7.36 Hz, 3H, Ph), 7.32 (t, $J_{H,H}$ = 7.36 Hz, 2H, Ph), 7.22–7.17 (m, 5H, Ph), 7.11–6.99 (m, 17H, Ph), 6.84–6.78 (m, 13H, Ph), 5.22 (s, 1H, CH), 1.31 ppm (s, 9H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K): δ = 151.66, 140.17, 132.40, 129.93, 129.60, 129.49, 129.33, 129.02, 128.83, 128.21, 127.61, 125.94, 118.87, 30.80 ppm.

Preparation of [Al(OC$_6$H$_3$Ph$_2$)$_3$(4-CH$_3$OC$_6$H$_4$CHO)] (5): Complex **5** was synthesized by following the procedure used for the preparation of [Al(OC$_6$H$_3$Ph$_2$)$_3$(*p*-CH$_3$C$_6$H$_4$CHO)] (**3**), but by using 4-anisaldehyde (81 mg, 0.50 mmol) instead of 4-tolualdehyde. Yellow single crystals of X-ray quality were formed. Yield: 0.37 g, 82 %.

Preparation of [Al(OC$_6$H$_3$Ph$_2$)$_3$(2-CH$_3$OC$_6$H$_4$CHO)]·(CH$_2$Cl$_2$)$_{1.5}$ (6): Complex **6** was synthesized by following the procedure used for the preparation of [Al(OC$_6$H$_3$Ph$_2$)$_3$(*p*-CH$_3$C$_6$H$_4$CHO)] (**3**), but by using 2-anisaldehyde (81 mg, 0.50 mmol) instead of 4-tolualdehyde. Yellow single crystals of X-ray quality were deposited. Yield: 0.39 g, 87 %. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): δ = 7.48 (d, $J_{H,H}$ = 8.44 Hz, 3H, Ph), 7.40 (t, $J_{H,H}$ = 7.32 Hz, 3H, Ph), 7.31 (t, $J_{H,H}$ = 7.92 Hz, 2H, Ph), 7.20–7.16 (m, 5H, Ph), 7.10–7.00 (m, 13H, Ph), 6.9–6.8 (m, 10H, Ph), 6.82 (t, $J_{H,H}$ = 7.32 Hz, 7H, Ph), 5.33 (s, 1H, CH), 3.74 ppm (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 293 K): δ = 151.78, 140.14, 137.85, 132.47, 129.86, 129.44, 129.33, 129.02, 128.83, 128.21, 127.44, 125.77, 125.28, 118.77, 21.46 ppm.

Solid-state CD spectroscopy: Solid-state CD spectra were recorded using thin (100 mg) KBr disks of 13 mm diameter. No spectral changes caused by rotation of the disk in the beam could be discerned. Controlled dilution was accomplished by selecting a crystalline sample (approximately 1 mg) under a microscope and then manually mixing and grinding it with KBr (approximately 1 g). The best result was obtained by adding KBr in four smaller portions, each addition being followed by careful manual grinding, until a homogeneous mixture was obtained. Approximately 100 mg of the mixture was collected and pressed into a disk for 2 min at 8 ton. This resulted in a thin disk containing approximately 0.1 mg crystal mass. All complexes will eventually lose aldehyde upon grinding, but **2** in particular loses benzaldehyde upon extensive grinding, which made it difficult to obtain high quality spectra for the enantiomers of **2**.

Solution CD spectroscopy: Solutions were prepared by dissolving enantiopure (and homochiral) single crystals in dichloromethane and CD spectra were recorded immediately. No CD signal from the complex could be detected indicating rapid racemization had occurred.

General procedure for solid-state alkylation reactions of 1–5: Crystals of the relevant ATPH–aldehyde complex (approximately 30 mg, 0.03 mmol) were added to an excess of the solid organometallic reagent (approximately 3 mmol) in a Schlenk tube and the resulting mixture was ground with a magnetic stirring bar for 24 h. The Schlenk tube was then lowered into a dry-ice bath and a saturated NH_4Cl solution was added very slowly. (In a blind test, quenching and work up was performed directly after mixing the solid substrate and reagent. No adduct could be identified showing that the reaction occurs between the solid reagents and not in solution during quenching.) Diethyl ether (2 mL) was added to the quenched reaction and the organic phase was dried with $NaSO_4$ and transferred to a vial. Conversions and enantiomeric excesses were determined by chiral GC. The data in Table 3 are typically mean values from five separate reactions.

Preparation of [LiMe(dee)$_x$]: A solution of 1.6 M MeLi in DEE was evaporated to dryness under vacuum. The remaining white solid must be handled with care since it is pyrophoric.

Preparation of [MgEt$_2$(dioxane)]: Magnesium turnings (4.0 g, 164 mmol) and ethyl bromide (14.0 g, 130 mmol) were stirred for 10 h at ambient temperature in DEE (100 mL). 1,4-Dioxane (14.3 g, 0.16 mmol) was then added to the greyish suspension. The resulting mixture was centrifuged to give a white precipitate and a clear solution. The solution was transferred, using a syringe, to a Schlenk tube and allowed to cool to −30 °C.

Colorless single crystals, suitable for X-ray determination, were formed after 6 h. The identity of the crystals was determined from the unit cell dimensions.[37] Yield: 7.00 g, 65%.

X-ray crystallography: Crystal and experimental data for **2**–**6** are summarized in Table 1. Crystals were selected and mounted under nitrogen or at low temperature and transferred to a Rigaku AFC6 diffractometer equipped with an evacuated beam tunnel. The beam tunnel and the low-temperature equipment prohibited collection of data at 2θ angles larger than 120°. Diffracted intensities were measured at a low temperature using graphite-monochromated $Cu_{K\alpha}$ ($\lambda = 1.54178$ Å) radiation from a RU200 rotating anode operated at 50 kV and 180 mA. Stationary background counts were recorded on each side of the reflection, the ratio of peak counting time to background counting time being 2:1. Weak reflections ($I < 10.0\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. For complexes **2** and **3**, as many Friedel pairs as possible were collected in order to obtain a low standard deviation in the Flack parameter determination.[30] The intensities of three reflections were monitored regularly after measurement of 150 reflections and indicated crystal stability during the diffraction experiment. Cell constants were obtained by least-squares refinement from the setting angles of at least 20 reflections. An empirical correction for the effects of absorption was made based on several ψ-scans. All structures were solved using SHELXS-97[38] or SIR97[39] and refined using SHELXL-97[38] (full-matrix least-squares calculations on F^2) operating in the WinGX program package.[40] Anisotropic thermal displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined using a riding model except for the disordered carbon atoms in **4**, for which the hydrogen atoms were not located. Structural illustrations have been drawn with ORTEP-3 for Windows[41] and PLATON[42] under WinGX.

CCDC-261279 (Δ-**2**), CCDC-261280 (Λ-**3**), CCDC-261281 (Δ-**4**), CCDC-261282 (Λ-**5**), and CCDC-261283 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Acknowledgements

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[1] B. L. Feringa, R. A. Van Delden, *Angew. Chem.* **1999**, *111*, 3624–3645; *Angew. Chem. Int. Ed.* **1999**, *38*, 3418.
[2] M. Avalos, R. Babiano, P. Cintas, J. L. Jimenez, J. C. Palacios, L. D. Barron, *Chem. Rev.* **1998**, *98*, 2391.
[3] R. G. Kostyanovsky, V. R. Kostyanovsky, G. n. K. Kadorkina, K. A. Lyssenko, *Mendeleev Commun.* **2001**, 1.
[4] D. A. Singleton, L. K. Vo, *Org. Lett.* **2003**, *5*, 4337.
[5] K. Mislow, *Collect. Czech. Chem. Commun.* **2003**, *68*, 849.
[6] K. Soai, I. Sato, T. Shibata, S. Komiya, M. Hayashi, Y. Matsueda, H. Imamura, T. Hayase, H. Morioka, H. Tabira, J. Yamamoto, Y. Kowata, *Tetrahedron: Asymmetry* **2003**, *14*, 185.
[7] M. Sakamoto, *Chem. Eur. J.* **1997**, *3*, 684.
[8] M. Vestergren, J. Eriksson, M. Håkansson, *Chem. Eur. J.* **2003**, *9*, 4678.
[9] M. Vestergren, B. Gustafsson, O. Davidsson, M. Håkansson, *Angew. Chem.* **2000**, *112*, 3577; *Angew. Chem. Int. Ed.* **2000**, *39*, 3435.
[10] M. Vestergren, J. Eriksson, M. Håkansson, *J. Organomet. Chem.* **2003**, *681*, 215.
[11] B. Mueller, M. Ruf, H. Vahrenkamp, *Angew. Chem.* **1994**, *106*, 2164; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2089.
[12] D. Walther, *Z. Chem.* **1975**, *15*, 490.
[13] J. Jacques, M. Leclercq, M. J. Brienne, *Tetrahedron* **1981**, *37*, 1727.
[14] W. Clegg, M. R. J. Elsegood, R. Snaith, A. E. H. Wheatley, *Acta Crystallogr., Sect. E* **2003**, *59*, M225.
[15] S. Saito, M. Shiozawa, H. Yamamoto, personal communication, CCDC 112322, QULXUQ, **2001**.
[16] S. Saito, T. Nagahara, M. Shiozawa, M. Nakadai, H. Yamamoto, *J. Am. Chem. Soc.* **2003**, *125*, 6200.
[17] S. Saito, S. Yamazaki, H. Yamamoto, *Angew. Chem.* **2001**, *113*, 3725; *Angew. Chem. Int. Ed.* **2001**, *40*, 3613.
[18] S. Saito, M. Shiozawa, T. Nagahara, M. Nakadai, H. Yamamoto, *J. Am. Chem. Soc.* **2000**, *122*, 7847.
[19] S. Saito, M. Shiozawa, H. Yamamoto, *Angew. Chem.* **1999**, *111*, 1884; *Angew. Chem. Int. Ed.* **1999**, *38*, 1769.
[20] S. Saito, M. Ito, H. Yamamoto, *J. Am. Chem. Soc.* **1997**, *119*, 611.
[21] K. Maruoka, M. Ito, H. Yamamoto, *J. Am. Chem. Soc.* **1995**, *117*, 9091.
[22] K. Maruoka, H. Imoto, S. Saito, H. Yamamoto, *J. Am. Chem. Soc.* **1994**, *116*, 4131.
[23] D. K. Kondepudi, R. J. Kaufman, N. Singh, *Science* **1990**, *250*, 975.
[24] D. K. Kondepudi, J. Laudadio, K. Asakura, *J. Am. Chem. Soc.* **1999**, *121*, 1448.
[25] J. M. McBride, R. L. Carter, *Angew. Chem.* **1991**, *103*, 298; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 293.
[26] M. Håkansson, M. Vestergren, B. Gustafsson, G. Hilmersson, *Angew. Chem.* **1999**, *111*, 2336; *Angew. Chem. Int. Ed.* **1999**, *38*, 2199.
[27] A. Lennartson, M. Vestergren, M. Håkansson, *Chem. Eur. J.* **2005**, *11*, 1757.
[28] M. Vestergren, A. Johansson, A. Lennartson, M. Håkansson, *Mendeleev Commun.* **2004**, *14*, 258.
[29] R. Kuroda, T. Honma, *Chirality* **2000**, *12*, 269.
[30] H. D. Flack, G. Bernardinelli, *J. Appl. Crystallogr.* **2000**, *33*, 1143.
[31] H. D. Flack, G. Bernardinelli, *Acta Crystallogr., Sect. A* **1999**, *55*, 908.
[32] K. Tanaka, F. Toda, *Chem. Rev.* **2000**, *100*, 1025.
[33] K. Penzien, G. M. J. Schmidt, *Angew. Chem.* **1969**, *81*, 628; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 608.
[34] N. Conley, R. N. Compton, R. M. Pagni, *Mendeleev Commun.* **2004**, *14*, 296.
[35] M. Nishio, *CrystEngComm* **2004**, *6*, 130.
[36] M. Håkansson, *Inorg. Synth.* **1998**, *32*, 222.
[37] R. Fischer, D. Walther, P. Gebhardt, H. Goerls, *Organometallics* **2000**, *19*, 2532.
[38] G. M. Sheldrick, SHELX97 - Programs for Crystal Structure Analysis (Release 97–2), Universität Göttingen, Göttingen (Germany), **1998**.
[39] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115.
[40] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.
[41] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.
[42] A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht (The Netherlands), **2002**.

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