Synthesis of (*P*)- and (*M*)-6,7-Bis[(diphenylphosphanyl)methyl]-8,12-diphenylbenzo[*a*]heptalenes – Potential Ligands for Homogeneous Asymmetric Catalysis

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The title bis(phosphane) ligands have been prepared starting from optically pure diisopropyl (*P*)- and (*M*)-8,12-diphenylbenzo[*a*]heptalene-6,7-dicarboxylates ((*P*)-**1b** and (*M*)-**1b**) that had been obtained by HPLC separation of *rac*-**1b** on a semi-preparative *Chiralcel OD* column. Reduction of (*P*)-**1b** and (*M*)-**1b** with diisobutylaluminum hydride (DIBAH) gave optically pure (*P*)- and (*M*)-dimethanols **3** (*Scheme 6* and *Fig. 5*). Unfortunately, the almost quantitative chlorination of *rac*-**3** with PCl_5 in $CHCl_3$ at $-60°$ led with (*M*)-**3** to nearly complete loss of optical integrity. However, mesylate formation of (*P*)-**3**, followed by phosphanylation with $LiP(BH_3)Ph_2$ gave (*P*)-**6** with only a small loss of optical activity. Optically pure (*P*)-**6** was obtained by crystallization from Et_2O/hexane, which removed the nearly insoluble *rac*-**6**. The pure bis(phosphane) ligands (*P*)-**2** and (*M*)-**2** can be liberated quantitatively from **6** by warming **6** in toluene in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO). First Rh^I-catalyzed asymmetric hydrogenation reactions of (*Z*)-α-(acetamido)cinnamic acid ((*Z*)-**14**) in the presence of (*P*)-**2** led to (*R*)-*N*-acetylphenylalanin ((*R*)-**15**) in optical purities up to 77% (see *Table 1*).

1. Introduction. – The inherently chiral skeletal backbone of heptalenes (*cf.* [1] [2]) stimulates to experimentally investigate the question whether it would be useful as a template for bidentate ligands for homogeneous transition-metal catalysis. In contrast to the well-established class of unsymmetrically 2,2′-substituted 1,1′-biphenyls, including α,α-binaphthyls (see [3] and especially [4] and refs. cit. therein), with more or less free adjustable torsion angles at the axis of chirality, *peri*-substituted heptalenes show defined torsion angles at the central C(5a)–C(10a) bond, which also determine the 'opening angle' at the adjacent *peri*-positions, as well as at the C=C and C–C bonds of the perimeter (*cf. Fig. 1*) [5] [6]. The energies of activation and thus the temperatures for the racemization of heptalenes, which is characterized by double ring inversion, are dependent on the size and number of *peri*-substituents (*cf.* [7] [8]) and may be adjustable well above the working temperatures for homogeneous catalysis. In addition, unsymmetrically substituted heptalenes always occur in two double bond-shifted (DBS) isomers, which are interconvertible thermally or photochemically with retention of configuration [9] (see also [8]). The E_a (DBS) value is hereby regularly smaller than the E_a(*rac*) value. Therefore, heptalenes, substituted vicinally at their perimeter with *n*-donor groups for transition-metal complexation, can principally be switched thermally or photochemically between two torsion-angle regions of *ca.* 0 and 30° (*Fig. 2*). There is, however, one exceptional case, where heptalenes carry the

[1]) Part of the Ph. D. thesis of *P.M.*, University of Zürich, 1999.

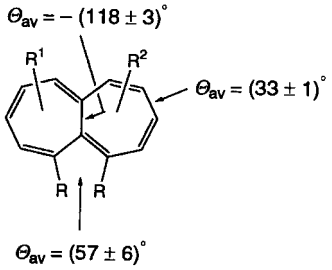


Fig. 1. *Average torsion angles of* peri-*substituted heptalenes according to X-ray crystal-structure analyses*

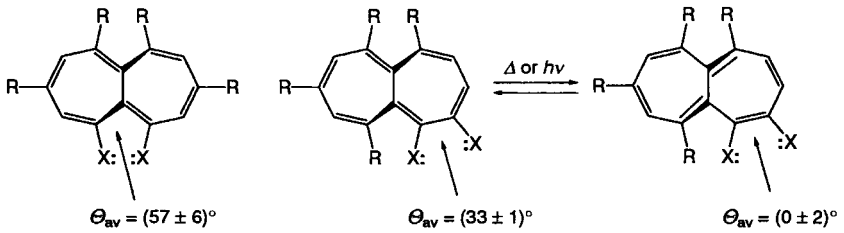
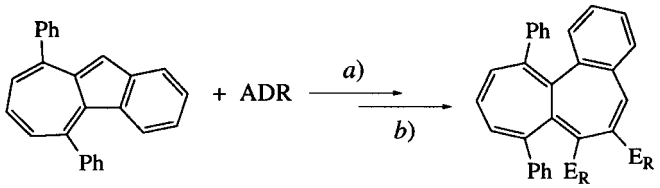


Fig. 2. *Possible substitution patterns of heptalenes with n-donor groups for transition metal complexation*

same substituents symmetrically distributed over both seven-membered rings. In this case, the C_2-axis of symmetry is preserved in the course of the DBS process, *i.e.*, the DBS process becomes isoenergonic, because reactant and product are identical. Benzo[*a*]-anellation of heptalenes suppresses the DBS process completely, since it would lead to an energetically unfavorable *o*-quinomethane substructure of heptalenes [10] [11] (see also [12]). All these specific properties make heptalenes attractive for their chemical modification into chiral ligands for homogeneous transition-metal catalysis.

2. Synthesis of (*P*)- and (*M*)-6,7-Bis[(diphenylphosphanyl)methyl]-8,12-diphenylbenzo[*a*]heptalene ((*P*)-2 and (*M*)-2, resp.). – The most facile access to heptalenes is by no means *Hafner*'s synthesis of dialkyl heptalene-1,2-dicarboxylates and/or heptalene-4,5-dicarboxylates from azulenes and dialkyl acetylenedicarboxylates [8b] [13], which, as we found, can also be applied to the synthesis of benzo[*a*]heptalenes if one attempts at the synthesis with benz[*a*]azulenes [10] [11b] [14]. An example that we have discussed in detail in a preceding publication [15] is shown in *Scheme 1*. The X-ray crystal-structure analysis of the dimethyl benzo[*a*]heptalene-6,7-dicarboxylate **1a** exhibits a torsion angle $\Theta = 40.1^\circ$ between the two carbonyl C-atoms at C(6) and C(7), which is by 7° larger than in dimethyl 1,2,6,8,10-pentamethylheptalene-4,5-dicarboxylate, an analog, which shows the same substitution pattern at its heptalene core as **1a**. The enlargement of the peripheral torsion angle of **1a** as compared with the corresponding heptalene pendant is an effect of the benzo[*a*]-anellation and not attributable to the Ph substituent at C(8) of **1a**, since the unsubstituted dimethyl benzo[*a*]heptalene-6,7-dicarboxylate shows a torsion angle of $\Theta = 44.0^\circ$ between the

Scheme 1



***rac*-1a** R = Me
***rac*-1b** R = i-Pr

For R = Me: *a*) 3 mol-equiv. ADM/MeCN, 100°/18 h; *b*) DMF, 150°; 83% [15]. For R = i-Pr: *a*) 3 mol-equiv. ADiP + 2 mol-% [$RuH_2(PPh)_4$]/MeCN, 100°/72 h; *b*) DMF, 150°/5 h; 81% [15].

carbonyl C-atoms at C(6) and C(7) (*cf.* Table 6 in [15]). The good accessibility of **1**, the thermal stability of **1a** against racemization up to 150° [10], the frozen DBS process, and the comparably large torsion angle between the carboxylic groups make this type of heptalenes ideal precursors of the bis[(diphenylphosphanyl)methyl]-substituted heptalenes (+)-**2** and (−)-**2** as first examples of a new class of chiral ligand systems for homogeneous asymmetric transition-metal catalysis (*cf.* [3]).

2.1. *Synthesis of* rac-**2**. The general procedure for the formation of *rac*-**2** is depicted in *Scheme 2*. The reduction of *rac*-**1a** to the corresponding dimethanol *rac*-**3** with diisobutylaluminum hydride (DIBAH) in THF has already been described by us [16]. Two by-products that result from the selective reduction of the sterically less hindered MeOCO group at C(6) can easily be removed by column chromatography on silica gel (*cf.* [16]). In the meantime, we identified a third by-product, which is present in $< 1\%$ in the reaction mixture. Its structure, **7** (*Scheme 3*), was elucidated by an X-ray crystral-structure analysis (see *Exper. Part*). Obviously, compound **7** is the result of a 1,4-reduction of the MeOCO group at C(6), followed by reduction of MeOCO−C(7) and subsequent lactonization (*Scheme 3*)[2]). After column chromatography, purified *rac*-**3** was obtained as a solid yellow foam, which was not crystallized.

Whereas chlorination of *rac*-**3** with CCl_4/PPh_3 (25°/72 h) [17] or *N*-chlorosuccinimide (NCS)/Me_2S (0°/15 h) [18] gave the expected dichloride *rac*-**4** in yields of only $< 10\%$, the reaction of *rac*-**3** with PCl_5 in $CHCl_3$ at −60°, a procedure that had already been successfully applied to heptalene-dimethanols by *Hafner et al.* [19], provided *rac*-**4** almost quantitatively. Dichloride *rac*-**4** was isolated as yellow foam after column chromatography.

The nucleophilic exchange of the two Cl substituents of *rac*-**4** by diphenylphosphanyl groups could easily be realized in good yield with a 50% molar excess of lithium diphenylphosphanide in THF at 0°. However, the purification of the bis[(diphenylphosphanyl)methyl]heptalene *rac*-**2** was difficult, since it decomposed on column chromatography on silica gel, and the sole product that could be isolated in small

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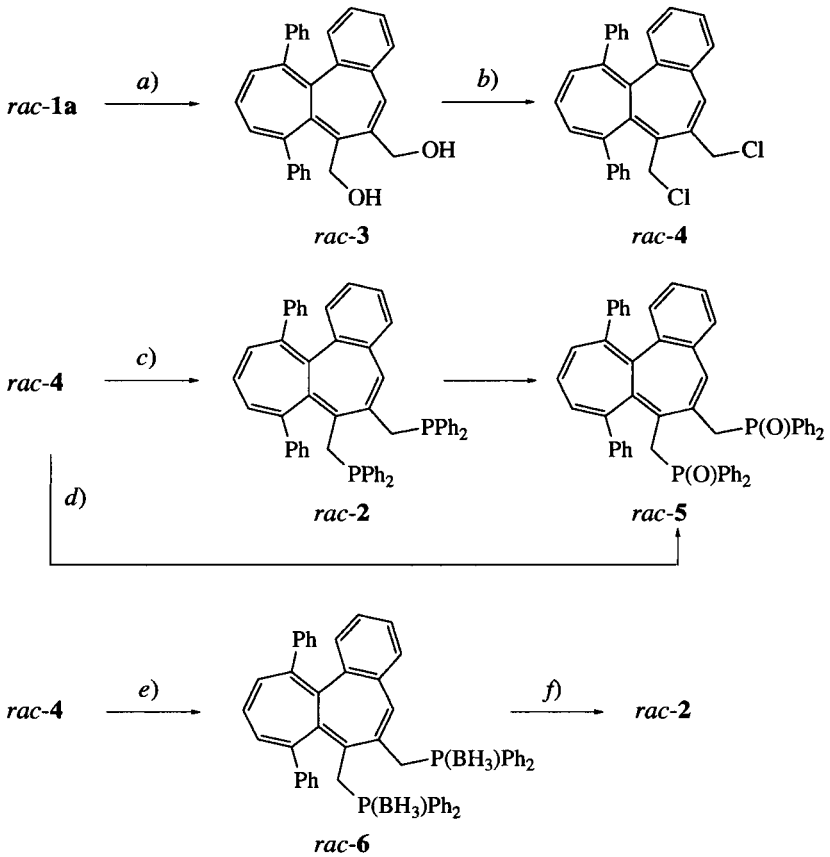
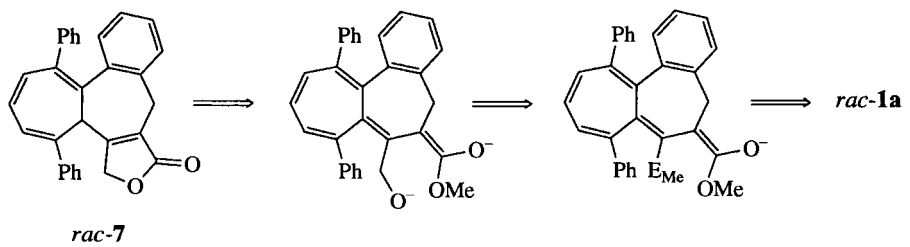
[2]) We can definitely exclude that *rac*-**7** is formed *via* a 1,4-reduction of the furan-3-one that could be generated by selective reduction of MeOCO−C(7) of *rac*-**1a,** followed by lactonization, since reduction of this furan-3-one, which is available by dehydrogenation of *rac*-**3** with MnO_2 (*cf.* [16]), with DIBAH in THF does not lead to the formation of *rac*-**7**.

Scheme 2



a) DIBAH (20%)/hexane, THF, 0°/2.5 h; 89% [16]. *b*) $PCl_5/CHCl_3$, −60°/2 h; 97%. *c*) 3 mol-equiv. $LiPPh_2$/THF, 0° → r.t./2.5 h; 89%. *d*) 3 mol-equiv. $LiP(O)Ph_2$/THF, 0° → r.t./2.5 h; 77%. *e*) 6 mol-equiv. $LiP(BH_3)Ph_2$/THF, 0° → r.t./12 h; 83%. *f*) DABCO/toluene, 60°/4 h; quant.

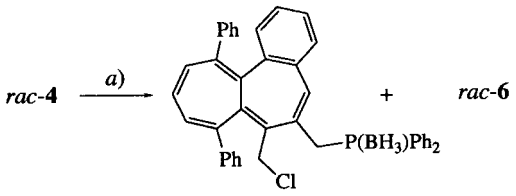
Scheme 3



amounts was the corresponding bis(phosphane oxide) *rac*-**5**. The latter compound was available in pure form (yellow needles) by reaction of *rac*-**4** with lithium oxidodiphenylphosphanide in THF (*Scheme 2*).

In principle, phosphane oxides such as *rac*-**5** can be reduced with Cl_3SiH or $PhSiH_3$ to the corresponding phosphanes (*cf.*, *e.g.*, [20]). However, in view of the difficulties to purify *rac*-**2** by chromatographic means, we looked for a protecting group of the two phosphane moieties of *rac*-**2** that could be removed more easily and also much smoother than oxido substituents. Recently, BH_3 has been successfully introduced as an excellent protecting group for phosphanes [21–23] (*cf.* also [24–25]), which withstands strongly basic media and oxidation by air [26], but can readily be removed with amines such as 1,4-diazabicyclo[2.2.2]octane (DABCO) [22] or with acids, *e.g.*, HBF_4 [27], under mild conditions. The reaction of *rac*-**4** with 2.2 mol-equiv. of lithium boranyldiphenylphosphanide in THF at $-78°$ to room temperature gave *rac*-**6** only in trace amounts. The main product was the mono-substitution product *rac*-**8** that was isolated in a yield of 42% (*Scheme 4*). However, in the presence of 6 mol-equiv. of $Ph_2(BH_3)PLi$ at 0° to room temperature both Cl substituents were smoothly exchanged by the boranyldiphenylphosphanyl group to give *rac*-**6** in 83% yield. The heptalenes *rac*-**6**, as well as *rac*-**8**, could easily be purified by column chromatography on silica gel and further by crystallization.

Scheme 4



a) 2.2 mol-equiv. $LiP(BH_3)Ph_2$/THF, $-78 \rightarrow 0°$/12.5 h; 42% of *rac*-**8**; trace amounts of *rac*-**6**.

The bis[(boranyldiphenylphosphanyl)methyl]heptalene *rac*-**6** crystallized from CH_2Cl_2/hexane in pale yellow, triangular prisms with one molecule of CH_2Cl_2. The X-ray crystal-structure analysis of one of these crystals gave only a poor quality of the refinement results (see *Exper. Part*), which may be partly due to the presence of the highly disordered CH_2Cl_2 molecules and partly due to the quality of the original data related to the quality of the crystals. Nevertheless, the overall geometry of *rac*-**6** is clearly defined (*Fig. 3*), whereas the accuracy of the atomic parameters is of substandard quality. Obviously, the crystal conformation of *rac*-**6** is mainly determined by an optimal spatial arrangement of the four Ph groups at the P-atoms of the two phosphanylmethyl substituents and the two Ph groups at C(8) and C(12) in relation to the inward tilted benzo ring at the C_2-twisted heptalene skeleton. The orientations of the two phosphanylmethyl substituents are more or less interrelated by a pseudo-C_2 axis, passing through the middle of the C(6)–C(7) bond, with the BH_3 groups at the two P-atoms pointing inward (*i.e.*, towards the pseudo-C_2 axis), whereby the two sterically bulkier Ph groups at each P-atom are placed outward. This spatial situation leads to interactions with the two Ph groups at C(8) and C(12). Whereas the *pro-S*-Ph group of $Ph_2(BH_3)PCH_2$–C(6) in the displayed (*M*)-configuration of the heptalene skeleton (*cf. Fig. 3*) shows no recognizable interactions with the heptalene core, the orientation of the *pro-R*-Ph group is influenced by the Ph group at C(12), with the

result that both are situated in nearly parallel planes (deviation from perfect parallelism 6°) with a distance of 3.5 Å between the planes and 4.6 Å between the centroids of the Ph rings. On the other hand, the *pro-R*-Ph group of $Ph_2(BH_3)PCH_2-C(7)$ matches an edge-to-face orientation across the heptalene skeleton with the benzo ring (distances of the corresponding H_o- and H_m-atoms to the centroid of the benzo ring are 3.4 and 3.3 Å, resp.) and a loose face-to-face arrangement with the Ph group at C(8). The latter one is also involved in a quite short perpendicular contact with the corresponding H_o-atom of the pro-*S*-Ph group of $Ph_2(BH_3)PCH_2-C(7)$ (distance of the H_o-atom to the centroid of Ph group 2.8 Å), which, on the other hand, exhibits no further intramolecular interactions. In this manner, a cavity between the two P-atoms is formed that is occupied by the two BH_3 groups, but may also accommodate exchangeable ligands carrying transition metals instead of the boranyl groups.

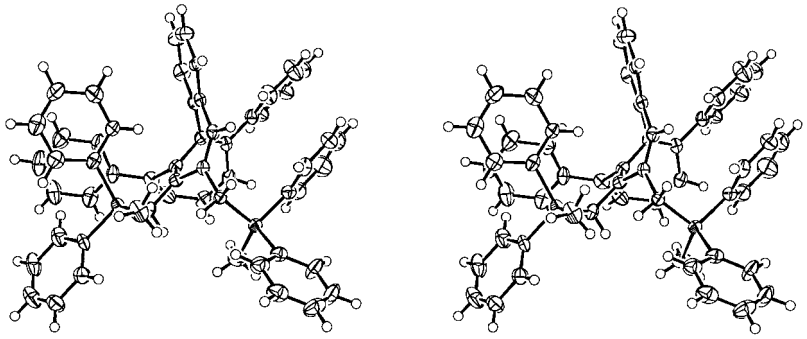


Fig. 3. *Stereoscopic view of the crystal structure of* rac-*6,7-bis[(boranyldiphenylphosphanyl)methyl]-8,12-diphenylbenzo[*a*]heptalene* (*rac*-**6**; displayed in ORTEP representation and (*M*)-configuration[3]))

Heating *rac*-**6** with DABCO in toluene at 60° during 4 h, followed by extraction of DABCO with 2N aqueous HCl and removal of the solvent after drying, gave the pure diphosphane *rac*-**2** (^{1}H-NMR control) which was not further purified.

2.2. *Optical Resolutions and Synthesis of* (P)-**2** *and* (M)-**2**. For the first time, heptalenes have been separated into their antipodes *via* fractionated crystallization of the ammonium salts of 5(4)-methoxycarbonylheptalene-4(5)-carboxylic acids with (+)-(*R*)-1-phenylethylamine or (−)-(1*R*,2*S*)-ephedrine [28] [29] (see also [8b] [17b], as well as [30]). As other dimethyl heptalene-4,5-dicarboxylates, *rac*-**1a** can selectively be saponified at the sterically less congested ester group at C(6) to the mono-acid *rac*-**9** (*Scheme 5*). Unfortunately, we were not able to crystallize the ammonium salts of this acid with the above-mentioned amines. The fractionated crystallization of the brucine salts of *rac*-**9** gave also unsatisfactory results[4]). Therefore, we did not further follow the optical resolution of *rac*-**9**.

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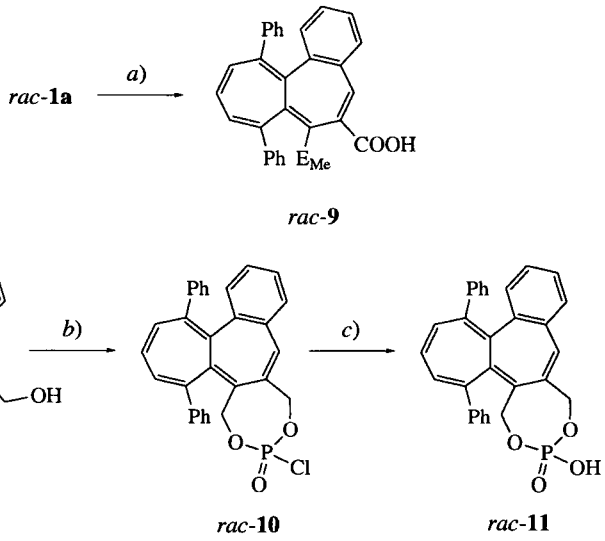
[3]) The helicity descriptors (*M*) and (*P*) refer to the central C(7a)–C(12a) heptalene bond. The designation of the helicity at the C(12a)–C(12b) bond that characterizes the heptalene-benzo ring junction is omitted. Its helicity is always opposite to that at the central heptalene bond that determines the overall chirality of the benzo[*a*]heptalenes (see also later).

[4]) In AcOEt, salt formation was observed after 16 month! However, the HPLC analysis of **1a**, which was formed of the recovered mono-acid **9** from the crystallized salt with CH_2N_2, on an analytical *Chiralcel OD* column (*cf.* [15] and later) indicated an enantiomeric excess (ee) of only 18% of (+)-(*M*)-**1a**.

Scheme 5



a) KOH in EtOH/H_2O (1:1), 50°/22 h; 82%. *b*) $POCl_3 + Et_3N/CH_2Cl_2$, r.t./1 h; 56%; *c*) 2% aq. Na_2CO_3, r.t./1 h, then HCl, 100°/10 min; 18%.

Cram et al. [31] resolved [1,1′-binaphthalene]-2,2′-diol by formation of the cyclic phosphoric acid diester, which was separated into the antipodes by salt formation with cinchonine. Since the phosphoric acid diester forms with [1,1′-binaphthalene]-2,2′-diol a seven-membered phosphadioxa ring, we applied the procedure to the heptalene-dimethanol *rac*-**3**, which should form a comparable seven-membered phosphadioxa ring. Indeed, reaction of the diol with $POCl_3$ gave the cyclic diester chloride *rac*-**10** in a yield of 56% as a 1:1 mixture of diastereoisomers (*Scheme 5*). Since the hydrolysis of this mixture according to the procedure of *Cram et al.* gave the acid *rac*-**11** in yields of only $\leq 18\%$, we abandoned resolution experiments of the acid with cinchonine.

Recently, *Cai et al.* [32] separated the antipodes [1,1′-binaphthalene]-2,2′-diol by complex formation with *N*-benzylcinchonidinium chloride in boiling MeCN. The pure diastereoisomeric complex was then decomposed with aqueous 1N HCl. Indeed, we observed with *rac*-**3** and the cinchonidinium salt the formation of a powdery precipitate, but the decomposition of this precipitate with 1N HCl gave back *rac*-**3**.

Finally, we tried to form diastereoisomeric benzo[*a*]heptaleno-pyrrolidinium chlorides by reaction of the dichloride *rac*-**4** with (−)-(1*R*,2*S*)-ephedrine in boiling $MeCN/C_6H_6$, in analogy with a procedure of *Maigrot* and *Mazaleyrat* [33]. Ephedrine hydrochloride separated after a short time from the reaction mixture, but, after its removal by filtration, no crystallization of the pyrrolidinium salts occurred, and no further experiments were undertaken.

Since all our attempts for a chemical resolution had failed, we returned to our earlier observation that the antipodes of the diester *rac*-**1a** can be separated chromatographically – at least on an analytical scale – on an HPLC *Chiralcel OD* column [10]. In principle, all simple dialkyl esters of type *rac*-**1** can be resolved on a *Chiralcel OD* column, however,

the best separation factors ($t_R(P)$-form/$t_R(M)$-form) are observed for *rac*-**1a** and *rac*-**1b** [15]. The HPLC results for *rac*-**1a** and *rac*-**1b** with hexane/i-PrOH 95 : 5 as eluant under optimized conditions are displayed in *Fig. 4*. The separation factors of 1.55 and 1.42, respectively, are excellent for both diesters. Nevertheless, the solubility of *rac*-**1a** is with a 3 mg/ml eluant mixture three times smaller than for *rac*-**1b** with 10 mg/ml. Therefore, we resolved *rac*-**1b** on a semi-preparative *Chiralcel OD* column (see *Exper. Part*), which allowed 4-ml injections of *rac*-**1b** without loss of base-line separation of the antipodes, *i.e.*, each 40-mg injection led to 20 mg of optically pure (+)-(*M*)-**1b** and (−)-(*P*)-**1b**. The CD spectrum of (+)-(*M*)-**1b**, which correlates at the long-wavelength heptalene-band region (364 nm) perfectly with that of dimethyl (+)-(*M*)-1,6,8,10-tetramethyl-heptalene-4,5-dicarboxylate (*cf.* [7] [10] [29]), as well as of other pentamethoxy-benzo-[*a*]heptalenes [11] or tetra- and pentamethyl-heptaleno[1,2-*c*]furans [16] (*Fig. 5,a*).

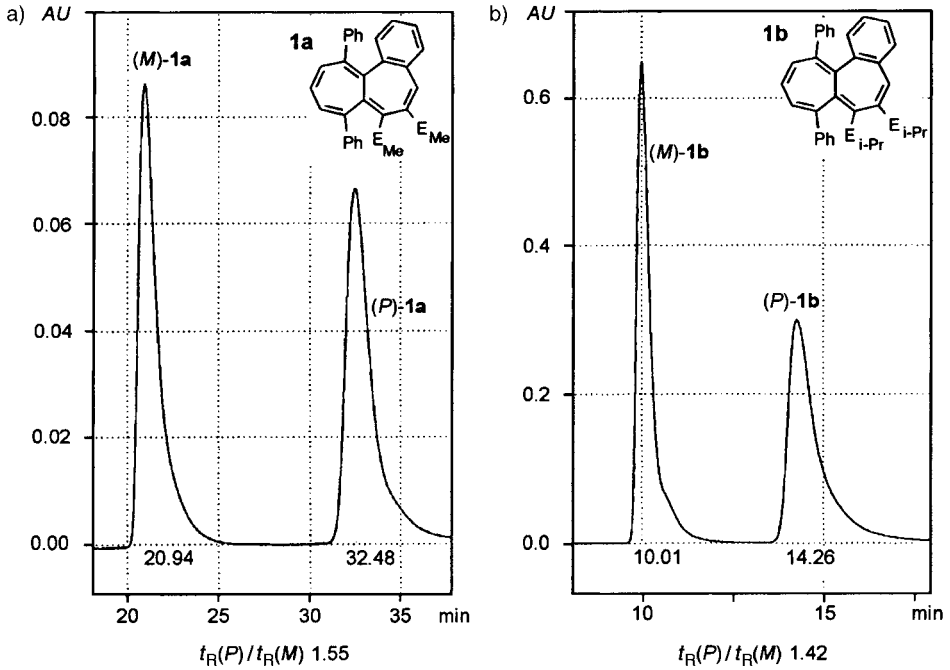


Fig. 4. *Optical resolution of* a) rac-**1a** *and* b) rac-**1b** *on an analytical* Chiralcel *OD column* (eluant: hexane/i-PrOH 95 : 5; flow rate: 0.8 ml/min; temp.: 20°; detection wavelength: 284 nm)

Reduction of the enantiomers of **1b** with DIBAH in THF at ambient temperature led to the corresponding enantiomers of the dimethanol **3** in somewhat lower yields than the reduction of the dimethyl diester *rac*-**1a** (see *Scheme 6*). The CD spectrum of (+)-(*M*)-**3** is displayed in *Fig. 5,b*. As expected, there is almost no change in the position of the heptalene band at 361 nm[5]). Only a slight hypochromic effect of $\Delta\varepsilon$

[5]) (−)-(*P*)-1,5,6,8-Tetramethylheptalene-4,5-dimethanol exhibits its longest-wavelength, negative *Cotton* effect (− CE) in cyclohexane (dioxane) at 345 (349) nm [7] [29] and its DBS isomer, the (−)-(*P*)-1,2-dimethanol, the corresponding − CE (cyclohexane) at 365 nm [16].

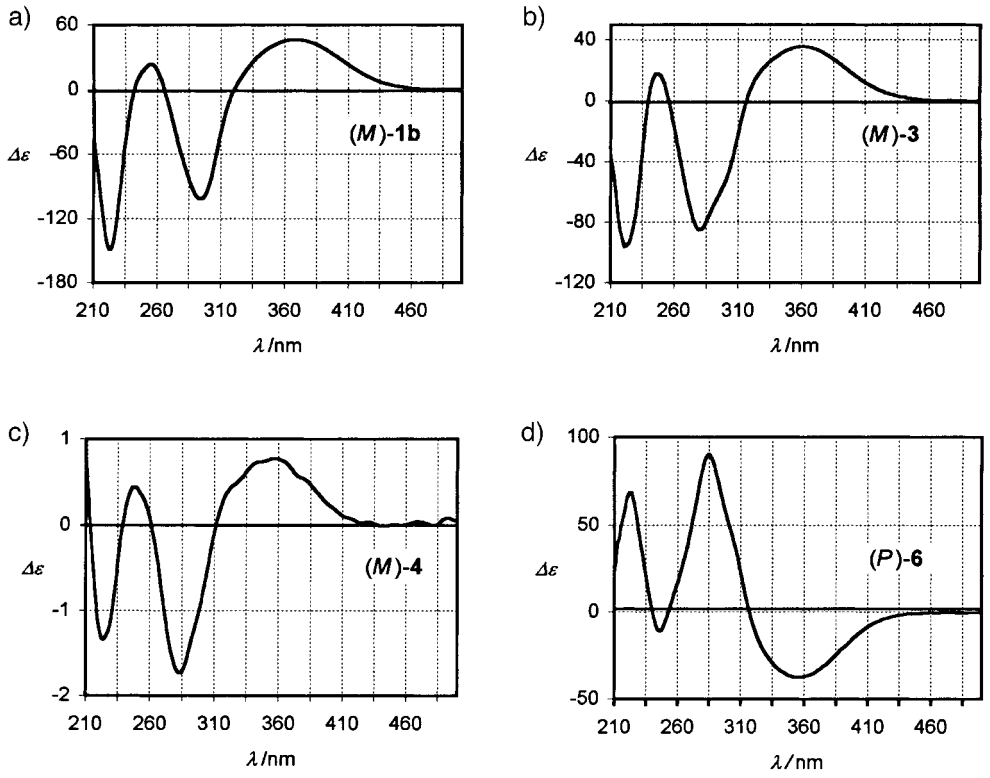
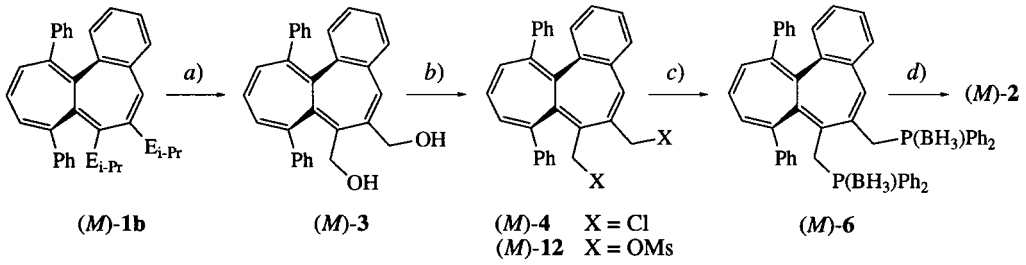


Fig. 5. *CD Spectra of* a) *optically pure (+)-(*M*)-***1b*** (EtOH); b) *optically pure (+)-(*M*)-***3*** (hexane); c) (+)-(*M*)-***4*** (hexane) *from the reaction of (+)-(*M*)-***3*** with $PCl_5/CHCl_3$ at −60°*; d) *(−)-(*P*)-***6*** (enantiomeric purity >99%; hexane)

Scheme 6



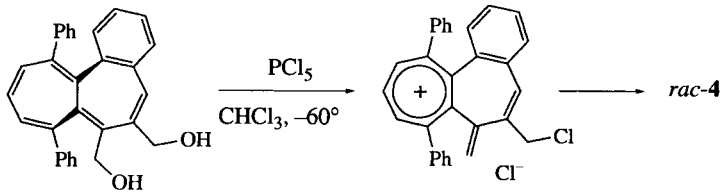
a) 2M DIBAH/hexane, THF, 0° → r.t./3 h; 66%. *b*) X = Cl: $PCl_5/CHCl_3$, −60°/1.5 h; 71%; X = MsO: MsCl + Et_3N/CH_2Cl_2, 0°/30 min, then r.t./2 h; 90%. *c*) X = Cl: see *e*) in *Scheme 2*; X = MsO: in analogy to step *e*) in *Scheme 2*; 33%. *d*) see *f*) in *Scheme 2*.

(+43.2 for **1b** *vs.* +35.9 for **3**) is observed, which may be due to the loss of ester-heptalene conjugation in going from **1b** to **3**.

Hafner et al. [17] (see also [30]) have reported that the reaction of the optical isomers of 1,6,8,10-tetramethylheptalene-4,5-dimethanol with PCl_5 in $CHCl_3$ at −60°

leads not only to an nearly complete loss of optical purity of the formed dichloride, but, in a consecutive step, also to the double-bond shifted heptalene-1,2-bis(methyl chloride). Presumably, in the presence of the formed HCl, planar heptalenium ions are generated that are responsible for racemization and the formation of DBS isomers. The heptalene-6,7-dimethanol **3** cannot undergo the DBS process, and the *peri*-positions of the central heptalene part are occupied by Ph groups and the benzo ring, which may hinder the formation of planar heptalenium ions of type **13** (*Scheme 7*). However, when optically pure (+)-(*M*)-**3** was reacted with PCl_5 at $-60°$ (*Scheme 6*), we obtained also almost *rac*-**4** with a residual optical purity of *ca.* 2% according to its CD spectrum in comparison with that of optical pure (+)-(*M*)-**3** (see *Fig. 5,b* and *c*). The optical purity (2%) of (+)-(*M*)-**4** was corroborated by its transformation with $LiP(BH_3)Ph_2$ into (+)-(*M*)-**6** (*cf. Scheme 6*), which also displayed an optical purity of *ca.* 2% on the basis of the CD spectrum of the optically pure material (*cf. Fig. 5,d*). The latter was obtained by reaction of optically pure (−)-(*P*)-**3** with MsCl, followed by substitution of the bis(methanesulfonate) (*P*)-**12** with 6 mol-equiv. of $LiP(BH_3)Ph_2$ in THF (*Scheme 6*). The resulting compound (−)-(*P*)-**6** showed, on an analytical, chiral HPLC column (type (*S,S*)-*Whelk-01*; *cf. Exper. Part*), an enantiomeric composition of 90% (*P*)-**6** and 10% (*M*)-**6**, *i.e.*, some racemization had also occurred on the bis(methanesulfonate) path. Fortunately, *rac*-**6** is much less soluble in hexane/CH_2Cl_2 mixtures than the pure enantiomers so that *rac*-**6** could be separated almost completely by one crystallization. The mother liquor contained (−)-(*P*)-**6** in an enantiomeric purity of $>99\%$ according to HPLC analysis (*i.e.*, ee $\geq 98\%$). The CD spectrum of (−)-(*P*)-**6** (*Fig. 5,d*) exhibits the longest-wavelength heptalene CE at 354 nm ($\Delta\varepsilon = -37.4$) of comparable intensity as that of the dimethanol (+)-(*M*)-3, which appears, slightly bathochromically shifted, at 361 nm. This shift effect clearly indicates a stronger twisting of the heptalene skeleton of the bis[(boranyldiphenylphosphanyl)methyl]-substituted derivative **6** in comparison with the dimethanol **3** due to the sterically much bulkier substituents at C(6) and C(7) of **6** (see also the discussions in [11] [16]).

Scheme 7



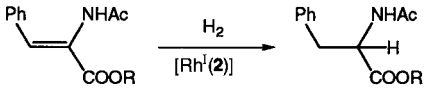
(*M*)-**3** **13**

The liberation of the free bis(phosphanes) (+)-(*M*)-**2** and (−)-(*P*)-**2** was performed as for the racemic material (*Scheme 6*). They were used without further characterization in first homogeneous catalysis experiments.

3. Homogeneous Hydrogenation of (*Z*)-α-Acetamidocinnamic Acid in the Presence of (*M*)-2 and (*P*)-2. (*Z*)-α-Acetamidocinnamic acid ((*Z*)-**14**) has mostly been used as a test compound in Rh^I-catalyzed, homogeneous asymmetric hydrogenation

experiments (see *Table 1*). The optical or the enantiomeric purity of the formed *N*-acetylphenylalanin (**15**) can easily be derived from the $[\alpha]_D$ values of the free acid and/or by HPLC of the corresponding methyl ester **16** on a chiral phase. Therefore, we tested our new ligands also in the Rh^I-catalyzed hydrogenation of (*Z*)-**14** and its methyl ester (*Z*)-**17**. We generated the corresponding complexes with (*M*)-**2** and (*P*)-**2** *in situ* by stirring of the [Rh(olefin)] complex with the heptalene ligands in the corresponding solvent or solvent mixture for the hydrogenation experiment[6]). The results of some non-optimized Rh^I-catalyzed hydrogenation reactions of (*Z*)-**14** and (*Z*)-**17** in the presence of (*P*)-**2** and (*M*)-**2** are summarized in *Table 1*. With the optically pure ligand, we observed for (*Z*)-**14** optical inductions of up to 88.5% (77% ee). These values are comparable with those that had been observed by *Kagan* and *Dang* in their first Rh^I-catalyzed hydrogenation experiments of (*Z*)-**14** in the presence of diop (*Table 2*). Less good results were obtained by *Kumada* and co-workers with the naphos ligand. Both ligands possess like **2** bis(diphenylphosphanylmethyl) substituents link to a chiral backbone. However, whereas diop, like **2**, forms by complex formation with Rh^I ions a seven-membered ring, a nine-membered ring is formed with naphos. On the other hand, ligands such as bppm, bdpp, or norphos that carry bis(diphenylphosphanyl) groups at centers of chirality show higher values of optical inductions in hydrogenation reactions of (*Z*)-**14** (*Table 2*). Nevertheless, the hydrogenation reactions of (*Z*)-**14** or (*Z*)-**17** follow the empirical rule, established by *Noyori* (*cf.* [3c]), that Rh^I-catalyzed hydrogenations of (*Z*)-α-(acylamino)acrylic acids result, with λ-configured bis(diarylphosphanyl)-Rh rings, in the formation of (*S*)-configured α-(acylamino) acids and, in turn, with δ-configured bis(diarylphosphanyl)-Rh rings in the antipodes with (*R*)-

Table 1. *Rh^I-Catalyzed Asymmetric Hydrogenation of (*Z*)-**14** and (*Z*)-**17** in the Presence of (*P*)-**2** and (*M*)-**2***[a])



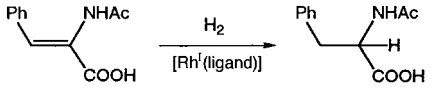
R = H: (*Z*)-**14** (*R*)-**15**/(*S*)-**15**
R = Me: (*Z*)-**17** (*R*)-**15**/(*S*)-**16**

Entry	Substrate	Configuration of ligand **2** (o.p. [%])	Solvent mixture	Chem. yield [%]	Yield of enantiomer **15**(**16**)		ee [%]	Remarks[b])
					(*R*)	(*S*)		
1	(*Z*)-**14**	(*P*) (≥ 99)	THF	93	84.5	15.5	69	HPLC
2	(*Z*)-**14**	(*P*) (≥ 99)	THF	100	88.5	11.5	77	HPLC
3	(*Z*)-**14**	(*M*) (~ 2)	THF	99	36.5	63.5	27	$[\alpha]_D$
4	(*Z*)-**14**	(*M*) (~ 2)	EtOH	100	37	63	26	$[\alpha]_D$
5	(*Z*)-**14**	(*M*) (~ 2)	EtOH/CH_2Cl_2 1 : 1	98	37.5	62.5	25	$[\alpha]_D$
6	(*Z*)-**17**	(*M*) (~ 2)	THF	98	40.5	59.5	19	HPLC
7	(*Z*)-**14**	(*M*) (~ 2)	THF	100	47	53	6	$[\alpha]_D$; 50 mol-% of Et_3N were added

[a]) All hydrogenations were performed at 40°/5 bar; reaction time 24 h (for details, see *Exper. Part*).
[b]) $[\alpha]_D$: only acid **15** was measured; HPLC: determination of amounts of (*R*)-**16** and (*S*)-**16** (for *Entries 1* and *2*, after ester formation).

6) Complex formation with the heptalene ligands could always be recognized by the change of the color of the solution from yellow ([Rh(olefin)] complex) to deep orange ([Rh(**2**)] complex).

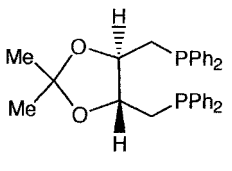
Table 2. *Examples of Rh^{I}-Catalyzed Asymmetric Hydrogenations of (Z)-***14**



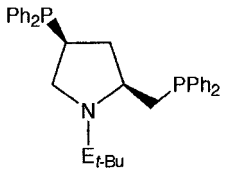
(*Z*)-**14** (*R*)-**15**/(*S*)-**15**

Bisphosphane[a])	Yield of enantiomers of **15** [%]		ee [%]	Ref.
	(*R*)	(*S*)		
(*R*,*R*)-diop	86	14	72	[20c]
(*S*,*S*)-bppm	95.5	4.5	91	[34]
(*S*,*S*)-bdpp	96	4	92	[35]
(*M*)-naphos	23	77	54	[36]
(*S*,*S*)-norphos	2	98	96	[20f]

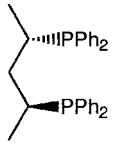
[a])



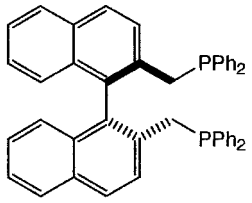
(*R*,*R*)-diop



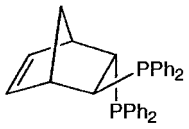
(*S*,*S*)-bppm



(*S*,*S*)-bdpp



(*M*)-naphos

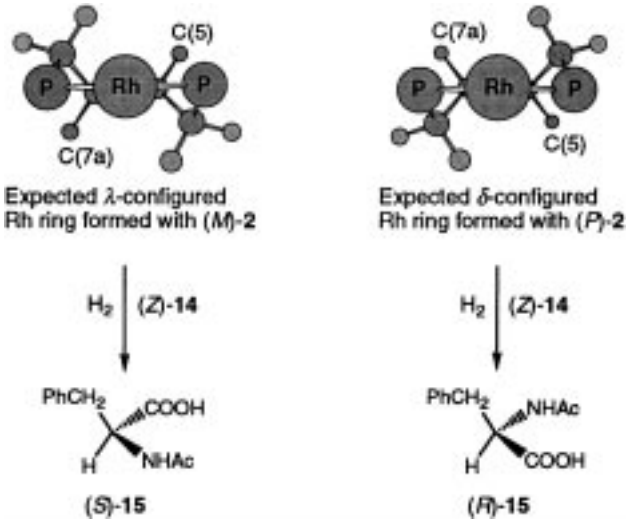


(*S*,*S*)-norphos

configuration (*Scheme 8*). Since (*M*)-**6** (*Fig. 3*) and (*M*)-**2** possess in their $CH_2-C(6)-C(7)-CH_2$ moiety a $+sc$-configuration, in agreement with the case of (*S*,*S*)-diop, for example, they can form with Rh^{I} ions only a λ-configured seven-membered ring, which will induce the preferred formation of (*S*)-α-(acylamino) acids from (*Z*)-α-(acylamino)acrylic acids, as observed with both ligands.

However, much more amazing for us were the results of hydrogenation experiments of (*Z*)-**14** in the presence of (*M*)-**2** that showed an optical purity of only 2%, but led to optical inductions of up to 63.5% (27% ee). This corresponds to an >10fold enhancement in the optical yield. Such 'chiral amplification' effects have been observed, for example, in alkylation reactions of benzaldehydes with dialkylzinc in the presence of catalytic amounts of chiral β-amino alcohols (*cf.* [3c] [37]) and has been attributed to the fact that corresponding homochiral bis(ligand)-Zn complexes are catalytically much more active than the optically inactive heterochiral bis(ligand)-Zn complexes. We should consider a similar situation in the Rh^{I}-catalyzed hydrogenation of (*Z*)-**14** or (*Z*)-**17** in the presence of our highly unsymmetrical ligands (*P*)-**2** and (*M*)-**2**. The fact that a substantial breakdown of the optical yield of (*S*)-**15** is observed, when

Scheme 8



(*Z*)-**14** is hydrogenated in the presence of 50 mol-% of Et_3N with respect to the amount of the substrate (see *Table 2*, *Entry 7*), supports these assumptions. We will come back to this point in a forthcoming publication.

We thank Prof. *M. Hesse* and his co-workers for mass spectra, our NMR Laboratory for specific NMR measurements, Dr. *A. Linden* for the two X-ray crystal-structure analyses, and our Analytical Laboratory for elemental analyses. The financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. See [15]. Specific rotations ($[\alpha]_D$): on a *Perkin-Elmer* polarimeter (model 241 MC). CD Spectra: on a *Jasco* instrument (model *J*-715); maxima (λ_{max}) and minima (λ_{min}) in nm, and $\Delta\varepsilon$ ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$). Anal. HPLC in addition to [15] *LiChroCART® 250-4* HPLC cartridge type (*S,S*)-*Whelk-01* (5 μm; 4.6 × 250 mm) from *Merck*; t_R in min. Prep. HPLC separation of the enantiomers of *rac*-**1b**: on a semi-prep. *Chiralcel OD* column (5 μm; 20 × 250 mm) from *Daicel Chemical Industries*.

1. Racemic Compounds. – 1.1. *Dimethyl and Diisopropyl 8,12-Diphenylbenzo[a]heptalene-6,7-dicarboxylates* (*rac*-**1a** and *rac*-**1b**, resp.). See [15].

1.2. *DIBAH Reduction of* rac-**1a**. See [15]. In addition to the described products, we isolated from the mother liquors of the semi-reduced forms (furan-1-one and 6-(hydroxymethyl)-7-carboxylate) in small amounts (≤1%) pale yellow crystals, which consisted of *5a,6,8,9-tetrahydro*-1,5-diphenylbenzo[4,5]heptaleno[1,2-*c*]furan-8-one (*rac*-**7**).

Data of rac-**7**: M.p. 192.2–193.2° (Et_2O/hexane). R_f (Et_2O/hexane 5:1) 0.26. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.31 (*d* with f.s., $^3J(10,11) = 7.6$, H–C(10)); 7.17–7.03 (*m*, 8 arom. H, H–C(11), H–C(12)); 7.00 (*d*, $^3J(2,3) = 11.1$, H–C(2)); 6.81–6.76 (*m*, 2 arom. H, H–C(3), H–C(4)); 6.42 (*dd*, $^3J(12,13) = 7.7$, $^4J(11,13) = 1.1$, H–C(13)); 4.34, 3.92 (2*d* with f.s., *AB*, $^2J_{AB} \approx 16.8$, $^5J = 2.9$, 2.6, 1.4, 2 H–C(9)); 4.17, 3.78 (2*d* with f.s., *AB*, $^2J_{AB} \approx 15.6$, $^5J = \approx 3.2$, 2.9, 2 H–C(6)); 3.36 (*d*, $^3J(5a,9) = 4.0$, H–C(5a)). EI-MS: 415 (30, $[M+1]^{+\cdot}$), 414 (100, $M^{+\cdot}$), 370 (21, $[M - CO_2]^{+\cdot}$), 369 (26, $[M - CO_2 - 1]^{+\cdot}$), 355 (24, $[M - 59]^{+\cdot}$), 279 (35), 276 (38), 265 (50), 252 (45).

The structure of *rac*-**7** was confirmed by an X-ray crystal-structure analysis (*cf. Table 3*).

1.3. *DIBAH Reduction of* rac-**1b**. The heptalene-diester (0.592 g; 1.12 mmol) was dissolved in THF (25 ml) and 2M DIBAH in hexane (5.6 ml; 11.2 mmol) was added at 0° in a rate that the temp. did not raise. After stirring for 3 h at ambient temp., the mixture was worked up in the usual manner (*cf.* [15]), and the product, *8,12-*

*diphenylbenzo[*a*]heptalene-6,7-dimethanol* (*rac*-**3**), was separated and purified by CC on silica gel. Pure *rac*-**3** (0.308 g, 66%) was obtained as a yellow foam.

Reduction of *rac*-**1b** with $LiAlH_4$ in boiling Et_2O gave *rac*-**3** in a yield of only 19%.

1.4. *6,7-Bis(chloromethyl)-8,12-diphenylbenzo[*a*]heptalene* (*rac*-**4**). Dimethanol **3** (0.417 g, 1.0 mmol) was dissolved in $CHCl_3$ (25 ml) and cooled to $-60°$. Simultaneously, PCl_5 was dissolved in $CHCl_3$ (20 ml), cooled to $-60°$, and then added slowly to the soln. of **3**, thereby avoiding an increase in temp. The color of the mixture turned slowly from yellow to dark orange. DC after 1.5 h showed that all **3** had been consumed, and a new product, *rac*-**4** (R_f (hexane/Et_2O 7:1) 0.39), formed. A sat. aq. soln. of $NaHCO_3$ (50 ml) was added to avoid further reaction, and the $CHCl_3$ phase was washed three times with the $NaHCO_3$ soln. After drying of the $CHCl_3$ phase ($MgSO_4$) and removal of the solvent in a rotatory evaporator, the residue was purified by chromatography over silica gel with hexane/Et_2O 7:1. Pure *rac*-**4** (0.440 g, 97%) was obtained as a stiff yellow foam, which could be crystallized from Et_2O/hexane.

Data of rac-**4**: M.p. 158.6–159.6°. R_f (hexane/Et_2O 7:1) 0.39. UV (hexane): λ_{max} 336 (sh) (3.68), 280.5 (4.47), 229 (sh) (4.57); λ_{min} 257.7 (4.38). IR (KBr): 3055*m*, 3016*m*, 1950*w*, 1596*m*, 1489*m*, 1474*m*, 1443*m*, 1434*m*, 1349*w*, 1304*w*, 1256*m*, 1224*w*, 1178*w*, 1160*w*, 1107*w*, 1075*w*, 1021*w*, 964*w*, 948*w*, 916*w*, 882*w*, 863*w*, 839*w*, 795*m*, 755*s*, 720*s*, 696*s*, 653*m*, 620*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.42 (*d* with f.s., $^3J(4,3) = 7.4$, H–C(4)); 7.41 (*s*, H–C(5)), 7.29–7.23 (*m*, 2 arom. H, H–C(3)); 7.17–7.15 (*m*, 3 arom. H); 7.12–7.06 (*m*, 3 arom. H, H–C(2)); 7.01 (*d*, $^3J(9,10) = 6.1$, H–C(9)); 6.87–6.83 (*m*, 2 arom. H); 6.80 (*dd*, $^3J(10,9) = 6.1$, $^3J(10,11) = 11.5$, H–C(10)); 6.66 (*d*, $^3J(11,10) = 11.5$, H–C(11)); 6.56 (*d* with f.s., $^3J(1,2) = 7.6$, H–C(1)); 4.76 (*d* with f.s., *A* of *AB*, $^2J_{AB} = 11.8$, 1 H, CH_2–C(6)); 4.35 (*d*, *B* of *AB*, $^2J_{AB} = 12.0$, 1 H, CH_2–C(6)); 4.21 (*s*, CH_2–C(7)). ^{13}C-NMR (150 MHz, $CDCl_3$): 40.93 (*t*); 48.49 (*t*); 125.38 (*d*); 126.81 (*d*, 3 × enhanced intensity); 127.25 (*d*); 127.58 (*d*, 2 × enhanced intensity), 127.62 (*d*); 128.47 (*s*); 128.67 (*d*, 2 × enhanced intensity), 128.90 (*d*); 129.23 (*d*); 129.92 (*d*); 130.48 (*d*, 2 × enhanced intensity), 130.70 (*d*); 132.00 (*s*); 133.92 (*d*); 134.26 (*s*); 136.22 (*s*); 136.74 (*d*); 136.74 (*s*); 136.99 (*s*); 137.86 (*s*); 138.55 (*s*); 139.56 (*s*); 139.56 (*s*). EI-MS: 456/454/452 (8/44/79, $M^{+\cdot}$), 419/417 (20/60, $[M-Cl]^{+\cdot}$), 405/403 (6/20, $[M-CH_2Cl]^{+\cdot}$), 381 (72), 367 (41), 365 (26), 330 (100, $[M-(ClH_2C)_2]^{+\cdot}$), 329 (34), 303 (34), 302 (32), 289 (64), 276 (32), 253 (53), 252 (52). Anal. calc. for $C_{30}H_{22}Cl_2$ (453.41): C 79.47, H 4.89; found C 78.71, H 4.90.

1.5. *8,12-Diphenylbenzo[*a*]heptalene-6,7-dimethyl Bis(methanesulfonate)* (*rac*-**12**). A soln. of MsCl (0.093 ml, 1.20 mol) in CH_2Cl_2 (1 ml) was added dropwise at 0° to a soln. of *rac*-**3** (0.208 g, 0.50 mmol) and Et_3N (0.181 ml, 1.30 mmol) in CH_2Cl_2 (5 ml) under stirring. After 30 min, the temp. was raised to ambient temp., and stirring was continued for 2 h. A sat. soln. of NH_4Cl was added, and the aq. phase extracted three times with CH_2Cl_2 and then dried (Na_2SO_4). The solvent was distilled off *in vacuo*, and the solid yellow residue (0.280 g, 106%) was used for the phosphanylation reaction (see *1.7.2*).

Data of rac-**12**: R_f (Et_2O/hexane 4:1) 0.20. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.54 (*s*, H–C(5)); 7.48 (*d* with f.s., $^3J(4,3) = 7.5$, H–C(4)); 7.33 (*td*, $^3J(3,4) = 7.5$, $^4J(3,1) = 1.2$, H–C(3)); 7.29–7.02, 6.87–6.79, 6.67–6.52 (3*m*, 10 arom. H, H–C(1), H–C(2), H–C(9), H–C(10), H–C(11)); 5.33 (*d* with f.s., *A* of *AB*, $^2J_{AB} = 12.9$, 1 H, CH_2–C(6)); 5.11 (*d*, *B* of *AB*, $^2J_{AB} = 12.9$, 1 H, CH_2–C(6)); 4.87 (*d*, *A* of *AB*, $^2J_{AB} = 11.1$, 1 H, CH_2–C(7)); 4.72 (*d*, *B* of *AB*, $^2J_{AB} = 11.1$, 1 H, CH_2–C(7)); 2.88 (*s*, *Me*SO_2OCH_2–C(6)); 2.19 (*s*, $MeSO_2OCH_2$–C(7)).

1.6. *6-[(Boranyldiphenylphosphanyl)methyl]-7-(chloromethyl)-8,12-diphenylbenzo[*a*]heptalene* (*rac*-**8**). $LiP(BH_3)Ph_2$ was prepared by stirring $P(BH_3)Ph_3$ (0.364 g, 1.32 mmol) and Li dust (0.0183 g, 2.64 mmol) in THF (3 ml) at 0°. After 4 h, the originally colorless mixture had turned orange-brown. Then, *t*-BuCl (0.145 ml, 1.32 mmol) was added, and stirring was continued for 30 min. A portion of this soln. (0.5 ml, containing 0.22 mmol of $LiP(BH_3)Ph_2$) was slowly added to a soln., kept at $-78°$, of *rac*-**4** (0.0453 g, 0.10 mmol) in THF (3 ml), whereby the originally yellow mixture turned orange. The mixture was warmed to 0° and then stirred overnight (12.5 h) at ambient temp. 1N HCl (10 ml) was added, and the aqueous phase was extracted three times with Et_2O (10 ml). The combined extracts were washed with sat. NaCl soln. and dried ($MgSO_4$). The residue of the Et_2O extracts, which contained mainly *rac*-**8** and only trace amounts of *rac*-**6**, was chromatographically purified on silica gel (R_f (hexane/Et_2O 7:1) 0.12) to give pure *rac*-**8** (0.042 g, 42%) as yellow crystals.

Data of rac-**8**: M.p. 192° (dec.). R_f (hexane/Et_2O 7:1) 0.12. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.69–7.60 (*m*, 4 arom. H); 7.48–6.97 (*m*, 14 arom. H, H–C(2), H–C(3), H–C(4), H–C(5), H–C(9)); 6.88 (*dd*, $^3J(10,11) = 11.3$, $^3J(10,9) = 6.1$, H–C(10)); 6.70 (*d*, $^3J(11,10) = 11.3$, H–C(11)); 6.58–6.55 (*m*, 2 arom. H); 6.46 (*d*, $^3J(1,2) = 7.7$, H–C(1)); 4.18 (*d*, *A* of *AB*, $^2J_{AB} = 12.5$, 1 H, CH_2–C(7)); 4.09 (*d*, *B* of *AB*, $^2J_{AB} = 12.6$, 1 H, CH_2–C(7)); 3.77 (*dd*, *A* of *ABX*, $^2J_{AB} = 14.1$, $^2J_{AX} = 9.8$, 1 H, CH_2–C(6)); 3.42 (*t*-like, *B* of *ABX*, $^2J_{AB} = 14.5$, $^2J_{BX} = 14.5$, 1 H, CH_2–C(6)); 1.6–0.4 (br. *q*, BH_3).

1.7. *6,7-Bis[(boranyldiphenylphosphanyl)methyl]-8,12-diphenylbenzo[*a*]heptalene* (*rac*-**6**). 1.7.1. *By Phosphanylation of* rac-**4**. $LiP(BH_3)Ph_2$ in THF (4 ml) was prepared from $P(BH_3)Ph_3$ (1.139 g, 4.00 mmol) and Li

dust (0.056 g, 8.00 mmol) at 0°. After 4 h, *t*-BuCl (0.441 ml, 4.00 mmol) was added, and stirring was continued for further 30 min. This soln. (3.0 ml, 3.00 mmol of $LiP(BH_3)Ph_2$) was added at 0° to a second soln. of *rac*-**4** (0.227 g, 0.50 mmol) in THF (15 ml). Thereafter, the mixture was stirred overnight (12 h) at ambient temp. The usual workup (see *1.6*), followed by chromatography on silica gel with hexane/CH_2Cl_2 1:1 (R_f(*rac*-**6**) 0.23) delivered pure *rac*-**6**, which was further purified by crystallization from hexane/CH_2Cl_2, to give rac-**6** as yellow triangular prisms (0.327 g, 83%).

Data of rac-**6**: M.p. 148° (dec.). R_f (hexane/Et_2O 1:1) 0.32. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.59–7.52 (*m*, 2 arom. H); 7.48–7.16 (*m*, 12 arom. H, H–C(3), H–C(4), H–C(5)); 7.08 (*t*, $^3J(1,2) \approx {}^3J(2,3) \approx 7.1$, H–C(2)); 7.03–7.01 (*m*, 2 arom. H)); 6.96 (*d*, $^3J(9,10) = 7.6$, H–C(9)); 6.93–6.65 (*m*, 12 arom. H, H–C(10)); 6.61 (*d*, $^3J(11,10) = 11.1$, H–C(11)); 6.47–6.42 (*m*, 2 arom. H, H–C(1)); 3.93 (*dd*, *A* of *ABX*, $^2J_{AB} = 14.2$, $^2J_{AX} = 10.7$, 1 H, CH_2–C(6)); 3.17 (*t*-like, *B* of *ABX*, $^2J_{AB} \approx {}^2J_{BX} \approx 14.9$, 1 H, CH_2–C(6)); 3.52 (*dd*, *A* of *ABX*, $^2J_{AB} = 15.6$, $^2J_{AX} = 13.5$, 1 H, CH_2–C(7)); 3.33 (*dd*, *B* of *ABX*, $^2J_{AB} = 15.7$, $^2J_{BX} = 9.9$, 1 H, CH_2–C(7)); 1.6–0.4 (br.*q*, 2 BH_3).

The structure of *rac*-**6** was confirmed by an X-ray crystal-structure analysis (see *Fig. 3* and *Table 3*).

1.7.2. *By Phosphanylation of* rac-**12**. The bis(methanesulfonate) *rac*-**12** of *Exper. 1.5* (0.280 g, *ca.* 0.5 mmol) in THF (10 ml) was reacted according to *1.7.1* with 3 mmol of $LiP(BH_3)Ph_2$ in THF. Formed *rac*-**6** (R_f (CH_2Cl_2/hexane 7:3) 0.23) was purified by column chromatography to give *rac*-**6** as a yellow foam (0.130 g, 33% with respect to *rac*-**3** as starting material).

1.8. *6,7-Bis[(diphenylphosphanyl)methyl]-8,12-diphenylbenzo[*a*]heptalene* (*rac*-**2**). 1.8.1. *By Deprotection of* rac-**6** *with DABCO*. The bis(boranyl) compound *rac*-**6** (0.156 g, 0.02 mmol) and DABCO (0.0067 g, 0.06 mmol) were dissolved in toluene (2 ml), and the mixture was heated during 4 h at 60°. After this time, DC indicated that all *rac*-**6** had been consumed, and only *rac*-**2** (R_f (hexane/Et_2O 1:1) 0.57) was present. The mixture was extracted three times with 2N aq. HCl, dried ($MgSO_4$), and the solvent was distilled off *in vacuo*. The ligand *rac*-**2** was obtained in quant. yield as a yellow foam, which was not further purified.

Data of rac-**2**: R_f: see *1.8.1*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.80–6.95 (*m*, 22 arom. H, H–C(2), H–C(3), H–C(4), H–C(5)); 6.90–6.83 (*m*, 4 arom. H, H–C(9)); 6.78–6.73 (*m*, 2 arom. H, H–C(10)); 6.65–6.56 (*m*, 2 arom. H, H–C(11)); 6.47 (*d* with f.s., $^3J(1,2) = 7.5$, H–C(1)); 3.16 (*dd*, *A* of *ABX*, $^2J_{AB} = 14.2$, $^2J_{AX} = 1.8$, 1 H, CH_2–C(6)); 3.00 (*dd* with f.s., *B* of *ABX*, $^2J_{AB} = 14.2$, $^2J_{BX} = 1.8$, 1 H, CH_2–C(6)); 2.89 (*d*, *A* of *ABX*, $^2J_{AB} = 13.7$, $^2J_{AX} \leq 0.3$, 1 H, CH_2–C(7)); 2.61 (*dd*, *B* of *ABX*, $^2J_{AB} = 13.9$, $^2J_{BX} = 3.4$, 1 H, CH_2–C(7)).

1.8.2. *By Deprotection with* $Et_2O \cdot HBF_4$. Compound rac-**6** (0.0156 g, 0.02 mmol) was dissolved in CH_2Cl_2 (2 ml) and treated at −5° with a fivefold excess of HBF_4 (0.3 ml of a 54% soln. in Et_2O, 0.2 mmol). The soln. was then stirred for 20 h at ambient temp. The isolated compound *rac*-**2** was contaminated with several by-products (DC) so that this deprotection procedure of *rac*-**6** was abandoned.

1.8.3. *Phosphanylation of* rac-**4** *with Lithiumdiphenylphosphane*. Ph_2PH (0.186 g, 1.00 mmol) was dissolved in THF (1.5 ml) and, at 0°, lithiated with 1.6M BuLi in hexane (0.66 ml, *ca.* 1 mmol). The dark orange-colored soln. of $LiPPh_2$ was added dropwise at 0° to a solution of *rac*-**4** (0.151 g, 0.33 mmol) in THF (2 ml), as long as the mixture changed its color from olive-green (after addition of a drop of $LiPPh_2$ soln.) to yellow (color of *rac*-**4** as well as of *rac*-**2**). Thereafter, the ice bath was removed, and stirring was continued at ambient temp. for 2.5 h. H_2O was added, and the organic phase was washed five times with H_2O and then dried ($MgSO_4$). After removal of the solvent and drying the residue at 80° for 6 h in high vacuum, *rac*-**2** was obtained as a yellow foam (0.223 g, 89%), which could not further purified by column chromatography on silica gel, since decomposition took place. Only *rac*-**5** could be identified in small amounts after chromatography.

1.9. *8,12-Diphenyl-6,7-bis[(diphenylphosphinoyl)methyl]benzo[*a*]heptalene* (*rac*-**5**). A solution of lithium-oxodiphenylphosphorus in THF (1.5 ml) was prepared by lithiation of hydrido oxodiphenylphosphorus(V) (0.202 g, 1.00 mmol) with 1.6M BuLi in hexane (0.66 ml, *ca.* 1 mmol) at 0°. This soln. was added dropwise to a soln. of *rac*-**4** (0.151 g, 1.00 mmol) in THF (2 ml), according to the procedure in *1.8.2.* Compound *rac*-**5** was purified by isothermal crystallization from THF with pentane, giving yellow crystals of *rac*-**5** (0.202 g, 77%).

Data of rac-**5**: M.p. 130° (dec.). R_f (Et_2O) < 0.05. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.94–7.82 (*m*, 4 arom. H); 7.55–7.49 (*m*, 2 arom. H); 7.44–7.39 (*m*, 2 arom. H, H–C(4), H–C(5)); 7.34–7.23 (*m*, 9 arom. H, H–C(3)); 7.18 (*td*, $^3J(2,1) \approx {}^3J(2,3) = 7.5$, $^4J(2,4) = 1.2$, H–C(2)); 7.09–6.82 (*m*, 8 arom. H, H–C(9), H–C(10), H–C(11)); 6.53–6.29 (*m*, 5 arom. H, H–C(1)); 4.70 (*dd*, *A* of *ABXY*, $^2J_{AB} = 15.6$, $^2J_{AX} = 13.3$, $^4J_{AY} < 0.3$, 1 H, CH_2–C(6)); 3.61 (*td*-like, *B* of *ABXY*, $^2J_{AB} = 15.6$, $^2J_{BX} = 15.6$, $^4J_{BY} = 1.0$, 1 H, CH_2–C(6)); 3.40 (*t*-like, *A* of *ABX*, $^2J_{AB} \approx {}^2J_{AX} \approx 15.7$, 1 H, CH_2–C(7)); 3.32 (*dd*, *B* of *ABX*, $^2J_{AB} \approx 15.7$, $^2J_{BX} \approx 12.4$, 1 H, CH_2–C(7)).

2. Optical Resolution Experiments. 2.1. *7-(Methoxycarbonyl)-8,12-diphenylbenzo[*a*]heptalene-6-carboxylic Acid* (*rac*-**9**). Diester *rac*-**1a** (0.0945 g, 0.20 mmol) was suspended in EtOH (1.25 ml) and aq. KOH (1.25 ml of a soln. of 10 g of KOH in 50 ml of H_2O) was added. The yellow suspension was heated at 50° with stirring,

until a clear yellow soln. was formed (22 h). The cooled mixture was acidified with aq. HCl (1.25 ml of 25% HCl), the yellow precipitate was isolated, dissolved in Et_2O, dried ($MgSO_4$), and, after removal of Et_2O, crystallized from Et_2O/hexane to give pure yellow crystals of *rac*-**9** (0.0765 g, 82%).

Data of rac-**9**: M.p. 191–194° (under evolution of MeOH and anhydride formation). R_f (EtOH) 0.54. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.0 (br.*s*, COOH); 8.49 (*s*, H–C(5)); 7.57 (*d* with f.s., $^3J(4,3) = 7.5$, H–C(4)); 7.31 (*td*, $^3J(3,2) \approx {}^3J(3,4) \approx 7.5$, $^4J(3,1) \approx 1.1$, H–C(3)); 7.18 (*td*, $^3J(2,1) \approx {}^3J(2,3) \approx 7.6$, $^4J(2,4) \approx 1.1$, H–C(2)); 7.15–7.03 (*m*, 8 arom. H); 6.94–6.82 (*m*, 2 arom. H, H–C(9), H–C(10)); 6.68 (*dd*, $^3J(11,10) = 10.9$, $^4J(11,9) = 0.8$, H–C(11)); 6.61 (*d*, $^3J(1,2) = 7.5$, H–C(1)); 3.21 (*s*, MeOCO).

2.1.1. *Attempted Resolution with Brucin.* Acid *rac*-**9** (0.0917 g, 0.20 mmol) and brucin (0.0868 g, 0.22 mmol) were dissolved in AcOEt, whereby instantaneous salt formation occurred. The salt was redissolved at 40° in additional AcOEt (3 ml). For fractionated crystallization, the soln. was stored in a refrigerator at 4°. Crystals were formed after 16 months. The mother liquor was decanted, and the crystals were dried in a stream of N_2, whereby they decomposed to a yellow powder. From the latter, *rac*-**9** (0.011 g, 12%) was recovered and re-esterified with CH_2N_2 in Et_2O. HPLC Analysis (*Chiralcel OD* column; hexane/i-PrOH 93:7; flow rate 0.8 ml/min) indicated the presence of 59% of (*M*)-**1a** and 41% of (*P*)-**1a**.

Resolution experiments of *rac*-**9** with (−)-ephedrine or (+)-1-phenylethylamine in AcOEt were unsuccessful, since no salt formation was observed.

2.2. *Resolution Experiments with* rac-**3**. 2.2.1. *8-Hydroxy-1,5-diphenylbenzo[4,5]heptaleno[1,2-*e*][1,3,2]dioxaphosphepin 3-Oxide* (*rac*-**11**). 2.2.1.1. *8-Chloro-1,5-diphenylbenzo[4,5]heptaleno[1,2-*e*][1,3,2]dioxaphosphepin 3-Oxide* (*rac*-**10**). To *rac*-**3** (0.105 g, 0.25 mmol) in CH_2Cl_2 (5 ml), $POCl_3$ (0.033 ml, 0.36 mmol) was added, followed by Et_3N (0.086 ml, 0.61 mmol), whereby the temp. raised gently until boiling of the mixture. After 1 h, DC revealed that all *rac*-**3** had been consumed, and *rac*-**10** was formed (R_f (Et_2O/hexane 5:1) 0.19 (*rac*-**3**) and 0.35 (*rac*-**10**)). H_2O (5 ml) was added, the org. phase was washed three times with H_2O and then dried ($MgSO_4$). The residue was subjected to CC on silica gel with Et_2O/hexane 2:1. Compound *rac*-**10** (0.070 g, 56%) was obtained as a 1:1 mixture of diastereoisomers as yellow crystals. As a second fraction, *rac*-**4** was isolated (0.021 g, 19%).

Data of rac-**10**. M.p. 120° (dec.). R_f: ^{1}H-NMR (300 MHz, $CDCl_3$; 1:1 mixture of diastereoisomers): 7.56 (*s*, 0.5 H, H–C(11)); 7.50, 7.43 (2*d* with f.s., $^3J(12,13) = 7.7$, 0.5/0.5 H, H–C(12)); 7.32–7.03 (*m*, 0.5/0.5 H, H–C(13), 0.5 H, H–C(11), 10 arom. H); 6.90–6.78 (*m*, 0.5/0.5 H, H–C(14), 0.5 H, H–C(4), and 0.5 H, H–C(3)); 6.69, 6.65 (2*d*, $^3J(2,3) = 11.3$, 0.5 H, H–C(2)); 6.57, 6.44 (2*d*, $^3J(14,15) \approx 6.9$, 0.5 H, H–C(15)); 5.18 (*t* with f.s., $^2J_{AB} = 14.8$, 0.5 H, H–C(10)); 5.08–4.67 (*m*, total 3.0 H, H–C(6), H–C(10)); 4.38 (*dd*, $^2J_{AB} = 12.8$, $^2J_{BX} = 10.6$, 0.5 H, H–C(6)). ^{31}P-NMR (161 MHz, $CDCl_3$; 1:1 mixture of diastereoisomers): 4.97, 4.41 (2*s*, 1:1 ratio). EI-MS: 498/496 (36/100, $M^{+\bullet}$), 497 (34, $[M+1]^{+\bullet}$).

2.2.1.2. *Hydrolysis of* rac-**10**. Compound *rac*-**10** (0.058 g, 0.116 mmol) was suspended in 2% aq. Na_2CO_3 (25 ml), stirred for 1 h, and then acidified with dil. HCl. The mixture was heated at 100° for 10 min and, after cooling, extracted several times with CH_2Cl_2. After drying ($MgSO_4$), CH_2Cl_2 was distilled off, and the residue (0.051 g) was recrystallized from CH_2Cl_2/Et_2O/hexane to give a small amount of *rac*-**11** (0.010 g, 18%) as yellow crystals.

Data of rac-**11**. M.p.: dec. on heating and formation of brown crystals which did not melt up to 300°. R_f (Et_2O/hexane 5:1) < 0.05. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.44 (*d* with f.s., $^3J(12,13) = 7.6$, H–C(12)); 7.34 (*s*, H–C(11)); 7.26 (*t* with f.s., $^3J(12,13) \approx {}^3J(13,14) \approx 7.5$, H–C(13)); 7.13–7.02 (*m*, H–C(14), H–C(4), 8 arom. H)); 6.81 (*dd*, $^3J(2,3) = 11.4$, $^3J(3,4) = 6.1$, H–C(3)); 6.84–6.78 (*m*, 2 arom. H); 6.64 (*d*, $^3J(2,3) = 11.4$, H–C(2)); 6.51 (*d* with f.s., $^3J(14,15) = 7.5$, H–C(15)); 5.96 (br.*s*, OH); 4.94 (*t*-like, *A* of *ABX*, $^2J_{AB} = 12.4$, $^3J_{AX} = 10.5$, 1 H–C(6)); 4.65 (*dd*-like, *A′* and *B′* of *A′B′X*, $^2J_{A'B'} = 19.1$, $^3J_{A'X} = {}^3J_{B'X} = 13.6$, 2 H–C(10)) 4.31 (*t*-like, *B* of *ABX*, $^2J_{AB} = {}^2J_{BX} = 13.4$, 1 H–C(6)). ESI-MS: 980 (100, $[2M + Na]^+$), 958 ($[2M+1]^+$), 501 ($[M + Na]^+$), 479 ($[M+1]^+$).

Since the yield of *rac*-**11** could not be improved and was $< 18\%$ in further runs, no resolution experiments of *rac*-**11** with cinchonine were performed.

2.2. *With* N-*Benzylcinchonidinium Chloride.* Compound *rac*-**3** (0.230 g, 0.55 mmol) and *N*-benzylcinchonidinium chloride (0.128 g, 0.30 mmol) were dissolved in MeCN (3 ml), and the mixture was boiled for 4 h. The soln. was cooled, stirred at ambient temp. overnight, and then stored at 4° for crystallization. The formed powder-like precipitate was dissolved in AcOEt, washed with 1N HCl and sat. NaCl soln. and dried ($MgSO_4$). HPLC on an anal. column (*Bio-Sil C 18 HL 90-5 S* column; hexane/EtOH 9:1; flow rate: 0.6 ml/min) revealed a 1:1 ratio of the enantiomers of **3**. No further experiments were performed.

2.3. *HPLC Separation of Diisopropyl* (M)*- and (*P*)-8,12-diphenylbenzo[*a*]heptalene-6,7-dicarboxylate* ((*M*)-**1b** and (*P*)-**1b**, resp.). Separation studies on dialkyl diesters of type **1** on an anal. *Chiralcel OD* column had

revealed that *rac*-**1a** and *rac*-**1b** are best suited for chromatographic resolution [15]. Since stationary phases of the *Chiralcel* type are only compatible with eluants consisting mainly of hydrocarbons (*e.g.*, hexane) with small amounts of alcohols (*e.g.*, 1–8% of EtOH, i-PrOH *etc.*), the solubility of the diesters in such solvent mixtures was also a parameter to be optimized. It turned out that *rac*-**1b** is much better soluble in hexane/i-PrOH 95:5 (10 mg/ml) than *rac*-**1a** (3 mg/ml). The enantiomers of both diesters **1** exhibited with this solvent mixture on the anal. *Chiralcel OD* column (flow rate 0.8 ml/min) comparable good separation factors α of the antipodes of **1a** ($\alpha = 1.55$) and **1b** ($\alpha = 1.42$), with the (*M*)-enantiomers as the faster moving form (see *Fig. 4*). On the semi-prep. *Chiralcel OD* column, (*M*)-**1b** and (*P*)-**1b** showed $\alpha = 1.30$ (t_R (hexane/i-PrOH 95:5) 23 and 30 min, resp.; flow rate: 7 ml/min). It allowed separations of 10 mg of *rac*-**1b**/injection (4 ml), which led to 100% optically pure (+)-(*M*)-**1b** and (−)-(*P*)-**1b** as yellow foams after removal of the eluant *in vacuo*. Crystallizations were not attempted.

*Data of (+)-(*M*)-***1b*** (see [15] for **1a**)*[7]): $[\alpha]_{589} = +975.6$, $[\alpha]_{578} = +1078.8$, $[\alpha]_{546} = +1494.8$ (20°; CH_2Cl_2, $c =$ 0.5 g/ml). CD (EtOH, $c = 4.018 \cdot 10^{-5}$ mol/l, r.t.; *cf. Fig. 5,a*): 368.2 (pos. max., +46.21), 320.2 (0), 294.0 (neg. max., −101.65), 265.4 (0), 255.0 (pos. max., +23.48), 241.8 (0), 223.0 (neg. max., −148.78).

2.4. *(+)-(*M*)- and (−)-(*P*)-8,12-Diphenylbenzo[*a*]heptalene-6,7-dimethanol* ((+)-(*M*)-**3** and (−)-(*P*)-**3**, resp.). 2.4.1. *(+)-(*M*)-***3***. Diester (+)-(*M*)-**1b** (0.562 g, 1.12 mmol) in THF (25 ml) and 2M DIBAH in hexane (5.6 ml, 11.2 mmol) were combined dropwise at 0°, and then the mixture was stirred for 3 h at ambient temp. The usual workup [16], followed by chromatography on a short silica gel column, gave pure material as a yellow foam (0.306 g, 66%). Crystallization of (+)-(*M*)-**3** was not attempted. The antipode (−)-(*P*)-**3** was prepared in the same way.

*Data of (+)-(*M*)-***3***. CD (hexane, $c = 4.975 \cdot 10^{-5}$ mol/l r.t.; *cf. Fig. 5,b*): 361.2 (pos. max., +35.88), 316.6 (0), 298.4 (sh, −56.63), 280.4 (neg. max., −85.21), 255.8 (0), 246.2 (pos. max., +17.92), 239.6 (neg. max., −95.94).

2.5. *(+)-(*M*)-6,7-Bis(chloromethyl)-8,12-diphenylbenzo[*a*]heptalene* ((+)-(*M*)-**4**). Dimethanol (+)-(*M*)-**3** (*cf.* 2.4.1; 0.306 g, 0.73 mmol) in $CHCl_3$ (20 ml) was reacted with PCl_5 (0.608 g, 2.92 mmol) in $CHCl_3$ (30 ml) at −60° for 1.5 h. The workup as described in *1.4* gave pure (+)-(*M*)-**4** as a yellow foam (0.235 g, 71%) which was not further purified.

CD (hexane; $c = 4.358 \cdot 10^{-5}$ mol/l, r.t.; *cf. Fig. 5,c*): 356.6 (pos. max., +0.78), 311.2 (0), 283.4 (neg. max., −1.73), 261.0 (0), 248.2 (pos. max., +0.45), 238.4 (0), 223.6 (neg. max., −1.34).

Based on the CD of the optically pure starting material (+)-(*M*)-**3**, the residual optical purity of (+)-(*M*)-**4** amounts to 2.2% (*cf.* also *2.6.1*).

2.6. *(+)-(*M*)- and (−)-(*P*)-6,7-Bis[(diphenylphosphanyl)methyl]-8,12-diphenylbenzo[*a*]heptalene* ((+)-(*M*)-**2** and (−)-(*P*)-**2**). 2.6.1. *From (+)-(*M*)-***4***. Compound (+)-(*M*)-**4** from *Exper. 2.5* (0.235 g, 0.52 mmol) in THF (5 ml) was reacted with *ca.* 1.2 mol-equiv. of $LiPPh_2$ in THF (3 ml) as described in *1.8.3*. Workup without chromatography gave (+)-(*M*)-**2** (0.350 g, 89%) as a yellow foam. ^{1}H-NMR showed that the chemical purity of (+)-(*M*)-**2** amounted to *ca.* 90%. CD (hexane, $c = 3.69 \cdot 10^{-5}$ mol/l; r.t.): 357.8 (pos. max., +0.49), 315.8 (0), 299.6 (sh, −0.72), 283.4 (neg. max., −1.34), 248.2 (0), 242.6 (pos. max., +0.13), 238.4 (0), 226.8 (neg. max., −1.22).

Based on the chemical purity and the CD of optically pure (−)-(*P*)-**6** (*cf. 2.7*), the residual optical purity of (+)-(*M*)-**2** amounts to *ca.* 1.5%.

2.6.2. *From (−)-(*P*)-***4***. Compound (−)-(*P*)-**4** (0.151 g, 0.33 mmol) in THF (3 ml) was reacted with *ca.* 0.7 mol-equiv. of LiPPh2 in THF (2 ml) as described in *1.8.3*. Workup without chromatography gave (−)-(*P*)-**2** (0.289 g, 116%) as a yellow foam, which could not be further purified, *i.e.*, the chemical purity of (−)-(*P*)-**4** was ≤83%. A CD spectrum was not recorded.

2.7. *(−)-(*P*)-6,7-Bis[(boranyldiphenylphosphanyl)methyl]-8,12-diphenylbenzo[*a*]heptalene* ((−)-(*P*)-**6**) via *Bis(methanesulfonate) (*P*)-***12***. As described in *1.5*, (*P*)-**12** was formed from optically pure (−)-(*P*)-**3** (0.208 g, 0.50 mmol), Et_3N (0.180 ml, 1.3 mmol) in CH_2Cl_2 (5 ml), and mesyl chloride (0.083 ml, 1.06 mmol) in CH_2Cl_2 (5 ml). According to *1.6*, the isolated, crude compound (*P*)-**12** was reacted with 6 mol-equiv. of $LiP(BH_3)Ph_2$ in THF to give finally, after purification by chromatography on silica gel, chemically pure (−)-(*P*)-**6** (0.130 g, 33%). HPLC with CH_2Cl_2 on the anal. *Whelk-01* column ($\alpha = 1.07$) indicated the presence of 10% of the (*M*)- and 90% of the (*P*)-enantiomer. After dissolution in Et_2O and addition of hexane, only *rac*-**6** crystallized. The mother liquor contained (−)-(*P*)-**6** with an enantiomeric purity of >99% (HPLC on the *Whelk-01* column). CD (hexane, $c = 3.659 \cdot 10^{-5}$ mol/l r.t.; *cf. Fig. 5,d*): 354.4 (neg. max., −37.41), 316.8 (0), 301.8 (sh, +47.51), 284.6 (pos. max., +90.14), 252.8 (0), 246.0 (neg. max., −10.79), 240.4 (0), 222.8 (pos. max., +68.70).

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[7]) Here and in the following sections the optical properties of only one of the antipodes are reported.

3. Rh^{I}-Catalyzed Hydrogenation of (*Z*)-α-Acetamidocinnamic Acid ((*Z*)-14) in the Presence of (*M*)-2 and (*P*)-2. 3.1. *General Remarks.* Acid (*Z*)-**14**, as well as (*R*)- and (*S*)-phenylalanin, which were transformed to the corresponding *N*-acetylated forms (*R*)-**15** and (*S*)-**15**, resp., were purchased from *Fluka* (quality: *puriss.* resp. *BioChemika*) and used without further purification. The precursor complex $[Rh(cod)_2]BF_4$ (purity 97%) was from *Aldrich*. Esterification of (*R*)-**15** and (*S*)-**15** with CH_2N_2 in AcOEt gave the corresponding methyl esters (*R*)-**16** and (*S*)-**16**, which showed, on the analytical *Chiralcel OD-H* column with hexane/EtOH 93:7, base-line separation of the antipodes t_R((*R*)-**16**) 9.48 min and t_R((*S*)-**16**) 10.18 min (flow rate: 1 ml/min; detection wavelength: 254 nm). Pure (*Z*)-**17** was prepared from (*Z*)-**14** with $SOCl_2$ and MeOH *via* the acid chloride. The $[\alpha]_D$ values of (*R*)-**15** and (*S*)-**15** were measured in EtOH ($c = 1$). The optically pure forms showed under these conditions $-45.6°$ for (*R*)-**15** and $+46.0°$ for (*S*)-**15**. The latter one was chosen as reference value.

The hydrogenations were performed in specifically constructed stainless steel autoclaves from *Medimex* (total volume 40 ml; upper working temp./pressure 300°/300 bar), equipped with a manometer from *SITEC* (pressure range up to 1000 bar). The filling of the autoclave was performed in a glove-box (dew point $-80°$, residual O_2 content < 10 ppm). The residual O_2 content of the used H_2 gas was 6 ppm. In general, the autoclave was charged with the corresponding solvent or solvent mixture, and the heptalene ligand **2** and $[Rh(cod)_2]BF_4$ were added under magnetic stirring. After formation of the Rh^{I}-heptalene complex, (*Z*)-**14** was added and the autoclave closed. Outside the glove-box, the autoclave was connected with the H_2 line, flushed three times with H_2, and then the working pressure was adjusted. After the hydrogenation, the solvent was removed under reduced pressure, the residue was dissolved in warm water (40°), and the soln. was filtered through a frit (size *G4*). H_2O was distilled off under reduced pressure, and the colorless glassy residue of *N*-acetylphenylalanin **15** was dried in high vacuum. After measurement of the $[\alpha]_D$ value, esterification with CH_2N_2 to **16** was performed, and the enantiomeric composition was determined by HPLC.

3.2. *Hydrogenation Reactions* (*cf. Table 2*). 3.2.1. *In the Presence of Optically Pure (*P*)-***2***. Entry 1:* The catalyst was prepared from (*P*)-**2** (13.6 mg, 0.018 mmol; generated from (*P*)-**6**) and $[Rh(cod)_2]BF_4$ (6.1 mg, 0.015 mmol) in THF (6 ml) during 1 h. Compound (*Z*)-**14** (0.308 g, 1.50 mmol) was added and hydrogenated at 40°/5 bar during 24 h. Yield of (*R*)-**15**: 0.289 g (93%): $[\alpha]_D^{26°} = -29.5$ (EtOH; $c = 1$), 65% o.p. HPLC of methyl ester: 74.5% of (*R*)-**16** and 25.5% of (*S*)-**16**, 69% *ee*.

Entry 2: The hydrogenation as described in *Entry 1* was repeated. Yield of (*R*)-**15**: 0.311 g (quant.); $[\alpha]_D^{26°} = -33.0$ (EtOH; $c = 1$), 72% o.p. HPLC of methyl ester: 88.5% of (*R*)-**16** and 11.5% of (*S*)-**16**, 77% ee.

3.2.2. *In the Presence of* ca. *2% Optically Pure (*M*)-***2***. Entry 3.* Amounts and conditions were those of *Entry 1* (*3.2.1*). However, (*M*)-**2**, prepared from (*M*)-**4** (*cf.* 2.5), was employed in 5 ml of THF. Yield of (*S*)-**15**: 0.308 g (99%): $[\alpha]_D^{26°} = +12.5$ (EtOH; $c = 1$), 27% o.p.

Entry 4: Amounts and conditions were those of *Entry 1* (*3.2.1*). However, (*M*)-**2**, prepared from (*M*)-**4** (*cf. 2.5*), was employed in 5 ml of EtOH. Yield of (*S*)-**15**: 0.308 g (99%); $[\alpha]_D^{26°} = +12.0$ (EtOH; $c = 1$), 26% o.p.

Entry 5: Amounts and conditions were those of *Entry 1* (*3.2.1*). However, (*M*)-**2**, prepared from (*M*)-**4** (*cf. 2.5*), was employed in 5 ml of EtOH/CH_2Cl_2 1:1. Yield of (*S*)-**15**: 0.308 g (99%). $[\alpha]_D^{26°} = +11.7$ (EtOH, $c = 1$), 25% o.p.

Entry 6: The methyl ester of (*Z*)-**14** (0.329 g, 1.50 mmol) was employed. All other amounts and conditions were as in *Entry 1*. However, (*M*)-**2**, prepared from (*M*)-**4** (*cf. 2.5*), was employed in 5 ml of THF. Yield of (*S*)-**16**: 0.326 g (98%). HPLC: 59.5% of (*S*)-**16** and 40.5% of (*R*)-**16**, 19% ee.

Entry 7: Amounts and conditions were those of *Entry 1* (*3.2.1*). However, (*M*)-**2**, prepared from (*M*)-**4** (*cf. 2.5*), was employed in 5 ml of THF in the presence of Et_3N (0.076 g, 0.75 mmol). Yield of (*S*)-**15**: 0.311 g (quant.). $[\alpha]_D^{26°} = +2.7$ (EtOH; $c = 1$), 6% o.p.

4. X-Ray Crystal-Structure Determinations of Compounds *rac*-6 and *rac*-7[8]. – 4.1. *Experimental.* See [15]. 4.2. *Discussion of* rac-**6**. The structure of $C_{54}H_{48}B_2P_2 \cdot CH_2Cl_2$ has been determined, but the results are of substandard quality. A highly disordered CH_2Cl_2 molecule is present in the structure. It was very difficult to model the solvent molecule adequately. Partial occupancy atoms were assigned to peaks of electron density in the solvent region so that the residual density was reasonably well accounted for, but no effort was made to

[8] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Center* as supplementary publication No. CCDC-133889 and CCDC-133890 for *rac*-**6** and *rac*-**7**, respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-(0)1223-336033; email: deposit@ccdc.cam.ac.uk).

generate a sensible geometry from these atoms. Another method was also tried (the SQUEEZE routine of *Spek* [38]) where the contribution to the reflection intensities from the solvent region of the structure is calculated and subtracted from the original intensities so that the model can be generated without needing to define any solvent atoms. This method yielded similar *R* factors to the refinement using the model which included solvent. Thus, it is suspected that the poor quality of the refinement results may be partly due to the presence of disordered solvent and partly due to the quality of the original data (which is related to crystal quality). The overall geometry of the organic molecule is clearly defined, and the desired features are visible, however, the accuracy of the atomic parameters and thus the bond lengths and angles is considerably poorer than normal. These results should, therefore, be used with caution.

4.3. *Discussion of* rac-**7**. The structure of $C_{30}H_{22}O_2$ has been solved and refined successfully with no unusual feature. The unknown part of the molecule was the five-membered lactone ring. The compound crystallizes in a chiral space group, even though it is a racemate. The hand of the chirality, and thus the space group, has been chosen arbitrarily. The alternate enantiomorphous space group is $P4_3$.

Table 3. *Crystallographic Data of* rac-**6** *and* rac-**7**

	rac-**6**	*rac*-**7**
Crystallized from	CH_2Cl_2/hexane	Et_2O/CH_2Cl_2
Empirical formula	$C_{54}H_{48}B_2P_2 \cdot CH_2Cl_2$	$C_{30}H_{22}O_2$
Formula weight	865.47	414.50
Crystal color, habit	pale yellow, triangular prism	pale yellow, prism
Crystal dimensions [mm]	$0.16 \cdot 0.42 \cdot 0.40$	$0.25 \cdot 0.33 \cdot 0.43$
Temp. [K]	173(1)	173(1)
Crystal system	triclinic	tetragonal
Space group	$P\bar{1}$	$P4_1$
Z	2	4
Lattice parameters		
Reflections for cell determination	25	25
2θ range [°]	32–39	37–40
a [Å]	13.339(4)	12.6441(7)
b [Å]	17.497(6)	12.6441(7)
c [Å]	12.295(5)	13.650(2)
α [°]	95.19(3)	90
β [°]	117.16(2)	90
γ [°]	105.13(3)	90
V [Å^3]	2390 (2)	21822.2(4)
D_x [g cm^{-3}]	1.202	1.262
Absorption coefficient		
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	0.238	0.0776
2θ(max) [°]	55	55
Total reflections measured	11441	3335
Symmetry independent reflections	10973	2822
R_{int}	0.031	0.017
Reflections used [$I > 2\sigma(I)$]	6328	2187
Parameters refined	577	289
Final R	0.0965	0.0378
wR	0.1082	0.0318
Goodness of fit	3.959	1.406
Final $\Delta_{\max}/\sigma$	3.8	0.0002
$\Delta\rho$ (max; min) [e Å^{-3}]	0.86; −0.82	0.15; −0.17

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