35. Axially Dissymmetric Diphosphines in the Biphenyl Series: Synthesis of (6,6'-Dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine) ('MeO-BIPHEP') and Analogues *via* an *ortho*-Lithiation/Iodination *Ullmann*-Reaction Approach

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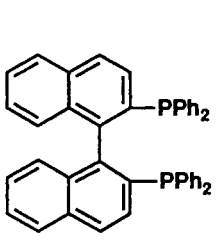
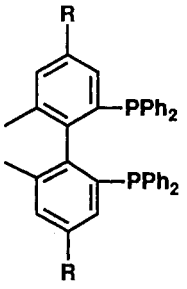
The new axially dissymmetric diphosphines (*R*)- and (*S*)-(6,6'-dimethoxybiphenyl-2,2'-diyl)bis(diphenyl phosphine) ((*R*)- and (*S*)-**5a**; 'MeO-BIPHEP') and the analogues (*R*)- and (*S*)-**5b** and **5c** have been synthesized in enantiomerically pure form. These ligands have become readily available by a synthetic scheme which employs, as key steps, an *ortho*-lithiation/iodination reaction of the (*m*-methoxyphenyl)diphenylphosphine oxides **8** and a subsequent *Ullmann* reaction of the resulting iodides **9** to provide the racemic bis(phosphine oxides) **10**. The bis(phosphine oxides) **10** subsequently are resolved with (–)-(2*R*,3*R*)- and (+)-(2*S*,3*S*)-*O*-2,3-dibenzoyltartaric acid and reduced to diphosphines **5**. The *Ullmann* reaction constitutes a new and efficient route to 2,2'-bis(phosphinoyl)-substituted biphenyl systems. Absolute configurations were established for (*R*)-**5a** by X-ray analysis of the derived Pd complex (*R*,*R*)-**17a**, and for **5b** and **5c** by means of ^{1}H-NMR comparisons of the derived Pd complexes **16** or **17**, respectively, and by means of CD comparisons. The MeO-BIPHEP diphosphine **5a** proved to be as efficient as the previously described BIPHEMP diphosphine ((6,6'-dimethylbiphenyl-2,2'-diyl)bis(diphenylphosphine)) in enantioselective isomerizations and hydrogenations.

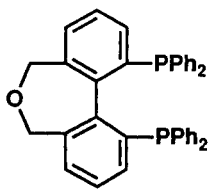
1. Introduction. – The potential of axially dissymmetric diphosphines such as the prototype compound BINAP (**1**) as asymmetry-inducing ligands has been amply demonstrated for various transition-metal-catalyzed reactions, in particular for Rh^{I}- and Ru^{II}-catalyzed hydrogenations [1]. Therefore, it is not surprising that considerable efforts have been undertaken for the design and synthesis of other atropisomeric diphosphine ligands. Some time ago, the parent compound in the atropisomeric biphenyl series, the BIPHEMP ligand **2a** has been synthesized by us [2] as well as independently by *Freyd* and coworkers [3], and by *Miyashita et al.* [4]. Moreover, the substituted analogues **2b**, **2c**, and the bridged analogue **3** have also been synthesized [2]. The BIPHEMP ligand was shown to be at least as efficient as the BINAP ligand in Rh^{I}-catalyzed allylamine-to-enamine isomerizations [2] and in Ru^{II}-catalyzed hydrogenations of allylic alcohols and β-keto esters [5]. Recently, the bis(dicyclohexyl) analogue **4** (BICHEP) has been synthesized by *Miyashita et al.* [6] and shown to provide excellent enantioselectivity in Rh^{I}-catalyzed hydrogenations of dimethyl itaconate. Since the diphosphines of the biphenyl series are obviously a highly useful class of chiral ligands, it seemed interesting to further study this field with the dual goal of developing new synthetic methodology and the synthesis of novel chiral ligands. We have developed a new approach to the synthesis of **2a** and **4** which employs an *Ullmann* reaction as the crucial step [7]. In this paper, we report the synthesis of (*R*)- and (*S*)-(6,6'-dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine) ((*R*)- and (*S*)-**5a**, hereafter abbreviated 'MeO-BIPHEP') and of the two analogues **5b** and **5c**. Synthetically, these new biphenyl-diphosphines with MeO substituents at C(6) and C(6') have become very readily available through a sequence of an *ortho*-lithiation/iodination followed by an *Ullman* reaction for the construction of the C-skeleton.



1 (BINAP)



2a R = H (BIPHEMP)
b R = Me
c R = Me_2N



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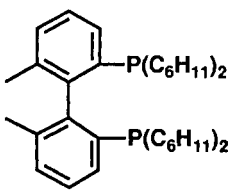
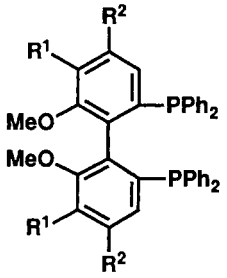


4 (BICHEP)



5a $R^1 = R^2 = H$ (MeO-BIPHEP)
b R^1 = MeO, R^2 = H
c $R^1 = R^2$ = MeO

2. Synthesis of Diphosphines. – Our synthetic approach to the biphenyl-diphosphines **5** with MeO substituents at C(6) and C(6′) is depicted in *Scheme 1*. It relies on a sequence of *1*) an *ortho*-lithiation/iodination reaction of the *m*-MeO-substituted phosphine oxides **8** to provide the iodides **9**, *2*) *Ullmann* reaction of the iodides **9** to prepare the racemic bis(phosphine oxides) **10**, *3*) their resolution by complex formation with (−)-(2*R*,3*R*)- or (+)-(2*S*,3*S*)-2,3-*O*-dibenzoyltartaric acid [8], and finally *4*) reduction of the enantiomerically pure bis(phosphine oxides) **10** to the corresponding enantiomerically pure diphosphines **5**.

Directed *ortho*-lithiation [9] at C(2) of the *m*-MeO-substituted phosphine oxides **8** followed by iodination appeared to be an attractive, straightforward method to provide access to iodides **9** which are required as substrates for the *Ullmann* reaction. Such an *ortho*-lithiation was expected to be assisted by and directed with high 'in-between' regioselectivity by the cooperative activating and directing effects of the 1,3-interrelated MeO (*cf.* [9]) and phosphinoyl substituents [10][1][2]).

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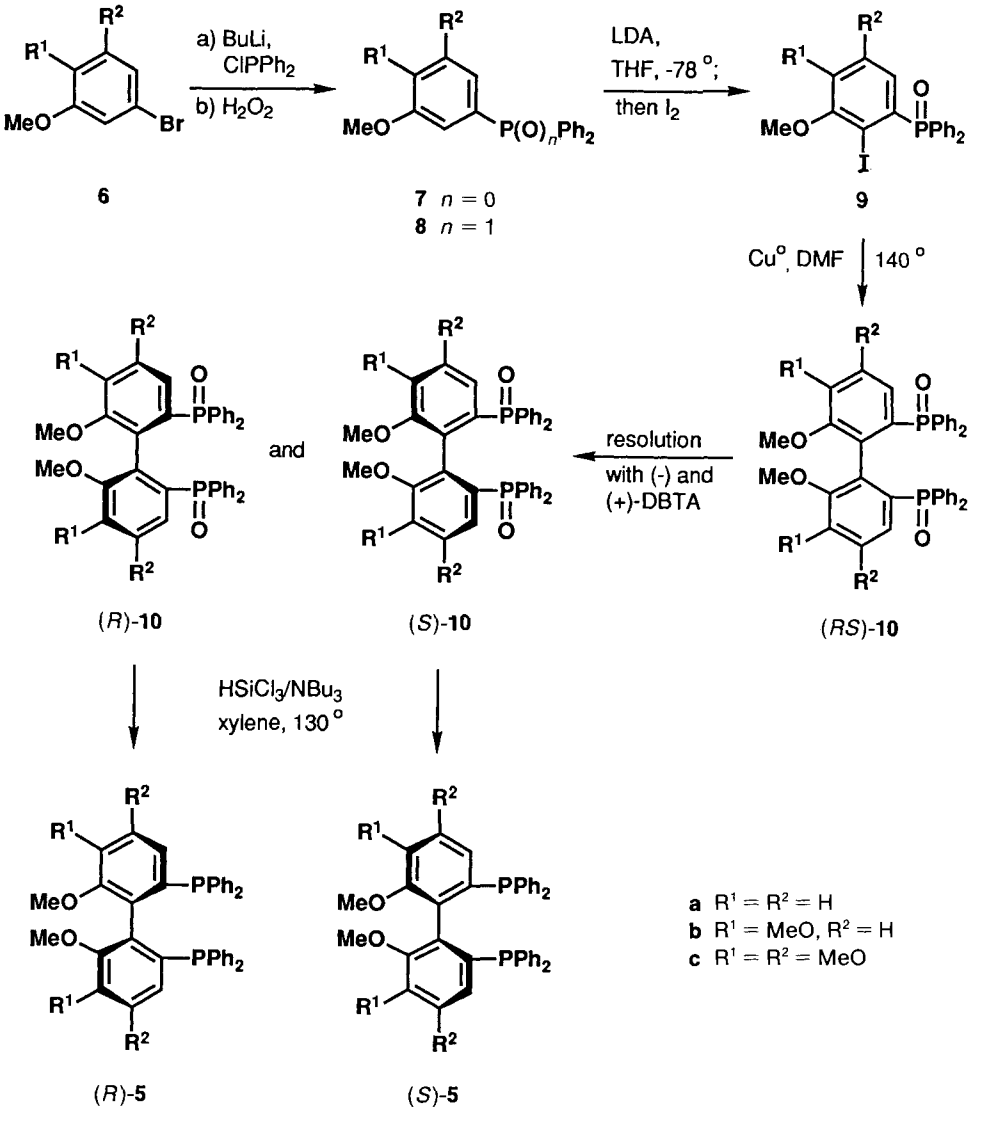
[1]) Directed *ortho*-lithiations of aromatic or heteroaromatic rings having phosphinoyl substituents have scarcely been described and rarely been exploited for synthetic purposes. In fact, to the best of our knowledge, there exist only two examples of such *ortho*-lithiations: *a*) of (β-thienyl)diphenylphosphine oxide by BuLi (lithiation at C(2) of the thiophene ring) (*Lampin* and *Mathey* [10a]) and *b*) of triphenylphosphine oxide itself by PhLi or *t*-BuLi (*Schlosser* and coworkers [10b]). In addition, there exist a few examples of *ortho*-lithiations of aromatic rings of other P-compounds, *i.e.* of triphenylphosphine *N*-phenylimide (PhLi; *Stuckwish* [11a]), of phenylphosphonic bis(dimethylamide) (BuLi; *Dashan* and *Tripett* [11b]), and of triphenylphosphono methylid (*s*- or *t*-BuLi; *Schlosser* and coworkers [10b]).

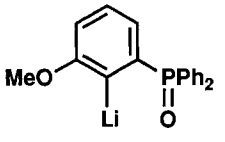
[2]) After our work had been completed [12], the *ortho*-lithiation at C(2) of (3,6-dimethoxyphenyl)diphenylphosphine oxide with *t*-BuLi and the subsequent reaction of the resulting Li species with various electrophiles, among them also I_2, has been disclosed by *Brown et al.* [13]. We thank Prof. *J. M. Brown* for discussions and for providing us with a preprint of his work [13b].

Scheme 1



After some experimentation, we have found that lithium diisopropylamide (LDA) is the reagent of choice for such *ortho*-lithiations. Thus, in the parent series **a** ($R^1 = R^2 = H$), treatment of **8a** with 1.06 mol-equiv. of LDA in THF at −78° followed by quenching of the reaction with 1.1 mol-equiv. of I_2 provided **9a** in 77–82% isolated yield. Similarly, **9b** and **9c** were obtained from **8b** and **8c**, respectively, in yields of 82 and 66–68%. The substrates of type **8** required for lithiation were synthesized in 77–88% yields from bromides **6** by standard methods (a) BuLi/THF, $ClPPh_2$; b) H_2O_2, MeOH; *cf.* [14]).

The *ortho*-lithiation/iodination reaction deserves further comment. The reaction proceeds with high chemo- and regioselectivity and is almost devoid of formation of by-products, however, *ca.* 20% of unreacted starting material **8** is recovered. A closer examination of the reaction conditions in the parent series **a** showed that the temperature is critical: lithiation at low temperatures (−78°) apparently is important; at this temperature the Li species **11** precipitates as a solid, and good yields of **9a** are obtained. At reaction temperatures above −30°, no precipitate is formed, and the yield of product is substantially reduced. This suggests that the lithiation with LDA is a thermodynamically controlled process (*cf.* [15]). Lithiations with BuLi or PhLi proceeded with much lower selectivities and afforded lower yields (BuLi/THF, −78°, 26% **9a**; PhLi/LiBr/THF, −30°; 20–41% **9a**). Varying the solvent, using BuLi as lithiation reagent also did not lead to improved yields. An experiment attempting 'catalyzed lithiation' (1.1 mol-equiv. BuLi, 0.1 mol-equiv. $(i\text{-Pr})_2NH$) (*cf.* [15]) proceeded non-selectively and produced **9a** only in low yield. Experiments to effect *ortho*-lithiation/bromination of **8a** were not promising; treatment of **8a** with LDA (THF, −78°) and Br_2 afforded only 10% of bromide **12**, while use of 1,2-dibromoethane as a bromination agent gave no **12**. It is also noteworthy that attempted lithiation/iodination of the phosphine **7a** (rather than the phosphine oxide **8a**) produced the iodide **13**, albeit in low yield (10%). Thus, lithiation of the phosphine was taking place, at least to some extent, at C(4), rather than at the 'in-between' C(2)-atom[3]).



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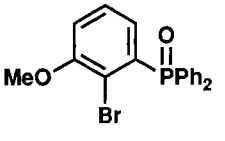

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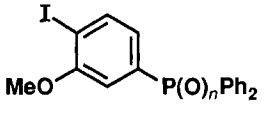


13 $n = 0$
14 $n = 1$

The *Ullmann* reaction of iodides **9**, carried out according to *Kornblum* and *Kendall* [17] in DMF solution, proceeded with surprising ease (starting at temperatures as low as 120° and being completed usually after 1–4 h at 140°) and in high yield (91% (*RS*)-**10a**, 82% (*RS*)-**10b**, 79–90% (*RS*)-**10c**). Reduction to compounds **8** is observed as a side reaction; **8a** was formed in 6% yield. The corresponding bromide **12** underwent the *Ullmann* reaction with similar ease and led to equally high yield as the iodide **9a**. The smooth course of these *Ullmann* reactions is remarkable, particularly in view of the presence of the sterically bulky diphenylphosphinoyl substituent in the *ortho*-position. Obviously, the strong electron-withdrawing effect of this group (*cf.* [14c]) is important. Together with the two examples developed for the synthesis of (*RS*)-**2a** and (*RS*)-**4** [7], these examples are the first *Ullmann* reactions of aryl halides containing a P-substituent, specifically a phosphinoyl substituent *ortho* to the halogen atom.

The optical resolution of the bis(phosphine oxides) (*RS*)-**10** was carried out by complex formation with (−)-(2*R*,3*R*)- and (+)-(2*S*,3*S*)-2,3-*O*-dibenzoyltartaric acid

[3]) Metalation of Ph_3P by BuLi occurs to some extent in the *meta*-position and gives an 8% yield of '(3-carboxyphenyl)diphenylphosphine', after carbonation [16].

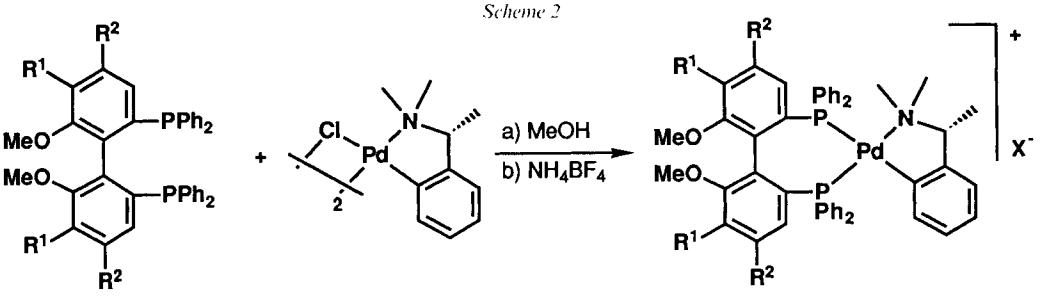
((−)- and (+)-DBTA, respectively) as resolving agents [8]. In the parent series, the diastereoisomerically pure 1:1 complex (*R*)-**10a**/(−)-DBTA crystallized from CH_2Cl_2/AcOEt containing equimolar amounts of (*RS*)-**10a** and (−)-DBTA. Treatment of the tartrate complex with aqueous base provided enantiomerically pure (*R*)-**10a** in 78% yield based on (*RS*)-**10a**. Enantiomerically enriched (*S*)-**10a** was recovered from the mother liquor by treatment with aqueous base and further purified by formation of the crystalline complex with (+)-DBTA. Enantiomerically pure (*S*)-**10a** was obtained, after decomposition of the complex, in 88% yield based on (*RS*)-**10a**.

Reduction of the resolved **10a** was performed by heating with an excess of Cl_3SiH in xylene [18] in the presence of Bu_3N (*cf.* [19]). These reductions proceeded with complete retention of the biphenyl configuration to afford the enantiomerically pure diphosphines (*R*)- and (*S*)-**10a** ((*R*)- and (*S*)-MeO-BIPHEP) in yields of 97–98% after simple trituration with EtOH, or in 84–86% yields after subsequent crystallization from toluene/EtOH.

Resolutions of the analogues (*RS*)-**10b** and (*RS*)-**10c** were carried out similarly with (−)- and (+)-DBTA. Surprisingly, the resolution of (*RS*)-**10b** was stereochemically opposite to the parent series; *i.e.* complexes (*S*)-**10b**/(−)-DBTA and (*R*)-**10b**/(+)-DBTA preferentially formed when crystallizing from $CHCl_3$/EtOH or CH_2Cl_2/EtOH mixtures. In this series, a 'through process' **8b** → **9b** → (*RS*)-**10b** was also developed in which crude iodide **9b** was directly subjected to the *Ullmann* reaction and bis(phosphine oxide) (*RS*)-**10b** was isolated from the crude reaction product upon crystallization of (*RS*)-**10b** as complex(es) with (−)-DBTA from CH_2Cl_2/AcOEt. The yield of the (*RS*)-**10b** tartrate complex in this 'through process' amounted to 63–66% based on **8b**. Recrystallization of this material from a different solvent system, $CHCl_3$/EtOH, then provided the diastereomerically pure complex (*S*)-**10b**/(−)-DBTA in 84% yield from which enantiomerically pure (*S*)-**10b** was recovered in virtually quantitative yield. Enantiomerically pure (*R*)-**10b** was obtained in 58% yield *via* crystallization of the (*R*)-**10b**/(+)-DBTA complex. With the analogue (*RS*)-**10c**, the stereochemical preferences for complex formation with DBTA depended on the crystallization solvent and on the enantiomer ratio of **10c**. Thus, crystallization from an i-PrOH solution of an equimolar mixture of (*RS*)-**10c** and (−)-DBTA led to the formation of the (*S*)-**10c**/(−)-DBTA complex; the enantiomerically enriched (*R*)-**10c** recovered from the mother liquor provided the (*R*)-**10c**/(+)-DBTA complex. Both complexes were of high diastereoisomeric purity after a single crystallization. On the other hand, when crystallizing from a CH_2Cl_2/AcOEt solution of (*RS*)-**10c** and (−)-DBTA, the complex (*R*)-**10c**/(−)-DBTA formed preferentially, and the enantiomerically enriched (*S*)-**10c** recovered from the mother liquor then provided the (*S*)-**10c**/(+)-DBTA complex. Both complexes required 2–3 further recrystallizations from i-PrOH to become diastereoisomerically pure. In one case, the (*R*)-**10c**/(+)-DBTA complex crystallized preferentially from a mother liquor enriched in (*R*)-**10c**. Resolution of (*RS*)-**10c** using only one resolving agent proved also feasible by consecutive isolation of the (*R*)-**10c**((+)-DBTA and the (*S*)-**10c**/(+)-DBTA complexes (*cf. Exper. Part*). It was also shown that all four possible 1:1 complexes can readily be obtained in crystalline form when starting from the optically pure bis(phosphine oxides) **10c** and either (+)- or (−)-DBTA upon crystallization from i-PrOH. Reductions of enantiomerically pure **10b** and **10c** proceeded uneventfully to provide enantiomerically pure **5b** and **5c**, respectively, in 90–96% yields.

3. Absolute Configurations and Enantiomeric Purities of the Diphosphines 5. – The absolute configuration (+)-(*R*)-**5a** ((*R*)-MeO-BIPHEP) was established by X-ray structure analysis of the derived Pd complex (*R,R*)-**17a** (*Scheme 2*). This complex and its stereoisomer (*S,R*)-**17a** were synthesized according to the method developed by *Otsuka et al.* [20], and *Roberts* and *Wild* [21] by reaction of racemic diphosphine **5a** with Pd reagent (*R*)-**15** (a) MeOH, b) aqueous NH_4BF_4) and diastereoisomer separation *via* fractional precipitation and crystallization (*cf. Exper. Part*). Degradation of the diastereoisomerically pure Pd complexes (a) CF_3CO_2H; b) $KCN/CH_2Cl_2/H_2O$, *cf.* [2b]) produced the enantiomerically pure diphosphines (+)-(*R*)-**5a** and (−)-(*S*)-**5a**.

Scheme 2



(*RS*)-**5** (*R*)-**15** (*R,R*)- and (*S,R*)-**16** X = Cl
(*R,R*)- and (*S,R*)-**17** X = BF_4

a $R^1 = R^2 = H$ **b** $R^1 = MeO$, $R^2 = H$ **c** $R^1 = R^2 = MeO$

An ORTEP plot including the atomic-numbering scheme and a stereoscopic drawing of the cationic moiety of the Pd complex (*R,R*)-**17a** are given in *Figs. 1* and *2*, respectively. The coordination of the Pd-atom by the P(1)- and P(2)-atoms of the diphosphine and the C(39)- and N(46)-atoms of the (palladated) *N,N*-dimethyl-α-phenylethylamine moiety is considerably distorted from square-planar geometry. The dihedral angle of 20.1° between the P(1)/Pd/P(2) and C(39)/Pd/N(46) planes indicates this distortion. It appears to have been determined by the minimization of repulsive forces between Ph rings (C(15)–C(20)) and (C(39)–C(44)) which have some close contacts (non-bonded distances C(39)–C(20): 3.133 Å; C(40)–C(15): 3.106 Å). The Pd–P distances are grossly different from each other, the Pd–P(2) bond located *trans* to the σ-bonded C-atom being long 2.403(2) Å) and the other (Pd–P(1)), located *trans* to the N ligand, being short (2.258(2) Å). Presumably, the difference must be ascribed to the *trans*-influence of the C- and N-ligand atoms in the coordination sphere of the Pd-atoms[4]). The five-membered Pd cycle (Pd–C(39)–C(44)–C(45)–N(46)) assumes an envelope conformation in which the N-atom is out of the plane of the other ring atoms, and where the Me substituent at C(45) is located in a *pseudo*-equatorial orientation. The seven-membered chelate ring (Pd–P(1)–C(2)–C(1)–C(8)–C(9)–P(2)) adopts a distorted skew (v) boat conformation

[4]) A similar *trans*-influence was observed in the corresponding Pd complex with (*S,S*)-*ortho*-phenylene bis(methylphenylarsine), the Pd–As bond *trans* to the σ-bonded C-atom being long (2.462 Å) and the Pd–As bond *trans* to the N-ligand atom short (2.339 Å) [22].

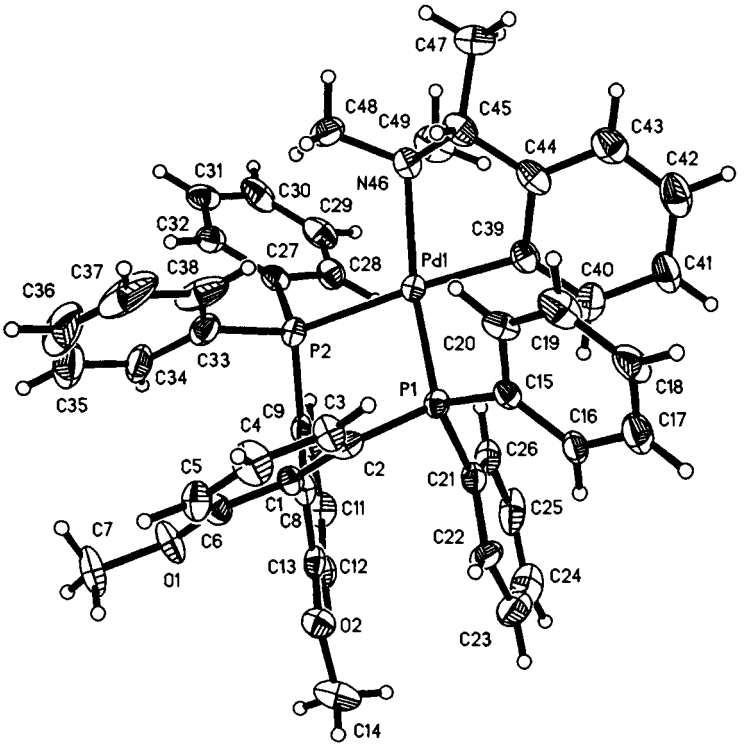


Fig. 1. *ORTEP Plot and atomic-numbering scheme of the cationic moiety of the Pd complex (*R,R*)*-**17a** (the BF_4^- counterion has been omitted). Top view; thermal ellipsoids are drawn at the 50% probability level. Selected bond distances [Å] and angles [deg] are as follows: Pd–P(1) = 2.258(3), Pd–P(2) = 2.403(2), Pd–C(39) = 2.034(7), Pd–N(46) = 2.196(6); P(1)–Pd–P(2) = 91.7(1), C(39)–Pd–N(46) = 78.7(3).

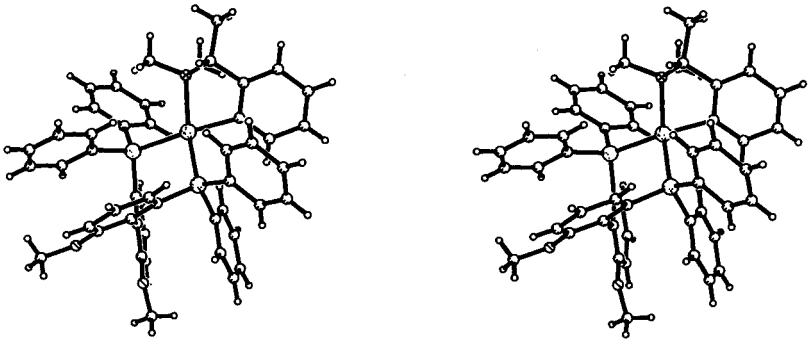


Fig. 2. *Stereoscopic drawing of the cationic moiety of Pd complex (*R,R*)*-**17a**

of λ helicity [23]. In the diphosphine part, a dihedral angle, θ, between the least-squares planes of the two Ph rings of the biphenyl system, of 70.3° is observed. This value is very similar to the θ value of 71.8° found for the cationic complex [Rh((*S*)-**2a**) (norbornadiene)]BF_4 derived from the BIPHEMP diphosphine (*S*)-**2a** [2b]. As has been already found for that complex, two pairs of stacked Ph rings (C(1)–C(6))/(C(33)–C(38)) and (C(8)–C(13))/(C(21)–C(26)) are observed in the complex (*R,R*)-**17a**; the dihedral angles of the two Ph rings of these pairs amount to 12.4° and 14.1°, respectively. The MeO substituents at C(6) and C(6′) assume coplanar conformations with respect to the biphenyl rings thus providing maximal orbital overlap. The Me groups of the MeO substituents are oriented outwards, the torsion angles C(1)–C(6)–O(1)–C(7) and C(8)–C(13)–O(2)–C(14) being −178.5° and −173.4°, respectively. The X-ray structure determination establishes the absolute configuration of the diphosphine **5a** in the complex to be (*R*) relative to the known (*R*)-configuration of the chiral center C(45) [20] [21].

Absolute configurations of **5a** and of its analogues **5b** and **5c** could also be deduced from ^{1}H-NMR spectra of the Pd complexes **16** or **17** and by comparison of their CD spectra. As already observed for the BIPHEMP congeners **2** [2b], the individual diastereoisomers of the (*R,R*)- and of the (*S,R*)-series of Pd complexes **16** or **17** display highly characteristic ^{1}H-NMR chemical shifts for the signals of the Me_2NCHCH_3 group (see *Table 1*). In particular, a low-field *quadruplet* absorption at 5.2–5.35 ppm for the methine H-atom of the Me_2NCHCH_3 group is characteristic for the (*R,R*)-diastereoisomers, while, for the (*S,R*)-diastereoisomers, this signal is observed at *ca.* 3.5 ppm (*cf.* also [2b])[5]).

Table 1. *Selected ^{1}H-NMR Data*[a]) *of Pd Complexes* **16** *and* **17**[b]) *Derived from the Diphosphines* **5a**, **5b**, *and* **5c**

Diphosphine	Pd complex	NC*H*Me	NCH*Me*	NMe_a	NMe_b	MeO[c])
(*R*)-**5a**	(*R,R*)-**17a**	5.20 (*q*, 6.5)	1.34 (*d*, 6.5)	2.55 (~ *t*, 3.5)	1.56 (*d*, 2.5)	3.47, 3.16
(*R*)-**5b**	(*R,R*)-**16b**	5.20 (*q*, 6.5)	1.31 (*d*, 6.5)	2.50 (*m*)	1.38 (*d*, 2)	3.71, 3.70, 3.68, 3.13
(*R*)-**5c**	(*R,R*)-**16c**	5.35 (*q*, 6.5)	1.33 (*d*, 6.5)	2.56 (*m*)	1.44 (*m*)	3.73, 3.64, 3.59, 3.58, 3.50, 3.22
(*S*)-**5a**	(*S,R*)-**17a**	3.49 (~ *quint.*, 6)	2.26 (*d*, 6.5)	2.22 (br. *s*)	1.94 (*d*, 2)	3.52, 3.19
(*S*)-**5b**	(*S,R*)-**16b**	3.47 (*m*)	2.23 (*d*, 6.5)	2.11 (br. *s*)	1.78 (*m*)	3.74, 3.70, 3.68, 3.20
(*S*)-**5c**	(*S,R*)-**16c**	3.55 (*m*)	2.26 (*d*, 6.5)	2.17 (br. *s*)	(br. *s*)	3.78, 3.65, 3.57. 3.53, 3.47, 3.27

[a]) In $CDCl_3$, at 400 MHz; chemical shifts (ppm] relative to TMS (= 0) (*J* in Hz).

[b]) The ^{1}H-NMR spectra of the Pd complexes **16** and **17** are not dependent on the counterion chloride or tetrafluoroborate, respectively.

[c]) *Singlet* signal.

[5]) It has been presumed in [2b] that the unusual low-field chemical shift of the methine H of the (*R,R*)-diastereoisomers is due to deshielding effects of the aromatic ring of the 'benzpalladazol' system. Evidently, this cannot be the case, since the X-ray structure analysis of (*R,R*)-**17a** reveals a virtually perpendicular arrangement of this methine H-atom with respect to the aromatic ring (*cf. Fig. 2*).

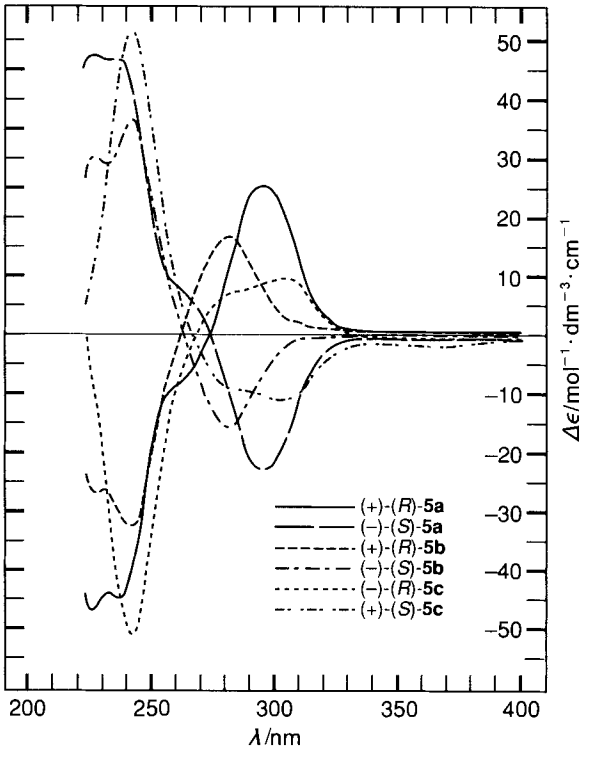


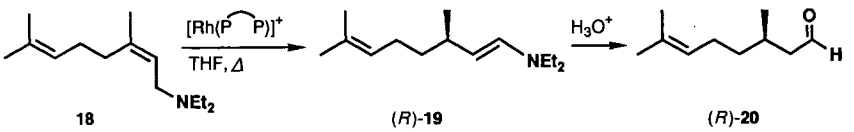
Fig. 3. *CD Spectra of diphosphines* **5a**–**5c** *in* $CHCl_3$

The assignment of the absolute configurations of the diphosphines **5** is further corroborated by CD spectra (*cf. Fig. 3*). As found already for the BIPHEMP congeners **2** [2b], a characteristic and strong negative CE at 235–240 nm and a weaker positive CE at 280–290 nm is observed for the (*R*)-series.

The *enantiomeric purities* of the diphosphines **5** were determined, after oxidation by H_2O_2 in MeOH, by HPLC analysis of the corresponding bis(phosphine oxides) **10** on chiral phases (*Pirkle* or (+)-poly(trityl methacrylate)). Generally, the enantiomeric purities were found to be in the order of 99% or higher. The ^{1}H-NMR spectra of the diphosphine-derived Pd complexes **16** may also be used for the determination of the enantiomeric purity as has already been described for the BIPHEMP congeners **2** (*cf.* [2b]). Diastereoisomeric purities of the Pd complexes **16** – formed *in situ* by dissolving the diphosphines **5** and 0.5 mol-equiv. of Pd reagent (*R*)-**15** in $CDCl_3$ (*Scheme 2*) – were determined by ^{1}H-NMR to be in the order of 98.5% de or higher based on the ratios of the *singlet* absorptions of one or more of the MeO groups. In some cases, ^{13}C-satellite bands served to calibrate the intensities of signals due to the minor diastereoisomers. It should be noted that a sample of (*S*)-**5a** containing 0.15% of (*R*)-**5a** by HPLC displayed *ca.* 0.7% of the minor diastereoisomer (*S,R*)-**16a** by the ^{1}H-NMR method. This may suggest that the Pd reagent (*R*)-**15** [20] [21] used by us for complex formation was not 100% enantiomerically pure.

4. Applications in Rh^{I}-Catalyzed Asymmetric Isomerizations and Ru^{II}-Catalyzed Asymmetric Hydrogenations. – Preliminary experiments indicate that the MeO-BIPHEP ligand **5a** is as efficient as the BIPHEMP or the BINAP ligand in enantioselective isomerizations and hydrogenations. Cationic Rh^{I} complexes of the type $[Rh((R)\text{-}\mathbf{5a})(diene)]^{+}X^{-}$ (diene = cod, or nbd[6]), X = BF_4 or ClO_4) and $[Rh((R)\text{-}\mathbf{5a})_2]^{+}X^{-}$ have been prepared by standard methods [24]. The complexes $[Ru((R)\text{-}\mathbf{5a})(diene)]^{+}X^{-}$ afforded enantioselectivites of up to 98.5% ee in the isomerization of *N,N*-diethylnerylamine (**18**)

Table 2. *Asymmetric Isomerization of* N,N-*Diethylnerylamine* (**18**)[a])



18 (*R*)-**19** (*R*)-**20**

Entry	$[Rh(P\frown P)]^{+}$	S/C[b])	Temp. [°C]	Time [h]	(*R*)-Citronellal ((*R*)-**20**)	
					Yield[c]) [%]	ee[d]) [%]
1	$[Rh((R)\text{-}\mathbf{5a})(cod)]BF_4$	250	85–90	16	89.5	98
2	$[Rh((R)\text{-}\mathbf{5a})(cod)]ClO_4$	300	65	48	88.5	98.5
3	$[Rh((R)\text{-}\mathbf{5a})nbd)]BF_4$	400	75	16	[e])	
4	$[Rh(cod)_2]BF_4/(R)\text{-}\mathbf{5a}$[f])	200	65	20	93	98.5
5	$[Rh((R)\text{-}\mathbf{5a})_2]BF_4$	1000	110	30	7	95.5
6	$[Rh((R)\text{-}\mathbf{5a})_2]ClO_4$	500	100	64	26	97

[a]) The isomerizations were carried out in THF in sealed, degassed tubes (reaction temp. > 75°) or in sealed *Schlenk* tubes under Ar (reaction temp. 65°).

[b]) Molar substrate/catalyst ratio.

[c]) Isolated yield after enamine hydrolysis (20–50% AcOH) and bulb-to-bulb distillation.

[d]) Determined by GC diastereoisomer analysis after reduction of (*R*)-**20** to the alcohol and esterification with (*S*)-Trolox™ methyl ether [26].

[e]) Conversion < 5%.

[f]) Catalyst prepared *in situ* from 1.0 mol-equiv. of $[Rh(cod)_2]BF_4$ and 1.1 mol-equiv. of (*R*)-**5a**.

to the enamine (*R*)-**19** [25] (*Table 2*). The Rh^{I} catalyst is preferentially prepared *in situ* from $[Rh(cod)_2]BF_4$ and **5a** (*Entry 4*). Interestingly, the bis(MeO-BIPHEP) complexes $[Rh((R)\text{-}\mathbf{5a})_2]^{+}X^{-}$ (X = BF_4 or ClO_4) were of much lower activity in these isomerizations. Only at temperatures > 100° did slow isomerization occur but with lower enantioselectivities (*Entries 5* and *6*). This result should be contrasted to those obtained with the corresponding bis(BINAP) [25c] or bis(BIPHEMP) [27] complexes, indicating a higher thermodynamic and/or kinetic stability of the bis(MeO-BIPHEP) complexes with respect to the dissociation of one of the diphosphine ligands. The MeO-BIPHEP ligand **5a** was also investigated in Ru^{II}-catalyzed enantioselective hydrogenations of allylic alcohols and of one β-keto ester and found to lead to asymmetric inductions of 97–98% ee (see [5]).

5. Concluding Remarks. – The new atropisomeric diphosphine ligands (*R*)- and (*S*)-(6,6′-dimethoxybiphenyl-2,2′-diyl)bis(diphenylphosphine) ((*R*)- and (*S*)-**5a**, (*R*)- and (*S*)-MeO-BIPHEP, respectively) have been prepared in enantiomerically pure form *via*

[6]) nbd = norbornadiene; cod = (*Z,Z*)-cycloocta-1,5-diene.

an *ortho*-lithiation/iodination reaction directed in concert by MeO and diphenylphosphinoyl substituents and a subsequent *Ullmann* reaction as the key steps. The synthesis is efficient (48–54% overall yield), simple (no chromatography required), and readily amenable to multigram scale-up. Overall, the MeO-BIPHEP ligand **5a** has become synthetically more readily available than the previously developed BIPHEMP ligand **2a**. The synthesis scheme is flexible and allows the preparation of MeO-BIPHEP analogues such as **5b** and **5c**. In terms of structural and electronic properties, the MeO-BIPHEP ligand differs only marginally from its BIPHEMP congener and gives similar results in the asymmetric isomerization of *N,N*-diethylnerylamine and in hydrogenation reactions of allylic alcohols and of one β-keto ester. There are, however, some applications where **5a** proved clearly superior to **2a** or **1**; these results will be reported in due course. Further synthetic work in this area is in progress, and results will be reported later.

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Experimental Part

General. Cf. [2b]. ^{1}H-NMR at 250 MHz (*Bruker AC*) in $CDCl_3$ solns., unless otherwise noted. IR spectra: KBr, unless otherwise noted. DMF was dried by storing over 4-Å molecular sieves. M.p. higher than 250° were determined by thermal analysis (*Mettler TA-2000/A*). ^{31}P-NMR: at 202.46 MHz (*Bruker AC*) in $CDCl_3$ solns. with H_3PO_4 as external standard.

1. Synthesis of Diphosphines 5a (MeO-BIPHEP). – 1.1. *(3-Methoxyphenyl)diphenylphosphine* (**7a**). The synthesis of **7a** was carried out according to literature procedures [14a–d] but using the lithio derivative of 3-bromoanisole instead of the *Grignard* reagent: to a soln. of *3-bromoanisole* (**6a**) (120 g, 0.641 mol) in dry THF (400 ml) was added dropwise BuLi soln. (400 ml, 1.6M in hexane, 0.664 mol) at −70° within 45 min. The resulting beige-colored suspension was stirred for an additional 1 h at −78°. Then, freshly distilled Ph_2PCl (150 g, 0.703 mol) was added dropwise at such a rate that the reaction temp. did not exceed −60°. The yellow soln. was allowed to warm to 0° within 2 h and quenched by addition of sat. NH_4Cl soln. (500 ml). The org. layer was separated, washed with sat. NaCl soln. (2 × 500 ml), dried ($MgSO_4$), filtered, and evaporated. The solid residue was triturated with warm hexane (750 ml), yielding a suspension which was stirred overnight at r.t; the solid was collected by filtration, washed with hexane, and dried *in vacuo* to yield **7a** (171 g, 91%) as white powder. M.p. 57–58° [(14a, b]: 60–61°, [14c]: 62–64°, [14d]: 55–56°).

1.2. *(3-Methoxyphenyl)diphenylphosphine Oxide* (**8a**). To a suspension of **7a** (171 g, 0.585 mol) in MeOH (750 ml) was added dropwise at ≤ 40° 35% aq. H_2O_2 soln. (65 ml, 0.65 mol). The resulting clear soln. was stirred at amb. temp. for 1 h, treated for 1 h with sat. Na_2SO_3 soln. (150 ml) and 1N HCl soln. (100 ml), and the mixture was concentrated at the rotavapor at 40° to remove the MeOH. Usual workup of the residue with CH_2Cl_2 (300 ml) afforded an oil which was crystallized from hexane (500 ml) at 40°. Filtration, washing with hexane, and drying *in vacuo* provided spectroscopically pure **8a** (175 g, 97%) as white powder. M.p. 108–109° ([14a]: 110–111°, [14c]: 107.9–108.5°, [14e]: 112–113°).

1.3. *(2-Iodo-3-methoxyphenyl)diphenylphosphine Oxide* (**9a**). To a soln. of $(i\text{-Pr})_2NH$ (21.4 g, 0.211 mol) in dry THF (170 ml) was added, at −78°, within 15 min, BuLi soln. (113 ml, 1.65M in hexane, 0.186 mol). After stirring for 15 min at −78° to −40°, the LDA soln. was cooled again to −78° and added, *via* cannula, at ≤ −70° over 20 min, to a flask containing a soln. of **8a** (52.5 g, 0.170 mol) in dry THF (350 ml). During the addition, the mixture turned reddish-brown, and eventually a beige suspension formed. After stirring for an additional 15 min at −78°, a soln. of I_2 (47.4 g, 0.187 mol) in THF (170 ml) was added dropwise at ≤ −70°. Towards the end of the addition, the formation of a reddish-brown viscous paste began. At this point, the mechanical stirrer was stopped, the cooling bath was removed, and the mixture was allowed to warm to 0° to obtain a clear red soln. The mixture was quenched

by addition of an aq. $Na_2S_2O_3$ soln. (12 g in 100 ml of H_2O), then worked up as usual to yield a brown paste. This material was crystallized from *t*-BuOMe (300 ml) at reflux temp. After standing at amb. temp. overnight, the solid was collected by filtration, washed with *t*-BuOMe (100 ml) and dried *in vacuo* at 70° to provide spectroscopically pure **9a** (55.7 g, 75.5%) as an off-white powder. M.p. 186–189°. An identical second experiment afforded 58.6 g of a solid consisting, by ^{1}H-NMR analysis, of 97% of **9a** and 3% of starting material **8a**; chemical yield 56.5 g (76.5%). An anal. sample of **9a** was obtained by crystallization from toluene/hexane 1:1; yellowish needles. M.p. 188–190°. IR: 1557 (Ar.); 1455, 1434 (P-Ar.); 1257, 1152, 1044 (Ar.-ether); 1186 (P = O). ^{1}H-NMR: 7.8–7.6 (*m*, 4 arom. H); 7.6–7.4 (*m*, 6 arom. H); 7.30 (*td*, *J* = 8, 3, H–C(5)); 6.96 (*d*, *J* = 8, H–C(4)); 6.80 (*dd*, *J* = 12, 8, H–C(6)); 3.91 (*s*, CH_3O). MS: 434 (100, $M^{+\cdot}$), 433 (86, $[M - H]^+$), 307 (56, $[M - I]^+$). Anal. calc. for $C_{19}H_{16}IO_2P$ (434.21): C 52.56, H 3.71, I 29.23; found: C 53.43, H 3.77, I 28.15.

1.4. *(RS)-(6,6'-Dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide)* ((*RS*)-**10a**). A mixture of **9a** (113.0 g, 0.260 mol), Cu powder (49.5 g, 0.78 mol; activated by I_2 treatment according to [28]) and DMF (500 ml) was stirred at 140° (oil-bath temp.) for 1 h. The cold mixture was evaporated to dryness at the rotavapor at 70°. The residue was treated for a few min with hot CH_2Cl_2 (500 ml), the solid parts were removed by filtration and washed with CH_2Cl_2 (250 ml), and the combined filtrate and wash solns. were washed with sat. NH_4Cl soln. (2 × 250 ml), dried ($MgSO_4$), and evaporated. The solid residue (89 g) was triturated 4 times with hot hexane (500 ml) and dried *in vacuo* at 70° for 1 h to afford (*RS*)-**10a** (79.8) as beige powder. M.p. 307–308°. This material, according to its ^{1}H-NMR spectrum, contained 0.73 mol-equiv. (9.2% by weight) of CH_2Cl_2 which could not be removed by prolonged drying *in vacuo* at 80°; calculated chemical yield of (*RS*)-**10a**: 72.5 g (91%). Evaporation of the combined hexane trituration solns. afforded 6.0 g of a white powder consisting, by ^{1}H-NMR, of a 87:13 mixture **8a**/**9a**; calc. yield of **8a**: ca. 5.2 g (6.5%). An analytical sample of (*RS*)-**10a** was obtained by crystallization from CH_2Cl_2/AcOEt 3:10; white needles. M.p. 308–309°. This material again retained 0.65 mol-equiv. of CH_2Cl_2 and traces of AcOEt. IR: 1572 (Ar.); 1460, 1436 (P-Ar.); 1255, 1154, 1050 (Ar.-ether); 1205 (P = O). ^{1}H-NMR: 7.75–7.20 (*m*, 22 arom. H); 6.9–6.75 (*m*, 4 arom. H); 3.11 (*s*, 2 CH_3O). MS: 613 (1, $[M - H]^+$), 583 (1, $[M - OMe]^+$), 537 (3, $[M - Ph]^+$), 413 (100, $[M - P(O)Ph_2]^+$).

1.5. *Resolution of (RS)-***10a**. 1.5.1. *(R)-(6,6'-Dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide)* ((*R*)-**10a**). Compound (*RS*)-**10a** (79.5 g, containing 9.2% of CH_2Cl_2, 0.117 mol) was dissolved in boiling CH_2Cl_2 (440 ml). To the soln. was added, in one portion, a hot (50°) soln. of (−)-(2*R*,3*R*)-2,3-*O*-dibenzoyltartaric acid ((−)-DBTA) (56.3 g, 0.157 mol) in AcOEt (520 ml). Crystallization started immediately and the suspension was stirred for 3 h while slowly lowering the temp. to 20°. The solid was collected by filtration, washed with a CH_2Cl_2/AcOEt mixture (220 ml/260 ml), and dried at 80°/15 mbar to provide the 1:1 complex (*R*)-**10a**/(−)DBTA (46.0 g, 80% of theory based on (*RS*)-**10a**) as white crystals. M.p. 209–210°; $[\alpha]_D^{20} = +19.2$ (*c* = 0.8, EtOH). ^{1}H-NMR (DMSO): 14.0 (br. *s*, 2 OH); 8.03 (*d*, *J* = 7.5, 4 arom. H); 7.8–7.4 (*m*, 26 arom. H); 7.25 (*m*, 2 arom. H); 6.87 (*d*, *J* = 7, 2 arom. H); 6.65 (*dd*, *J* = 12, 7.5, 2 arom. H); 5.88 (*s*, 2 CHO); 2.94 (*s*, 2 CH_3O). (Mother liquor and the wash solns. of the crystallization were stored for the recovery of the enantiomer (*S*)-**10a**, see *1.5.2*). The complex (*R*)-**10a**/(−)-DBTA (46.0 g) was stirred with CH_2Cl_2 (500 ml) and 2N NaOH (200 ml), until the solid had completely dissolved (30 min). The org. layer was separated, washed with 2N NaOH (200 ml) and H_2O (2 × 250 ml), dried ($MgSO_4$), filtered, and evaporated. The solid residue was triturated with hot hexane (100 ml) and dried for 4 h at 80°/15 mbar to provide (*R*)-**10a** (28.4 g, 79% based on (*RS*)-**10a**) as white crystals. M.p. 338°. $[\alpha]_D^{20} = +129.9$ (*c* = 1.0, $CHCl_3$). This material was enantiomerically pure (≥ 99% ee) according to HPLC on a *Pirkle* phase. An anal. sample was obtained from another experiment by crystallization from CH_2Cl_2/hexane. M.p. 337°. $[\alpha]_D^{20} = +129.5$ (*c* = 1.0, $CHCl_3$), $[\alpha]_D^{20} = +98.4$ (*c* = 1.0, EtOH). IR, ^{1}H-NMR, MS: identical to the corresponding spectra of (*RS*)-**10a**. CD (*c* = 0.046, EtOH): 206 (+52, pos. max.); 218 (0); 230 (−35, neg. max.); 252 (0); 258 (+1.2, pos. max.); 266 (+0.4, pos. min.); 279 (+5.1, sh); 288 (+7.6, pos. max.); 301 (0); 313 (−3.9, neg. max.). ^{31}P-NMR: 29.9 (*s*). Anal. calc. for $C_{38}H_{32}O_4P_2$ (614.62): C 74.26, H 5.25; found: C 74.16, H 5.23.

1.5.2. *(S)-(6,6'-Dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide)* ((*S*)-**10a**). The residue obtained after evaporation of the combined mother liquor and wash solns. from *1.5.1* was treated under stirring with CH_2Cl_2 (750 ml) and 2N NaOH (250 ml), until a clear two-layer system resulted (30 min.) The org. layer was separated, washed with 2N NaOH (250 ml) and H_2O (3 × 250 ml), dried ($MgSO_4$), filtered, and evaporated. The solid residue (45 g), consisting by HPLC on a *Pirkle* phase of a 12:88 mixture (*R*)-**10a**/(*S*)-**10a**, was dissolved in boiling CH_2Cl_2 (250 ml), and to the soln. was added, in one portion, a soln. of (+)-(2*S*,3*S*)-2,3-*O*-dibenzolytartaric acid ((+)-DBTA) (28.8 g, 0.080 mol) in hot (50°) AcOEt (275 ml). The resulting suspension was stirred overnight while slowly allowing the temp. to attain 20°. The precipitate was filtered, washed with a CH_2Cl_2/AcOEt mixture (90 ml/110 ml), and dried for 1 h at 100°/15 mbar to provide the 1:1 complex (*S*)-**10a**/(+)-DBTA (51.0 g, 89.5% of theory based on (*RS*)-**10a**) as white crystals. M.p. 211–212°. $[\alpha]_D^{20} = -19.4$ (*c* = 1.0, EtOH). This complex was further processed as described in *1.5.1* to provide (*S*)-**10a** (31.8 g, 88.5% of theory based on (*RS*)-**10a**) as white crystals. M.p. 336.5°.

$[\alpha]_D^{20} = -130.4$ ($c = 1.0$, $CHCl_3$). This material was enantiomerically pure ($\geq 99\%$ ee) according to HPLC on a *Pirkle* phase. An anal. sample was obtained by crystallization from CH_2Cl_2/hexane. M.p. 338°. $[\alpha]_D^{20} = -130.4$ ($c = 1.0$, $CHCl_3$), $[\alpha]_D^{20} = -98.9$ ($c = 1.0$, EtOH). IR, ^{1}H-NMR, ^{31}P-NMR, MS: identical to the corresponding spectra of (*R*)-**10a**. CD ($c = 0.076$, EtOH): 216 (0); 229 (39.6, pos. max.); 251 (0); 258 (−1.6, neg. max.); 264 (−0.7, neg. min.); 288 (−8.3, neg. max.); 302 (0); 310 (+2.8, pos.max.). Anal. calc. for $C_{38}H_{32}O_4P_2$ (614.62): C 74.26, H 5.25; found: C 73.98, H 5.36.

1.6. *Reduction to Diphosphines* **5a**. 1.6.1. *(R)-(6,6'-Dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine)* ((*R*)-**5a**; (*R*)-MeO-BIPHEP). To a suspension of (*R*)-**10a** (27.9 g, 54.4 mmol) in dry xylene (isomer mixture, 300 ml) were added Bu_3N (95 ml, 0.40 mol) and Cl_3SiH (34.9 g, 257 mmol). The mixture was heated at reflux temp. for 3 h. After cooling to 0°, deoxygenated 30% aq. NaOH (200 ml) was added carefully to the opaque mixture at a rate which allowed to keep the reaction temp. at *ca.* 70°. CH_2Cl_2 (100 ml) was added and the mixture stirred at 60°, until the org. and aq. layers became clear. The aq. layer was removed *via* cannula, and the org. layer was treated again with deoxygenated 30% aq. NaOH (200 ml), diluted with CH_2Cl_2 (100 ml), and washed with H_2O (3 × 200 ml), sat. NaCl-soln. (200 ml), dried ($MgSO_4$), filtered, and evaporated. The residue was dried *in vacuo* at 80°, then EtOH (250 ml) was added and the suspension heated to 80° for a few min. After cooling to 0°, the solid was collected by filtration, washed with EtOH (250 ml) and pentane (100 ml) and dried at 100°/15 mbar for 1 h to yield (*R*)-**5a** (25.75 g, 97%). M.p. 214–215°. $[\alpha]_D^{20} = +42.4$ ($c = 1.0$, $CHCl_3$). This material, according to its ^{1}H-NMR spectrum, contained 1% of Bu_3N but was otherwise pure. Its enantiomeric purity, based on the ^{1}H-NMR spectra of the *in situ* formed Pd complex (*R,R*)-**16a** was $\geq 99\%$ ee. Recrystallization from a hot mixture of toluene (80 ml) and EtOH (100 ml) followed by filtration, washing with a toluene/EtOH mixture (80 ml/100 ml) and pentane (100 ml), and drying *in vacuo* (110°/2 h) afforded (*R*)-**5a** (22.8 g, 86%) as white crystals. M.p. 214–215°. $[\alpha]_D^{20} = +42.3$ ($c = 1.0$, $CHCl_3$). CD ($c = 0.096$, $CHCl_3$): 225 (−48.1, neg. max.); 232 (−45.5, neg. min.); 236 (−46.5, neg. max.); 259 (−8.7, sh.); 272 (0); 293 (+26.4, pos. max.); 317 (0); 370 (−1.2, neg. max.). IR: 1561 (Ar.); 1457 (P-Ar.); 1254, 1150, 1040 (Ar.-ether). ^{1}H-NMR: 7.3–7.15 (*m*, 18 arom. H); 7.08 (*m*, 4 arom. H); 6.8–6.7 (*m*, 4 arom. H); 3.15 (*s*, 2 CH_3O). ^{31}P-NMR: −13.9 (*s*). MS: 505 (4, $[M - Ph]^+$), 397 (100, $[M - PPh_2]^+$). Anal. calc. for $C_{38}H_{32}O_2P_2$ (582.62): C 78.34, H 5.54; found: C 78.09, H 5.86.

1.6.2. *(S)-(6,6'-Dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine)* ((*S*)-**5a**; (*S*)-MeO-BIPHEP). Reduction of (*S*)-**10a** (31.5 g, 51.25 mmol) as described in *1.6.1* afforded spectroscopically pure (*S*)-**5a** (29.3 g, 98%), white powder. M.p. 214–215°. $[\alpha]_D^{20} = -41.7$ ($c = 1.0$, $CHCl_3$); enantiomeric purity based on ^{1}H-NMR spectrum of the *in situ* formed Pd complex (*S,R*)-**16a** > 99% ee. Recrystallization as described in *1.6.1* yielded (*S*)-**5a** (25.1 g, 84%) as white crystals. M.p. 214–215°. $[\alpha]_D^{20} = -42.5$ ($c = 1.0$, $CHCl_3$). The enantiomeric purity of this material was determined to be 99.7% ee by oxidation (H_2O_2, MeOH) to (*S*)-**10a** and HPLC on a *Pirkle* phase. CD ($c = 0.086$, $CHCl_3$): 225 (+47.5 pos. max.); 231 (+46.6, pos. min.); 237 (+46.8, pos. max.); 259 (8.4, sh); 272 (0); 294 (−22.6, neg. max.). IR, ^{1}H-NMR, ^{31}P-NMR, MS: identical to the corresponding spectra of (*R*)-**5a**. Anal. calc. for $C_{38}H_{32}O_2P_2$ (582.62): C 78.34, C 5.54; found: C 78.27, C 5.69.

1.6.3. *(RS)-(6,6'-Dimethoxybiphenyl-2,2'-diyl)bis(dihenylphosphine)* ((*RS*)-**5a**; (*RS*)-MeO-BIPHEP). An analogous reduction of (*RS*)-**10a** (10.5 g, 17.08 mmol) afforded (*RS*)-**5a** (10.0 g, 99%) as white powder. Recrystallization from MeOH (100 ml) and toluene (80 ml) gave (*RS*)-**5a** (4.96 g, 50%). M.p. 218–219°. IR, ^{1}H-NMR, MS: identical to the corresponding spectra of (*R*)-**5a**. Anal. calc. for $C_{38}H_{32}O_2P_2$ (582.62): C 78.34, C 5.54; found: C 78.58, C 5.78.

1.7. *Resolution of Diphosphines (RS)-***5a** via *Pd Complexes* **17a**. 1.7.1. *{(R)-2-[1-(Dimethylamino)ethyl]-phenyl-C,N}[(R)- and (S)-(6,6'-dimethoxybiphenyl-2,2'-diyl)bis(diphenylphospine)]palladium(II) Tetrafluoroborate* ((*R,R*)-**17a** and (*S,R*)-**17a**). A suspension of (*RS*)-**5a** (4.96 g, 8.52 mmol) and Pd complex (*R*)-**15** [21b] (*cf.* [2b]) (2.47 g, 4.26 mmol) in MeOH (100 ml) was stirred for 3.5 h at 40°. To the resulting yellow soln. was added dropwise, at amb. temp., an aq. soln. of NH_4BF_4 (0.529 g, 5.05 mmol, in 23 ml of H_2O), and the resulting suspension was stirred at amb. temp. overnight. The precipitates were collected by filtration, washed with MeOH/H_2O 4:1, and dried *in vacuo* to afford 3.35 g (85% of theory) of a 99:1 diastereoisomer mixture (*R,R*)-**17a**/(*S,R*)-**17a** (^{1}H-NMR). Recrystallization from CH_2Cl_2/AcOEt (30 ml/55 ml) afforded 3.05 g (77.5% of theory) of diastereoisomerically pure ($\geq 99\%$ de) (*R,R*)-**17a**. The filtrate obtained above was treated with a second portion of an aq. soln. of NH_4BF_4 (0.575 g, 5.48 mmol, in 25 ml of H_2O) and the suspension stirred for 2 h. The precipitates were collected by filtration, washed with MeOH/H_2O 3:1, and dried *in vacuo*. The yellow powder (3.4 g), consisting of a 10:90 diastereoisomer mixture (*R,R*)-**17a**/(*S,R*)-**17a** (^{1}H-NMR), was dissolved in the minimum amount of CH_2Cl_2, and AcOEt was added, until precipitation started. After standing overnight, the precipitates (0.8 g of a 25:75 mixture (*R,R*)-**17a**/(*S,R*)-**17a** according to ^{1}H-NMR) were removed by filtration, the filtrate was evaporated and the residue (2.4 g) recrystallized from CH_2Cl_2/AcOEt to provide diastereoisomerically pure ($\geq 99\%$ de) (*S,R*)-**17a** (1.53 g, 39% of theory).

*Data of (*R,R*)*-**17a**. Yellowish crystals. M.p. 215–218° (dec., darkening from 150°). $[\alpha]_D^{20} = +342.3$ ($c = 0.74$, $CHCl_3$). IR: 1570 (Ar.); 1262, 1155 (Ar.-ether); 1049 (br., BF_4^-). ^{1}H-NMR: 7.9–6.9 (*m*, 23 arom. H); 6.73 (*m*, 3 arom. H); 6.5–6.25 (*m*, 4 arom. H); 5.25 (*q*, $J = 6.5$, $NCHCH_3$); 3.45, 3.15 (2*s*, 2 CH_3O); 2.55 (*m*, NCH_3); 1.54 ($\sim$ *d*, $J = 2.5$, NCH_3); 1.32 (*d*, $J = 6.5$, $NCHCH_3$). ^{31}P-NMR: 36.66 (*d*, $J = 45$); 11.24 (*d*, $J = 45$). X-Ray analysis: see *1.7.2*. Anal. calc. for $C_{48}H_{46}BF_4NO_2P_2Pd$ (924.05): C 62.39, H 5.02, N 1.52; found: C 61.81, H 5.13, N 1.51.

*Data of (*S,R*)*-**17a**. Yellowish crystals. M.p. 218–219° (dec., darkening from 150°). $[\alpha]_D^{20} = -346.2$ ($c = 1.0$, $CHCl_3$). IR: 1574 (Ar.); 1265, 1158, 999 (Ar.-ether); 1055 (br., BF_4^-). ^{1}H-NMR: 7.9–7.0 (*m*, 21 arom. H); 7.0–6.9 (*m*, 3 arom. H); 6.8–6.6 (*m*, 2 arom. H); 6.45–6.2 (*m*, 4 arom. H); 3.52, 3.19 (2*s*, 2 CH_3O); 3.48 (*m*, $NCHCH_3$); 2.26 (*d*, $J = 6.5$, $NCHCH_3$); 2.12 (*m*, NCH_3); 1.95 ($\sim$ *d*, $J = 2$, NCH_3). ^{31}P-NMR: 35.95 (*d*, $J = 44.5$); 11.72 (*d*, $J = 44.2$). Anal. calc. for $C_{48}H_{46}BF_4NO_2P_2Pd$ (924.05): C 62.39, H 5.02, N 1.52; found: C 61.50, H 5.29, N 1.53, H_2O 0.66.

1.7.2. *X-Ray Analysis of (*R,R*)*-**17a**. $C_{48}H_{46}NO_2P_2Pd \cdot BF_4$ (924.042): $F(000) = 1896$. *Space Group and Cell Dimensions:* orthorhombic: $P2_12_12_1$; $a = 11.776(2)$, $b = 18.723(3)$, $c = 19.117(6)$ Å; $D = 1.46$ (Mgm^{-3}, $Z = 4$; $\mu(Mo/K_\alpha) = 0.56$ mm^{-1}. *Data Collection:* crystal size $0.25 \times 0.35 \times 0.45$ mm^3; temp. 180° K; wavelenght: 0.71069 Å; scan mode: $\theta/2\theta$; scan speed: 5.2°/min minimum speed; strong reflexions measured at up to 20°/min; scan width: 2.2° $\theta_{min}/\theta_{max}$ 0/28°; peak: background ratio 5:1, intensity from profile analysis; total data measured: 5629 excluding standards; total data observed: 4341 rejection criterion: $I > 2.5\ \sigma(I)$; number of parameters: 578; weigths: $w = 1/(\sigma^2|F|^2 + 0.001|F|^2)$. Data were collected on a *Nicolet P3m* four-circle diffractometer fitted with a graphite monochromator and the *LT1* cooling apparatus. *Structure Determination and Refinement*: The structure was determined by *Patterson* methods. Refinement proceeded smoothly to convergence at $R = 0.0480$ with anisotropic refinement of all non-H-atoms. The H-atom coordinates were calculated using known geometries. All calculations were carried out with the SHELXTL/1 [29] package of the *R3m* system. Coordinates and thermal parameters have been deposited with the *Cambridge Crystallographic Data Centre*, Cambridge, University Chemical Lab, Cambridge CB2 1EW, England.

1.7.3. *(*R*)-(6,6'-Dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine)* ((*R*)-**5a**; (*R*)-MeO-BIPHEP). A suspension of (*R,R*)-**17a** (2.40 g, 2.59 mmol) in acetone (20 ml) and CF_3COOH (5 ml) was stirred at amb. temp. for 18 h. The resulting yellow soln. was evaporated by solvent condensation into a cold trap. The yellow residue was dissolved in CH_2Cl_2 and the soln. evaporated again. To the residue were added KCN (2.0 g), CH_2Cl_2 (20 ml), and H_2O (5 ml), and the two-layer system was stirred vigorously for 2 h. The org. layer was separated, washed with H_2O (3×5 ml), dried (Na_2SO_4), filtered through a short pad of silica gel, and evaporated. Crystallization of the residue (1.7 g) from toluene/EtOH (9 ml/11 ml) afforded 1.15 g (76%) of (*R*)-**5a**. M.p. 214–215°. $[\alpha]_D^{20} = +41.3$ ($c = 1.0$, $CHCl_3$). Anal. calc. for $C_{38}H_{32}O_2P_2$ (582.62): C 78.34, H 5.54; found: C 78.26, H 5.70.

1.7.4. *(*S*)-(6,6'-Dimethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine)* ((*S*)-**5a**; (*S*)-MeO-BIPHEP). Degradation of (*S*)-**17a** (1.20 g, 1.245 mmol) as described in *1.7.3* afforded 0.70 g (96%) of (*S*)-**5a**, white needles. M.p. 214–215°. $[\alpha]_D^{20} = -43.4$ ($c = 1.0$, $CHCl_3$).

1.8. *(2-Bromo-3-methoxyphenyl)diphenylphosphine Oxide* (**12**). Phosphine oxide **8a** (4.50 g, 14.6 mmol) was lithiated with LDA as described in *1.3*, and a soln. of Br_2 (3.57 g, 22.4 mmol) in THF (15 ml) was added at −70°. The reaction was allowed to warm to r.t. Usual workup followed by chromatography on silica gel (AcOEt) provided **12** (0.60 g, 10.5%) as white powder. The sample for analysis was recrystallized from CH_2Cl_2/Et_2O/hexane. M.p. 149–150°. IR: 1557 (Ar.); 1460 (P-Ar.); 1270, 1187, 1046 (Ar.-ether, P=O). ^{1}H-NMR: 7.72 (*m*, 4 arom. H); 7.6–7.4 (*m*, 6 arom. H); 7.3 (*m*, H–C(5)); 7.08 (*d*, $J = 8$, H–C(4)); 6.96 (*ddd*, $J = 12.5$, 8, 1.5, H–C(6)). MS: 388/386 (38/42, $M^{+\cdot}$), 387/385 (100/96, $[M-H]^+$), 307 (53, $[M-Br]^+$). Anal. calc. for $C_{19}H_{16}BrO_2P$ (387.21): C 58.94, H 4.17, Br 20.64; found: C 59.10, H 4.24, Br 20.62.

Treatment of **12** (0.31 g, 0.80 mmol) as described in *1.4* (4 h, 140°) yielded (*RS*)-**10a** (0.24 g, 97%) as white powder.

1.9. *Lithiation/Iodination of* **7a**. 1.9.1. *(4-Iodo-3-methoxyphenyl)diphenylphosphine* (**13**). A soln. of BuLi (12.5 ml, 1.6M in hexane, 20.0 mmol) was added dropwise to **7a** (5.80 g, 20.0 mmol) in THF (20 ml) at −10°. The yellow soln. was allowed to warm to 0° stirred at this temp. for 1 h. Then, a soln. of I_2 (2.50 g, 9.85 mmol) in THF (20 ml) was added at −10°. The reaction was allowed to warm to r.t., treated with aq. $Na_2S_2O_5$ soln., and the org. layer was washed with sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated. Chromatography on silica gel (hexane/CH_2Cl_2 9:1 followed by crystallization from hexane/toluene gave **13** (0.80 g, 10%). M.p. 121–123°. IR: 1566 (Ar.); 1373, 1249, 1024, 1010 (Ar.-ether). ^{1}H-NMR: 7.71 (*dd*, $J = 8$, 1.5, H–C(5)); 7.4–7.25 (*m*, 10 arom. H); 6.76 (*dd*, $J = 8$, 1.5, H–C(2)); 6.57 (*t* with fine struct., $J = 8$, H–C(6)); 3.73 (*s*, CH_3O). MS: 418 (100, $M^{+\cdot}$). Anal. calc. for $C_{19}H_{16}IOP$ (418.21): C 54.45, H 4.36; found: C 54.60, H 4.40.

1.9.2. *(4-Iodo-3-methoxyphenyl)diphenylphosphine Oxide* (**14**). Oxidation of a sample of **13** as described in *1.2* provided, after crystallization from hexane/Et_2O, **14**. M.p. 184–185°. IR: 1572 (Ar.); 1377, 1243, 1117, 1029

(Ar-ether); 1178 (P=O). ^{1}H-NMR: 7.83 (*dd*, *J* = 8, 3.5, H–C(5)); 7.7–7.4 (*m*, 10 arom. H); 7.34 (*dd*, *J* = 12.5, 1.5, H–C(2)); 6.74 (*ddd*, *J* = 9.5, 8, 1.5, H–C(6)); 3.87 (*s*, CH_3O). MS: 434 (69, $M^{+\cdot}$), 433 (100). Anal. calc. for $C_{19}H_{16}IO_2P$ (434.1): C 52.56, H 3.71; found: C 52.40, H 3.62.

2. Synthesis of the Diphosphines 5b. – 2.1. *(3,4-Dimethoxyphenyl)diphenylphosphine* (**7b**). Treatment of *4-bromo-1,2-dimethoxybenzene* (**6b**) (45.27 g, 0.208 mol) as described in *1.1* provided crude **7b** (75 g) as a yellow oil which crystallized on standing, and which was carried on into the next step without purification. An anal. sample was obtained by filtration through a short pad of silica gel (CH_2Cl_2) and crystallization from EtOH, white needles. M.p. 102.5–103.5° ([14f]: 127°). IR: 1591, 1508 (Ar.); 1433 (P-Ar.); 1254, 1145, 1021 (Ar.-ether). ^{1}H-NMR: 7.35–7.25 (*m*, 10 arom. H); 6.9–6.85 (*m*, 3 arom. H); 3.88, 3.75 (2*s*, 2 CH_3O). MS: 322 (100, $M^{+\cdot}$). Anal. calc. for $C_{20}H_{19}O_2P$ (322.34): C 74.52, H 5.94; found: C 74.41, H 5.93.

2.2. *(3,4-Dimethoxyphenyl)diphenylphosphine Oxide* (**8b**). Oxidation of **7b** (75 g of crude material, *ex* 0.208 mol of **6b**) afforded a solid which was crystallized from AcOEt/hexane (450 ml/450 ml) to provide **8b** (54 g, 77% based on **6b**) as a off-white powder. M.p. 154.5–156°. The anal. sample was obtained by recrystallization from THF/hexane. M.p. 156–157°. IR: 1589, 1509 (Ar.); 1438 (P-Ar.); 1260, 1161, 1020 (Ar.-ether); 1115 (P=O). ^{1}H-NMR: 7.7–7.6 (*m*, 4 arom. H); 7.6–7.4 (*m*, 6 arom. H); 7.32 (*dd*, *J* = 13, 1.5, 1 arom. H); 7.05 (*m*, 1 arom. H); 6.89 (*dd*, *J* = 8, 3, 1 arom. H); 3.91, 3.65 (2*s*, 2 CH_3O). MS: 338 (66, $M^{+\cdot}$), 337 (100). Anal. calc. for $C_{20}H_{19}O_3P$ (338.34): C 71.00, H 5.66; found: C 71.06, H 5.73.

2.3. *(2-Iodo-3,4-dimethoxyphenyl)diphenylphosphine Oxide* (**9b**). Treatment of **8b** (3.38 g, 10 mmol) with LDA (–78°/2 h) and I_2 as described in *1.3* followed by chromatography on silica gel (200 g, AcOEt) and recrystallization from *t*-BuOMe provided **9b** (3.8 g, 82%) as beige crystals. M.p. 178–179°. IR: 1571, 1472 (Ar.); 1264, 1144, 1017 (Ar.-ether); 1190 (P=O). ^{1}H-NMR: 7.8–7.65 (*m*, 4 arom. H); 7.6–7.4 (*m*, 6 arom. H); 6.95–6.8 (*m*, 2 arom. H); 3.88, 3.82 (2*s*, 2 CH_3O). MS: 464 (98, $M^{+\cdot}$), 463 (100), 337 (38). Anal. calc. for $C_{20}H_{19}IO_3P$ (464.24): C 51.74, H 3.91, I 27.34; found: C 51.59, H 4.02, I 27.09.

2.4. *(RS)-(5,5',6,6'-Tetramethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide)* ((*RS*)-**10b**). Treatment of **9b** (3.0 g, 6.46 mmol) as described in *1.4* (140°/4 h) followed by crystallization of the crude material from AcOEt provided (*RS*)-**10b** (1.80 g, 82%) as white crystals. M.p. 169–170°. IR: 1583, 1477 (Ar.); 1435 (P-Ar.); 1265, 1147, 1023 (Ar.-ether); 1202 (P=O). ^{1}H-NMR: 7.7–7.55 (*m*, 8 arom. H); 7.45–7.15 (*m*, 12 arom. H); 7.0–6.8 (*m*, 4 arom. H); 3.83 (*s*, 2 CH_3O); 3.41 (*s*, 2 CH_3O). MS: 643 (9, $[M - OCH_3]^+$), 597 (4, $[M - Ph]^+$), 473 (100, $[M - P(O)Ph_2]^+$). Anal. calc. for $C_{40}H_{36}O_6P_2$ (674.67): C 71.21, H 5.38; found: C 71.05, H 5.46.

2.5. *Resolution of (RS)-***10b**. 2.5.1. *Through-Reactions for the Synthesis of (RS)-***10b** *and Its Isolation as Complex with (–)-DBTA*. Treatment of **8b** (20.0 g, 59.1 mmol) as described in *2.3* afforded a brown solid (28.7 g) which was subjected without purification to the *Ullman* reaction (*cf. 2.4*). The resulting crude material (*ca.* 30 g of a brown solid) was dissolved in CH_2Cl_2 (130 ml), and the soln. was combined with a soln. of (–)-(2*R*,3*R*)-2,3-*O*-dibenzoyltartaric acid ((–)-DBTA) (12.5 g, 34.9 mmol) in AcOEt (260 ml). After stirring overnight, the precipitates were collected by filtration and dried at 100°/15 mbar for 3 h to afford 20.2 g of complex (*RS*)-**10b**/(–)-DBTA as off-white powder. Another 2 identical experiments afforded 20.3 g and 19.5 g of the complex, respectively. Yields over the 2 steps amounted to 63–66% based on **8b**.

2.5.2. *(S)-(5,5',6,6'-Tetramethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide)* ((*S*)-**10b**). The (*RS*)-**10b**/(–)-DBTA complex (39.0 g, 37.7 mmol, from *2.5.1*) was dissolved in $CHCl_3$ (600 ml) and EtOH (15 ml) at reflux temp. After stirring overnight at amb. temp. a first crop (1.5 g) of (*S*)-**10b**/(–)-DBTA was recovered by filtration. The filtrate was concentrated at the rotavapor, $CHCl_3$ (100 ml) was added to the crystal slurry, and the suspension was stirred at 50° for ½ h and at amb. temp. for 3 h. Filtration and drying *in vacuo* afforded a second crop (15.2 g) of (*S*)-**10b**/(–)-DBTA. (The mother liquor was stored for the recovery of the other enantiomer, *cf. 2.5.3.*) The enantiomeric purity of (*S*)-**10b** in both crops was > 99% ee by HPLC (*Pirkle* phase); combined yield 16.7 g (84% of theory). An anal. sample was obtained by recrystallization from $CHCl_3$/EtOH. $[\alpha]_D^{20} = -75$ (*c* = 1.0, MeOH).

The (*S*)-**10b**/(–)-DBTA complex (25.7 g, 24.9 mmol, combined material from 2 experiments) was stirred with CH_2Cl_2 (200 ml) and 2N NaOH (100 ml), until the solid had completely dissolved (30 min). The org. layer was separated, washed with 2N NaOH, H_2O and sat. NaCl soln., dried ($MgSO_4$), filtered, and evaporated to afford a white solid. The material was dissolved in CH_2Cl_2, *t*-BuOMe (100 ml) was added, and the soln. was concentrated at the rotavapor. The precipitates were collected by filtration, washed with hexane, and dried *in vacuo* to provide (*S*)-**10b** (26.7 g; 99.5% based on complex (*S*)-**10b**/(–)-DBTA); white powder. M.p. 140–150°. $[\alpha]_D^{20} = -21.3$ (*c* = 1.0, $CHCl_3$). This material contained *ca.* 0.3 mol-equiv. (3.5%) of *t*-BuOMe (^{1}H-NMR). An anal. sample was obtained by recrystallization from CH_2Cl_2/AcOEt/hexane. M.p. 169–170°. $[\alpha]_D^{20} = -23.6$ (*c* = 1.0, $CHCl_3$). IR, ^{1}H-NMR, MS: identical to the corresponding spectra of (*RS*)-**10b**.

2.5.3. *(R)-(5,5',6,6'-Tetramethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide)* ((*R*)-**10b**). The residue obtained after evaporation of the mother liquor from *2.5.2* (*ex* 27.7 mmol (*RS*)-**10b**) together with the corresponding

material from another resolution experiment (*ex* 19.55 mmol (*RS*)-**10b**) was stirred with CH_2Cl_2 (200 ml) and 5N NaOH (100 ml), until the solid had completely dissolved (1 h). The org. layer was separated, washed with 2N NaOH, H_2O and sat. NaCl soln., dried (Na_2SO_4), filtered, and evaporated to provide enantiomerically enriched (*R*)-**10b** as a brown solid (23.3 g). A soln. of this material in $CHCl_3$ (100 ml) and EtOH (15 ml) was combined with a soln. of (+)-(2*S*,3*S*)-2,3-*O*-dibenzoyltartaric acid ((+)-DBTA) (14.0 g, 26.2 mmol) in $CHCl_3$ (90 ml) and EtOH (10 ml), and the soln. was concentrated at the rotavapor to obtain a crystal slurry. After addition of $CHCl_3$ (100 ml), the crystals were collected by filtration and dried *in vacuo*: 17.8 g (60% of theory) of (*R*)-**10b**/(+)-DBTA. The enantiomeric purity of (*R*)-**10b** was 99% ee according to HPLC (*Pirkle* phase). The sample for analysis was recrystallized from $CHCl_3$/EtOH. $[\alpha]_D^{20} = +72.5$ ($c = 1.0$, MeOH).

The (*R*)-**10b**/(+)-DBTA complex (22.9 g, 22.1 mmol, combined materials from 2 experiments) was decomposed as described in *2.5.2* to provide (*R*)-**10b** (14.4 g, 96% based on complex) as white powder. M.p. 140–150°. $[\alpha]_D^{20} = +20.6$ ($c = 0.5$, $CHCl_3$). This material contained 0.2 mol-equiv. (2.5%) of *t*-BuOMe (^{1}H-NMR). The sample for analysis was recrystallized from AcOEt/*t*-BuOMe. M.p. 167–169°. $[\alpha]_D^{20} = +21.6$ ($c = 0.5$, $CHCl_3$). IR, ^{1}H-NMR, MS: identical to the corresponding spectra of (*RS*)-**10b**. Anal. calc. for $C_{40}H_{36}O_6P_2$ (674.67): C 71.21, H 5.38; found: C 70.65, H 5.60.

2.6. *Reduction to Diphosphines* **5b**. 2.6.1. *(R)-(5,5',6,6'-Tetramethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine)* ((*R*)-**5b**). The crude material, obtained by reduction of (*R*)-**10b** (14.0 g, 209.75 mmol) as described in *1.6.1*, was crystallized by dissolution in CH_2Cl_2 (200 ml), addition of EtOH (100 ml) and concentration at the rotavapor to about $^1/_3$ of the original volume. The white precipitates were collected, washed with EtOH and pentane, and dried *in vacuo* at 80° for 4 h: 12.1 g (91%) (*R*)-**5b**. White powder. M.p. 171–172°. $[\alpha]_D^{20} = +5.8$ ($c = 1.0$, $CHCl_3$). CD ($c = 0.080$, $CHCl_3$): 227 (−22.8, neg. max.); 229 (−22.9, neg. min.); 240 (−28.8, neg. max.); 261 (0); 280 (+16.1, pos. max.). IR: 1557 (Ar.); 1466, 1430 (P-Ar.); 1287, 1146, 1023 (Ar.-ether). ^{1}H-NMR: 7.4–7.1 (*m*, 20 arom. H); 6.9 (*s*, with fine struct., 4 arom. H); 3.81 (*s*, 2 CH_3O); 3.32 (*s*, 2 CH_3O). ^{1}H-NMR (400 MHz) of derived Pd complex (*R,R*)-**16b** (formed *in situ* by addition of 0.5 mol-equiv. of (*R*)-**15**): 8.5–7.55 (br. *m*, 7 arom. H); 7.5–7.35 (*m*, 10 arom. H); 7.2 (*m*, 1 arom. H); 7.1 (*m*, 2 arom. H); 6.99 (*dd*, $J = 12$, 8, 1 arom. H); 6.75 (*m*, 4 arom. H); 6.46 (*m*, 2 arom. H); 6.30 (*m*, 1 arom. H); 5.20 (*q*, $J = 6.5$, NC*H*CH_3); 3.71, 3.70, 3.68, 3.13 (4*s*, 4 CH_3O); 2.50 (*m*, NCH_3); 1.38 ($\sim d$, $J = 2$, NCH_3); 1.31 (*d*, $J = 6.5$, NCHCH_3); additionally: 3.19 (*s*, CH_3O) of *ca.* 0.7% of diastereoisomer (*S,R*)-**16b**; enantiomeric purity of (*R*)-**5b** ≥ 98.5% ee. MS: 611 (8, $[M - OMe]^+$), 565 (6, $[M - Ph]^+$), 458 (90), 457 (100, $[M - PPh_2]^+$), 290 (41). Anal. calc. for $C_{40}H_{36}O_4P_2$ (642.67): C 74.76, H 5.65; found: C 74.60, H 5.72.

2.6.2. *(S)-(5,5',6,6'-Tetramethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine)* ((*S*)-**5b**). An analogous reduction of (*S*)-**10b** (16.4 g, 24.3 mmol) provided (*S*)-**5b** (14.0 g, 90%) as white powder. M.p. 171–172°. $[\alpha]_D^{20} = -5.8$ ($c = 1.0$, $CHCl_3$). CD ($c = 0.082$, $CHCl_3$): 226 (+26.1, pos. max.); 230 (+25.2, pos. min.); 241 (+32.8, pos. max.); 261 (0); 281 (−15.0, neg. max.). IR, ^{1}H-NMR, MS: identical to the corresponding spectra of (*R*)-**5b**. ^{1}H-NMR (400 MHz) of derived Pd complex (*S,R*)-**16b** (formed *in situ* by addition of 0.5 mol-equiv. of (*R*)-**15**): 8.3 (br., 1 arom. H); 7.75 (br., 1 arom. H); 7.6 (br. *s*, 3 arom. H); 7.5–6.9 (several *m*, 18 arom. H); 6.73 (*m*, 2 arom. H); 6.69 (*dd*, $J = 9$, 7.5, 1 arom. H); 6.46 (*dd*, $J = 9$, 1, 1 arom. H); 6.37–6.22 (*m*, 2 arom. H); 3.74, 3.70, 3.68 (3*s*, 3 CH_3O); 3.47 (*m*, NC*H*CH_3); 3.20 (*s*, 1 CH_3O); 2.23 (*d*, $J = 6.5$, NCHCH_3); 2.11 (*m*, NCH_3); 1.78 (*m*, NCH_3); additionally: 3.13 (*s*, CH_3O) of *ca.* 0.5% of diastereoisomer (*R,R*)-**12b**; enantiomeric purity of (*S*)-**5b** ≥ 99% ee. Anal. calc. for $C_{40}H_{36}O_4P_2$ (642.67): C 74.76, H 5.65; found: C 74.48, H 5.78.

2.6.3. *(RS)-(5,5',6,6'-Tetramethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine)* ((*RS*)-**5b**). Reduction of (*RS*)-**10b** according to *1.6.1* using CH_3CN instead of xylene as solvent followed by chromatography on silica gel (hexane/CH_2Cl_2) and crystallization from EtOH provided (*RS*)-**5b** as white crystals. M.p. 217–219°. IR, ^{1}H-NMR, MS: identical to the corresponding spectra of (*R*)-**5b**.

3. Synthesis of the Diphosphines 5c. – 3.1. *(3,4,5-Trimethoxyphenyl)diphenylphosphine* (**7c**). Treatment of *5-bromo-1,2,3-trimethoxybenzene* (**6c**) [30] (10.0 g, 40.5 mmol) as described in *1.1* provided crude **7c** as an oil. Crystallization occurred upon dissolving the oil in MeOH and concentration of the soln. at the rotavapor. The crystals were collected by filtration, washed with MeOH, and dried *in vacuo*: 9.83 g of **7c**. M.p. 88–89°, GC purity 99%. A second crop of 1.93 g of **7c** was obtained from the mother liquor. M.p. 87.5–88.5°, GC purity 98%; combined yield 11.75 g (82.5%). An analogous experiment starting from 50.0 g (0.202 mol) of **6c** afforded 60.75 g (85%) of **7c**. M.p. 87.5–88.5°. IR: 1574, 1498 (Ar.); 1431 (P-Ar.); 1237, 1124, 1001 (Ar.-ether). ^{1}H-NMR: 7.3 (*m*, 10 arom. H); 6.53 (*d*, $J = 8$, 2 arom. H); 3.86 (*s*, 1 CH_3O); 3.71 (*s*, 2 CH_3O). MS: 352 (100, M^+). Anal. calc. for $C_{21}H_{21}O_3P$ (352.37): C 71.58, H 6.01; found: C 71.40, H 6.11.

3.2. *(3,4,5-Trimethoxyphenyl)diphenylphosphine Oxide* (**8c**). Oxidation of **7c** (11.76 g, 33.4 mmol) as described in *1.2* gave an oil which was crystallized from Et_2O/hexane (20 ml/5 ml) to provide **8c** (11.6 g, 94%) as white crystals. M.p. 125.5–126°. An analogous experiment starting from 56.0 g (0.519 mol) **7c** afforded 56.4 g (96%) **8c**.

IR: 1580, 1502 (Ar.); 1435 (P-Ar.); 1236, 1124, 1002 (Ar.-ether); 1184 (P=O). ^{1}H-NMR: 7.75–7.65 (*m*, 14 arom. H); 7.6–7.4 (*m*, 6 arom. H); 6.86 (*d*, *J* = 13, 2 arom. H); 3.90 (*s*, 1 CH_3O); 3.78 (*s*, 2 CH_3O). MS: 368 (85, M^+), 367 (100), 353 (15, $[M - Me]^+$). Anal. calc. for $C_{21}H_{21}O_4P$ (368.37): C 68.47, H 5.75; found: C 68.56, H 6.00.

3.3. *(2-Iodo-3,4,5-trimethoxyphenyl)diphenylphosphine Oxide* (**9c**). Treatment of **8c** (11.0 g, 29.9 mmol) with LDA (−78°, 2 h) and I_2 as described in *1.3* followed by chromatography on silica gel (hexane/AcOEt 3:1) and crystallization from *t*-BuOMe provided **9c** (9.7 g, 66%) as white crystals. M.p. 139.5–140.5°. In an analogous experiment starting from 50.0 g (136 mmol) **8c**, the crude material was directly crystallized from AcOEt to afford 45.7 g (68%) **9c**. M.p. 137–138°. IR: 1547, 1474 (Ar.); 1301, 1178, 1149, 1100, 991 (Ar.-ether, P=O). ^{1}H-NMR: 7.8–7.7 (*m*, 4 arom. H); 7.6–7.4 (*m*, 6 arom H); 6.78 (*d*, *J* = 14, H–C(6)); 3.93, 3.85, 3.59 (3*s*, 3 CH_3O). MS: 494 (67, M^+), 493 (100), 367 (35, $[M - I]^+$). Anal. calc. for $C_{21}H_{20}IO_4P$ (494.26): C 51.03, H 4.08, I 25.68; found: C 51.03, H 4.08, I 25.41.

3.4. *(RS)-(4,4',5,5',6,6'-Hexamethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide)* ((*RS*)-**10c**). Treatment of **9c** (9.7 g, 19.6 mmol) as described in 1.4 (140°/3 h) followed by crystallization of the crude material from CH_2Cl_2/hexane provided (*RS*)-**10c** (5.7 g, 79%) as white powder. M.p. > 250°. In an analogous experiment, starting from 45.7 g (92.5 mmol) **9c**, a yield of 30.67 g (90%) of (*RS*)-**10c** was achieved. IR: 1584, 1480 (Ar.); 1301, 1199, 1113, 1027 (Ar.-ether, P=O). ^{1}H-NMR: 7.75–7.55 (*m*, 8 arom. H); 7.5–7.2 (*m*, 12 arom. H); 6.44 (*d*, *J* = 14.5, H–C(3), H–C(3')); 3.72, 3.57, 3.49 (3*s*, 2 CH_3O each). MS: 703 (7, $[M - OMe]^+$), 657 (3, $[M - Ph]^+$), 534 (33), 533 (100, $[M - P(O)Ph_2]^+$). Anal. calc. for $C_{42}H_{40}O_8P_2$ (734.72): C 68.66, H 5.49; found: C 68.36, H 5.56.

3.5. *Resolution of (RS)-***10c**. 3.5.1. *Resolution* via *Complexes (S)-***10c***/(−)-DBTA and (R)-***10c***/(+)-DBTA*. a) *(S)-(4,4',5,5',6,6'-Hexamethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide)* ((*S*)-**10c**). Compound (*RS*)-**10c** (4.0 g, 5.44 mmol) and (−)-DBTA (2.0 g, 5.6 mmol) were dissolved in i-PrOH (20 ml) at reflux temp. After stirring and cooling to r.t. overnight, the precipitates were collected by filtration to provide complex (*S*)-**10c**/(−)-DBTA (2.50 g, 1:1 complex by ^{1}H-NMR, (*R*)-**10c**/(*S*)-**10c** 2:98 by HPLC on (+)-poly(trityl methacrylate)) as white crystals. $[\alpha]_D^{20} = -24$ (*c* = 1.0, $CHCl_3$). Recrystallization from i-PrOH (15 ml) gave pure (*S*)-**10c**/(−)-DBTA (1.90 g, (*R*)-**10c**/(*S*)-**10c** 0.2:99.8 by HPLC). (The mother liquors were stored for the recovery of the enantiomer, *vide infra*.) The complex was treated with CH_2Cl_2 (50 ml) and 2N NaOH (40 ml) as described in *1.5.1* to provide (*S*)-**10c** (1.30 g, 65% of theory based on (*RS*)-**10c**) as white powder. M.p. 284°. $[\alpha]_D^{20} = -51.3$ (*c* = 1.0, $CHCl_3$). IR, ^{1}H-NMR, MS: identical to the corresponding spectra of (*RS*)-**10c**. Anal. calc. for $C_{42}H_{40}O_8P_2$ (734.72): C 68.66, H 5.49; found: C 68.56, H 5.71.

b) *(R)-(4,4',5,5',6,6'-Hexamethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine oxide)* ((*R*)-**10c**). The residue obtained after evaporation of the mother liquors from above (*ex* 5.44 mol (*RS*)-**10c**) was treated in the usual way with CH_2Cl_2/2N NaOH. The resulting solid (2.6 g) and (+)-DBTA (1.50 g, 4.18 mmol) were dissolved in refluxing i-PrOH (15 ml). After stirring and cooling to r.t. overnight, the precipitates were collected by filtration to provide complex (*R*)-**10c**/(+)-DBTA (2.7 g, 1:1 complex by ^{1}H-NMR, (*R*)-**10c**/(*S*)-**10c** 99:1 by HPLC). Treatment of this material with 2N NaOH/CH_2Cl_2 in the usual way provided (*R*)-**10c** (1.70 g, 85% of theory based on (*RS*)-**10c**) as white powder. M.p. 284°. $[\alpha]_D^{20} = +54.7$ (*c* = 1.0, $CHCl_3$). IR, ^{1}H-NMR, MS: identical to the corresponding spectra of (*RS*)-**10c**. Anal. calc. for $C_{42}H_{40}O_8P_2$ (734.72): C 68.66, H 5.49; found: C 68.54, H 5.66.

3.5.2. *Resolution* via *Complexes (R)-***10c***/(−)-DBTA and (S)-***10c***/(+)-DBTA*. Solns. of (*RS*)-**10c** (35.63 g, 48.5 mmol) in CH_2Cl_2 (180 ml) and (−)-DBTA (23.3 g, 65.1 mmol) in AcOEt (215 ml) were combined. After stirring overnight, the precipitates were collected by filtration to give the complex (**10c**/(−)-DBTA (18.93 g, (*R*)-**10c**/(*S*)-**10c** 67:33 by HPLC on (+)-poly(trityl methacrylate)). (The mother liquor was stored for recovery of the other enantiomer.) The complex was recrystallized 3 times from i-PrOH to afford diastereoisomerically almost pure complex (*R*)-**10**/(−)-DBTA (4.4 g, (*R*)-**10c**/(*S*)-**10c** 99.5:0.5 by HPLC). From this material, (*R*)-**10c** (2.9 g, 16% of theory based on (*RS*)-**10c**) was isolated by the usual 2N NaOH/CH_2Cl_2 treatment, enantiomeric purity 99% ee (HPLC).

Compound **10c** recovered from the above mother liquor by the usual 2N NaOH/CH_2Cl_2 treatment (22.5 g) was dissolved together with (+)-DBTA (14.7 g, 41.0 mmol) in warm i-PrOH (150 ml). After stirring and cooling to r.t. overnight, the precipitate was collected by filtration to provide complex (*S*)-**10c**/(+)-DBTA (10.8 g, (*R*)-**10c**/(*S*)-**10c** 4:96 by HPLC) which was recrystallized from i-PrOH to give diastereoisomerically almost pure complex (*S*)-**10c**/(+)-DBTA (6.4 g, (*R*)-**10c**/(*S*)-**10c** 0.5:99.5 by HPLC). From this material, (*S*)-**10c** (4.3 g, 24% of theory based on (*RS*)-**10c**) was isolated by the usual 2N NaOH/CH_2Cl_2 treatment; enantiomeric purity 99.3% ee (HPLC).

3.5.3. *Resolution* via *Complexes (R)-***10c***/(+)-DBTA and (S)-***10c***/(+)-DBTA*. A soln. of (*RS*)-**10c** (20.5 g, 27.9 mmol) and (+)-DBTA (10.5 g, 29.3 mmol) in i-PrOH was stirred at 50° until crystallization started, then at amb. temp. overnight. The solid obtained after filtration (17.0 g, (*R*)-**10c**/(*S*)-**10c** 73:27 by HPLC) was recrystallized twice from i-PrOH (70 ml and 40 ml) to provide complex (*R*)-**10c**/(+)-DBTA (10.0 g, 1:1 complex by ^{1}H-NMR; (*R*)-**10c**/(*S*)-**10c** ≥ 99:1 by HPLC). $[\alpha]_D^{20} = +26$ (*c* = 0.5, $CHCl_3$). (The mother liquors of the 3

crystallizations were stored for the recovery of the enantiomer.) The complex was treated with 5N NaOH/CH_2Cl_2 in the usual manner to provide, subsequent to crystallization from *t*-BuOMe/CH_2Cl_2, (*R*)-**10c** (6.60 g, 64.5% of theory based on (*RS*)-**10c**) as white powder. M.p. 284°. $[\alpha]_D^{20} = +51.0$ (*c* = 1.0, $CHCl_3$).

Solns. of **10c** (12.0 g, 16.4 mmol, (*R*)-**10c**/(*S*)-**10c** 20:80 by HPLC, recovered in the usual way from the above mother liquors) in CH_2Cl_2 (60 ml) and (+)-DBTA (6.60 g, 18.4 mol) in i-PrOH (60 ml) were combined and concentrated at the rotavapor at 50°/400 mbar. The precipitate was filtered, washed with i-PrOH, and pentane and dried *in vacuo* to provide the 1:1 complex (*S*)-**10c**/(+)-DBTA (8.0 g); $[\alpha]_D^{20} = +16.5$ (*c* = 1.0, $CHCl_3$). Usual treatment of this material with 5N NaOH/CH_2Cl_2 provided (*S*)-**10c** (5.30 g, 52% of theory based on (*RS*)-**10c**) as white powder. M.p. 284°. $[\alpha]_D^{20} = -51.5$ (*c* = 1.0, $CHCl_3$); ee ≥ 99% (HPLC).

3.5.4. *Isolation of the DBTA Complexes from Optically Pure* **10c**. Compound (*R*)- or (*S*)-**10c** (0.734 g, 1.0 mmol) and (–)- or (+)-DBTA (0.360 g, 1.0 mmol) were dissolved in hot i-PrOH (20 ml). After standing overnight, the precipitates were filtered, washed (i-PrOH) and dried to provide the complexes (1:1 adducts by ^{1}H-NMR): (*R*)-**10c**/(–)-DBTA (70 mg, 6.5%); $[\alpha]_D^{20} = -20.7$ (*c* = 1.0, $CHCl_3$); (*R*)-**10c**/(+)-DBTA (1.0 g, 91%); $[\alpha]_D^{20} = +25.0$ (*c* = 1.0, $CHCl_3$); (*S*)-**10c**/(–)-DBTA (0.80 g, 73%); $[\alpha]_D^{20} = -24.3$ (*c* = 1.0, $CHCl_3$); (*S*)-**10c**/(+)-DBTA (0.20 g, 18%); $[\alpha]_D^{20} = +21.4$ (*c* = 1.0, $CHCl_3$).

3.6. *Reduction to Diphosphines* **5c**. 3.6.1. *(R)-(4,4',5,5',6,6'-Hexamethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine)* ((*R*)-**5c**). Reduction of (*R*)-**10c** (6.30 g, 8.5 mmol) as described in *1.6.1* provided, after crystallization from CH_2Cl_2/EtOH, (*R*)-**5c** (5.80 g, 96%), white platelets. M.p. 238°. $[\alpha]_D^{20} = -2.4$ (*c* = 1.16, $CHCl_3$). CD (*c* = 0.106, $CHCl_3$): 220 (0); 241 (–50.6, neg. max.); 266 (0); 284 (+7.5, sh); 291 (+8.3, sh.); 304 (+9.8, pos. max.); 329 (0). IR: 1580, 1474 (Ar.); 1460 (P-Ar.); 1295, 1153, 1025 (Ar.-ether). ^{1}H-NMR: 7.3–7.2 (*m*, 20 arom. H); 6.38 (*m*, 2 arom. H); 3.65, 3.56, 3.36 (3*s*, 2 CH_3O each). ^{1}H-NMR (400 MHz) of derived Pd complex (*R*,*R*)-**16c** (formed *in situ* by addition of 0.5 mol-equiv. of (*R*)-**15**): 8.4–7.4 (br. *m*, 17 arom H); 7.25–7.1 (*m*, 3 arom H); 6.75 (*m*, 2 arom H); 6.53–6.44 (*m*, 2 arom H); 6.29 (*m*, 2 arom H); 5.35 (*q*, *J* = 6.5, NC*H*CH_3); 3.73, 3.64, 3.59, 3.58, 3.50, 3.22 (6*s*, 6 CH_3O); 2.56 (*m*, NCH_3); 1.44 (*m*, NCH_3); 1.33 (*d*, *J* = 6.5, NCHCH_3); additionally: 3.27 (*s*, CH_3O) of *ca.* 0.5% of diastereoisomer (*S*,*R*)-**16c**; enantiomeric purity of (*R*)-**5c**: ≥ 99% ee. MS: 671 (2, $[M - OMe]^+$), 517 (100, $[M - PPh_2]^+$). Anal. calc. for $C_{42}H_{40}O_6P_2$ (702.72): C 71.79, H 5.74; found: C 71.74, H 5.78.

3.6.2. *(S)-(4,4',5,5',6,6'-Hexamethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine)* ((*S*)-**5c**). Analogous reduction of (*S*)-**10c** (5.0 g, 6.8 mmol) provided (*S*)-**5c** (4.5 g, 94%), white platelets. M.p. 243°. $[\alpha]_D^{20} = +2.7$ (*c* = 1.04, $CHCl_3$). CD (*c* = 0.218, $CHCl_3$): 240 (+51.7, pos. max.); 264 (0); 283 (–9.2, sh); 291 (–9.9, sh); 303 (–11.0, neg. max.). IR, ^{1}H-NMR, MS: identical to the corresponding spectra of (*R*)-**5c**. ^{1}H-NMR (400 MHz) of derived Pd complex (*S*,*R*)-**16** (formed *in situ* by addition of 0.5 mol-equiv. of (*R*)-**15**): 8.0–7.35 (br. *m*, 15 arom H); 7.3–7.1 (*m*, 5 arom H); 6.98 (*m*, 1 arom H); 6.76 (*t*, *J* = 7, 1 arom H); 6.49 (*d*, *J* = 13, 1 arom H); 6.35 (*q*, *J* = 7, 1 arom. H); 6.28 (*m*, 1 arom H); 6.20 (*d*, *J* = 10, 1 arom H); 3.78, 3.65, 3.57, 3.53, 3.47, 3.27 (6*s*, 6 CH_3O); 3.55 (*m*, NC*H*CH_3); 2.26 (*d*, *J* = 6.5, NCHCH_3); 2.17 (br. *s*, NCH_3); 1.84 (br. *s*, NCH_3); additionally: 3.22 (*s*, CH_3O) of *ca.* 0.5% of diastereoisomer (*S*,*R*)-**16c**; enantiomeric purity of (*S*)-**5c**: ≥ 99% ee. Anal. calc. for $C_{42}H_{40}O_6P_2$ (702.72): C 71.79, H 5.74; found: C 71.69, H 5.83.

3.6.3. *(RS)-(4,4'-5,5'-6,6'-Hexamethoxybiphenyl-2,2'-diyl)bis(diphenylphosphine)* ((*RS*)-**5c**). Analogous reduction of (*RS*)-**10c** (4.80 g, 6.5 mmol) afforded (*RS*)-**5c** (4.40 g, 96%) as white powder. M.p. 234.5°. IR, ^{1}H-NMR; MS: identical to the corresponding spectra of (*R*)-**5c**. Anal. calc. for $C_{42}H_{40}O_6P_2$ (702.72): C 71.79, H 5.74; found: C 71.94, H 5.85.

4. Rh^I Complexes. – Cationic Rh^I complexes were prepared according to literature procedures [24] (*cf.* [2b]). *[Rh((R)-5a)(cod)]BF$_4$*. A mixture of $[Rh(cod)_2]BF_4$ (203 mg, 0.50 mmol) and (*R*)-**5a** (291 mg, 0.50 mmol) in THF (30 ml) was stirred overnight. After evaporation to dryness, the residue was treated with Et_2O (30 ml), and the precipitates were filtered, washed with Et_2O and dried *in vacuo* to provide [Rh((*R*)-**5a**)(cod)]BF_4 (359 mg, 91%) as an orange microcrystalline powder. IR: 1568 (Ar.); 1264, 1155 (Ar.-ether); 1053 (br., BF_4^-). ^{1}H-NMR: 7.75–7.2 (*m*, 22 arom. H); 7.05 (*t*, *J* = 8, 2 arom. H); 6.37 (*d*, *J* = 8, 2 arom. H); 4.7, 4.55 (2*m*, 2 × 2 olefin. H); 3.34 (*s*, 2 CH_3O); 2.7, 2.45, 2.2, 2.1 (4*m*, 4 CH_2). Anal. calc. for $C_{46}H_{44}BF_4O_2P_2Rh$ (880.51): C 62.75, H 5.04; found: C 61.99, H 5.55.

[Rh((R)-5a)(cod)]ClO$_4$. A analogous reaction of $[Rh(cod)_2]ClO_4$ (209 mg, 0.50 mmol) and (*R*)-**5a** (291 mg, 0.50 mmol) provided [Rh((*R*)-**5a**)(cod)]ClO_4 (431 mg, 96%) as an orange powder. IR: 1568 (Ar.); 1263, 1155 (Ar.-ether); 1092 (br., ClO_4^-). ^{1}H-NMR: identical to ^{1}H-NMR of [Rh((*R*)-**5a**)(cod)]BF_4; contains *ca.* 20 mol-% of Et_2O.

[Rh((R)-5a)(nbd)]BF$_4$. A mixture of $[Rh(nbd)Cl]_2$ (247 mg, 0.536 mmol) and (*R*)-**5a** (624 mg, 1.07 mmol) in MeOH (20 ml) was stirred at r.t. (4 h) to obtain a homogeneous soln. A soln. of $NaBF_4$ (93 mg, 0.85 mmol) in H_2O (9 ml) was added dropwise, and the precipitates were filtered, washed with H_2O and dried *in vacuo* to give an orange powder (410 mg). Crystallization from CH_2Cl_2/EtO 1:1 yielded, after washing with AcOEt and drying *in vacuo*,

130 mg of an orange powder. A second crop of 180 mg was obtained from the mother liquor; combined yield: 310 mg (33%) of [Rh((*R*)-**5a**)(nbd)]BF_4. ^{1}H-NMR: 7.8–7.2 (*m*, 22 arom. H); 7.05 (*m*, 2 arom H); 6.4 (*m*, 2 arom H); 4.95, 4.65 (2*m*, 2 × 2 olefin. H); 4.05 (*m*, 2 CH); 3.34 (*s*, 2 CH_3O); 1.55 (br. *s*, CH_2); contains *ca.* 50 mol-% of AcOEt.

*[Rh((R)-***5a***)$_2$]BF_4.* A mixture of [Rh(cod)$_2$]BF_4 (203 mg, 0.50 mmol) and (*R*)-**5a** (612 mg, 1.05 mmol) in THF (25 ml) was stirred at amb. temp. (4 h) to give a clear soln., then at 60° overnight to produce an orange suspension. Filtration, washing with Et_2O, and drying *in vacuo* yielded [Rh((*R*)-**5a**)$_2$]BF_4 (470 mg, 69%) as an orange powder. $[\alpha]_D^{20} = +187$ ($c = 0.2$, $CHCl_3$). IR: 1567 (Ar.); 1460 (P-Ar.); 1263, 1182 (Ar.-ether); 1054 (br., BF_4^-). ^{1}H-NMR: 7.87 (*m*, 8 arom. H); 7.35–6.95 (*m*, 20 arom. H); 6.8–6.6 (*m*, 20 arom. H); 6.53 (*d*, $J = 8$, 4 arom. H); 3.49 (*s*, 4 CH_3O). Anal. calc. for $C_{76}H_{64}BF_4O_4P_4Rh$ (1354.95): C 67.37, H 4.76; found: C 67.27, H 4.57.

*[Rh((R)-***5a***)$_2$]ClO_4.* A mixture of [Rh(cod)$_2$]ClO_4 (105 mg, 0.25 mmol) and (*R*)-**5a** (291 mg, 0.50 mmol) in THF (25 ml) was stirred at 60° overnight. Filtration of the precipitates, washing with Et_2O, and drying *in vacuo* provided [Rh((*R*)-**5a**)$_2$]ClO_4 (259 mg, 76%) as an orange powder. $[\alpha]_D^{20} = +191.5$ ($c = 0.2$, $CHCl_3$). IR: 1567 (Ar.); 1460 (P-Ar.); 1263, 1154, 1045 (Ar.-ether); 1090 (br., ClO_4^-). ^{1}H-NMR: identical to that of [Rh((*R*)-**5a**)$_2$]BF_4; contains *ca.* 50 mol-% of H_2O.

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