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# Rigid P-chiral mono and diphosphines. Configurative stability and P-inversion barrier

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**Abstract**—A group of P-chiral monophosphine oxides and one diaryl diphosphine oxide based on the dibenzophosphole skeleton have been synthesized. Preparative enantioselective chromatography of 4-trimethylsilyl-5-phenyl-5*H*-dibenzophosphol oxide followed by a simple transformation with exchange of substituents (and a homo-coupling reaction in one case) and a stereoselective reduction step furnished the corresponding phosphines in fair to good yield. Their relative and absolute configurations were determined by crystal structure analysis. It turned out that racemization of the phosphines through P-inversion takes place at ambient temperature and depends markedly on *ortho* substituents (104–114 kJ mol$^{-1}$). In the case of the diphosphine, racemization can be suppressed when forming a chelate with Pd(II) or Ni(II) complexes.


## 1. Introduction

The dramatically increased importance of transition metal catalyzed asymmetric transformations[1] over the last few decades has been paralleled by the growing desire for chiral ligands. Among these especially P(III)-compounds have proven to be versatile modifiers, useful in numerous types of transition metal catalyzed reactions. An impressive number of applications have been reported where almost enantiopure products were obtained in high chemical yield.

Nevertheless, it became obvious that a perfect fit of ligand and substrate is a prerequisite for high asymmetric induction. This stimulated an intensive and continuous search for new and more efficient ligand structures. Since it is generally accepted that conformational stability, best accomplished through the formation of 5–7 membered chelates, is a favorable feature for efficient chiral catalysts, preferentially bidentate P-ligands have been applied. In contrast, the number of chiral monophosphines[2] is still comparably small, which might be due to the fact that only rather recently transition metal catalyzed reactions have been discovered, which are better catalyzed by monodentate ligands.[3] To counterbalance the lack of conformational stability in transition metal catalysts with monodentate ligands, frequently concomitant with decreased asymmetric induction, P-chiral phosphines,[4] which display their chiral interaction in immediate proximity to the metal center are of high interest. These compounds are typically prepared either by (1) resolution of preceding phosphine oxides, (2) stepwise attachment of three electronically and/or sterically different aryl or alkyl substituents to a sp$^3$ P-center replacing a chiral auxiliary, (3) by asymmetric deprotonation of enantiotopic $CH_3$ or $CH_2$ groups in corresponding phosphine oxides or borane complexes, or (4) via dynamic kinetic resolution of secondary phosphine borane complexes under the influence of BuLi/(−)sparteine or chiral transition metal complexes.[5] A sufficiently high inversion barrier provided stable enantiomers. Several calculations and empirical determinations of the barrier for the pyramidal inversion have been performed both, for open chain and cyclic phosphines,[6] including P-aromatic systems.[7]

For rigid compounds of general structures depicted in Figure 1, the inversion of P will be markedly influenced by the ring strain and the aromatic character of the heteroring (if $n = 0$). For the first investigation, we chose the dibenzophosphole unit (Fig. 1: R = aryl, $n = 0$) as a rigid prochiral

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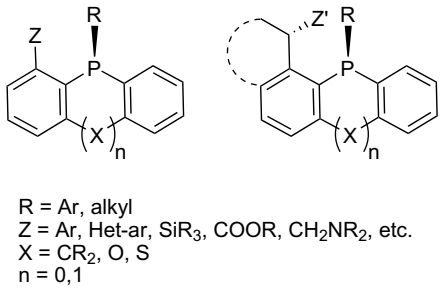



**Figure 1.** Examples of P-chiral auxiliaries through desymmetrization of P heterocycles.

precursor,[8] which can be conveniently desymmetrized by *ortho* substitution yielding P-chiral monophosphines. Based on the results of the calculations,[7] we expected moderate configurative stability, which eventually increased due to the presence of annelated benzene rings in a range of 100 and 150 kJ $mol^{-1}$.

In a subsequent homo-coupling reaction, $C_2$-symmetrical biaryl ligands[9] will be accessible (Scheme 1). With these ligands, sterically demanding metal complexes will be formed, in particular with $Z^1 \neq H$ in the case of biaryls, which can be applied as chiral catalysts. We expected an increased asymmetric induction in several reaction types, especially in cases where small and/or monocoordinating substrate molecules are involved, due to a more pronounced steric interaction with improved conformational stability in substrate complexes.

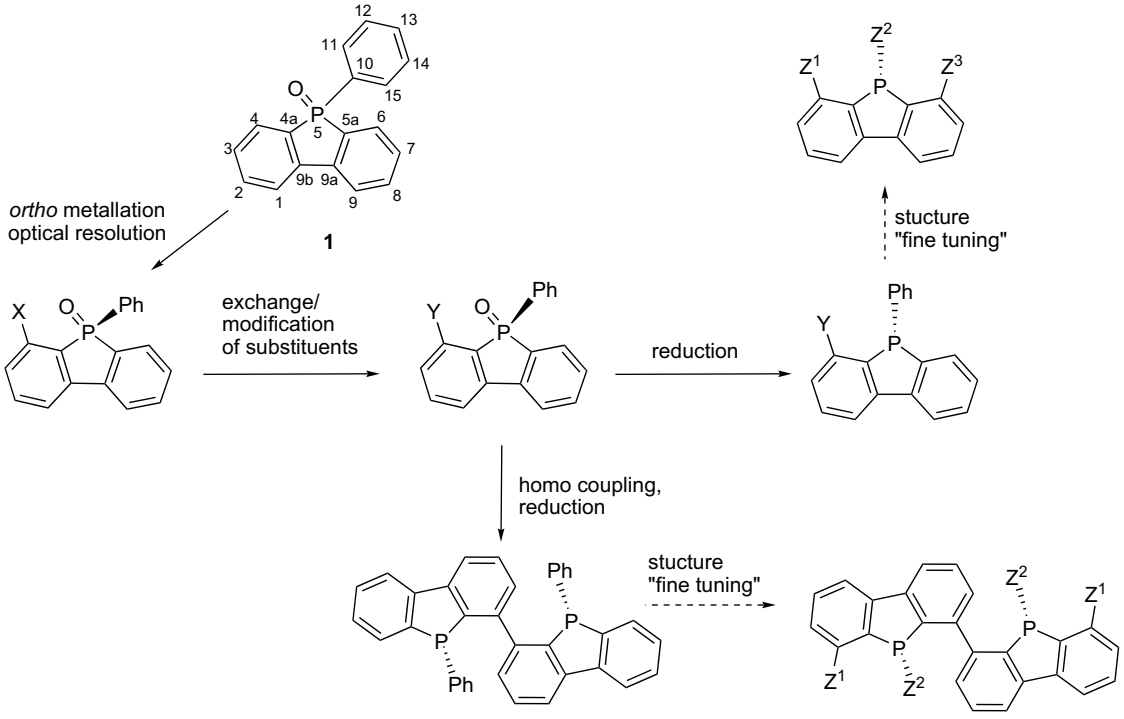
*P*-Phenyl-5*H*-dibenzophosphole oxide **1** appeared to be an inexpensive and versatile starting material since *ortho* metallation of one of the diastereotopic positions 4 or 6 followed by reaction with electrophiles yields rigid P-chiral phosphine oxides.[8e] After resolution of a suitable intermediate, the substituent at position 4 could be modified or exchanged before a final reduction step would afford the phosphine. Alternatively, a homo-coupling reaction resulted in a bidentate biaryl diphosphine ligand with P-chirality, a low rotational barrier, and—tentatively—with less conformational freedom than BINAP.[10] Structural variations are possible either with replacing P–Ph by other aromatic or aliphatic moieties or by introducing additional substituents at positions 6 and 6′.

Herein we report the synthesis of several P-chiral mono and the first diphosphine ligand as well as their oxides containing dibenzophosphole units, their preparation in enantiomerically pure or enriched form, determination of absolute configuration, and investigation of their racemization barrier due to P-inversion. Moreover, we describe the preparation and structure of a palladium complex.

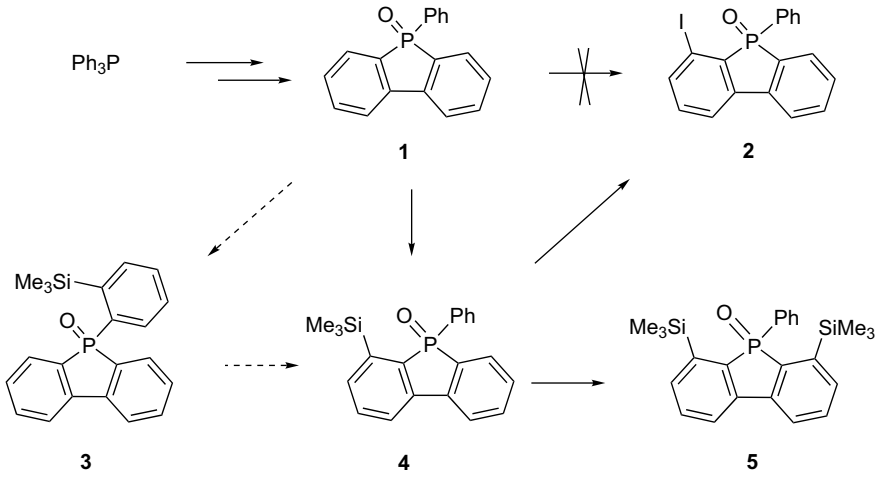
## 2. Results and discussion

### 2.1. Syntheses

The synthesis started from 5-phenyl-dibenzophosphole oxide **1**, which is easily prepared from triphenylphosphine oxide and Ph–Li in two steps (Scheme 2). As reported by Ogawa et al.[8e] **1** can be *ortho* metallated with LDA giving preferentially the 4-lithio compound, which reacts with various electrophiles. Quenching with TMS-Cl yielded **4**. In our hands, the yields were rather low (28%). A modified procedure with a shorter reaction time and excess of LDA




**Scheme 1.**




**Scheme 2.**

afforded **4** in 41% yield, together with some disubstituted product **5** (27%) and starting material **1** (9%). Treatment of **4** with excess of ICl gave 4-iodo-5-phenyl-dibenzophosphole oxide **2** (97%), which proved to be a versatile key intermediate for the synthesis of several P-chiral compounds (see below). Attempts to increase the yield of **4** by using the in situ trap protocol[11] (Li-TMP/TMS-Cl, −78 °C) resulted in a 1:1 mixture of **3** and **4** indicating that **4** is the thermodynamically favored species, while both *ortho* positions are attacked by LDA with equal ease. Attempts to access **2** directly from **1** failed. Under the conditions investigated [LDA, TMP-MgBr, $(TMP)_2Mg$; electrophile $I_2$ or 1,2-diiodoethane] only complex mixtures were obtained from which no **2** could be isolated.

For the preparation of enantiomerically pure phosphines, an economic access either to **2** or **4** was desired. Attempted resolution procedures via fractional crystallization of diastereomeric clathrates with 2,2′-binaphthol,[12] *O*,*O*-dibenzoyltartrate,[13] mandelic acid,[14] or camphor sulfonic acid[13] were unsuccessful. Fortunately, enantiomeric phosphine oxides **2** and **4** could be easily separated by enantioselective chromatography using a Chiralcel OD column. For **4**, with an extremely large separation factor ($\alpha = 4.6$), separation on a large scale was practical. Using a preparative column (5 × 50 cm, 20 μm), 300 mg samples per injection could be resolved within 1 h. The absolute configuration of the preferentially eluted enantiomer (−)-**4** was determined to be $(S)_P$ by crystal structure analysis of (−)-**2** (see below).

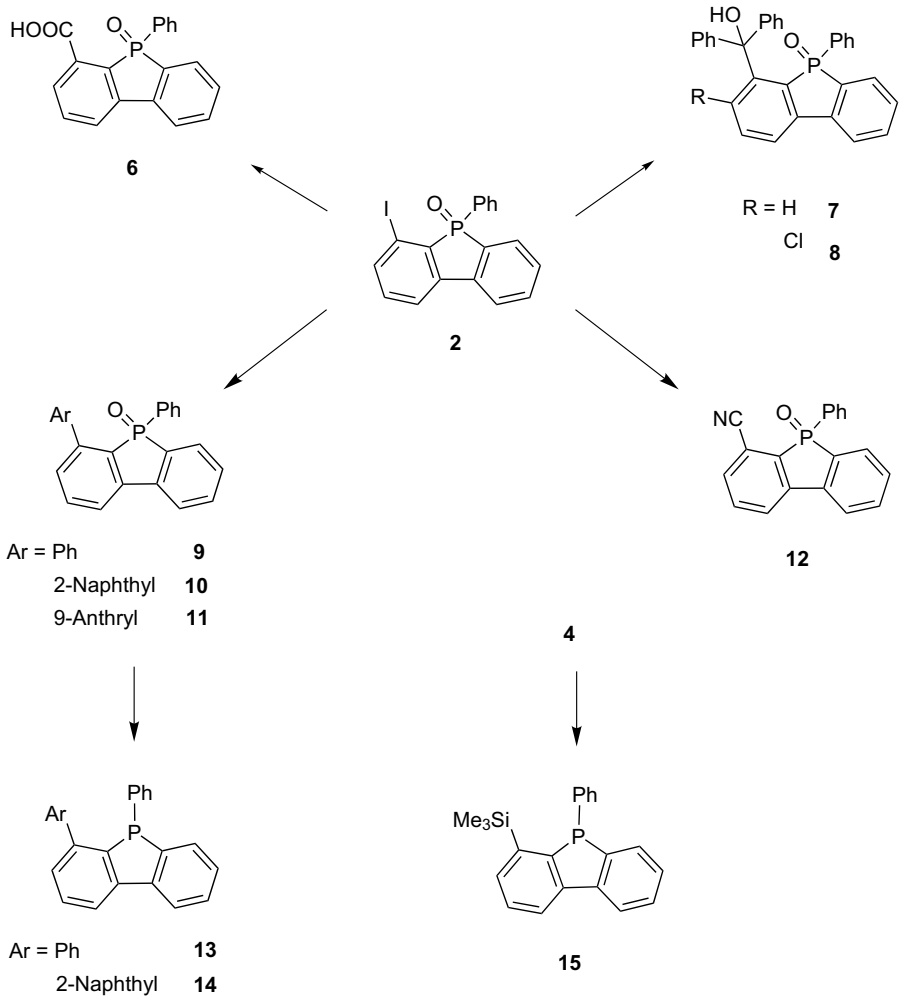
From **2**, P-chiral monophosphine oxides with various substituents at position 4 were obtained (Scheme 3). In view of their intended use in asymmetric catalysis either 'transformable' substituents (useful in further transformations) such as carboxyl or cyano group, or bulky substituents with increased steric interaction near to the P-center were synthesized. The corresponding Grignard intermediate with MgX at position 4 was not accessible directly from **1** but could be easily obtained from **2** by reaction with isopropyl magnesium chloride. However, the reaction was not straightforward; while quenching with $CO_2$ gave **6** in good yield, the reaction with benzophenone afforded comparable quantities of **7** and **8** in low yield. Their structures were confirmed by X-ray crystallography (see below). Both Pd mediated reactions, the introduction of the cyano group ($Pd(PPh_3)_4$, KCN, CuCN, **12**)[15] and arylation (Suzuki coupling with Ar–$B(OH)_2$, **9**, **10**) proceeded smoothly in good yield.[16]

Not unexpected, the introduction of the 9-anthryl unit was difficult; **11** could be isolated in only 11%, which was attributed to the steric hindrance and low stability of 9-anthryl boronic acid. An attempted coupling reaction with 9-phenanthryl boronic acid led to an inseparable mixture of (atropisomeric) products.

While the reduction of a non-stereogenic P═O group with various reagents are available ($HSiCl_3$/amine, polysiloxane, $AlH_3$, $LiAlH_4$, with or without Lewis acids, etc.)[17] the presence of a stereogenic center requires a stereoselective transformation in order to conserve P-chirality.[18] A mild method using MeOTf/$LiAlH_4$ in DME was recently shown to reduce several P-chiral mono and diphosphine oxides with a high degree of stereo inversion.[18b] With all phosphine oxides, including **4**, the final reduction step proceeded smoothly yielding phosphines **13**–**15** as moderately air stable compounds.

### 2.2. Racemization kinetics and configurative stability

During work-up of the phosphines, it was noticed that the specific rotation varied markedly depending on duration, temperature, and method of isolation. Hence, it became evident that significant racemization took place at ambient temperature. In a kinetic study on **13**, **14**, and **15**, rate constants of the pyramidal inversion of P and activation parameters were determined by following the decay of the specific rotation at 436 nm for 0.5–4 half lives. With these data and on the basis of a first order kinetics with $v_{rac} = 2 \times v_{inv}$, rate constants $k_{inv}$ and $\Delta G^{\neq}$ were calculated for three temperatures (Table 1). After graphical




**Scheme 3.**

determination of $\Delta E_A$ from the Arrhenius plot, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were obtained.[†] For further details see the Experimental. It turned out that the donor/acceptor ability of 4-substituents had a marked influence on the ease of racemization. While a trimethylsilyl group stabilized the P configuration ($t_{1/2} = 338$ h at 313 K), aromatic substituents with delocalization ability promoted the inversion ($t_{1/2} = 19$ h at 313 K), eventually through stabilization of a polar transition state as depicted in Figure 2. This is in qualitative agreement with the experimental findings and theoretical studies on the benzophosphol system.[6,7]

A minor stabilizing effect from the incorporation of P into a ring is overcompensated by formation of a heteroaromatic structure and a low-energy polar transition state with delocalization of the negative charge.

From these findings, we concluded that configurative stability in this system could be reached if the P-centers are part of a chelate structure. Therefore the synthesis of the $C_2$ symmetrical diphosphine **17** was attempted (Scheme 4). Various procedures for homo-coupling reactions[19] have been developed beginning with the 'classical' high temperature Ullmann coupling (Cu bronze, neat) and variants thereof (in DMF, NMP, pyridine or with Ni complexes and reducing agents). Also, the cross coupling methodology and Fe and Cu promoted coupling reactions of lithiated precursors can be adapted in order to obtain symmetrical products.[16,20] While the Cu catalyzed Ullmann coupling proved to be rather insensitive to steric hindrance, yielding tetra-*ortho* substituted biphenyls or 2,2′-substituted binaphthyls in high yield, the corresponding Pd and Ni catalyzed reaction often suffers from low yields accompanied by the formation of a dehalogenated substrate.[21] Conditions have been worked out which proved to be particularly useful for the coupling of Ar–P(O)$R_2$.[22]

In our case, the Ullmann type Ni catalyzed reaction using excess phosphine ligand, zinc dust, and NaH gave the most promising results.[23] Replacing $Ph_3P$ with 1,1′-bis(diphenylphosphino)ferrocene (dppf) and applying ultrasonification afforded the desired $C_2$-symmetrical dioxide *dl*-**16**. Under optimized conditions, 47% of *dl*-**16** was isolated as the exclusive stereoisomer. No NMR evidence for the

[†] The slight temperature dependence observed is attributed to insufficient accurancy of $T$ measurement.

**Table 1.** Kinetics of P-inversion and activation parameters

| Compd | $T$ (K) | $k_{inv} \times 10^{-6}$ s$^{-1}$ | $\Delta E_A$ (kJ mol$^{-1}$) | $\Delta G^{\neq}$ (kJ mol$^{-1}$) | $\Delta H^{\neq}$ (kJ mol$^{-1}$) | $\Delta S^{\neq}$ (J mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|---|---|---|
| **13**[a] | 303 | 2.95 | 98.6 | 106.3 | 96.1 | −33 |
| | 313 | 10.26 | | 106.6 | 96.0 | −34 |
| | 323 | 33.60 | | 106.9 | 96.0 | −34 |
| **14**[a] | 303 | 2.84 | 99.7 | 106.4 | 97.2 | −30 |
| | 313 | 10.11 | | 106.7 | 97.1 | −31 |
| | 323 | 33.10 | | 107.0 | 97.1 | −31 |
| **15**[a] | 313 | 0.569 | 114 | 114.1 | 111.4 | −9 |
| | 323 | 2.53 | | 113.9 | 111.3 | −8 |
| | 333 | 7.94 | | 114.3 | 111.2 | −9 |
| *dl*-**17**[b] | 293 | 1.55 | 124 | 104.2 | 121.7 | 59 |
| | 296 | 2.73 | | 104.1 | 121.6 | 59 |
| | 303 | 8.57 | | 103.6 | 121.6 | 59 |
| | 308 | 18.37 | | 103.4 | 121.5 | 59 |

[a] Based on the decay of the specific rotation at 436 nm.
[b] Based on integration of corresponding signals of *dl*-**17** and *meso*-**17** in $^1$H NMR spectra.

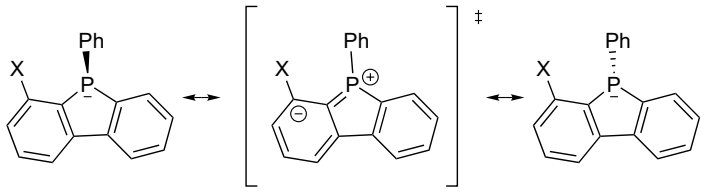
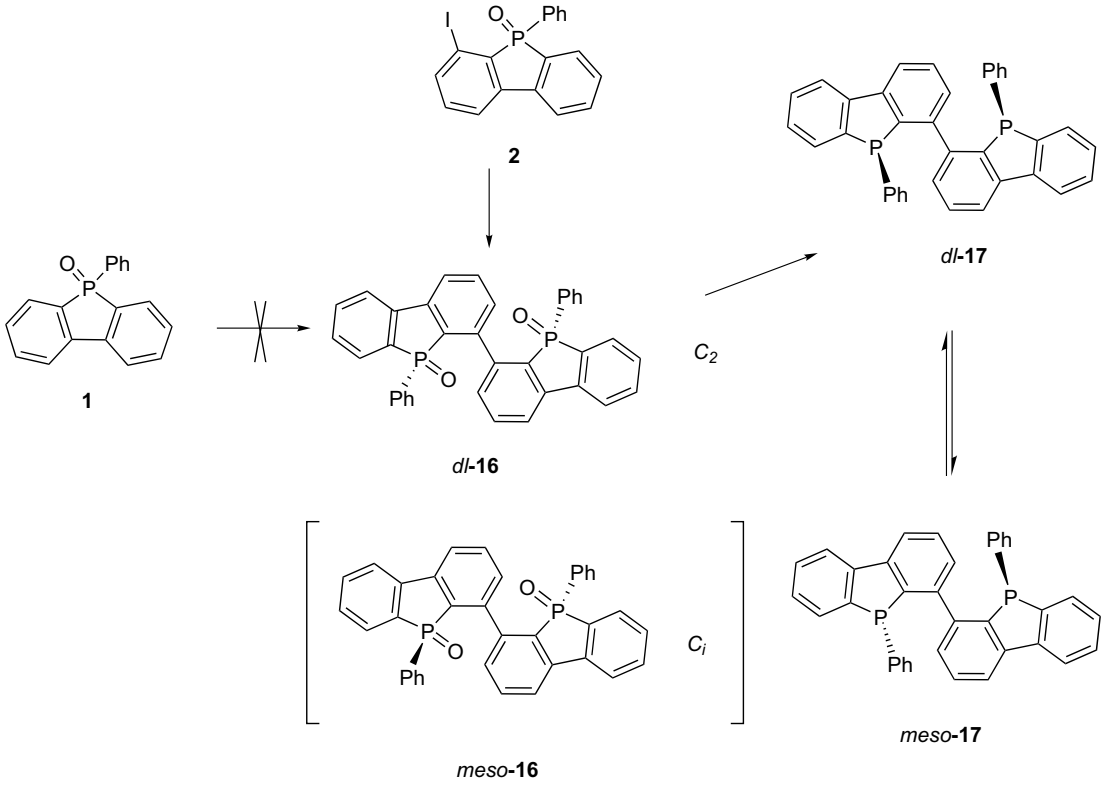



**Figure 2.**




**Scheme 4.**

presence of *meso*-**16** could be detected;[‡] repetition with enantiomeric (−)-(*S*)-**2** improved the yield of (+)-(*S*,*S*)-**16** to 69% (13% of **1** was recovered). To elucidate the preferred biaryl torsion of *dl*-**16**, its crystal structure was determined (see below) showing a relative configuration $(S^*,S^*)_P(S^*)_{axial}$ with a biaryl angle of 54.5(3)°. However, at room temperature no evidence from the NMR spectra for a restricted rotation around the biaryl axis could be found. Reduction of *dl*-**16** proceeded smoothly at low temperature to afford 66% of crude **17**. Analysis by NMR revealed that a (slow) epimerization of the predominating and obviously primarily formed diastereoisomer *dl*-**17** was taking place to give *meso*-**17**. By conducting the reduction with racemic *dl*-**16**, the main product could be selectively precipitated with MeOH. Its relative configuration was confirmed by crystal structure analysis of the corresponding $PdCl_2$ complex to be $(S^*,S^*)_P$ (see below).[§] In situ decomplexation of *dl*-**17**·$PdCl_2$ with KCN in a NMR tube yielded the spectrum of the original ligand *dl*-**17**. The epimer *meso*-**17** could be only obtained as an enriched mixture after chromatography together with *dl*-**17** (60:40). This process of epimerization resulted in the population of *meso*-**17** by P-inversion in a reversible reaction reaching equilibrium with a 1:1 mixture of the stereoisomers which was somewhat surprising but reflects the lack of steric or electronic interaction of P-centers. If enantiomerically pure **16** was used in the reduction, this process also resulted in a racemization of **17** through two P-inversions in sequence according to Eq. 1.

$$(S,S)_P\text{-}\mathbf{17} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{meso}\text{-}\mathbf{17} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} (R,R)_P\text{-}\mathbf{17} \quad k_1 \sim k_{-1} \qquad (1)$$

The kinetics were followed by $^1H$ NMR between 293 and 308 K, from which activation parameters were calculated and a half-life for the interconversion $t_{1/2} = 120$ h at 293 K (Table 1). *Note:* the half-life for the epimerization is 60 h.

Similarly a Ni(II) complex was prepared in the NMR tube; adding a methanolic solution of $NiCl_2·7H_2O$ to *dl*-**17** in $CDCl_3$ gave an immediate color change to deep violet. NMR spectra showed the formation of a single species with $C_2$ symmetry for which in analogy to the Pd complex, a dicoordinated Ni(II) complex was postulated. However, its structure remains undiscovered yet. Attempts to crystallize the compound remained unsuccessful and MS spectra (electrospray and MALDI) were not conclusive, showing fragments of *m*/*e* 576 and 1095 corresponding to a (P–P)M and $(P–P)_2M$. Since this species displays a pronounced solubility in polar solvents, either a monomeric or dimeric cationic species with coordination of solvate molecules is supposed. Both complexes are air stable compounds and no epimerization/racemization could be observed in solution (NMR, specific rotation) even at elevated temperature (up to 6 h at 50 °C).

### 2.3. Crystal structure analysis and solid state stereochemistry of (*S*)-2, 7, 8, (*S*,*S*)-16·$CH_2Cl_2$, and *dl*-17·$PdCl_2$·$CHCl_3$

In order to ascertain molecular structures, the absolute configuration in the case of (−)-(*S*)-**2** and (*S*,*S*)-**16**·$CH_2Cl_2$, and the stereochemistry of new compounds, crystal structures of five representatives were determined by X-ray diffraction. Technical details on this work are reported in the Experimental, and crystallographic data are shown in Table 2. Crystallographic data of a sixth compound, *meso*-**16**, are reported only in the supporting information (CCDC-294527). Selected geometric data are compiled in Table 3, views of the molecular structures are shown in Figures 3–7. All structures are based on the 4*H*-dibenzophosphol moiety which consists of a biphenyl entity bridged by phosphorus under the formation of a flat five-membered ring. The phosphorus imposes a significant in-plane bending of the biphenyl entity causing the inner angles C2–C1–C7/C8–C7–C1 to be smaller by about 12° than the outer angles C6-C1–C7/C12–C7–C6 (cf. Fig. 3). The bond lengths and bond angles in the phosphol rings are fairly constant (Table 3), showing mean values of P–C = 1.809(14) Å, aromatic C–C = 1.403(9) Å, aliphatic C–C = 1.477(4) Å, C–P–C = 92.5(4)°, P–C–C = 109.8(9)°, and C–C–C = 113.9(5)° for the four phosphol oxides and similar values for the phosphol complex *dl*-**17**·$PdCl_2$·$CHCl_3$ (Table 3). In all five compounds are the terminal phenyl rings [e.g., C13 though C18 in (*S*)-**2**] essentially perpendicular to the dibenzophosphol moieties and in bisecting orientations, as can be seen from the torsion angles C14–C13–P1–O1 in Table 3. Particularly regular in this respect is (*S*)-**2**, which served to fix the absolute configuration of the chiral members of the compounds presented here. The distinctly anisotropic displacement ellipsoids of the outer biphenyl atoms of this compound at 173 K (cf. Fig. 3) are in context with a pending phase transition, which at lower temperature leads to a change in the unit cell (see Experimental).

A remarkable situation was encountered with the two diphenylhydroxymethyl compounds **7** and **8**, which differ in constitution by only the Cl atom attached to C4 of compound **8**. In **7**, the phenyl rings C13–C18 and C20–C25 are oriented in such a fashion which permits a pronounced intramolecular arene–arene π-stacking interaction with a ring–ring separation of about 3.3 Å (shortest C–C distance is 3.34 Å and mutual ring inclination is 4.9°). This stereochemistry brings the hydroxy group of O2 in close vicinity of O1 and both are linked by a straight intramolecular hydrogen bond to O1···O2 = 2.735(2) Å (Fig. 4). In compound **8**, the chlorine attached to C4 hinders the diphenylhydroxymethyl group from adopting the same orientation as in **7** and consequently **8** is lacking an intramolecular arene–arene π-stacking. Because of this stereochemistry, the hydroxy oxygen O2 is now coplanar with the dibenzophosphol moiety and shows a remarkably short intramolecular distance to P1, P1–O2 = 2.581(2) Å (in **7** this distance is 3.31 Å, that is, close to 3.35 Å, the sum of van der Waals radii), while the accompanying intra-

[‡] In a preliminary coupling experiment using $Ph_3P$ instead of dppf, also *meso*-**16** was isolated as a side product (~5%). Its structure was confirmed by X-ray crystallography.

[§] Note that the stereochemical descriptors are unchanged although the configuration at P is inverted since the substituent '=O' is replaced by a lone pair changing the priority of substituents.

**Table 2.** Details for the crystal structure determinations of compounds (*S*)-**2**, **7**, **8**, (*S*,*S*)-**16**·$CH_2Cl_2$, and *dl*-**17**·$PdCl_2$·$CHCl_3$

| | (*S*)-**2** | **7** | **8** | (*S*,*S*)-**16**·$CH_2Cl_2$ | *dl*-**17**·$PdCl_2$·$CHCl_3$ |
|---|---|---|---|---|---|
| Formula | $C_{18}H_{12}IOP$ | $C_{31}H_{23}O_2P$ | $C_{31}H_{22}ClO_2P$ | $C_{37}H_{26}Cl_2O_2P_2$ | $C_{37}H_{25}Cl_5P_2Pd$ |
| *fw* | 402.15 | 458.46 | 492.91 | 635.42 | 815.16 |
| Cryst. size, mm | $0.55\times0.52\times0.33$ | $0.58\times0.28\times0.22$ | $0.65\times0.08\times0.07$ | $0.69\times0.45\times0.40$ | $0.48\times0.35\times0.07$ |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic | Orthorhombic | Orthorhombic |
| Space group | $P2_12_12_1$ (no. 19) | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) | $P2_12_12_1$ (no. 19) | $Pca2_1$ (no. 29) |
| *a* (Å) | 8.2459(4) | 15.1403(11) | 12.8448(6) | 10.0076(4) | 21.4238(11) |
| *b* (Å) | 13.0882(7) | 9.1133(7) | 16.5073(8) | 15.4231(6) | 10.8201(5) |
| *c* (Å) | 14.7084(8) | 16.5383(12) | 12.0212(6) | 20.0818(8) | 14.5902(7) |
| $\beta$ (°) | 90 | 92.524(1) | 110.414(1) | 90 | 90 |
| *V* (Å$^3$) | 1587.39(14) | 2279.7(3) | 2388.8(2) | 3099.6(2) | 3382.1(3) |
| *Z* | 4 | 4 | 4 | 4 | 4 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.683 | 1.336 | 1.371 | 1.362 | 1.601 |
| *T* (K) | 173(2) | 173(2) | 297(2) | 173(2) | 173(2) |
| $\mu$ (mm$^{-1}$) (Mo K$\alpha$) | 2.113 | 0.148 | 0.255 | 0.346 | 1.066 |
| *F*(000) | 784 | 960 | 1024 | 1312 | 1632 |
| $\theta_{max}$ (°) | 30 | 27 | 27 | 30 | 30 |
| No. of rflns measd | 9708 | 26350 | 23738 | 27740 | 48454 |
| No. of unique rflns | 4537 | 4971 | 5202 | 9005 | 9872 |
| No. of rflns $I > 2\sigma(I)$ | 4203 | 4276 | 3889 | 8612 | 9124 |
| No. of params | 190 | 311 | 320 | 388 | 406 |
| $R_1$ ($I > 2\sigma(I)$)[a] | 0.0422 | 0.0382 | 0.0499 | 0.0357 | 0.0230 |
| $R_1$ (all data) | 0.0457 | 0.0463 | 0.0699 | 0.0376 | 0.0270 |
| $wR_2$ (all data) | 0.1020 | 0.1092 | 0.1300 | 0.0944 | 0.0545 |
| Diff. four peaks min/max (e Å$^{-3}$) | −1.64/1.09 | −0.32/0.47 | −0.18/0.48 | −0.25/0.64 | −0.56/0.68 |

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\sum|F_o|$, $wR_2 = [\sum((w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

**Table 3.** Selected geometric data of compounds (*S*)-**2**, **7**, **8**, (*S*,*S*)-**16**·$CH_2Cl_2$, and *dl*-**17**·$PdCl_2$·$CHCl_3$ (Å, °)

| | (*S*)-**2** | **7** | **8** | (*S*,*S*)-**16**·$CH_2Cl_2$[a] | *dl*-**17**·$PdCl_2$·$CHCl_3$[a] |
|---|---|---|---|---|---|
| Pd–Cl1, Pd–Cl2 | | | | | 2.342(1), 2.347(1) |
| P1–O1 or –Pd | 1.489(2) | 1.493(1) | 1.483(1) | 1.493(1), 1.486(1) | 2.240(1), 2.246(1) |
| P1–C2 | 1.805(4) | 1.816(1) | 1.844(2) | 1.813(1), 1.818(1) | 1.824(2), 1.817(2) |
| P1–C8 | 1.798(4) | 1.794(1) | 1.811(2) | 1.801(1), 1.793(1) | 1.814(2), 1.809(2) |
| P1–C13 | 1.799(3) | 1.803(2) | 1.802(2) | 1.794(1), 1.802(2) | 1.812(2), 1.801(2) |
| C1–C2 | 1.411(6) | 1.409(2) | 1.413(3) | 1.408(2), 1.410(2) | 1.404(3), 1.405(3) |
| C7–C8 | 1.387(7) | 1.403(2) | 1.388(3) | 1.402(2), 1.402(2) | 1.397(3), 1.398(3) |
| C1–C7 | 1.470(8) | 1.483(2) | 1.477(3) | 1.476(2), 1.478(2) | 1.475(3), 1.472(3) |
| C2–P1–C8 | 92.2(2) | 93.1(1) | 92.0(1) | 92.5(1), 92.5(1) | 91.7(1), 91.6(1) |
| C2–P1–O1 or –Pd | 118.9(2) | 114.9(1) | 122.0(1) | 116.2(1), 118.5(1) | 121.4(1), 113.7(1) |
| C8–P1–O1 or –Pd | 117.1(2) | 118.2(1) | 111.2(1) | 115.4(1), 114.8(1) | 114.7(1), 115.7(1) |
| C13–P1–O1 or –Pd | 112.7(2) | 113.7(1) | 116.1(1) | 111.6(1), 113.9(1) | 112.1(1), 113.3(1) |
| C2–P1–C13 | 106.5(2) | 110.1(1) | 107.6(1) | 110.7(1), 107.3(1) | 104.9(1), 111.9(1) |
| C8–P1–C13 | 107.2(2) | 104.8(1) | 104.0(1) | 109.1(1), 107.5(1) | 110.1(1), 108.8(1) |
| C14–C13–P1–O1 or Pd | 2.7(4) | 19.2(1) | −15.0(2) | −5.3(1), 30.2(1) | 31.7(2), −23.8(3) |
| rms planarity (Å)[b] | 0.026 | 0.070 | 0.027 | 0.072, 0.030 | 0.074, 0.105 |
| C3–X | X = I 2.099(5) | X = C19 1.550(2) | X = C19 1.545(3) | X = C21 1.484(2) | X = C21 1.483(3) |
| O1…O2 intramol. | | 2.735(2) | 2.781(2) | | |
| P1…O2 intramol. | | 3.310(1) | 2.581(2) | | |
| C2–C3–C19–O2 | | −57.9(2) | −0.5(2) | | |
| C2–C3–C21–C20 | | | | 127.7(1) | 54.5(3) |

[a] Pairs of values for first and second dibenzophosphol moiety (atom numbers for second dibenzophosphol moiety increase by 18 for C and by 1 for P and O).

[b] rms deviation from a common least-squares plane of the C and P atoms of the dibenzophosphol moiety.

molecular O2–O1 distance of 2.781(2) Å is now not a hydrogen bond because the hydrogen atom is *exo*-oriented. Referring to systematic studies of Holmes et al.,[24] P1–O2 = 2.581(2) Å in **8** has to be classified as a P–O donor coordination by which an oxygen enters the coordination of a tetrahedral phosphorus and changes it gradually toward a trigonal bipyramidal geometry. Consistent with this are the trends in the bond angles around P1 when compared with those of **7** (cf. C2–P1–O1 and C8–P1–O1 of **7** and **8** in Table 3). In order to show how outstanding P1–O2 = 2.581 Å in **8** is, the corresponding P–O donor bond lengths in diphenylposphinoylbenzoic acid, P–O =

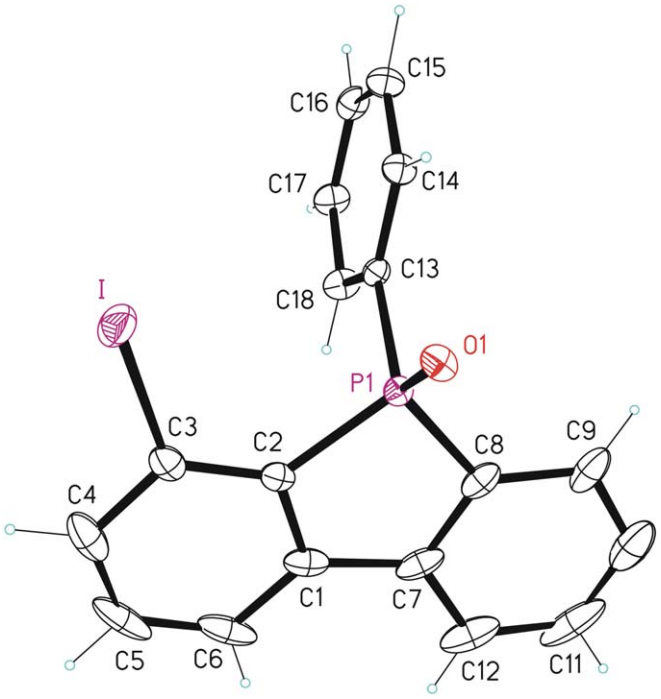



**Figure 3.** Structural view of (*S*)-**2** showing 20% thermal ellipsoids.

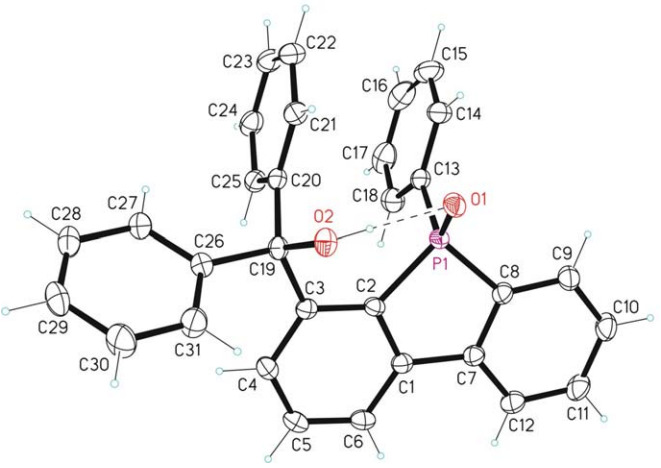



**Figure 4.** Structural view of **7** showing 40% thermal ellipsoids. Hydrogen bond O1···O2 = 2.735(2) Å shown as broken line.

3.075(2) Å, and its diethylammonium salt, P–O = 2.863(2) Å, can be quoted as examples.[25] The obvious shortness of P1–O2 in **8** may be at least in part attributable to the formation of a pair of intermolecular hydrogen bond from O2 to O1 [O2···O1 = 2.715(2) Å] of a neighboring molecule under formation of a hydrogen bonded dimer (Fig. 5). Moreover a push effect of the Cl at the *ortho*-position to O2 may be effective.

The stereochemistry of (*S*,*S*)-**16**·$CH_2Cl_2$ is shown in Figure 6 with geometric data in Table 3. Note that this solid state compound is formed from *dl*-**16** by spontaneous crystallization resolution under the formation of a conglomerate of both enantiomers. The angle between the two dibenzo-

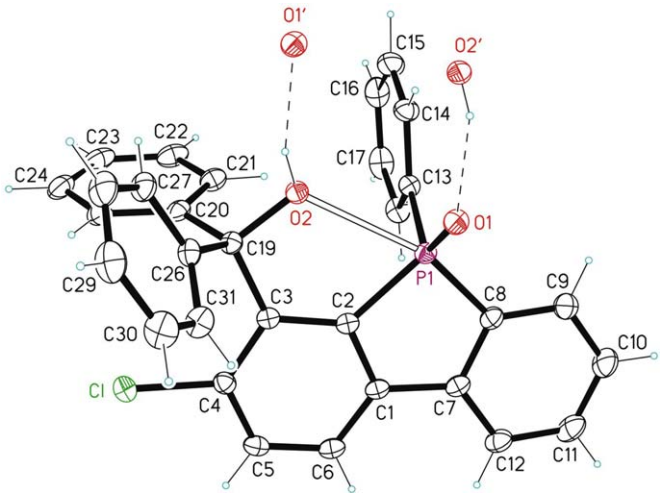



**Figure 5.** Structural view of **8** showing 20% thermal ellipsoids. The open bond P1–O2 = 2.581(2) Å represents a P–O donor coordination. Hydrogen bonds with O1′ and O2′ of a centrosymmetric neighbor molecule are shown as broken lines, O2···O1′ = O2′···O1 = 2.715(2) Å.

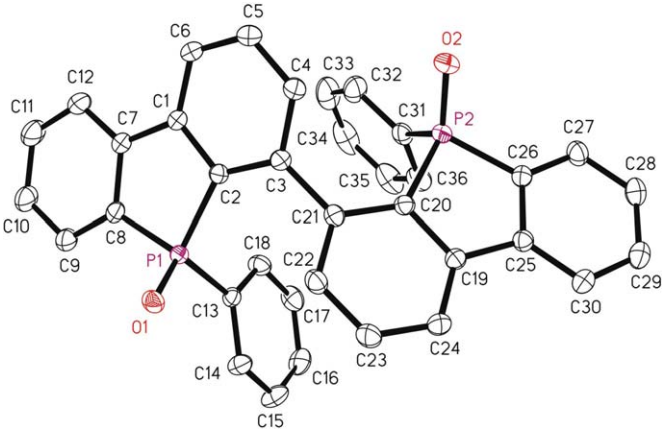



**Figure 6.** Structural view of (*S*,*S*)-**16**·$CH_2Cl_2$ (40% thermal ellipsoids, H atoms and $CH_2Cl_2$ omitted for clarity).

phosphol moieties is about 128° and results in an intramolecular P1–P2 distance of 5.67 Å. The distinct basicity of the phosphol oxide oxygen atoms is evident in this compound from the presence of hydrogen bond interactions with the $CH_2Cl_2$ solvent molecule, which bridges two molecules of **16** with C–H···O hydrogen bonds of C···O1 = 3.18 and C···O2 = 3.68 Å, both C–H—O angles being near 165°. When *dl*-**17** is reacted with $Pd(CH_3CN)_2Cl_2$, the chelate complex *dl*-**17**·$PdCl_2$ is formed, which crystallizes from chloroform as a stable stoichiometric $CHCl_3$ solvate. The molecular structure depicted in Figure 7 shows an essentially $C_2$-symmetric bis-dibenzophosphol moiety, but the $PdCl_2$ unit, as well as the two P-bound phenyl rings C13–C18 and C31–C36 deviate notably from this symmetry. The angle between the two dibenzophosphol moieties is about 55° and results in an intramolecular P1–P2 distance of 3.21 Å. Pd has a moderately twisted square-planar coordination by two P and two Cl with bond angles between 85.9° and 93.2°. The $CHCl_3$ molecule forms an

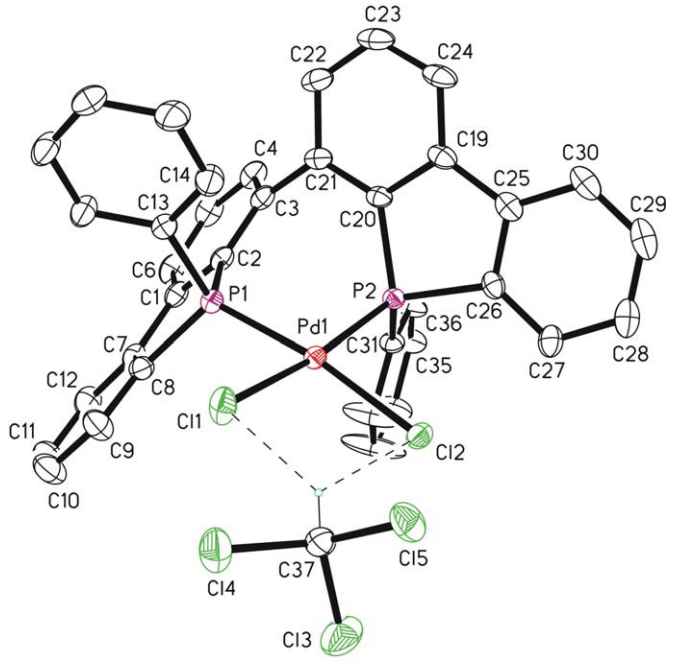



**Figure 7.** Structural view of *dl*-**17**·$PdCl_2$·$CHCl_3$ (40% thermal ellipsoids, most H atoms omitted for clarity) including the C–H···Cl hydrogen bonded $CHCl_3$ molecule.

asymmetrically bifurcated C–H–Cl hydrogen bond with the two $PdCl_2$ chlorine atoms, H37···Cl1 = 2.51 Å. and H37···Cl2 = 2.86 Å (Fig. 7).

## 3. Conclusions

In conclusion we have synthesized a group of P-chiral monophosphine oxides and one biaryl diphosphine oxide, all based on the dibenzophosphole skeleton as well as the corresponding phosphines. Preparative separation of the enantiomers of the key intermediate **4** by chromatography enabled their synthesis in enantiomerically pure form and determination of absolute configurations. It turned out that racemization of phosphines through P-inversion takes place at ambient temperature and depends markedly on the *ortho* substituents (104–114 kJ $mol^{-1}$). In the case of diphosphine **17**, racemization can be suppressed when forming a chelate with either Pd(II) or Ni(II) complexes.

## 4. Experimental

### 4.1. General

Melting points were determined on a Kofler melting point apparatus and are uncorrected. NMR: Bruker DRX 400 spectrometer at 400.13 MHz for protons ($^1$H), 161.92 MHz for phosphorus ($^{31}$P), and 100.57 MHz for carbon ($^{13}$C) as well as Bruker DRX 600 spectrometer at 600.13 MHz for protons ($^1$H), 242.88 MHz for phosphorus ($^{31}$P) and 150.86 MHz for carbon ($^{13}$C) in $CDCl_3$ if not otherwise stated. Chemical shifts $\delta$ are reported in parts per million rel to $CHCl_3$ (7.24 or 77.00 ppm, respectively). Coupling patterns are designated as s (singlet), d (doublet), t (triplet), p (pseudo), m (multiplet), and br (broad). $^{13}$C NMR spectra are recorded in a *J*-modulated mode; signals are assigned as $CH_3$, $CH_2$ or C for quaternary carbon; undesignated signals refer to CH-resonances. In spectral areas with extensive signal overlapping multiplets could not be identified; these signals of unclear relationship are underlined, ignoring probable multiplet structures. MS: MAT 8230 (EI, 70 eV) and MAT 900 (electrospray). Petroleum ether and ethyl acetate were distilled, absolute THF, dioxane, and DME from sodium benzophenone ketyl, $Et_2O$ from $LiAlH_4$. Commercially available solutions were used of PhLi (1.9 M, in dibutylether, Fluka), LDA (1.5 M as THF complex in cyclohexane, Aldrich), and 2-PrMgCl (2.0 M in THF). All other chemicals were of analytical grade and used without further purification. dppf[26] and $Ni(PPh_3)_2Cl_2$[27] were prepared according to published procedures. Zinc dust was activated by treatment with diluted HCl and stored under argon.[28]

### 4.2. Syntheses

**4.2.1. 5-Phenyl-5*H*-dibenzophosphol oxide 1.** The synthesis followed a literature procedure with modifications using triphenylphosphine[8c] and commercially available phenyllithium in dibutylether. The reaction proceeded with moderate yield (52%) and gave a product slightly contaminated with biphenyl, which was pure enough for the next step. For the oxidation with hydrogen peroxide, acetic acid was replaced by a mixture of toluene/methanol (9:1) as the solvent (100 mL/10 g of crude 5-phenyl-5*H*-dibenzophosphole oxide). After work-up the crude product was leached several times with boiling pentane to remove biphenyl. The remaining white powder given, was almost pure **1** as evidenced by NMR.

**4.2.2. 4-Trimethylsilyl-5-phenyl-5*H*-dibenzophosphol oxide 4 and 4,6-bis(trimethylsilyl)-5-phenyl-5*H*-dibenzophosphol oxide 5.** 5-Phenyl-5*H*-dibenzophosphol oxide **1** (11.28 g, 40.9 mmol) was placed in a three-necked flask equipped with dropping funnel and gas inlet. Freshly distilled abs THF (350 mL) was added and the solution degassed and set under argon. The reaction was cooled to −78 °C and 1.5 equiv LDA (40.9 mL, 61.4 mmol) was added dropwise over 10 min. After 1 h at the same temperature, TMS-Cl (17.77 g, 164 mmol, 4 equiv, 20.8 mL) was added over 15 min. The mixture was kept at −78 °C for 2 h and then warmed up to −40 °C over 1 h. The deep red solution was stirred for further 30 min and water (5 mL) was added. After removing the solvent under vacuum, the residue was treated with HCl (100 mL, 2%) and $CH_2Cl_2$ (100 mL). The aqueous phase was extracted with $CH_2Cl_2$ (2 × 100 mL) and the combined organic phases washed with satd $NaHCO_3$ (50 mL), water (2 × 100 mL), and satd NaCl solution (100 mL). After drying over $MgSO_4$ and removal of solvent the mixture was chromatographed (column 5 × 40 cm, ethyl acetate (50% → 100%)/petroleum ether). Yield: 4.27 g (27%) of **5**, 5.82 g (41%, 45% relative to recovered starting material) of **4**, and 1.06 g (9%) of **1**.

Compound **4**: $^1$H NMR ($CDCl_3$) $\delta$: 0.15 (s, 9H); 7.29 (ptdd, *J* = 7.4, 3.8, 0.8 Hz, 1H); 7.33 (m, 2H); 7.43 (m, 1H); 7.49

(ptpt, $J = 7.6$, 1.2 Hz, 1H); 7.54–7.62 (m, 5H); 7.76 (dd, $J = 7.8$, 2.9 Hz; 1H); 7.83 (ddd, $J = 7.3$, 2.8, 1.3 Hz, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$: 0.05 ($CH_3$); 120.79 (d, $J = 9.9$ Hz); 121.47 (d, $J = 9.9$ Hz); 128.50 (d, $J = 13.0$ Hz); 129.06; 129.16; 129.21; 129.32 (2 × d); 130.94 (d, $J = 10.7$ Hz); 131.74 (d, $J = 3.1$ Hz); 132.11 (d, $J = 2.3$ Hz); 132.86 (d, $J = 2.3$ Hz); 133.36 (C, d, $J = 50.5$ Hz); 134.70 (C); 135.80 (d, $J = 13.8$ Hz); 137.09 (C); 140.61 (C, d, $J = 21.4$ Hz); 142.51 (C, d, $J = 25.0$ Hz); 145.62 (C, d, $J = 16.2$ Hz). $^{31}$P NMR ($CDCl_3$) $\delta$: 35.24 (s).

Chromatographic separation of enantiomers, (*S*)-**4** and (*R*)-**4**: Chiralcel OD® (5 × 50 cm, 20 μm), solvent: 2-PrOH/petroleum ether (30:70), sample size: 200–300 mg per run, dissolved in 10 mL, flow: 40 mL min$^{-1}$, rt, *fraction* 1: $t_R \sim 20$ min, (−)-(*S*)-**4**, $[\alpha]_D^{20} = -276$ (*c* 1.15, $CHCl_3$); *fraction* 2: $t_R \sim 40$ min, (+)-(*R*)-**4**, $[\alpha]_D^{20} = +281$ (*c* 1.21, $CHCl_3$); recovery rate: 95%.

Compound **5**: $^1$H NMR ($CDCl_3$) $\delta$: 0.16 (s, 18H); 7.29 (m, 2H); 7.38 (m, 1H); 7.47–7.63 (m, 6H); 7.82 (ddd, $J = 7.5$, 2.8, 1.3 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$: 0.27 ($CH_3$); 121.17 (d, $J = 9.9$ Hz); 128.18 (d, $J = 12.2$ Hz); 131.44 (d, $J = 2.3$ Hz); 131.76 (d, $J = 2.3$ Hz); 132.10 (C, d, $J = 95.8$ Hz); 132.30 (d, $J = 9.9$ Hz); 135.86 (d, $J = 13.8$ Hz); 138.99 (C, d, $J = 106.7$ Hz); 141.42 (C, d, $J = 25.2$ Hz); 144.39 (C, d, $J = 17.4$ Hz). $^{31}$P NMR ($CDCl_3$) $\delta$: 36.31 (s). MS (40 °C) *m*/*z* (rel%): 420 (2.5, $M^+$); 405 (85, $M-CH_3$); 329 (100). HRMS: calcd for $C_{23}H_{26}OPSi_2$: 405.1260, found: 405.1267.

**4.2.3. 4-Iodo-5-phenyl-5*H*-dibenzophosphol oxide 2.** To a stirred solution of **4** (5.50 g, 15.8 mmol) in $CH_2Cl_2$ (230 mL) was added dropwise iodomonochloride (15.4 g, 94.7 mmol, 6 equiv) in $CH_2Cl_2$ (100 mL) at 0 °C over 1 h. Stirring was continued at room temperature and the progress followed by TLC. After complete consumption of starting material (approx. 48 h), $NaHSO_3$ solution (10%, 100 mL) was added. The organic phase was separated, washed with water (100 mL) and brine (100 mL), and dried over $MgSO_4$. Evaporation left a pale yellow solid which was found to be pure by NMR. Yield: 5.99 g (94%); mp: 191–194 °C. $^1$H NMR ($CDCl_3$) $\delta$: 7.22 (ptd, $J = 7.8$, 1.3 Hz, 1H); 7.38 (m, 3H); 7.50 (m, 1H); 7.58 (m, 1H); 7.65–7.73 (m, 4H); 7.78 (br ptd, $J = 7.8$, 3.0 Hz, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$: 97.00 (C, d, $J = 7.4$ Hz); 120.54 (d, $J = 9.2$ Hz); 121.07 (d, $J = 9.9$ Hz); 128.55 (d, $J = 13.0$ Hz); 128.77 (C, d, $J = 105.3$ Hz); 129.95; 130.03; 130.06, 130.14 (2 × d); 131.89 (d, $J = 11.5$ Hz); 132.24 (d, $J = 3.1$ Hz); 133.13 (C, d, $J = 109$ Hz); 133.44 (d, $J = 1.5$ Hz); 134.34 (d, $J = 1.5$ Hz); 139.43 (d, $J = 8.4$ Hz); 140.12 (C, d, $J = 19.6$ Hz); 144.70 (C, d, $J = 21.6$ Hz). $^{31}$P NMR ($CDCl_3$) $\delta$: 36.57 (s). MS: (40 °C) *m*/*z* (rel%): 401.9 (69, $M^+$); HRMS: calcd for $C_{18}H_{12}IOP$: 401.9670, found: 401.9682.

The same procedure applied to (*S*)-**4** yielded (*S*)-**2**; mp: 195–198 °C; $[\alpha]_D^{20} = -77.2$ (*c* 1.03, $CHCl_3$).

**4.2.4. 5-Phenyl-5*H*-dibenzophosphol oxide-4-carbonic acid 6.** To a degassed solution of **2** (539 mg, 1.34 mmol) in THF abs (5 mL) was added 2-propylmagnesium chloride (0.8 mL, 1.6 mmol) at −20 °C and the heterogeneous violet mixture stirred for 15 min. After cooling to −50 °C, excess solid $CO_2$ was added and the reaction was allowed to warm to −10 °C. Concd HCl (0.2 mL) was added and stirring was continued for 30 min. The white crystalline precipitate formed was separated, washed with distilled water and dried in vacuo to yield 365 mg (85%) of **6**. Mp: >310 °C (dec). $^1$H NMR (DMSO-$d_6$) $\delta$: 7.36–7.51 (m, 6H); 7.56 (br pt, $J = 8.0$ Hz, 1H); 7.66 (ptpt, $J = 7.6$, 1.3 Hz, 1H); 7.86 (ptd, $J = 7.9$, 1.3 Hz, 1H); 7.98 (ddd, $J = 7.6$, 4.3, 0.8 Hz, 1H); 8.14 (dd, $J = 7.6$, 2.5 Hz, 1H); 7.40 (ddd, $J = 7.6$, 2.5, 0.8 Hz, 1H); 13.41 (br s, 1H). $^{13}$C NMR (DMSO-$d_6$) $\delta$: 121.78 (d, $J = 9.2$ Hz); 125.85 (d, $J = 9.2$ Hz); 128.28 (d, $J = 12.2$ Hz); 129.19 (d, $J = 9.2$ Hz); 130.10; 130.25; 130.25 (d, $J = 10.7$ Hz); 130.33; 131.34 (C); 131.40 (d, $J = 2.3$ Hz); 132.11 (C); 132.43 (C); 133.10; 133.25 (C); 134.22; 134.36 (C); 135.41 (C); 139.17 (C, d, $J = 20.5$ Hz); 143.40 (C, d, $J = 20.7$ Hz); 165.44 (C). $^{31}$P NMR (DMSO-$d_6$) $\delta$: 33.52 (s). MS (electrospray): 319.1 (100, $M-1^+$). HRMS: calcd for $C_{19}H_{12}O_3P$: 319.0624, found: 319.0538.

**4.2.5. 4-Diphenylhydroxymethyl-5-phenyl-4*H*-dibenzophosphol oxide 7 and 3-chloro-4-diphenylhydroxymethyl-5-phenyl-4*H*-dibenzophosphol oxide 8.** To a degassed solution of 4-iodo-5-phenyl-dibenzophosphol oxide **2** (201 mg, 0.5 mmol) in abs THF (3 mL) was added 2-propylmagnesium chloride (0.3 mL of a 2 M solution in THF, 0.6 mmol) at −20 °C and the heterogeneous violet mixture was stirred at the same temperature for 20 min. Benzophenone (146 mg, 0.8 mmol) was added and the reaction slowly warmed up to rt overnight. To the yellow solution containing some white precipitate was added HCl (2 mL, 2%) and the mixture extracted with ethyl acetate (2 × 10 mL). The organic phase was washed with water and brine and dried over $MgSO_4$. The crude mixture obtained after evaporation was subjected to column chromatography ($SiO_2$, 60 × 2 cm, ethyl acetate) to yield 34 mg (15%) of **7** and 36 mg (14%) of **8** as crystalline solids.

Compound **7**: Mp: 235–240 °C. $^1$H NMR ($CDCl_3$) $\delta$: 5.83 (s, 1H); 6.86–7.00 (m, 6H); 7.15–7.38 (m, 11H); 7.44 (ptm, $J = 7.8$ Hz, 1H); 7.54 (m, 2H); 7.78 (dd, $J = 7.6$, 2.5 Hz, 1H); 7.82 (dd, $J = 7.6$, 2.5 Hz, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$: 83.21 (C, d, $J = 1.9$ Hz); 120.03 (d, $J = 9.9$ Hz); 120.92 (d, $J = 9.9$ Hz); 127.20; 127.51; 127.60; 127.80; 128.02; 128.32 (d, $J = 13.0$ Hz); 128.48; 129.56 (d, $J = 3.8$ Hz); 129.57 (d, $J = 17.6$ Hz); 129.72 (C, d, $J = 105.8$ Hz); 130.38 (d, $J = 11.5$ Hz); 130.85 (d, $J = 9.2$ Hz); 130.94 (d, $J = 3.1$ Hz); 131.90 (C, d, $J = 108.0$ Hz); 132.75 (d, $J = 2.3$ Hz); 133.05 (d, $J = 2.3$ Hz); 133.81 (C, d, $J = 108.0$ Hz); 140.80 (C, d, $J = 20.9$ Hz); 143.28 (C, d, $J = 23.4$ Hz); 145.24 (C); 146.49 (C); 152.57 (C, d, $J = 6.9$ Hz). $^{31}$P NMR ($CDCl_3$) $\delta$: 40.14 (s). MS (190 °C) *m*/*z* (rel%): 458 (84, $M^+$); 381 (100, M−Ph). HRMS: calcd for $C_{13}H_{23}O_2P$: 458.1436, found: 458.1428.

Compound **8**: Mp: 210–214 °C. $^1$H NMR ($CDCl_3$) $\delta$: 5.00 (s, 1H); 6.86 (m, 2H); 6.98 (m, 2H); 7.08 (ptt, $J = 7.2$, 1.4 Hz, 1H); 7.28–7.43 (m, 9H); 7.52–7.62 (m, 5H); 7.82 (m, 2H); $^{13}$C NMR ($CDCl_3$) $\delta$: 84.05 (C); 120.71 (d,

$J = 9.9$ Hz); 121.63 (d, $J = 11.5$ Hz); 126.84; 126.90 (d, $J = 13.0$ Hz); 128.06; 128.19; 128.23; 128.37; 128.88; 129.51; 129.67; 129.77; 129.85; 129.96; 130.34 (d, $J = 10.7$ Hz); 131.19 (d, $J = 3.1$ Hz); 132.25 (C); 132.30 (C); 132.96 (d, $J = 2.0$ Hz); 133.31 (C); 133.41 (C); 134.12 (C); 134.69 (C); 134.81 (C); 135.19 (C); 137.00 (d, $J = 1.2$ Hz); 139.41 (C, d, $J = 20.0$ Hz); 142.45 (C); 142.49 (C); 142.67 (C, d, $J = 23.0$ Hz); 149.36 (C, d, $J = 6.2$ Hz). $^{31}$P NMR ($CDCl_3$) $\delta$: 40.17 (s). MS (200 °C) $m/z$ (rel%): 492 (100, $M^+$); 415 (45, M−Ph). HRMS: calcd for $C_{31}H_{22}ClO_2P$: 492.1046, found: 492.1057.

**4.2.6. 4,5-Diphenyl-4*H*-dibenzophosphol oxide 9.** To a solution of **2** (201 mg, 0.5 mmol) in toluene (5 mL) was added phenyl boronic acid (122 mg, 1 mmol) dissolved in the minimum amount of EtOH (0.3 mL) and 2 M $Na_2CO_3$ (1.05 mL, 2.1 mmol) and the mixture degassed. A catalytic amount of $Pd(Ph_3P)_4$ (10 mg) was added and the mixture refluxed under Ar for 16 h. TLC indicated the complete absence of the starting material. Water (10 mL) was introduced and the mixture extracted with ethyl acetate (20 mL) and the organic phase washed with water and satd NaCl solution. After drying with $MgSO_4$ and evaporation, the crude product was chromatographed on $SiO_2$. Elution with ethyl acetate afforded 138 mg (78%) of **9**; mp: 210–211 °C. $^1$H NMR ($CDCl_3$) $\delta$: 7.14 (ptd, $J = 7.6$, 3.3 Hz, 2H); 7.21 (dm, $J = 6.8$ Hz, 1H); 7.24 (dm, $J = 6.8$ Hz, 1H); 7.30–7.38 (m, 5H); 7.43 (ptd, $J = 7.6$, 3.8 Hz, 1H); 7.54 (m, 2H); 7.64 (m, 2H); 7.72 (br dd, $J = 8.6$, 7.5H, 1H); 7.86 (dd, $J = 7.8$, 2.5 Hz, 1H); 7.90 (dd, $J = 7.8$, 2.8 Hz, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$: 119.78 (d, $J = 9.9$ Hz); 121.04 (d, $J = 10.7$ Hz); 127.86; 127.93 (d, $J = 12.2$ Hz); 127.94; 129.29; 129.48 (d, $J = 10.7$ Hz); 129.83 (d, $J = 9.9$ Hz); 130.27 (C, d, $J = 104$ Hz); 130.50 (d, $J = 9.2$ Hz); 130.74 (d, $J = 11.4$ Hz); 131.54 (d, $J = 3.1$ Hz); 131.67 (C, d, $J = 103$ Hz); 132.80 (C, d, $J = 109$ Hz); 133.17 (d, $J = 2.3$ Hz); 133.29 (d, $J = 2.2$ Hz); 139.17 (C, d, $J = 2.6$ Hz); 141.67 (C, d, $J = 21.6$ Hz); 142.26 (C, d, $J = 21.6$ Hz); 146.73 (C, d, $J = 7.9$ Hz). $^{31}$P NMR ($CDCl_3$) $\delta$. 35.54 (s). MS (120 °C) $m/z$ (rel%): 351.0 (100, M−1). HRMS: calcd for $C_{24}H_{17}OP$: 352.1017, found: 352.0976.

Applying the same procedure to (−)-(*S*)-**2** afforded (−)-(*S*)-**9**; mp: 198–202 °C, $[\alpha]_D^{20} = -199$ ($c$ 1.03, $CHCl_3$).

**4.2.7. 4-(2-Naphthyl)-5-phenyl-4*H*-dibenzophosphol oxide 10 and 4-(9-anthryl)-5-phenyl-4*H*-dibenzophosphol oxide 11.** Similar procedures as used for the preparation of **9** were applied using naphthalene-2-boronic acid and anthracene-9-boronic acid, respectively, instead of phenyl boronic acid to afford **10** and **11**. Analogue procedures using enantiopure iodide (−)-(*S*)-**2** gave (−)-(*S*)-**10** and (+)-(*S*)-**11**.

Compound **10**: 87%; mp: 104–107 °C; $^1$H NMR ($CDCl_3$) $\delta$: 7.00 (m, 2H); 7.14 (m, 2H); 7.23 (ptq, $J = 7.3$, 1.3 Hz, 1H); 7.36–7.42 (m, 2H); 7.43–7.49 (m, 2H); 7.54 (dd, $J = 8.6$, 1.8 Hz, 1H); 7.57–7.68 (m, 3H); 7.73–7.89 (m, 5H); 7.98 (d, $J = 1.2$ Hz, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$: 119.89 (d, $J = 9.2$ Hz); 121.08 (d, $J = 9.9$ Hz); 126.10; 126.20; 126.97; 127.49; 127.70; 128.00 (d, $J = 13.0$ Hz); 128.58; 128.79; 129.58 (d, $J = 11.5$ Hz); 129.84 (d, $J = 9.9$ Hz); 130.02 (C); 130.78 (2(!)d, $J = 10.7$ Hz); 131.05 (C); 131.41 (C); 131.56 (d, $J = 2.3$ Hz); 132.46 (C); 132.78 (C); 132.85 (C); 133.23 (d, $J = 2.2$ Hz); 133.39 (d, $J = 2.0$ Hz); 133.54 (C); 136.59 (C); 136.62 (C); 141.69 (C, d, $J = 21.0$ Hz); 142.50 (C, d, $J = 22.3$ Hz); 146.68 (C, d, $J = 8.6$ Hz). $^{31}$P NMR ($CDCl_3$) $\delta$: 35.46 (s). MS (120 °C) $m/z$ (rel%): 402.3 (6, $M^+$); 401.3 (9, M−1). HRMS: calcd for $C_{28}H_{19}OP$: 402.1174, found: 402.1145. (−)-(*S*)-**10**; mp: 86–89 °C; $[\alpha]_D^{20} = -357$ ($c$ 1.01, $CHCl_3$).

Compound **11**: 11%; pale yellow foam. $^1$H NMR ($CDCl_3$) $\delta$: 6.52 (dd, $J = 12.9$, 1.3 Hz, 1H); 6.54 (dd, $J = 13.1$, 1.3 Hz, 1H); 6.60 (m, 2H); 6.70 (ptdm, $J = 8.3$, 3.3 Hz, 2H); 6.98 (ptq, $J = 7.6$, 1.5 Hz, 1H); 7.12 (ddd, $J = 8.6$, 5.3, 2.3 Hz, 1H); 7.27 (ddd, $J = 7.6$, 4.3, 0.8 Hz, 1H); 7.36 (ptdd, $J = 7.3$, 3.5, 0.8 Hz, 1H); 7.41 (m, 1H); 7.48 (m, 1H); 7.52 (m, 1H); 7.63 (ptt, $J = 7.6$, 1.3 Hz, 1H); 7.70 (dm, $J = 8.8$ Hz, 1H); 7.74 (dd, $J = 7.6$, 1.3 Hz, 1H); 7.85 (br d, $J = 8.6$ Hz, 1H); 7.95 (ddm, $J = 7.8$, 2.8 Hz, 1H); 7.99 (ddd, $J = 7.8$, 2.3, 0.8 Hz, 1H); 8.04 (dm, $J = 8.3$ Hz, 1H); 8.49 (s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$: 120.54 (d, $J = 9.9$ Hz); 121.13 (d, $J = 9.9$ Hz); 124.18; 124.82; 125.30; 125.54; 125.67; 127.44; 127.61 (d, $J = 13.0$ Hz); 127.81; 127.94; 129.20 (C, d, $J = 67$ Hz); 129.35 (C); 129.57 (d, $J = 10.8$ Hz); 130.08 (d, $J = 9.2$ Hz); 130.44 (d, $J = 11.5$ Hz); 130.59 (C); 131.18 (C); 131.22 (d, $J = 3.1$ Hz); 132.14 (C); 132.23 (d, $J = 9.2$ Hz); 132.35 (C); 133.35 (d, $J = 1.4$ Hz); 133.41 (C); 133.76 (C); 134.80 (C); 141.89 (C, d, $J = 22.3$ Hz); 142.22 (C, d, $J = 21.2$ Hz); 142.75 (C, d, $J = 9.0$ Hz). $^{31}$P NMR ($CDCl_3$) $\delta$: 33.33 (s). MS (190 °C) $m/z$ (rel%): 452.1 (100, $M^+$). HRMS calcd for $C_{23}H_{21}OP$: 452.1330, found: 452.1327. (+)-(*S*)-**11**: Mp: 302–306 °C, $[\alpha]_D^{20} + 45$ ($c$ 0.43, $CHCl_3$).

**4.2.8. 4-Cyano-5-phenyl-5*H*-dibenzophosphol oxide 12.** To a solution of **2** (201 mg, 0.5 mmol) in THF (5 mL) was added KCN (98 mg, 1.5 mmol) and a catalytic amount of CuCN (5 mg). The mixture was degassed and after the addition of $Pd(PPh_3)_4$ (58 mg, 10 mol %) was heated under argon at reflux until TLC ($CHCl_3$/MeOH, 9:1) indicated complete conversion. The dark brown solution was diluted with $CH_2Cl_2$ (20 mL) and water (10 mL) was added. The aqueous phase was repeatedly extracted with $CH_2Cl_2$ ($3 \times 5$ mL) and the combined organic extracts washed with water, satd NaCl solution, and dried over $MgSO_4$. Evaporation of the solvent left **12** as a crystalline white powder; yield: 127 mg (84%); mp: 216–217 °C. $^1$H NMR ($CDCl_3$) $\delta$: 7.38–7.41 (m, 2H); 7.47 (ptdd, $J = 7.3$, 3.5, 0.8 Hz, 1H); 7.52 (m, 1 Hz, 1H); 7.54 (ddd, $J = 7.6$, 3.8, 1.0 Hz, 1H); 7.60–7.72 (m, 4H); 7.75 (br dd, $J = 9.9$, 7.3 Hz, 1H); 7.84 (dd, $J = 7.8$, 3.0 Hz; 1H); 7.99 (ddd, $J = 7.8$, 2.3, 1.0 Hz, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$: 113.76 (C, d, $J = 5.9$ Hz); 115.63 (C, d, $J = 4.5$ Hz); 121.59 (d, $J = 9.9$ Hz); 124.94 (d, $J = 9.2$ Hz); 127.70 (C, part of d); 128.83 (d, $J = 13.0$ Hz); 130.45 (d, $J = 9.9$ Hz); 130.62 (d, $J = 11.5$ Hz); 131.50 (d, $J = 11.5$ Hz); 132.53 (C, part of d); 132.84 (d, $J = 6.9$ Hz); 132.92 (d, $J = 3.1$ Hz); 133.57 (d, $J = 1.5$ Hz); 133.98 (d, $J = 2.3$ Hz); 136.85 (C, d, $J = 100$ Hz); 140.18 (C, d, $J = 20.0$ Hz); 142.74 (C, d, $J = 20.0$ Hz). $^{31}$P NMR ($CDCl_3$) $\delta$: 33.18 (s). MS (electrospray) $m/z$ (rel%): 324.1 (100, M+23). HRMS: calcd for $C_{19}H_{12}NOP$: 301.0657, found: 301.0662.

**4.2.9. Reduction of enantiopure phosphol oxides (*R*)-4, (*S*)-9, and (*S*)-10 (*general procedure*).** The phosphol oxide (0.7 mmol) was dissolved in dry DME (10 mL) and degassed. Methyltriflate (1.0 mmol, 113 μL) was added and the mixture stirred at rt for 2 h. After cooling to −55 °C, $LiAlH_4$ (137 mg, 1.75 mmol) was added and the reaction warmed up to +10 °C for 4 h. TLC control indicated complete consumption of the substrate and the reaction was quenched by careful addition of degassed dil HCl (2%, 10 mL) followed by degassed ethyl acetate (10 mL). The aqueous phase was washed with a second portion of ethyl acetate (10 mL) and the combined extracts were washed with water and satd NaCl solution and dried with $MgSO_4$. After removal of solvent, the crude product was chromatographed with degassed solvents on $SiO_2$ (10 × 2 cm, ethyl acetate/petroleum ether (50:50)).

Compound (*S*)-**13**: 84%, turbid oil. $^1$H NMR ($CDCl_3$) δ: 6.92 (ptm, $J = 8.3$ Hz, 2H); 7.05 (ptm, $J = 7.3$ Hz, 2H); 7.17 (m, 1H); 7.29 (ddd, $J = 7.6$, 4.0, 1.0 Hz, 1H); 7.29–7.36 (m, 4H); 7.39–7.43 (m, 2H); 7.49 (ptd, $J = 7.6$, 1.3 Hz, 1H); 7.56 (pt, $J = 7.8$ Hz, 1H); 7.65 (br dd, $J = 7.6$, 4.8 Hz, 1H); 7.98 (d, $J = 7.8$ Hz, 1H); 8.01 (br d, $J = 7.8$ Hz, 1H). $^{13}$C NMR ($CDCl_3$) δ: 120.22; 121.47; 127.37; 127.65 (d, $J = 7.6$ Hz); 127.94 (d, $J = 3.8$ Hz); 128.12 (d, $J = 7.6$ Hz); 128.16; 128.50; 128.76 (d, $J = 3.8$ Hz); 128.97; 129.34; 130.21 (d, $J = 22.9$ Hz); 133.14 (d, $J = 20.7$ Hz); 135.22 (C, d, $J = 19.4$ Hz); 141.84 (C); 142.08 (C, d, $J = 6.0$ Hz); 143.13 (C, d, $J = 1.6$ Hz); 143.68 (C, d, $J = 2.4$ Hz); 144.27 (C, d, $J = 2.9$ Hz); 145.11 (C, d, $J = 16.2$ Hz). $^{31}$P NMR ($CDCl_3$) δ: −9.79 (s). MS (40 °C) *m*/*z* (rel%): 336.1 (100, $M^+$). HRMS: calcd for $C_{24}H_{17}P$: 336.1068, found: 336.1061. $[\alpha]_D^{20} = -164$ (*c* 1.00, $CHCl_3$).

Compound (*S*)-**14**: 96%, pale yellow oil. $^1$H NMR ($CDCl_3$) δ: 6.89 (ptm, $J = 8.2$ Hz, 2H); 6.99 (ptm, $J = 7.5$ Hz, 2H); 7.14 (ptm, $J = 7.4$ Hz, 1H); 7.29 (ptdd, $J = 7.3$, 2.8, 1.0 Hz, 1H); 7.36 (ddd, $J = 7.6$, 4.0, 1.0 Hz, 1H); 7.42–7.49 (m, 3H); 7.51 (dd, $J = 8.6$, 1.8 Hz, 1H); 7.56–7.62 (m, 3H); 7.67 (br s, 1H); 7.79 (d, $J = 8.6$ Hz, 1H); 7.83 (m, 1H); 7.99 (dm, $J = 7.8$ Hz, 2H). $^{13}$C NMR ($CDCl_3$) δ: 120.32; 121.49; 125.96; 126.05; 127.01 (d, $J = 3.1$ Hz); 127.61; 127.74 (d, $J = 6.9$ Hz); 127.84; 127.94 (d, $J = 3.8$ Hz); 128.23; 128.27 (d, $J = 8.4$ Hz); 128.33 (d, $J = 3.8$ Hz); 128.49; 129.10; 129.45; 130.18 (d, $J = 22.2$ Hz); 132.62 (C); 133.04 (C); 133.35 (d, $J = 19.9$ Hz); 135.78 (C, d, $J = 18.6$ Hz); 139.32 (C); 142.17 (C, d, $J = 5.6$ Hz); ∼143.5 (C, m); ∼144.6 (C, m); 145.19 (C, d, $J = 16.2$ Hz). $^{31}$P NMR ($CDCl_3$) δ: −10.31 (s). MS (110 °C) *m*/*z* (rel%): 366.0 (100, $M^+$). HRMS of $BH_3$ complex: calcd for $C_{28}H_{19}P{\cdot}BH_3$: 400.1557, found: 400.1546. $[\alpha]_D^{20} = -162$ (*c* 1.00, $CHCl_3$).

Compound (*R*)-**15**: 89%, oil. $^1$H NMR ($CDCl_3$) δ: 0.15 (s, 9H); 7.13–7.29 (m, 6H); 7.38 (ptm, $J = 7.5$ Hz, 1H); 7.49 (pt, $J = 7.5$ Hz, 1H); 7.53–7.59 (m, 2H); 7.91 (br d, $J = 7.8$ Hz, 1H); 7.99 (br d, $J = 7.6$ Hz, 1H). $^{13}$C NMR ($CDCl_3$) δ: −0.17 ($CH_3$), 121.14; 121.93; 127.54 (d, $J = 7.6$ Hz); 128.09; 128.24; 128.56 (d, $J = 7.6$ Hz); 129.36; 129.51 (d, $J = 22.9$ Hz); 133.51 (d, $J = 20.7$ Hz); 133.86 (d, $J = 9.2$ Hz); 136.89 (C, d, $J = 19.0$ Hz); 142.46 (C, d, $J = 2.4$ Hz); 143.50 (C, d, $J = 24.4$ Hz); 144.42 (C); 144.46 (C); 144.47 (C); 144.50 (C); 147.93 (C, d, $J = 5.1$ Hz). $^{31}$P NMR ($CDCl_3$) δ: −9.87 (s). MS (50 °C) *m*/*z* (rel%): 332 (100, $M^+$); 317 (55, $M-CH_3$). HRMS: calcd for $C_{21}H_{21}PSi$: 332.1150, found: 332.1154. $[\alpha]_D^{20} = +291$ (*c* 0.74, $CHCl_3$).

**4.2.10. *dl*-5,5′-Diphenyl-4,4′-bis(5*H*-dibenzophosphol oxide) *dl*-16.** NaH (960 mg, 40 mmol), $Ni(PPh_3)_2Cl_2$ (1.64 g, 2.5 mmol), Zn dust (activated, 980 mg, 15 mmol), and **2** (2.01 g, 5 mmol) were placed in a Schlenk tube under argon and abs toluene (100 mL) was added through a rubber septum. After stirring for 10 min, dppf (1.39 g, 2.5 mmol) was added and the mixture degassed. The carefully sealed Schlenk tube was sonificated in an ultrasonic bath at 75–80 °C for 4 h with occasional shaking. During this time, the color of the reaction mixture changed from green to dark yellow. Subsequently the reaction was stirred for 10–12 h at 80 °C. After cooling to room temperature, HCl (5%, 50 mL) was added carefully followed by $CHCl_3$ (300 mL) and the mixture stirred for 30 min. Filtration removed remaining Zn dust and Ni residues and the organic phase was separated and dried with $MgSO_4$. Evaporation of solvent left a semi-solid mixture which was triturated with $CH_2Cl_2$/ethyl acetate (1:4) to give *dl*-**16** as a crystalline powder which was filtered off and washed with ethyl acetate and $Et_2O$ (>95% pure by NMR). The mother liquor was subjected to column chromatography ($SiO_2$, 40 × 4 cm, acetone/$CH_2Cl_2$, 1:1) to give a further crop of *dl*-**16**. Total yield: 631 mg (46%); mp: 237–240 °C.

$^1$H NMR ($CDCl_3$) δ: 6.70 (br dd, $J = 13.1$, 8.3 Hz, 4H); 6.85 (br td, $J = 7.8$, 3.0 Hz, 4H); 7.11 (m, 2H); 7.34 (ptdd, $J = 7.6$, 3.8, 0.8 Hz, 2H); 7.50 (br dd, $J = 9.3$, 7.2 Hz, 2H); 7.58 (ptpt, $J = 7.6$, 1.3 Hz, 2H); 7.78 (ptd, $J = 7.6$, 1.3 Hz, 2H); 7.83 (m, 4H); 8.35 (br dd, $J = 6.8$, 5.6 Hz, 2H). $^{13}$C NMR ($CDCl_3$) δ: 120.85 (d, $J = 9.9$ Hz); 121.02 (d, $J = 9.9$ Hz); 128.02 (d, $J = 12.2$ Hz); 129.15 (C, d, $J = 103$ Hz); 129.43 (d, $J = 11.5$ Hz); 129.83 (d, $J = 9.9$ Hz); 130.61 (d, $J = 10.7$ Hz); 131.29 (d, $J = 3.1$ Hz); 131.42 (C, d, $J = 101$ Hz); 132.15 (C, d, $J = 110$ Hz); ∼133.3 (m); 141.68; 141.89; 141.95; 142.17 (2 × C, 2 × d); ∼142.96 (C, m). $^{31}$P NMR ($CDCl_3$) δ: 36.76 (s). MS (electrospray) *m*/*z* (rel%): 573.1 (70, M+Na); 551.1 (60, M+H); 473.1 (100, M−Ph). HRMS: calcd for $C_{30}H_{19}O_2P_2$ (M−Ph): 473.0860, found: 473.0871. The same procedure applied to (*S*)-**2** yielded 69% of (*S*,*S*)-**16**; mp: >345 °C; $[\alpha]_D^{20} = +213$ (*c* 0.736, $CH_2Cl_2$).

**4.2.11. 5,5′-Diphenyl-4,4′-bis(5*H*-dibenzophosphol) 17.** Bis(phosphine oxide) *dl*-**16** (330 mg, 0.6 mmol) was suspended in abs DME (20 mL) in a Schlenk tube and degassed. To this was added MeOTf (390 mg, 1.8 mmol, 267 μL) and the mixture was stirred under Ar to give, after 1.5 h, an orange solution. After cooling to −50 °C $LiAlH_4$ (183 mg, 5.1 mmol) was added in one portion. The reaction was warmed up within 3 h to −10 °C and quenched with HCl (3 mL, 1 M). The cold mixture was filtered over Celite which was carefully washed with ethyl acetate (15 mL) and the filtrate evaporated at rt. The residue was treated with MeOH (3 mL) and kept overnight to give a white crystalline precipitate which was separated and dried. Yield:

174 mg (56%, 90–95% pure racem form, mp: ~325 °C). The mother liquor was chromatographed (ethyl acetate/petroleum ether, 1:9, $SiO_2$ deactivated with 13% of water) to give an additional product (33 mg, 10%) which was a mixture of racemate (40%) and *meso* (60%) forms.

Compound *dl*-**17**: $^1$H NMR[¶] (600 MHz, $CDCl_3$) $\delta$: 6.90 (br m, H-3); 6.98 (br m, H-12, H-14); 7.14 (pt, $J = 7.5$ Hz, H-13); 7.20 (br pt, $J = 7.4$ Hz, H-2); 7.27 (ptq, $J = 7.3$, 1.4 Hz, H-7); 7.47 (ptd, $J = 7.6$, 1.2 Hz, H-8); 7.57 (dm, $J = 7.4$ Hz, H-6); 7.60 (br m, H-11, H-15); 7.92 (dd, $J = 7.9$, 1.0 Hz, H-1); 7.80 (d, $J = 7.5$ Hz, H-9). $^{13}$C NMR[¶] (600 MHz, $CDCl_3$) $\delta$: 120.42 (C-1); 121.34 (C-9); 127.53 (pt, $J = 3.9$ Hz, C-7); 127.97 (pt, $J = 4.5$ Hz, C-12, C-14); 128.38 (C-8); 128.53 (C-2); 128.60 (pt, $J = 3.1$ Hz, C-3); 129.01 (C-13); 130.52 (pt, $J = 11.5$ Hz, C-6); 133.67 (pt, $J = 10.9$ Hz, C-11, C-15); 142.43 (pt, $J = 2.4$ Hz, C-4a); 143.41 (C-5a); 143.49 (C-4); 143.94 (pt, $J = 1.2$ Hz, C-9a, C-9b); C-10 was not observed. $^{31}$P NMR (600 MHz, $CDCl_3$) $\delta$: −10.03 (s). MS (150 °C) *m*/*z* (rel%): 518 (55, $M^+$); 441 (100, M−Ph). HRMS: calcd for $C_{36}H_{24}P_2$: 518.1353, found: 518.1362.

Compound *meso*-**17**: $^1$H NMR[¶] (600 MHz, $CDCl_3$) $\delta$: ~6.5 (br m, H-3); 6.76 (br m, H-12, H-14); 6.88 (br m, H-11, H-15); 6.98 (br m, H-13); 7.25 (ptdd, $J = 7.3$, 2.8, 1.1 Hz, H-7); 7.38 (br m, H-2); 7.44 (ptd, $J = 7.6$, 1.3 Hz, H-8); 7.46 (m, H-6); 7.94 (d, $J = 8.2$ Hz, H-1); 7.96 (d, $J = 8.6$ Hz, H-9). $^{13}$C NMR[¶] (600 MHz, $CDCl_3$) $\delta$: 120.51 (C-1); 121.21 (C-9); 127.45 (d, $J = 7.3$ Hz, C-7); 127.91 (d, $J = 8.1$ Hz, C-12, C-14); 128.26 (C-8); 128.36 (d, $J = 6.8$ Hz, C-3); 129.02 (C-13); 130.10 (d, $J = 12.7$ Hz; C-6); 133.59 (d, $J = 21.6$ Hz, C-11, C-15); 142.42 (d, $J = 1.9$ Hz, C-4a); 143.38 (C-5a); 143.68 (C-9a); 143.74 (C-9b); 143.81 (C-4); signals due to C-2 and C-10 were not observed. $^{31}$P NMR (600 MHz, $CDCl_3$) $\delta$: −11.54 (br s).

**4.2.12. Nickel dichloride complex of *dl*-17.** To a solution of 5.2 mg (0.01 mmol) of *dl*-**17** in $CDCl_3$ (0.7 mL) was added 1.1 equiv $NiCl_2{\cdot}6H_2O$ (0.1 M solution in $CD_3OD$) immediately giving a dark violet solution. $^1$H NMR ($CDCl_3/CD_3OD$, ~7:1) $\delta$: 6.54 (d, $J = 7.6$ Hz, H-3); 6.99 (pt, $J = 7.6$ Hz, H-12, H-14); 7.16 (t, $J = 7.3$ Hz, H-13); 7.29 (pt, $J = 7.8$ Hz, H-7); 7.31 (pt, $J = 7.8$ Hz, H-2); 7.42 (d, $J = 7.8$ Hz, H-11, H-15); 7.59 (pt, $J = 7.6$ Hz, H-8); 7.72 (d, $J = 7.8$ Hz, H-1); 7.87 (d, $J = 7.8$ Hz, H-9); 8.31 (d, $J = 7.6$ Hz, H-6). $^{13}$C NMR ($CDCl_3/CD_3OD$, ~7:1) $\delta$: 120.92 (C-1); 121.40 (C-9); 128.29 (C-12, C-14); 128.78 (C-3); 129.16 (C-7); 131.50 (C-13); 132.56 (C-8); 133.38 (C-2); 133.50 (C-11, C-15); 135.90 (C-6); 141.70–142.22 (m, C). $^{31}$P NMR ($CDCl_3/CD_3OD$, ~7:1) $\delta$: ~15 (br s).

**4.2.13. Palladium dichloride complexes of *dl*-17 and (*S*,*S*)-17.** Ligand *dl*-**17** (52 mg, 0.1 mmol) was dissolved in degassed $CH_2Cl_2$ (1 mL) and a solution of $Pd(CH_3CN)_2Cl_2$ (26 mg, 0.1 mmol) in 2.5 mL of the same solvent was added dropwise with stirring over 5 min to give a clear yellow solution. This was followed by the addition of EtOH (5 mL) and the slightly turbid mixture was concentrated in vacuo to afford a yellow precipitate. The crude complex was collected, washed with $Et_2O$ and dried. The solid was dissolved in $CHCl_3$, filtered over Celite, and evaporated to yield 56 mg (80%) of the pure complex. $^1$H NMR ($CDCl_3$) $\delta$: 6.69 (dd, $J = 7.3$, 4.8 Hz, H-3); 7.07 (ptd, $J = 7.7$, 1.6 Hz, H-12, H-14); 7.26 (br t, $J = 7.5$ Hz, H-13); 7.36–7.45 (m, H-2, H-7, H-11, H-15); 7.61 (pt, $J = 7.6$ Hz, H-8); 7.73 (d, $J = 7.8$ Hz, H-1); 7.84 (br d, $J = 7.6$ Hz, H-9); 8.64 (pt, $J = 7.8$ Hz, H-6). $^{13}$C NMR ($CDCl_3$) $\delta$: 121.11 (m, C-1); 121.27 (m, C-9); 124.63 (d, $J = 52$ Hz, C-10); 128.56 (m, C-12, C-14); 129.06 (m, C-7[‖]); 129.23 (m, C-3); 131.96 (C-13); 132.67 (C-8); 132.97–133.58 (m, $C_{quat.}$); 133.70 (C-2[‖]); 134.01 (m, C-11, C-15); 136.36 (m, C-6); 141.31 (m, $C_{quat.}$); 142.66 (m, C). $^{31}$P NMR ($CDCl_3$) $\delta$: 17.27 (s). MS (electro spray, sample in $CH_3CN$): *m*/*z* (rel%) 698 (40), 699 (20), 700 (95), 701 (50), 702 (100), 703 (43), 704 (50), 705 (21), 706 (10); the isotopic pattern is in agreement with $C_{38}H_{27}ClNP_2Pd$ corresponding to the fragment $[\mathbf{17}{\cdot}PdCl{\cdot}CH_3CN]^+$.

The same procedure applied to $(S,S)_P$-**17** (90% d.e.) afforded stereoselectively $(S,S)_P$-**17**·$PdCl_2$; $[\alpha]_D^{20} = -373$ (*c* 0.105, $CH_2Cl_2$,).

### 4.3. Kinetics

Kinetics of racemization for compounds **13**–**15** during 0.5–4 half lives was followed by polarimetry at 436 nm using a thermostated 1 dm cell. The calculations were based on a first order rate law[29] for $[R] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [S]$ with $[R] > [S]$.

$$(k_1 + k_{-1})t = \ln \frac{[R]_0 - [R]_{equ}}{[R]_t - [R]_{equ}}$$

with $k = k_1 = k_{-1}$ and taking into account that the specific rotation decreases with a rate twice the P-inversion, this transforms to

$$2kt = \ln \frac{\alpha_{max}}{\alpha_t}$$

A linear plot $\ln(\alpha_{max}/\alpha_t)$ versus $t$ yielded the rate constant $k_{inv}$ from which $\Delta G^{\neq}$ was calculated. From rate constants at three temperatures the slope of the Arrhenius plot ($\lg k$ vs $1/T$) yielded the activation energy $E_A$ and therefrom $\Delta H^{\neq} = E_A - RT$ and $\Delta S^{\neq} = (\Delta H^{\neq} - \Delta G^{\neq})/T$.

The kinetics of the epimerization of *dl*-**17** was followed by $^1$H NMR (600 MHz) using the integration ratio of signals at 7.99 ppm (*dl*) and 7.95 ppm (*meso*). The determination of thermodynamic parameters was performed as described above. For all plots, $R^2 \geqslant 0.996$ was found.

### 4.4. Crystallography

Crystals of (*S*)-**2**,**7**,**8**, *dl*-**16**, and *dl*-**17**·$PdCl_2$ were obtained either by evaporation ((*S*)-**2** from acetone, **7** from DMF) or by diffusion of pentane into $CH_2Cl_2$ (**8**, *dl*-**16** crystallizing as chiral (*S*,*S*)-**16**·$CH_2Cl_2$) or $CHCl_3$ solutions (*dl*-**17**·$PdCl_2$

[¶] Assignment was made by 2D NMR methods and numbering refers to Scheme 1.

[‖] Exchangeable.

giving *dl*-**17**·$PdCl_2$·$CHCl_3$). X-ray data were collected on a Bruker Smart CCD area detector diffractometer with graphite monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, and 0.3° ω-scan frames covering mostly entire spheres of the reciprocal space. After frame data integration with program SAINT, the reflection data were corrected for absorption by the multi-scan method and for $\lambda/2$ effects with program SADABS.[30] Space group assignments were made on the basis of systematic absences and intensity statistics by using the XPREP program.[30] The structures were then solved by direct methods and refined by full-matrix least-squares on $F^2$ using the program suite SHELX97.[31] The non-hydrogen atoms were refined with anisotropic thermal parameters and carbon-bound hydrogen atoms were included in idealized positions. The hydrogen atoms of the OH-groups in **7** and **8** were refined in *x*, *y*, *z*, and $U_{iso}$. Crystallographic data are presented in Table 2, selected geometric data are given in Table 3, and views of the molecular structures are shown in Figures 3–7. The structure of (*S*)-**2** showed at $T = 173$ K, strongly anisotropic displacement parameters for the phenyl carbon atoms indicating disorder. On cooling below $T = 173$ K, a phase transformation occurred, which caused the *b*-axis and the unit cell volume to double, but this low temperature structure could not be solved as yet. Another feature of interest is that racemic **16** crystallized as a $CH_2Cl_2$-solvate in the chiral space group $P2_12_12_1$ and formed a conglomerate of enantiopure left- and right-handed crystals, one of which with an (*S*,*S*)-configuration was investigated by X-ray diffraction. Therefore, the term racemic was omitted for the solid state material. In addition, compound *meso*-**16** was studied with X-ray diffraction, but is reported only in the supplementary material. CCDC 294522-294527 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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