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P-Chirogenic Benzo-Fused Phenoxaphosphane: Synthesis, Resolution and Study of the Stereochemical Properties of the Corresponding Palladium Complexes

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The synthesis and resolution of chiral phenoxaphosphane **3**, with the stereogenic center at the phosphorus atom, is described. Compound **3** has been synthesized following a well-known procedure for trapping a phosphorus atom within a six-membered ring. The resolution of the racemic mixture of **3** was achieved through separation of its diastereomeric palladacycle derivatives **7a**,**b** and **9a**,**b**. The absolute configuration of enantiopure phosphanes **3a**,**b** was assigned unequivocally by means of X-ray crystal structure determination for complex **9a** and by combination of NOE(^{1}H–^{1}H)/COSY(^{1}H,^{1}H) spectroscopy and DFT calculations for complexes **7a**,**b**, which in both cases led to identical results.

Introduction

Chiral phosphacyclic compounds are currently attracting the interest of the homogeneous catalysis community after having been neglected for many decades.[1,2] This attention for these P-heterocycles can be ascribed to the incessant search for novel structures, suitable as chiral ligands in asymmetric catalysis, pursued by researchers involved in the field of ligand development. In this regard, chiral phosphacycle-based ligands, which as a consequence of their ring constraints bear unique steric and electronic properties often remarkably different from their acyclic counterparts, are a new intriguing class of enantio-inductors for asymmetric transformations.[3] The first major breakthrough in the application of phosphacyclic ligands in asymmetric catalysis is represented indubitably by the five-membered DuPhos ligands.[4a,4b] An increasing variety of chiral phosphacycles of different ring extensions, ranging from four to seven units, have since then been prepared and applied successfully in asymmetric catalysis.[2,3,5,6]

Benzo-fused phenoxaphosphanes, a class of conjugated phosphorus-based heterocycles, were initially introduced by Mann and Millar in the late 1950's and since then have found applications mostly in the development of new polymeric materials.[7,8] The potential of these cyclic analogues of triphenylphosphane in catalysis has remained hitherto unexpressed as is demonstrated by the very few articles regarding the applications of these compounds.[9,10] Despite the scarce interest in this class of phosphanes, our group has extensively worked with phenoxaphosphane-based systems and in particular with phenoxaphosphanyl-substituted XantPhos ligands which have been successfully applied in metal-catalyzed reactions, such as hydroformylation of internal alkenes, outperforming their diphenylphosphane counterparts.[10]

In this context, the synthesis of chiral benzo-fused phenoxaphosphane compounds represents the next step due to the high degree of enantio-discrimination chiral phosphacycles can induce in asymmetric metal-catalyzed reactions.[1–6] In this work we describe the synthesis and optical resolution of the first benzo-fused phenoxaphosphane **3** in which a hydroxyl moiety, amenable to further functionalization, is attached to the rigid phenoxaphospanyl skeleton. Moreover, given the influence exerted by the ligand/metal stereoelectronic interactions in controlling a catalytic process and in view of the employment of chiral phenoxaphosphane-based ligands in asymmetric catalysis we carried out an in-depth investigation of the stereochemical properties of **3** and derivatives thereof.

Results and Discussion

Racemic **3** was prepared starting from *m*-phenoxyphenol, successively protected as 1-(1-ethoxyethoxy)-3-phenoxybenzene (**1**). Metallation of **1** with *n*-butyllithium, in the presence of TMEDA, followed by internal ring closure with dichlorophenylphosphane gives **2**, which after deprotection affords the racemic mixture **3** (Scheme 1).[11]

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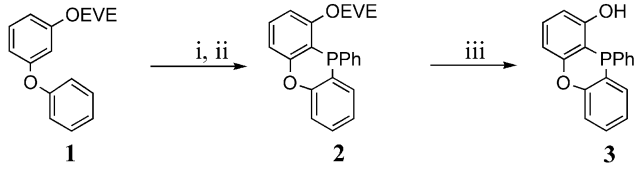
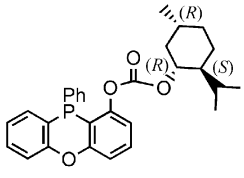
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.



Scheme 1. Synthesis of chiral phosphane **3** (EVE = ethyl vinyl ether or 1-ethoxyethoxy group). i) 2 equiv. TMEDA, 2 equiv. BuLi, Et_2O/hexane, 0 °C to r.t., overnight; ii) 1.1 equiv. $PhPCl_2$, –70 °C, 3 h; iii) PPTS, ethanol/CH_2Cl_2, reflux; overall yield 32%.

Resolution of racemic phosphanes based on the transformation of both enantiomers into a pair of diastereoisomers is common practice.[12] In our particular case, we envisaged that derivatization of the hydroxyl group in **3** to a chiral menthyl carbonate would be exploitable for the separation of the resultant diastereomeric mixture. Functionalization of phosphane **3** was successfully accomplished to yield the mixture of diastereoisomers **4a**,**b**, but all attempts towards resolution failed.[13]



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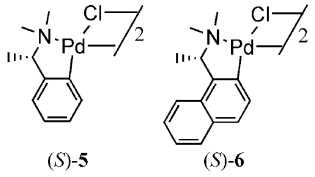
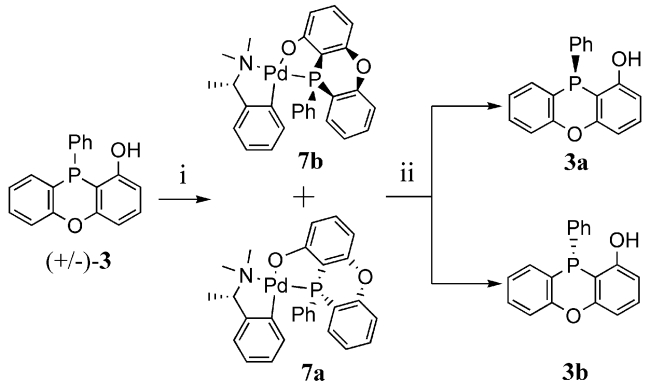
Alternatively, it was considered to employ chiral metal complexes as resolving agents. Thus *ortho*-palladated derivatives of (*S*)-dimethyl(1-phenylethyl)amine (*S*)-**5** and (*S*)-dimethyl(1-naphthylethyl)amine (*S*)-**6**, which have demonstrated their effectiveness towards a wide range of racemic phosphanes, were chosen (Figure 1).[14–16]



(*S*)-**5** (*S*)-**6**

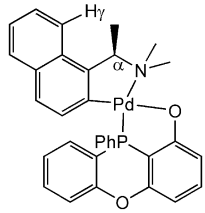
Figure 1. Chiral palladacycles.

The diastereomeric mixture of **7a**,**b** was prepared by reaction of the racemate of **3** with palladate complex (*S*)-**5** in CH_2Cl_2 in the presence of triethylamine. The ^{31}P-NMR spectrum of compounds **7a**,**b** showed a set of two well resolved singlets of equal intensity at δ = –5.76 and –4.97 ppm. Compounds (*S*,*S*a)-**7a** and (*R*,*S*a)-**7b** were successfully separated by careful radial chromatography and characterized by IR, mass analysis, ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy. Moreover, it was possible to determine the absolute configurations at the phosphorus atom and assign the λ/δ conformations of the organometallic five-membered Pd–C–N ring in the same complexes, see below. Enantiopure phosphanes **3a** and **3b** were obtained by decomplexation from their corresponding diastereomeric palladium complexes, respectively **7b** and **7a**, using 1,2-bis(diphenylphosphanyl)ethane (dppe) in the presence of excess ammonium chloride as proton source (Scheme 2).[14]



Scheme 2. Chiral resolution of phosphane **3**. i) 0.5 equiv. of (*S*)-**5**, NEt_3, CH_2Cl_2, room temp., 30 min; ii) dppe, NH_4Cl, CH_2Cl_2, room temp., 1 h.

Isolation of adequate amounts of enantiopure **3a**,**b**, which might be required at a later stage for purposes such as ligand screening for homogeneous catalysis, is an essential prerequisite of any considered chiral resolution technique. Consequently, the scale up of the aforementioned chromatography separation was investigated, but led only to the recovery of diastereomerically enriched mixtures. Clearly the structures of complexes **7a**,**b** do not differ sufficiently for being optimally separated. In order to enhance the structural differences between **3a**,**b** derivatives we turned our attention towards the more conformationally rigid palladacycle (*S*)-**6** and for this purpose the synthesis of compound **8** was undertaken and successfully accomplished, following the same procedure reported for **7**. Disappointingly, the chromatographic separation of the diastereomeric mixture of **8**, despite the large array of solvents employed as eluents was fruitless and at best, afforded only diastereomerically enriched mixtures and decomposed material.



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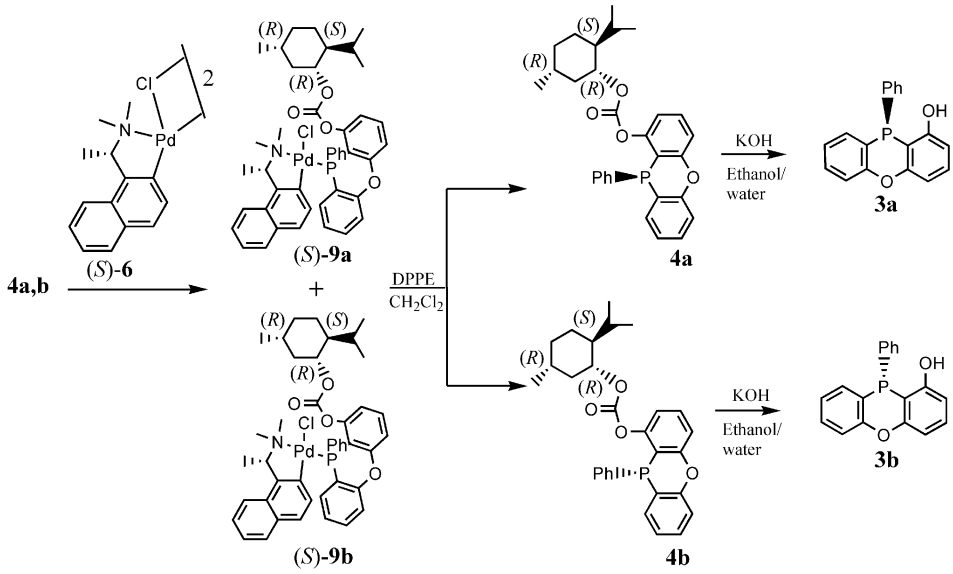
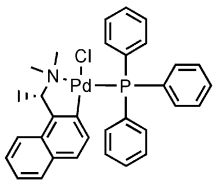
The Pd–C–N ring of palladacycle (*S*)-**6** is known to adopt a λ conformation, with the Me_α taking up the axial position, which is normally retained in its derivatives in order to avoid the steric congestion that would be present otherwise between H_γ and an equatorial Me_α in a conformation of type δ.[17] Indeed, the ^{1}H NMR spectrum of the diastereomeric mixture of complex **8** shows, for H_α, two peaks partially overlapping with chemical shifts in the range



Scheme 3. Chiral resolution of phosphanes **3** and **4**.

δ = 4.3–4.6 ppm, in agreement with a conformation type λ for both diastereoisomers. Much to our dismay, the strain caused by both the Pd–C–N ring and the heterobidentate phosphane in **8** is not beneficial, in contrast with previous reports, for the resolution of this diastereomeric mixture and furthermore is at the origin of the instability of these highly strained complexes.[17]

Thus, the resolution route employing directly P,O-phosphane **3** was discarded and another route, employing protected phosphane **4a**,**b**, was considered instead. This resolution method consists as a first step in reacting diastereomeric mixture **4a**,**b**, which as such could not be resolved, to palladacycle (*S*)-**6**.[15] The resultant diastereomeric mixture **9a**,**b** was successfully resolved by chromatography into its two components **9a** and **9b** with high yields (Scheme 3). Most importantly, employing this route we could scale up the separation of these diastereoisomers by at least one order of magnitude compared to the separation of diastereoisomers **7a**,**b**. Diastereopure phosphanes **4a**,**b** were obtained by decomplexation from their corresponding diastereomeric palladium complexes using dppe.[15] Hydrolysis of the carbonate group of **4a** and **4b** affords enantiopure **3a** and **3b**, respectively.[13] The enantiopure ligands were isolated in good yields and found to be configurationally stable after refluxing in water/ethanol overnight. This was confirmed by preparing compound **4** and checking the diastereopurity by ^{1}H and ^{31}P NMR spectroscopy.



(*S*)-**6**-(PPh_3)

Yellow crystals of **9a**, suitable for X-ray diffraction, were obtained by slow diffusion of hexane into a solution of **9a** in dichloromethane. Due to the disorder of the menthyl group the geometrical parameters of this group have large standard uncertainties. However, this does not affect the Flack parameter[29] for the determination of the absolute configuration, which is established to be *S* at the phosphorus atom (Figure 2). Selected bond lengths and bond angles of structure **9a** are given in Table 1.

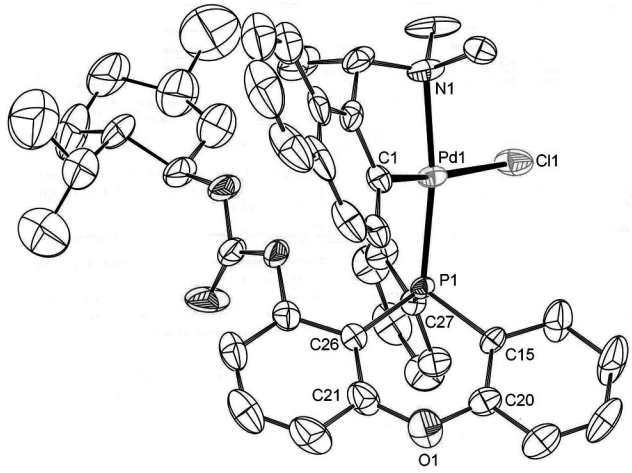


Figure 2. Displacement ellipsoid plot of the structure of **9a** in the crystal (50% probability level). Hydrogen atoms and disordered solvent molecules are omitted for clarity. Only the major disordered component of the menthyl moiety is shown (58.3% occupancy).

Table 1. Selected bond lengths [Å] and angles [°] for **9a**.

P1–Pd1	2.2405(8)	C26–P1–C15	99.48(15)
P1–C15	1.807(3)	P1–C26–C21	123.2(3)
P1–C26	1.808(3)	C26–C21–O1	124.5(3)
P1–C27	1.826(3)	O1–C20–C15	125.7(3)
Pd1–Cl1	2.4019(9)	P1–C15–C20	123.0(3)
N1–Pd1	2.123(3)	C15–P1–C27	105.51(15)
Pd1–C1	2.009(3)	C26–P1–C27	102.52(14)

As expected, the tertiary phosphane is coordinated *trans* to the NMe_2 group of the naphthylamine.[14] The palladium–phosphorus distance of this structure is very similar to those observed in related complexes such as (*S*)-**6**-(PPh_3), containing an unstrained triphenylphosphane. The sum of the three C–P–C angles of **9a** (307.5°) is smaller than that of (*S*)-**6**-(PPh_3) (310.9°) hence confirming that the phosphorus atom is slightly pyramidalized owing to its incorporation in a six-membered ring.[18,20] As a consequence, the P-lone pair of **3** has a greater s-character than its analogue PPh_3. This is further confirmed by the enhancement of the π-acceptor properties of phenoxaphosphane-based ligands compared to strainless analogues, which was established previously by high pressure FT-IR studies of the stretching frequencies of CO, in phenoxaphosphane-based ligand/rhodium carbonyl complexes.[19,20]

Assignment of the Absolute Stereochemistry in 7: Compound **7** represents one of the few examples of neutral chiral palladacycles containing a hetero-bidentate phosphane and the only known example with a P,O-hetero-bidentate phosphane reported to date. Such a low level of diversity, amid this class of complexes, finds its rationalization in that chiral organopalladium complexes, such as **5**–**6**, have been mainly used as resolving agents for monophosphanes.[14a,21,22] Consequently, the uniform, large body of data regarding their structural and spectroscopic features, available in literature, turned out to be particularly useful for investigating stereochemical properties of chiral phosphanes.[23]

The absolute configuration of the phosphorus atom, in compounds **7a**,**b**, has been unambiguously assigned by complementing the study of the NOE(^{1}H–^{1}H) contacts and the NMR chemical shift regularities with DFT calculations performed using SPARTAN.[23,24] The assignment of all the resonances from ^{1}H NMR spectra of complexes **7a**,**b** was accomplished by analyzing the COSY(^{1}H,^{1}H) spectra and NOE(^{1}H–^{1}H) interactions. In the case of complex **7a**, the NOE(^{1}H–^{1}H) signals of the contacts between Me^{17} and H^{19} and between H^{22} and H^3 permitted the full characterization, by COSY(^{1}H,^{1}H), respectively, of the metallated phenyl ring and the adjacent benzo-fused phenyl ring of the phosphacycle. The resonance of H^{11} is determined by analysis of the COSY(^{1}H,^{1}H) spectrum, which shows interactions with both upfield H^{10} and H^{12} protons. The signals of the protons P^{ortho}, P^{meta} and P^{ipso} of the uncondensed phenyl group of the phosphacycle were assigned by analysis of the COSY(^{1}H,^{1}H) spectrum (Figure 3). The spatial disposition of the Me groups was established by NOE (^{1}H–^{1}H) experiments. The ^{1}H NMR spectrum of **7a** (Figure 4) is shown below along with the enlargement of the aromatic region of the corresponding COSY(^{1}H,^{1}H) spectrum and the complete list of NOE(^{1}H–^{1}H) contacts. Complex **7b** was fully characterized in a similar manner.

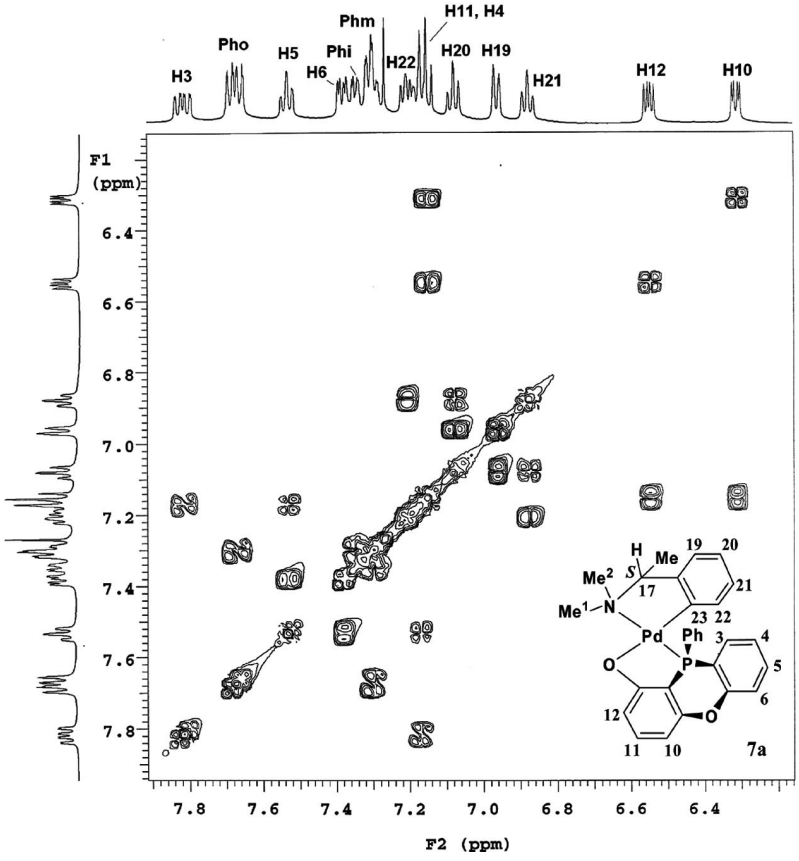


Figure 3. COSY(^{1}H,^{1}H) spectrum of the aromatic region of **7a**.

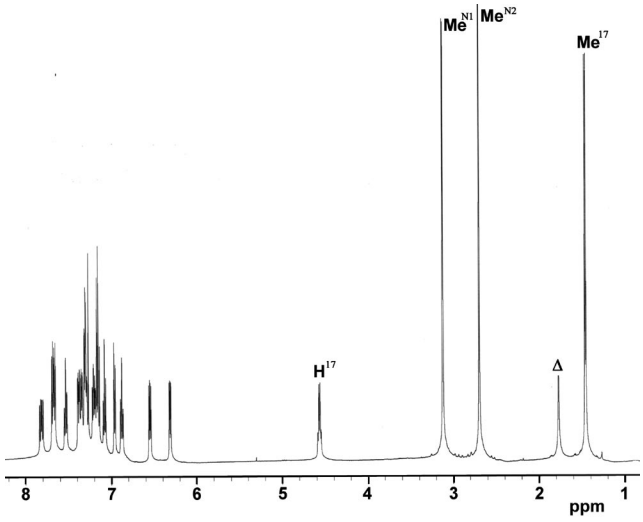


Figure 4. ^{1}H NMR of **7a**. The symbol Δ refers to H_2O.

The 1D ^{1}H-NMR NOE data for structure **7a** clearly show a strong interaction between Me^{N1} and H^{17} while they do not show any interaction between Me^{N2} and H^{17} (Table 2). The Newman projection of this structure is in agreement with a conformation type δ where H^{17} is axial and Me^{N1} and Me^{N2} correspond to Me(eq) and Me(ax), respectively. On the contrary, for complex **7b** it was possible to see a NOE(^{1}H–^{1}H) signal for the interaction between H^{17} with both $Me^{N1,N2}$, albeit weak, in agreement with a conformation type λ with Me^{17} axial (Figure 5). Irradiation of Me^{17} for both complexes **7a**,**b** did not show any appreciable NOE(^{1}H–^{1}H) interaction with $Me^{N1,N2}$. Furthermore, the ^{1}H NMR spectra of both complexes **7a** and **7b** show for H^{17} a chemical shift difference of about 1 ppm on the δ scale, pointing out a totally different magnetic field experienced by this proton in the δ–λ conformations of the Pd–C–N ring.[17]

Table 2. Selected 1D ^{1}H-NMR NOE data for **7a**.

Me^{N1} (3.11) – H^{17} (4.56) (m)
Me^{17} (1.46) – H^{17} (4.56) (m), H^{19} (6.95) (m)
Me^{N2} (2.69) – Me^{N1} (3.11) (w), Me^{17} (1.46) (w)
H^{19} (6.96) – H^{20} (7.07) (s), H^{17} (4.56) (m), Me^{17} (1.46) (s)
H^{17} (4.56) – H^{19}(6.96) (m), Me^{N1} (3.11) (s), Me^{17} (1.46) (s)
H^{22} (7.2) – H^3 (7.8) (s), H^{21} (6.87) (s)
H^3 (7.8) – H^{22} (7.2) (s)
H^{20} (7.07) – H^{19} (6.96) (s), H^{21} (6.87) (s)
H^{21} (6.87) – H^{20} (7.07) (s), H^{22} (7.2) (s)

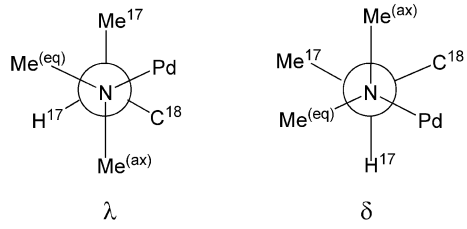


Figure 5. Newman projections for the λ and δ conformations of the palladacycle in **7**.

Calculations at the HF-DFT SDF level of theory, using RB3LYP as method and LACVP* as basis set, have been carried out for the four most stable conformers **7**, namely the structures containing the combination of the two different absolute configurations at the phosphorus atom *R*/*S* with the two possible conformations δ–λ of the palladacycles, (Figure 6). The distance between H^3–H^{22} in complex (*S*)-δ-**7** (I) is 2.08 Å while in (*S*)-λ-**7** (II) it is 2.58 Å. Clearly,

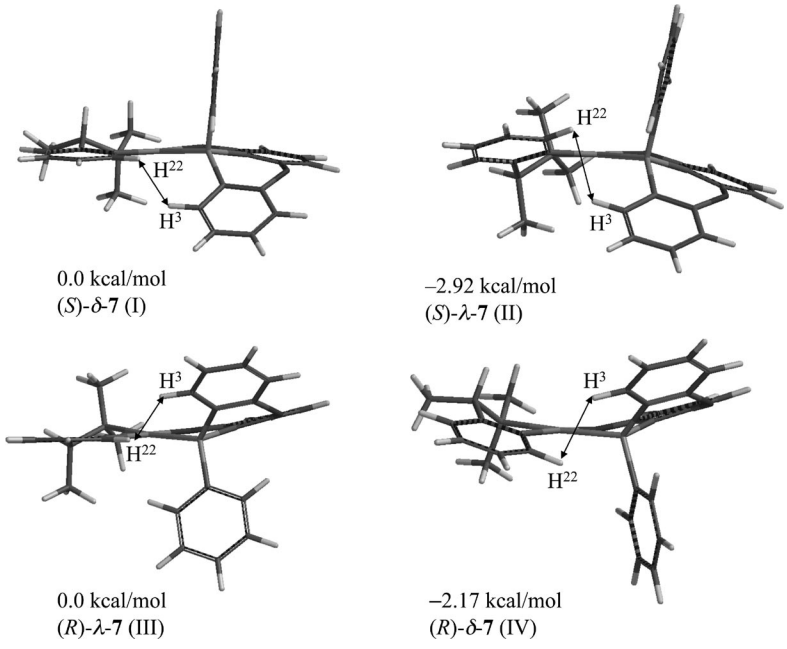


Figure 6. Structures of the four most stable conformers calculated at the HF-DFT SDF level of theory. (*S*)-δ-**7** (I), (*S*)-λ-**7** (II), (*R*)-λ-**7** (III), (*R*)-δ-**7** (IV).

the second structure experiences a higher steric relief compared to the former, which results in an energy difference of 2.92 kcal/mol. This value indicates the presence of only one of the two possible structures I–II in solution thus suggesting that **7b** corresponds to (*S*)-λ-**7** (II). The determination of the absolute configuration at the phosphorus atom was applied likewise for (*R*)-**7**-(III–IV) complexes. In this case, the distance between H^3–H^{22} in complex (*R*)-λ-**5** (III) is 2.01 Å while in (*R*)-δ-**7** (IV) it is 2.46 Å hence favouring the formation of the latter by 2.17 kcal/mol. These results are consistent with **7a** corresponding to structure (*R*)-δ-**7** (IV). The modelled structures reported in Figure 6 show that steric relief is indeed achieved when the Pd–C–N ring flips in response to the tension caused by the rigid P–O ligand. Enantiopure phosphanes **3a**,**b** have been freed from complexes **7a**,**b** and further reacted with (–)-menthyl chloroformate to give rise to compounds **4a**,**b** of which the ^{1}H, ^{31}P-NMR spectra corroborated the correct assignment of the absolute configuration at the phosphorus atom.

In summary, we have synthesized the first chiral benzo-fused phenoxaphosphane **3** and determined the absolute configuration at the phosphorus atom in its metal complexes. DFT calculations underpin structural features of the molecules determined spectroscopically and give more insight into structural preferences in solution. Currently compound **3** and other achiral benzo-fused phenoxaphosphane are being used as building blocks in the syntheses of monodentate and bidentate phenoxaphosphane-based ligands. Results regarding the applications of these ligands, as enantio-inductors in asymmetric catalysis, will be published in due course.

Experimental Section

General: All chemical manipulations were carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures and freshly distilled under nitrogen atmosphere. NMR spectra were recorded at 295°K on a Varian Gemini 300 spectrometer operating at 300.07 MHz (^{1}H), 121.47 MHz (^{31}P) and 75.46 MHz (^{13}C) unless otherwise stated; NOESY, COSY and NOE were recorded at 499.79 MHz (^{1}H) on a Varian Gemini 500 spectrometer. Chemical shifts are quoted with reference to Me_4Si (^{1}H) and 85% H_3PO_4 (^{31}P). The optical rotations were measured using a Perkin–Elmer 241-MC polarimeter. Infrared spectra were recorded as KBr pallets on a Nicolet Nexus 670-FT-IR spectrometer and processed with the OMNIC software. High resolution mass spectra were measured on a JEOL IMS-SX/SX102A. Elemental analyses were performed at the H. Kolbe Mikroanalytisches Laboratorium in Mülheim (Germany). Chiral compounds **7a**–**b** were obtained in pure form by preparative thin layer radial chromatography (Chromatotron®, Harrison Research, model 7924T) employing silica gel 60 PF254 containing gypsum. The resolving agents di-μ-chlorobis[(*S*)-dimethyl(1-phenylethyl)aminato-C_2,N]dipalladium(II) (*S*)-**5** and di-μ-chlorobis[(*S*)-dimethyl(1-naphthylethyl)aminato-C_2,N]dipalladium(II) (*S*)-**6** were prepared according to literature procedure.[14,15]

All the calculations were performed with the Spartan "04 1,0,0 (Sept. 17, 2003) suite of programs.[31]

1-(1-Ethoxyethoxy)-3-phenoxybenzene (1):[25] To a solution of 3-phenoxyphenol (15.4 g, 83 mmol) in dichloromethane (250 mL) was added (pyridinium *p*-toluenesulfonate) PPTS (2.08 g, 8.3 mmol) at room temperature. The resultant mixture was cooled to 0 °C and subsequently ethyl vinyl ether (EVE) (132.8 mmol) was added dropwise. The mixture was allowed to stir overnight at room temperature. The resultant solution was washed with brine (20 mL) and the phases were subsequently separated. The organic layer was washed twice with aqueous 1 M NaOH (20 mL) and dried with $MgSO_4$. The solvent and all volatiles were removed in vacuo. The crude of reaction is a yellow oil which after filtration through silica (eluent: CH_2Cl_2) yielded a colorless oil (20.12 g, 78 mmol, 94%). ^{1}H NMR ($CDCl_3$): δ = 1.19 (t, ^3J = 7.1 Hz, 3 H), 1.48 (d, ^3J = 5.3 Hz, 3 H), 3.50 (m, 1 H), 3.70 (m, 1 H), 5.35 (q, ^3J = 5.3 Hz, 1 H), 6.64 (dd, ^3J = 8.10 Hz, 1 H), 6.68 (t, ^3J = 2.3 Hz, 1 H), 6.76 (dd, ^3J = 8.2 Hz, 1 H), 7.03 (d, ^3J = 7.6 Hz, 2 H), 7.10 (t, ^3J = 7.3 Hz, 1 H), 7.20 (t, ^3J = 8.2 Hz, 1 H), 7.34 (t, ^3J = 7.6 Hz, 2 H) ppm. EI-MS (70 eV): *m*/*z* = 258, 213, 186, 73, 45.

(±)-1-(1-Ethoxyethoxy)-10-phenyl-10*H*-phenoxaphosphane (2): To a solution of *O*-protected 3-phenoxyphenol (4.4 g, 17.0 mmol) and TMEDA (35.90 mmol, 3.5 mL) in 300 mL of diethyl ether/hexane (1:2) was added dropwise a solution of *n*-butyllithium in hexane (2.5 M, 36 mmol, 14.4 mL) at 0 °C and the reaction mixture was allowed to stir overnight at room temperature. The resultant orange solution was cooled to –60 °C and subsequently a solution of Cl_2PPh, (19.30 mmol, 2.7 mL) in 5 mL of hexane, was slowly added. The reaction mixture was slowly warmed to room temperature and allowed to stir for 5 h. The color of the solution changed from orange to colorless with the formation of a precipitate (LiCl). The solution was canulated into another Schlenk tube and the solvent was removed in vacuo. The crude of reaction was dissolved in CH_2Cl_2 and washed with deoxygenated 0.1 M aqueous HCl. The crude product is a yellow oil which after filtration through silica (eluent: CH_2Cl_2) and removal of the solvent in vacuo is obtained as colorless oil (2.6 g, 7.14 mmol, 42%). ^{31}P NMR ($CDCl_3$): δ = –63.80, –64.80 ppm. ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, ^3J = 7.2 Hz, 3 H), 1.12 (t, ^3J = 7.2 Hz, 3 H), 1.27 (d, ^3J = 5.1 Hz, 3 H), 1.32 (d, ^3J = 5.1 Hz, 3 H), 2.95 (m, 1 H), 3.20 δ (m, 1 H), 3.50 (m, 1 H), 3.72 (m, 1 H), 5.35 (m, 2 H), 6.60–7.50 (m, ^3J = 7.3 Hz, 12 H) ppm. EI-MS (70 eV): *m*/*z* = 364, 335, 320, 282, 215.

(±)-10-Phenyl-10*H*-phenoxaphosphan-1-ol (3): 1-(1-Ethoxyethoxy)-10-phenyl-10*H*- phenoxaphosphane (2.6 g, 7.14 mmol) was dissolved in a 3:1 mixture of degassed ethanol and dichloromethane (80 mL). PPTS (0.07 mmol) was added and the solution was heated to 65 °C and stirred overnight. The mixture was cooled down and subsequently the solvent and all volatiles were evaporated in vacuo to leave a white viscous oil. The product is filtered through silica (eluent: CH_2Cl_2) after that the solvent was removed in vacuo to yield a white solid (1.7 g, 5.8 mmol, 81%). ^{31}P NMR ($CDCl_3$): δ = –72.78 ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 105.83, 110.18, 110.56, 116.93, 118.22, 124.03–124.19, 128.80, 128.88–129.04, 131.63–131.76, 131.83–132.02, 135.21, 135.71, 139.09–139.33, 155.59, 156.43, 158.31, 158.53 ppm. ^{1}H NMR ($CDCl_3$): δ = 6.10 (s, 1 H, OH), 6.70 (m, 1 H) 6.82 (d, ^3J = 8.2 Hz, 1 H), 7.10–7.35 (m, 8 H), 7.40 (m, 1 H), 7.60 (m, 1 H) ppm. (HRMS, FAB+): *m*/*z* calcd. for $C_{18}H_{13}O_2P$: 292.070; found: 292.065. $C_{18}H_{13}O_2P$ (292.07): calcd. C 73.97, H 4.48; found C 73.82, H 4.41.

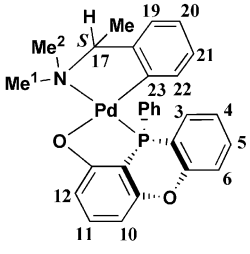
(1*R*)-(–)-Menthyl 10-Phenyl-10*H*-phenoxaphosphan-1-yl Carbonate (4a,b): To a solution of 10-phenyl-10*H*-phenoxaphosphan-1-ol (100 mg, 0.342 mmol) in dichloromethane (5 mL) was added NEt_3 (0.1 mL) and the resultant mixture was allowed to stir for 30 min at room temperature. Subsequently (–) menthyl chloroformate

(1 equiv.) was added and the solution was stirred for an additional 2h at room temp. The solvent and all the volatiles were removed in vacuo and the product obtained was dissolved again in toluene (1 mL) and filtered through a short silica column (eluent: toluene). The evaporation of the volatiles yields the product as a white oil (138 mg, 0.29 mmol, 86%). ^{31}P NMR ($CDCl_3$): δ = –66.36, –65.54 ppm. (HRMS, FAB+): *m*/*z* calcd. for $C_{29}H_{31}O_4P$: 474.319; found: 475.200 $[M + H]^+$.

Compound 7: To a solution of **3** (25 mg, 0.086 mmol) in dichloromethane (5 mL) was added triethylamine (1.1 equiv.) and the solution was stirred for 30 min. At this point (*S*)-**5** (25 mg, 0.043 mmol) was added and the solution was stirred for an additional hour. The solution was filtered through a short pad of silica (eluent: CH_2Cl_2), next the solvent was evaporated off to give rise to the diastereomeric mixture of compounds **7a**,**b** as a yellow solid (36 mg, 0.066 mmol, 72%). Subsequently the diastereoisomers were separated by radial chromatography (eluent: CH_2Cl_2/hexane = 20:1). ^{31}P NMR ($CDCl_3$): δ = –5.76, –4.97 ppm. (HRMS, FAB+): *m*/*z* calcd. for $C_{28}H_{26}NO_2PPd$: 545.070; found: 545.070. $C_{28}H_{26}NO_2PPd$ (545.07): calcd. C 61.60, H 4.80; found C 61.55, H 4.76.

Compound (R^P)-7a: First diastereoisomer eluted (21 mg, 84%). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –5.76 ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 10.59, 42.07–42.10, 47.63–47.65, 72.14–72.16, 101.95–101.98, 106.13, 106.57, 112.98, 113.42, 113.93–114.00, 119.50, 124.27–124.49, 126.32–126.36, 128.97–129.06, 130.89–130.91, 132.44–132.56, 132.78, 133.42–133.53, 134.21–134.57, 140.32–140.41, 148.65–148.68, 152.94–152.96, 157.88–157.89, 158.54–158.56, 175.37–175.47 ppm. ^{1}H NMR (499.8 MHz, $CDCl_3$): δ = 1.46 (d, ^3J = 6.6 Hz, 3 H, Me^{17}), 2.70 (d, ^3J = 1.8 Hz, 3 H, Me^{N2}), 3.10 (d, ^3J = 1.8 Hz, 3 H, Me^{N1}), 4.50 (q, 1 H, H^{17}), 6.30 (dd, 1 H, H^{10}), 6.55 (dd, 1 H, H^{12}), 6.88 (t, ^3J = 7.5 Hz, 1 H, H^{21}), 6.96 (d, ^3J = 7.8 Hz, 1 H, H^{19}), 7.08 (t, ^3J = 7.5 Hz, 1 H, H^{20}), 7.10–7.20 (m, 2 H, H^{11}, H^4), 7.20–7.25 (m, 1 H, H^{22}), 7.30 (m, 1 H, Ph^m), 7.34 (m, 1 H, Ph^i), 7.40 (m, 1 H, H^6), 7.53 (t, ^3J = 8.7 Hz, 1 H, H^5), 7.66 (m, 2 H, Ph^o), 7.80 (m, 1 H, H^3), ppm (complex **7a** see Figure 3). $[\alpha]_D^{25}$ = +46.6 (*c* = 0.42, $CHCl_3$). IR (KBr): $\tilde{\nu}_{max}$ = 1588 (s), 1541 (m), 1447(s), 1429 (m), 1312 (m), 1218 cm^{-1} (m). (HRMS, FAB+): *m*/*z* calcd. for $C_{28}H_{26}NO_2PPd$: 545.070; found: 545.074.

Compound (S^P)-7b: Second diastereoisomer eluted (7 mg, 29%). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –4.97 ppm. ^{13}C NMR (126.7 MHz, $CDCl_3$): δ = 25.22, 46.19–46.21, 51.41–51.44, 75.40–75.43, 101.97–102.00, 106.22, 106.65, 113.17, 113.61, 113.97–114.03, 119.51–119.54, 123.32, 124.47, 124.57, 125.81–125.85, 128.95–129.04, 130.88–130.90, 132.41–132.52, 132.74–132.75, 133.41–133.53, 134.15–134.51, 140.51–140.85, 145.02–145.06, 156.53–156.55, 157.93–157.95, 158.55–158.57, 175.55–175.65 ppm. ^{1}H NMR (499.8 MHz, $CDCl_3$): δ = 1.70 (d, ^3J = 6.3 Hz, 3 H, Me^{17}), 2.87 (d, ^3J = 3.3 Hz, 3 H, Me^N), 2.92 (d, ^3J = 1.8 Hz, 3 H, Me^N), 3.70 (m, 1 H, H^{17}), 6.30 (dd, 1 H, H^{10}), 6.53 (dd, 1 H, H^{12}), 6.83 (t, ^3J = 7.2 Hz, 1 H, H^{21}), 7.02 (t, ^3J = 7.5 Hz, 1 H, H^{20}), 7.10 (d, ^3J = 8.4 Hz, 1 H, H^{19}), 7.10–7.30 (m, 3 H), 7.3 (m, 1 H, Ph^m), 7.35 (m, 1 H, Ph^i), 7.40 (m, 1 H, H^6), 7.52 (t, ^3J = 7.5 Hz, 1 H, H^5), 7.66 (m, 2 H, Ph^o), 7.80 (m, 1 H, H^3) ppm. $[\alpha]_D^{25}$ = –33.9 (*c* = 0.24, $CHCl_3$). IR (KBr): $\tilde{\nu}_{max}$ = 1588 (s), 1535 (m), 1452 (s), 1429 (m), 1312 (m), 1218 cm^{-1} (m). (HRMS, FAB+): *m*/*z* calcd. for $C_{28}H_{26}NO_2PPd$: 545.07; found: 545.07.



7b

Compound 8: Experimental procedure as reported for **7**; yield 63%. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –5.40 ppm. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 1.80 (m, 6 H), 2.8–3.1 (m, 12 H), 4.30–4.60 (m, 2 H), 6.20–6.50 (m, 2 H), 6.60–6.80 (m, 3 H), 7.00–8.20 (m, 29 H) ppm. (HRMS, FAB+): *m*/*z* calcd. for $C_{32}H_{28}NO_2PPd$: 595.09; found 595.09.

Compounds 9a,b: Compound **4a**,**b** (498 mg, 0.975 mmol) and (*S*)-**6** (333 mg, 0.427 mmol) were placed in a Shlenk tube and subsequently solubilized in dichloromethane (20 mL).The resultant solution was allowed to stir for 30 min. Next, the solvent was evaporated to give rise to the diastereomeric mixture of compounds **9a**,**b** as a yellow solid. Subsequently the diastereoisomers were separated by chromatography (eluent: CH_2Cl_2). ^{31}P NMR: δ = –8.20, –12.70 ppm.

Compounds (S^P)-9a: First diastereoisomer eluted (300 mg, 86%). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –12.72 ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 15.89, 21.17, 22.27, 22.90–22.96, 25.71, 31.58, 31.83, 34.14, 41.18, 47.44, 48.50, 51.5, 73.67, 79.83, 107.08, 107.76, 110.20, 110.85, 114.70, 117.40–117.45, 117.75, 123.54, 124.01, 124.64–124.73, 124.73–125.00, 125.65, 128.11, 128.25, 128.83, 130.50, 131.23, 132.34, 133.12, 133.40, 133.60, 134.11, 134.59, 134.75, 137.00, 137.23, 148.78–148.81, 151.53, 151.90, 151.95, 153.53, 154.36 ppm. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.65 (d, ^3J = 6.6 Hz, 3 H), 0.80–2.00 (m, 15 H), 2.16 (d, *J* = 6.6 Hz, 3 H), 2.59 (s, 3 H), 3.03 (d, ^3J = 3.6 Hz, 3 H), 4.20–4.50 (m, 2 H), 6.60 (m, 2 H), 6.90 (d, ^3J = 8.7 Hz, 3 H), 7.10 (d, ^3J = 8.4 Hz, 3 H), 7.20–7.80 (m, 13 H), 8.6 (m, 1 H) ppm. $[\alpha]_D^{25}$ = +107 (*c* = 0.42, $CHCl_3$). IR (KBr): $\tilde{\nu}_{max}$ = 1753 (s) (C=O), 1588 (m), 1453 (m), 1435 (s), 1218 cm^{-1} (s). (HRMS, FAB+): *m*/*z* calcd. for $C_{43}H_{47}ClNO_4PPd$: 813.20, found: 813.1967. $C_{43}H_{47}ClNO_4PPd$ (813.20): calcd. C 63.39, H 5.81; found C 63.42, H 5.93.

Compounds (R^P)-9b: Second diastereoisomer eluted (250 mg, 72%). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –8.20 ppm. ^{13}C NMR (126.7 MHz, $CDCl_3$): δ = 16.32, 20.72, 22.24, 23.11, 24.29, 25.83, 31.68, 34.32, 40.96, 46.98, 48.88, 51.79–51.81, 73.45–73.48, 80.38, 108.8, 109.24, 110.93, 111.34, 115.18–115.21, 116.73–116.77, 118.23–118.26, 123.60, 124.24, 124.45–124.50, 124.68–124.79, 125.81, 128.30–128.39, 128.85, 129.12, 130.49–130.50, 131.41, 131.91, 132.78–133.13, 133.35, 136.41, 136.57–136.59, 136.69, 149.82, 150.00–150.02, 152.27–152.34, 153.79–153.81, 154.80 ppm. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.46 (d, ^3J = 6.6 Hz, 3 H), 0.80–2.00 (m, 15 H), 2.14 (d, ^3J = 6.6 Hz, 3 H), 2.74 (s, 3 H), 2.95 (d, ^3J = 3.6 Hz, 3 H), 4.20 (m, 1 H), 4.60 (m, 1 H), 6.70 (m, 2 H), 6.90 (d, 1 H), 7.00–7.80 (m, 14 H), 8.20 (m, 1 H) ppm. $[\alpha]_D^{25}$ = –85 (*c* = 0.78, $CHCl_3$). IR (KBr): $\tilde{\nu}_{max}$ = 1753 (s) (C=O), 1588 (m), 1453 (m), 1429 (s), 1218 cm^{-1} (s). (HRMS, FAB+): *m*/*z* calcd. for $C_{43}H_{47}ClNO_4PPd$: 813.20; found: 813.20. $C_{43}H_{47}ClNO_4PPd$ (813.20): calcd. C 63.39, H 5.81; found C 63.78, H 6.01.

(–)-(1*R*)-Menthyl (R^P)-10-Phenyl-10*H*-phenoxaphosphan-1-yl Carbonate (4a): Compound **9a** (30.0 mg) and 1,2-bis(diphenylphosphanyl)ethane (14.7 mg) were placed in a Shlenk tube and dissolved in dichloromethane (3 mL). The resultant light yellow solution was stirred for 30min at room temperature and subsequently the volume of solvent was reduced to about half mL. The solution

was filtered through a short pad of silica (eluent: CH_2Cl_2) and the organic solvent removed in vacuo to give a colourless oil (17 mg, yield 97%). ^{31}P NMR (121.4 MHz, $CDCl_3$): δ = –65.60 ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 16.70, 21.02, 22.23, 23.54, 26.33, 31.60, 34.27, 40.69, 47.23, 79.95, 115.89, 117.01, 117.27, 117.95, 124.05–124.19, 128.69–129.09, 131.05, 131.29, 132.31, 132.59, 135.09, 135.60, 139.38, 139.67, 153.03, 153.24–153.45, 154.70, 155.61 ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.80–1.20 (m, 14 H), 1.51 (m, 2 H), 1.70 (m, 2 H), 1.96 (m, 1 H), 2.22 (m, 1 H), 4.60 (m, 1 H), 6.90–7.00 (m, 1 H), 7.00–7.50 (m, 11 H) ppm. $[a]_D^{25}$ = –110 (c = 0.21, $CHCl_3$). IR (KBr): $\tilde{\nu}_{max}$ = 2953 (s), 2879 (m), 1759 (s) (C=O), 1453 (m), 1429 (s), 1259 (s), 1212 cm^{-1} (s).

(+)-(1*R*)-Menthyl (*S*^{P})-10-Phenyl-10*H*-phenoxaphosphan-1-yl Carbonate (4b): The same procedure described for **4a** was followed to obtain **4b**. ^{31}P NMR (121.4 MHz, $CDCl_3$): δ = –66.40 ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 16.40, 21.02, 22.25, 23.42, 26.23, 31.65, 34.27, 40.76, 47.13, 79.97, 115.89, 116.83, 117.36, 117.98, 124.22–124.06, 128.66–128.90, 131.13, 131.41, 131.96, 132.22, 135.22, 135.73, 139.27, 139.56, 153.00, 153.47–153.70, 155.06, 155.91 ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.60–1.80 (m, 16 H), 1.98 (m, 1 H), 2.20 (m, 1 H), 4.60 (m, 1 H), 7.02 (m, 1 H), 7.06–7.45 (m, 10 H), 7.53 (t, 1 H) ppm. $[a]_D^{25}$ = +44 (c = 0.39, $CHCl_3$). IR (KBr): $\tilde{\nu}_{max}$ = 2953 (s), 2879 (m), 1759 (s) (C=O), 1588 (m), 1453 (m), 1429 (s), 1250 (s), 1212 cm^{-1} (s).

(–)-(*R*)-10-Phenyl-10*H*-phenoxaphosphanyl-1-ol (3a). Method A: Compound **4a** (151.6 mg, 0.32 mmol) was dissolved in a small amount of THF (1 mL). To this solution was added a degassed KOH ethanolic solution (600 mg of KOH, 20 mL H_2O, 20 mL EtOH) and subsequently the reaction mixture was set to the temperature of 85 °C and vigorously stirred for 2 h. The reaction mixture was cooled down and ethanol removed in vacuo. The aqueous solution was extracted several times with dichloromethane, next the organic solution was dried with magnesium sulfate and the solvent evaporated off. The residue was filtered through a short pad of silica using as eluent CH_2Cl_2 and subsequently the solvent was evaporated off to yield a white solid (73 mg, 0.25 mmol, 78%).

Method B: Compound **7b** (30.2 mg, 0.055 mmol), 1,2-bis(diphenylphosphanyl)ethane (22 mg, 0.055 mmol) and ammonium chloride (100 mg) were dissolved in dichloromethane (3 mL). The heterogeneous solution was stirred for 30min at room temp. and subsequently the solution was filtered through a short pad of silica. The organic solvent was removed in vacuo to give a white solid (4 mg, 25%). ^1H NMR, ^{31}P NMR, ^{13}C NMR and HRMS, FAB+ are in agreement with the data of the racemic mixture (+/–)-**3**. $[a]_D^{25}$ = –59 (c = 0.26, $CHCl_3$), 98.5% *ee*; chiral HPLC, Chiracel AD-H column (hexane/2-propanol = 90:10), 0.5 mL/min, wavelength: 230 nm, t_{3a} = 10.12 min, t_{3b} = 16.65 min.

(+)-(*S*)-10-Phenyl-10*H*-phenoxaphosphan-1-ol (3b): This compound was obtained from **4b** (method A) and from **7a** (method B) using the procedures reported above for **3a**. $[a]_D^{25}$ = +61 (c = 0.5, $CHCl_3$).

X-ray Crystal Structure Determination of 9a: $C_{43}H_{47}ClNO_4PPd$ + disordered solvent, Fw = 814.64,[30] yellow plate, 0.36 × 0.33 × 0.03 mm^3, monoclinic, C2 (no. 5), a = 22.4031(4), b = 9.6277(3), c = 19.5494(3) Å, β = 97.813(1)°, V = 4177.49(15) $Å^3$, Z = 4, D_x = 1.295 g/cm^3,[30] μ = 0.59 mm^{-1}.[30] 38633 Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) at a temperature of 150K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.61 $Å^{-1}$. The reflections were corrected for absorption on the basis of multiple measured reflections (0.66–0.98 correction range). 7778 Reflections were unique (R_{int} = 0.0321). The structure was solved with the program DIRDIF-99[26] using automated Patterson Methods. The crystal structure contains voids (398 $Å^3$/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the routine SQUEEZE of the program PLATON,[27] resulting in 66 electrons/unit cell. The structure was refined with SHELXL-97[28] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. The menthyl moiety was refined with a disorder model. 533 Parameters were refined with 119 restraints. $R1/wR_2$ [$I > 2\sigma(I)$]: 0.0301/0.0661. $R1/wR_2$ (for all reflections): 0.0360/0.0682, S = 1.085, Flack x parameter: –0.07(3).[29] Residual electron density was between –0.37 and 0.53 e/$Å^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[27]

CCDC-657165 (for **9a**) contains supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): ^1H NMR, ^{31}P NMR, ^{13}C-NMR spectra of compounds **1**, **2**, **3**, **4a**, **4b**, **7a**, **7b**, **8**, **9a**, **9b** and three-dimensional coordinates of the calculated structures I–IV (**7**) are provided. HPLC chromatograms of racemic **3** and enantiopure **3a** are provided.

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