Water-Soluble Phosphanes, 11[+]

Syntheses and Coordination Chemistry of Chiral Phosphanyl Glycerols and Their Derivatives – X-ray Structure of (*R*)-$Ph_2P–CH_2–C^aH–O–B(Ph)–O–C^bH_2$($C^a$–$C^b$)

David J. Brauer,[a] Peter Machnitzki,[a] Thomas Nickel,[a] and Othmar Stelzer*[a]

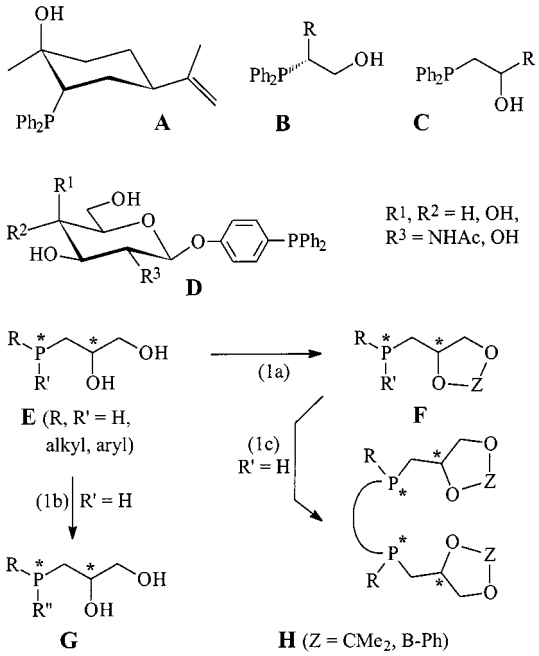
Dedicated to Professor Dr. R. Schmutzler on the occasion of his 65th birthday

Keywords: (*R*)-(+)-2,3-Epoxy-1-propanol / 2,3-Dihydroxyalkyl phosphanes / 1,3,2-Dioxaborolane / 1,3-Dioxolane ring / Enantiopure phosphanes / Complexes

Reaction of (*R*)-(+)-2,3-epoxy-1-propanol with Ph_2PH, Ph(Me)PH, or $PhPH_2$ in the superbasic medium KOH/DMSO affords the novel chiral phosphanes **1a**–**1c**. While **1a** is obtained enantiomerically pure, **1b** and the secondary phosphane **1c** are formed as mixtures of diastereoisomers (R_PR_C, S_PR_C) with homochiral β carbon atoms. Derivatization of **1a** with phenylboronic acid or 2,2-dimethoxypropane yields **2a** and **3a** with 1,3,2-dioxaborolane and 1,3-dioxolane ring systems, respectively. The X-ray structure of **2a** (space group $P2_1$) reveals the presence of four molecules of *R* configuration in the unit cell. Nucleophilic phosphanylation of (*R*)-(–)-2,3-*O*-isopropylideneglycerol tosylate with Ph_2PH, Ph(Me)PH, or $PhPH_2$ yields chiral **3a**–**3d**. Compound **3b** was obtained enantiomerically pure. The secondary phosphane **3c** has been employed in syntheses of the hydrophilic tertiary phosphanes **3e**, **3f** and of the novel bidentate phosphane ligands **3g**, **3h**, all of which have homochiral β carbon atoms. Pd^{II} complexes PdL_2Cl_2 of **1a**, **2a**, **3a** (L) are formed as mixtures of *cis*/*trans* isomers. Rh^I complexes of **1a**, **3a**, and bidentate **3h** have also been synthesized.

Functionalized hydrophilic phosphanes have attracted considerable interest in recent years, mainly because of their application as ligands in catalytically active coordination compounds and organometallic complexes.[2] The hydrophilic character was introduced by modification of the neutral phosphane ligands with polar groups.[3–5] The concept of attaining hydrophilicity by incorporation of hydroxyl groups at the periphery of the ligands has attracted much less attention.[6a] Chiral and achiral ligands containing monohydroxylated alkyl groups, e.g. **A**, have been obtained by addition of phosphides to oxiranes.[6b,6c] These reactions proceed with high regioselectivity,[7a,7b] i.e. the phosphorus nucleophile attacks preferentially at the least substituted carbon atom of the epoxide ring system. Using enantiopure epoxides obtained by Sharpless epoxidation[6d] of allyl alcohols, optically active hydroxylated phosphanes have been obtained by this method.[6e] The experimentally observed preference for inversion of configuration at the carbon atom attacked in the nucleophilic ring-opening of epoxides has been supported by theoretical studies.[7b]

Enders and Berg[8] developed a multi-step synthesis of optically active 2-hydroxyalkyl diphenylphosphanes (*R*)-$Ph_2P–CH(R)–CH_2–OH$ (**B**) starting from simple aldehydes. Kinetic resolution of the racemate of $Ph_2P–CH_2–$CH(OH)R (**C**) (R = Me, Et, *n*Pr) through acylation with isopropenyl acetate under rabbit gastric lipase catalysis yielded the corresponding ligands in enantiomerically enriched form. Hydrophilic hydroxyalkylphosphanes containing carbohydrate moieties (**D**) have also been reported.[10]



[+] Part 10: Ref.[1]

[a] Fachbereich 9, Anorganische Chemie, Bergische Universität-GH Wuppertal,
Gaußstraße 20, D-42097 Wuppertal, Germany

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Their dual functionality renders hydroxyalkylphosphanes hemilabile (P,O) ligands,[11] which are of great potential in homogeneous catalysis. Their physical properties may be tuned by derivatization of the OH groups.[12] The introduction of additional OH groups in vicinal positions and functionalization of the phosphorus atoms (**E**, R′ = H) add further interesting possibilities in the context of a systematic ligand tailoring, allowing the formation of 1,3-dioxolane and 1,3-dioxaborolane ring systems at the 1,2-diol moieties (**F**) (Equation 1a) and P−C coupling reactions to yield chiral mono- or bidentate tertiary phosphane ligands (**G**, **H**) (Equations 1b, 1c).

We report herein on the synthesis of ligands of type **E** and their derivatives **F**−**H**, which may formally be derived from glycerol by replacement of a terminal OH group by a phosphanyl substituent ("phosphanyl glycerols").

Results

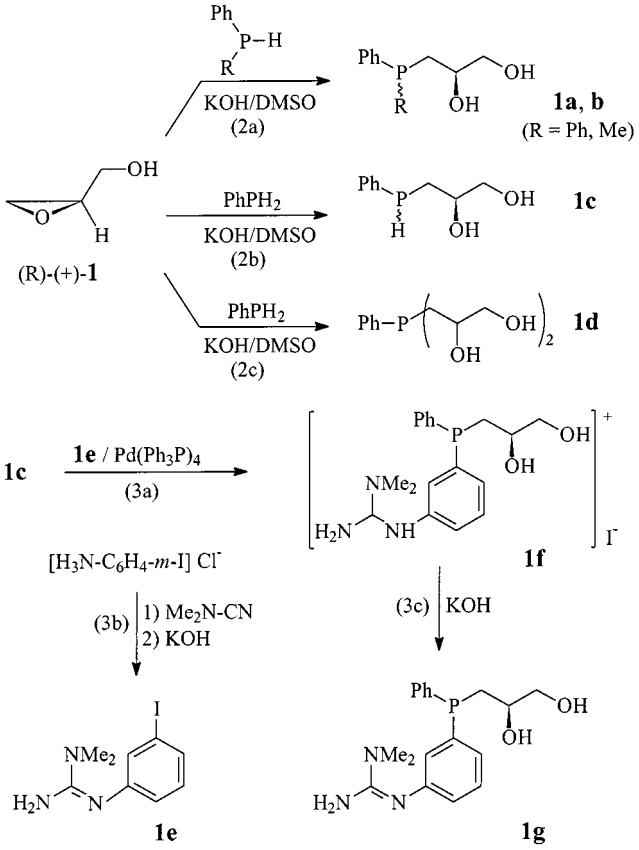
Chiral Phosphane Ligands with 2,3-Dihydroxypropyl Substituents

The synthesis of type **E** ligands containing 2,3-dihydroxypropyl substituents was achieved by nucleophilic opening of the epoxide ring system in glycidol (2,3-epoxy-1-propanol, **1**) using primary or secondary phosphanes in the superbasic medium DMSO/KOH.[13] Thus, **1a** and **1b** were formed in high yields by reaction of Ph_2PH[14a] or Ph(Me)PH[14b] with racemic **1** under these conditions (Equation 2a).

While **1a** shows only one signal at δP = −21.2 in its $^{31}P\{^1H\}$-NMR spectrum, **1b** with two centers of chirality (P, β-C) exhibits two resonances (δP = −39.1, −41.0, intensity ratio 1:1), which may be assigned to the *erythro* and *threo* isomers (R_PR_C/S_PS_C and R_PS_C/S_PR_C). Optically active **1a** {$[\alpha]_D^{20}$ = −19.4° (*c* = 1.3, CH_2Cl_2), δP = −21.2} is formed if commercially available (*R*)-(+)-**1** ($[\alpha]_D^{23}$ = +12°, neat, enantiomeric purity ≈98% *ee*) is employed in this reaction. This has been established from analysis of the $^{31}P\{^1H\}$-NMR spectrum of the disubstituted Pd complex **4** of **1a** (see below). Due to the chiral carbon atom in the β-position, the phenyl groups of the Ph_2P substituent in **1a** are non-equivalent, as indicated by the observation of two sets of resonances for the *ipso*, *ortho*, and *meta* carbon atoms in the $^{13}C\{^1H\}$-NMR spectrum.

The technique developed for the syntheses of **1a** and **1b** can also be used to prepare secondary phosphanes containing 2,3-dihydroxypropyl substituents with chiral β carbon atoms. Thus, reaction of $PhPH_2$[14c] with one equivalent (*R*)-(+)-glycidol gave **1c** in high yields (Equation 2b). The $^{31}P\{^1H\}$-NMR spectrum of **1c** features two resonances of about equal intensity at δP = −63.05 and −63.39, which may be assigned to the *erythro* and *threo* isomers. Under proton coupling, these signals are split into doublets [$^1J(^{31}P\text{-}^1H)$ = 212 Hz] showing additional fine structure [^nJ(PH), *n* = 2, 3].

Treatment of $PhPH_2$ with two equivalents of racemic **1** gave the tertiary phosphane **1d** as a mixture of three diastereoisomers (two *meso* forms and an enantiomeric pair; $^{31}P\{^1H\}$-NMR spectrum: δP = −32.8, −33.8, −34.4, intensity ratio 1:2:1) (Equation 2c). An analogous effect of two asymmetric carbon centers in the α- or β-positions on the $^{31}P\{^1H\}$-NMR spectra of chiral secondary phosphanes with H−P(−C*−C−)$_2$ or H−P(−C−C*−)$_2$ skeletons has been reported.[15] If (*R*)-(+)-**1** is employed instead of racemic **1**, one diastereoisomer of **1d** with homochiral β carbon atoms is formed {$[\alpha]_D^{20}$ = −25.7° (neat); −11.0° (*c* = 10, MeOH)}, which shows a single resonance at δP = −33.8 in its $^{31}P\{^1H\}$-NMR spectrum. Signals of low intensity (ca. 3% of the main signal) at δ = −32.8 and −34.4 may be assigned to the *meso* forms obtained, since the enantiomeric purity of (*R*)-(+)-**1** was only 97% *ee*. The formation of **1d** evidently proceeds with high stereoselectivity. However, in order to achieve a complete transformation of $PhPH_2$ and the intermediate secondary phosphane **1c** to **1d**, an excess of **1** or (*R*)-(+)-**1** (ca. 10−15%) had to be applied. The excess **1** and side-products formed during the reaction could not be completely separated by distillation due to the thermal instability of **1d**.



Scheme 1

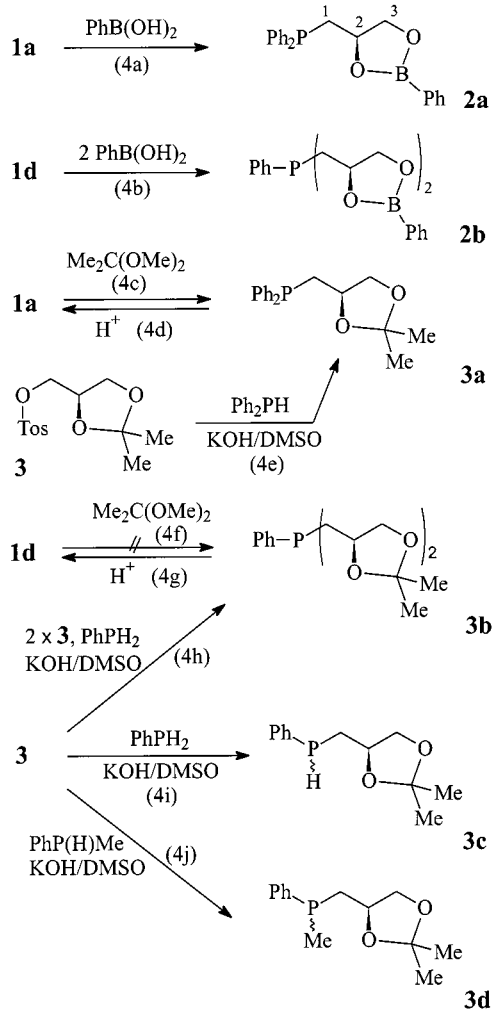
The secondary phosphane **1c** can be used as a building block for the synthesis of tertiary phosphanes containing dihydroxylated propyl substituents with chiral carbon and phosphorus atoms. In the context of a research program aimed at the development of chiral, water-soluble phosphanes for two-phase catalysis, the introduction of substituents bearing polar cationic or anionic groups was of pri-

mary interest.[5b] Nucleophilic phosphanylation[16a] or Pd-catalyzed P−C coupling,[16b,17] as developed earlier by us, could be used as the fundamental synthetic principles. Thus, reaction of **1c** with the iodophenyl guanidine **1e**[18] in the presence of a catalytic amount of $Pd(Ph_3P)_4$[19] gave the guanidinium phosphane **1f** (Equation 3a). In order to isolate it from the reaction mixture and to allow its further purification, **1f** was deprotonated with KOH to give the neutral guanidinophosphane ligand **1g** (Equation 3c). **1e** was obtained from 3-iodoanilinium chloride by reaction with Me_2NCN and subsequent deprotonation of the intermediate guanidinium salt with KOH.[18]

Direct and Indirect Derivatization of 1a, 1c, and 1d

The 2,3-dihydroxypropyl substituents and the PH functionality in **1a**−**1d** offer numerous possibilities for fine tuning of their ligand properties.

Chiral ligands **2a**, **2b** bearing Lewis acidic sites are accessible by reaction of enantiomerically pure **1a** or **1d**, respectively, with phenylboronic acid (Equation 4a, 4b). This access to aromatic boronate esters has been exploited in the synthesis of boron analogues of DIOP by Fields and Jacobsen.[20]



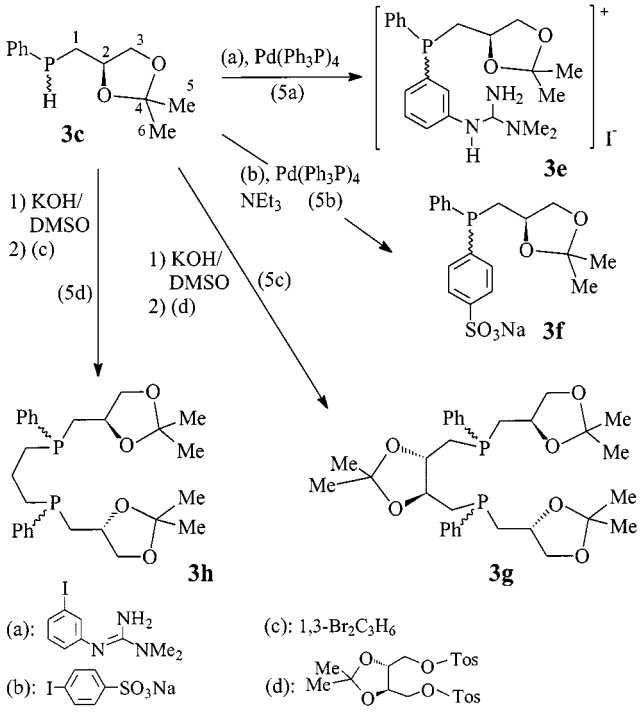
Scheme 2

The formation of **2a** from enantiopure (*R*)-(−)-**1a** proceeds with retention of configuration at the β carbon atom (see X-ray structural analysis of **2a**). The $^{31}P\{^1H\}$-NMR spectrum of **2b** features an intense signal at δP = −37.39 corresponding to the main (*RR*)-isomer. Additional resonances of low intensity at δP = −36.41 and −39.57 may be assigned to the two *meso* forms of **2b**, derived from the *meso* isomers present in the starting material **1d** (see above). If racemic **1d** is employed in this reaction (Equation 4b), a 1:2:1 mixture of three diastereoisomers of **2b** is obtained, which gives rise to resonances at δP = −36.46, −37.42, and −39.60 in the $^{31}P\{^1H\}$-NMR spectrum.

Ketalization of optically active **1a** with 2,2-dimethoxypropane using *p*-toluenesulfonic acid as catalyst yields (*R*)-(+)-2,3-*O*-isopropylideneglycerol-1-diphenylphosphane **3a** (Equation 4c). However, attempts to synthesize oligofunctional **3b** by ketalization of **1d** were not successful, a multi-component mixture being formed (Equation 4f). The phosphane ligand (*R*)-(+)-Glyphos (**3a**) was first prepared by Brunner and Leyerer[21a] in moderate yield by reaction of Ph_2PK in dioxane with (*R*)-(−)-2,3-*O*-isopropylidene-1-glycerol tosylate **3**. Very recently, Kerr et al.[21b] published an analogous synthetic procedure for (*R*)-(+)-Glyphos starting from D-mannitol. We have now found that this ligand may be obtained much more easily and in substantially higher yields by nucleophilic phosphanylation of enantiomerically pure (*R*)-(−)-**3** with Ph_2PH in the superbasic medium DMSO/KOH (Equation 4e). Using this methodology, the tertiary and secondary phosphanes **3b**−**3d** have also been prepared by employing $PhPH_2$ or Ph(Me)PH and (*R*)-(−)-**3** as the starting materials (Equations 4h−4j). **3b** shows only one signal (δP = −35.57) in its $^{31}P\{^1H\}$-NMR spectrum, indicating that it is formed stereoselectively [(*R,R*)-isomer] according to Equation 4h. In **3b**, with homochiral β carbon atoms, the two CH_2−P, CH−O, and CH_2O groups are non-equivalent. Compared with the spectra of **3a**, a doubling of the line patterns in the ^1H- and $^{13}C\{^1H\}$-NMR spectra is therefore observed.

The phosphanes **3c** and **3d** with two centers of chirality give rise to two $^{31}P\{^1H\}$-NMR signals [δP = −62.94, −63.44 (**3c**): δP = −38.96, −41.22 (**3d**)], which, in the case of **3c**, are split into doublets under proton coupling [^1J(PH) = 211.1 or 208.6 Hz]. The isopropylidene protecting group in **3a** may be cleaved by reaction with small amounts of *p*-toluenesulfonic acid, leading to the formation of **1a** without loss of optical activity (Equation 4d). Very recently, this method has been used by Brunner and Rückert[22] for the synthesis of **1a** using **3a** as starting material.

The PH functionality renders **3c** a valuable synthon for the preparation of further functionalized mono- or bidentate phosphanes. The bidentate ligand **3h** was thus obtained by alkylation of **3c** using 1,3-dibromopropane in the superbasic medium DMSO/KOH (Equation 5d). As evidenced by the $^{31}P\{^1H\}$-NMR spectrum, **3h**, with homochiral β carbon atoms, is formed as a mixture of three diastereoisomers ($R_CR_PR_PR_C$, $R_CS_PS_PR_C$, and $R_CR_PS_PR_C$), two of them ($R_CR_PR_PR_C$, $R_CS_PS_PR_C$) with equivalent (δP =



Scheme 3

−29.81, −31.46, respectively) and one ($R_CR_PS_PR_C$) with chemically non-equivalent phosphorus atoms [δP = −29.68, −31.32, ^4J(PP) = 1.0 Hz]. The value observed for ^4J(PP) is typical for long-range coupling constants (0−5 Hz) in trimethylene-bridged diphosphorus compounds.[23] If (*R,R*)-(+)-1,4-di-*O*-*p*-toluenesulfonyl-2,3-*O*-isopropylidene-D-threitol is used instead of 1,3-dibromopropane for coupling to **3c**, the bidentate ligand **3g** is obtained as a mixture of three diastereoisomers [$R_CR_P(S_C)_2R_PR_C$, $R_CS_P(S_C)_2S_PR_C$, $R_CR_P(S_C)_2S_PR_C$], in one of which [$R_CR_P(S_C)_2S_PR_C$] the P atoms are non-equivalent, as reflected in the $^{31}P\{^1H\}$-NMR spectrum (Equation 5c).

Derivatization of **3c** is also possible by means of Pd-catalyzed P−C coupling reactions with iodoaromatic compounds.[16b,17] Thus, on reaction of **3c** with iodophenyl guanidine **1e**, the cationic phosphane ligand **3e** is obtained in high yield (Equation 5a). Using sodium *p*-iodobenzenesulfonate[24] in the presence of NEt_3, the anionic phosphane **3f** is formed (Equation 5b). **3e** and **3f** are obtained as mixtures of diastereoisomers.

X-ray Structure of (*R*)-$Ph_2P-CH_2-C^aH-O-B(Ph)-O-C^bH_2$ [*C*^{a}−*C*^{b}]

Crystals suitable for X-ray structural analysis were obtained by recrystallization of (*R*)-(+)-**2a** from ethanol. The unit cell of the crystal of **2a** (space group $P2_1$) used for the X-ray analysis contains two crystallographically independent molecules forming pairs of antiparallel oriented molecules A and B both showing (*R*) configuration at the β carbon atom. The numbering scheme for **2a** and selected bond lengths and angles are collected in Figure 1.

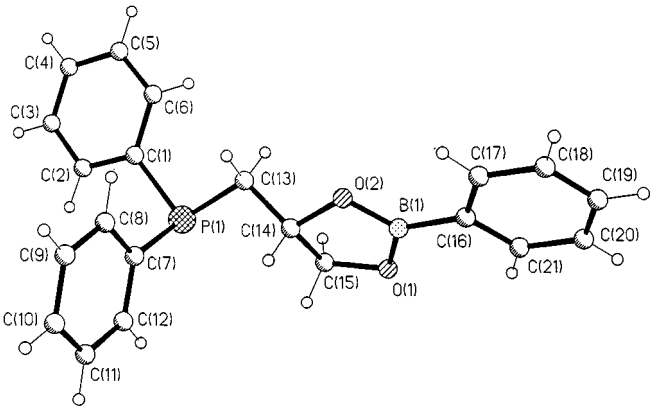


Figure 1. Molecular structure of **2a**; selected interatomic distances [Å] and angles [°]: P(1)−C(1) 1.836(6), P(1)−C(7) 1.822 (7), P(1)−C(13) 1.851(6), C(14)−O(2) 1.463(7), C(15)−O(1) 1.443(7), C(14)−C(15) 1.525, B(1)−O(1) 1.384(8), B(1)−O(2) 1.369(8), B(1)−C(16) 1.509(9); C(1)−P(1)−C(7) 101.76(29), C(1)−P(1)−C(13) 101.83(30), C(7)−P(1)−C(13) 101.46(28), O(1)−B(1)−O(2) 111.9(5)

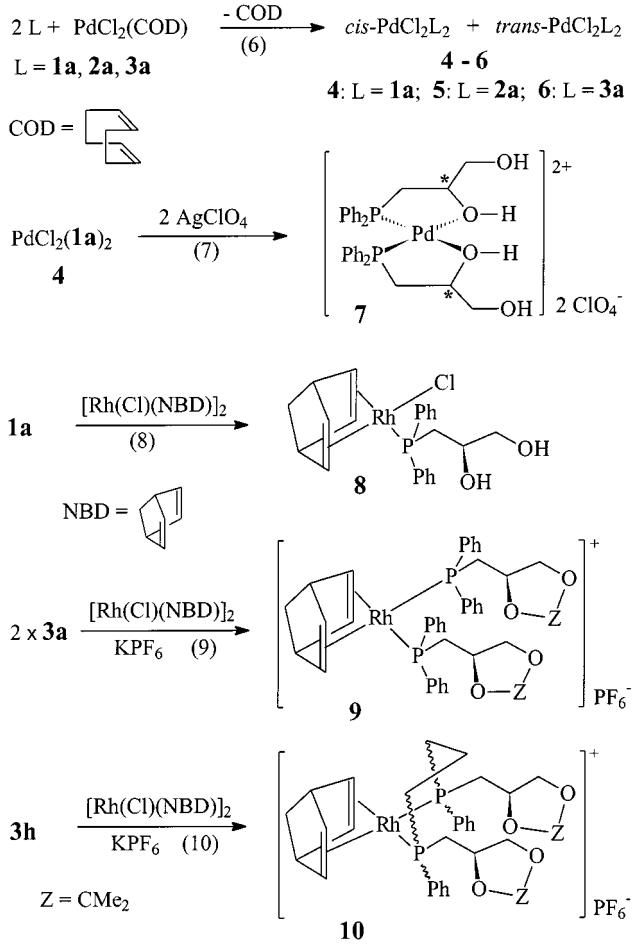
In the two independent molecules (A, B), the geometrical parameters of the PC_3 skeleton are slightly different, the P−C distances [P(1)−C(1) 1.836(6), P(1)−C(7) 1.822(7), P(1a)−C(1a) 1.805(7), P(1a)−C(7a) 1.836(6) Å] and C−P−C bond angles [C(1)−P(1)−C(7) 101.8(3), C(1a)−P(1a)−C(7a) 101.2(3)°] within the Ph_2P groups being comparable to those in Ph_3P.[25,26] The torsional arrangements of the aromatic ring planes within the Ph_2P units of the two independent molecules A and B are also different.

The atoms within the cyclic boronic diester moieties O(1)−C(14)−C(15)−O(2)−B(1)[*O(1)−B(1)*] are coplanar to within 0.084 Å, the coordination at B(1) or B(1a) being distorted trigonal planar [O(1)−B(1)−O(2) 111.9(5), O(2)−B(1)−C(16) 123.0(6), O(1)−B(1)−C(16) 125.1(6)°]. The aromatic substituent at B(1) or B(1a) and the BO_2C_2 cyclic boronic diester unit are arranged in an almost coplanar fashion, the interplanar angle between the plane of the aromatic ring system and the plane defined by B(1), O(1), O(2), and C(16) being just 4.42°. Similar coplanarity of the BO_2 group with the aromatic ring has been found in other aromatic boronic acids and their esters.[27]

Palladium(II) and Rhodium(I) Complexes of 1a, 2a, 3a, 3h

On reaction of enantiomerically pure **1a**, **2a**, or **3a** with $PdCl_2$(COD) in a 2:1 molar ratio, complexes of the composition $PdCl_2L_2$ are formed (Equation 6), which show two signals in their $^{31}P\{^1H\}$-NMR spectra in the ranges δ = 40−28 and δ = 15−13. By analogy with literature data for *cis*- and *trans*-Cl_2PdL_2 complexes,[28,29] the low field signals are assigned to the *cis* isomers and the high field resonances to the *trans* isomers of **4**−**6**. The relative intensities of the $^{31}P\{^1H\}$-NMR signals of both isomers (*cis*/*trans*) vary from 10:1 (**4**), through 1:1 (**6**), to 1:7 (**5**). The assignment of the $^{31}P\{^1H\}$-NMR resonances to *cis*/*trans* isomers is corroborated by analysis of the $^{13}C\{^1H\}$-NMR spectra, which fea-

ture signals (e.g. for C1, C3, C_{ipso}, C_{ortho}, C_{meta}) of corresponding intensity with doublet or triplet fine structures (for the numbering of the aliphatic C atoms, see Scheme 3). Thus, **4**, which exists predominantly as the *cis* isomer, shows signals with doublet fine structure for C1 and C3, while a singlet is observed for C2. In the case of **6**, two $^{13}C\{^1H\}$-NMR resonances are observed for the carbon atoms C1 and C_o, C_m of the phenyl substituents with doublet or triplet fine structures (X parts of ABX spin systems,[30] A, B = ^{31}P, X = ^{13}C) for the *cis* and *trans* isomers, respectively. Each of the two isomers show singlets for C2, C3, and C4. The Me groups of the CMe_2 units (C5, C6) in the two isomers of **6** (*cis*, *trans*) are diastereotopic due to the center of asymmetry at the β carbon. The same applies to the two Ph substituents of the Ph_2P groups in **5** (existing mainly as the *trans* isomer) and **6**; two sets of $^{13}C\{^1H\}$-NMR resonances with triplet fine structure are observed for the aromatic carbon atoms C_{ipso}, C_{ortho}, and C_{meta} of the *trans* isomer.



Scheme 4

Treatment of a toluene solution of **4** with $AgClO_4$ gave the dicationic complex **7** (Equation 7). Similar types of reactions have been reported by Pringle et al.[31–33] for palladium(II) and platinum(II) complexes of phosphanyl alcohols $Ph_2P-CH_2-CRR'-OH$ (R, R′ = H, Me). Complex **7** shows one signal at δP = 52.46 in its $^{31}P\{^1H\}$-NMR spectrum, in a range consistent with a *cis* geometry. A resonance of low intensity at δP = 47.63 may possibly be due to the *trans* isomer of **7**. The assignment of the main signal to the *cis* isomer is in accord with the filled-in doublet appearance of the $^{13}C\{^1H\}$-NMR resonances of the aromatic carbon atoms (C_o, C_m) at δC = 136.48, 134.59, 131.28, 130.83 (X parts of ABX-type spin systems,[30] A, B = ^{31}P, X = ^{13}C) in the $^{13}C\{^1H\}$-NMR spectrum.

On reaction of $[RhCl(NBD)Cl]_2$ with **1a**, complex **8** is formed (Equation 8). A signal at δP = 23.54 observed in the $^{31}P\{^1H\}$-NMR spectrum of **8** is split into a doublet by ^{103}Rh-^{31}P coupling [$J(^{103}Rh$-$^{31}P)$ = 168.7 Hz]. If **3a** is treated with $[RhCl(NBD)Cl]_2$ in a 2:1 molar ratio in the presence of KPF_6 using acetone as solvent, the cationic complex **9** is obtained (Equation 9). A similar procedure has been used by Schrock and Osborn[34] for the preparation of the corresponding Ph_3P complex. The $^{31}P\{^1H\}$-NMR spectrum features a doublet at δP = 24.41 [$J(^{103}Rh$-$^{31}P)$ = 155.7 Hz] and a septet at δP = 142.97 [$J(^{31}P$-$^{19}F)$ = 707.8 Hz] for the PF_6^- ion. An analogous reaction with the bidentate ligand **3h** affords complex **10** as a mixture of three diastereoisomers (Equation 10), two of them giving rise to a simple doublet in the $^{31}P\{^1H\}$-NMR spectrum {symmetrical isomers, δP = 7.73 [$J(^{103}Rh$-$^{31}P)$ = 143.9 Hz], 7.48 [$J(^{103}Rh$-$^{31}P)$ = 146.1 Hz]}. The unsymmetrical diastereoisomer with non-equivalent phosphorus atoms (AB part of an ABX spin system, A, B = ^{31}P, X = ^{103}Rh) gives rise to eight lines (δP(A) = 5.62 {$J[^{103}Rh$-$^{31}P(A)]$ = 145.9 Hz}; δP(B) = 7.37 {$J[^{103}Rh$-$^{31}P(B)]$ = 145.9 Hz, $J[^{31}P(A)$-$^{31}P(B)]$ = 52.32 Hz})

Experimental Section

General: For experimental details, see Part 10 of this series.[1] – NMR spectra were recorded on a Bruker AMX 400 or a Bruker AC 250 instrument. – Mass spectra were obtained on a Varian MAT 311 A. – Racemic and (*R*)-(+)-glycidol (2,3-epoxy-1-propanol), 3-iodoaniline, phenylboronic acid, (*S*)-(+)-2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane were purchased from Aldrich GmbH and used without further purification. 1,5-Cyclooctadiene dichloro palladium(II),[35] norbornadienechlororhodium(I) dimer,[36] (*R*)-(−)-2,3-*O*-isopropylideneglycerol tosylate **3**,[37] and $Pd(Ph_3P)_4$[19] were prepared according to literature methods. 3-Iodophenyl guanidine (**1e**)[5b,18] and sodium *p*-iodobenzenesulfonate[24] were prepared according to methods that we have described previously.

Preparation of *rac*- and (*R*)-(−)-2,3-Dihydroxypropyl-1-diphenylphosphane [*rac*-1a and (*R*)-(−)-1a]: 2.0 g (11.0 mmol) or 12.6 g (67.5 mmol) of diphenylphosphane was added to a suspension of 0.83 g (13.0 mmol) or 4.90 g (77.0 mmol) of KOH powder (88%) in 10 or 50 mL of dimethyl sulfoxide (DMSO). The reaction mixture was stirred for 1 h at ambient temperature. On addition of 0.90 g (12.0 mmol) of *rac*-glycidol or 5.0 g (68.0 mmol) of (*R*)-(+)-glycidol, the orange color of the solution disappeared. 10 mL of water was then added and thereafter the solvents were removed in vacuo (70°C, 0.01 mbar). The remaining residue was redissolved in 10 or 50 mL of ethanol and the solution was neutralized with conc. HCl. The precipitate of KCl formed was filtered off and the solvent was stripped off in vacuo (80°C, 0.01 mbar) leaving the phosphanes *rac*-**1a** (2.4 g, 84%) and (*R*)-(−)-**1a** (14.8 g, 84%) as colorless oily liquids. They were purified by distillation in vacuo (oil bath temperature 180°C, 0.01 mbar). – (*R*)-(−)-**1a**: $C_{15}H_{17}O_2P$ (260.3):

calcd. C 69.22, H 6.63; found C 69.14, H 6.63. – MS: *m/z* (%): 260 (32) [M^+], 243 (18) [$M^+ - OH$], 229 (4) [$M^+ - CH_2OH$], 199 (100) [$M^+ - C_2H_3(OH)_2$], 183 (65) [$M^+ - C_6H_5$]. – ^{1}H NMR (C_6D_6): δ = 2.21–2.43 (2 H), 3.55–3.72 (2 H), 3.92 (1 H), 4.1 (2 H, OH), 7.04–7.19, 7.46–7.55 (10 H). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 33.49 (14.2), 67.51 (9.2), 70.60 (16.3), 128.63 (9.2), 128.75, 128.83 (6.1), 133.03 (18.3), 133.45 (19.3), 139.18 (13.2), 139.49 (12.2). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −21.22. – $[\alpha]_D^{20}$ = −19.4° (*c* = 1.3, CH_2Cl_2).

Preparation of [(*R*,*S*)$_P$,*R*$_C$]-2,3-Dihydroxypropyl-1-phenylmethylphosphane (1b): 1.05 g (16.5 mmol) of KOH, 1.8 g (14.5 mmol) of Ph(Me)PH, and 1.07 g (14.5 mmol) of (*R*)-(+)-glycidol were reacted according to the same procedure as described for **1a**. Yield: 2.33 g (81%). – *rac*-**1b**: $C_{10}H_{15}O_2P$ (198.2): calcd. C 60.60, H 7.63; found C 59.98, H 7.67. – MS: *m/z* (%): 198 (29) [M^+], 181 (17.6) [$M^+ - OH$], 138 (100) [$M^+ - C_2H_2(OH)_2$]. – ^{1}H NMR (CD_3OD): δ = 1.33 (3.4, 3 H), 1.35 (3.1, 3 H), 1.74–1.97 (2 H), 3.32–3.71 (1 H), 4.15 (OH), 7.36, 7.54 (5 H). – $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 12.56 (13.4), 13.24 (13.0), 36.68 (13.5), 37.08 (12.6), 67.81 (8.5), 68.19 (9.2), 71.26 (13.0), 71.89 (14.8), 129.44 (6.1), 132.54 (18.3), 132.64 (19.3), 141.84 (13.2), 129.55, 129.64. – $^{31}P\{^1H\}$ NMR (CD_3OD): δ = −39.13, −40.95.

Preparation of *rac*- or [(*R*,*S*)$_P$,*R*$_C$]-2,3-Dihydroxypropyl-1-phenylphosphane (1c): 2.0 g (18.2 mmol) or 1.5 g (13.5 mmol) of phenylphosphane was reacted with 1.4 g (22.0 mmol) or 1.0 g (15.7 mmol) of KOH and 1.48 g (20.0 mmol) or 1.1 g (14.8 mmol) of *rac*- or (*R*)-(+)-glycidol according to the same procedure as described for **1a**. 2.78 g (83%) of *rac*-**1c** and 1.98 g (80%) of [(*R*,*S*)$_P$,*R*$_C$]-**1c** were obtained as oily liquids. – *rac*-**1c**: $C_9H_{13}O_2P$ (184.2): calcd. C 58.69, H 7.11; found C 58.43, H 6.89. – MS: *m/z* (%): 184 (34) [M^+], 167 (7) [$M^+ - OH$], 153 (7) [$M^+ - CH_2OH$], 125 (100) [$M^+ - C_2H(OH)_2$], 109 (84) [PhPH]. – ^{1}H NMR (C_6D_6): δ = 1.74–2.22 (2 H), 3.46–3.64, 3.72–3.94 (3 H), 4.38 (211.4, 1 H), 4.34 (211.3, 1 H), 7.05–7.19, 7.45–7.51 (5 H). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 27.92 (14.2), 27.97 (13.2), 67.35 (8.1), 67.40 (6.1), 71.00 (8.1), 71.30 (9.2), 128.34, 128.44, 128.72, 128.77 (2.0), 134.00 (16.3), 134.08 (16.3), 135.68 (10.2), 135.75 (10.2). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −3.28 (212), −3.05 (212). – ^{31}P NMR (C_6D_6): δ = −63.05 (212), −63.39 (212).

Preparation of *rac*- or (*R*,*R*)-(−)-Bis(2,3-dihydroxypropyl)-1-phenylphosphane [*rac*-1d and (*R*,*R*)-(−)-1d]: Reaction of 64 g (0.1 mol) or 2.1 g (33 mmol) of KOH and 4.62 g (42.0 mmol) or 1.5 g (13.6 mmol) of $PhPH_2$ with 6.88 g (92.8 mmol) or 2.22 g (30.0 mmol) of *rac*- or (*R*)-(+)-glycidol using the same procedure as described for **1a**, although at a higher temperature (80°C). Yields: 8.35 g (77%) of *rac*-**1d**, 2.6 g (74%) of (*R,R*)-(−)-**1d**. – (*R,R*)-(−)-**1d**: $C_{12}H_{19}O_4P$ (258.3): calcd. C 55.80, H 7.42; found C 55.40, H 7.18. – MS: *m/z* (%): 258 (17) [M^+], 241 (28) [$M^+ - OH$], 227 (18) [$M^+ - CH_2OH$], 198 (18) [$M^+ - C_2H_2(OH)_2$], 184 (21) [$M^+ - C_3O_2H_6$], 138 (100) [$M^+ - 2\,C_2H_2(OH)_2$]. – $^{31}P\{^1H\}$ NMR ([D$_6$]DMSO): δ = −35.2. – $[\alpha]_D^{20}$ = −11.0° (*c* = 10, MeOH) or −25.7° (neat).

Preparation of *rac*-2,3-Dihydroxypropyl-1-phenyl-1-[3-(*N*,*N*-dimethylguanidino)phenyl]phosphane (*rac*-1g): A solution of 2.5 g (8.6 mmol) of 3-iodophenyl guanidine and 1.6 g (8.6 mmol) of *rac*-**1d** in 10 mL of acetonitrile was heated to 60°C and then 0.2 g (2 mol-%) of $Pd(Ph_3P)_4$ was added. After stirring for 3 h, the solvent was removed in vacuo (60°C, 0.01 mbar) and the remaining residue was redissolved in 20 mL of *n*-hexanol. The precipitate (**1f**; $^{31}P\{^1H\}$ NMR: δ = −18.6, −19.2) deposited following the addition of 150 mL of diethyl ether was filtered off and dried in vacuo. It was then treated with excess aqueous KOH and the resulting solution was extracted three times with 30 mL of dichloromethane. After evaporation of the solvent from the combined extracts, **1g** was obtained as a cream-colored powder. Yield: 1.8 g (55%). – *rac*-**1g**: $C_{18}H_{24}N_3O_2P \cdot 2.5\,H_2O$ (390.4): calcd. C 55.45, H 7.37, N 10.78; found C 55.70, H 7.20, N 10.62. – MS: *m/z* (%): 345 (39) [M^+], 289 (66) [$M^+ - HNCNMe$], 274 (19) [$M^+ - HNCNMe_2$]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.72 (14.3), 37.48, 66.88 (6.7), 66.94 (7.6), 69.81 (10.5), 69.94 (9.5), 124.06, 124.30, 126.42 (21.4), 126.68 (21.4) 127.38 (17.3), 127.73 (17.3), 128.21 (6.1), 128.27 (7.1), 129.28 (6.1), 129.35 (6.1), 130.28, 130.61, 132.32 (18.3), 132.63 (18.3), 138.57 (12.2), 138.61 (13.2), 138.86 (11.2), 138.93 (11.2), 149.91 (12.2), 149.98 (12.2), 152.29, 152.72, 153.17, 153.19. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −21.54, −21.73.

Preparation of *rac*- or (*R*)-(+)-(2-Phenyl-1,3,2-dioxaborolano-4-methyl)diphenylphosphane [*rac*-2a, (*R*)-(+)-2a] and *rac*- or (*R*,*R*)-(−)-Bis(2-phenyl-1,3,2-dioxaborolano-4-methyl)phenylphosphane [*rac*-2b, (*R*,*R*)-(−)-2b]: To a suspension of 0.9 g (3.5 mmol) or 1.47 g (5.6 mmol) of racemic or (*R*)-(−)-**1a** in 20 mL of dichloromethane, a CH_2Cl_2 solution of 0.42 g (3.46 mmol) or 0.7 g (5.6 mmol) of benzeneboronic acid was added with stirring. After 1 h, all volatiles were removed from the clear solution leaving a colorless solid, which was recrystallized from ethanol for further purification. Yields: 0.90 g (74%) of *rac*-**2a**, 1.49 g (77%) of (*R*)-(+)-**2a**. – *rac*-**2a**: $C_{21}H_{20}BO_2P$ (346.2): calcd. C 72.85, H 5.82, P 8.95; found C 72.52, H 5.92, P 9.30. – MS: *m/z* (%): 346 (32) [M^+], 199 (100) [$M^+ - C_2H_3O_2B(Ph)$], 183 (44) [$M^+ - C_3H_5O_2B(Ph) - H_2$], 121 (23) [$M^+ - C_2H_3O_2B(Ph) - Ph$], 108 (22) [$M^+ - C_3H_5O_2B(Ph) - Ph$]. – ^{1}H NMR ($C_6D_6$): δ = 1.98–2.03 (2 H), 2.45–2.50 (2 H), 3.82–3.86 (2 H), 3.99–4.04 (2 H), 4.37–4.46 (1 H), 7.07–8.12 (15 H). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 36.40 (15.26), 71.96 (10.18), 75.82 (19.33) 128.11, 128.68 (4.1), 128.74, 128.80 (4.1), 128.90, 131.69, 133.10 (20.4), 133.19 (19.3), 135.43, 138.50 (13.2), 138.93 (13.2). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −22.8. – (*R*)-(+)-**2a**: $C_{21}H_{20}BO_2P$ (346.2): calcd: C 72.85, H 5.82, P 8.95; found C 72.37, H 5.90, P 9.13. – $[\alpha]_D^{20}$ = +9.0° (*c* = 2, $CHCl_3$).

rac-**2b** and (*R,R*)-(−)-**2b** were prepared in a manner analogous to that described for *rac*-**2a** and (*R*)-(+)-**2a** employing 3.58 g (13.9 mmol) or 1.06 g (4.1 mmol) of **1c** [*rac* or (*R*)-(+) form] and 3.38 g (27.7 mmol) or 1.0 g (8.2 mmol) of benzeneboronic acid. Yields: 4.6 g (77%) of *rac*-**2b**, 1.4 g (80%) of (*R*)-(−)-**2b**. – *rac*-**2b**: $C_{24}H_{25}B_2O_4P$ (430.0): calcd. C 67.03, H 5.96; found C 66.59, H 6.07. – MS: *m/z* (%): 430 (6.2) [M^+], 312 (12) [$M^+ - CH_2OB(Ph)$], 284 (7) [$M^+ - C_2H_2O_2B(Ph)$], 270 (6) [$M^+ - C_3H_4O_2B(Ph)$], 138 (100) [$M^+ - 2\,C_2H_2O_2B(Ph)$]. – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 36.0 (15.3), 36.28 (16.3), 36.47 (14.2), 37.10 (15.3), 71.84 (8.1), 71.95 (10.2), 72.12 (9.2), 72.16 (9.2), 75.56 (15.3), 75.70 (14.2), 76.21 (19.3), 76.24 (19.3). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −36.46, −37.42, −39.60. – (*R,R*)-(−)-**2b**: $C_{24}H_{25}B_2O_4P$ (430.0): calcd. C 67.03, H 5.96; found C 66.59, H 6.07. – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 36.28 (16.3), 36.45 (14.2), 71.95 (9.2), 72.11 (9.2), 75.68 (15.3), 76.20 (18.3), 128.11, 128.15, 128.76 (7.1), 129.46, 131.70, 131.75, 133.01 (21.4), 135.36, 137.78 (13.2). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −37.39. – $[\alpha]_D^{20}$ = −13.8° (*c* = 1.68, C_6H_6).

Preparation of *rac*- and (*R*)-(+)-2,3-*O*-Isopropylideneglycerol-1-diphenylphosphane [*rac*-3a, (*R*)-(+)-3a]: To a suspension of 1.9 g (29.6 mmol) or 1.0 g (14.7 mmol) of KOH powder (88%) in 30 mL of DMSO, 5.5 g (29.6 mmol) or 2.5 g (13.4 mmol) of diphenylphosphane was added at ambient temperature. 7.7 g (27.0 mmol) or 3.85 g (13.4 mmol) of *rac*- or (*R*)-(−)-2,3-*O*-isopropylideneglycerol-1-tosylate was then added to the intensely red-colored reaction mixture within a period of 30 min. After stirring for 8 h, 20 mL of water was added and the reaction mixture was extracted with toluene (3 × 50 mL). The combined toluene phases were dried with

$MgSO_4$ and the solvent was evaporated in vacuo (20°C, 0.01 mbar). The remaining oily residue was dried in vacuo (80°C, 0.01 mbar). Yields: 6.5 g (80%) of *rac*-**3a**, 3.1 g (77%) of (*R*)-(+)-**3a**. For further purification, the products were distilled in vacuo (oil bath temperature 180°C, 0.01 mbar). – (*R*)-(+)-**3a**: $C_{18}H_{21}O_2P$ (300.3): calcd. C 71.98, H 7.05, P 10.31; found C 71.71, H 6.65, P 9.76. – MS: *m/z* (%): 300 (32) [M^+], 285 (7) [$M^+ - CH_3$], 242 (7) [$M^+ - C_3H_6O$], 199 (47) [$M^+ - C_2H_3O_2C_3H_6$], 186 (100) [Ph_2PH]. – ^1H NMR (C_6D_6): δ = 1.28 (3 H), 1.42 (3 H), 2.15, 2.54 (2 H), 3.56, 3.88 (2 H), 4.19 (1 H), 7.08–7.44 (10 H). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 26.01, 27.26, 33.87 (15.3), 70.34 (9.2), 74.31 (20.3), 108.94, 128.69 (7.1), 128.79 (9.2), 133.00 (18.3), 133.20 (19.3), 138.89 (13.2), 139.20 (14.2). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −21.66. – $[\alpha]_D^{20}$ = +14.5° (*c* = 1, C_6H_6).

Preparation of (*R*,*R*)-(+)-Bis[2,3-*O*-isopropylideneglycerol]-1-phenylphosphane [(*R*,*R*)-(+)-3b]: 2.16 g (33.9 mmol) of KOH, 1.64 g (14.9 mmol) of $PhPH_2$, and 8.53 g (29.8 mmol) of (*R*)-(−)-2,3-*O*-isopropylideneglycerol-1-tosylate were reacted according to the same procedure as described for **3a**. Yield: 4.1 g (81%) of **3b**. – (*RR*)-(+)-**3b**: $C_{18}H_{27}O_4P$ (338.4): calcd. C 63.89, H 8.04; found C 63.55, H 7.81. – MS: *m/z* (%): 338 (29) [M^+], 323 (2) [$M^+ - CH_3$], 280 (6) [$M^+ - C_3H_6O$], 222 (18) [$M^+ - 2\ C_3H_6O$], 166 (100) [$M^+ - C_6H_{10}O_2 - C_3H_6O$]. – ^1H NMR (C_6D_6): δ = 1.21, 1.26 (6 H), 1.37 (6 H), 1.65–1.71, 1.85–1.92, 2.01–2.07 (4 H), 3.26–3.30, 3.59–3.64 (6 H), 7.08–7.16, 7.39–7.44 (5 H). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 25.99, 26.01, 27.19, 27.23, 33.80 (15.3), 34.31 (13.2), 70.21 (9.2), 70.52 (8.1), 74.18 (16.3), 74.75 (20.3), 108.88, 108.89, 128.68 (7.1), 129.36, 132.96 (20.3), 138.48 (14.2). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −35.57. – $[\alpha]_D^{20}$ = +32.8 (neat).

Preparation of [(*R*,*S*)$_P$,*R*$_C$]-2,3-*O*-Isopropylideneglycerol-1-phenylphosphane (3c) and [(*R*,*S*)$_P$,*R*$_C$]-2,3-*O*-Isopropylideneglycerol-1-phenylmethylphosphane (3d): These ligands were prepared in an analogous manner as (*R,R*)-(+)-**3b**, employing 5.04 g (45.8 mmol) of $PhPH_2$ or 1.08 g (8.7 mmol) of Ph(Me)PH, 3.20 g (50.3 mmol) or 0.63 g (9.6 mmol) of KOH, and 13.1 g (45.8 mmol) or 2.49 g (8.7 mmol) of (*R*)-(−)-2,3-*O*-isopropylideneglycerol tosylate. Yields: 6.7 g (65%) of **3c**, 1.48 g (71%) of **3d**. Purification of **3c** and **3d** was achieved by vacuum distillation (**3c**: 74–76°C, 0.01 mbar, **3d**: 104°C, 0.01 mbar). – **3c**: $C_{12}H_{17}O_2P$ (224.2): C 64.27, H 7.64; found C 63.83, H 7.67. – MS: *m/z* (%): 224 (7.4) [M^+], 209 (11.2) [$M^+ - CH_3$], 166 (83.9) [$M^+ - C_3H_6O$], 125 (100) [$M^+ - C_5H_8O_2$], 110 (46.4) [$PhPH_2$]. – ^1H NMR (C_6D_6): δ = 1.24, 1.25, 1.35, 1.37 (6 H), 1.62–1.70, 1.75–1.91, 2.08–2.15 (2 H), 3.28–3.38, 3.63–3.84, 3.91–4.05, 4.32–4.47 (4 H), 7.03–7.38 (5 H). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 25.84, 25.98, 27.23, 27.27, 28.27 (15.3), 28.30 (14.3), 70.00 (5.2), 70.02 (5.1), 74.83 (10.2), 74.92 (8.1), 108.86, 109.13, 128.24, 128.65 (5.1), 128.70 (4.1), 133.84 (16.3), 134.08 (16.3), 135.29 (11.2), 135.33 (11.2). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −62.94 (211.1), −63.44 (208.6). – **3d**: $C_{13}H_{19}O_2P$ (238.3): C 65.53, H 8.04; found C 65.25, H 7.91. – MS: *m/z* (%): 238 (20.7) [M^+], 223 (80) [$M^+ - CH_3$], 138 (45.8) [$M^+ - C_5H_8O_2$], 124 (100) [PhMePH]. – ^1H NMR (C_6D_6): δ = 1.15 (4.1), 1.20 (3.6, 3 H), 1.28, 1.32, 1.41, 1.42 (6 H), 1.64–1.74, 1.81–2.04 (2 H), 3.33–4.16 (3 H), 7.07–7.71 (5 H). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 12.49 (14.3), 12.82 (15.3), 26.05, 27.26 (4.1), 35.57 (16.3), 36.56 (15.3), 70.29 (9.2), 70.67 (9.2), 74.23 (15.3), 74.94 (18.3), 108.85, 128.60 (7.1), 128.61 (7.1), 128.73, 128.76, 131.89 (19.3), 140.56 (14.2), 140.95 (14.2). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −38.96, −41.22.

Preparation of 2,3-*O*-Isopropylideneglycerol-1-[3-(*N*,*N*-dimethylguanidinium)phenyl]phosphane Iodide (3e): 0.55 g (2.45 mmol) of [(*R*,*S*)$_P$,*R*$_C$]-**3c** and 0.71 g (2.45 mmol) of 3-iodophenylguanidine were dissolved in 10 mL of acetonitrile and 2.8 mg (1.0 mol-%) of the catalyst $Pd(Ph_3P)_4$ was added. After stirring the reaction mixture at 60°C for 5 h, all volatiles were removed in vacuo. [(*R*,*S*)$_P$,*R*$_C$]-**3e** was obtained as an off-white powder, which was recrystallized from acetone. Yield: 1.13 g (90%). – [(*R*,*S*)$_P$,*R*$_C$]-**3e**: $C_{21}H_{29}IN_3O_2P$ (513.3): calcd. C 49.13, H 5.69, N 8.19; found C 49.81, H 5.57, N 7.77. – ^1H NMR ([D$_6$]acetone): δ = 1.23, 1.24, 1.31, 1.33 (6 H), 3.30 (6 H), 2.47–2.55, 3.58–3.66, 3.92–4.10, 4.15–4.22 (5 H). – $^{13}C\{^1H\}$ NMR ([D$_6$]acetone): δ = 26.72, 27.86, 34.27 (11.2), 41.26, 71.21 (10.2), 71.31 (10.2), 75.18 (19.3), 109.88, 109.86, 126.19, 126.27, 129.59 (3.8), 129.76 (5.7), 130.01 (6.7), 130.03 (7.6), 130.99, 131.07, 131.94 (20.3), 132.28 (22.4), 134.38 (19.1), 134.64 (20.4), 134.88 (20.3), 137.86 (7.1), 137.92 (6.1), 139.22 (13.2), 139.35 (13.2), 142.17 (15.3), 142.45 (16.3), 157.34, 157.36. – $^{31}P\{^1H\}$ NMR ([D$_6$]acetone): δ = −20.68, −20.87.

Preparation of (2,3-*O*-Isopropylideneglycerol)[4-(sodiumsulfonato)-phenyl]phenylphosphane (3f): 0.73 g (3.25 mmol) of the secondary phosphane [(*R*,*S*)$_P$,*R*$_C$]-**3c** and sodium *p*-iodobenzenesulfonate were dissolved in 15 mL of methanol and 0.36 g (3.58 mmol) of NEt_3 was added. After the addition of 38.0 mg (1.0 mol-%) of the catalyst $Pd(Ph_3P)_4$, the reaction mixture was heated to 60°C and stirred for 24 h. The solvent was then removed in vacuo and the remaining residue was extracted with 25 mL of dichloromethane. On concentration of the combined extracts to dryness, **3f** was obtained as a pale-yellow powder. Yield: 1.3 g (99%). The sample was found to contain a small amount of $HNEt_3I$, which could not be completely removed by extraction. – **3f**: $C_{18}H_{20}NaO_5PS$: (402.4): calcd C 53.73, H 5.01; found C 53.09, H 5.51. – ^1H NMR (D_2O): δ = 1.14, 1.24 (6 H), 2.14–2.36 (2 H), 3.36–3.49, 3.77–4.02 (3 H), 7.02–7.94 (9 H). – $^{13}C\{^1H\}$ NMR (D_2O): δ = 27.41, 28.59, 34.50 (14.2), 34.55 (13.2), 71.76 (9.2), 75.92 (18.3), 111.48, 127.93, 131.07 (6.1), 131.52, 131.71, 134.75 (19.3), 135.04 (20.3), 135.24 (19.4), 135.58 (20.4), 139.05 (11.2), 143.99 (13.2), 144.11 (13.2), 145.66, 145.83. – $^{31}P\{^1H\}$ NMR (D_2O): δ = −22.1, −22.5.

Preparation of (*S*,*S*)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis[(*R*,*R*)-2′,3′-*O*-isopropylideneglycerol-1-phenylphosphano]butane (3g), Diastereomeric Mixture: To a solution of 0.36 g (11.0 mmol) of KOH in 10 mL of DMSO, 1.11 g (4.95 mmol) of **3c** was added and the solution was stirred for 1 h. A solution of 1.16 g (2.47 mmol) of (*R*,*R*)-(+)-1,4-di-*O*-*p*-toluolsulfonyl-2,3-isopropylidene-D-threitol in 20 mL of DMSO was then added and the mixture was stirred for 10 h. After the addition of 15 mL of water, the mixture was extracted with 50 mL of CH_2Cl_2. Evaporation of all volatiles in vacuo (20°C, 0.01 mbar) left **3g** as an off-white solid, which was dried in vacuo at 80°C. Yield: 1.32 g (93%). – **3g**: $C_{31}H_{44}O_6P_2$ (574.6): calcd. C 64.79, H 7.72; found C 65.20, H 7.63. – MS: *m/z* (%): 574 (<1) [M^+], 559 (2) [$M^+ - CH_3$], 558 (4) [$M^+ - CH_3 - H$], 459 (100) [$M^+ - C_6H_{11}O_2$], 351 (29) [$M^+ - C_6H_{11}O_2 - C_6H_5P$]. – ^1H NMR (C_6D_6): δ = 1.17–1.41 (18 H), 1.78–2.30 (8 H), 3.31–4.24 (8 H), 7.11–7.53 (10 H) – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −33.50 (isomer A), −37.50 (isomer B), −33.81, −37.24 (1.5) (isomer C).

Preparation of 1,3-Bis[(*R*,*R*)-2,3-*O*-isopropylideneglycerol-1-phenylphosphano]propane (3h), Diastereomeric Mixture: 1.84 g (8.2 mmol) of [(*R*,*S*)$_P$,*R*$_C$]-**3c** was added to a suspension of KOH powder (88%) in 20 mL of DMSO. 0.83 g (4.1 mmol) of 1,3-dibromopropane was added and the reaction mixture was stirred at ambient temperature for 8 h. The product was then extracted with dichloromethane (3 × 20 mL). The extracts were pooled and dried with $MgSO_4$. After removing the solvent in vacuo, **3h** was obtained as a colorless oily liquid. Yield: 1.56 g (78%). – **3h**: $C_{27}H_{38}O_4P_2$ (488.5): calcd. C 66.38, H 7.84; found C 66.28, H 7.86. – MS: *m/z* (%): 488 (2)

[M^+], 473 (15) [$M^+ - CH_3$], 374 (100) [$M^+ - C_6H_{10}O_2$], 373 (92) [$M^+ - C_6H_{11}O_2$], 259 (18) [$M^+ - 2\ C_6H_{11}O_2 + H$], 258 (18) [$M^+ - 2\ C_6H_{11}O_2$]. – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −29.81 (isomer A), −31.46 (isomer B), −29.68, −31.32 (1.0) (isomer C).

Syntheses of the Complexes L_2PdCl_2 (L = 1a, 2a, 3a) (4−6): The ligands **1a** (1.46 g, 5.6 mmol), **2a** (0.42 g, 1.2 mmol), and **3a** (0.5 g, 1.66 mmol) were dissolved in 10 mL aliquots of dichloromethane and stirred with 0.80 g (2.8 mmol) or 0.17 g (0.6 mmol) or 0.24 g (0.83 mmol) of 1,5-cyclooctadiene dichloropalladium(II) for 3 h. After evaporation of the solvent in vacuo, the complexes were obtained as yellow or cream-colored solids. Yields: 1.92 g (98%) of **4**, 0.43 g (83%) of **5**, 0.62 g (96%) of **6**. – Bis[(*R*)-(−)-2,3-dihydroxypropyl-1-diphenylphosphane]dichloropalladium(II) (**4**): $C_{30}H_{34}Cl_2O_4P_2Pd$ (697.9): calcd. C 51.63, H 4.91; found C 50.99, H 5.24. – $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 38.31 (*N* = 35.5 Hz), 66.37 (*N* = 14.9 Hz), 72.84, 127.75 (*N* = 58.0 Hz), 129.87 (*N* = 11.2 Hz), 130.19 (*N* = 11.2 Hz), 132.65, 132.67, 133.72 (*N* = 11.2 Hz), 135.85 (*N* = 11.2 Hz). – $^{31}P\{^1H\}$ NMR (CD_3OD): δ = 26.38 (*trans*), 43.02 (*cis*). – Bis[(*R*)-(+)-1,3,2-dioxaborolano-4-methyl-2-phenyldiphenylphosphane]dichloropalladium(II) (**5**): $C_{42}H_{40}B_2Cl_2O_4P_2Pd$ (869.7): calcd. C 58.00, H 4.64; found C 57.82, H 4.58. – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.91 (*N* = 27.8 Hz), 72.37, 74.01, 127.68, 128.21 (*N* = 10.7 Hz), 128.31, 128.44 (*N* = 10.2 Hz), 129.1 (*N* = 47.8), 129.9 (*N* = 47.3 Hz), 130.69, 130.75, 131.42, 133.55 (*N* = 12.2 Hz), 134.39 (*N* = 13.2 Hz), 134.88. – $^{31}P\{^1H\}$ NMR: ($CDCl_3$): δ = 13.63 (*trans*), 30.95 (*cis*). – Bis[(*R*)-(+)-2,3-*O*-isopropylideneglycerol-1-diphenylphosphane]dichloropalladium(II) (**6**): $C_{36}H_{42}Cl_2O_4P_2Pd$ (778.0): calcd. C 55.58, H 5.44; found C 55.31, H 5.28. – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 25.56, 25.81, 26.82, 26.95, 30.77 (*N* = 28.5 Hz), 32.76 (*N* = 33.6 Hz), 70.22, 70.35, 72.25, 73.01, 108.90, 109.31, 128.18 (*N* = 10.5 Hz), 128.34 (*N* = 11.5 Hz), 128.49 (*N* = 9.5 Hz), 128.64 (*N* = 11.5 Hz), 130.40, 130.49, 131.55, 133.75 (*N* = 10.5 Hz), 134.14 (*N* = 12.4 Hz), 134.19 (*N* = 9.5 Hz), 134.49 (*N* = 12.4 Hz). – $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 13.63 (*trans*), 28.13 (*cis*).

Preparation of Bis[(*R*)-(−)-2,3-dihydroxypropyl-1-diphenylphosphane]palladium(II) Diperchlorate (7): 0.22 g (1.06 mmol) of silver(I) perchlorate (in 5 mL of toluene) was added to a solution of 0.17 g (0.24 mmol) of **4** in 15 mL of toluene and the reaction mixture was stirred for 2 h. The solvent was then removed in vacuo and the remaining residue was extracted with 20 mL of CH_2Cl_2. The combined extracts were concentrated in vacuo to a volume of 10 mL. The precipitate formed on addition of 10 mL of diethyl ether was filtered off and the filtrate was concentrated to dryness in vacuo. Yield: 0.18 g (92%). – **7**: $C_{30}H_{34}Cl_2O_{12}P_2Pd$ (825.9): calcd. C 43.63, H 4.15; found C 43.65, H 3.87. – $^{13}C\{^1H\}$ NMR ([D_6]acetone): δ = 37.04 (*N* = 32.4 Hz), 65.27 (*N* = 15.0 Hz), 75.72, 123.10 (*N* = 60.0 Hz), 125.28 (*N* = 62.1 Hz), 130.86 (*N* = 11.2 Hz), 131.30 (*N* = 13.2 Hz), 134.61 (*N* = 11.2 Hz), 135.0, 135.34, 136.49 (*N* = 13.2 Hz). – $^{31}P\{^1H\}$ NMR ([D_6]acetone): δ = 51.50 (*cis*).

Preparation of (Bicyclo[2.2.1]hepta-2,5-diene)chloro[(*R*)-(−)-2,3-dihydroxypropyl-1-diphenylphosphane]rhodium(I) (8): To a suspension of 0.49 g (1.06 mmol) of bicyclo[2.2.1]hepta-2,5-dienechlororhodium(I) dimer in 8 mL of methanol, a solution of 0.55 g (2.12 mmol) of **1a** was added and the reaction mixture was stirred for 2 h. After removal of the solvent, **8** was obtained as an orange powder. Yield: 0.98 g (94%). – **8**: $C_{22}H_{25}ClO_2PRh$ (490.8): calcd. C 53.84, H 5.13; found C 53.32, H 5.11. – ^1H NMR ($CDCl_3$): δ = 1.39 (2 H), 3.63, 3.65, 3.77 (6 H), 2.39−2.47 (2 H), 2.61−2.69 (2 H), 4.16−4.25 (1 H), 7.30−7.69 (10 H). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 33.29 (23.4), 63.81 (3.1), 67.18 (12.2), 67.77, 128.30 (9.2), 128.46 (9.2), 129.89 (2.0), 130.43 (2.0), 131.19 (41.7), 132.19 (42.7), 132.50 (10.2), 133.66 (11.2 Hz). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 23.54 [^1J(Ph−P) = 168.7 Hz].

Preparation of (Bicyclo[2.2.1]hepta-2,5-diene)bis[(*R*)-(+)-2,3-*O*-isopropylideneglycerol-1-diphenylphosphane]rhodium(I) Hexafluorophosphate (9): 1.0 g (3.33 mmol) of **3a** and 0.38 g (0.83 mmol) of bicyclo[2.2.1]hepta-2,5-dienechlororhodium(I) dimer were dissolved in 15 mL of acetone. After addition of 0.31 g (1.67 mmol) of KPF_6, the reaction mixture was stirred for 12 h at ambient temperature and then concentrated in vacuo to a volume of 5 mL. The precipitate deposited on addition of 20 mL of diethyl ether was filtered off and dried in vacuo. Yield: 1.5 g (96%). – **9**: $C_{43}H_{50}F_6O_4P_3Rh$ (940.7): calcd. C 54.90, H 5.36; found C 54.06, H 5.33. – $^{13}C\{^1H\}$ NMR ([D_6]acetone): δ = 26.64, 26.74, 31.60 (*N* = 23.4 Hz), 54.49, 69.14, 71.81 (*N* = 10.9 Hz), 74.71, 93.1 (*N* = 92.4 Hz), 110.92, 130.20, 130.26, 132.10, 132.19 (*N* = 42.7 Hz), 132.62 (*N* = 44.8 Hz), 132.68, 134.38 (*N* = 10.2 Hz), 135.22 (*N* = 11.2 Hz). – $^{31}P\{^1H\}$ NMR ([D_6]acetone): δ = 24.4 (155.7); PF_6^-: δ = −142.97 [^1J(P−F) = 707.8 Hz]. – $[\alpha]_D^{20}$ = −78° (*c* = 5, CH_3CN).

Preparation of (Bicyclo[2.2.1]hepta-2,5-diene)-[1,3-bis{(*R*,*R*)-2,3-*O*-isopropylideneglycerol-1-phenylphosphano}propane]rhodium(I) Hexafluorophosphate (10): 0.79 g (1.62 mmol) of **3e**, 0.39 g (0.84 mmol) of bicyclo[2.2.1]hepta-2,5-dienechlororhodium(I) dimer, and 0.31 g (1.68 mmol) of KPF_6 were reacted according to the same procedure as described for **9**. The complex **10** was obtained as an orange powder. Yield: 1.32 g (98%). – **10**: $C_{34}H_{46}F_6O_4P_3Rh$ (828.6): calcd. C 49.29, H 5.60; found C 49.10, H 5.58. – $^{31}P\{^1H\}$ NMR ([D_6]acetone): δ = 7.48 [J(^{103}Rh−^{31}P) = 146.1 Hz] (isomer A), 7.72 [J(^{103}Rh−^{31}P) = 143.9 Hz] (isomer B), 5.62 [P(A)], 7.37 [P(B)] {J[^{31}P(A)−^{31}P(B)] = 52.3 Hz, J[^{103}Rh−^{31}P(A)] = 145.9 Hz, J[^{103}Rh−^{31}P(B)] = 145.9 Hz}.

Crystal Structure Analysis of (*R*)-$Ph_2P-CH_2-C^aH-O-B(Ph)-O-C^bH_2$ [*C^a-C^b*]: A crystal of (*R*)-(+)-**2a** was mounted in a glass capillary. X-ray data were collected using a Siemens P3 diffractometer equipped with a graphite monochromator and employing Cu-K_α radiation. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using all unique data with all non-hydrogen atoms anisotropic and hydrogen atoms positioned geometrically. The value of the absolute

Table 1. Experimental data relating to the X-ray structure of **2a**

formula weight	346.2
temperature	293(2) K
crystal system	monoclinic
space group	$P2_1$
unit cell dimensions	*a* = 11.6050(11) Å
	b = 12.3033(13) Å
	c = 13.177(2) Å
	β = 98.769(8)°
V	1859.6(3) Å^3
Z	4
$D_{calcd.}$	1.236 Mg/m^3
absorption coefficient	1.383 mm^{-1}
crystal size	0.20 × 0.33 × 0.54 mm
θ range	3.4 to 57.2°
reflections collected	2807
independent reflections	2674
observed reflections [$I > 2\sigma(I)$]	1956
absorption correction	semiempirical
max. and min. transmission	0.690−0.354
data/restraints/parameters	2674/1/452
final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0465, *wR*2 = 0.1064
R indices all data	*R*1 = 0.0660, *wR*2 = 0.1150
largest diff. peak and hole	0.24/−0.18 eÅ^{-3}

structural parameter, −0.03(4), shows that the configurations of C(14) and C(14a) had been determined correctly. Crystal data and refinement details are given in Table 1. The program SHELX-93 was used for the refinement.[38]

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[1] P. Machnitzki, T. Nickel, O. Stelzer, C. Landgrafe, *Eur. J. Inorg. Chem.* **1998**, 1029.
[2] B. Cornils, W. A. Herrmann, in: *Applied Homogeneous Catalysis with Organometallic Compounds*, vol. 2 (Eds.: B. Cornils, W. A. Herrmann), VCH Verlagsgesellschaft, Weinheim, **1996**, p. 575.
[3] W. A. Herrmann, C. W. Kohlpaintner, *Angew. Chem*. **1993**, *105*, 1588; *Angew. Chem. Int. Ed. Engl*. **1993**, *32*, 1524; B. Cornils, W. A. Herrmann, in: *Aqueous-Phase Organometallic Catalysis* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, New York, Chichester, Brisbane, Singapore, Toronto, **1998**, p. 57.
[4] [4a] M. Hingst, M. Tepper, O. Stelzer, *Eur. J. Inorg. Chem*. **1998**, 73; M. Tepper, O. Stelzer, T. Häusler, W. S. Sheldrick, *Tetrahedron Lett*. **1997**, *38*, 2257. – [4b] M. Peuckert, W. Keim, *Organometallics* **1983**, *2*, 594.
[5] [5a] B. Mohr, D. M. Lynn, R. H. Grubbs, *Organometallics* **1996**, *2*, 4317. – [5b] A. Heßler, O. Stelzer, H. Dibowski, K. Worm, F. P. Schmidtchen, *J. Org. Chem*. **1997**, *62*, 2362; O. Stelzer, F. P. Schmidtchen, A. Heßler, M. Tepper, H. Dibowski, H. Bahrmann, M. Riedel, DE 19701245 (Celanese GmbH) 16. 1. 1997.
[6] [6a] J. Holz, M. Quirmbach, A. Börner, *Synthesis* **1997**, 983. – [6b] G. Muller, D. Sainz, *J. Organomet. Chem*. **1995**, *495*, 103. – [6c] Y. G. Shermolovich, A. V. Solovev, N. P. Kolesnik, L. N. Markowski, *Zh. Obshch. Khim*. **1990**, *60*, 1243. – [6d] M. G. Finn, K. B. Sharpless, in: *Asymmetric Synthesis*, vol. 5, *Chiral Catalysis* (Ed.: J. D. Morrison), Academic Press, New York, **1985**, p. 247; J. G. Hill, K. B. Sharpless, C. M. Exon, R. Regenye, *Org. Synth*. **1984**, *63*, 66. – [6e] H. Brunner, A. Sicheneder, *Angew. Chem*. **1988**, *100*, 730; *Angew. Chem. Int. Ed. Engl*. **1988**, *27*, 718.
[7] [7a] K. Issleib, H. R. Roleff, *Chem. Ber.* **1965**, *98*, 2091; K. Issleib, F. Ungvary, *Z. Naturforsch.* **1967**, *22b*, 1238; K. L. Marsi, M. E. Co-Sorno, *J. Org. Chem.* **1977**, *42*, 778. – [7b] H. Fujimoto, I. Hataue, N. Koga, T. Yamasaki, *Tetrahedron Lett*. **1984**, 5339; S. Harder, J. H. van Lenthe, N. J. R. van Eikema Hommes, P. von Rague-Schleyer, *J. Am. Chem. Soc*. **1994**, *116*, 2508.
[8] D. Enders, T. Berg, *Synlett* **1996**, 796; D. Enders, T. Berg, G. Raabe, J. Runsink, *Liebigs Ann./Recueil* **1997**, 345.
[9] H. B. Kagan, M. Tahar, J. C. Fiaud, *Tetrahedron Lett.* **1991**, *32*, 5959.
[10] [10a] N. Mitchell, K. Heesche-Wagner, *J. Organomet. Chem*. **1992**, *436*, 43. – [10b] M. Beller, J. G. Krauter, A. Zapf, *Angew. Chem*. **1997**, *109*, 793; *Angew. Chem. Int. Ed. Engl*. **1997**, *36*, 793.
[11] W. Keim, *Angew. Chem*. **1990**, *102*, 251; *Angew. Chem. Int. Ed. Engl*. **1990**, *29*, 235; A. Baader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27; M. Swamamura, Y. Ito, *Chem. Rev.* **1992**, *92*, 857.
[12] [12a] A. Börner, J. Ward, K. Kortus, H. B. Kagan, *Tetrahedron: Asymmetry* **1993**, *10*, 2219. – [12b] P. Pellon, *Tetrahedron Lett.* **1992**, *33*, 4451.
[13] K. P. Langhans, O. Stelzer, J. Svara, N. Weferling, *Z. Naturforsch*. **1990**, *45b*, 203; E. N. Tsvetkov, N. A. Bondarenko, I. G. Malakova, M. I. Kabachnik, *Synthesis* **1986**, 198.
[14] [14a] W. Gee, R. A. Shaw, B. C. Smith, *Inorg. Synth*. **1967**, *9*, 19. – [14b] N. K. Roberts, S. B. Wild, *J. Am. Chem. Soc*. **1979**, *101*, 6254. – [14c] F. Pass, H. Schindlbaur, *Monatsh. Chem.* **1959**, *90*, 148.
[15] A. J. Robertson, *Phosphorus and Sulfur* **1987**, *30*, 265.
[16] [16a] O. Herd, K. P. Langhans, O. Stelzer, N. Weferling, W. S. Sheldrick, *Angew. Chem*. **1993**, *105*, 1097; *Angew. Chem. Int. Ed. Engl*. **1993**, *32*, 1058; O. Herd, A. Heßler, K. P. Langhans, O. Stelzer, N. Weferling, W. S. Sheldrick, *J. Organomet. Chem.* **1994**, *475*, 99; F. Bitterer, O. Herd, A. Heßler, M. Kühnel, K. Rettig, O. Stelzer, W. S. Sheldrick, S. Nagel, N. Rösch, *Inorg. Chem*. **1996**, *35*, 4103. – [16b] O. Herd, A. Heßler, M. Hingst, M. Tepper, O. Stelzer, *J. Organomet. Chem.* **1996**, *522*, 69.
[17] O. Herd, A. Heßler, M. Hingst, P. Machnitzki, M. Tepper, O. Stelzer, *Catalysis Today* **1998**, *42*, 413.
[18] P. Machnitzki, M. Tepper, K. Wenz, O. Stelzer, E. Herdtweck, to be published.
[19] D. R. Coulson, *Inorg. Synth*. **1972**, *13*, 121.
[20] L. B. Fields, E. N. Jacobsen, *Tetrahedron: Asymmetry* **1993**, *4*, 2229.
[21] [21a] H. Brunner, H. Leyerer, *J. Organomet. Chem.* **1987**, *334*, 369; H. Brunner, K. Kramler, *Synthesis* **1991**, 1121. – [21b] W. J. Kerr, G. G. Kirk, D. Middlemiss, *J. Organomet. Chem.* **1996**, *519*, 93.
[22] H. Brunner, T. Rückert, *Monatsh. Chem.* **1998**, *129*, 339.
[23] M. Baacke, O. Stelzer, V. Wray, *Chem. Ber*. **1980**, *113*, 1356; S. Hietkamp, T. Lebbe, G. U. Spiegel, O. Stelzer, *Z. Naturforsch*. **1987**, *42b*, 177.
[24] I. Lukaschewisch, *Dokl. Akad. Nauk SSSR, Ser. Khim*. **1957**, *112*, 872.
[25] J. J. Daly, *J. Chem. Soc.* **1964**, 3799; B. J. Dunne, A. G. Orpen, *Acta Cryst.* **1991**, *C47*, 345.
[26] B. J. Dunne, R. B. Morris, A. G. Orpen, *J. Chem. Soc., Dalton Trans.* **1991**, 653; F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, *J. Chem. Soc., Perkin Trans. 2* **1987**, 1.
[27] H. Shimanouchi, N. Saito, Y. Sasada, *Bull. Chem. Soc. Jpn*. **1969**, *42*, 1239.
[28] [28a] S. O. Grim, R. L. Keiter, *Inorg. Chim. Acta* **1970**, *4*, 56. – [28b] B. E. Mann, B. L. Shaw, R. M. Slade, *J. Chem. Soc.(A)* **1971**, 2976. – [28c] G. Balimann, H. Motschi, P. S. Pregosin, *Inorg. Chim. Acta* **1977**, *23*, 191.
[29] T. Bartik, T. Himmler, *J. Organomet. Chem*. **1985**, *293*, 343.
[30] J. W. Emsley, J. Feeney, L. H. Suttcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, vol. 1, Pergamon Press, Oxford, London, New York, Toronto, Sydney, Paris, Braunschweig, **1966**, p. 280; H. J. Bernstein, J. A. Pople, C. W. Schneider, *Can. J. Chem*. **1957**, *35*, 65.
[31] N. W. Alcock, A. W. G. Platt, P. G. Pringle, *Inorg. Chim. Acta* **1987**, *128*, 215; *J. Chem. Soc., Dalton Trans.* **1989**, 139.
[32] A. W. G. Platt, P. G. Pringle, *J. Chem. Soc., Dalton Trans.* **1989**, 1193.
[33] N. W. Alcock, A. W. G. Platt, P. G. Pringle, *J. Chem. Soc., Dalton Trans.* **1987**, 2273.
[34] R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1971**, *93*, 2397.
[35] J. Chatt, L. M. Vallarino, L. M. Venanzi, *J. Chem. Soc*. **1957**, 3413.
[36] E. W. Abel, M. A. Bennett, G. Wilkinson, *J. Chem. Soc.* **1959**, 3178.
[37] E. Baer, H. O. L. Fischer, *J. Am. Chem. Soc.* **1948**, *70*, 609; Y. Tsuda, Y. Okada, M. Tanaka, N. Shigematsu, Y. Hori, *Chem. Pharm. Bull.* **1991**, *39*, 607.
[38] Further details of the crystal structure investigation are available from the Cambridge Crystallogaphic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44(0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk] on quoting the depository number CCDC-133697.

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