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A New Access to Chiral Phospholanes

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The hydrogenation of 5-oxo-5*H*-5λ^5-dibenzophosphol-5-ol gives, almost quantitatively, only one geometric isomer of 5-oxododecahydro-5λ^5-dibenzophosphol-5-ol (**2**). An X-ray structure analysis confirmed the formation of a *meso* isomer with a 4aβ,5aβ,9aβ,9bβ configuration (**2a**). Another possible way to get **2a** is the hydrogenation of (4aβ,5aβ)-5-oxo-2,3,4,4a,5,5a,6,7,8,9-decahydro-1*H*-5λ^5-dibenzophosphol-5-ol (**11**), which is easily available starting from cyclohexanone. Highly selective epimerization has been achieved using LDA as base at elevated temperature. Resolution of **2e** was achieved by salt formation with (*R*)-(+)- and (*S*)-(–)-*N*-benzyl-α-methylbenzylamine to give (+)- and (–)-(4aα,5aβ,9aβ,9bβ)-5-oxododecahydro-5λ^5-dibenzophosphol-5-ol. The geometry of **2e** was confirmed by X-ray structure analysis. Reduction of (+)- or (–)-**2e** gave diastereomeric phospholanes (4aα,5*R*/*S*,5aβ,9aβ,9bβ)-dodecahydrodibenzophosphole (**1a**), which were oxidized to the corresponding secondary phosphane oxides (SPOs) (4aα,5*R*/*S*,5aβ,9aβ,9bβ)-dodecahydrodibenzophosphole 5-oxide (**1b**). These phosphanes and phosphane oxides were used as ligands and preligands, respectively, in the Rh-catalyzed enantioselective hydrogenation of benchmark substrates, where up to 79% *ee* have been achieved. B3LYP density functional calculations reveal that among the three possible epimers at the ^{4a}C- and ^{5a}C-positions the *chiral* isomer (4aα,5aβ,9aβ,9bβ)-5-oxododecahydro-5λ^5-dibenzophosphol-5-ol (**2e**) is 3.52 kcal mol^{-1} more stable than the related *meso* isomer **2a** in Gibbs free energy.

Introduction

Chiral phospholanes are one of the most powerful classes of ligands in transition-metal-catalyzed asymmetric hydrogenation.[1] The pioneering work in this field was carried out by Brunner et al. in 1987.[2] Unfortunately, the 3,4-disubstituted bisphospholane, which was derived from chiral tartaric acid, induced only poor enantioselectivity in Rh-catalyzed hydrogenation. The decisive breakthrough was achieved by Burk and co-workers at DuPont a few years later with the synthesis of bisphospholanes bearing alkyl substituents at the 2,5-positions of the heterocyclic rings.[3] These ligands, now known under their trade names DuPHOS and BPE,[4] became the prototype of a range of other bisphosphanes based on four-, five- or six-membered P heterocycles.[5] A few of them, such as TangPHOS,[6] Butiphane,[7] RoPHOS[8] and some other bisphospholanes derived from D-mannitol[9] and ligands of the cat*AS*ium® M series,[10] are commercially available and operate even in an industrial scale.[11]

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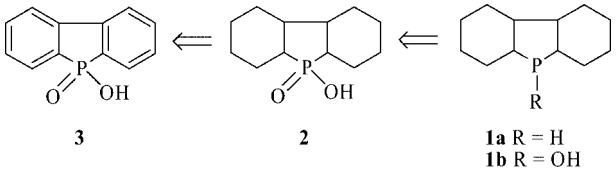
Currently there are three general approaches for the construction of these phospholanes. The most frequently employed access consists of the double nucleophilic substitution of a chiral dimesylate/ditosylate or a cyclic sulfate by a primary phosphane group, as originally suggested by Brunner and Burk, respectively.[2,3] This methodology, however, is hampered by the high price and limited variability of the required primary phosphane and by the synthetic restrictions due to patent claims.[12] Another approach, recently discovered by us, is based on the coupling of *P*-silylphospholanes with activated 1,2-dihaloolefins.[10] This is by far the most versatile method and has been used to establish one of the most comprehensive libraries of chiral phosphane ligands.[10c] The third and less frequently used route is based on the transformation of achiral phosphorus heterocycles into chiral phospholanes. Seminal work concerning the preparation of chiral ligands for asymmetric catalysis has come from the groups of Fiaud[13] and Pietrusiewicz,[14] who started their approaches with phosphole and phospholene derivatives, respectively.[15,16]

In order to broaden the scope of the third strategy, we present here the synthesis of the bicyclohexyl-fused phospholane **1a** and its phosphinous acid **1b**, respectively (Scheme 1). The pivotal steps of our approach are the heterogeneously catalyzed hydrogenation of a dibenzophosphol derivative **3**, followed by epimerization and resolution of the resultant chiral enantiomeric phosphinic acids **2**. Compounds **1a**,**b** can be used as bulky monodentate ligands in

asymmetric catalysis. Preliminary results in the Rh-catalyzed hydrogenation of benchmark olefins will also be detailed.



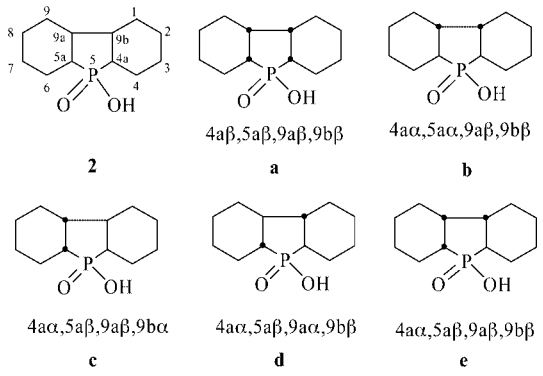
Scheme 1. Retrosynthetic approach to new chiral phospholanes.

Results and Discussion

5-Oxo-5*H*-5λ^5-dibenzophosphol-5-ol (**3**), which serves as a substrate for the saturation of the aromatic rings, was prepared from 1,2-dibromobenzene (**4**; Scheme 2). In the first synthetic step one equivalent of *n*-butyllithium was treated with two equivalents of **4** at low temperature to give 2,2′-dibromobiphenyl (**5**) as the main product in 82% yield.[17] The compound was transformed into 5-phenyl-5*H* dibenzophosphole (**6**) according to the procedure of Wittig and Maercker.[18] Thus, lithiation of **5**, followed by reaction with $PhPCl_2$, led to the closure of the ring and afforded the desired dibenzophosphole **6** in 82% yield. Cleavage of the Ph–P bond and subsequent oxidation of the resultant secondary phosphane[19] in situ with hydrogen peroxide at 45 °C[20] afforded 5-oxo-5*H*-5λ^5-dibenzophosphol-5-ol (**3**).

For the saturation of the aromatic rings in **3**, heterogeneous reduction with molecular hydrogen was envisaged. In the literature only one trial of this particular transformation has been described. In 1959 Freedman and Doak reported this reaction, but neither experimental details nor information about the stereochemistry of the product were given.[21] Moreover, expensive rhodium chloride was employed for the hydrogenation. We found that the less expensive Ru/Al_2O_3 can also be used successfully. At 50 °C and 50 bar initial H_2 pressure 5-oxododecahydro-5λ^5-dibenzophosphol-5-ol (**2**) was obtained in 95% yield within 7 h.

In principle five diastereomers **2a**–**e** can be formed as products of the hydrogenation (Scheme 3), but only a single isomer was obtained in this reaction.[22]



Scheme 3. Possible diastereomers of 5-oxododecahydro-5λ^5-dibenzophosphol-5-ol (**2**).

The ^1H and ^{13}C NMR spectra of the cyclic phosphinic acid **2** are characterized by a small set of signals. Unambiguous evidence for the structure came from the X-ray structure analysis.[23a] Suitable crystals could be obtained by crystallization from methanol/water. The molecular structure of compound **2** is shown in Figure 1, and selected bonds lengths and angles are listed in Table 1 along with the computed data. As can be clearly derived from this picture, the *meso* compound **2a**, where all H atoms of the phospholane ring are in a *cis* configuration, is formed as a result of a selective *cis* hydrogenation.

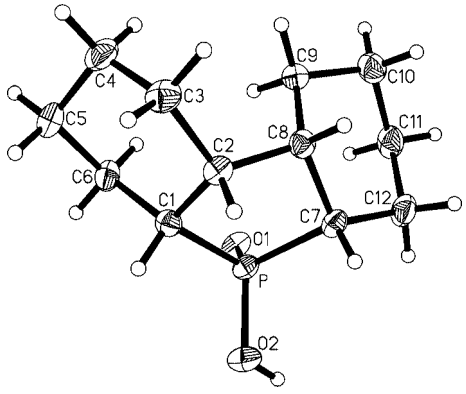
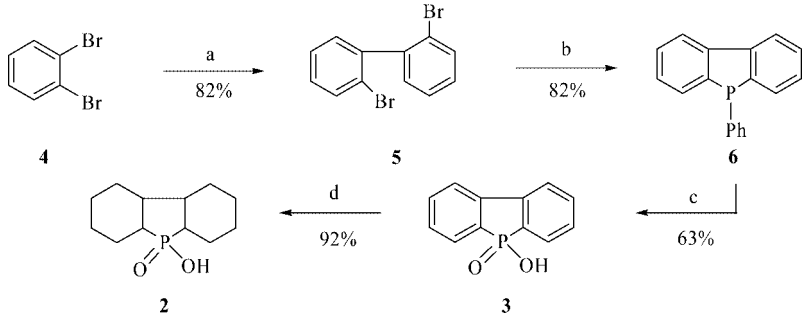


Figure 1. Molecular structure of **2a**. The thermal ellipsoids correspond to 30% probability.

As an alternative route to **2a** we investigated the McCormack cyclization between 1,3-dienes and dihalophosphanes,



Scheme 2. Synthesis of **2**. Reagents and conditions: a) *n*BuLi, aq. HCl; b) *n*BuLi, $PhPCl_2$; c) Li, H_2O_2, HOAc; d) H_2 (50 bar), Ru/Al_2O_3, MeOH, 50 °C, 7 h.

Table 1. X-ray structural and computational parameters (Å and degrees).[a]

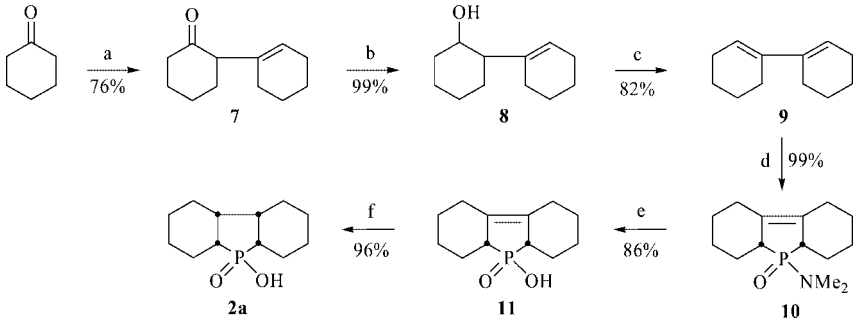
Parameter[b]	2a		2e		2b
P1–C1	1.813(2)	[1.8558]	1.793(2)	[1.8416]	[1.8322]
P1–C4	1.814(2)	[1.8435]	1.815(2)	[1.8530]	[1.8322]
P1–O1	1.5053(14)	[1.4979]	1.512(1)	[1.4969]	[1.4949]
P1–O2	1.5584(15)	[1.6487]	1.543(1)	[1.6495]	[1.6485]
C1–C2	1.556(3)	[1.5655]	1.538(2)	[1.5495]	[1.5521]
C2–C3	1.552(3)	[1.5602]	1.534(2)	[1.5526]	[1.5765]
C3–C4	1.547(3)	[1.5539]	1.540(2)	[1.5591]	[1.5521]
C1–P1–C4	97.72(9)	[96.82]	97.22(8)	[96.29]	[91.02]
O1–P1–O2	113.11(8)	[112.45]	113.50(7)	[122.88]	[113.01]

[a] The B3LYP/6-31G* computed values are given in square brackets. [b] Using the numbering system in Figure 2.

which has been widely used for the synthesis of phospholenes.[24] The required diene **9** was prepared by a simple three-step synthetic sequence (Scheme 4). In the first step the aldol condensation product **7** was formed by self-condensation of cyclohexanone.[25] Chemoselective reduction of the carbonyl group with $NaBH_4$ gave the alcohol **8**, which, in turn, was dehydrated with $POCl_3$ to give 1,1′-bicyclohexyl (**9**) in 62% overall yield.[26] The latter was subjected to the McCormack reaction. One of the main drawbacks of this transformation is the long reaction time usually required for completion (several days or weeks). An important improvement of this method is the application of chlorophosphenium cations $[(Alk_2N)(Cl)P]^+$ as reagent.[27] The latter can be generated, for example, by addition of $AlCl_3$ to dichloro(dimethylamino)phosphane. The product is formed in a clean and fast reaction with **9** to afford **10** quantitatively. The latter was subjected, without further purification, to hydrolysis with aqueous HCl solution to give the phosphinic acid **11** as colorless crystals. Heterogeneous hydrogenation of the double bond in **11** using Ru/Al_2O_3 gave exclusively **2a** in excellent yield. With Pd/C as a catalyst we observed the formation of the *meso* forms **2a** and **2b** in a ratio of approximately 1:1.

In order to prove the possibility of the epimerization of the stereogenic ^{4a}C and ^{5a}C atoms of **2a**, all three diastereomers (**2a**, **2b**, and **2e**) were optimized at the B3LYP density functional level of theory (see computational part for details). The B3LYP/6-31G(d) optimized structures are shown in Figure 2; the computed bond parameters in Table 1 agree well with the X-ray data. In all three structures the fused six-membered cyclohexane rings have the chair conformation. Structure **2b** is C_s-symmetric and the five-membered heterocyclic ring has a conformation in an envelope shape, while structures **2a** and **2e** are C_1-symmetric and their five-membered rings are twisted. These calculations reveal that the chiral derivative **2e** is thermodynamically more favored than the *meso* compounds **2a** and **2b**, by 3.52 and 4.57 kcal mol^{-1} in Gibbs free energy (ΔG), respectively (Figure 2). These energetic differences explain the formation of **2e** as the only product and the absence of **2b** during the epimerization of **2a**.

As anticipated by the calculations, **2e** can be prepared by treatment of **2a** with a strong base. In a first trial we used



Scheme 4. Reagents and conditions: a) *p*TsOH, reflux; b) $NaBH_4$; c) $POCl_3$/Py; d) $Me_2NPCl_2/AlCl_3$, H_2O; e) aq. HCl; f) H_2 (50 bar), Ru/Al_2O_3, MeOH, 50 °C, 7 h.

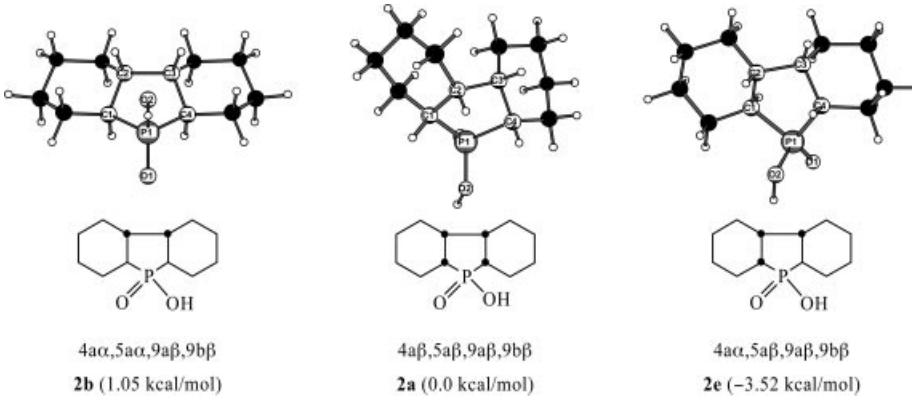
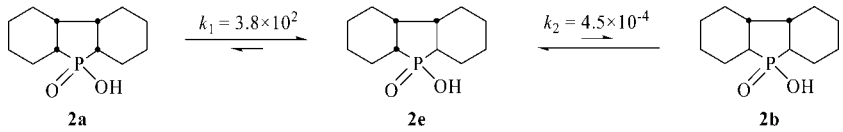


Figure 2. Relative Gibbs free energies (ΔG) of diastereomers of *meso*-**2** and *rac*-**2**.



Scheme 5. Rate constants of the epimerization of **2a**.

sodium methoxide as a base in methanol at reflux, but this method failed. We subsequently found that refluxing **2a** in THF for 3 h in the presence of LDA gave deprotonation at the α-carbon atom. Upon subsequent acidification the chiral compound **2e** was obtained in 76% yield (Scheme 5). Taking the computed relative Gibbs free energies in Figure 2, the estimated epimerization rate constants (at 298.15 K) are 3.8×10^2 for **2a** to **2e**, and 4.5×10^{-4} for **2e** to **2b**.

The structure of **2e** was determined by means of X-ray crystallography. Crystals suitable for X-ray structure analysis were obtained by crystallization from methanol/water. The ORTEP diagram is shown in Figure 3, and clearly indicates the asymmetric structure of the compound.[23b] The selected bond parameters are listed in Table 1 alongside the computed values.

Chiral amines have been suggested as possible reagents for the resolution of racemic phosphinic acids.[28] The acid *rac*-**2e** was neutralized with (*R*)-(+)-*N*-benzyl-α-methylbenzylamine in order to get the diastereomeric salts. The NMR spectra of the mixture of the latter are depicted in Figure 4, a. Even after a single recrystallization step one diastereomeric salt can be separated in high optical purity (Figure 4, b). The optically pure salt was obtained after washing with *n*-pentane. The enantiopure acid (–)-**2e** of hitherto unknown absolute configuration was liberated in good yield after treatment of the salt with an excess of aqueous NaOH. The mother liquor was used for a further resolution step with (*S*)-(–)-*N*-benzyl-α-methylbenzylamine to give (+)-**2e**.

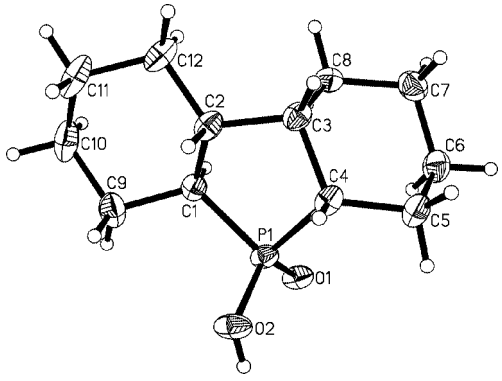


Figure 3. Molecular structure of racemic **2e**. The thermal ellipsoids correspond to 30% probability.

Upon substitution of the OH group with chloride and subsequent reduction of the intermediate chlorophospholane oxide with $LiAlH_4$, secondary phosphanes **1a** were obtained as a diastereomeric mixture in a ratio of 1:1 in 80% total yield (Scheme 6). The diastereomers were separated as their borane adducts by chromatography. However, during the removal of the borane protective group epimeri-

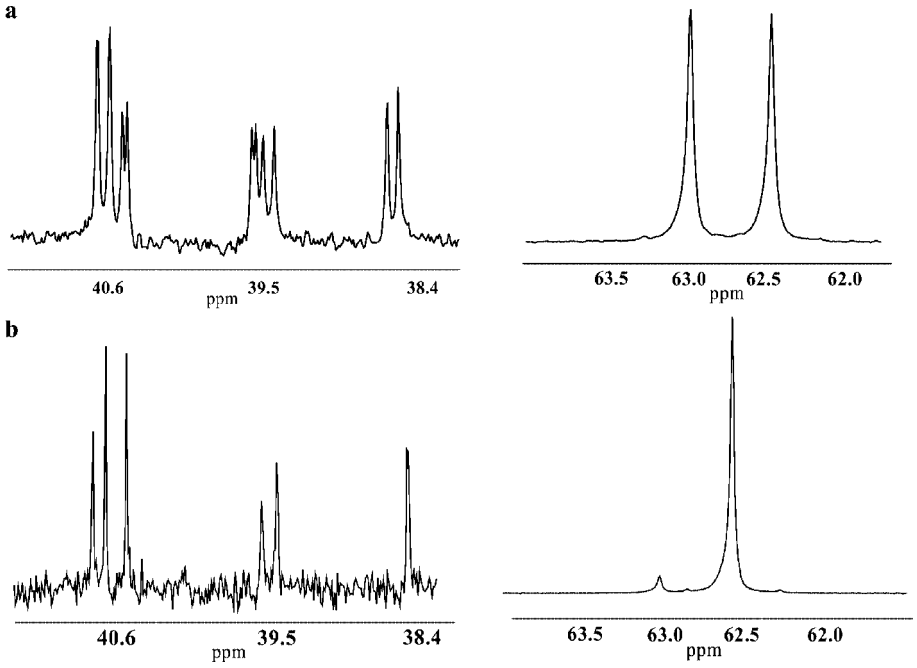
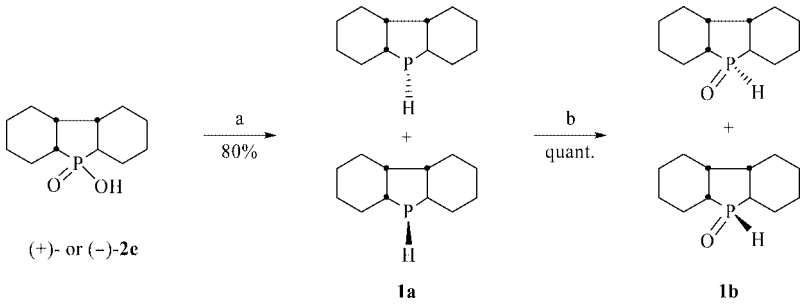


Figure 4. ^{13}C and ^{31}P NMR spectra of the diastereomeric salt of **2e** with (*R*)-(+)-*N*-benzyl-α-methylbenzylamine a) after neutralization and b) after one crystallization from *n*-hexane.



Scheme 6. Synthesis of diastereomeric phospholanes **1a** and *P*-oxides **1b** from enantiopure (+)- or (–)-(4aα,5aβ,9aβ,9bβ)-**2e**. Reagents and conditions: a) $SOCl_2$, $CHCl_3$, reflux; THF, –20 °C, $LiAlH_4$; b) air, *i*PrOH.

zation at the P atom again took place. DFT calculations indicated only a very small energy difference of 0.16 kcal mol^{-1} between both secondary phosphanes.[29]

Controlled oxidation of the diastereomeric phospholanes **1a** by air[30] gave the diastereomeric phosphane oxides **1b** in quantitative yield. Remarkably, the mixture of phosphane oxides **1b** is not stable in air, and it oxidizes into the corresponding phosphinic acid **2e** within a few days.

As expected, exchange of the protons at the phosphorus atom in compounds **1a** and **1b** by deuterium occurs in deuterated MeOH (Figure 5).

Both secondary phosphanes and phosphane oxides are interesting compounds for transition metal catalysis. The potential of secondary phosphanes in Rh-catalyzed enantioselective hydrogenation has been shown by Helmchen et al.[31] Secondary phosphane oxides (SPOs) such as **1b** can tautomerize to phosphinous acids and subsequently coordinate to a metal center, therefore the term preligand was coined.[32] We were furthermore interested in investigating the effect of heteroligand Rh complexes on enantioselective hydrogenation. From the pioneering work of Reetz and Feringa/de Vries it is known that mixed-ligand complexes can sometimes provide higher enantioselectivities than homoligand catalysts.[33]

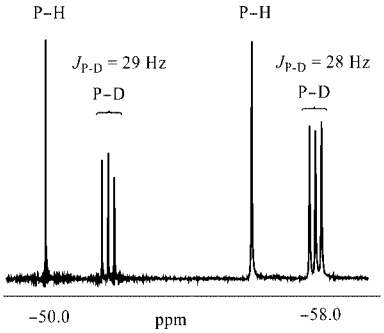
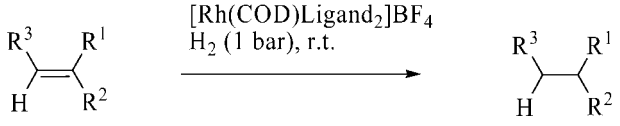


Figure 5. $^{31}P\{^1H\}$ NMR spectrum of the diastereomeric phospholanes **1a** after treatment with [D_4]methanol for 0.5 h; significant amounts of P–H are transformed into P–D.

Cationic Rh^I complexes for the hydrogenation experiments were synthesized in situ by reaction of two equivalents of the ligands **1a** or **1b** [from enantiopure (+)- or (–)-**2e**] with $[Rh(COD)_2]BF_4$. The ^{31}P NMR spectrum of the reaction of $[Rh(COD)_2]BF_4$ with preligand **1b** is depicted in Figure 6. It confirms that interconversion of the phosphane oxides into phosphinites by tautomerism has occurred. Since two diastereomers of **1b** were used in the reaction,

Table 2. Enantioselective hydrogenations with $[Rh(COD)(ligand)_2]BF_4$.[a]



Run	Ligands[b]	R^1	R^2	R^3	Conv. [%]	Solvent	*ee* [%][c]
1	**1a** [(+)-**2e**]	COOMe	CH_2COOMe	H	100	CH_2Cl_2	45 (*R*)[d]
2	**1a** [(+)-**2e**]	COOMe	CH_2COOMe	H	100	CH_3OH	52 (*R*)[d]
3	**1b** [(+)-**2e**]	COOMe	CH_2COOMe	H	100	CH_2Cl_2	79 (*R*)[d]
4	**1b** [(+)-**2e**]	COOMe	CH_2COOMe	H	100	CH_3OH	25 (*R*)[d]
5	**1b** [(–)-**2e**]	COOMe	CH_2COOMe	H	100	CH_2Cl_2	78 (*S*)[d]
6	**1b** [(–)-**2e**]	COOMe	CH_2COOMe	H	100	CH_3OH	9 (*S*)[d]
7	**1a** [(+)-**2e**]	COOMe	NHAc	Ph	100	CH_2Cl_2	23 (*S*)[e]
8	**1a** [(+)-**2e**]	COOMe	NHAc	Ph	100	CH_3OH	61 (*S*)[e]
9	**1b** [(+)-**2e**]	COOMe	NHAc	Ph	100	CH_2Cl_2	44 (*R*)[e]
10	**1b** [(+)-**2e**]	COOMe	NHAc	Ph	100	CH_3OH	9 (*R*)[e]
11	**1b** [(–)-**2e**]	COOMe	NHAc	Ph	100	CH_2Cl_2	30 (*S*)[e]

[a] Conditions: in situ hydrogenation, $[Rh(COD)_2]BF_4$/ligand/substrate = 1:2:100 (0.01:0.020:1.0 mmol) at 25.0 °C, 4 h, 1.0 atm overall pressure over the solution. [b] The origin of the ligand is given in parentheses. [c] Measured after consumption of the calculated amount of H_2. [d] Determined by GC, 25 m Lipodex E, 80 °C. [e] Determined by GC, 25 m Lipodex E, 145 °C.

two bis(homo-ligand) [d, $^1J_{P,Rh}$ = 169 Hz] and one hetero-ligand complex [dq, $^1J_{P,Rh}$ = 169, $^2J_{(P,P)}$ = 20 Hz] are formed.

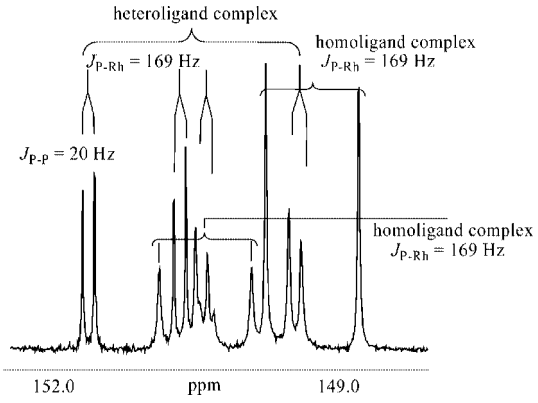


Figure 6. $^{31}P\{^1H\}$ NMR spectrum of the products of the reaction of $[Rh(COD)_2]BF_4$ with diastereomeric phosphane oxide preligand **1b**.

The results of the hydrogenation of the benchmark substrates methyl α-(*Z*)-acetylamino cinnamate and dimethyl itaconate are listed in Table 2.

The new complexes show varying enantiodiscriminatory abilities for the olefins investigated. Surprisingly, the best result was obtained with a mixture of diastereomeric phosphane oxides **1b** as preligands in CH_2Cl_2 (79% *ee*, run 3).

Conclusions

Heterogeneous hydrogenation of 5-oxo-5*H*-5λ^5-dibenzophosphol-5-ol (**3**) gives exclusively the *meso* isomer (4aβ,5aβ,9aβ,9bβ)-5-oxododecahydro-5λ^5-dibenzophosphol-5-ol (**2a**). The geometry of the product was determined by X-ray crystallography. Hydrogenation of (4aβ,5aβ)-5-oxo-2,3,4,4a,5,5a,6,7,8,9-decahydro-1*H*-5λ^5-dibenzophosphol-5-ol (**11**), which is easily available starting from cyclohexanone, has also been found to be an alternative route to **2a**. Base-catalyzed epimerization of **2a** leads to the chiral isomer (4aβ,5aβ,9aβ,9bβ)-5-oxododecahydro-5λ^5-dibenzophosphol-5-ol (**2e**). X-ray structural analysis confirmed the geometrical relationships in the molecule. Resolution of these racemic phosphinic acids by treatment with (*R*)-(+)- and (*S*)-(–)-*N*-benzyl-α-methylbenzylamine, respectively, gave enantiopure (+)- and (–)-**2e**. Subsequent reduction afforded the diastereomeric phospholanes (4aα,5*R*/*S*,5aβ,9aβ,9bβ)-dodecahydrodibenzophosphole (**1a**), which, in turn, were selectively oxidized to the phosphane oxides (4aα,5*R*/*S*,5aβ,9aβ,9bβ)-5-oxododecahydro-5λ^5-dibenzophosphol-5-ol (**1b**). The mixtures of diastereomeric secondary phosphanes **1a** and phosphane oxides **1b** were used as ligands and preligands, respectively, in the Rh-catalyzed enantioselective hydrogenation of benchmark substrates, where up to 79% *ee* can be achieved.

Experimental Sections

General: All reagents, unless otherwise mentioned, were purchased from commercial sources and used without additional purification. Solvents were dried and freshly distilled under argon before use. Ru/Al_2O_3 (5%) was purchased from Degussa AG (G, 204 R/D 5%). All reactions involving phosphanes were performed under argon using standard Schlenk techniques. Melting points are corrected. The optical rotations were measured on a "gyromat-HP" instrument (Fa. Dr. Kernchen). NMR spectra were recorded at the following frequencies: 400.13 (^{1}H), 100.63 (^{13}C), 161.98 MHz (^{31}P). Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in ppm relative to TMS as an internal standard. Chemical shifts of ^{31}P NMR spectra are referred to H_3PO_4 as an external standard. Elemental analyses were performed with a LEGO CHNS-932. Mass spectra were recorded on an AMD 402 spectrometer.

(4aβ,5aβ,9aβ,9bβ)-5-Oxododecahydro-5λ^5-dibenzophosphol-5-ol (2a): 5-Oxo-5*H*-5λ^5-dibenzophosphol-5-ol (**3**; 3.00 g, 13.8 mmol) in CH_3OH (30 mL) was hydrogenated with 5% Ru/Al_2O_3 (9.00 g) at 50 °C and 50 bar initial H_2 pressure for 7 h. The catalyst was then filtered off and washed with ethanol. The filtrate was concentrated to dryness under reduced pressure and the resulting solid was crystallized from methanol/water to give **2a** as colorless crystals. Yield: 2.92 g (92%); m.p. 152–153.5 °C. ^{1}H NMR ($CDCl_3$): δ = 1.22–2.11 (m, 20 H), 9.96 (s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.5–23.8 (CH_2), 24.4 (CH_2), 27.3 (CH_2), 36.8 (CH), 37.7 (CH), 40.5 (CH), 40.7 (CH) ppm. ^{31}P NMR ($CDCl_3$): δ = 82.2 (s) ppm. MS (70 eV, EI): *m*/*z* (%) 229 (23) [M^+ + H], 228 (53) [M^+], 199 (13), 173 (34), 146 (40), 82 (100), 81 (59). HRMS ($C_{12}H_{20}O_2P$, M = 228.27): calcd. 228.12791; found 228.12952.

(4aα,5aβ,9aβ,9bβ)-5-Oxododecahydro-5λ^5-dibenzophosphol-5-ol (2e): A solution of 1.8 M LDA (45.5 mL, 81.9 mmol) was added dropwise, whilst stirring, to a solution of **2a** (6.24 g, 27.3 mmol) in THF (350 mL) at –20 °C. The reaction mixture was warmed up to room temperature, then refluxed for 4 h. Afterwards, the solution was cooled to 0 °C, aqueous HCl (2 N, 280 mL) was added slowly, and the product was extracted with diethyl ether. The organic layer was washed with brine (3 × 100 mL) and the organic solvent removed under reduced pressure. The oily residue was crystallized from Et_2O to give the product **2e** as colorless crystals. Yield: 4.40 g (71%); m.p. 148.5–149.5 °C. ^{1}H NMR ($CDCl_3$): δ = 1.03–2.18 (m, 20 H), 12.2 (s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.8 (CH_2), 23.1 (CH_2), 24.1 (CH_2), 24.9 (CH_2), 25.4 (CH_2), 26.5 (CH_2), 26.8 (CH_2), 29.5 (CH_2), 38.3 (d, $^1J_{C,P}$ = 80Hz, CH), 39.2 (d, $^1J_{C,P}$ = 83 Hz, CH), 40.2 (d, $^2J_{C,P}$ = 10 Hz, CH), 45.3 (d, $^2J_{C,P}$ = 12 Hz, CH) ppm. ^{31}P NMR ($CDCl_3$): δ = 76.8 (s) ppm. MS (70 eV, EI): *m*/*z* (%) 227 (100) [M^+ – H], 226 (19) [M^+ – 2H], 198 (20), 172 (56), 147 (21), 145 (84).

Resolution of (4aα,5aβ,9aβ,9bβ)-5-Oxododecahydro-5λ^5-dibenzophosphol-5-ol (2e): (*R*)-(+)-*N*-Benzyl-α-methylbenzylamine (3.10 g, 14.0 mmol) was added, whilst stirring, to a mixture of **2e** (3.20 g, 14.0 mmol) in $CHCl_3$ (30 mL) at room temperature. The solution was stirred for 2 h and then the solvent was evaporated to give the diastereomeric salts. The oily residue was crystallized from hexane (50 mL) to give the product as colorless crystals. Yield: (3.10 g, 49%), enantiopurity 90% (^{31}P NMR: major δ = 62.2 (s), minor δ = 62.7 (s)]. The product was washed with pentane (3 × 10 mL) to give the diastereomerically pure salt (confirmed by NMR spectroscopy). Yield: 2.22 g (35.3%). $[\alpha]_D^{25}$ = 19.5 (*c* = 0.6, $CHCl_3$). ^{13}C NMR ($CDCl_3$): δ = 23.2 (s, CH_2), 23.6 (d, CH_2), 24.2 (s, CH_2), 25.4 (s, CH_2), 26.1 (d, CH_2), 26.7 (d, CH_2), 27.1 (d, CH_2), 29.7 (d, CH_2), 38.5 (s, CH), 39.4 (d, CH), 40.3 (m, CH), 45.6 (d, CH), 57.4 (CH) ppm. ^{31}P NMR ($CDCl_3$): δ = 62.2 (s) ppm. The mother

liquor, enriched with the opposite enantiomeric phosphinic acid **2e**, was used for another resolution step with (*S*)-(–)-*N*-benzyl-α-methylbenzylamine to give (+)-**2e**.

(–)-(4aα,5aβ,9aβ,9bβ)-5-Oxododecahydro-5λ^5-dibenzophosphol-5-ol [(–)-2e]: An excess of aqueous NaOH (2 M) was added to a solution of the diastereomerically pure salt (2.22 g, 4.9 mmol) in $CHCl_3$ (20 mL). The solution was stirred at room temperature for 30 min. The organic layer was then separated and washed with aqueous NaOH solution (2 M, 2×20 mL). The basic water layer was then acidified with an excess of aqueous HCl solution (2 M) and the compound extracted with CH_2Cl_2 (3×50 mL). The organic solvent was removed under reduced pressure to give the pure product. Yield: 0.93 g (58%); m.p. 173.5–174.5 °C. $[a]_D^{25}$ = –21.0 (*c* = 0.6, MeOH).

(+)-(4aα,5aβ,9aβ,9bβ)-5-Oxododecahydro-5λ^5-dibenzophosphol-5-ol [(+)-2e]: Yield: 1.44 g (90%); m.p. 173–174 °C, $[a]_D^{25}$ = 18.0 (*c* = 0.6, MeOH).

Dimethyl-(4aβ,5aβ)-(5-oxo-2,3,4,4a,5,5a,6,7,8,9-decahydro-1*H*-5λ^5-dibenzophosphol-5-yl)amine (10): Me_2NPCl_2 (16.4 g, 0.113 mol) was added to a suspension of $AlCl_3$ (14.1 g, 0.106 mol) in CH_2Cl_2 (150 mL). After the addition the mixture was stirred for 40 min until complete dissolution had occurred. A solution of dien **9** (16.7 g, 0.103 mol) in CH_2Cl_2 (100 mL) was added dropwise to this solution in an ice bath. The resulting red solution was stirred at 0 °C for 8 h and at room temperature overnight. The mixture was slowly poured into ice (200 mL) and stirred with ice/water for 1 h. The crude product was obtained by extraction with dichloromethane and evaporation of the organic solvent. This oily material was hydrolyzed to give the phospholanic acid **1a**. Yield: 23.07 g (99%). ^{1}H NMR ($CDCl_3$): δ = 1.03–2.18 (m, 20 H), 2.73 (d, *J* = 8 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 24.0 (d, $J_{P,C}$ = 6 Hz, CH_2), 25.5 (s, CH_2), 25.8 (d, $J_{P,C}$ = 12 Hz, CH_2), 26.7 (d, $J_{P,C}$ = 10 Hz, CH_2), 37.9 (d, $J_{P,C}$ = 2 Hz, CH_3), 42.1 (d, $J_{C,P}$ = 82 Hz, CH), 131.2 (d, $J_{C,P}$ = 15 Hz, C=) ppm. ^{31}P NMR ($CDCl_3$): δ = 69.5 (s) ppm. MS (70 eV, EI): *m*/*z* (%) 253 (20) [M$^+$], 163 (65) [M$^+$ – $HOPNMe_2$], 94 (100), 92 (46), 91 (73).

(4aβ,5aβ)-5-Oxo-2,3,4,4a,5,5a,6,7,8,9-decahydro-1*H*-5λ^5-dibenzophosphol-5-ol (11): An aqueous solution of HCl (6 M) was added to a solution of the amide **10** (6.5 g, 25.8 mol) in EtOH (50 mL) and the mixture was stirred overnight. The mixture was then made alkaline by careful addition of an aqueous NaOH solution (4 M) and extracted with CH_2Cl_2 (2×40 mL). The aqueous layer was acidified with concentrated HCl. The crude product was obtained by extraction with dichloromethane (5×70 mL) and evaporation of the organic solvent. An analytically pure sample was obtained by recrystallization from EtOH. Yield: 5.70 g (86%); m.p. 172.5–173.5 °C. ^{1}H NMR ($CDCl_3$): δ = 1.10–2.72 (m, 18 H), 9.17 (s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 26.2 (d, $J_{C,P}$ = 13 Hz, CH_2), 26.7 (s, CH_2), 27.0 (d, $J_{C,P}$ = 5 Hz, CH_2), 27.3 (d, $J_{C,P}$ = 10 Hz, CH_2), 41.9 (d, $J_{C,P}$ = 95 Hz, CH), 131.2 (d, $J_{C,P}$ = 15 Hz, C=) ppm. ^{31}P NMR ($CDCl_3$): δ = 73.8 (s) ppm. MS (70 eV, EI): *m*/*z* (%) 226 (20) [M$^+$], 162 (100) [M$^+$ – HPO_2]. $C_{12}H_{19}O_2P$ (226.25) calcd. C 63.70, H 8.46, P 13.69; found C 63.13, H 8.57, P 14.03.

(4aα,5*R*/*S*,5aβ,9aβ,9bβ)-Dodecahydrodibenzophosphole (1a): $SOCl_2$ (6.19 g, 5.2 mmol) was added dropwise to a solution of optically pure **2e** (2.37 g, 10.4 mmol) in $CHCl_3$ (25 mL) and the mixture was refluxed for 1 h. The solvent was removed under reduced pressure and the residue was dissolved in THF (20 mL). $LiAlH_4$ (0.79 g, 20.8 mmol) was added carefully to the resulting solution at –20 °C and the mixture was stirred for 1 h at the same temperature. Aqueous NaOH (7%, 5 mL) was then added to the mixture. Extraction with *n*-hexane and filtration, followed by concentration in vacuo, yielded the product **1a** as a colorless oil (two diastereomers in a ratio of 1:1). Yield: 1.63 g (80%). ^{1}H NMR (C_6D_6): δ = 0.94–2.28 (m, 18 H), 2.45 (m, 1 H, CH), 2.92 (m, 1 H, CH), 3.05 (dt, $^1J_{P,H}$ = 183, $^2J_{H,H}$ = 12 Hz, 1 H, P-H of one diastereomer), 3.55 (dt, $^1J_{P,H}$ = 181, $^2J_{H,H}$ = 11 Hz,1 H, P-H of other diastereomer) ppm. ^{13}C NMR (C_6D_6): δ = 21.0, 22.2–22.4 (CH_2), 24.6 (CH_2), 25.3–25.5 (CH_2), 26.8–26.9 (CH_2), 28.2–29.0 (CH_2), 32.1 (d, $J_{C,P}$ = 8 Hz, CH), 32.6–33.3 (CH_2), 35.3 (d, $J_{C,P}$ = 7 Hz, CH), 35.5 (d, $J_{C,P}$ = 10 Hz, CH), 38.9 (d, $J_{C,P}$ = 8 Hz, CH), 45.7 (CH), 46.1 (d, $J_{C,P}$ = 4 Hz, CH), 55.9 (CH), 56.7 (d, $J_{C,P}$ = 5 Hz; CH) ppm. ^{31}P NMR (C_6D_6): δ = –47.3 (s, one diastereomer), δ = –55.9 (s, other diastereomer). Treatment of the phosphanes **1a** with selenium in $CDCl_3$ at room temperature afforded the corresponding phosphane selenides, which were characterized in the ^{31}P NMR spectrum by a triplet at δ = 12.4, ($J_{P,Se}$ = 704 Hz) and another at δ = 23.1 ($J_{P,Se}$ = 710 Hz). The diastereomers were purified as their BH_3 adducts, which were prepared by addition of a small excess of a solution of BH_3-dimethylsulfide complex in toluene to the phosphanes.

First Diastereomer: ^{1}H NMR ($CDCl_3$): δ = 0.05–0.82 (br. m, 3 H, BH_3), 0.88–2.21 (m, 17 H), 2.25 (m, 2 H), 4.29 (m, 1 H, CH), 5.16 (m, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.0 (CH_2), 23.8 (CH_2), 24.0 (CH_2), 24.9 (CH_2), 26.3 (CH_2), 27.0–27.4 (CH_2), 29.0 (CH_2) 31.1 (d, $^1J_{C,P}$ = 33 Hz, CH), 38.7 (d, $^1J_{C,P}$ = 35 Hz, CH), 44.1 (CH), 51.5 (CH) ppm. ^{31}P NMR ($CDCl_3$): δ = –7.7 (br. m) ppm.

Second Diastereomer: ^{1}H NMR ($CDCl_3$): δ = 0.05–0.82 (br. m, 3 H, BH_3), 0.88–2.26 (m, 17 H), 2.67 (m, 2 H), 3.93 (m, 1 H, CH), 4.81 (m, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.4 (CH_2), 24.5–24.8 (CH_2), 26.5 (CH_2), 27.3 (CH_2), 28.6 (CH_2), 29.7 (m, CH_2), 33.2 (d, $^1J_{C,P}$ = 35 Hz, CH), 37.7 (d, $^1J_{C,P}$ = 35 Hz, CH), 43.7 (CH), 51.3 (CH) ppm. ^{31}P NMR ($CDCl_3$): δ = 11.8 (br. m) ppm. MS (70 eV, EI): *m*/*z* (%) 209 (6) [M$^+$ – H], 208 (8) [M$^+$ – 2H], 196 (100) [M$^+$ – BH_3], 154 (14). $C_{12}H_{24}BP$ (210.10): calcd. C 68.60, H 11.51, P 14.74; found C 68.21, H 11.18, P 14.43.

Liberation of the phosphanes from their BH_3 adducts was carried out by treatment with DABCO in THF at room temperature and subsequent chromatography on a short column of celite.

(4aα,5*R*/*S*,5aβ,9aβ,9bβ)-Dodecahydrodibenzophosphole 5-Oxide (1b): Phospholane **1a** (0.39 g, 2.0 mmol) was dissolved in *i*PrOH (10 mL) and stirred for 1 h in air. Evaporation of the solvent yielded the product **1b** as a colorless oil (two diastereomers in a ratio of 1:1). Yield: 0.42 g (100%).

First Diastereomer: ^{1}H NMR ($CDCl_3$): δ = 1.12–2.41 (m, 20 H), 7.02 (d, $^1J_{H,P}$ = 445 Hz, PH) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.2 (m, CH_2), 24.5–25.0 (m, CH_2), 24.4 (m, CH_2), 27.9 (m, CH_2), 29.1 (CH_2), 36.9 (d, $^1J_{C,P}$ = 66 Hz, CH), 38.5 (d, $^1J_{C,P}$ = 67 Hz, CH), 40.9 (d, $^2J_{C,P}$ = 8 Hz, CH), 41.8 (d, $^2J_{C,P}$ = 5 Hz, CH) ppm. ^{31}P NMR ($CDCl_3$): δ = 48.0 (s) ppm.

Second Diastereomer: ^{1}H NMR ($CDCl_3$): δ = 1.12–2.41 (m, 20 H), 7.53 (d, $J_{P,H}$ = 445 Hz, PH) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.2 (m, CH_2), 24.5–25.0 (m, CH_2), 24.4 (m, CH_2), 27.9 (m, CH_2), 29.1 (CH_2), 42.6 (d, $^1J_{C,P}$ = 62 Hz, CH), 43.3 (d, $^1J_{C,P}$ = 63 Hz, CH), 44.8 (d, $^2J_{C,P}$ = 11 Hz, CH), 48.8 (d, $^2J_{C,P}$ = 6 Hz, CH) ppm. ^{31}P NMR ($CDCl_3$): δ = 55.1 (s) ppm. MS (70 eV, EI): *m*/*z* (%) 212 (100) [M$^+$], 211 (32) [M$^+$ – H].

Preparation of [Rh(COD)(ligand)$_2$]BF$_4$: A solution of the ligand (1.20 mmol) in CH_2Cl_2 (5 mL) was added slowly to a solution of $[Rh(COD)_2]BF_4$ (0.24 g, 0.60 mmol) in CH_2Cl_2 (5 mL) at –40 °C. The mixture was stirred overnight, while warming up to room temperature. The clear reddish brown solution was used directly for the hydrogenation.

Computational Details: All calculations were carried out with the Gaussian 03 program.[34] All structures were first optimized at the B3LYP level[35] of density functional theory with the 6-31G(d) basis set,[36] and the optimized structures on the potential energy surface (PES) were characterized as energy minima (without imaginary frequencies) by frequency calculation at the same level of theory [B3LYP/6-31(d)].[36] Frequency calculations also provided the zero-point energies (ZPE) and thermal energies as well as entropies at the given temperature (T = 298.15 K), all these data were used for the thermodynamic parameters. Single-point energies were calculated at the B3LYP/6-311+G(d,p) level of theory on the B3LYP/6-31G(d) optimized structures. The relative energies for discussion and interpretation (rate constant of epimerization) are the Gibbs free energies ($\Delta G = \Delta H - T\Delta S$), which were calculated at the B3LYP/6-311+G(d,p) level including the B3LYP/6-31G(d) thermal corrections at T = 298.15 K. The computed total Gibbs free energies are –961.71083 (**2a**), –961.70915 (**2b**), and –961.71644 (**2e**).

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