Chiral Oxo- and Oxy-Functionalized Diphosphane Ligands Derived from Camphor for Rhodium(I)-Catalyzed Enantioselective Hydrogenation

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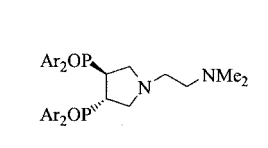
Keywords: Asymmetric synthesis / Camphor / Hydrogenation / Phosphanes / Rhodium

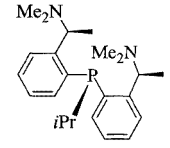
The synthesis of two series of diastereomeric oxo- and oxy-substituted diphosphanes **7a**–**9a** and **7b**–**9b**, as well as an analogous nonfunctionalized diphosphane **17**, was performed starting from (*R*)-camphor. The new diphosphanes were used as ligands in the enantioselective rhodium(I)-catalyzed hydrogenation of functionalized olefins – α- and β-dehydroamino acids and their esters – in order to elucidate the effect of the oxo- and oxy-functional groups. The enantioselectivities, ranging from 2–90% *ee*, and the rates were strongly dependent on the type and relative position of the oxo or oxy substituent in the catalyst. Possible explanations for the effects are given.

Introduction

The vast majority of ligands used in Rh-, Ir- and Ru-based catalysts for enantioselective hydrogenation and many other reactions are chiral diphosphanes,[1] which usually possess no additional functional groups.[2] Their stereodifferentiating properties are believed to be caused mainly by steric repulsion. In contrast, some very efficient and selective natural catalysts − enzymes − are highly functionalized. Attractive interactions between enzyme and substrate, primarily hydrogen bonds and electrostatic interactions, are responsible for their amazing selectivity and reactivity.[3] There are only a few examples of homogeneous hydrogenation catalysts which exploit additional functional groups in ligands to achieve high enantioselectivity. For example, asymmetric catalytic hydrogenation of prochiral dehydroacylamino acids and dehydrodipeptides in the presence of Rh^I complexes bearing ligands **1** and **2** was suggested to proceed with high enantioselectivity because of electrostatic attraction between carboxylate ion and the protonated amino group in the ligands.[4]



1, Ar = *p*-$MeOC_6H_4$



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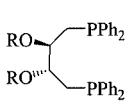

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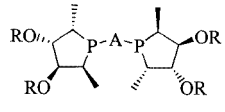

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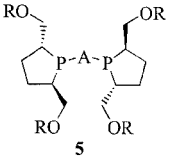

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(R = H, Alk, A = 1,2-phenylene, 1,2-ethylene)

The presence of hydroxy and alkoxy groups in diphosphane ligands such as **3**,[5] **4** (RoPHOS)[6] and **5** (BASPHOS)[7] were shown to influence − dramatically in some cases − the selectivity and activity of the Rh^I catalysts. Mechanistic studies provided evidence that these effects might be caused by secondary interactions of the hydroxy groups with the metal centre or the substrate.[8] In all cases the effects were strongly dependent on the spatial orientations of the additional functional group(s) and the substrate employed.

It is obvious that the synthesis of functionalized ligands and their employment in catalysis not only provides a great academic challenge but also has unexplored industrial potential. Up to now, however, the design of functionalized diphosphane ligands has received neither theoretical nor sufficient empirical support, and so the synthesis of series of structurally related ligands and their subsequent screening in metal-catalyzed asymmetric reactions is currently the most practical approach to find efficient catalysts and elucidate the role of the additional functionality.

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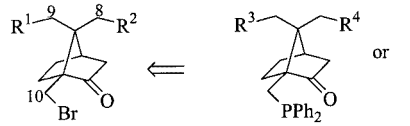
This study was directed toward the synthesis of a set of isomeric chiral chelating diphosphane ligands bearing different oxo- and oxy-functionalities. Hydroxy, oxo and acetal groups were chosen, representing functional groups with different hydrogen bond donor and acceptor properties. The new chiral diphosphanes were prepared from camphor and subsequently tested in the Rh^{I}-catalyzed enantioselective hydrogenation of functionalized olefins of academic and industrial relevance.

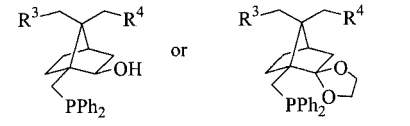
Results and Discussion

Synthesis of New Ligands

The rich chemistry of camphor[9] and its availability from the "chiral pool" prompted us to use it as a starting material for the synthesis of new diphosphanes. Although camphor is widely used in syntheses of chiral auxiliaries,[10] and in total syntheses of natural compounds,[11,12] its potential in homogeneous catalysis is largely unexplored, as already pointed out in a recent paper.[13] Camphor can easily be converted into many mono- and dibromo-substituted derivatives, which are useful intermediates in ligand synthesis.[14] Especially attractive for the synthesis of functionalized diphosphanes are 9,10- and 8,10-dibromocamphors **6a** and **6b**, available from camphor by stereospecific bromination/rearrangement reaction sequences.[15] Thus, the bromomethyl groups in **6a** and **6b** can be advantageously used for nucleophilic substitution with phosphorus nucleophiles to obtain **7a** and **7b**, whereas the carbonyl group can be further converted into, for example, the hydroxy group by reduction, giving rise to hydroxy derivative of the diphosphanes **8a** and **8b**, or transformed into an acetal group (**9a**, **9b**).[16]

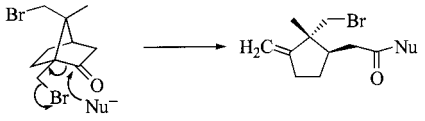


6a (R^1 = Br, R^2 = H) **7a** (R^3 = PPh_2, R^4 = H)
6b (R^1 = H, R^2 = Br) **7b** (R^3 = H, R^4 = PPh_2)



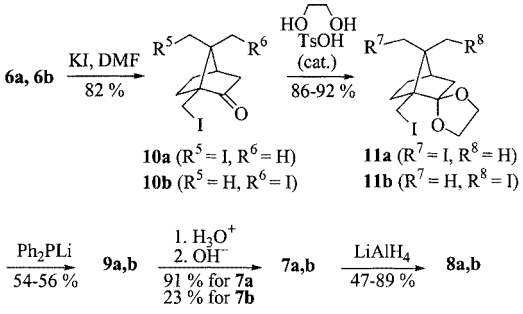
8a (R^3 = PPh_2, R^4 = H) **9a** (R^3 = PPh_2, R^4 = H)
8b (R^3 = H, R^4 = PPh_2) **9b** (R^3 = H, R^4 = PPh_2)

On the way to the desired ligands we were confronted with two major obstacles. The first was the Grob-type fragmentation shown for 9,10-dibromocamphor in Scheme 1. This fragmentation is a well-known reaction of α,α-disubstituted β-halocarbonyl compounds.[17] This forced us to use carbonyl group protection in the early stages of the synthesis.



Scheme 1

Another problem is the need to use rather drastic conditions to perform nucleophilic substitution of the bromo substituents at the neopentyl-like positions in **6a** and **6b**. This results in side reactions caused by the basic nature of the nucleophilic phosphide reagent, even if the carbonyl group is protected. To solve this problem, both isomeric dibromocamphors were transformed into the corresponding diiodocamphors **10a** and **10b** (Scheme 2). The weakly basic and highly nucleophilic iodide ion smoothly substitutes bromide in the dibromocamphors. On the other hand, the diiodocamphors, possessing good leaving groups, are much more reactive than the bromo derivatives in reactions with phosphides. With the above considerations in mind, the following syntheses of the target functionalized ligands (**7a**, **7b**; **8a**, **8b**; **9a**, **9b**) were performed.



10a (R^5 = I, R^6 = H) **11a** (R^7 = I, R^8 = H)
10b (R^5 = H, R^6 = I) **11b** (R^7 = H, R^8 = I)

Scheme 2

The configurations at C-2 in the hydroxy derivatives **8a** and **8b** were confirmed by NOE experiments (Figure 1).

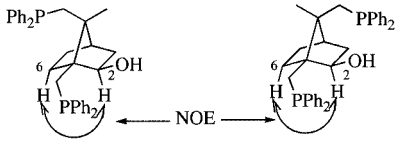
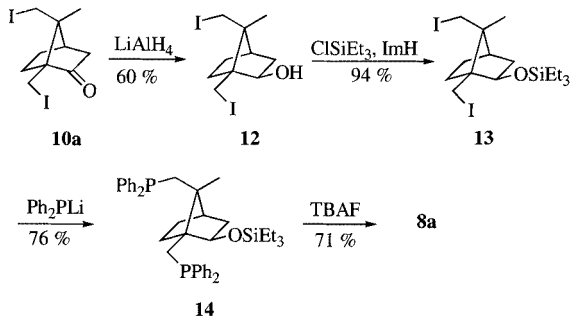


Figure 1. Strong positive NOEs between 2-H and *endo*-6-H

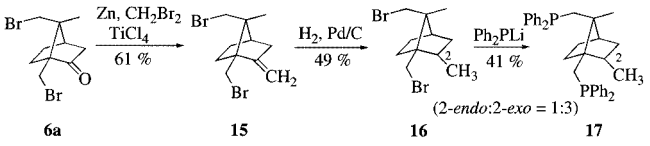
For the synthesis of the hydroxy derivative of the diphosphane **8a** we also used an alternative strategy, which involved reduction of the carbonyl group in 9,10-diiodocamphor **10a** and protection of the formed hydroxy group prior to the nucleophilic substitution. As in the case of the oxo derivatives **7a** and **7b**, reduction of **10a** by $LiAlH_4$ proceeded with satisfactory *exo* diastereoselectivity. The hydroxy group in **12** was then protected by $SiEt_3$ as shown recently for 10-iodoisoborneol.[13] Subsequent treatment

with Ph_2PLi and deprotection yielded the hydroxy derivative of the diphosphane **8a** (Scheme 3).



Scheme 3

For the synthesis of the analogous unfunctionalized ligands we planned to convert the carbonyl groups in the dibromocamphors into $C{=}CH_2$ groups by use of a "Ti^0" reagent,[18] followed by hydrogenation of the double bond and subsequent treatment with Ph_2PLi. This was achieved only when starting from the 9,10-dibromocamphor **6a** (Scheme 4). Ligand **17** was obtained as a mixture of *endo* and *exo* isomers in a ratio of 1:3 (the configurations at C-2 in both isomers were verified by NOE experiments). Treatment of the titanium-based reagent with the 8,10-dibromocamphor gave a complex mixture of unidentified products.

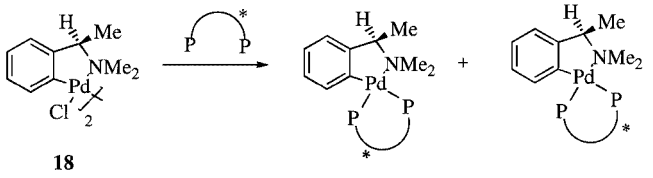


Scheme 4

Optical Purities of Ligands

The optical purity of commercially available natural camphor is not perfect: 99.2−99.5% *ee* for (*R*)-camphor and 78.6−92.8% *ee* for (*S*)-camphor.[19] In most cases, high optical purity of ligands is desired for achievement of maximum enantioselectivity in catalytic reactions. The optical purities of some diphosphanes prepared both from 9,10- and 8,10-dibromocamphors were therefore determined.

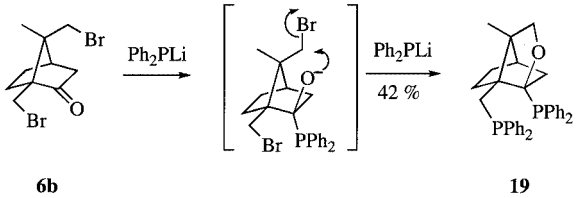
The analysis was carried out by $^{31}P\{H\}$ NMR spectroscopy in the presence of (−)-bis(μ-chloro)bis[(*R*)-dimethyl(α-methylbenzyl)aminato-C^2,N]dipalladium(II) (**18**). This method has been widely used for analysis of the optical purities of chelating diphosphanes.[20] In the case of C_1-symmetrical diphosphane ligands as studied in this work, each enantiomer of a ligand forms two complexes with **18** (Scheme 5). Usually all four complexes formed from a mixture of enantiomers have different $^{31}P\{H\}$ NMR shifts (singlets or pairs of doublets). The optical purity can be determined by integration of the signals.



Scheme 5

In the 9,10-$(PPh_2)_2$-substituted series we analyzed the optical purity of ligand **7a**, prepared for the analysis in both enantiomeric forms, starting from (*R*)- and (*S*)-camphor. In the presence of 1 equiv. of **18**, each enantiomer of **7a** gave a $^{31}P\{H\}$ NMR spectrum containing two singlets with integral intensity ratio of approximately 1:1, corresponding to two palladium complexes. ^{31}P-^{31}P coupling was not observed, probably due to rapid site-site exchange of the ligands. A similar effect has been reported for (*R*,*R*)-DIOP.[20] For each enantiomer of **7a**, the signals characterizing the other enantiomer were below the detection limits, which establishes the high (> 98% *ee*) optical purity of the ligand. It is surprising that the optical purity of the ligand prepared from (*S*)-camphor turned out to be higher than that of the (*S*)-camphor itself. This is presumably due to the recrystallization of the intermediate bromocamphors during the synthesis of the ligand.

The analysis of the 8,10-$(PPh_2)_2$-substituted ligands was complicated by the additional coordination of the oxo- and oxy-functionality with Pd. We therefore prepared the oxatricyclic ligand **19**, as previously described from 8,10-dibromocamphor, again in both enantiomeric forms (Scheme 6).[14] No crystallization was used during the synthesis, in order to avoid enantiomer enrichment. The optical purity of **19** was determined without any problems with the help of the palladium complex **18**. Thus, the $^{31}P\{H\}$ NMR spectrum of this compound in the presence of 0.5 equiv. of **18** revealed two pairs of doublets [δ = 36.3 and 8.9 ppm, $J(^{31}P$-$^{31}P)$ = 54.1 Hz, and δ = 34.4 and 11.9 ppm, $J(^{31}P$-$^{31}P)$ = 51.3 Hz, in a ratio of 1:0.86], which correspond to two complexes formed between the enantiomerically pure ligand and the palladium reagent. Signals corresponding to the complexes derived from the other enantiomer of **19** [δ = 33.8 and 10.6 ppm, $J(^{31}P$-$^{31}P)$ = 54.1 Hz, and δ = 29.0 and 17.4 ppm, $J(^{31}P$-$^{31}P)$ = 54.1 Hz] had overall integral intensities of less than 2%.



Scheme 6

We confirmed the high optical purity of **19** by an independent method. The enantiomeric diphosphanes were oxidized to the corresponding phosphane oxides with H_2O_2.

HPLC analysis of the phosphane oxides on a chiral column showed that both enantiomers were of high optical purity. We were unable to detect the opposite enantiomer in each case (> 98% *ee*).

Since the analysis of **19** unambiguously showed its high optical purity, this should also hold for ligands **7b**−**9b**. It is highly unlikely that any racemization would happen during the synthesis of 8,10-diiodocamphor, acetal formation, nucleophilic substitution with Ph_2PLi and hydrolysis of the acetal [in fact, it did not happen in the 9,10-$(PPh_2)_2$-substituted series of ligands; see the above analysis of **7a**]. We thus assume that the optical purity of 8,10-$(PPh_2)_2$-substituted ligands should be similarly high as that of the ligand **19**.

Synthesis and Structure of Precatalysts

The new diphosphanes **7a**, **7b**, **8a**, **8b**, **9a**, **9b** and **17** (**L**) were used to prepare Rh^I complexes of the type [Rh(**L**)(COD)]BF_4 by mixing [Rh(acac)(COD)] and the ligand in THF, followed by addition of 1 equiv. of HBF_4. In all cases the crystalline complexes were formed in moderate yields. They were fully characterized by spectroscopic methods. It was found in the case of the nonfunctionalized ligand **17** that crystallization yielded the complex with only the *exo* isomer of the ligand, although a mixture of the *endo* and *exo* isomers had been used for the synthesis.

For Rh^I chelate complexes with diphosphanes of C_1 symmetry there are typically two sets of double doublets in the $^{31}P\{H\}$ NMR spectra. Relevant chemical shifts and coupling constants are listed in Table 1. Resonances in the region between δ = 9 and 16 ppm are typical for phosphorus atoms involved in seven-membered chelate rings with Rh.[21] Interestingly, the signals of the COD methine groups were not visible in the ^1H NMR spectrum of [Rh(**8b**)(COD)]BF_4, whereas the CH_2 groups appeared as two very broad signals. This indicates slow (on the NMR timescale) motion of the COD ligand in the coordination sphere of Rh.[22]

Table 1. $^{31}P\{H\}$ NMR spectroscopic data for complexes [Rh(**L**)(COD)]BF_4 (solvent: CD_3OD)

Ligand (**L**)	δ [ppm]	Δδ [ppm]	$J(^{103}Rh\text{-}^{31}P)$ [Hz]	$J(^{31}P\text{-}^{31}P)$ [Hz]
7a	12.8, 9.3	3.5	142.9	36.1
8a	15.2, 14.3	0.9	142.3	42.5
9a	14.3, 13.5	0.8	142.8	42.1
17	15.6, 14.3	1.3	142.0	43.0
7b	13.2, 3.7	9.5	142.5	32.3
8b	14.9, 5.3	9.6	141.5	31.9
9b	15.6, 5.2	10.4	142.9	33.3

Crystals suitable for X-ray analysis were obtained for the isomeric pair of the precatalysts [Rh(**7b**)(COD)]BF_4 and [Rh(**7a**)(COD)]BF_4 by slow crystallization from methanol. A single-crystal X-ray structural analysis established the structures of the cations, as shown in Figure 2. All Rh−P and Rh−C bond lengths and angles of the examined complexes are closely related to those in other (diphosphane)-rhodium(I) precatalysts.[23]

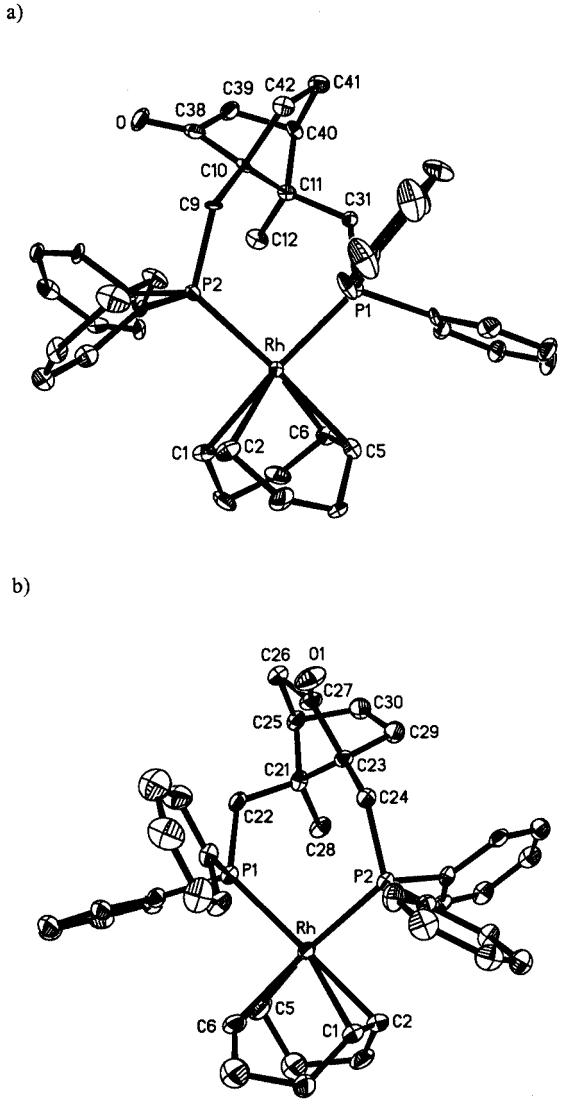


Figure 2. Crystal structures of cations of [Rh(**7a**)(COD)]BF_4 (a) and [Rh(**7b**)(COD)]BF_4 (b); hydrogen atoms are omitted for clarity, the thermal ellipsoids are shown at 30% level of probability; selected bond lengths [Å] and angles [°]: [Rh(COD)(**7a**)]BF_4: Rh−P(1) 2.327(2), Rh−P(2) 2.343(2) P(1)−Rh−P(2) 92.94(9), C(9)−C(10)−C(11)−C(31) 62.57; [Rh(COD)(**7b**)]BF_4: Rh−P(1) 2.3555(15), Rh−P(2) 2.3341(17), P(1)−Rh−P(2) 93.72(7), C(24)−C(23)−C(21)−C(22) 56.53

One particular aspect of the crystal structures, namely the conformation of the seven-membered chelate rings, needs special attention. The C−C−C−C unit in these rings is a part of the rigid camphor skeleton, which fixes this unit in the *synclinal* conformation (the C−C−C−C torsion angle is about 60°). In most (diphosphane)Rh precatalysts used for asymmetric hydrogenation, in which this unit is also fixed by *trans* fusion of a five- and a seven-membered ring (e.g., DIOP and its analogues) this conformation is closer to *anticlinal*, and the C−C−C−C torsion angles are

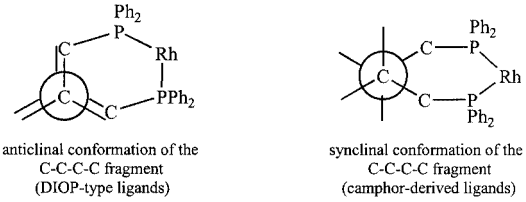


Figure 3. Conformations around a C(4)−C(5) bond of the seven-membered chelate ring in different Rh^I precatalysts

usually more than 60° (Figure 3, see also the caption of Figure 2).[24]

Consequently, unlike most of related (diphosphane)Rh complexes possessing seven-membered chelate rings in twist-chair or boat B_4−B_5 conformations,[25] this ring in complexes [Rh(**7a**)(COD)]BF_4 and [Rh(**7b**)(COD)]BF_4 adopts the boat B_3 conformation (Figure 4, λ-chiral in the former complex and δ-chiral in the latter). As can be seen from Figure 4, the B_3 conformation is characterized by a slightly distorted chiral alternating pseudoaxial-pseudoequatorial arrangement of the *P*-phenyl groups, which expose their *edge* or *face* to the Rh atom depending on whether they are pseudoaxial or pseudoequatorial (*edge-on-face-on* model). As shown in many examples, this arrangement may have a beneficial influence on the degree of enantioselection in the hydrogenation.[26]

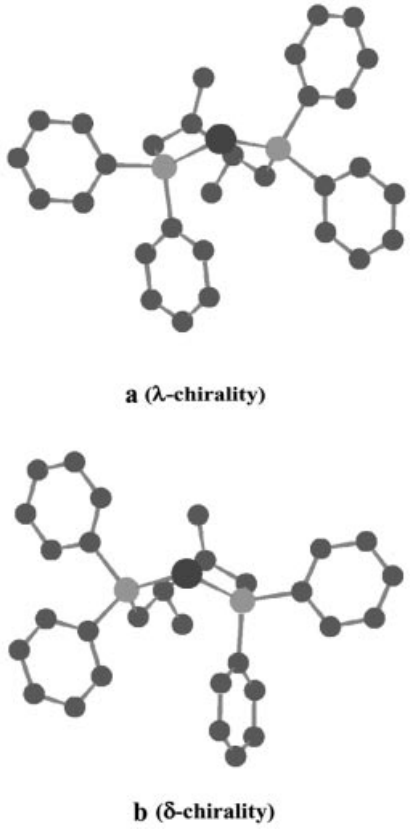
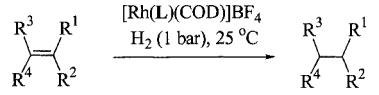


Figure 4. Fragments of the structures of complexes [Rh(**7a**)(COD)]BF_4 (a) and [Rh(**7b**)(COD)]BF_4 (b) showing conformations of the seven-membered rings and position of their substituents − phenyl rings and CH_3 (CH_2) groups of the camphor skeleton; hydrogen atoms are omitted for clarity

Hydrogenation Results

The new precatalysts based on 9,10- and 8,10-$(PPh_2)_2$-substituted ligands were employed for the hydrogenation of (*Z*)-2-acetamidocinnamic acid (AH) and its methyl ester (AMe), as well as of (*Z*)- and (*E*)-3-acetamidoacrylic acids and their methyl esters[27] (Scheme 7). The reactions were performed under identical conditions: at 1 bar pressure of hydrogen, 25 °C, in methanol or dichloromethane, with molar catalyst/substrate ratios of 1:100 or 1:1000.



21, R^1 = COOMe, R^2 = NHAc, R^3 = H, R^4 = Ph
22, R^1 = COOH, R^2 = NHAc, R^3 = H, R^4 = Ph
23, R^1 = COOMe, R^2 = H, R^3 = CH_3, R^4 = NHAc
24, R^1 = COOMe, R^2 = H, R^3 = NHAc, R^4 = CH_3
25, R^1 = COOH, R^2 = H, R^3 = CH_3, R^4 = NHAc
26, R^1 = COOH, R^2 = H, R^3 = NHAc, R^4 = CH_3

Scheme 7

Striking differences between pairs of isomeric catalysts in terms of activity and enantioselectivity were observed. Catalysts derived from ligands **7a**, **8a** and **9a** are highly active and give moderate or good enantioselectivies in the hydrogenation of AH and AMe (Table 2). The hydrogenation proceeded within a few minutes, with enantioselectivities of up to 90% *ee*. A reduction in the catalyst/substrate molar ratio to 1:1000 reduced the rates of the hydrogenation only slightly, and with almost no loss of selectivity. The high enantioselectivity of these catalysts might be explained in terms of the *edge-on-face-on* model discussed above. Chiral alternating (pseudo)axial-(pseudo)equatorial arrangements of the Ph substituents around Rh as found in the crystal structure for one of the precatalysts are likely to be maintained in catalytic intermediates, due to the rigidity of the camphor skeleton, and might have a decisive influence on the stereochemical outcome of the hydrogenation. Similarly high enantioselectivities have previously been achieved with related ligands forming seven-membered chelate rings and showing alternating *edge-to-face* disposition of the *P*-phenyl groups.[28] It should be pointed out, however, that while in most known cases the λ-chiral conformation of the precatalysts produces (*S*) isomers of the α-amino acids,[1] our precatalyst [Rh(**7a**)(COD)]BF_4 has λ-chiral conformation (see Figure 4) but gives (*R*)-amino acids (Table 2). β-Amino acid precursors were also reduced with good *ee*s (up to 82% *ee*). In general, a change in the solvent from methanol to dichloromethane affected the enantioselectivity. In agreement with some literature data,[29] (*Z*) isomers of the β-amino acid precursors were hydrogenated with better selectivity in MeOH, the corresponding (*E*) isomers in CH_2Cl_2. Close inspection of the hydrogenation data for complexes bearing

Table 2. Hydrogenation results of various substrates with complexes Rh[$\mathbf{L^a}$(COD)]BF_4 where $\mathbf{L^a}$ is a ligand of the 9,10-$(PPh_2)_2$-substituted series (**7a**−**9a**, **17**)[a]

Substrate	Solvent	Ligand ($\mathbf{L^a}$)											
		7a			**8a**			**9a**			**17**		
		Time [min]	Conv. [%]	*ee* [%]	Time [min]	Conv. [%]	*ee* [%]	Time [min]	Conv. [%]	*ee* [%]	Time [min]	Conv. [%]	*ee* [%]
21	MeOH	2	100	70 (*R*)	1	100	80 (*R*)	2.5	100	81 (*R*)	1.5	100	79 (*R*)
	MeOH[b]	7	100	78 (*R*)	2	100	77 (*R*)	4	100	65 (*R*)			
	CH_2Cl_2	5	100	73 (*R*)	15	93	81 (*R*)	3	100	83 (*R*)	3	100	82 (*R*)
22	MeOH	2	100	90 (*R*)	2	100	90 (*R*)	1.5	100	81 (*R*)			
	CH_2Cl_2	7	100	80 (*R*)	6	100	88 (*R*)	8	100	88 (*R*)			
23	MeOH	300	100	68 (*S*)	170	87	58 (*S*)	350	97	40 (*S*)	180	51	61 (*S*)
	CH_2Cl_2	30	96	82 (*S*)	40	87	71 (*S*)	30	95	69 (*S*)	30	62	77 (*S*)
24	MeOH	120	99	13 (*R*)	80	100	22 (*R*)	100	100	25 (*R*)			
	CH_2Cl_2	80	56	7 (*S*)	250	48	9 (*R*)	160	48	17 (*R*)			
25	MeOH	800	93	41 (*S*)	1400	85	36 (*S*)	1100	75	36 (*S*)	180	19	27 (*S*)
	CH_2Cl_2	400	31	65 (*S*)	1400	19	27 (*S*)	1400	25	52 (*S*)	1400	25	45 (*S*)
26	MeOH	600	69	19 (*S*)	220	71	8 (*S*)	2400	43	15 (*S*)			

[a] Molar catalyst-substrate ratio 1:100 (if otherwise not stated), 1 bar H_2, 25 °C. [b] Molar catalyst-substrate ratio 1:1000.

9,10-$(PPh_2)_2$-substituted ligands reveals their similarity in catalytic performance, despite the fact that they possess different functional groups. Moreover, the rates of hydrogenation and the *ee*s were essentially the same with the complex based on the nonfunctionalized ligand **17**. Therefore, we assume that none of the O groups in this series of catalysts participates actively in the enantioselective step.

Analogous ligands in the 8,10-$(PPh_2)_2$-substituted series (**7b**, **8b** and **9b**) form catalysts with entirely different and inferior hydrogenation properties (Table 3). The highest *ee*s were achieved with the oxo derivative **7b** and AH as the substrate (73% *ee*), but this value is still lower than that obtained in the case of the corresponding isomeric ligand **7a** (81% *ee*). Large differences in the *ee*s of up to 80% for different O groups were observed when the same substrates were reduced. In many cases, products with opposite configuration were obtained (compare, for example, the hydrogenation of AH and AMe by complexes based on **7b** and **8b**). The differences in selectivity and activity within the 8,10-$(PPh_2)_2$-substituted ligand series are much larger than those within the 9,10-$(PPh_2)_2$-substituted series. This is a clear demonstration that the oxo and oxy functionalities disturb the catalytic action of the metal ion in the case of the 8,10-$(PPh_2)_2$-substituted ligands. One reason for such a disturbance could be coordination of the functional groups to the metal centre, shown to influence the hydrogenation rate and selectivity in related ligands.[8] MMX calculations[30] revealed that such coordination is possible in principle for complexes with ligands **7b**−**9b**, while in the case of isomeric ligands **7a**−**9a** it is impossible for steric reasons.

There is spectroscopic evidence for the functional group coordination to Rh in solutions of complexes with diphosphanes **7b**−**9b**. In the series of 9,10-$(PPh_2)_2$-substituted ligands (**7a**, **8a**, **9a** and **17**) both phosphorus atoms are characterized by similar shifts ($\Delta\delta$ = 0.9−3.5, Table 1) indicating similar chemical environments around the phosphorus nuclei. In contrast, the ^{31}P NMR shifts of the Rh precatalysts with ligands based on the 8,10-$(PPh_2)_2$-substituted camphor skeleton (**7b**, **8b**, **9b**) are quite different, $\Delta\delta$ being in the range of 9.5−10.4. One of the signals is essentially the same as for the complexes with 9,10-$(PPh_2)_2$-substituted ligands, but the other is shifted upfield. This unusual shift can be explained by assuming hemilabile coordination[31] of the oxo- and oxy-functionalities to Rh. Because of the coordination, a six-membered P−Rh−O chelate ring is formed in addition to the seven-membered P−Rh−P chelate ring. Phosphorus nuclei involved in six-membered rings are in general characterized by a shift of their ^{31}P NMR signals to higher field (around 10 ppm).[21,32] The participation in both a six-membered and a seven-membered ring holds only for the diphenylphosphanyl group at C-10 in **7b**−**9b**. A ^{31}P-^{1}H correlation spectrum of [Rh(**9b**)(COD)]BF_4 gave evidence that it is the signal at C-10, which is shifted upfield.

Further support for hemilabile coordination of the O functionalities to Rh in complexes with 8,10-$(PPh_2)_2$-substi-

Table 3. Hydrogenation results of various substrates with complexes Rh[$\mathbf{L^b}$(COD)]BF_4 where $\mathbf{L^b}$ is a ligand of the 8,10-$(PPh_2)_2$-substituted series (**7b**−**9b**)[a]

Substrate	Solvent	Ligand ($\mathbf{L^b}$)								
		7b			**8b**			**9b**		
		Time [min]	Conv. [%]	*ee* [%]	Time [min]	Conv. [%]	*ee* [%]	Time [min]	Conv. [%]	*ee* [%]
21	MeOH	90	100	43 (*S*)	1400	67	49 (*R*)	100	100	4 (*R*)
	CH_2Cl_2	150	100	49 (*S*)	1400	55	27 (*R*)	800	34	3 (*R*)
22	MeOH	200	100	73 (*S*)	20	100	35 (*R*)	500	100	19 (*R*)
	CH_2Cl_2	600	76	64 (*S*)	600	100	27 (*R*)	1600	45	34 (*R*)
23	MeOH	1400	33	28 (*R*)	800	74	44 (*R*)	1800	60	7 (*R*)
	CH_2Cl_2							200	12	19 (*R*)
24	MeOH	2500	54	4 (*S*)				1400	13	3 (*S*)
	CH_2Cl_2							no reaction	−	−
25	MeOH	1400	30	2 (*S*)				1400	30	14 (*R*)
	CH_2Cl_2							1400	8	45 (*R*)
26	MeOH	1400	18	2 (*S*)				1400	18	15 (*S*)

[a] Molar catalyst-substrate ratio 1:100, 1 bar H_2, 25 °C.

tuted ligands can be derived from their ^{103}Rh NMR spectra. By use of a reverse detection technique we determined the ^{103}Rh NMR shifts (relative to Ξ = 3.16 MHz)[33] for complexes [Rh(**9a**)(COD)]BF_4 and [Rh(**9b**)(COD)]BF_4. For the former, δ = −157 ppm, while for the latter δ = −29 ppm was observed. The observation of such a downfield shift for the complex [Rh(**9b**)(COD)]BF_4 indicates changes in the coordination sphere of Rh.[34]

At a first glance, the crystal structure data for complexes [Rh(**7b**)(COD)]BF_4 and [Rh(**7a**)(COD)]BF_4 (Figure 2) appear to disprove the hemilabile coordination hypothesis. In both complexes the oxygen atom is well separated from the Rh (5.899 and 6.025 Å for complexes with **7b** and **7a**, respectively). However, the crystal structures do not say anything about the behavior of the complexes in solutions, and (most importantly) about the structure of the true catalytic intermediates. (The latter is, of course, also true for the NMR solution data of the precatalysts.) The hemilabile coordination might be more facile in the intermediates, as reported previously.[8] Thus, the difference in ^{31}P NMR shifts for [Rh(**9b**)(COD)]BF_4 mentioned above disappears on hydrogenation of its COD ligand in CD_3OD [presumably with formation of the bis(CD_3OD) complex with no hemilabile coordination] and appears again on addition of the substrate AMe (restoration of the hemilabile coordination in the catalyst−substrate adduct).

Low-temperature measurements on CD_2Cl_2 solutions of both [Rh(**9a**)(COD)]BF_4 and [Rh(**9b**)(COD)]BF_4 complexes revealed no significant changes in the ^{31}P and ^{1}H NMR spectra (in the aliphatic regions) up to −90 °C. This, together with the X-ray data for complexes [Rh(**7b**)(COD)]BF_4 and [Rh(**7a**)(COD)]BF_4, casts some doubts on the hemilabile coordination hypothesis. The other possible reason for the observed functional group effect on the rate and selectivity of the catalytic hydrogenation could be secondary interaction − noncovalent ligand−substrate interactions in the catalytic intermediates. Work is in progress to find evidence for or disprove this proposal.

Conclusions

In general, all the catalysts based on 9,10-$(PPh_2)_2$-substituted camphor ligands (**7a**, **8a**, **9a**, **17**) show the same tendencies in their catalytic behavior. In contrast, complexes bearing ligands of the 8,10-$(PPh_2)_2$-substituted series (**7b**, **8b**, **9b**) differ significantly in their stereodifferentiating properties. Catalysts based on ligands **7a**, **8a** and **9a** are superior to their isomeric counterparts both in their activity and in their enantioselectivity. Our results provide evidence that structurally similar ligands with additional functional groups can differ greatly in their catalytic performances. As possible reasons for this, coordination of the functional groups to the Rh centre or secondary ligand−substrate interaction can be suggested. Whatever the reason, the effect of the oxo- and oxy-functional groups in diphosphane ligands can be seriously damaging for catalytic performance of the corresponding hydrogenation catalysts, in terms both of activity and of selectivity.

Experimental Section

General Remarks: All reagents were obtained from Aldrich and Merck. Solvents were dried and freshly distilled under argon before use. Reactions involving phosphanes and organometallic compounds were performed under argon by use of standard Schlenk techniques. Thin layer chromatography was performed on pre-coated TLC plates (silica gel 60 F_{254}, Merck). Flash chromatography was carried out with silica gel 60 (particle size 0.040−0.063 mm, Merck). Melting points were measured on a hotplate and are not corrected. NMR spectra were recorded at the following frequencies: 400.13 MHz (^{1}H), 100.63 MHz (^{13}C), 161.98 MHz (^{31}P). ^{103}Rh NMR shifts were determined by inverse detected (four-pulse HMQC) triple-resonance experiments ^{31}P,^{103}Rh{^{1}H}.[35] Each determination was carried out at least twice, with variation of the pulse frequency and the t_1 increment to ensure that the signals in the F_1 dimension were not folded. Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in ppm downfield from TMS as an internal standard. Chemical shifts of ^{31}P NMR spectra are referenced to H_3PO_4 as an external standard. Signals are quoted as s (singlet), d (doublet), br. (broad) and m (multiplet). Elemental analyses were performed with a LECO CHNS-932. Hydrogenation experiments of functionalized olefins were carried out under normal pressure and isobaric conditions with automatic recording of the gas uptake (1.0 atm overall pressure over the solution). The experiments were performed in 15.0 mL of solvent at 25.0 °C. The degrees of conversion of the prochiral dehydroamino acids and the *ee*s of the products were determined by GC. The acids were esterified with trimethylsilyl diazomethane before GC measurements: FID; carrier gas: Ar, 1 mL/min; methyl *N*-acetylphenylalaninate; fused silica, 10 m, XE-60-L-valine-*tert*-butylamide, i.d. 0.2 mm; oven temperature 150 °C. The conversion into methyl 3-*N*-acetylaminobutanoate and its *ee* were determined by GC: Chiraldex β-PM 50 m × 0.25 mm (Astec), 130 °C. Optical purity analyses of the phosphane oxides prepared from both enantiomers of **19** were accomplished by HPLC on a Chiralcel OD-H column (Merck), with hexane/ethanol (95:5) as eluent (flow 1.0 mL/min).

(1*S*,4*R*,7*R*)-1,7-Bis(iodomethyl)-7-methylbicyclo[2.2.1]heptan-2-one (10a): A solution of 9,10-dibromocamphor (10 g, 32.2 mmol), obtained as described previously,[15] and KI (53.5 g, 322.0 mmol) in dry DMF (150 mL) was stirred under argon at 110 °C overnight. A precipitate formed. The mixture was then cooled and diluted with water (500 mL), and the product was extracted with Et_2O (500 mL). The diethyl ether extract was washed with water (3 × 200 mL) and dried (Na_2SO_4), and the solvents were evaporated. The residue was recrystallized from heptane. White crystals, m.p. 133 °C, 10.6 g (81.8%). $C_{10}H_{14}I_2O$ (404.03): calcd. C 29.73, H 3.49; found C 29.92, H 3.46. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.47 (dq, *J* = 0.2, 10.1 Hz, 1 H) and 3.33 (d, *J* = 10.1 Hz, 1 H, 7-CH_2I), 3.43 (d, *J* = 11.3 Hz, 1 H) and 3.17 (d, *J* = 11.3 Hz, 1 H, 1-CH_2I), 2.46 (t, *J* = 4.0 Hz, 1 H, 4-H), 2.37 (dt, *J* = 4.0, 18.6 Hz, 1 H) and 1.97 (d, *J* = 18.6 Hz, 1 H, 3-CH_2), 2.12 (t, *J* = 10.9 Hz, 1 H), 1.85−1.95 (m, 1 H), 1.43−1.60 (m, 2 H, 5-CH_2 and 6-CH_2), 1.04 (s, 3 H, 7-CH_3) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 213.6 (C=O), 59.4 (C), 51.5 (C), 43.8 (4-CH), 41.9 (*C*H_2C=O), 29.3 (CH_2), 25. 9 (CH_2), 17.9 (CH_3), 15.6 (CH_2I), 0.0 (CH_2I) ppm. MS (EI): *m*/*z* (%) = 404 (0.12) [M^+], 277 (77.8), 235 (12.6), 149 (40.2), 122 (40.8), 121 (100), 108 (21.1), 107 (90.5), 94 (13.3), 93 (66.5), 91 (27.9), 79 (65.2), 53 (24.5), 41 (44.2), 39 (39.6).

(1*S*,4*R*,7*S*)-1,7-Bis(iodomethyl)-7-methylbicyclo[2.2.1]heptan-2-one (10b): This compound was obtained analogously to **10a**, from 8,10-dibromocamphor, obtained as described previously,[15] in 81.5% yield. White crystals, m.p. 115−116 °C. $C_{10}H_{14}I_2O$ (404.03): calcd. C 29.73, H 3.49; found C 29.77, H 3.37. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.28 (d, *J* = 10.8 Hz, 1 H) and 3.15 (d, *J* = 10.8 Hz, 1 H, 1-CH_2I), 3.17 (d, *J* = 10.6 Hz, 1 H) and 2.97 (dq, *J* = 1.0, 10.6 Hz, 1 H, 7-CH_2I), 2.42 (d, *J* = 3.7 Hz, 1 H, 4-CH), 2.40 (dt, *J* = 3.7, 17.0 Hz, 1 H) and 2.01 (d, *J* = 17.0 Hz, 1 H, 3-CH_2), 2.14 (tm, 1 H), 1.86−2.05 (m, 1 H), 1.83 (ddd, *J* = 3.7, 9.3, 9.3 Hz, 1 H), 1.41 (ddd, *J* = 3.7, 9.1, 9.1 Hz, 1 H, 5,6-CH_2), 1.24 (d, *J* = 1.0 Hz, 3 H, 7-CH_3) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 213.8 (C=O), 58.7 (C), 52.3 (C), 45.5 (4-CH), 42.6 (CH_2), 34.1 (CH_2), 26.0 (CH_2), 18.6 (CH_3), 14.1 (CH_2I), −0.8 (CH_2I) ppm.

(1*S*,4*R*,7*R*)-1,7-Bis(iodomethyl)-7-methylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]dioxolane] (11a): A mixture of 9,10-diiodocamphor (**10a**, 7.2 g, 17.9 mmol), ethylene glycol (35 mL), benzene (150 mL; ***caution, toxic!***) and *p*-toluenesulfonic acid (monohydrate, 150 mg) was heated at reflux in a Dean−Stark apparatus for ca. 5 d. Every 12 h a cartridge made of glass wool packed with P_2O_5 was put in the apparatus to remove water efficiently. It is very important to protect the reaction flask from moisture. The reaction was monitored by TLC (hexane/diethyl ether, 3:1). After the reaction was complete, the mixture was cooled to room temperature, diluted with diethyl ether (200 mL) and washed with brine and water (3 × 100 mL), dried (Na_2SO_4) and concentrated. The product was purified by column chromatography (hexane/diethyl ether, 3:1, as an eluent). Pale yellow oil, 7.4 g (92% yield). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.95−4.10 (m, 3 H), 3.75−3.80 (m, 1 H, OCH_2CH_2), 3.51 (dq, *J* = 1.2, 9.6 Hz, 1 H), 3.16 (d, *J* = 9.6 Hz, 1 H, 7-CH_2I), 3.36 (d, *J* = 10.3 Hz, 1 H), 3.17 (d, *J* = 10.3 Hz, 1 H, 1-CH_2I), 2.12 (t, *J* = 4.4 Hz, 1 H, 4-CH), 2.17 (m, 1 H), 2.01 (ddd, *J* = 2.2, 4.7, 13.3 Hz, 1 H), 1.70−1.80 (m, 2 H), 1.48 (d, *J* = 13.3 Hz, 1 H), 1.34 (m, 1 H, 3-, 5-, 6-CH_2), 1.21 (d, *J* = 1.2 Hz, 3 H, 7-CH_3) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 116.6 (2-C), 64.9, 62.9 (OCH_2CH_2), 53.7 (C), 52.7 (C), 45.8 (4-CH), 43.8 (CH_2), 28.9 (CH_2), 25.3 (CH_2), 17.7 (CH_2I), 17.6 (CH_3), 2.5 (CH_2I).

(1*S*,4*R*,7*S*)-1,7-Bis(iodomethyl)-7-methylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]dioxolane] (11b): This compound was prepared analogously to **11a**, from 8,10-diiodocamphor (**10b**, 6.58 g, 16.3 mmol), ethylene glycol (33 mL), benzene (150 mL), and *p*-toluenesulfonic acid monohydrate (150 mg). Pale yellow oil, 6.24 g (85.5% yield). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.87−4.10 (m, 4 H), 3.75−3.85 (m, 1 H, OCH_2CH_2O, HC*H*I), 3.37 (d, *J* = 9.9 Hz, 1 H), 3.10 (d, *J* = 9.9 Hz, 1 H, CH_2I), 3.03 (d, *J* = 10.3 Hz, 1 H, HC*H*I), 2.40 (dd, *J* = 3.2, 12.5 Hz, 1 H), 2.14 (t, *J* = 4.6 Hz, 1 H, 4-CH), 1.97 (ddd, *J* = 2.8, 4.6, 13.5 Hz, 1 H), 1.65−1.80 (m, 2 H), 1.55 (d, *J* = 13.5 Hz, 1 H), 1.25−1.35 (m, 1 H), 1.13 (s, 3 H, 7-CH_3) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 115.6 (2-C), 66.1, 63.9 (OCH_2CH_2O), 54.4 (C), 53.9 (C), 46.9 (4-CH), 45.5 (CH_2), 33.3 (CH_2), 25.7 (CH_2), 19.5 (CH_3), 17.6 (CH_2I), 2.7 (CH_2I) ppm.

Diphenyl({(1*S*,4*R*,7*S*)-1-[(diphenylphosphanyl)methyl]-7-methylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]dioxolan]-7-yl}methyl)-phosphane (9a): A Ph_2PLi solution [prepared from Ph_2PCl (4.5 mL, 25.11 mmol) and Li (520 mg, 75.33 mmol) in 40 mL of THF, by stirring at room temperature for 1 h and then heating at reflux for 2 h] was added at 0 °C (ice bath) whilst stirring (under argon) to a solution of the diiodo acetal **11a** (3.75 g, 8.37 mmol) in THF (10 mL). The ice bath was removed, and the mixture was heated at reflux for 12 h. The mixture was cooled to room temperature, water was added (20 mL), and the product was extracted with diethyl ether (50 mL). The extract was washed twice with water and concentrated, and the product was purified by column chromatography (eluent hexane/diethyl ether, 3:1). Colorless, amorphous solid, 2.2 g (54.4% yield). $C_{36}H_{38}O_2P_2$ (564.64): calcd. C 76.58, H 6.78; found

C 76.50, H 6.82. ^{1}H NMR (400.13 MHz, C_6D_6): δ = 7.65−7.85 (m, 8 H), 7.15−7.35 (m, 12 H, arom.), 3.80 (q, *J* = 6.9 Hz, 1 H), 3.60−3.75 (two overlapped q, *J* = 6.9 Hz, 2 H), 3.49 (q, *J* = 6.9 Hz, 1 H, OCH_2CH_2O), 2.87 (d, *J* = 14.4 Hz, 1 H), 2.40−2.65 (m, 5 H), 2.17 (dm, *J* = 16.8 Hz, 1 H), 1.72 (s, 3 H, 7-CH_3), 1.60−1.85 (m, 2 H), 1.52 (d, *J* = 13.0 Hz, 1 H), 1.30 (m, 1 H) ppm. ^{13}C NMR (100.63 MHz, C_6D_6): δ = 127−143 (arom. signals), 117.1 (d, $^3J_{C\text{-}P}$ = 3.8 Hz, 2-C), 65.2 (s), 63.1 (s, O−CH_2CH_2−O), 57.2 (dd, $J_{C\text{-}P}$ = 4.8, 9.5 Hz), 54.0 (dd, $J_{C\text{-}P}$ = 4.8, 14.3 Hz, 1,7-C), 45.2 (s, 3-CH_2), 43.5 (d, $J_{C\text{-}P}$ = 11.5 Hz, 4-CH), 35.5 (d, $^1J_{C\text{-}P}$ = 14.3 Hz, P−CH_2), 28.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 27.4 (s, 5,6-CH_2), 26.6 (d, $^1J_{C\text{-}P}$ = 20.0 Hz, P−CH_2), 20.1 (d, $^3J_{C\text{-}P}$ = 12.0 Hz, 7-CH_3) ppm. ^{31}P NMR (161.98 MHz, C_6D_6): δ = −20.7, −21.9 ppm.

Diphenyl({(1*S*,4*R*,7*R*)-1-[(diphenylphosphanyl)methyl]-7-methylspiro[bicyclo[2.2.1]heptane-2,2′-[1,3]dioxolan]-7-yl}methyl)phosphane (9b): This compound was prepared analogously to the isomer **9a**, from **11b** in 55.5% yield, as colorless crystals, m.p. 111 °C. Purification was performed by column chromatography (hexane/diethyl ether, 5:1, as eluent). $C_{36}H_{38}O_2P_2$ (564.64): calcd. C 76.58, H 6.78; found C 76.52, H 6.80. ^{1}H NMR (400.13 MHz, C_6D_6): δ = 7.65−7.85 (m, 8 H), 7.10−7.35 (m, 12 H, arom.), 3.76 (q, *J* = 7.0 Hz, 1 H), 3.67 (q, *J* = 7.0 Hz, 1 H), 3.59 (q, *J* = 7.0 Hz, 1 H), 3.42 (q, *J* = 7.0 Hz, 1 H, OCH_2CH_2O), 3.51 (dd, *J* = 2.7, 14.7 Hz, 1 H), 2.92 (d, *J* = 14.3 Hz, 1 H), 2.40−2.50 (m, 4 H), 2.01 (dt, *J* = 3.2, 12.9 Hz, 1 H), 1.70 (m, 1 H), 1.56 (m, 1 H), 1.43 (d, *J* = 13.3 Hz, 1 H), 1.35 (m, 1 H), 1.24 (s, 3 H, 7-CH_3) ppm. ^{13}C NMR (100.63 MHz, C_6D_6): δ = 141.0−143.0, 132.0−135.0, 127.0−130.0 (arom. carbon atoms), 117.2 (s, 2-C), 65.2 (s), 63.0 (s, OCH_2CH_2O), 57.4 (dd, $J_{C\text{-}P}$ = 4.8, 9.5 Hz, C), 53.9 (dd, $J_{C\text{-}P}$ = 5.7, 13.4 Hz, C), 45.0 (s, CH_2), 43.3 (d, $J_{C\text{-}P}$ = 7.2 Hz, 4-CH), 34.5 (d, $^1J_{C\text{-}P}$ = 16.2 Hz, P−CH_2), 28.9 (d, $J_{C\text{-}P}$ = 6.7 Hz, CH_2), 27.61 (s, CH_2), 26.6 (d, $^1J_{C\text{-}P}$ = 21.0 Hz, P−CH_2), 20.2 (d, $^3J_{C\text{-}P}$ = 10.5 Hz, 7-CH_3) ppm. ^{31}P NMR (161.98 MHz, C_6D_6): δ = −19.5, −21.7 ppm.

(1*S*,4*R*,7*S*)-1,7-Bis[(diphenylphosphanyl)methyl]-7-methylbicyclo[2.2.1]heptan-2-one (7a): The acetal **9a** (300 mg, 0.53 mmol) was dissolved in a mixture of concd. HCl (1 mL), water (2 mL) and THF (5 mL), and the solution was brought to reflux under argon for 5 h. The mixture was cooled to room temperature, and aq. NaOH (2.5 N, 10 mL) was added carefully. The product was extracted with diethyl ether (20 mL), and the extract was washed with water (2 × 20 mL) and concentrated. The phosphane was purified by column chromatography (hexane/diethyl ether, 5:2, as eluent). Colorless crystals (from hexane), m.p. 118 °C (150 mg, 49% yield, calculated from the diiodo acetal **11a**). $C_{34}H_{34}OP_2$ (520.59): calcd. C 78.44, H 6.58; found C 78.40, H 6.59. ^{1}H NMR (400.13 MHz, C_6D_6): δ = 7.72−7.85 (m, 4 H), 7.60−7.70 (m, 4 H), 7.25−7.35 (m, 12 H, arom. protons), 3.05 (dd, *J* = 3.6, 15.4 Hz, 1 H), 2.56 (dd, *J* = 2.2, 12.1 Hz, 1 H), 2.48 (s, 2 H), 2.45 (dd, *J* = 2.2, 12.1 Hz, 1 H), 2.31 (dt, *J* = 4.2, 18.2 Hz, 1 H), 2.17 (t, *J* = 13.3 Hz, 1 H), 1.75 (d, *J* = 18.2 Hz, 1 H), 1.65 (m, 1 H), 1.51 (m, 1 H), 1.02 (s, 3 H), 0.99 (m, 1 H) ppm. ^{31}C NMR (100.63 MHz, C_6D_6): δ = 215.4 (d, $^3J_{C\text{-}P}$ = 3.8 Hz, C=O), 129−140 (arom. signals), 62.2 (dd, $J_{C\text{-}P}$ = 5.7, 12.6 Hz, C), 51.7 (d, $J_{C\text{-}P}$ = 15.2 Hz, C), 42.9 (s, CH_2), 41.3 (d, $J_{C\text{-}P}$ = 10.4 Hz, 4-CH), 34.2 (dd, $J_{C\text{-}P}$ = 5.7, 19.1 Hz, CH_2), 28.2 (d, $J_{C\text{-}P}$ = 14.3 Hz, CH_2), 27.2 (s, CH_2), 25.4 (d, $J_{C\text{-}P}$ = 17.2 Hz, CH_2), 19.8 (d, $J_{C\text{-}P}$ = 10.5 Hz, CH_3) ppm. ^{31}P NMR (161.98 MHz, C_6D_6): δ = −23.49 (d, *J* = 2.8 Hz), −23.82 (d, *J* = 2.8 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1739 (C=O) cm^{-1}.

(1*S*,4*R*,7*R*)-1,7-Bis[(diphenylphosphanyl)methyl]-7-methylbicyclo[2.2.1]heptan-2-one (7b): This compound was obtained analogously to the isomer **7a**, from **9b** in 23% yield. White crystals. ^{1}H NMR (400.13 MHz, C_6D_6): δ = 7.50−7.61 (m, 4 H), 7.30−7.40 (m, 2 H), 7.20−7.30 (m, 2 H), 6.90−7.10 (m, 12 H, arom.), 2.74 (dd, *J* = 3.2, 15.0 Hz, 1 H), 2.28 (dd, *J* = 2.5, 15.0 Hz, 1 H, P−CH_2), 2.17 (t, *J* = 4.2 Hz, 1 H, 4-CH), 2.03 (d, *J* = 3.2 Hz, 2 H, PCH_2), 1.88 (m, 1 H), 1.75 (m, 1 H), 1.42 (d, *J* = 18.2 Hz, 1 H), 1.40 (m, 2 H), 0.83 (m, 1 H, 3-, 5-, 6-CH_2), 1.05 (s, 3 H, 7-CH_3) ppm. ^{13}C NMR (100.63 MHz, C_6D_6): δ = 215.5 (s, C=O), 126−147 (arom.), 62.4 (dd, $J_{C\text{-}P}$ = 5.7, 12.4 Hz, C), 51.6 (dd, $J_{C\text{-}P}$ = 2.9, 14.3 Hz, C), 42.5 (s, CH_2), 40.9 (d, $J_{C\text{-}P}$ = 8.6 Hz, 4-CH), 35.0 (d, $J_{C\text{-}P}$ = 19.1 Hz, CH_2), 28.2 (d, $J_{C\text{-}P}$ = 13.4 Hz, CH_2), 27.1 (s, CH_2), 25.6 (d, $J_{C\text{-}P}$ = 18.1 Hz, CH_2), 19.2 (dd, $J_{C\text{-}P}$ = 4.8, 11.5 Hz, 7-CH_3) ppm. ^{31}P NMR (161.98 MHz, C_6D_6): δ = −21.4, −23.2 ppm.

(1*S*,2*R*,4*R*,7*R*)-1,7-Bis[(diphenylphosphanyl)methyl]-7-methylbicyclo[2.2.1]heptan-2-ol (8b): The oxo derivative **7b** (255 mg, 0.49 mmol) was dissolved in THF (5 mL), and $LiAlH_4$ (50 mg, 1.3 mmol) was added to the solution. The mixture was stirred at room temperature for 5 h, and water was then added to quench excess $LiAlH_4$ (the reaction flask was cooled in an ice bath). The product was extracted with diethyl ether (3 × 20 mL), concentrated and purified by column chromatography (hexane/diethyl ether, 2:1 as an eluent). White crystals (120 mg, 47% yield). ^{1}H NMR (400.13 MHz, C_6D_6): δ = 7.64 (t, *J* = 8.1 Hz, 2 H), 7.58 (t, *J* = 8.1 Hz, 2 H), 7.52 (m, 2 H),7.41 (t, *J* = 8.1 Hz, 2 H), 6.95−7.10 (m, 12 H, arom.), 3.88 (dd, *J* = 3.4, 7.6 Hz, 1 H, 2-CH),3.49 (dd *J* = 4.0, 14.5 Hz, 1 H, CH_2P), 2.65 (d *J* = 13.5, 1 H, CH_2P), 2.15−2.25 (m, 4 H, OH, 4-CH, CH_2P), 1.76 (dq, *J* = 3.4, 13.3 Hz, 1 H), 1.46 (dd, *J* = 4.2, 13.3 Hz, 1 H, 3-CH_2), 1.38 (m, 1 H), 1.18 (m, 1 H), 0.89 (m, 1 H), 0.72 (m, 1 H, 5-, 6-CH_2), 0.95 (s, 3 H, 7-CH_3) ppm. ^{13}C NMR (100.63 MHz, C_6D_6): δ = 127−142 (arom.), 77.5 (d, $^3J_{C\text{-}P}$ = 4.8 Hz, 2-CH), 54.1 (dd, $J_{C\text{-}P}$ = 4.8, 9.5 Hz, C), 52.1 (dd, $J_{C\text{-}P}$ = 7.6, 13.4 Hz, C), 42.8 (d, $J_{C\text{-}P}$ = 10.5 Hz, 4-CH), 39.9 (s, CH_2), 33.9 (d, $^1J_{C\text{-}P}$ = 16.2 Hz, PCH_2), 32.9 (s, CH_2), 27.6 (s, CH_2), 27.5 (d, $^1J_{C\text{-}P}$ = 18.1 Hz, PCH_2), 19.6 (d, *J* = 11.5 Hz, 7-CH_3) ppm. ^{31}P NMR (161.98 MHz, C_6D_6): δ = −19.5, −23.0 ppm.

(1*R*,2*R*,4*R*,7*R*)-1,7-Bis(iodomethyl)-7-methylbicyclo[2.2.1]heptan-2-ol (12): 9,10-Diiodocamphor (**10a**, 1.64 g, 4.06 mmol) was added in portions at 0−5 °C (ice bath) under an inert gas to a stirred suspension of $LiAlH_4$ (300 mg) in THF (20 mL). The mixture was then stirred for 1.5 h at 0 °C, after which water was carefully added to quench excess $LiAlH_4$. Diethyl ether (50 mL) was added, and the precipitate was filtered off and washed with diethyl ether and THF. The filtrate was concentrated, and the residue was applied to a column. The desired product was eluted first by hexane/EtOAc (3:1) (1 g, 2.46 mmol, 60.1% yield), followed by 7-(iodomethyl)-1,7-dimethylbicyclo[2.2.1]heptan-2-ol and then by 2-[2-(iodomethyl)-2-methyl-3-methylenecyclopentyl]ethanol. White crystals, m.p. 80 °C. $C_{10}H_{16}I_2O$ (406.05): calcd. C 29.58, H 3.97; found C 30.29 H, 4.03. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.95 [pseudo p (ddd), *J* = 4.3 Hz, 1 H, C*H*OH], 3.47 (d, *J* = 9.3 Hz, 1 H), 3.17 (d, *J* = 9.3 Hz, 1 H, CH_2I), 3.36 (dd, *J* = 9.9, 1.2 Hz, 1 H), 3.00 (d, *J* = 9.9 Hz, 1 H, CH_2I), 2.30 (t, *J* = 4.0 Hz, 1 H, 4-H), 2.22 (d, *J* = 4.2 Hz, 1 H, OH), 1.60−1.75 (m, 4 H, 2 × CH_2), 1.35−1.42 (m, 1 H), 1.13−1.21 (m, 1 H, CH_2), 1.24 (d, *J* = 1.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 80.5 (CH_2OH), 51.1 (C), 51.8 (C), 47.8 (CH), 38.5 (CH_2), 33.2 (CH_2), 26.3 (CH_2), 18.4 (CH_3), 17.6 (CH_2), 9.6 (CH_2) ppm.

(1*S*,2*R*,4*R*,7*S*)-1,7-Bis(iodomethyl)-7-methyl-2-(triethylsilyloxy)bicyclo[2.2.1]heptane (13): Chlorotriethylsilane (0.985 mL, 5.87 mmol) was added to a solution of the alcohol **12** (1.986 g, 4.89 mmol) and imidazole (0.433 g, 6.36 mmol) in DMF (10 mL), cooled in an ice bath. The resulting solution was stirred for 15 min at 0 °C and then overnight at room temperature. Ice-cold water

(20 mL) was added, and the product was extracted with CH_2Cl_2, dried with Na_2SO_4, concentrated and purified by flash chromatography (hexane/EtOAc, 10:1; R_f = 0.8). Colorless oil (2.38 g, 4.57 mmol), 93.5% yield. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.91 (dd, *J* = 7.1, 3.4 Hz, 1 H, C*H*OH), 3.48 (d, *J* = 9.1 Hz, 1 H), 3.12 (d, *J* = 9.1 Hz, 1 H, 1-CH_2I), 3.36 (dq, *J* = 9.1, 1.0 Hz, 1 H), 3.02 (d, *J* = 9.1 Hz, 1 H, 7-CH_2I), 2.2 (t, *J* = 3.8 Hz, 1 H, 4-H), 1.6−1.8 (m, 4 H, CH_2), 1.34 (m, 1 H), 1.14 (m, 1 H, CH_2), 1.23 (d, *J* = 1 Hz, 3 H, CH_3), 0.98 (t, *J* = 7.9 Hz, 9 H, SiCH$_2$C*H*$_3$), 0.64 (q, *J* = 7.9 Hz, 6 H, SiC*H*$_2$CH$_3$) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 79.4 (CHOH), 52.8 (C), 51.3 (C), 47.9 (CH), 40.1 (CH_2), 33.8 (CH_2), 26.0 (CH_2), 18.0 (CH_2), 8.4 (CH_2), 7.0 (SiCH$_2$*C*H$_3$), 6.4 (CH_3), 5.1 (Si*C*H$_2$CH$_3$) ppm.

(1*S*,2*R*,4*R*,7*S*)-1,7-Bis[(diphenylphosphanyl)methyl]-7-methylbicyclo[2.2.1]heptan-2-ol (8a). Method A: The compound was prepared from **7a** and $LiAlH_4$ analogously to **8b**, in 89% yield. **Method B:** A solution of Ph_2PLi [prepared from Ph_2PCl (1.97 mL, 10.97 mmol) and Li (207 mg, 30 mmol) in 30 mL of THF, stirring at room temperature, 1 h and at reflux, 2 h] was added dropwise at 0−5 °C (ice bath), whilst stirring under argon, to a solution of the protected hydroxy diiodide **13** (2.38 g, 4.57 mmol) in THF (10 mL). The reaction mixture was stirred for 30 min in the ice bath and for 30 min at room temperature, and then heated at reflux for 1.5 h. Degassed water was added, and the product **14** was extracted with diethyl ether (100 mL). The diethyl ether solution was washed twice with water and concentrated, and the product was dried in high vacuum at 50 °C for 4 h. The diphosphane **14** thus obtained was characterized by NMR, and used for the next step without further purification. ^{1}H NMR (400.13 MHz, C_6D_6): δ = 7.08−7.40 (m, 8 H), 6.65−6.95 (m, 12 H, arom.), 3.93 (dd, *J* = 4.9, 2.6 Hz, 1 H, 2-H), 2.42 (d, *J* = 13.5 Hz, 1 H), 2.24 (dd, *J* = 5.9, 13.5 Hz, 1 H, PCH_2), 1.98 (dd, *J* = 13.2, 3.6 Hz, 1 H), 1.85 (dd, *J* = 13.2, 2.2 Hz, 1 H, PCH_2), 1.91 (m, 1 H, 4-H), 1.60 (m, 2 H, 3-CH_2), 1.32 (m, 2 H, CH_2), 1.22 (s, 3 H, CH_3), 1.01 (m, 2 H, CH_2), 0.78 (t, *J* = 8.0 Hz, 9 H, SiCH$_2$C*H*$_3$), 0.45 (q, *J* = 8.0 Hz, 6 H, SiC*H*$_2$CH$_3$) ppm. ^{31}P NMR (161.98 MHz, C_6D_6): δ = −19.9, −23.5 ppm. The Et_3Si-protected diphosphane **14** was dissolved in degassed THF (20 mL), tetrabutylammonium fluoride hydrate (3.36 g, 11.4 mmol) was added, and the solution was stirred overnight at room temperature. Degassed water was added (20 mL), and the product was extracted with diethyl ether (100 mL). The diethyl ether solution was washed with water and concentrated, and the residue was purified by column chromatography (under argon; pentane/Et_2O, 2:1, as eluent) to give **8a** as a colorless, amorphous solid (1.7 g, 3.25 mmol, 71.1% yield calculated from **12**). $C_{34}H_{36}OP_2$ (522.61): calcd. C 78.14, H 6.94; found C 78.18, H 6.90. ^{1}H NMR (400.13 MHz, C_6D_6): δ = 7.5−7.7 (m, 8 H), 7.0−7.2 (m, 12 H, arom.), 3.97 (dd, *J* = 4.5, 2.0 Hz, 1 H, 2-H), 2.63 and 2.42 (ABq, *J* = 13.5 Hz, 2 H, P−CH_2), 2.3 (br. s, 1 H, OH), 2.21 (m, 3 H, 3-H and PCH_2), 1.97 (d, *J* = 13 Hz, 1 H, 3-C*H*$_2$), 1.60 (d, s, *J* = 13 Hz, 4 H, CH_3 and 3-CH_2), 1.33 (m, 2 H, 6-CH_2 and 5-CH_2), 0.96 (m, 1 H, 6-CH_2), 0.71 (m, 1 H, 5-CH_2) ppm. ^{13}C NMR (100.63 MHz, C_6D_6): δ = 127−142 (arom.), 77.8 (d, *J* = 3 Hz, CHOH), 54.2 (dd, $J_{C\text{-}P}$ = 4.8, 9.5 Hz, C), 52.5 (dd, $J_{C\text{-}P}$ = 7.6, 14.3 Hz, C), 43.1 (d, $J_{C\text{-}P}$ = 9.5 Hz, 4-CH), 40.2 (s, 3-CH_3), 35.6 (d, $^1J_{C\text{-}P}$ = 18.1 Hz, PCH_2), 33.0 (d, $J_{C\text{-}P}$ = 5.7 Hz, 6-CH_2), 27.8 (d, $^1J_{C\text{-}P}$ = 15.3 Hz, PCH_2), 27.6 (s, 5-CH_2), 19.5 (d, $J_{C\text{-}P}$ = 12.4 Hz, 7-CH_3, assignments were made using H,H- and C,H-COSY) ppm. ^{31}P NMR (161.98 MHz, C_6D_6): δ = −20.2, −23.1 ppm. IR (KBr): $\tilde{\nu}$ = 3550 (OH) cm^{-1}.

(1*R*,4*R*,7*R*)-1,7-Bis(bromomethyl)-7-methyl-2-methylenebicyclo[2.2.1]heptane (15): Titanium tetrachloride (4.04 g, 21.3 mmol) was dissolved under argon in dry CH_2Cl_2 (10 mL), and this solution was added dropwise to a stirred suspension of Zn dust (< 10 micron, 98% purity, 5.69 g, 87.1 mmol) in a CH_2Br_2/THF mixture (2.04 mL and 20 mL, respectively) at −40 °C. The mixture was then kept in a refrigerator at 0−5 °C for 3 d. This reagent was added to a solution of 9,10-dibromocamphor (2 g, 6.45 mmol) in THF (5 mL), and the resulting mixture was stirred for 2 d at room temperature. It was then neutralized with sat. aq. $NaHCO_3$ and filtered. The deposit was washed on the filter with CH_2Cl_2. The filtrate was washed with water (3 × 20 mL), dried with Na_2SO_4 and concentrated. The crude product was purified by chromatography (eluent hexane/Et_2O, 3:1). Colorless oil (1.25 g, 60.5% yield). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.89 (t, *J* = 2.5 Hz, 1 H, =CH), 4.75 (t, *J* = 2.0 Hz, 1 H, =CH), 3.67, 3.49 (ABq, 2 H, CH_2Br), 3.64, 3.54 (ABq, 2 H, CH_2Br), 2.41 (br. d, *J* = 16.4 Hz, 1 H), 2.23 (t, *J* = 4.4 Hz, 1 H), 2.12 (dt, *J* = 4.0, 13.0 Hz, 1 H), 2.01 (dt, *J* = 2.0, 16.4 Hz, 1 H), 1.87 (ddd, 1 H), 1.54 (ddd, *J* = 4.0, 9.7, 13.0 Hz, 1 H), 1.04 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 155.7, 104.3, 55.8, 53.7, 43.7, 40.7, 35.9, 33.1, 31.9, 26.8, 16.6 ppm.

(1*R*,2*R*/*S*,4*R*,7*R*)-1,7-Bis(bromomethyl)-2,7-dimethylbicyclo[2.2.1]heptane (16): Compound **15** was dissolved in methanol (15 mL), Pd on charcoal (10%, 100 mg) was added to the solution, and the double bond was hydrogenated in an autoclave at 55 bar of hydrogen and room temperature. The uptake of hydrogen stopped after about 16 h. The mixture was then filtered and concentrated, and the product was purified by column chromatography with hexane as the eluent. The NMR spectroscopic data showed that the product was a mixture of the *endo* and *exo* isomers in a ratio of 1:3. Colorless oil (146 mg, 48.5% yield). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.71 (dd, *J* = 1.1, 10.3 Hz), 3.52 (d, *J* = 10.3 Hz, CH_2Br, minor isomer), 3.43 (s, CH_2Br, minor), 3.57 (dd, *J* = 1.0, 10.1 Hz), 3.26 (d, *J* = 10.1 Hz, CH_2Br, major), 3.52 (d, *J* = 9.9 Hz), 3.46 (d, *J* = 9.9 Hz, CH_2Br, major), 2.2−2.3 (overlapped m), 1.9−2.1 (overlapped m), 1.45−1.85 (overlapped m), 1.25−1.35 (overlapped m), 1.19 (d, *J* = 0.8 Hz, 7-CH_3, minor), 1.16 (d, *J* = 0.8 Hz, 7-CH_3, major), 1.13 (d, *J* = 7.4 Hz, 2-CH_3, major), 0.98 (d, *J* = 6.9 Hz, 2-CH_3, minor), 0.78 (dd, *J* = 10.8, 3.5 Hz) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ (major isomer) = 17.3 (CH_3), 19.3 (CH_3), 26.6 (CH_2), 36.1 (CH_2), 37.2 (CH_2), 37.4 (CH_2), 42.2 (CH), 42.3 (CH_2), 46.1 (CH), 53.0 (C), 53.9 (C) ppm; δ (minor isomer) = 15.9 (CH_3), 16.1 (CH_3), 25.7 (CH_2), 27.8 (CH_2), 35.1 (CH_2), 37.2 (CH_2), 38.4 (CH), 42.2 (CH_2), 45.2 (CH), 53.2 (C), 55.0 (C) ppm.

Diphenyl({(1*S*,2*R*/*S*,4*R*,7*S*)-1-[(diphenylphosphanyl)methyl]-2,7-dimethylbicyclo[2.2.1]hept-7-yl}methyl)phosphane (17): A Ph_2PLi solution [prepared from Ph_2PCl (0.219 mL, 1.22 mmol) and Li (25 mg, 3.66 mmol) in 5 mL of THF, by stirring at room temperature for 1 h and then heating at reflux for 2 h] was added at 0 °C (ice bath) whilst stirring (under argon) to a solution of the dibromide **16** (146 mg, 0.47 mmol) in THF (3 mL). The ice bath was then removed, and the mixture was heated at reflux for 12 h. The mixture was cooled to room temperature, water was added (20 mL), and the product was extracted with diethyl ether (20 mL). The extract was washed twice with water and concentrated, and the diphosphane was purified by column chromatography (eluent hexane/diethyl ether, 10:1). The NMR spectroscopic data showed that the product was a mixture of the *endo* and *exo* isomers in the ratio of 1:3. Colorless, amorphous solid, 100 mg (41% yield). ^{1}H NMR (400.13 MHz, C_6D_6): δ = 7.77 (t, *J* = 7.3 Hz), 7.55−7.70 (m), 7.10−7.25 (m, arom.), 2.67 (dd, *J* = 5.7, 14.0 Hz), 2.34 (d, *J* = 14.0 Hz, PCH_2, major isomer), 2.55 (dd, *J* = 4.8, 13.2 Hz), 2.48

(dd, J = 5.1, 13.2 Hz, PCH_2, minor isomer), 2.29 (m, PCH_2, major and minor isomer, 2-CH major and minor, 4-CH major and minor), 1.57 (d, J = 7.9 Hz), 1.40−1.90 (overlapped m), 1.31 (d, J = 7.4 Hz, 2-CH_3 major), 1.28 (s, 7-CH_3 major), 1.23 (s, 7-CH_3 minor), 1.10 (d, J = 6.9 Hz, 2-CH_3 minor), 0.80−1.10 (overlapped m) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ (major isomer) = 125−145 (arom.), 53.1 (d, $J_{C\text{-}P}$ = 13.0 Hz, C), 52.4 (d, $J_{C\text{-}P}$ = 10.3 Hz, C), 43.8 (CH), 41.0 (CH), 38.7 (CH_2), 38.3 (CH_2), 35.5 (d, $^1J_{C\text{-}P}$ = 22.0 Hz, PCH_2), 28.6 (d, $^1J_{C\text{-}P}$ = 18.0 Hz, PCH_2), 27.7 (CH_2), 20.8 (CH_3), 19.7 (d, $J_{C\text{-}P}$ = 4.3 Hz, CH_3) ppm. ^{31}P NMR (161.98 MHz, C_6D_6): δ (major isomer) = −19.6, −22.6 ppm. δ (minor isomer) −19.5, −23.2 ppm.

(1*R*,3*S*,6*S*,7*S*)-3-Diphenylphosphanyl-7-[(diphenylphosphanyl)-methyl]-6-methyl-4-oxatricyclo[4.3.0.0^{3,7}]nonane (19): A solution of Ph_2PLi [prepared from Ph_2PCl (2.89 mL, 16.1 mmol) and Li (550 mg) in THF (20 mL), room temperature for 1 h and heating at reflux for 2 h) was added dropwise at −78 °C under argon to a solution of 8,10-dibromocamphor (2 g, 6.45 mmol) in THF (5 mL). The reaction mixture was stirred at −78 °C for 0.5 h and 1 h at room temperature, and then heated at reflux for 5 h. Water (50 mL) was added, and the product was extracted with diethyl ether (100 mL), washed with water and concentrated. Column chromatography (hexane/diethyl ether, 8:1, as eluent) gave the diphosphane as a white solid, which could be recrystallized from hexane. White crystals, m.p. 154 °C (1.41 g, 2.71 mmol, 42% yield). $C_{34}H_{34}OP_2$ (520.59): calcd. C 78.44, H 6.58; found C 78.43, H 6.60. ^{1}H NMR (400.13 MHz, C_6D_6): δ = 8.50 (t, J = 8 Hz, 2 H), 8.25 (t, J = 8 Hz, 2 H), 7.54 (t, J = 8 Hz, 2 H), 7.45 (t, J = 8 Hz, 2 H), 7.05−7.29 (m, 12 H), 3.75 (d, J = 7.8 Hz, 1 H), 3.62 (d, J = 7.8 Hz, 1 H), 2.70 (dd, J = 2.2 and 15 Hz, 1 H), 2.33 (d, J = 15 Hz, 1 H), 2.07 (m, 1 H), 1.75−1.92 (m, 2 H), 1.55−1.68 (m, 2 H), 1.35 (m, 2 H), 1.04 (s, 3 H) ppm. ^{13}C NMR (100.63 MHz, C_6D_6): δ = 127−141 (arom), 92.9 (dd, $J_{C\text{-}P}$ = 3.8, 26.7 Hz, P−C), 72.1 (OCH_2), 58.7 (d, $J_{C\text{-}P}$ = 13.4 Hz, C), 55.2 (C), 44.4 (CH), 41.4 (d, $^1J_{C\text{-}P}$ = 13.4 Hz, P−CH_2), 30.6 (CH_2), 28.9 (CH_2), 24.9 (d, $J_{C\text{-}P}$ = 9.5 Hz, CH_2), 13.4 (d, J = 9.5 Hz, CH_3) ppm. ^{31}P NMR (161.98 MHz, C_6D_6): δ = −18.2 (d, J = 18 Hz), −25.6 (d, J = 18 Hz) ppm.

General Procedure for the Preparation of the Precatalysts with Ligands 7a, 7b, 8a, 8b, 9a, 9b and 17: [Rh(COD)(acac)] (311 mg, 1 mmol) was added to a stirred solution of the diphosphane (1 mmol) in THF (2 mL). The solution was stirred for 15 min, a stoichiometric amount of aq. 40% HBF_4 was then added, and stirring was continued for another 15 min. The complex was precipitated with diethyl ether (20 mL), dissolved in CH_2Cl_2 (0.5 mL), again precipitated by diethyl ether, and dried under vacuum for 5 h at 50 °C. Yellow powders, containing nonstoichiometric amounts of THF and diethyl ether, making the elemental analyses of the complexes incorrect. However, the complexes were fully characterized spectroscopically.

[Rh(COD)(7a)]BF_4: ^{1}H NMR (400.13 MHz, CD_3OD): δ = 8.20−8.30 m, 2 H), 7.80−7.90 (m, 4 H), 7.50−7.80 (m, 14 H, arom.), 5.14 (br. s, 1 H), 4.61 (br. s, 1 H), 4.50 (br. s, 1 H), 4.21 (br. s, 1 H, COD CH), 3.62 (m, 1 H), 3.05 (tm, J = 12.9 Hz, 1 H), 2.88 (dd, J = 11.9, 15.6 Hz, 1 H), 2.77 (m, 1 H, P−CH_2), 2.15−2.55 (m, 11 H), 1.85−2.00 (m, 2 H), 1.59 (s, 3 H, CH_3), 1.45 (m, 1 H),1.35 (m, 1 H) ppm. ^{13}C NMR (100.63 MHz, CD_3OD): δ = 212.0 (C=O), 125−135 (arom), 116.6, 104.8, 98.4, 98.3 (=CH), 47.9 (CH), 41.6, 41.2, 34.2, 32.1, 31.9, 31.3, 30.8, 30.5, 29.9, 28.6, 26.3, 18.8 (CH_3) ppm. ^{31}P NMR (161.98 MHz, CD_3OD): δ = 12.8 (dd, J = 36.1 and 142.9 Hz), 9.3 (dd, J = 36.1 and 142.9 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1742 [ν(C=O)] cm^{-1}.

[Rh(COD)(8a)]BF_4: ^{1}H NMR (400.13 MHz, $CD_3OD/CDCl_3$, ca. 1:1): δ = 8.10−8.25 (m, 4 H), 7.20-7.70 (m, 14 H, arom.), 4.37 (br. s, 1 H), 4.15−4.30 (m, 3 H, =CH), 3.34 (dd, J = 4.2, 7.1 Hz, 1 H, 2-CH), 2.92 (t, J = 16.8 Hz, 1 H), 2.72 (d, J = 13.8 Hz, 1 H), 2.53 (m, 1 H), 2.00−2.55 (m, 5 H), 1.55−1.70 (m, 8 H), 1.43 (m, 1 H), 0.98 (m, 1 H), 0.77 (s, 3 H, CH_3), 0.41 (m, 1 H) ppm. ^{13}C NMR (100.63 MHz, $CD_3OD/CDCl_3$, ca. 1:1): δ = 127−134 (arom.), 105.2, 104.4, 97.3, 95.4 (=CH), 81.3 (d, J = 10.5 Hz, 2-CH), 55.8, 53.1, 47.8 (4-CH), 41.2, 35.8, 32.3 (d, J = 28.3 Hz), 31.6, 30.5, 30.4 (d, J = 18 Hz), 29.8, 29.1, 27.4 (CH_2), 21.3 (CH_3) ppm. ^{31}P NMR (161.98 MHz, $CD_3OD/CDCl_3$, ca. 1:1): δ = 15.2 (dd, J = 42.5 and 142.3), 14.3 (dd, J = 42.5 and 142.3, chemical shifts and coupling constants were obtained by g NMR simulation of the observed AB part of the ABX spin system) ppm. IR (KBr): $\tilde{\nu}$ = 3530 [ν(OH)] cm^{-1}.

[Rh(COD)(9a)]BF_4: ^{1}H NMR (400.13 MHz, CD_3OD): δ = 7.95 (m, 2 H), 7.80 (m, 2 H), 7.0−7.5 (m, 16 H, arom.), 4.24 (br. s, 1 H), 4.03 (br. s, 1 H), 3.94 (br. s, 1 H), 3.87 (br. s, 1 H, COD CH), 3.54 (m, 2 H), 3.25−3.40 (m, 3 H), 3.14 (m, 1 H, OCH_2CH_2), 2.59 (d, J = 9.8 Hz, 1 H), 2.38 (t, J = 14.8 Hz, 1 H), 2.27 (s, 1 H), 1.50−2.20 (m, 12 H), 1.08 (m, 1 H), 0.9 (m, 1 H), 0.6 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.63 MHz, CD_3OD): δ = 127−135 (arom.), 116.5 (d, $J_{C\text{-}P}$ = 7.6 Hz, OCO), 103.3, 101.9, 99.2, 95.1 (=CH), 65.1, 63.3 (OCH_2CH_2O), 53.9 (C), 52.9 (C), 46.1 (d, $J_{C\text{-}P}$ = 10.5 Hz, 4-CH), 44.3 (3-CH_2), 37.7 (m, CH_2), 26−31 (overlapped CH_2), 19.6 (CH_3) ppm. ^{31}P NMR (161.98 MHz, CD_3OD): δ = 14.3 (dd, J = 42.1 and 142.8 Hz), 13.5 (dd, J = 42.1 and 142.8 Hz) ppm.

[Rh(COD)(7b)]BF_4: ^{1}H NMR (400.13 MHz, CD_3OD): δ = 7.73 (m, 2 H), 7.51 (m, 2 H), 6.8−7.4 (m, 12 H), 6.59 (m, 2 H), 6.21 (m, 2 H, arom.), 5.05 (br. s, 1 H), 4.32 (br. s, 1 H), 4.12 (br. s, 1 H), 3.87 (br. s, 1 H, COD CH), 2.74 (t, J = 17 Hz, 1 H), 1.2−2.5 (m, 15 H), 1.48 (s, 3 H, CH_3), 0.65 (m, 1 H), 0.33 (m, 1 H) ppm. ^{13}C NMR (100.63 MHz, CD_3OD): δ = 217.1 (d, $^3J_{C\text{-}P}$ = 12.4 Hz, C=O), 127−138 (arom.), 105.7, 100.3, 99.4, 90.8 (=CH), 58.3 (C), 55.3 (C), 44.1 (d, $J_{C\text{-}P}$ = 8.5 Hz, 4-CH), 41.6 (3-CH_2), 36.9 (d, $^1J_{C\text{-}P}$ = 21 Hz, P−CH_2), 34.3, 33.8, 26.0−28.0 (CH_2), 24.8 (CH_3) ppm. ^{31}P NMR (161.98 MHz, CD_3OD): δ = 13.2 (dm, J = 154 Hz), 3.7 (dm, J = 154 Hz) ppm.

[Rh(COD)(8b)]BF_4: ^{1}H NMR (400.13 MHz, CD_3OD): δ = 8.42 (t, J = 8.7 Hz, 2 H), 8.06 (t, J = 8.7 Hz, 2 H), 7.81 (t, J = 8.7 Hz, 1 H), 7.55−7.70 (m, 5 H), 7.47 (t, J = 8.7 Hz, 1 H), 7.25−7.45 (m, 5 H), 7.10 (br. s, 2 H), 6.90 (t, J = 8.7 Hz, 2 H, arom.), 4.3−5.5 (br. signals, 4 H, =CH), 4.16 (t, J = 14.5 Hz, 1 H, 2-H), 2.85 (d, J = 14.5 Hz, 1 H), 2.41 (dd, J = 10.3, 15.2 Hz, 1 H), 2.34 (br. s, 5 H), 2.22 (m, 1 H), 2.04 (br. s, 5 H), 1.85 (m, 1 H), 1.71 (m, 1 H), 1.54 (m, 1 H), 0.90 (m, 1 H), 0.54 (td, J = 4.6, 11.9 Hz, 1 H), 0.36 (tt, J = 3.7, 9.5 Hz, 1 H, CH_2), 1.92 (s, 3 H, CH_3) ppm. ^{13}C NMR (100.63 MHz, CD_3OD): δ = 127−134 (arom.), 80.6 (d, $^3J_{C\text{-}P}$ = 10.8 Hz, 2-CH), 55.3, 52.3, 48.2 (4-CH), 41.6, 36.2, 33.1 (d, $J_{C\text{-}P}$ = 28.3 Hz), 30.9, 30.4, 30.1 (d, J = 18 Hz), 30.0, 29.6, 27.1 (CH_2), 20.8 (CH_3) ppm. ^{31}P NMR (161.98 MHz, CD_3OD): δ = 14.9 (dd, J = 31.9 and 141.5 Hz), 5.3 (dd, J = 31.9 and 141.5 Hz) ppm.

[Rh(COD)(9b)]BF_4: ^{1}H NMR (400.13 MHz, CD_3OD): δ = 8.36 (br. m, 2 H), 7.98 (t, J = 7.3 Hz, 2 H), 7.20−7.70 (m, 12 H), 7.12 (br. m, 2 H), 6.84 (t, J = 7.3 Hz, 2 H, arom.), 5.29 (br. s, 1 H), 4.54 (br. s, 1 H), 4.24 (br. s, 1 H), 3.70 (br. s, 1 H, =CH−), 3.80 (t, J = 8.2 Hz, 1 H), 3.68 (m, 1 H), 3.59 (q, J = 6.7 Hz, 1 H), 3.48 (q, J = 6.7 Hz, 1 H, OCH_2CH_2O), 2.83 (m, 1 H), 2.56 (dd, J = 2.5, 12.0 Hz, 1 H), 2.35−2.50 (m, 3 H), 2.10−2.25 (m, 3 H), 1.89 (m, 1 H), 1.87 (s, 3 H, CH_3), 1.52 (m, 1 H), 1.34 (d, J = 12.0 Hz, 1 H), 1.23 (m, 1 H), 1.02 (m, 1 H), 0.45 (td, J = 2.5, 11.7 Hz, 1 H)

ppm. ^{13}C NMR (100.63 MHz, CD_3OD): δ = 128−137 (arom.), 117.1 (d, $^3J_{C\text{-}P}$ = 12.4 Hz, 2-C), 103.9, 100.4, 98.9, 88.8 (=CH−), 64.9, 63.8 (OCH_2CH_2), 55.5, 50.3 (C), 47.9 (d, $J_{C\text{-}P}$ = 9.5 Hz, 4-CH), 43.6, 39.4 (d, $J_{C\text{-}P}$ = 21. Hz), 33.9, 33.2, 25.7−27.9 (CH_2), 25.9 (d, $J_{C\text{-}P}$ = 16 Hz, CH_3) ppm. ^{31}P NMR (161.98 MHz, CD_3OD): δ = 15.6 (dd, *J* = 33. 3 and 142.9 Hz), 5.2 (dd, *J* = 33. 3 and 142.9 Hz) ppm.

[Rh(COD)(17)]BF_4: ^1H NMR (400.13 MHz, CD_3OD): δ = 8.30−8.50 (m, 4 H), 7.80−7.90 (m, 4 H), 7.40-7-70 (m, 12 H, arom.), 4.43 (br. s, 1 H), 4.37 (br. s, 1 H), 4.31 (br. s, 2 H), (COD CH), 3.00 (m, 1 H), 2.85 (m, 1 H), 2.75 (d, *J* = 15.0 Hz, 1 H), 1.00−2.60 (overlapped m, 17 H), 0.96 (d, *J* = 7.1 Hz, 3 H, 2-CH_3), 0.75 (s, 3 H, 7-CH_3) ppm. ^{13}C NMR (100.63 MHz, CD_3OD): δ = 125−135 (arom), 113.2, 103.1, 98.6, 98.5 (=CH), 47.9 (CH), 43.2 (CH), 41.6, 41.8, 33.4, 32.8, 32.9, 31.6, 30.8, 30.0, 28.9, 28.6, 25.6, 20.3 (CH_3), 18.8 (CH_3) ppm. ^{31}P NMR (161.98 MHz, CD_3OD): δ = 15.6 (dd, *J* = 43.0 and 142.0 Hz), 14.3 (dd, *J* = 43.0 and 142.0 Hz) ppm.

Crystal Structure Determinations: Crystals of [Rh(**7b**)(COD)]BF_4 and [Rh(**7a**)(COD)]BF_4 for the X-ray analyses were obtained by slow crystallization from MeOH solutions of the rhodium complexes. Diffraction data were collected with a STOE-IPDS diffractometer with graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods (SHELXS-97)[36] and refined by full-matrix, least-squares techniques against F^2 (SHELXL-97).[37] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. The non-hydrogen atoms {except the atoms of disordered groups and solvent molecules of [Rh(COD)(**7b**)BF_4]} were refined anisotropically. The hydrogen atoms were placed in theoretical positions and were refined by using the riding model. Crystal and refinement data of [Rh(COD)-(**7a**)]BF_4: crystal size = 0.3 × 0.2 × 0.2 mm, space group $P2_12_12_1$, orthorhombic, *a* = 9.867(2), *b* = 18.742(4), *c* = 19.908(4) Å, *V* = 3681.5(13) Å^3, *Z* = 4, $\rho_{calcd.}$ = 1.477 g/cm^3, μ (Mo-K_α) = 0.605 mm^{-1}, *T* = 200 K, *F*(000) = 1688, Θ range for data collection = 1.49−21.13°, index range (*h*,*k*,*l*) = −9/9, −18/19, −20/19, reflections collected = 13768, observed reflections = 2988, refined parameters = 460, *R*1 [2σ(I)] = 0.0369, *R*1 (all data) = 0.0532. Crystal and refinement data of [Rh(COD)(**7b**)]BF_4: crystal size = 0.4 × 0.3 × 0.2 mm, space group $P2_1$, monoclinic, *a* = 9.583(2), *b* = 19.029(4), *c* = 11.457(2) Å, β = 106.00(3), *V* = 2008.3(7) Å^3, *Z* = 2, $\rho_{calcd.}$ = 1.380 g/cm^3, μ (Mo-K_α) = 0.557 mm^{-1}, *T* = 200 K, *F*(000) = 862, Θ range for data collection = 2.14−24.34 °, index range (*h*,*k*,*l*) = −10/10, −22/21, −13/13, reflections collected = 10914, observed reflections = 5122, refined parameters = 469, *R*1 [2σ(*I*)] = 0.0433, *R*1 (all data) = 0.0530. CCDC-186344 ([Rh-(COD)(**7a**)]BF_4) and -186343 ([Rh(COD)(**7b**)]BF_4) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors are grateful for a grant given by the Alexander von Humboldt Foundation to I. K. We thank Dr. A. Kless for helpful discussions. We are indebted to the Degussa AG (Frankfurt) and the Fonds der Chemischen Industrie for financial support. It is a pleasure for us to acknowledge skilled technical assistance by S. Buchholz.

[1] *Asymmetric Synthesis* (Ed.: J. D. Morrison), Academic Press, Orlando, **1985**, vol. 5. R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, **1994**. *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Heidelberg, **1999**, vol. I−III. *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima), Wiley-VCH, New York, **2000**.
[2] See, for example: H. Brunner, W. Zettlmeier, *Handbook of Enantioselective Catalysis with Transition Metal Compounds, Ligands*, VCH Verlagsgesellschaft, Weinheim, **1993**, vol. II.
[3] W. P. Janks, *Catalysis in Chemistry and Enzymology*, McGraw-Hill, New York, **1969**.
[4] M. Yatagai, M. Zama, T. Yamagishi, M. Hida, *Chem. Lett.* **1983**, 1203. I. Yamada, M. Yamaguchi, T. Yamagishi, *Tetrahedron: Asymmetry* **1996**, *7*, 3339.
[5] S. Borns, R. Kadyrov, D. Heller, W. Baumann, A. Spannenberg, R. Kempe, J. Holz, A. Börner, *Eur. J. Inorg. Chem.* **1998**, 1291−1295. S. Borns, R. Kadyrov, D. Heller, W. Baumann, J. Holz, A. Börner, *Tetrahedron: Asymmetry* **1999**, *10*, 1425−1431.
[6] J. Holz, M. Quirmbach, U. Schmidt, D. Heller, R. Stürmer, A. Börner, *J. Org. Chem.* **1998**, *63*, 8031−8034. W. Li, Z. Zhang, D. Xiao, X. Zhang, *Tetrahedron Lett.* **1999**, *40*, 6701−6704. Y.-Y. Yan, T. V. RajanBabu, *J. Org. Chem.* **2000**, *65*, 900−906. W. Li, Z. Zhang, D. Xiao, X. Zhang, *J. Org. Chem.* **2000**, *65*, 3489−3496. Y.-Y. Yan, T. V. RajanBabu, *Org. Lett.* **2000**, *2*, 199−202.
[7] J. Holz, D. Heller, R. Stürmer, A. Börner, *Tetrahedron Lett.* **1999**, *40*, 7059−7062. T. V. RajanBabu, Y.-Y. Yan, S. Shin, *J. Am. Chem. Soc.* **2001**, *123*, 10207−10213. J. Holz, R. Stürmer, U. Schmidt, H.-J. Drexler, D. Heller, H.-P. Krimmer, A. Börner, *Eur. J. Org. Chem.* **2001**, 4615−4624.
[8] For reviews on the effect of oxy groups in Rh-catalyzed asymmetric hydrogenation see: A. Börner, *Eur. J. Inorg. Chem.* **2001**, 327−337. A. Börner, *Chirality* **2001**, *13*, 625−628. For a more general review of ambifunctional catalysts, see: G. J. Rowland, *Tetrahedron* **2001**, *57*, 1865−1882.
[9] T. Money, *Nat. Prod. Rep.* **1985**, *2*, 253−289.
[10] J. Seyden-Penne, *Chiral Auxiliaries and Ligands in Asymmetric Synthesis*, John Wiley & Sons, New York, **1995**.
[11] J. H. Hutchinson, T. Money, S. E. Piper, *Can. J. Chem.* **1986**, *64*, 854−860.
[12] V. Vaillancourt, M. R. Agharahimi, U. N. Sundram, O. Richou, D. J. Faulkner, K. F. Albizati, *J. Org. Chem.* **1991**, *56*, 378−387.
[13] T. Sell, S. Laschat, I. Dix, P. G. Jones, *Eur. J. Org. Chem.* **2000**, 4119−4124.
[14] I. V. Komarov, M. V. Gorichko, M. Y. Kornilov, *Tetrahedron: Asymmetry* **1997**, *8*, 435−445.
[15] W. M. Dadson, M. Lam, T. Money, S. E. Piper, *Can. J. Chem.* **1983**, *61*, 343−346.
[16] Reviews for the synthesis of hydroxy phosphanes see: J. Holz, M. Quirmbach, A. Börner, *Synthesis* **1997**, 983−1006. J. Holz, M. Quirmbach, L. Götze, A. Börner, *Rec. Develop. Org. Chem.* **1998**, *2*, 685−711.
[17] K. B. Becker, C. A. Grob, in *The Chemistry of the Double-bonded Functional Groups. Part II, Suppl.* (Ed.: A. S. Patai), Interscience, New York, **1977**.
[18] J. A. Clase, D. L. F. Li, L. Lo, T. Money, *Can. J. Chem.* **1990**, *68*, 1829−1836.
[19] V. Rautenstrauch, M. Lindström, B. Bourdin, J. Currie, E. Oliveros, *Helv. Chim. Acta* **1993**, *76*, 607−615.
[20] E. P. Kyba, S. P. Rines, *J. Org. Chem.* **1982**, *47*, 4800−4801.
[21] P. E. Garrou, *Chem. Rev.* **1981**, *81*, 229−266.
[22] I. Toth, B. E. Hanson, *Organometallics* **1993**, *12*, 1506−1513.
[23] M. P. Anderson, L. H. Pignolet, *Inorg. Chem.* **1981**, *20*, 4101−4107.
[24] G. Balavoine, S. Brunie, H. B. Kagan, *J. Organomet. Chem.* **1980**, *187*, 125−139.
[25] R. Kadyrov, A. Börner, R. Selke, *Eur. J. Inorg. Chem.* **1999**, 705−711.

[26] B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, D. J. Weinkauff, *J. Am. Chem. Soc.* **1977**, *99*, 5946−5952. H. Brunner, A. Winter, J. Breu, *J. Organomet. Chem.* **1998**, *553*, 285−306. V. A. Pavlov, E. I. Klabunovskii, Yu. T. Struchkov, A. A. Voloboev, A. I. Yanovsky, *J. Mol. Catal.* **1988**, *44*, 217−243. D.-R. Hou, J. Reibenspies, T. J. Colacot, K. Burgess, *Chem. Eur. J.* **2001**, 5391−5400.
[27] G. Zhu, Z. Chen, X. Zhang, *J. Org. Chem.* **1999**, *64*, 6907−6908. D. Heller, J. Holz, H.-J. Drexler, J. Lang, H.-P. Krimmer, K. Drauz, A. Börner, *J. Org. Chem.* **2001**, *66*, 6816−6817. D. Heller, H.-J. Drexler, Y. You, W. Baumann, K. Drauz, H.-P. Krimmer, A. Börner, *Chem. Eur. J.*, in press.
[28] T. V. RajanBabu, B. Radetich, K. K. You, T. A. Ayers, A. L. Casalnuovo, J. C. Calabrese, *J. Org. Chem.* **1999**, *64*, 3429−3447.
[29] S. G. Lee, Y. J. Zhang, *Org. Lett.* **2002**, *4*, 2429−2431.
[30] A. Kless, unpublished results.
[31] J. C. Jeffrey, T. B. Rauchfuss, *Inorg. Chem.* **1979**, *18*, 2658−2666. A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27−110. J. J. Schneider, *Nachr. Chem.* **2000**, *48*, 614−620. P. Braunstein, F. Naud, *Angew. Chem.* **2001**, *113*, 702−722; *Angew. Chem. Int. Ed.* **2001**, *40*, 680−699.
[32] D. A. Slack, I. Greveling, M. C. Baird, *Inorg. Chem.* **1979**, *18*, 3125−3132.
[33] R. J. Goodfellow in *Multinuclear NMR* (Ed.: J. Mason), Plenum Press, New York, **1987**, p. 521.
[34] M. Bühl, W. Baumann, R. Kadyrov, A. Börner, *Helv. Chim. Acta* **1999**, *82*, 811−820.
[35] R. Benn, C. Brevard, *J. Am. Chem. Soc.* **1986**, *108*, 5622−5624. R. Benn, A. Rufińska, *Magn. Reson. Chem.* **1988**, *26*, 895−902. D. Nanz, PhD Thesis, Universität Zürich, **1993**.
[36] G. M. Sheldrick, *SHELXS-97*, University of Göttingen, Germany, **1997**.
[37] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1997**.

Received May 31, 2002
[O02293]