P/O Ligand Systems: Facile Synthesis, Structure, and Catalytic Tests of 2′-Phosphanyl-1,1′-biphenyl-2-ols and 2′-Phosphanyl-1,1′-binaphthyl-2-ols

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A facile synthesis of 2′-phosphanyl-1,1′-biphenyl- and 2′-phosphanyl-1,1′-binaphthyl-2-ols and their silyl ethers has been developed, consisting of electron-transfer-catalyzed ring-opening of dibenzofuran and dinaphthofuran, respectively, subsequent reaction with chlorophosphanes, and work-up with acetic acid or $ClSiMe_3$. Studies of the molecular and crystal structures reveal the presence of P···H−O bridging bonds in the more basic *t*BuPhP derivative and a nearly perpendicular arrangement of the aryl planes in the biphenyl derivatives. The barrier to rotation of the aryl planes about the C−C axis was determined by NMR in the case of the P-asymmetric derivative **3d**, using the appearance of diastereoisomers by atropisomerism and P-asymmetry. Comparative screening tests of the title compounds, phosphanylphenols and phosphanylnaphthols in homogeneous Rh-catalyzed reactions demonstrate catalytic activity in hydroformylation reactions and superior properties of the biphenyl- and binaphthyl-2-ol derivatives in relation to other P−O ligands.

P/O-hybrid ligands have attracted considerable interest in homogeneous catalysis. P−O chelate nickel complexes derived from phosphanylacetic acid are used in the Shell Higher Olefin Process[1], while *O*-substituted *o*-phosphanylphenol or phosphanylbinaphthol ethers, providing a hemilabile temporary coordination, have been applied in transition-metal-catalyzed asymmetric hydrogenation, hydroformylation[2], and enantioselective hydroboration/hydrosilylation[3]. Phosphanyl phosphites, obtained by *O*-functionalization of hydroxyarylphosphanes[4], are also of interest, and gave high *ee*'s in asymmetric catalytic hydroformylation using a 2′-diphenylphosphanyl-1,1′-binaphthyl-2-yl phosphite ligand[5]. In the course of investigations of *o*-hydroxyarylphosphanes[6][7], mainly P-asymmetrically substituted derivatives, we have also studied some 2′-phosphanyl-1,1′-biphenyl-2-ol and 2′-phosphanyl-1,1′-binaphthyl-2-ol derivatives and report here on their synthesis and structures, as well as on screening tests of their catalytic activity.

Results and Discussion

Synthesis: The synthesis of hydroxy-substituted aryl phosphanes is accomplished most frequently by metalorganic strategies: (i) metallation of *o*-bromoaryl phosphinites followed by an intramolecular carbanionic rearrangement[6]; (ii) the formation of C,O-dilithio reagents and coupling with chlorophosphanes[7]; and (iii) synthesis of *O*-protected derivatives by substitution of chlorophosphanes with RM^1 and subsequent ether cleavage[8]. An alternative Pd-catalyzed coupling of iodophenol and other functionally substituted iodoarenes with primary and secondary arylphosphanes, affording the respective phosphanes, has recently been reported[9]. 2-Chloro-1,2-bihydrodibenzo[*c,e*]-1,2-oxaphosphorin, a precursor of 2′-phosphanyl-1,1′-diphenyl-2-ol derivatives, has been synthesized from 2-hydroxydiphenyl and PCl_3 in the presence of Lewis acid catalysts[10].

We studied the use of C,O-dilithio reagents in obtaining the title compounds, and made comparisons with the behavior of C,O-Li_2 species derived from *o*-bromophenols and 1-bromonaphth-2-ols. Suspensions of lithium 2-lithio-1,1′-biphenyl-2-olate **1** can be obtained by C−O bond cleavage of dibenzofuran with lithium under prolonged reflux in diethyl ether or dioxane, whereas tetrahydrofuran was found to be unsuitable[11][12]. We observed that, using conventional lithium suspensions, reaction times of about 4 d were necessary to achieve sufficient and reproducible conversion to **1** and reasonable yields of 2′-phosphanyl-1,1′-biphenyl-2-yl silyl ethers **2** or 2′-phosphanyl-1,1′-biphenyl-2-ols **3** in the subsequent reaction with chloro- or alkoxyphosphanes and work-up with $ClSiMe_3$ or acids (Scheme 1). A consider-

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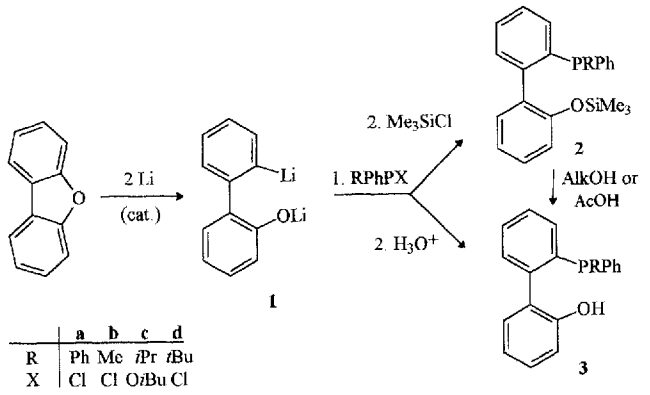
able acceleration of the reductive ring-opening reaction could be achieved by employing ultrasound, probably by removing the dilithium reagent from the surface of the metal. Recent work by Yus and co-workers on direct lithiation[13] with electron-transfer catalysts prompted us to attempt the ring cleavage in the presence of 4,4′-di-*tert*-butyldiphenyl. We found a significantly reduced reaction time (from 4 d to ca. 12 h) and an improved yield of the coupling product **3a**. The solvent THF is itself not attacked under these conditions, although it was found to be cleaved in the presence of $BF_3 \cdot OEt_2$[14]. The initial green color of the lithium arene-radical anion turns to brown during the course of the C–O cleavage and a greenish-brown color remains upon completion of the reaction. The superimposed intense brown color prevents a clear, visible monitoring of the consumption of dibenzofuran by the ultimately formed lithium arene-radical anion. The brown color disappears after reaction with chlorophosphanes.

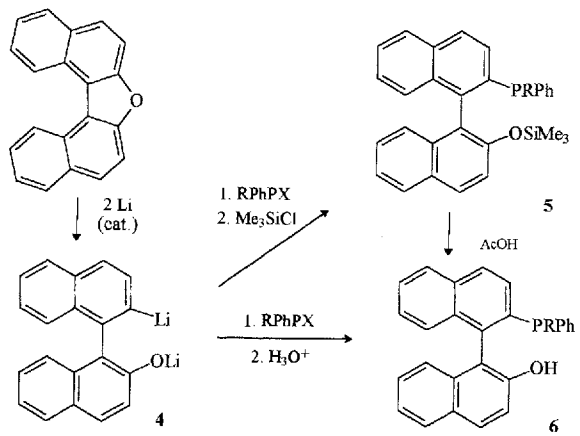
Scheme 1



The substitution of **1** by chloro- or alkoxyphosphanes proceeds chemoselectively at the carbon atom. C,O-disubstitution, observed especially with rigid, sterically stressed di-*tert*-butyl-2-lithiophenolate[7a], is not significant. Reaction of the somewhat bulkier *t*BuPhPCl with **1** affords **2d** in reasonable yield. Nevertheless, the yield of the methylphenyl derivative **2b** by reaction of **1** with chloro(methyl)phenylphosphane is relatively low (ca. 30%); base-induced elimination of HCl may interfere. Side reactions also occur, such as ether cleavage or competing formation of diphosphanes and lithium phosphides caused by excess lithium, which is not easily to separate from the ethereal suspension of **1**. The use of THF/4,4′-di-*tert*-butylbiphenyl circumvents this problem, since **1** is soluble in THF and can be separated from excess lithium simply by filtration through glass wool. Final *O*-silylation allows purification of **2b–d** by distillation and subsequent conversion to **3** by alcoholysis under completely neutral conditions. Deprotection of **2b** proceeds rapidly, whereas **2c,d** are less sensitive to alcoholysis or hydrolysis and must be heated for some time. The high-boiling diphenylphosphanyl derivative **2a** was treated with alcohol and the resulting crude **3a** was purified by column chromatography.

The analogous cleavage of dinaphthofuran, producing the C,O-dilithio reagent **4**, and subsequent reaction with chlorophosphanes offers a facile synthetic route to a racemate of atropisomeric 2′-phosphanyl-1,1′-binaphthyl-2-ol derivatives. The C,O-bond cleavage by lithium in diethyl ether proceeds faster (12 h) and in higher yields than in the case of dibenzofuran, possibly as a result of the greater steric stress. The reaction is accelerated in THF by the electron-transfer catalyst 4,4′-di-*tert*-butyl-1,1′-biphenyl and under these conditions is complete within 1 h. Further reaction of **4** with chlorodiphenylphosphane proceeds selectively at the carbon atom. The resulting naphtholate can be worked-up by trimethylsilylation to give **5a** or with aqueous acids affording **6a** (Scheme 2).

Scheme 2

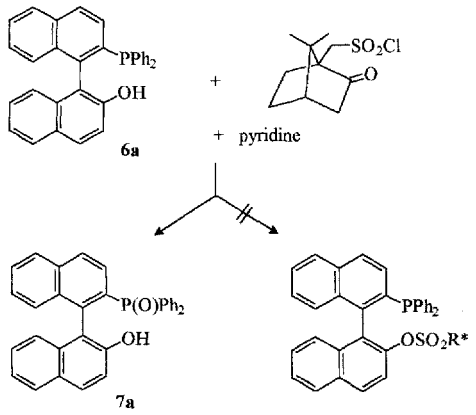


(**a**: R = Ph, X = Cl, **c**: R = *i*Pr, X = (–)-Menth)

The silyl ether **5a** is surprisingly stable towards alcohols and may be recrystallized from boiling ethanol. Deprotection to **6a** is accomplished by treatment with glacial acetic acid. Reaction of **4** with isopropylphenylphosphinous acid (1*R*,2*S*,5*R*)-menthyl ester followed by treatment with $ClSiMe_3$ furnishes **5c** in low yield. The diastereoselectivity was not high; a ratio of 2:1 was observed in the crude product. Attempts to separate the atropisomers of **6a** via diastereomeric sulfonic acid esters failed. Reaction of **6a** with (1*R*)-(–)camphor sulfonic acid chloride produced the phosphane oxide **7a** rather than a sulfonic acid ester (Scheme 3). The preparative-scale separation of the enantiomers by esterification with (1*S*)-(–)camphanic acid chloride is the subject of ongoing studies. Use of this reagent is more promising, as shown by the separation of the diastereoisomers formed with the P-asymmetric 2-(isopropylphenylphosphanyl)-4-methylphenol[7a]. Small amounts of pure enantiomers of **6a** for catalytical studies were resolved by HPLC using Chiracel OD-H as a chiral stationary phase and eluting with hexane/ethanol (98.5:1.5).

Dinaphthofuran is not commercially available and was initially prepared by oxidative dehydration of β-naphthol in the presence of V_2O_5[15] or potassium hydrogen sulfate[16]. The low yields, caused by sublimation of unreacted β-naphthol together with the product at the required high reaction temperature, prompted us to search for an improved synthesis. We obtained dinaphthofuran in high yield (91%) and

Scheme 3



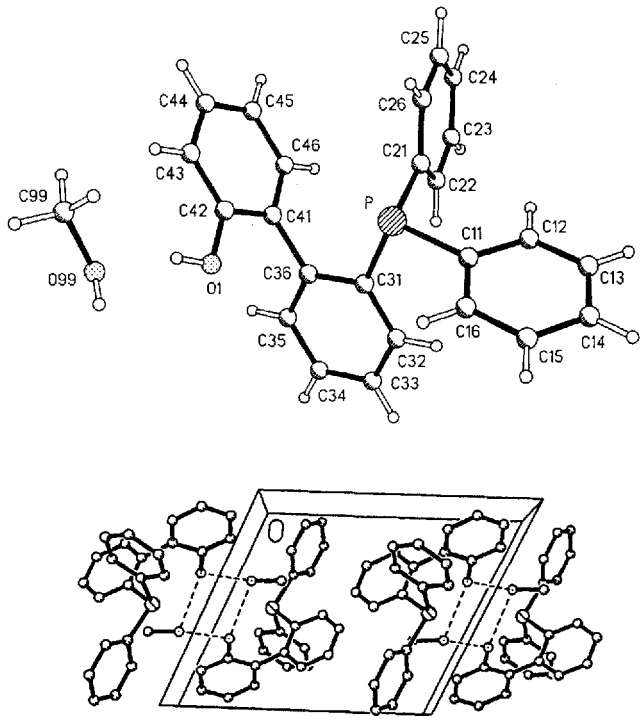
under mild conditions by use of a strongly acidic, perfluorinated sulfonic acid ion-exchange resin (Nafion-H), which had previously been successfully applied in the synthesis of dibenzofuran[17]. Subsequently, the dinaphthofuran thus obtained was treated with catalytic amounts of V_2O_5. This was found to be necessary to ensure the cleavage of the C–O bond by lithium in diethyl ether[18].

Structures: 2,2′-Disubstituted biphenyl and binaphthyl derivatives form atropisomers as a result of the steric repulsion of the substituents and hindered rotation about the 1,1′-C–C bond. An additional center of asymmetry due to the presence of different substituents at the inversion-stable phosphorus atom, gives rise to two pairs of diastereoisomers. Investigation of the crystal and molecular structures of **3a** · **MeOH** (Figure 1) and **3d** · **MeOH** (Figure 2) revealed that both crystallize in the centrosymmetric space group $P\bar{1}$ and are thus racemates. In both cases, the aryl planes of the biphenyl unit subtend a large angle (87° and 64°, respectively) thereby inducing chirality. In **3a** · **MeOH**, dimeric units are linked via inversion centres by hydrogen bonds [ArO–H···O: O···O 266.8(3) pm; MeO–H···O: O···O 278.6(3) pm]. In the P-asymmetrically substituted **3d** · **MeOH**, hydrogen-bonded dimers with inversion symmetry are also observed but, in contrast to **3a** · **MeOH**, the H bonds are ArO–H···O [O···O 270.3(2) pm] and MeO–H···P [O···P 332.7(2) pm] due to the increased basicity at the phosphorus atom. The conformation of the 2-hydroxybiphenyl group in the crystals is close to *trans-bisectional*, (X–P–C31–C36) = −169.7° in **3a** and (X–P–C1–C2) = 169.8° in **3d** (X is the centre of gravity of the three C atoms bound at phosphorus), while the phenyl groups prefer approximately *eclipsed* or *staggered* orientations.

The NMR spectra of the mixtures of diastereoisomeric alkylphenylphosphanyl hydroxybiphenyl derivatives **2b–d** and **3b–d** each feature two sets of signals. One of the diastereomeric pairs is preferred in the case of the bulkier *O*-silylated derivatives, with a larger influence being exerted by the isopropyl than by the rotationally symmetric methyl and *tert*-butyl groups (diastereoisomer ratio in **2** with R = Me, *i*Pr, *t*Bu: 1:2, 1:3, 1:2, respectively). The preference decreases slowly upon storage, e.g. of **2b**. Alcoholysis of **2** affords **3**, initially with an unchanged diastereoisomer ratio, as shown by in situ ^{31}P-NMR experiments with **2c**. Broad signals and racemization of **3** within a short time indicate an exchange process and a relatively low barrier to rotation about the C1–C1′ axis. In order to get some appraisal of the activation enthalpy and rate of rotation, we studied the temperature dependence of the ^{31}P-NMR signals of **3d**, and our results are presented in Figure 3. Using the temperature-dependent populations of the diastereomers, determined from the integration of ^{31}P resonances, the differences between the free enthalpies of the diastereoisomers $\Delta G^\circ = -RT\ln K$ was calculated. The plot against T was found to be linear and led to the expression ΔG° [kcal/mol] = −0.66 (±0.02) + 0.0014·T, showing that the lower enthalpy (ΔH° = −0.66 kcal/mol) diastereoisomer also possesses the lower entropy [ΔS° = 1.4 cal/(mol·K)] and is less populated at higher temperatures. A line-form analysis[19] (reference to the half-widths $w_{1/2}$ of the Ph_3PO signal) furnished the k values (Table 1). The temperature dependence of the ΔG^+ values (Table 1), calculated using the Eyring equation $k = (k_BT/h)\exp(-\Delta G^+/RT)$, led to ΔH^+ = 12.87(±0.06) kcal/mol and ΔS^+ = 3.8(±0.2) cal/mol·K.

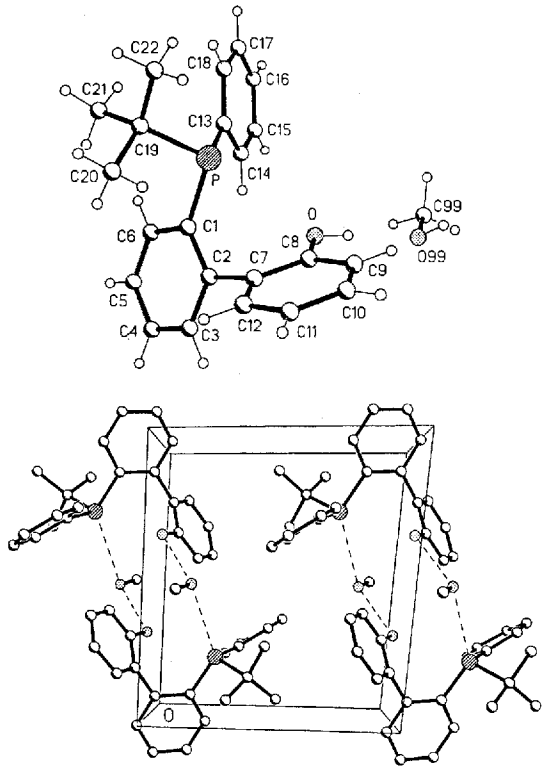
The barriers to internal rotation in biphenyl derivatives have been the subject of numerous classical studies[20][21]. The free energy of activation ΔG^+ in **3d** is lower than for biphenyls with other *ortho* substituents of similar van der

Figure 1. Crystal and molecular structure of **3a**[a]



[a] Selected distances [pm] and angles [°]: P–C11 183.0(3), P–C21 182.8(3), P–C31 183.7(3); C11–P–C21 102.2(2), C11–P–C31 101.89(14), C21–P–C31 100.71(14); O1–H1···O99: O···O 266.8(3), O–H···O 164; O99–H99···O1 (1 − x, 1 − y, −z): O···O 278.6(3), O–H···O 159; dihedral angles (X = center of gravity of C11, C21, C31): X–P–C11–C12 67.5, X–P–C21–C22 58.5, X–P–C31–C32 12.1.

Figure 2. Crystal and molecular structure of **3d**[a]



[a] Selected distances [pm] and angles [°]: P–C1 183.5(2), P–C13 183.2(2), P–C19 189.1(2); C1–P–C13 101.89(9), C1–P–C19 103.18(10), C13–P–C19 107.17(10); O–H···O99: O···O 270.3(2), O–H···O 174; O99–H···P (1 − *x*, 2 − *y*, 1 − *z*): O···P 332.7(2), O–H···P 171; dihedral angles (X = gravity center of C1, C13, C19): X–P–C1–C6 7.4, X–P–C13–C14 −83.8, X–P–C31–C32 12.1.

Figure 3. The observed and calculated ^{31}P-NMR spectra of **3d**

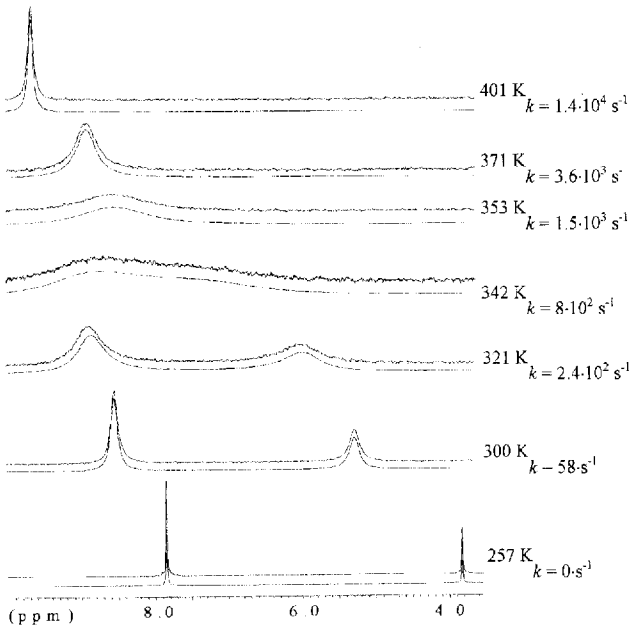


Table 1. Results of line-form analysis using WIN-DYNAMICS 1.0[19]: Temperature-dependent rate constants for the exchange and free enthalpy of activation $\Delta G^{\neq}$ calculated by the Eyring equation $k = (k_B T/h)\exp(-\Delta G^{\neq}/RT)$

T(K)	k_1	$\Delta G^{\neq}_{1\rightarrow 2}$
278.3	10	11.87
289.4	26	11.79
297.9	52	11.73
299.5	58	11.73
310	120	11.69
320.5	240	11.64
331.2	440	11.63
342.1	800	11.61
353.3	1490	11.55
362.1	2400	11.50
371.2	3600	11.49
381.7	5900	11.44
391.3	8700	11.42
401.4	14000	11.34

Waals radii. The reason for this is that the entropy of activation in most *ortho*-substituted biphenyls has a negative value between −3 and −20 cal/mol K, while it is positive in **3d** ($\Delta S^{\neq}$ = 3.8 cal/mol K). This may be attributed to the breaking of the hydrogen bond in the transition state.

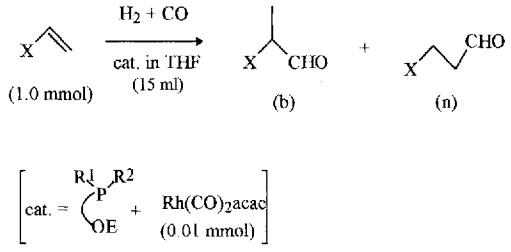
Catalysis: The advantageous *properties* of hemilabile P–O ligands in Rh-catalyzed hydrogenation and hydroformylation reactions[2][3][5] render interesting the behavior of related hydroxyl or *O*-silylated derivatives, which constitute potential P–O$^-$ precursors. The OH group promises an improved selectivity by directing interactions with O- or N-containing substrates or by the different *trans*-effect of O- and P-donors in P,O-chelate intermediates. The key factor relevant to the use of P,O-ligands might be the stability and lifetime of rhodium(I) P,O$^-$ chelate complexes, since neutral complexes are usually less active than cationic species. In this context, we became interested in comparing the co-catalytic behavior of the 2-hydroxy-2′-phosphanyl-1,1′-diphenyl and -dinaphthyl compounds with that of *o*-phosphanylphenol and 1-phosphanylnaphth-2-ol derivatives, the latter of which are known to form stable five-membered rhodium chelate complexes[2a][22].

Attempts at the homogeneous Rh-catalyzed hydrogenation of (*Z*)-PhCH=C(NHCOMe)COOMe (1 mmol at 25 °C, 0.1 MPa H_2, 0.01 mmol $[Rh(COD)_2]BF_4$ and 0.01 mmol P/O-ligand) showed that 2-phosphanylphenol and 1-phosphanylnaphth-2-ol ligands strongly impede the reaction. Low yields of the hydrogenation products were observed after prolonged reaction times, e.g. 7% in MeOH and 15% in THF with $PhP(2\text{-}OH\text{-}4\text{-}MeC_6H_3)_2$ after 24 h; 25% in MeOH and 46% in THF with *rac*-2-*t*BuPhP-4Me-$C_6H_3OSiMe_3$ after 70 h. The use of the 2-hydroxy-2′-diphenylphosphanyl-1,1′-binaphthyl ligand did not lead to any enhancement of the catalytic activity (conversion of 9% after 19 h in MeOH). It seems that by addition of the above ligands to $[Rh^I(COD)_2]BF_4$ under the reaction conditions, in situ complexes of the type $[(COD)Rh^I(P{\sim}O)_2]^+$ are formed, producing COD + 2 H^+ + $[Rh^I(P\frown O)_2]^-$ or $[Rh^{II}(P\frown O)_2]$[2a][23], which are inefficient hydrogenation catalysts. The low catalytic activity can be explained by assuming the presence of a small amount of the complex

[(COD)Rh(P⌒O)]$^+$. The formation of this type of complex is favored in THF more so than in MeOH[22c]. Accordingly, we observe a slight increase of the activity in THF.

Better results may be expected in catalytic reactions under more vigorous conditions and with components that compete more effectively with the P–O ligands for coordination sites. Studies of homogeneously Rh-catalyzed hydroformylation reactions with vinyl acetate at 80 °C/50 bar and a metal/ligand ratio of 1:1 (Scheme 4) were successful, whereas attempts using allyl acetate or with a metal/ligand ratio of 1:2 resulted in much lower conversions. The results of the hydroformylation of vinyl acetate in the presence of equimolar amounts of $Rh(CO)_2(acac)$ and some selected P–O ligands show the following trends (Table 2): *o*-Phosphanylphenols and 1-phosphanylnaphth-2-ols impede or prevent the catalysis. The activity increases, however, with the steric demand of the substituents at phosphorus, as observed for 2-*t*BuPhP-4-MeC_6H_3OH and the phosphanylnaphthol derivative. However, even then it is much lower than for phosphanylphenol ethers, as exemplified by 2-$Ph_2PC_6H_4OMe$. The secondary nature of the phosphanyl group in 2-PhHP-4-$MeC_6H_3OCH_2OMe$ does not strongly affect the catalytic behavior, activity or selectivity, although the complex chemistry is different; phosphido-bridging complexes are formed rather than P–O chelates[24]. Catalysts obtained with the title compounds, the 2-hydroxy-2′-phosphanyl-1,1′-biphenyl and -1,1′-binaphthyl derivatives **3** and **6** exhibit a high activity, while the 2-trimethylsilyloxy derivatives **2** and **5** are somewhat less effective.

Scheme 4



An increase in the ligand/Rh ratio causes inhibition of the hydroformylation. In the case of phosphanylphenols and -naphthols, catalysis is completely suppressed; for more active phosphanylphenol ethers or the binaphthyl-2-ol derivative **6a** it is markedly reduced. A decrease in activity with increasing ligand/metal ratio has also been observed for other mixed bidentate ligands[25] and can be rationalized in terms of the formation of unreactive complexes of the type [Rh(P⌒O)$_2$], which are better stabilized in the case of five- than in the case of seven-membered chelates.

The enantioselectivity induced by single enantiomer chiral ligands (+)-**6a** and (−)-**6a** was invariably less than 2%. A similarly low stereoselectivity (14%) has been reported previously for the Rh-catalyzed hydroformylation of styrene using analogous 2,2′-P,S substituted 1,1′-binaphthyl derivatives[26]. No *ee* was recorded with catalysts containing pyridylphosphane ligands able to form eight-membered rings by P,N chelation[27]. It seems that the smaller chelate effect in complexes with large heterobidentate ligands and the consequent facile ring-opening to form monodentate P-coordinated species during the hydroformylation, might be responsible for the low stereoselectivity as well as the high activity. Studies of the complex chemical behavior of **3** and **6** aimed at consolidating this interpretation will be carried out in due course.

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Experimental Section

General: Solvents were dried over appropriate drying agents and freshly distilled under argon prior to use. Me_3SiCl was distilled under argon, chloromethylphenylphosphane[28] and chloro-*tert*-butylphenylphosphane[29] were prepared according to literature procedures, and chloroisopropylphenylphosphane was obtained by an appropriate adaptation of the latter. All reactions were carried out under an argon atmosphere by using standard Schlenk techniques.

Table 2. Results of the Rh-catalyzed hydroformylation of vinyl acetate and allyl acetate in the presence of P–O ligands[a]

	R^1	R^2	E	aryl	L/Rh ratio	Pressure [bar]	Temp. [°C]	Time [h]	Conv. [%]	Selectivity (b/n) [%]
R–OAc										
	*i*Pr	H	H	4-MeC_6H_3	1	60	80	24	<1	–
	Ph	*t*Bu	H	4-MeC_6H_3	1	50	80	24	10	99 : 1
	Ph	*i*Pr	H	$C_{10}H_6$	1	50	60	24	45	b only
	Ph	Ph	Me	C_6H_4	1	54	60	17	99	b only
	Ph	Ph	Me	C_6H_4	2	50	40	18	10	b only
	Ph	H	CH_2OMe	4-MeC_6H_3	1	60	80	24	71	b only
3d	Ph	*t*Bu	H	C_6H_4-C_6H_4	1	55	81	24	91	98 : 2
2a	Ph	Ph	$SiMe_3$	C_6H_4-C_6H_4	1	60	80	24	83	96 : 4
5a	Ph	Ph	$SiMe_3$	$C_{10}H_6$-$C_{10}H_6$	1	60	80	24	81	b only
6a	Ph	Ph	H	$C_{10}H_6$-$C_{10}H_6$	1	42	60	70	96	b only
6a	Ph	Ph	H	$C_{10}H_6$-$C_{10}H_6$	2	50	60	60	46	b only
R=CH_2OAc										
	Ph	*i*Pr	R*[b]	4-MeC_6H_3	4	60	40	17	79	1.9
6a	Ph	Ph	H	$C_{10}H_6$-$C_{10}H_6$	1	55	60	2	74	1.1
6a	Ph	Ph	H	$C_{10}H_6$-$C_{10}H_6$	2	50	40	72	36	2.9

[a] 0.01 to 0.04 mmol of ligand, 0.01 mmol of $Rh(CO)_2(acac)$, 1 mmol of substrate CH_2=CHR in 15 ml of THF; *o*-phosphanylphenols, phosphanylnaphthols[7a][7b]. – [b] R* = (1*S*)-camphanoyl.

– NMR data were recorded on a multinuclear FT-NMR spectrometer ARX 300 (Bruker) at 300.1 (^{1}H), 75.5 (^{13}C), and 121.5 MHz (^{31}P) with reference to TMS and H_3PO_4 (85%), respectively. $CDCl_3$ was used as solvent unless otherwise indicated. – Mass spectra (EI, 70 eV) were measured on a single-focussing sector-field mass spectrometer AMD40 (Intectra). – HPLC was performed using a Model 1090 Scries II Liquid Chromatograph, equipped with a diode-array detector (Hewlett-Packard) and a Chiralyser (IBZ Messtechnik, Hannover, Germany). Separation was achieved using Chiracel OD-H analytical columns (250 × 4.6 mm I.D., Deicel).

The experimental procedures for the hydrogenation, the synthesis of the substrate, the derivatization and the determination of the hydrogenated products are described in ref.[30]. Gas chromatographic analyses were carried out on a Hewlett-Packard 5890 Series II gas chromatograph with flame ionization detector using a 25-m fused silica (HP101 or Lipodex E) capillary column.

2-[2'-(Diphenylphosphanyl)phenyl]phenyl Trimethylsilyl Ether (**2a**) *and 2-[2'-(Diphenylphosphanyl)phenyl]phenol* (**3a**): A suspension of lithium (1.5 g, 216 mmol) was added to a solution of dibenzofuran (16.8 g, 100 mmol) in 250 ml of diethyl ether and the mixture was heated for 25 h with sonication (120 W ultrasound bath, Bandelin) affording a red-brown solution and ultimately a brown suspension of **1**. After cooling to 0–5 °C, a solution of 22.0 g (100 mmol) of $ClPPh_2$ in THF (60 ml) was added dropwise. Stirring was continued at room temperature for 2 h (or overnight) and then 13 ml (103 mmol) of $ClSiMe_3$ was added slowly. The precipitate was removed by filtration and the solvent was evaporated in vacuo, leaving a viscous residue (42 g) containing **2a** ($\delta^{31}P$ = −11.8), tetraphenyldiphosphane ($\delta^{31}P$ = −14.6), Ph_2PSiMe_3 ($\delta^{31}P$ = −55.9, δ^1H_{SiMe3} = 0.23, d, J_{PH} = 4.8 Hz), and 2-Me_3SiO-C_6H_4-Ph. 17.0 g of the residue was distilled to give 2.4 g of unreacted dibenzofuran (80 °C/0.02 Torr) and a mixture with a boiling range of 110–180 °C/0.02 Torr. The remaining residue (25 g) was dissolved in hot methanol (50 ml), allowed to cool, poured into water (50 ml) and extracted with diethyl ether (3 × 50 ml). After drying with Na_2SO_4, the solvent was removed and the extract was purified by preparative column chromatography on silica (overload chromatography, substrate:silica 1:10), using petroleum ether/ethyl acetate (6:4) as the mobile phase. Removal of the solvent from the product fractions left a syrup, which was crystallized from methanol affording 9.4 g (41%, rel. to chromat. work-up) of pure **3a** · **MeOH**, m.p. 128 °C. – ^{31}P NMR ($CDCl_3$): δ = −12.3. – $C_{25}H_{23}O_2P$ (386.4): calcd. C 77.70, H 6.00; found C 77.70, H 6.06. – X-ray crystal structure analysis see Figure 1.

2-[2'-(Methylphenylphosphanyl)phenyl]phenyl Trimethylsilyl Ether [**2b(A,B)**]: A solution of dibenzofuran (4.2 g, 25 mmol) in diethyl ether (200 ml) was stirred for 60 h at room temperature with lithium suspension (0.4 g, 57 mmol). Then, Ph(Me)PCl (4.0 g, 25 mmol) was added at 0 °C and the brown suspension was stirred for a further 2 h. Thereafter, $ClSiMe_3$ (6.5 ml) was added, the precipitate was filtered off, the solvent was removed and the residue was distilled. The fraction obtained at 150–170 °C/0.1 Torr (4.0 g) was redistilled at 130–135 °C/10^{-3} Torr affording 2.7 g (30%) of a mixture of diastereoisomers **2b(A)** and **2b(B)**. The product was found to be slightly contaminated by an unidentified compound with $\delta^{31}P$ = 84.7, which constituted the main component of the residue. **2b(A,B)**. – ^{1}H NMR ($CDCl_3$): δ = 0.52, 0.53 (2 s, $SiMe_3$, **B,A**), 1.61 (d, $^2J_{PH}$ = 2.8 Hz, PMe, **B**), 1.75 (d, $^2J_{PH}$ = 4.0 Hz, PMe, **A**, int. **A/B** = 8:5), 6.8–7.8 (m, aryl H). – ^{31}P NMR ($CDCl_3$): δ = −34.4 and −33.1 (**A/B**, int. roughly 2:1). – $C_{22}H_{25}OPSi$ (364.5): calcd. C 72.49, H 6.91; found C 73.45, H 7.09. Chromatography of a degassed ethereal solution of crude **2b** on silica gel was accompanied by partial hydrolysis of **2b** to **3b**, $\delta^{31}P$ = −35.5, −39.1 (ca. 1:1, broad singlets).

2-[2'-(Isopropylphenylphosphanyl)phenyl]phenyl Trimethylsilyl Ether [**2c(A,B)**]: Ph(*i*Pr)PO*i*Bu (25 g, 111 mmol) was added dropwise to a suspension of the C,O-dilithium reagent, obtained by stirring 18.2 g (108 mmol) of dibenzofuran in diethyl ether (200 ml) with lithium suspension (1.49 g, 216 mmol) for 4 d. It was allowed to react for 1 d at room temperature, then 6.5 ml of $ClSiMe_3$ was added. The precipitate was filtered off, the solvent was removed from the filtrate, and the remainder was distilled to give 16.2 g (38%) of viscous oily **2c(A,B)**, b.p. 140–145 °C/0.005 Torr. – ^{1}H NMR ($CDCl_3$): δ = 0.0 , 0.12 (2 s, $SiMe_3$, **B,A**, ca. 1:3), 1.01, 1.22 (each dd, $^3J_{HH}$ = 6.9, $^3J_{PH}$ = 15.6 Hz, $Me_{A,B}$, **A**), ca. 0.99, ca. 1.06 (each dd, $Me_{A,B}$, **B**; **A**+**B**, 6 H), 2.42, 2.52 (2q, $^3J_{HH}$ = 6.6, 6.9 Hz, PC*H*, **B,A**, 1 H); **A**: 6.67 (d, 1 H), 6.86 ("t", 1 H), 7.00 (d, *J* = 8.1 Hz, 1 H), 7.58 (m, 2 H), 7.90 (d, 1 H); **B**: ca. 6.93 (d, 1 H), ca. 7.15 ("t", 1 H), 7.2–7.5 (m, aryl H). – ^{31}P NMR ($CDCl_3$): δ = −9.7 and −10.0 (**A/B**, intensity roughly 3:1). – $C_{24}H_{29}OPSi$ (392.6): calcd. C 73.43, H 7.45; found C 73.22, H 7.54.

2-[2'-(Isopropylphenylphosphanyl)phenyl]phenol [**3c(A,B)**]: 5.7 g of **2c(A,B)** was dissolved in warm methanol (10 ml). 2.35 g (50%) of colorless crystals formed after 1 h. Attempts at recrystallization furnished an oil, consisting of spectroscopically pure (NMR) diastereoisomers **3c(A,B)** with a low tendency to crystallize.The product distilled at 147–151 °C/10^{-3}Torr. – ^{1}H NMR ($CDCl_3$): δ = 0.96, 1.17 (each dd, $^3J_{HH}$ = ca. 6.7, $^3J_{PH}$ = ca. 16.3 Hz, Mc, **A**), 0.93, 1.04 (each dd, $^3J_{HH}$ = 6.9, $^3J_{PH}$ = 15.3 Hz, Me, **B**; **A**+**B**, 6 H), 2.43 (m, PC*H*, **B,A**, 1 H), 1.80 (br. s, 1 H, OH); **A**: 6.47 (d, *J* = 7.2 Hz, 1 H), 6.70 ("t", 1 H), 6.99 (d, *J* = 7.8 Hz, 1 H), ca. 7.60 (m, 2 H), ca. 7.75 (d, 1 H); **B**: 6.82 (d, 1 H), 7.00 ("t", 1 H), 7.2–7.5 (m, aryl H). – ^{31}P NMR ($CDCl_3$): δ = −8.6 and −9.8 (**A**:**B**, intensity ca. 55:45%). – $C_{21}H_{21}OP$ (320.4): calcd. P 9.67; found P 9.62.

2-[2'-(tert-Butylphenylphosphanyl)phenyl]phenyl Trimethylsilyl Ether (**2d**): A solution of 14.0 g (70 mmol) of *t*BuPhPCl in diethyl ether (20 ml) was added to the C,O-dilithium reagent, prepared by reaction of dibenzofuran (11.7 g, 70 mmol) with lithium (1.0 g, 144 mmol) in 200 ml of diethyl ether (30 h reflux, sonication bath). After stirring overnight, 8.8 ml of $ClSiMe_3$ was added, the precipitate was filtered off and the solvent was evaporated. 17 g (60%) of viscous oily **2d(A,B)** was obtained, distilling at 170–174 °C/0.01 Torr. – ^{1}H NMR ($CDCl_3$): δ = −0.08, 0.09 (2 s, $SiMe_3$, **A/B** 63:37), 1.06 (d, $^3J_{PH}$ = 12.3 Hz, C*Me*$_3$ **A**), 1.15 (d, $^3J_{PH}$ = 12.5 Hz, C*Me*$_3$ **B**); **A**: 6.55 (d, 1 H), 6.67 ("t", 1 H), 6.84 (d, *J* = 8 Hz, 1 H), ca. 7.57 (m, 2 H), ca. 7.84 (1 H); **B**: 6.85 (d, 1 H), 7.03 ("t", 1 H), 7.2–7.5 (m, aryl H). – ^{31}P NMR ($CDCl_3$): δ = 7.4 and 6.7 (**A/B**, int. 2:1). The product was found to be contaminated by ca. 5 mol% (tBuPhP)$_2$, identified by NMR[6a]; this diphosphane constituted about one-third of the crude product.

2-[2'-(tert-Butylphenylphosphanyl)phenyl]phenol (**3d**): **2d(A,B)** was heated with 10 ml of methanol. A 1:1 adduct with methanol, **3d(A,B)** · MeOH, crystallized at room temperature, m.p. 45–47 °C. – ^{1}H NMR ($CDCl_3$): δ = 1.10 (d, $^3J_{PH}$ = 12.7 Hz, C*Me*$_3$ **A**), 1.19 (d, $^3J_{PH}$ = 12.9 Hz, C*Me*$_3$ **B**); **A**: 6.37 (d, 7.6 Hz, 1 H), 6.57 ("t", 1 H), 6.94 (d, 8 Hz, 1 H), ca. 7.70 (dm, 1 H), ca. 7.95 (dm, 1 H); **B**: 6.80 (d, 1 H), 6.95 ("t", 1 H), 7.1–7.5 (m, aryl H). – ^{31}P NMR ($CDCl_3$): δ = 8.0 and 8.2 (**A/B**, int. 1:1). – $C_{23}H_{27}O_2P$ (366.4): calcd. C 75.39, H 7.43; found C 74.83, H 7.83. – X-ray crystal structure analysis see Figure 2.

Dinaphtho[2,1-b;1',2'-d]furan: 30 g (263 mmol) of β-dinaphthol and 15 g of strongly acidic ion-exchange resin, Nafion-NR50 (Aldrich), were refluxed in *o*-xylene (100 ml) in an apparatus fitted with a water separator until ca. 2.3 ml of water had been collected (ca. 16 h). The hot solution was then decanted from the ion-exchange resin and ca. 3/4 of the solvent was evaporated in vacuo. Pale-yellow crystals of dinaphtho[2,1-*b*;1',2'-*d*]furan were collected, the solvent was removed from the filtrate and the residue was crystallized from toluene/heptane (ca. 1:2). The total yield was 25.2 g (91%), m.p. 153–155 °C (cf. 156 °C ref.[31]). To obtain reproducible results in the lithium cleavage, the entire material was refluxed for 1 h with vanadium pentoxide and crystallized once more. – ^{1}H NMR ($CDCl_3$): δ = 7.44 (ddd, J_{H6H5} = 8.1, J_{H6H7} = 6.9, J_{H6H8} = 1.0 Hz, 6-H), 7.60 (ddd, J_{H7H8} = 8.5, J_{H7H6} = 6.9, J_{H7H5} = 1.3 Hz, 7-H), 7.64 [d(AB), J_{H4H3} = 8.9 Hz, 4-H], 7.75 [d(AB), J_{H3H4} = 8.9 Hz, 3-H], 7.88 (dd, J_{H5H6} = 8.1, J_{H7H5} = 1.3 Hz, 5-H), 8.98 (d, J_{H8H7} = 8.5 Hz, 8-H). – ^{13}C NMR (cf. ref.[16], $CDCl_3$): δ = 112.5 (C-3), 119.3 (C-1), 124.2, 125.5, 126.0, 128.1, 129.3 (C-4 to C-8), 128.5, 131.1 (C-4a, C-8a), 154.1 (C-2). – MS (70 eV); *m/z* (%): 269 (34) [M + 1$^+$], 268 (100) [M$^+$].

1-[2'-(Diphenylphosphanyl)naphth-1'-yl]naphth-2-yl Trimethylsilyl Ether (**5a**): A solution of 2.68 g (10 mmol) of dinaphthofuran in diethyl ether (60 ml) was stirred with a suspension of lithium (0.14 g, 20 mmol) affording a solution of **4**. The reaction was accompanied by a color change from blue through violet to dark-red. Stirring was continued overnight, then a solution of $ClPPh_2$ (2.2 g, 10 mmol) in diethyl ether (5 ml) was added dropwise to the mixture at 0 °C. After 1 h, $ClSiMe_3$ (1.5 ml) was added, the precipitate was removed and the solvent was evaporated in vacuo. The residue was refluxed for 2 h in ethanol (10 ml). 1.6 g (32%) of colorless crystals of **5a** separated, m.p. 107–109 °C. – ^{1}H NMR ($CDCl_3$): δ = –0.05 (s, 9 H, $SiMe_3$), 7.12 (d, *J* = 8.4 Hz, 1 H), 7.25 (t, *J* = ca. 7.3 Hz, 1 H), 7.28–7.38 (m, 6 H), 7.42–7.52 (m, 6 H), 7.62–7.68 (m, 2 H), 8.02 (d, *J* = 8.1 Hz, 1 H), 8.02–8.10 (m, 3 H). – ^{31}P NMR ($CDCl_3$): δ = –12.6. – MS (CI, isobutane); *m/z* (%): 583 (20) [M + isobutane$^+$], 528 (40) [M + 1$^+$], 527 (100) [M$^+$]. – IR (Nujol): no OH band. – $C_{35}H_{31}OPSi$ (526.7): calcd. C 79.82, H 5.93, P 5.88; found C 79.78, H 8.08, P 6.20.

1-[2'-(Diphenylphosphanyl)naphth-1'-yl]naphth-2-ol (**6a**): *(A):* Dinaphthofuran (3.10 g, 11.5 mmol) and 0.16 g (12 mmol) of lithium in diethyl ether (60 ml) were reacted as described above and a solution of 2.53 g (11.5 mmol) of $ClPPh_2$ in diethyl ether (20 ml) was added at 0 °C. After 1 h, 10 ml of dilute sulfuric acid (10%) was added, the organic layer was separated and the aqueous phase was extracted twice with CH_2Cl_2. The solvent was distilled off and the residue was purified by column chromatography on silica, using toluene as the eluent. Evaporation of the solvent in vacuo afforded 3.32 g (64%) of colorless crystals of **6a**, m.p. 197–200 °C, which were found to be readily soluble in CH_2Cl_2, and moderately soluble in MeOH. – ^{31}P NMR ($CDCl_3$): δ = –13.2 (ref.[3c] δ = –13.67). – $C_{32}H_{23}OP$ (454.5): calcd. C 84.56, H 5.10; found C 83.60, H 5.73.

(B): A solution of 360 mg (0.68 mmol) of the silyl ether **5a** in 3 ml of glacial acetic acid was heated for 10 min. over a water bath. The volatiles were then removed in vacuo and the residue was crystallized from methanol (2 ml) to yield 210 mg (68%) of **6a**, identified on the basis of its NMR spectra.

1-[2'-(Isopropylphenylphosphanyl)naphth-1'-yl]naphth-2-yl Trimethylsilyl Ether (**5c**): Dinaphthofuran (2.29 g, 8.5 mmol) in diethyl ether (100 ml) was stirred for 2 d with an excess of lithium suspension (0.165 g, 23.6 mmol). A solution of 2.65 g (8.5 mmol) of Ph(*i*Pr)PO(1*R*,2*S*,5*R*)-menthyl in THF (5 ml) was added, followed 2 h later by 3.0 ml of $ClSiMe_3$. After stirring overnight, 30 ml of degassed water was added, the organic phase was dried and most of the solvent was evaporated. The ^{31}P-NMR spectrum of the residue showed it to be a diastereoisomeric mixture of **5c** [signals at δ = –11.36, –11.51 (ratio ca. 2:1)] contaminated by impurities (δ = –24.9, 39.7, and 47.4) and a large amount of unreacted Ph(*i*Pr)PO-menthyl (δ = 122.3). Column chromatography on silica gel 60 (80 g) with degassed toluene as eluent furnished **5c** in low yield. The 5th and 6th fractions (each 20 ml) were found to contain **5c** in a diastereoisomeric ratio of ca. 1:1, contaminated by 2-Me_3-$SiC_{10}H_6$-1,1'-$C_{10}H_6OSiMe_3$.

1-(2'-Hydroxynaphth-1'-yl)naphth-2-yl-diphenylphosphane Oxide **7a** *by Reaction of* **6a** *with (R)-(–)-Camphor-10-sulfonyl Chloride:* 280 mg (1.03 mmol) of (*R*)-(–)-camphor-10-sulfonyl chloride was added to a solution of 450 mg (1 mmol) of **6a** in pyridine (5 ml) and the mixture was heated for 30 min. at 100 °C. After cooling, the mixture was added to water, the precipitate was filtered off, washed with water and dried in vacuo. Crystallization from ethanol afforded 300 mg of **6a**, m.p. > 265 °C. – ^{1}H NMR ([D$_6$]DMSO): δ = 6.40 (d, *J* = 8.3 Hz, 3'-H), 6.73 (td, *J* = ca. 7.0 and 1.3 Hz, 1 H), 6.82–6.94 (m, 5 H), 6.99 (m, 1 H), 7.07–7.18 (m, 3 H), 7.2–7.28 (m, 3 H), 7.37–7.47 (m, 3 H), 7.86 (d, *J* = 8.1 Hz, 1 H), 7.92 (dd, *J* = 8.6, 2.1 Hz, 1 H), 9.29 (s, 1 H, OH). – ^{31}P NMR ([D$_7$]DMF): δ = 28.5 (ref.[3c] δ = 30.8). – $C_{32}H_{23}O_2P$ (470.5): calcd. P 6.58; found P 6.45. – MS (70 eV); *m/z* (%): 471 (31) [M + 1$^+$], 470 (84) [M$^+$], 269 (21), 268 (100).

Catalysis Experiments Hydrogenation: For hydrogenation at 25 °C and 0.1 MPa H_2, 1 mmol of substrate was added to a catalyst solution prepared in situ from 0.01 mmol of $[Rh(COD)_2]BF_4$ and 0.01 mmol of phosphanylphenol in 15 ml of solvent (MeOH or THF) under anacrobic conditions.

Hydroformylation: A mixture of 1 mmol of substrate (vinyl acetate or allyl acetate), 0.01 mmol of $Rh(CO)_2(acac)$ and 0.01–0.05 mmol of ligand in 15 ml of THF was placed in a 40-ml autoclave (Ernst Haage, Mühlheim, Germany), pressurized to the appropriate initial pressure with syngas (CO/H_2 = 1:1) and heated to the reaction temperature. During the course of the reaction, several samples were withdrawn from the autoclave. Conversion, selectivity and enantiomeric excess were determined by GC.

Crystal Structure Analyses **3a · MeOH**: *Crystal data:* $C_{25}H_{23}O_2P$, 386.40, triclinic, space group $P\bar{1}$, *a* = 1024.7(2), *b* = 1063.8(3), *c* = 1148.9(3) pm, α = 111.96(1), β = 90.24(1), γ = 115.78(1)°, *V* = 1.0248(4) nm^3, *Z* = 2, D_{calc} = 1.252 Mg m^{-3}, μ(Mo-K_α) = 0.15 mm^{-1}, *F*(000) = 408, λ(Mo-K_α) = 0.71073 Å, *T* = –130 °C. – *Data collection and reduction:* A colorless prism 0.5 × 0.5 × 0.3 mm was mounted in inert oil and transferred to the cold gas stream of the diffractometer (Stoe STADI-4). A total of 3669 intensities were collected to $2\theta_{max}$ 50° using ω.2θ scans, of which 3612 were independent. – *Structure solution and refinement:* The structure was solved by direct methods and refined anisotropically on F^2 using the program SHELXL-93[32]; methyl and hydroxyl H-atoms as rigid groups, other H' quotation mark, rights riding. The final $wR(F^2)$ was 0.146 for all reflections, with conventional *R*(*F*) 0.056; 256 parameters; $S(F^2)$ 1.10; max. Δρ 253 e nm^{-3}.

3d · MeOH: *Crystal data:* $C_{23}H_{27}O_2P$, 366.42, triclinic, space group $P\bar{1}$, *a* = 980.7(3), *b* = 984.2(4), *c* = 1118.7(4), α = 83.78(2), β = 70.66(3), γ = 81.03(2), *V* = 1.0045(6) nm^3, *Z* = 2, D_{calc} = 1.211 Mg m^{-3}, μ(Mo-K_α) = 0.15 mm^{-1}, *F*(000) = 392, *T* = –130 °C. *Data collection and reduction:* Colorless tablet 0.7 × 0.7 × 0.3 mm, 3556 intensities, 3546 independent. *Structure refinement:* $wR(F^2)$ 0.117, *R*(*F*) 0.044; 241 parameters; $S(F^2)$ 1.04; max. Δρ 355 e nm^{-3}. All other details as above.

X-ray structural data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under deposition number 100448. Copies may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England [Fax (internat.): +44 (0)1223/336033; e-mail: deposit@chemcrys.cam.ac.uk].

[1] [1a] W. Keim, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 235. – [1b] W. Keim, *New J. Chem.* **1994**, *18*, 93.

[2] [2a] W. S. Knowles, *Acc. Chem. Res.* **1983**, *16*, 106. – [2b] A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27.

[3] [3a] Y. Uozumi, T. Hayashi, *J. Am. Chem. Soc.* **1991**, *91*, 9887. – [3b] Y. Matsumoto, M. Naito, Y. Uozumi, T. Hayashi, *J. Chem. Soc., Chem. Commun.* **1993**, 1468. – [3c] Y. Uozumi, A. Tanahashi, S.-Y. Lee, T. Hayashi, *J. Org. Chem.* **1993**, *58*, 1945–1948.

[4] [4a] R. Schmutzler, D. Schomburg, R. Bartsch, O. Stelzer, *Z. Naturforsch.* **1984**, *B39*, 1177. – [4b] F. Balegroune, P. Braunstein, D. Grandjean, D. Matt, D. Nobel, *Inorg. Chem.* **1988**, *27*, 3320. – [4c] M. J. Baker, P. G. Pringle, *J. Chem. Soc., Chem. Commun.* **1993**, 314.

[5] [5a] N. Sakai, S. Mano, K. Nozaki, H. Takaya, *J. Am. Chem. Soc.* **1993**, *115*, 7033. – [5b] N. Sakai, K. Nozaki, H. Takaya, *J. Chem. Soc., Chem. Commun.* **1994**, 395. – [5c] T. Higashizima, N. Sakai, K. Nozaki, H. Takaya, *Tetrahedron Lett.* **1994**, *35*, 2023. – [5d] K. Nozaki, N. Sato, H. Takaya, *J. Am. Chem. Soc.* **1995**, *117*, 9911.

[6] [6a] J. Heinicke, E. Nietzschmann, A. Tzschach, *J. Organomet. Chem.* **1986**, *310*, C 17. – [6b] J. Heinicke, R. Kadyrov, *J. Organomet. Chem.* **1996**, *520*, 131.

[7] [7a] J. Heinicke, R. Kadyrov, M. K. Kindermann, M. Koesling, P. G. Jones, *Chem. Ber.* **1996**, *129*, 1547. – [7b] J. Heinicke, R. Kadyrov, M. K. Kindermann, M. Kloss, A. Fischer, P. G. Jones, *Chem. Ber.* **1996**, *129*, 1061. – [7c] J. Heinicke, U. Jux, R. Kadyrov, M. He, *Heteroatom Chem.* **1997**, in print.

[8] [8a] H. D. Empsall, B. L. Shaw, B. L. Turtle, *J. Chem. Soc., Dalton Trans.* **1976**, 1500. – [8b] T. B. Rauchfuss, *Inorg. Chem.* **1977**, *16*, 2966.

[9] O. Herd, A. Heßler, M. Hingst, M. Tepper, O. Stelzer, *J. Organomet. Chem.* **1996**, *522*, 69.

[10] H. J. Kleiner (Hoechst), Eur. Pat. Appl. 582,957 (Cl. C07 F9/6571); *Chem. Abstr.* **1994**, *120*, 270819.

[11] [11a] H. Gilman, D. L. Esmay, *J. Am. Chem. Soc.* **1953**, *75*, 2947. – [11b] H. Gilman, J. J. Dietrich, *J. Org. Chem.* **1957**, *22*, 851.

[12] A. G. Evans, P. B. Roberts, B. J. Tabner, *J. Chem. Soc.* (B) **1966**, 269.

[13] M. Yus, *Chem. Soc. Rev.* **1996**, 155.

[14] J. Ramón, M. Yus, *Tetrahedron* **1992**, *48*, 3585.

[15] G. R. Clemo, R. Spence, *J. Chem. Soc.* **1928**, 2811.

[16] M. L. Poutsma, C. W. Dyer, *J. Org. Chem.* **1982**, *47*, 3367.

[17] T. Yamamoto, *J. Org. Chem.* **1991**, *56*, 3192.

[18] It might be that fluoride impurities are removed which passivate the lithium surface.

[19] Line-form analysis was carried out using the program WINDYNAMICS 1.0, Bruker-Franzen Analytik GmbH.

[20] E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, Wiley-Interscience Publication, New York, **1994**, pp. 1142–1150.

[21] G. Bott, L. D. Field, S. Sternhell, *J. Am. Chem. Soc.* **1980**, *102*, 5618.

[22] [22a] H. D. Empsall, E. M. Hyde, C. E. Jones, B. L. Shaw, *J. Chem. Soc., Dalton Trans.* **1974**, 1980. – [22b] K. R. Dunbar, J. H. Matonic, V. P. Saharan, *Inorg. Chem.* **1994**, *33*, 25. – [22c] A. Börner, A. Kless, J. Holz, W. Baumann, A. Tillack, R. Kadyrov, *J. Organomet. Chem.* **1995**, *490*, 213.

[23] M. Alvarez, N. Lugan, R. Mathieu, *J. Organomet. Chem.* **1994**, *468*, 249.

[24] U. Jux, Dissertation, EMA-Universität Greifswald, **1996**.

[25] [25a] S. Gladiali, L. Pinna, C. G. Arena, E. Rotondo, F. Faraone, *J. Mol. Catal.* **1991**, *66*, 183. – [25b] C. Abu-Gnim, I. Amer, *J. Chem. Soc., Chem. Commun.* **1994**, 115; C. Abu-Gnim, I. Amer, *J. Organomet. Chem.* **1996**, *516*, 235.

[26] S. Gladiali, A. Dore, D. Fabbri, *Tetrahedron: Asymmetry* **1994**, *5*, 1143.

[27] C. Basoli, C. Botteghi, M. A. Cabras, G. Chelucci, M. Marchetti, *J. Organomet. Chem.* **1995**, *488*, C20.

[28] L. Maier, *J. Inorg. Nucl. Chem.* **1962**, *24*, 1073.

[29] V. L. Foss, V. A. Solodenko, Yu. A. Veits, I. F. Lutsenko, *Zh. Obshch. Khim.* **1979**, *49*, 1724.

[30] R. Selke, H. Pracejus, *J. Mol. Catal.* **1986**, *37*, 213.

[31] G. R. Clemo, R. Spence, *J. Chem. Soc.* **1928**, 2811.

[32] G. M. Sheldrick, University of Göttingen, **1993**.

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