193. Catalytic Enantioselective Hydrosilylation of Aromatic Ketones Using Rhodium Complexes of TADDOL-Derived Cyclic Phosphonites and Phosphites

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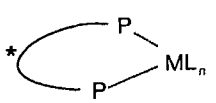
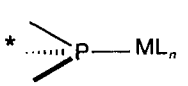
Cyclic phosphonites and phosphites **2–4** are readily available from Cl_2PR and (*R,R*)- or (*S,S*)-α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanols (= TADDOLs **1**, which, in turn, are only two steps away from tartrate); the X-ray crystal structure of one representative, the phenyl phosphonite **2b**, was determined. Five previously described and six new ones of the chiral P derivatives were tested as ligands for Rh^I- and Pd^0-catalyzed reactions such as hydrocarbonylations, hydroborations, and hydrosilylations of C=C bonds; while the resulting catalysts were highly active and regioselective, they did not lead to useful enantiomer enrichment in the products (*Scheme 1*). In contrast, hydrosilylation of phenyl and 2-naphthyl methyl or ethyl ketone by Ph_2SiH_2 (1.2 equiv.) gave, after desilylation, the corresponding secondary alcohols of (*R*)-configuration with up to 87% ee in the presence of 0.1 equiv. of the penta(2-naphthyl)-substituted phosphonite **3d** and 0.02 mol-equiv. of Rh (*Table 1*).

Introduction. – *Mono-* vs. *Bidentate Phosphorous Ligands in Enantioselective Catalysis.* While monodentate phosphorous(III) derivatives, especially phosphites with very bulky substituents, may form catalytically highly active complexes with certain transition metals[2]), enantioselective catalysis has been shown to be generally *much* more effective with bidentate, preferably C_2-symmetric ligands (see **A** *vs.* **B**) [3]. Thus, the hydrogenation of α,β-unsaturated carboxylic acids with $H_2/[Rh^IL_n]$ was found to be hardly enantioselective with monodentate phosphines [4–9] and phosphinites [10]. Hydrocyanation of C–C bonds has been studied employing Ni/chiral phosphites, and again the bidentate ligands led to higher enantioselectivity [11]. A notable exception is the recent finding by *Hayashi* and *Uozumi* [12] that the Pd-catalyzed hydrosilylation[3]) of mono- and dialkyl-substituted C=C bonds[4]) is highly enantioselective in the presence of the monodentate



A



B

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[2]) Examples are the hydroformylation and the hydrocyanation of C=C bonds using Rh [1] and Ni [2] catalysts, respectively.

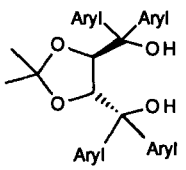
[3]) For review on hydrosilylations, see [13].

[4]) For an early review article on enantioselective hydrosilylations, including a chapter on ketone reduction, see [14].

P-ligand MOP. Also, the transition-metal-catalyzed hydrosilylation of C=O bonds[4]) was found to be reasonably enantioselective with the classical monodentate *Horner* phosphines [14], the pioneering work having been done with Pt complexes by *Kumada* and coworkers [15]. It has been confirmed by some more recent investigations that the use of bidentate P ligands does normally not lead to better enantioselectivities, also in Rh-catalyzed hydrosilylations of C=O bonds [16–19]; the highest values observed with simple ketones (bearing no additional function groups) are in the order of 65% ee. On the other hand, cationic Rh catalysts with bi- and tridentate chiral N-containing ligands have been found to reduce the keto groups with up to 200:1 selectivity [20].

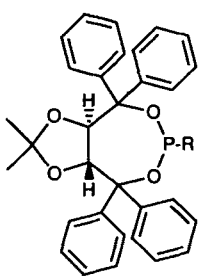
We wondered whether the cyclic monodentate phosphonites and phosphites readily available from TADDOLs **1** [21][5]) could be used in various transition-metal-catalyzed enantioselective transformations.

Preparation of TADDOL-Derived Ligands and Attempted Application to Hydrocarbonylation, Hydroboration, and Hydrosilylation of Olefins. – As phosphonite and phosphite ligands for the present investigation, we employed the TADDOL derivatives **2**, **3**, and **4**. These were prepared as described previously [21] by treating TADDOL **1a** or **1b** with BuLi in THF, followed by the addition of Cl_2PR or Cl_2POR. Procedures for the preparation of the cyclic phosphonites **2a**, **2b**, and **3a**, and for the phosphites **4a** and **4b** have been already published [21], the other six cyclic phosphinic-acid esters used herein are described in the *Exper. Part.*

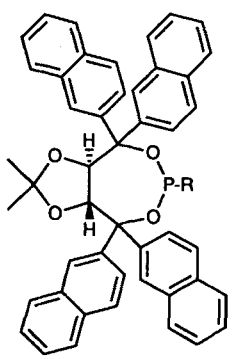


1

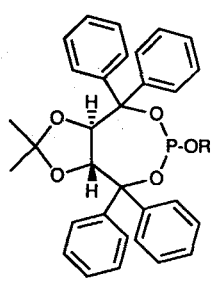
1a Aryl = Ph
b Aryl = 2-Naphth



2a R = Me
b R = Ph
c R = 4-Me–C_6H_4
d R = 2,4,6-Me_3–C_6H_2
e R = 2-Naphth



3a R = Ph
b R = 4-Me–C_6H_4
c R = 2,4,6-Me_3–C_6H_2
d R = 2-Naphth



4a R = Me
b R = Ph

[5]) TADDOL = α,α,α′,α′-Tetraaryl-2,2-dialkyl-1,3-dioxolane-4,5-dimethanol.

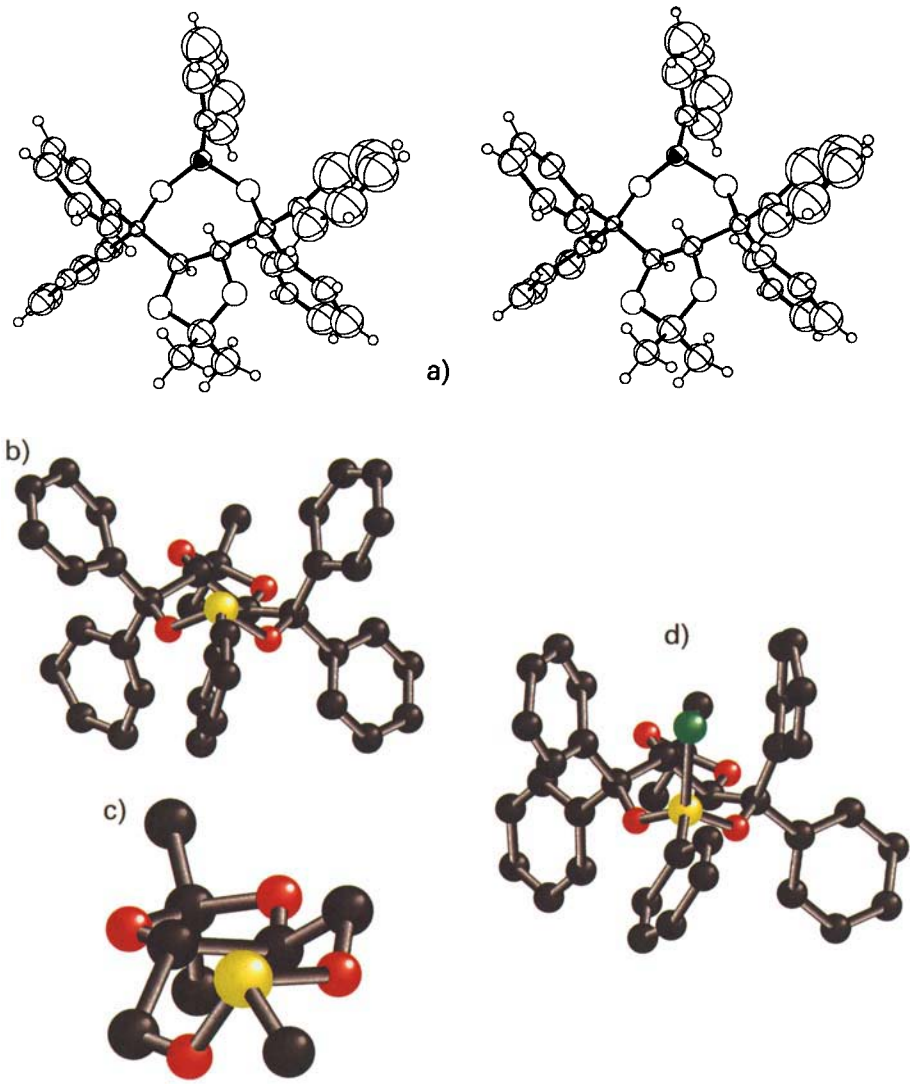
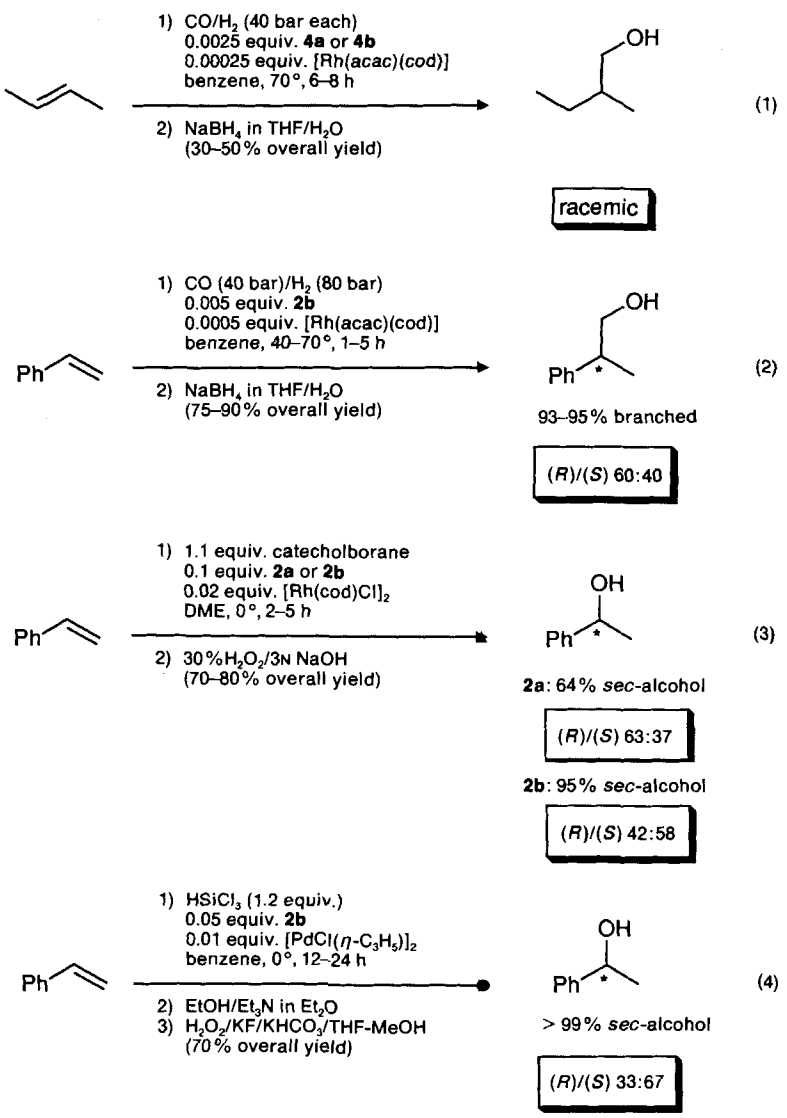


Figure. *Structure of the phosphonite* **2b** (C: black, O: red, P: yellow, Rh: green). *a*) ORTEP [22] stereoview of a single molecule of the crystal structure of **2b.** Vibrational ellipsoids are drawn at the 40% level (because of an exceptionally long unit cell axis of 116 Å, only isotropic refinement was possible, see *Exper. Part*). *b*) Projection showing the *quasi*-axial and *quasi*-equatorial disposition of the Ph groups in **2b**. *c*) Chair-type conformation of the seven-membered ring in **2b**. *d*) Modelling of a Rh complex of **2b** with SYBYL [22]. In the crystal structure, the space of the Rh-atom is occupied by a Ph ring of another molecule. The Rh-atom was attached to the P-atom at a distance of 2.2 Å (mean value of Rh–P fragments found in the *Cambridge Data Base* [23]). For the relaxation of the constructed complex, the Rh–P distance was fixed and only *van der Waals* repulsion between the Rh-atom and the rest of the molecule contributed to the energy calculation. Projections *b–d* were generated with PLUTO78 [23] and SYBYL [22].

To define possible geometries around a metal bonded to the P-atom of these cyclic esters, we determined the X-ray crystal structure of the pentaphenyl-substituted compound **2b** (see *Fig. 1*). The environment of the coordination site (direction of the non-bonding electron pair) on the P-atom is clearly evident from the projections of the structure in the *Figure, a–c*, and a Rh complex is modelled in the *Figure, d.*

We first tested the cyclic monodentate P-ligands for additions to C=C bonds (see the *Scheme*). Our phosphorous derivatives gave quite active catalysts with Rh and Pd for

Scheme[a])



[a]) cod = (Z,Z)-Cycloocta-1,5-diene, acac = acetylacetonate, THF = tetrahydrofuran, DME = dimethoxyethane.

effecting hydroformylations of but-2-ene and of styrene (*Eqns. 1* and *2*), for hydroboration (*Eqn. 3*), and for hydrosilylation (*Eqn. 4*). It is noteworthy that these reactions were also highly regioselective; no product resulting from but-1-ene was formed in the reaction of but-2-ene, a fact which may be interpreted as an indication that no C=C bond shift has occurred (*Eqn. 1*). Also, the additions of H/CHO, H/B(OR)$_2$, and H/SiCl$_3$ to styrene gave branched C-skeletons or secondary-alcohol derivatives with high preferences (*Eqns. 2* and *3/4*). On the other hand, the enantioselectivities were poor or not observable at all, results which are in agreement with previous experiences using monodentate P-ligands, as referred to above.

Enantioselective Hydrosilylation of Aromatic Ketones Catalyzed by the Rh Complexes of the Phosphonites 2 and 3. – We next turned our attention to enantioselective reductions of unsymmetrical ketones, a reaction which is now most successfully done by the *Corey-Itsuno* method [24]. We decided to test our ligands in the Rh^I-catalyzed reduction of aromatic ketones[6]) by diethyl-, diphenyl-, and (1-naphthyl)(phenyl)silane. It turned out that, under certain conditions, surprizingly high enantioselectivities (up to 87% ee) may be observed, despite the fact that monodentate ligands are employed (see the *Table*; in all cases the workup procedure was such that the silyl group was removed to facilitate identification and analysis of the alcohol formed).

A thorough investigation uncovered the following facts. *i*) The catalysts are highly active; 0.02 equiv. of Rh and as little as 0.025 equiv. of the chiral ligand are sufficient to reduce the aromatic ketones at 0 to 20° with 1.2 equiv. of the silane overnight[7]). *ii*) Of the silanes used, the diethyl derivative gave poor enantioselectivities. Diphenylsilane was superior to the other silanes[8]). *iii*) The nature of the substituent on the P-atom of the chiral ligand plays a decisive role. Thus, the phosphites **4** (MeO and PhO on P) are less efficient than the phosphonites **2** and **3**; the methyl phosphonite gives a modest selectivity for formation of the (*S*)-product from acetophenone; with phenyl, *p*-tolyl, and 2-naphthyl groups on phosphorous, and other conditions being identical, the (*R*)-alcohol is formed from acetophenone with about the same selectivity; the mesityl group with a 2,6-disubstituted Ph ring on the P-atom leads to a total loss of enantioselectivity, and also to a marked decrease of the catalytic activity. *iv*) Finally, we found that, as in the Ti-TADDOLate-catalyzed nucleophilic addition of R$_2$Zn to aldehydes [25], replacement of the Ph groups on the methanol groups by 2-naphthyl substituents leads to better results; as is evident from the numbers listed in the *Table*, the penta(2-naphthyl)-substituted phosphonite **3d** gives best results. *v*) Besides the aryl methyl and ethyl ketones shown in the *Table*, we also reduced isobutyrophenone and pivalophenone catalytically, with the result that the increased steric hindrance did not reduce the rate of the reaction (96 and 93% yield under standard conditions with ligand **2b**), but that the smaller difference in size of the substituents attached to the C=O group diminished the enantioselectivity essentially to nil.

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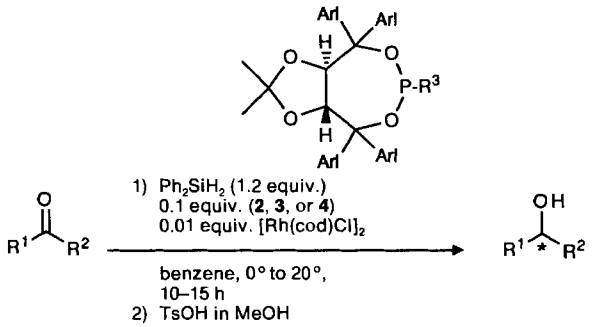
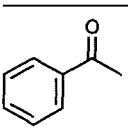
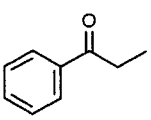
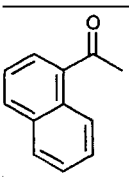
[6]) Certain aliphatic ketones are known to be reduced also by silanes in the presence of Rh^I [14], but these ketones were not employed in the present study.

[7]) Thus, 84, 83, and 80% ee of the (*R*)-alcohol were obtained in *ca.* 80% yield when reducing methyl 1-naphthyl ketone with 1.2 equiv. of Ph_2SiH_2/0.02 Rh^I in the presence of 0.1, 0.05, and 0.025 equiv. **3a**, respectively.

[8]) In one case, we compared diphenyl- with (1-naphthyl)(phenyl)silane to find that the latter one gave much poorer optical and chemical yields, a result which is opposite to previous reports using the silane in the presence of Rh complexes with other P-ligands [14].

Table. *Hydrosilylation of Aromatic Ketones Catalyzed by Rh^I in the Presence of Phosphonites* **2**, **3** *and Phosphites* **4**. Enantiomer ratios of *sec*-alcohols were determined by using a chiral GC column (details are given in the *Exper. Part*).



Ketone	P-Derivative			*sec*-Alcohol	
		Arl	R^3	Yield [%]	Ratio (*R*)/(*S*)
	**2a**	Ph	Me	50	29.5:70.5
	b	Ph	Ph	59	77.5:22.5
	c	Ph	4-Me–C_6H_4	92	81:19
	d	Ph	2,4,6-Me_3–C_6H_2	60	45:55
	e	Ph	2-Naphth	74	76.5:23.5
	3a	2-Naphth	Ph	91	91:9
	b	2-Naphth	4-Me–C_6H_4	76	89.5:10.5
	c	2-Naphth	2,4,6-$(Me)_3$–C_6H_2	46	50.5:49.5
	d	2-Naphth	2-Naphth	99	92:8
	4a	Ph	MeO	28	45:55
	b	Ph	PhO	40	37.5:62.5
	**2b**	Ph	Ph	59	78:22
	c	Ph	4-Me–C_6H_4	98	78.5:21.5
	3a	2-Naphth	Ph	98	83:17
	**2b**	Ph	Ph	82	80.5:19.5
	c	Ph	4-Me–C_6H_4	60	82.5:17.5
	e	Ph	2-Naphth	56	79:21
	3a	2-Naphth	Ph	84	92:8
	b	2-Naphth	4-Me–C_6H_4	95	90:10
	d	2-Naphth	2-Naphth	92	93.5:6.5

With the results so far obtained, it is fair to state that the readily available phosphonites **2** and **3** may be useful monodentate chiral ligands for certain transition-metal-catalyzed reactions. However, it is not possible to even speculate at this stage on the mechanism of the most successful application, which we have found, *i.e.* the enantioselective hydrosilylation of aryl alkyl ketones.

We thank the *Japanese Society for the Promotion of Science* for a stipend granted to *J. Sakaki*. Continuing support by the *Sandoz AG* (Basel) is gratefully acknowledged. The TADDOLs used in this investigation were partially supplied by the *Kilolabor of Sandoz Pharma AG* (*cf.* [26]). Finally, we would like to express our sincere thanks to Prof. Dr. *E. Consiglio* of the Laboratorium für Technische Chemie der ETH-Zürich for helpful guidance and discussions concerning asymmetric hydroformylations, and for allowing us to use equipment of his laboratory.

Experimental Part

General. Abbreviations: Mes (mesityl); *p*-Tol (p-tolyl); 2-Naphth (2-naphthyl). THF was distilled under Ar over LAH ($LiAlH_4$) prior to use and transferred with syringes. Solvents for extraction, recrystallization, and asymmetric reactions were purchased from *Fluka*, degassed, and stored over molecular sieves (4 Å) under Ar. The TADDOLs (**1a** [26–28], **b** [26]) were prepared by following reported procedures. The preparation of phosphonite ligands **2a,b** and **3a** and phosophite ligands **4a,b** was reported in our previous paper [21]. Phosphorus reagents $RPCl_2$: (R=MeO, PhO, Me, and Ph) were commercially available, others with R = Mes [29], *p*-Tol [30], and 2-Naphth [30] were prepared by slightly modified ways of reported procedures. Silane derivatives $R^1R^2SiH_2$ ($R^1 = R^2 =$ Et, Ph) were commercially available, (1-naphthyl)(phenyl)silane (R^1 = Ph, R^2 = 1-naphthyl) was prepared by the method analogous to that described in [31] [32]. All other commercially available chemicals used were of *p.a.* quality, or purified and dried according to standard methods. Flasks, pressure filter funnels, and stirring bars were dried at *ca.* 150° for *ca.* 12 h and allowed to cool in a desiccator. TLC: *Merck* precoated silica gel *60 F-254* plates. Chromatography: Flash column chromatography was performed on silica gel *60* (230–400 mesh, *Fluka*), using degassed solvents and N_2 pressure, and avoiding contact air as far as possible. M.p.: open glass capillaries, *Büchi 510* apparatus, values uncorrected. Optical rotations: at r.t., *Perkin-Elmer 241* polarimeter, in 10-cm cells. IR: *Perkin-Elmer 1600*, in cm^{-1}. Cap. GC: *HRGC 5160* or *4160* (*Carlo Erba*); column: *WCOT*-fused silica, *CP-Cyclodextrin-β-2,3,6-M-19*, 50 m × 0.25 mm (*Chrompack*). ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra: *Bruker AMX 400* (400, 100, and 162 MHz, resp.), *Varian XL 300* (300, 75, and 121 MHz, resp.), or *Varian Gemini 200* (200 MHz, ^{1}H-NMR). ^{19}F-NMR Spectra: *Varian XL 300* (282 MHz); δ in ppm downfield of TMS ($\delta = 0$), *J* in Hz. MS: *Hitachi-Perkin-Elmer RMU-6M*.

Mesitylphosphonous Dichloride. BuLi (60 mmol, 1.55M soln. in hexane) was added to a soln. of bromomesitylene (9.96 g, 50 mmol) in Et_2O (20 ml) below −20° and the mixture was refluxed for 2 h. A soln. of PCl_3 (17.2 g, 125 mmol) in Et_2O (20 ml) was added to the mixture at −78°. The mixture was warmed up to r.t. slowly and stirred overnight. The suspension was filtered through a pressure filter funnel under Ar. The filtrate was concentrated *in vacuo* and distilled under reduced pressure to give the title compound: 4.2 g, 38%. B.p. 128–130°/0.4 Torr (b.p. 145–150°/2 Torr [29]).

Chlorobis(diethylamino)phosphine [33]. A soln. of Et_2NH (70 g, 0.96 mol) in Et_2O (100 ml) was dropped to a soln. of PCl_3 (32.9 g, 0.24 mol) in Et_2O (500 ml) at −70° over 2 h. The mixutre was allowed to warm up to r.t. The suspension was filtered and washed several times with Et_2O. The filtrate and washings were concentrated *in vacuo*. The residue was distilled under reduced pressure to give the title compound (quant.). B.p. 78–79°/(0.5 Torr) (b.p. 87–90°/2 mmHg [33]).

(p-*Tolyl)phosphonous Dichloride.* (*p*-Tolyl)magnesium-bromide (prepared from 4-bromotoluene (11.29 g, 66 mmol) and Mg turnings (1.60 g, 66 mmol)) soln. of Et_2O (70 ml) was dropped to a soln. of chlorobis(diethylamino)phosphine [33] (9.15 g, 60 mmol) in Et_2O (120 ml) at −50° over 1.5 h. The mixture was warmed up to r.t. slowly and stirred overnight. HCl (8.76 g, 0.24 mol) in Et_2O (100 ml) was then slowly added under ice-cooling. The mixture was stirred for 2 h at r.t. and filtered. The filtrate was concentrated *in vacuo* and distilled under reduced pressure to give the title compound: 4.7 g, 41%. B.p. 71°/0.4 Torr (b.p. 116.5°/12 mmHg [34]).

(2-Naphthyl)phosphonous Dichloride. (2-Naphthyl)magnesium bromide (prepared from 2-bromonaphthalene (11.4 g, 55 mmol) and Mg turnings (1.34 g, 55 mmol)) soln. of Et_2O (80 ml) was dropped to a soln. of Chloro-bis(diethylamino)phosphine [33] (7.63 g, 50 mmol) in Et_2O (100 ml) at −70° over 1.5 h. The mixture was warmed up to r.t. slowly and stirred overnight, then refluxed for 0.5 h. HCl (7.3 g, 0.2 mol) in Et_2O (100 ml) was slowly added under ice-cooling. The mixture was stirred for 2 h at r.t. and filtered. The filtrate was concentrated *in vacuo* and distilled under reduced pressure to give a title compound (2.88 g, 25%). B.p. 100°/0.2 Torr (b.p. 110°/0.2 mmHg [34]).

Preparation of Phosphorus Ligands **2** *and* **3** *(General Procedure).* BuLi (42 mmol, 1.55M soln. in hexane) was added to a stirred soln. of **1a** or **1b** (20 mmol) in 80 ml of THF under Ar at −70°. During this addition, the temp. rose up to −50°. The mixture was cooled again to −70° and stirred at this temp. for 5 min, and then warmed up to r.t. within 1 h. The mixture was cooled again to −70° and dichlorophosphorus reagent (22 mmol) was added slowly without allowing the temp. to rise. The mixture was warmed up again to r.t. within 1 h and stirred for 5 h at this temp. After evaporation of the solvent under reduced pressure by high-vacuum pump, 50 ml of pentane were added to the residue. The suspension was stirred for 1 h and filtered through a pressure filter funnel under Ar. To this solid residue were added 100 ml of toluene. The suspension was stirred for 10 h and filtered through a pressure filter funnel again. The filtrate was concentrated *in vacuo* to give a solid which was purified as described for the individual compound. The ligands obtained were stored under Ar.

(1R,7R)-9,9-Dimethyl-4-(4-methylphenyl)-2,2,6,6-tetraphenyl-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane (**2c**). The *General Procedure* was applied with 2.33 g (5 mmol) of **1a** and 1.06 g (5.5 mmol) of (*p*-Tol)PCl_2. Purification by recrystallization (AcOEt/$CHCl_3$) provided 1.87 g (64%) of **2c** as a colourless solid. M.p. 207–211° (dec.). $[\alpha]_D^{r.t.} = -80.7$ ($c = 1.08$, $CHCl_3$). IR ($CHCl_3$): 3061, 3008, 1600, 1494, 1447, 1384, 1373, 1253, 1164, 1102, 1083, 1048, 1033, 1016, 918, 879, 831, 812, 644, 633. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.20 (*s*, Me); 1.55 (*s*, Me); 2.42 (*s*, Me); 4.77 (*d*, $J = 8.63$, CH); 5.61 (*dd*, $J = 8.63$, 4.66 CH); 7.15–7.88 (*m*, 24 arom. H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 21.63; 24.76; 27.87; 82.01; 82.06; 82.48; 82.72; 83.07; 83.15; 83.92; 83.96; 111.30; 127.11; 127.16; 127.20; 127.33; 127.43; 127.51; 127.61; 127.94; 128.10; 128.54; 128.57; 129.17; 129.24; 129.39; 129.83; 130.07; 137.92; 138.01; 141.03; 141.40; 141.41; 141.98; 145.91; 145.95; 146.86. ^{31}P-NMR ($CDCl_3$, 162 MHz): 157.4. EI-MS: 587 (28, $[M+1]^+$), 586 (< 1, M^+), 528 (23), 432 (77), 431 (98), 430 (9), 392 (43), 391 (91), 374 (66), 373 (42), 345 (39), 333 (61), 317 (27), 265 (42), 238 (80), 237 (96), 236 (91), 208 (38), 207 (90), 196 (32), 180 (79), 179 (100), 178 (97), 176 (77), 166 (49), 165 (80), 105 (41). HR-MS: $C_{38}H_{36}O_4P$ ($[M+1]^+$: calc. 587.2351; found: 587.2357).

(1R,7R)-9,9-Dimethyl-2,2,6,6-tetraphenyl-4-(2,4,6-trimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane (**2d**). Following the *General Procedure*, the reaction was performed with 1.17 g (2.5 mmol) of **1a** and 608 mg (2.75 mmol) of (Mes)PCl_2. After the addition of (Mes)PCl_2, the mixture was stirred at r.t. for 15 h. Then, THF was removed under reduced pressure and toluene (15 ml) added to the residue directly. The suspension was stirred for 3 h and filtered through a pressure filter funnel. The filtrate was concentrated *in vacuo*. The solid residue obtained was purified by silica-gel column chromatography (pentane/Et_2O 10:1) to give 812 mg (53%) of **2d** as a colourless solid. M.p. 205–208° (dec.). $[\alpha]_D^{r.t.} = -133.0$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3061, 3008, 1604, 1494, 1447, 1383, 1252, 1164, 1082, 1047, 1032, 1011, 917, 877, 824, 644, 629. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.28 (*s*, Me); 1.48 (*s*, Me); 2.29 (*s*, Me); 2.63 (*d*, $J = 1.89$, 2 Me); 4.98 (*d*, $J = 8.55$, CH); 5.52 (*dd*, $J = 8.55$, 4.60, CH); 6.88 (*d*, $J = 2.43$, 2 arom. H); 7.15–7.54 (*m*, 18 arom. H); 7.79–7.82 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 21.21; 22.10; 22.32; 24.67; 27.85; 82.78; 82.84; 83.07; 83.29; 83.34; 83.91; 84.03; 111.31; 127.09; 127.15; 127.22; 127.33; 127.48; 127.56; 127.64; 127.99; 128.48; 128.53; 129.21; 129.73; 129.78; 132.50; 132.71; 141.17; 141.48; 141.51; 142.33; 142.74; 142.96; 145.74; 145.77; 147.47; ^{31}P-NMR ($CDCl_3$, 162 MHz): 169.5. EI-MS: 615 (2, $[M+1]^+$), 556 (9), 431 (10), 430 (5), 420 (21), 419 (67), 361 (29), 265 (36), 238 (55), 237 (96), 236 (54), 207 (49), 180 (47), 179 (100), 178 (57), 167 (35), 166 (21), 165 (30), 49 (29). HR-MS: $C_{37}H_{33}O_3P$ ($[M - Me_2CO]^+$: calc. 556.2167; found: 556.2148).

(1R,7R)-9,9-Dimethyl-4-(2-naphthyl)-2,2,6,6-tetraphenyl-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane (**2e**). The *General Procedure* was applied with 1.4 g (3 mmol) of **1a** and 824 mg (3.6 mmol) of (β-Naphth)PCl_2. The dichloride was added as a soln. of THF (2 ml). Recrystallization (AcOEt/$CHCl_3$) provided 1.21 g (65%) of **2e** as a colourless solid. M.p. 201–202° (dec.). $[\alpha]_D^{r.t.} = -71.4$ ($c = 1.0$, $CHCl_3$). IR ($CHCl_3$): 3060, 3008, 1493, 1448, 1384, 1373, 1253, 1164, 1083, 1048, 1033, 1019, 918, 878, 852, 830, 817, 649. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.23 (*s*, Me); 1.56 (*s*, Me); 4.83 (*d*, $J = 8.62$, CH); 5.66 (*dd*, $J = 8.62$, 4.65 CH); 7.16–7.64 (*m*, arom. H); 7.89–7.94 (*m*, 4 arom. H); 7.99–8.07 (*m*, 2 arom. H); 8.24 (*d*, $J = 9.98$, 1 arom. H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 24.79; 27.88; 82.24; 82.29; 82.54; 82.77; 83.23; 83.30; 83.95; 83.99; 111.43; 125.54; 125.69; 126.41; 127.17; 127.22; 127.27; 127.32; 127.45; 127.58; 127.65; 127.90; 127.99; 128.16; 128.31; 128.36; 128.57; 128.60; 128.76; 129.38; 131.25; 131.59; 132.69; 132.80; 134.66; 138.41; 138.52; 141.36; 141.38; 141.92; 145.84; 145.88; 146.80. ^{31}P-NMR ($CDCl_3$, 162 MHz): 157.3. EI-MS: 623 (< 1, $[M+1]^+$), 622 (< 1, M^+), 564 (16), 431 (12), 430 (4), 428 (21), 427 (67), 386 (10), 374 (23), 370 (10), 369 (37), 356 (15), 353 (11), 344 (10), 265 (20), 238 (43), 237 (93), 236 (63), 208 (14), 207 (56), 196 (13), 192 (11), 190 (10), 180 (46), 179 (100), 178 (62), 167 (31), 166 (17), 165 (31), 127 (11), 105 (14), 84 (13), 77 (11), 49 (18). HR-MS: $C_{38}H_{29}O_3P$ ($[M-Me_2CO]^+$: calc.: 564.1854; found: 564.1737).

(1R,7R)-9,9-Dimethyl-4-(4-methylphenyl)-2,2,6,6-tetra(2-naphthyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane (**3b**). Following the *General Procedure*, the reaction was performed with 2.0 g (3 mmol) of **1b** and 695 mg (3.6 mmol) of (*p*-Tol)PCl_2. After the addition of (*p*-Tol)PCl_2, the mixture was stirred at r.t. for 15 h. Then, THF was removed under reduced pressure. To the residue obtained were added 10 ml of pentane. The suspension was stirred for 1 h and filtered through a pressure filter funnel under Ar. To this solid residue were added 20 ml of $CHCl_3$. The suspension was stirred for 3 h and filtered through a pressure filter funnel again. The filtrate was concentrated *in vacuo*. The residue was purified by recrystallization (hexane/AcOEt) to give 1.4 g (59%) of **3b** as a colourless solid. M.p. 167–168° (dec.). $[\alpha]_D^{r.t.} = -129.9$ ($c = 1.43$, $CHCl_3$). IR ($CHCl_3$): 3061, 3008, 1600, 1506, 1383, 1374, 1356, 1272, 1161, 1126, 1086, 1032, 1019, 946, 900, 880, 862, 823, 649, 637. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.16 (*s*, Me); 1.67 (*s*, Me); 2.45 (*s*, Me); 5.12 (*d*, $J = 8.55$, CH); 6.01 (*dd*, $J = 8.55$, 4.86, CH); 7.36–7.96 (*m*, 29 arom. H); 8.12 (*s*, 1 arom. H); 8.25 (*s*, 1 arom. H); 8.77 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 21.66; 25.23; 28.03; 82.59; 82.66; 82.70; 82.83; 83.51; 83.59; 83.92; 83.96; 111.82; 125.77; 125.87; 125.95; 125.97; 126.00; 126.04; 126.14; 126.16; 126.31; 126.44; 127.13; 127.16; 127.25; 127.31; 127.38; 127.40; 127.46; 127.57; 127.81; 127.98; 128.12; 128.16; 128.56; 128.67; 128.76; 129.29; 129.36; 129.88; 130.12; 132.49; 132.52; 132.61; 132.71; 132.77; 132.80; 137.88; 137.98; 138.77; 139.01; 141.17; 143.00; 143.04; 143.79. ^{31}P-NMR ($CDCl_3$, 162 MHz):

158.5. EI-MS: 786 (< 1, M^+), 728 (< 1), 631 (22), 630 (46), 545 (24), 544 (52), 365 (54), 336 (28), 308 (33), 307 (61), 296 (23), 281 (25), 280 (23), 279 (60), 278 (36), 276 (22), 268 (31), 267 (100), 266 (60), 265 (99), 264 (22), 263 (29), 252 (24), 155 (28), 91 (23), 50 (28). HR-MS: $C_{54}H_{43}O_4P$ (M^+: calc. 786.2899; found: 786.2778).

(1R,7R)-9,9-Dimethyl-2,2,6,6-tetra(2-naphthyl)-4-(2,4,6-trimethylphenyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane (**3c**). Following the *General Procedure*, the reaction was performed with 1.33 g (2 mmol) of **1b** and 530 mg (2.4 mmol) of (Mes)PCl_2. After the addition of (Mes)PCl_2 the mixture was stirred at r.t. for 15 h and heated at 50° for 2.5 h. Then, THF was removed under reduced pressure and 20 ml of toluene were added to the residue directly. The suspension was stirred for 3 h and filtered through a pressure filter funnel. The filtrate was concentrated *in vacuo* and the residue was purified by silica-gel column chromatography (pentane/Et_2O 10:1) to give 783 mg (48%) of **3c** as a pale-yellow solid. M.p. 174–178° (dec.). $[\alpha]_D^{r.t.} = -185.4$ ($c = 1.12$, $CHCl_3$). IR ($CHCl_3$): 3061, 3008, 2960, 2927, 2872, 1603, 1506, 1456, 1382, 1356, 1273, 1161, 1126, 1086, 1057, 1024, 946, 930, 900, 881, 861, 824, 648, 634. ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.25 (*s*, Me); 1.62 (*s*, Me); 2.34 (*s*, Me); 2.72 (*d*, $J = 1.94$, 2 Me); 5.30 (*d*, $J = 8.50$, CH); 5.86 (*dd*, $J = 8.50$, 4.61, CH); 6.94 (*d*, $J = 2.75$, arom. H); 7.39–7.88 (*m*, 24 arom. H); 8.03 (*s*, 1 arom. H); 8.19 (*s*, 1 arom. H); 8.25 (*s*, 1 arom. H); 8.66 (*s*, 1 arom. H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 21.27; 22.24; 22.46; 25.14; 28.01; 83.22; 83.27; 83.42; 83.48; 83.53; 83.68; 84.22; 84.34; 111.77; 125.71; 125.75; 125.84; 125.87; 125.96; 126.01; 126.04; 126.16; 126.34; 126.40; 127.13; 127.16; 127.22; 127.28; 127.36; 127.48; 127.64; 127.94; 128.16; 128.57; 128.62; 128.65; 128.69; 129.90; 129.94; 132.42; 132.53; 132.62; 132.69; 132.70; 132.72; 132.75; 132.82; 138.93; 138.96; 139.40; 141.37; 142.80; 142.84; 143.06; 144.45. ^{31}P-NMR ($CDCl_3$, 162 MHz): 169.7. EI-MS: 815 (< 1, $[M + 1]^+$), 814 (< 1, M^+), 756 (< 1), 630 (11), 365 (23), 337 (63), 336 (96), 307 (21), 296 (73), 294 (20), 293 (42), 279 (31), 278 (21), 268 (61), 267 (100), 266 (50), 265 (77), 263 (20), 252 (42), 184 (40), 165 (33), 119 (31), 105 (29). HR-MS: $C_{56}H_{47}O_4P$ (M^+: calc.: 814.3212; found: 814.3288).

(1R,7R)-9,9-Dimethyl-2,2,4,6,6-penta(2-naphthyl)-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane (**3d**). The *General Procedure* was applied with 2.0 g (3 mmol) of **1b** and 824 mg (3.6 mmol) of (2-Naphth)PCl_2. The dichloride was added as a soln. of THF (2 ml). After the addition of (2-Naphth)PCl_2, the mixture was stirred at r.t. for 15 h. Then, THF was removed under reduced pressure and 20 ml of toluene were added to the residue directly. The suspension was stirred for 3 h and filtered through a pressure filter funnel. The filtrate was concentrated *in vacuo* and the residue was chromatographed (silica gel, pentane/Et_2O 15:1) to give a pale yellow solid. To a soln. of this solid in 20 ml of Et_2O was added 1.0 g of activated charcol. The mixture was stirred for 3 min at r.t. and filtered off. The filtrate was evaporated *in vacuo* and the residue was purified by silica-gel column chromatography (pentane/Et_2O 15:1) again to 1.1 g (45%) of **3d** as a colourless solid. M.p. 171–173.5° (dec.). $[\alpha]_D^{r.t.} = -133.3$ ($c = 1.22$, $CHCl_3$). IR ($CHCl_3$): 3060, 3007, 2951, 2934, 1600, 1506, 1383, 1374, 1355, 1272, 1161, 1126, 1087, 1031, 964, 946, 929, 901, 880, 852, 824, 644. ^{1}H-NMR ($CDCl_3$, 400 MHz): 0.18 (*s*, Me); 1.68 (*s*, Me); 5.18 (*d*, $J = 8.54$, CH); 6.01 (*dd*, $J = 8.54$, 4.84, CH); 7.40–8.81 (*m*, 35 arom. H). ^{13}C-NMR ($CDCl_3$, 100 MHz): 25.27; 28.03; 82.63; 82.87; 82.91; 83.66; 83.73; 83.96; 84.00; 111.94; 125.54; 125.70; 125.81; 125.93; 125.96; 126.00; 126.04; 126.08; 126.10; 126.13; 126.21; 126.36; 126.51; 127.15; 127.18; 127.28; 127.32; 127.37; 127.40; 127.49; 127.60; 127.88; 127.94; 128.19; 128.40; 128.45; 128.58; 128.67; 128.69; 128.78; 128.81; 131.34; 131.67; 132.50; 132.54; 132.63; 132.73; 132.78; 132.81; 132.84; 134.71; 138.39; 138.50; 138.73; 138.96; 142.94; 142.98; 143.73. ^{31}P-NMR ($CDCl_3$, 121 MHz): 158.3. EI-MS: 822 (< 1, M^+), 746 (< 1), 631 (30), 630 (59), 572 (26), 545 (40), 544 (92), 366 (29), 365 (91), 308 (36), 307 (89), 281 (27), 280 (43), 279 (84), 278 (48), 277 (23), 276 (30), 268 (28), 267 (93), 266 (71), 265 (100), 264 (27), 263 (33), 50 (23). HR-MS: $C_{57}H_{43}O_4P$ (M^+: calc.: 822.2899; found: 822.2707).

General Procedure for the Enantioselective Hydroformylation of (E)-But-2-ene. A soln. of [Rh(acac)(cod)] (0.025 mmol, 0.025 mol-%) and ligand (0.25 mmol, 0.25 mol-%) in benzene (10 ml) was stirred under Ar for 15 h. The mixture was put in a 150 ml stainless steel autoclave under N_2. The autoclave was cooled by EtOH/dry ice and (*E*)-but-2-ene (0.1 mol) was condensed in it. The autoclave was pressurized with 40 atm of CO and shaken for 30 min at 70°. After cooling down by water, the autoclave was pressurized again with an additional 40 atm of H_2 and shaken at the same temp. Reaction was monitored by absorption of gas. After the reaction, the autoclave was cooled down by the ice. The mixture was dropped to a mixture of $NaBH_4$ (50 mmol), THF (90 ml), and H_2O (10 ml) under ice-cooling. The whole was stirred at the same temp. for 1 h. THF was evaporated off carefully. To the residue was added a sat. $NaHCO_3$ soln., and the mixture was extracted with Et_2O. The org. layer was washed with H_2O and dried ($MgSO_4$). After the evaporation of the solvent, the residue was distilled under reduced pressure to give 2-methylbutan-1-ol. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.84–0.92 (*m*, 2 Me); 1.01–1.18 (*m*, CH); 1.33–1.57 (*m*, MeCH_2); 1.97 (br. *s*, OH); 3.43 (*ddd*, $J = 20.9$, 10.6, 6.2, CH_2OH).

General Procedure for the Enantioselective Hydroformylation of Styrene. A soln. of [Rh(acac)(cod)] (0.025 mmol, 0.05 mol-%) and ligand (0.25 mmol, 0.5 mol-%) in benzene (10 ml) was stirred under Ar for 15 h. The catalyst soln. and styrene (5.8 ml, 50 mmol) were put in a 150-ml stainless steel autoclave under N_2. The autoclave was pressurized with 40 atm of CO and shaken for 30 min at 40–70°. After cooling down by water, the autoclave

was pressurized again with an additional 80 atm of H_2 and shaken at the same temp. Reaction was monitored by absorption of gas. The autoclave was cooled down by the ice. The mixture was dropped to a mixture of $NaBH_4$ (25 mmol), THF (50 ml), and H_2O (10 ml) under ice-cooling. The whole was stirred at the same temp. for 1 h. THF was evaporated off. To the residue was added a sat. $NaHCO_3$ soln., and the mixture was extracted with Et_2O. The org. layer was washed with H_2O and dried ($MgSO_4$). After the evaporation of the solvent, the residue was distilled under reduced pressure to give a mixture of 2-phenylpropan-1-ol and 3-phenylpropan-1-ol. 2-Phenylpropan-1-ol: ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.29 (*d*, $J = 7.0$, Me); 1.63 (br. *s*, OH); 2.87–3.04 (*m*, CH); 3.69 (*d*, $J = 7.0$, CH_2); 7.20–7.39 (*m*, arom. H).

General Procedure for the Enantioselective Hydroboration of Styrene. A soln. of $[Rh(cod)Cl]_2$ (20 mg, 0.04 mmol, 2 mol-%) and ligand (0.2 mmol, 10 mol-%) in THF or DME (2 ml) was stirred at r.t. under Ar for 1 h. To the catalyst soln. were added styrene (230 µl, 2 mmol), and then catecholborane (234 µl, 2.2 mmol) under ice-cooling, and the mixture was stirred at the same temp. for 2–7 h. The reaction was quenched with MeOH (4 ml) under ice-cooling. After the addition of 3N NaOH (5 ml) and 30% aq. H_2O_2 (0.6 ml), the mixture was allowed to warm to r.t. and stirred for 3 h. To the mixture was added 1N NaOH (10 ml) and extracted with Et_2O. The org. layer was washed with aq. NH_4Cl and dried ($MgSO_4$), then evaporated *in vacuo*. The residue obtained was purified by silica-gel column chromatography (pentane/Et_2O 5:1) to give a mixture of 1-phenylethanol and 2-phenylethanol.

General Procedure for the Enantioselective Hydrosilylation of Styrene. A soln. of $[PdCl(C_3H_5)]_2$ (36.6 mg, 0.1 mmol, 1 mol-%) and pentaphenyl ligand **2b** (286 mg, 0.5 mmol, 5 mol-%) in THF or benzene (4 ml) was stirred at r.t. under Ar for 1 h. Styrene (1.15 ml, 10 mmol) and then $HSiCl_3$ (1.21 ml, 12 mmol) were added to the catalyst soln. at 0°. The mixture was stirred for 1 day and concentrated under reduced pressure. The residue was dissolved in a mixture of EtOH (2 ml) and Et_2O (150 ml), then, Et_3N (30 ml) was added dropwise to the mixture under ice-cooling. The mixture was stirred at the same temp. for 30 min and at r.t. for 1.5 h. The suspension was filtered and the filtrate evaporated *in vacuo* to give a colourless oil. To a soln. of the residue in THF (50 ml) and MeOH (50 ml) were added $KHCO_3$ (3.0 g, 30 mmol) and KF (1.74 g, 30 mmol), and then 30% aq. H_2O_2 (23 ml, 200 mmol) under ice-cooling. The mixture was stirred at r.t. for 60 h and concentrated *in vacuo*. The residue was treated with H_2O and then extracted with Et_2O. The org. layer was dried ($MgSO_4$) and evaporated under reduced pressure. The residue obtained was purified by silica-gel column chromatography (pentane/Et_2O 5:1) to give (*S*)-1-phenylethanol.

General Procedure for the Enantioselective Hydrosilylation of Ketones. A soln. of $[Rh(cod)Cl]_2$ (9.9 mg, 0.02 mmol, 1 mol-%) and the ligand (0.2 mmol, 10 mol-%) in benzene (3 ml) was stirred at r.t. under Ar for 1 h. To this catalyst soln. were added slowly the ketone (2 mmol) at r.t. and the silane reagent (2.4 mmol) under ice-cooling. The mixture was allowed to warm to r.t. over 3 h and stirred overnight. To the mixture were added MeOH (5 ml) and TsOH (*ca.* 20–30 mg). The mixture was stirred at r.t. for 5 h and evaporated *in vacuo*. The residue was purified by silica-gel column chromatography (pentane/Et_2O 5:1) to give the secondary alcohol.

Hydrosilylation of Acetophenone Using the Pentaphenyl Ligand **2b**. The *General Procedure* was applied with $[Rh(cod)Cl]_2$ (9.9 mg, 0.02 mmol, 1 mol-%), ligand **2b** (114.4 mg, 0.2 mmol), acetophenone (233 µl, 2 mmol), and Ph_2SiH_2 (443 µl, 2.4 mmol). Purification by silica-gel column chromatography provided 143.7 mg (59%) of (*R*)-1-phenylethanol. $[\alpha]_D^{r.t.} = +27.3$ ($c = 1.29$, CH_2Cl_2) ((*S*)-isomer: $[\alpha]_D^{23} = -52.5$ ($c = 2.27$, CH_2Cl_2) [35]). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.50 (*d*, $J = 6.5$, Me); 1.89 (br. *s*, OH); 4.89 (*q*, $J = 6.5$, CH); 7.21–7.45 (*m*, 5 arom. H).

Hydrosilylation of Propiophenone Using the Pentaphenyl Ligand **2b**. The *General Procedure* was applied with $[Rh(cod)Cl]_2$ (9.9 mg, 0.02 mmol, 1 mol-%), ligand **2b** (114.4 mg, 0.2 mmol), propiophenone (266 µl, 2 mmol), and Ph_2SiH_2 (443 µl, 2.4 mmol). Purification by silica-gel column chromatography provided 160 mg (59%) of (*R*)-1-phenylpropan-1-ol. $[\alpha]_D^{r.t.} = +26.8$ ($c = 1.28$, $CHCl_3$) ((*S*)-isomer: $[\alpha]_D^{20} = -45.5$ ($c = 5.15$, $CHCl_3$) [36]). ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.92 (*t*, $J = 7.5$, Me); 1.67–1.88 (*m*, CH_2, OH); 4.60 (*t*, $J = 7.5$, CH); 7.25–7.37 (*m*, 5 arom. H).

Hydrosilylation of 1-Acetonaphthone Using the Pentaphenyl Ligand **2b**. The *General Procedure* was applied with $[Rh(cod)Cl]_2$ (9.9 mg, 0.02 mmol, 1 mol-%), ligand **2b** (114.4 mg, 0.2 mmol), 1-acetonaphthone (304 µl, 2 mmol), and Ph_2SiH_2 (443 µl, 2.4 mmol). Purification by silica-gel column chromatography provided 143.7 mg (82%) of (*R*)-1-(1-naphthyl)ethanol. $[\alpha]_D^{r.t.} = +40.8$ ($c = 1.93$, EtOH) ((*S*)-isomer: $[\alpha]_D = -74.4$ (EtOH) [36]). ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.68 (*d*, $J = 6.4$, Me); 1.45–1.90 (br. *s*, OH); 5.69 (*q*, $J = 6.4$, CH); 7.45–8.16 (*m*, 7 arom. H).

Crystal Structure Analysis of **2b**. Compound (**2b**): $C_{37}H_{33}O_4P$, hexagonal crystal system, space group $P6_522$, cell: $a = 9.460(15)$, $b = 9.460(9)$, $c = 116.5(3)$ Å, $\gamma = 120°$, $V = 9028.1$ Å^3, $Z = 12$, $D_c = 1.264$ g·cm^{-3}, $F(000) = 3624$. 3448 independent intensities of a suitable crystal (size 0.2 × 0.2 × 0.15 mm) were measured at r.t. with an *Enraf Nonius CAD4* diffractometer equipped with a graphite monochromator (CuK_α, $\lambda = 1.5418$ Å). The structure was solved by direct methods with SHELXS86 [37] and refined by full-matrix least-squares analysis [38].

Because of the exceptionally long *c*-axis and the relatively wide mosaic spread of the crystal the data collection suffered from reflection overlapping. Therefore, the data quality was poor and the limited number of reflexions (1168 with $I > 2\,\sigma(I)$) did not allow an anisotropic refinement of the non-H-atoms. For the same reason the disorder of the Ph rings were not resolved. The positions of the H-atoms were calculated and included in the final structure factor calculation. The weighting scheme used was $\sigma(F^2)^{-2}$. Final agreement factors (observed refl.): $R_w = 0.13$, $gof = 2.654$, residual electron-density = 0.429 e·Å^3. Positional and isotropic displacement parameters for the atoms are deposited with the *Cambridge Crystallographic Data Centre*, Cambridge, England.

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