[L*Rh(NBD)Cl] (L* = Chiral Cyclic Monophosphonite): A Novel Class of Rhodium(I) Complexes and Their Evaluation in the Asymmetric Hydrosilylation of Ketones. Investigations of the Effects of Temperature and Ligand Backbone†

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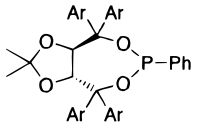
A series of new rhodium(I) complexes [L*Rh(NBD)Cl] (L* = chiral cyclic phosphonite with a fused 1,4-dioxane or cyclobutane ring in the backbone) was synthesized *via* the corresponding borane−phosphonite adducts. They turned out to be highly active catalysts in the asymmetric hydrosilylation of ketones in a broad temperature range. Evaluation of the temperature dependent measurements according to the Eyring formalism disclosed a nonlinear relationship between ln *P* (*P* = ratio of the enantiomeric product alcohols) and the reciprocal of temperature marked by the occurrence of points of inversion in the middle temperature region between −5 and 30 °C. These findings indicate a complexly composed selection mechanism that is controlled by at least two relevant partial steps. Furthermore, by comparison of different catalysts based on a 1,4-dioxane, a cyclobutane, or a 1,3-dioxolane ring in the backbone of L*, the conformational properties of the ligand backbone were revealed to be a crucial feature determining not only the extent but also the direction of chirality transfer, thus providing a versatile tool for the construction of stereocomplementary ligands. Accordingly, by proper choice of the ligand backbone and the temperature, fairly good enantioselectivities in the hydrosilylation of rather different ketones like acetophenone (82% ee) and pivalophenone (86% ee) can be achieved.

Introduction

The asymmetric hydrosilylation of prochiral ketones has been a subject of intensive studies over the past 25 years,[1] owing not only to the importance of optically active alcohols in organic synthesis but also to the exceedingly mild reaction conditions[2] as compared to the corresponding hydrogenation. However, up to the present the mechanistic understanding of transition metal catalyzed hydrosilylation is rather vague,[3,4] thus rendering a rationally guided design of suitable chiral ligands difficult. The most recent developments on this area are marked by the evolution of three very different types of ligands exhibiting promising properties in terms of asymmetric induction as well as catalytic activity. While the high enantioselectivities achieved with *trans*-chelating C_2-symmetric diphosphanes[5] and diamines[6] on the one hand, and oxazoline-phosphane hybrid ligands[7] on the other, correspond to the generally observed superiority of bidentate ligands in asymmetric synthesis,[1] the good results obtained with monodentate TADDOL-derived cyclic phosphonites **1a,b**[8] (Chart 1) constitute a notable exception. With efficient access to TADDOL analogues bearing a 1,4-dioxane backbone **3a**−**d** or a cyclobutane backbone **9** and **12** at our disposal,[9,10] we sought to prepare a series of structurally closely related phosphonites and their rhodium(I) complexes, designed to uncover the influence of structural properties on the potential of this novel class of compounds to function as catalysts in the asymmetric hydrosilylation of ketones.

Chart 1



1a: Ar = Ph
1b: Ar = 2-Naphthyl

† This work is dedicated to Prof. Dr. Peter Welzel on the occasion of his 60th birthday.

(1) (a) Ojima, I. *Catalytic Asymmetric Syntheses*; VCH Publishers: Weinheim, Germany, 1993. (b) Noyori, R. *Asymmetric Catalysis in Organic Syntheses*; J. Wiley & Sons: New York, 1994.
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(3) (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16. (b) Ojima, I.; Nihonyanagi, M.; Nagai, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3722. (c) Peyronel, J. F.; Kagan, H. B. *Nouv. J. Chim.* **1978**, *2*, 211.
(4) Zheng, G. Z.; Chan, T. H. *Organometallics* **1995**, *14*, 70.
(5) (a) Sawamura, M.; Kuwano, R.; Ito, Y. *Angew. Chem.* **1994**, *106*, 92; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 111. (b) Sawamura, M.; Kuwano, R.; Shirai, J.; Ito, Y. *Synlett* **1995**, 347.
(6) Nishibayashi, Y.; Singh, J. D.; Segawa, K.; Fukuzawa, S.; Uemura, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1375.
(7) (a) Nishibayashi, Y.; Segawa, K.; Ohe, K.; Uemura, S. *Oragnometallics* **1995**, *14*, 5486. (b) Nishibayashi, Y.; Segawa, K.; Takada, H.; Ohe, K.; Uemura, S. *Chem. Commun.* **1996**, 847. (c) Newman, L. M.; Williams, J. M. J.; McCague, R.; Potter, G. A. *Tetrahedron: Asymmetry* **1996**, *7*, 1597. (d) Langer, T.; Janssen, J.; Helmchen, G. *Tetrahedron: Asymmetry* **1996**, *7*, 1599.
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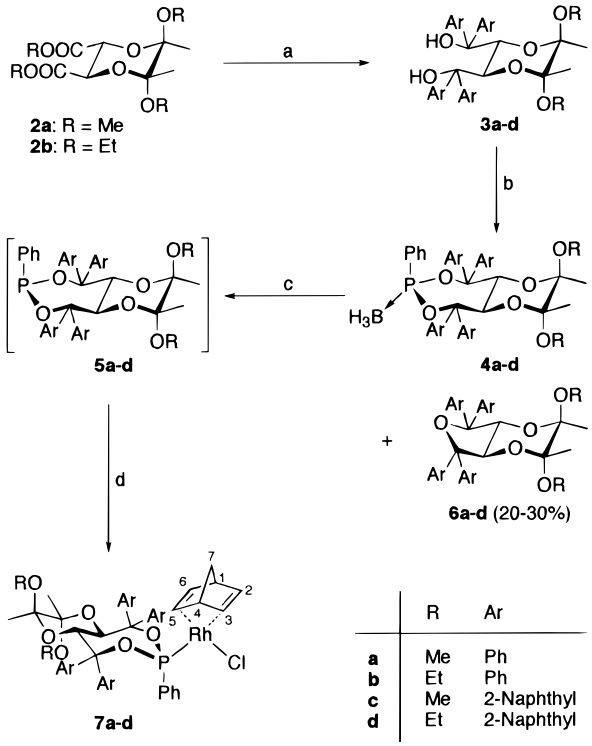
Scheme 1[a]



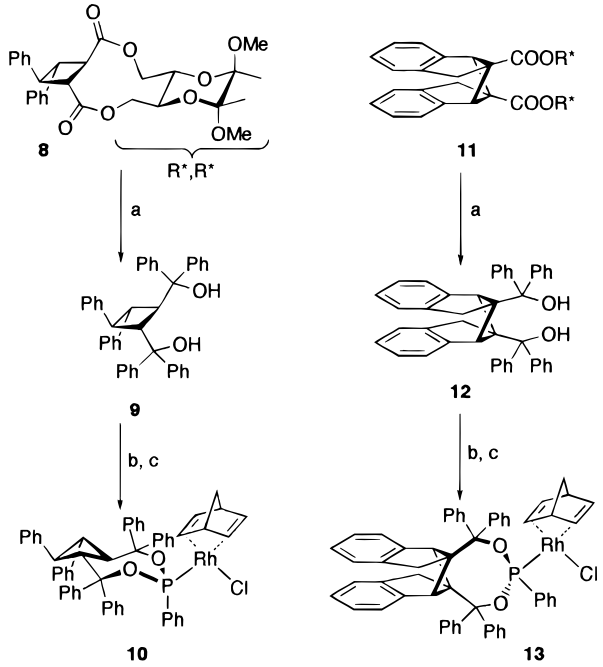
[a] Key: (a) excess ArMgBr, THF, Δ (53-79%); (b) (i) 2 equiv of BuLi, THF, -78 °C, then rt; (ii) $PhPCl_2$, -78 °C, then rt; (iii) BH_3SMe_2, toluene, rt (52-62%); (c) 1 equiv of DABCO, toluene, 50 °C (quantitative, contains ca. 5% of **6**); (d) 0.45-0.47 equiv of $[Rh(NBD)Cl]_2$, toluene, rt (71-89%).

The second objective of this work emerged from previous activities to determine the influence of the temperature on the enantioselectivity of the rhodium(I) catalyzed hydrosilylation. Although such investigations have been sparse, they clearly indicate that it is difficult to anticipate how the asymmetric induction is affected by the reaction temperature.[11] On the basis of the principle of isoinversion,[12] a stereochemical model which is compatible with such irregularities, we wondered whether the temperature dependence of the enantioselective hydrosilylation could be characterized by a nonlinear relationship featuring points of inversion.

Results and Discussion

Synthesis of Rhodium(I)−Phosphonite Complexes. The synthesis of the tartrate-derived rhodium(I)-phosphonite complexes **7a**−**d** bearing different alkoxy substituents in the 1,4-dioxane backbone and different aromatic substituents in the seven-membered phosphonite ring is outlined in Scheme 1. Starting from readily available diesters **2a**,**b** respectively,[9,10] the TARTROLs **3a**−**d** were obtained *via* Grignard reduction with an excess of the appropriate arylmagnesium bromide. Subsequent cyclization to the phosphonites **5a**−**d** was achieved following the protocol of Seebach.[8] The direct isolation of these very oxygen-sensitive compounds proved to be somewhat capricious, as the cylization reaction was notoriously accompanied by competitive formation of the corresponding tetrahydofurans **6a**−**d** (up to 30%) and incomplete conversion (∼90%), thus imposing a laborious purification procedure under an argon atmosphere. To circumvent this difficulty, the crude phosphonites **5a**−**d** were immediately converted into their borane adducts **4a**−**d**, which turned out not to be prone to oxidation and, therefore, could easily be purified by chromatography and/or crystallization. The liberation of the phosphonites **5a**−**d** succeeded with almost quantitative yield by treatment with equimolar amounts of DABCO at elevated temperatures.[13] Interestingly, even under these conditions the competitive formation of the corresponding tetrahydrofurans **6a**−**d** could not be suppressed completely. But, as exemplified for the phosphonite **5b** (*vide infra*), the crude compounds **5a**−**d** obtained in this manner were sufficiently pure (∼95%) for the *in-situ* preparation of rhodium catalysts for the hydrosilylation. The synthesis of the rhodium(I) complexes **7a**−**d** was best performed as a one-pot procedure comprising the cleavage of the borane−phosphonite adducts **4a**−**d** followed by immediate addition of $[Rh(NBD)Cl]_2$. Starting from diesters **8** and **11** (Scheme 2), which were obtained *via* highly diastereoselective intramolecular [2 + 2] photocycloaddition reactions,[10] the cyclobutane-based rhodium(I)−phosphonite complexes **10** and **13** were synthesized in a similar manner.

Scheme 2[a]



[a] Key: (a) excess PhMgBr, THF, Δ (82-88%); (b) (i) 2 equiv of BuLi, THF, -78 °C, then rt; (ii) $PhPCl_2$, -78 °C, then rt; (iii) BH_3SMe_2, toluene, rt (34-51%); (c) (i) 1 equiv of DABCO, toluene, 50 °C; (ii) 0.45-0.47 equiv of $[Rh(NBD)Cl]_2$, toluene, rt (82-87%).

(11) (a) Langlois, N.; Dang, T.-P.; Kagan, H. B. *Tetrahedron Lett.* **1973**, *14*, 4865. (b) Kolb, I.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1980**, *45*, 2224. (c) Semmelhack, M. F.; Misra, R. N. *J. Org. Chem.* **1982**, *47*, 2469. (d) Zhorov, E. Y.; Pavlov, V. A.; Koreshkov, Y. D.; Klabunovskii, E. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 1951. While in (a) and (b) it was found that lowering the reaction temperature led to improved stereoselectivities, in (c) and (d) the opposite trend was observed.

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(13) Brisset, H.; Gourdel, Y.; Pellon, P.; Le Corre, M. *Tetrahedron Lett.* **1993**, *34*, 4523.

Table 1. Effect of Various Reaction Parameters on the Rhodium(I)-Catalyzed Asymmetric Hydrosilylation of Acetophenone (14)[a]

T / °C	solvent	Rh:**5b**[b]	% ee	% cv
−27	toluene	1:1	17 (*S*)	57
0	toluene	1:1	53 (*S*)	96
+10	toluene	1:1	55 (*S*)	96
+20	toluene	1:1	51 (*S*)	95
−27	THF	1:1	15 (*S*)	39
0	THF	1:1	52 (*S*)	88
+10	THF	1:1	49 (*S*)	79
0	benzene	1:1	46 (*S*)	95
+20	benzene	1:1	49 (*S*)	86
+10[c]	toluene	1:1	54 (*S*)	86
+10	toluene	1:4	56 (*S*)	97
+10[d]	toluene	1:2	56 (*S*)	96
+10[d]	toluene	1:4	55 (*S*)	96

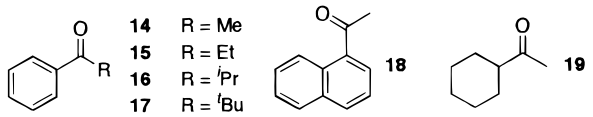
[a] Unless otherwise noted, reductions were carried out with 1.25 equiv of Ph_2SiH_2 in the presence of 1% of catalyst (0.5% $[Rh(NBD)Cl]_2$). [b] Catalysts were prepared *in-situ* from $[Rh(NBD)Cl]_2$ and ligand **5b**. [c] 1.0 equiv of Ph_2SiH_2 was used. [d] The amount of catalyst was increased to 2%.

Besides being stable to oxygen, the rhodium(I) complexes **7a**−**d**, **10**, and **13** also proved to be exceptionally thermally stable. Thus decomposition did not occur up to temperatures of 215 °C in any case. Consequently, one may assume that the bond between the phosphonite ligand and the central rhodium atom is sufficiently strong to permit the application of this type of complexes in asymmetric catalysis even at elevated temperatures and without addition of an excess of the chirality bearing ligand. Nevertheless, NMR spectroscopic measurements unambiguously disclosed a dynamic behavior of the 2,5-norbornadiene moiety. Indeed, in the conventional ^{1}H- and ^{13}C-NMR spectra of complex **7a** the resonances of all hydrogen and carbon atoms of the norbornadiene ligand appear at different chemical shifts according to their position relative to the phosphonite ligand. Due to the *trans*-effect of the latter imposing a weakening of the bond between the rhodium atom and the CH2−CH3 olefin substructure the corresponding NMR signals (^{1}H, 5.07 and 5.32 ppm; ^{13}C, 84.57 and 89.98 ppm) reflect a more olefinic character as compared with the CH5−CH6 double bond (^{1}H, 2.60 (CH5) and 4.12 ppm, ^{13}C: 50.07 and 51.20 ppm). Furthermore, the anisotropic shielding of the aryl groups gives rise to an additional shift to higher fields observed for the ^{1}H-NMR signal of CH5. On the contrary owing to saturation transfer, the protons arranged symmetrically at the C_2-axis of the norbornadiene ligand (e.g. CH2 and CH5) cannot be irradiated separately in ^{1}H-NOE experiments. Taking into account the mixing time of 0.5 s, this phenomenon corresponds to a formal rotation of the norbornadiene ligand with a frequency of at least 1 Hz.

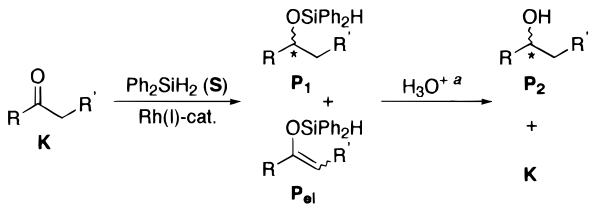
Temperature Dependence of Enantioselective Hydrosilylation. Before embarking on with temperature-dependent measurements of the enantioselective rhodium(I)-catalyzed hydrosilylation, our very first order of business was to elucidate the influence of other reaction parameters. For this purpose, hydrosilylation of acetophenone (**14**) employing ligand **5b** was performed as a model reaction.

The results obtained on varying the solvent, the amount of catalyst, the rhodium−ligand ratio, and the ketone−silane ratio are summarized in Table 1. With respect to chiral induction and conversion, the use of toluene as solvent with a slight excess of diphenylsilane appeared to be most favorable for our further investigations. The fact that an increase of the rhodium−ligand ratio from 1:1 to 1:4 did not effect the enantioselectivity is in line with the already mentioned thermal stability of the 1:1 rhodium−phosphonite complexes. Since doubling of the amount of catalyst did not show a noticeable influence on the outcome of the reaction, as little as 0.01 equiv of the isolated rhodium complex **7a**−**d**, **10**, or **13** can be regarded as adequate without jeopardizing enantioselectivity and conversion of the hydrosilylation reaction.

Chart 2



Scheme 3[a]



[a] The silyl group was removed to faciliate identification and analysis of the hydrosilylation products.

To gain a survey of the general temperature dependence of the asymmetric induction in the rhodium(I)-catalyzed hydrosilylation of ketones, the reduction of several substrates **14**, **15**, **18**, and **19** (Chart 2) in the presence of **7a** or **7b** was thoroughly examined in a temperature range from −30 to +90 °C.

The rather uniform influence of the temperature upon the conversion constitutes a conspicious feature common to all investigated systems (combinations ketone−catalyst). Throughout the middle temperature range from −15 to +45 °C almost complete conversion of the ketones was observed, whereas the substantial decrease of conversion (down to 22−87% depending on the ketone) at lower temperatures indicates a remarkable loss of catalytic activity of the rhodium complexes **7a**,**b**. On the other hand, reduced conversions (80−90%) at elevated temperatures are evoked by the competitive formation of the corresponding silyl enol ethers $\mathbf{P_{el}}$ (Scheme 3) *via* β-hydride elimination.[14]

Evaluation of the temperature-dependent enantioselectivities according to the modified Eyring formalism[15] is presented in Figures 1−4. These plots reveal a characteristic temperature profile which is marked by the existence of somewhat diffuse points of inversion in the temperature region between −5 and +25 °C. At both sides, this area is flanked by decreasing enantioselectivities. While the low-temperature region can be satisfactorily approximated by linear functions, the behavior in the high-temperature region appears to be more complex, as evidenced by the flattening of the slopes at temperatures above +50 °C.

(14) (a) Benes, J.; Hetflejs, J. *Collect. Czech. Chem. Commun.* **1976**, *41*, 2264. (b) Peyronel, J.-F.; Fiaud, J.-C.; Kagan, H. B. *J. Chem. Res. (M)* **1980**, 4055.

(15) Eyring, H. *J. Chem. Phys.* **1935**, *3*, 107.

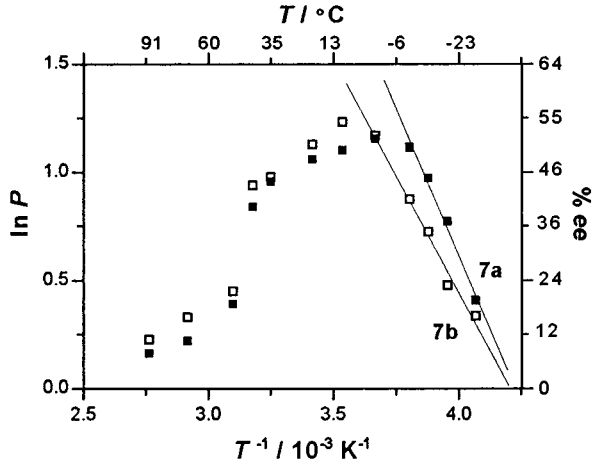


Figure 1. Eyring diagram for the hydrosilylation of acetophenone (**14**) catalyzed by **7a** and **7b** ($P = [S]/[R]$).

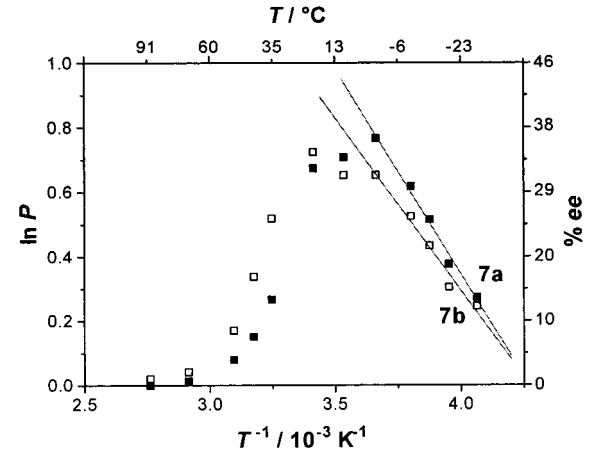


Figure 2. Eyring diagram for the hydrosilylation of propiophenone (**15**) catalyzed by **7a** and **7b** ($P = [S]/[R]$).

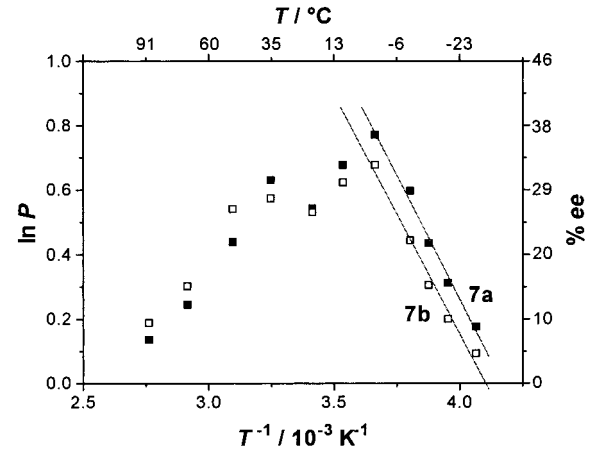


Figure 3. Eyring diagram for the hydrosilylation of cyclohexyl methyl ketone (**19**) catalyzed by **7a** and **7b** ($P = [S]/[R]$).

The mechanism of the rhodium-catalyzed hydrosilylation proposed by Ojima[3] (Scheme 4) may serve as an approach to rationalize the observed nonlinear relationship between ln P (P = ratio of enantiomers) and the reciprocal of temperature in the Eyring plots requiring the existence of at least two relevant partial steps within the selection mechanism.[12] Actually, the reversible enantioface differentiating coordination of ketone **K** to the rhodium hydride complex **B** and the subsequent

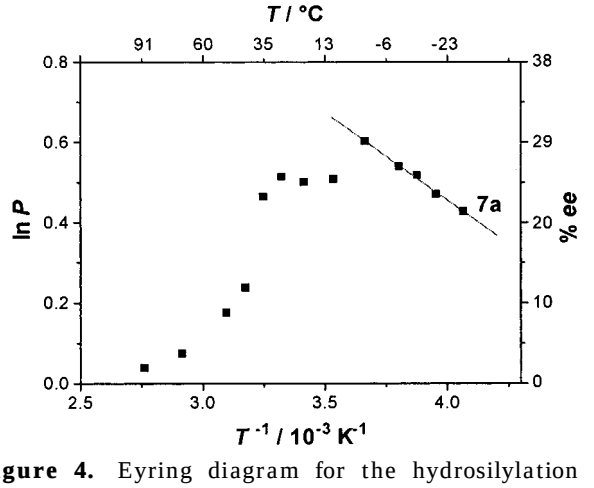
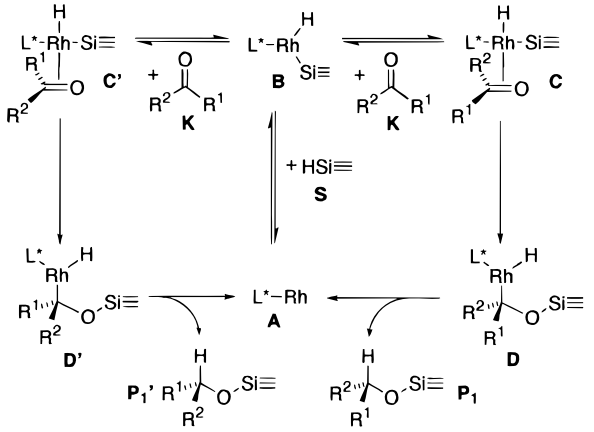
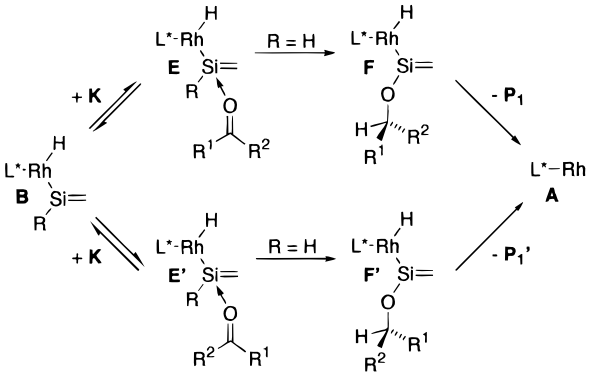


Figure 4. Eyring diagram for the hydrosilylation of 1-acetonaphthone (**18**) catalyzed by **7a** ($P = [S]/[R]$).

Scheme 4



Scheme 5[a]



[a] Assignment which of the both isomers **E** or **E'** leads to the formation of **F** and **F'** respectively was arbitrary.

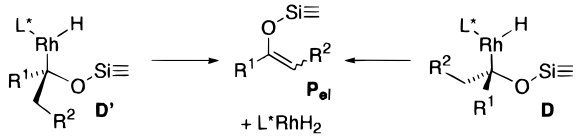
irreversible insertion of the carbonyl function of intermediate **C** and **C′**, respectively, into the rhodium silicon bond provide two stages at which the stereochemical outcome of the hydrosilylation can be determined. It is noteworthy that the alternative mechanism recently proposed by Zheng and Chan[4] (Scheme 5) is also characterized by the existence of two partial selection steps. Here, the reversible coordination of ketone **K** to the silicon atom of complex **B** giving adduct **E** and **E′**, respectively,[16] and the successive irreversible transfer of the silicon bound hydrogen to the carbonyl function represent the crucial features of the selection mechanism.

Table 2. Roughly Optimized Temperature-Dependent Enantioselectivities of the Hydrosilylation of Various Ketones (14−19) Using Chiral Rhodium(I) Catalysts with L-Tartaric Acid Derived Phosphonite Ligands 5a−d, 1a, and 1b

ketone	**5a**[a] % ee (*T*/°C)	**5b**[a] % ee (*T*/°C)	**5c**[a] % ee (*T*/°C)	**5d**[a] % ee (*T*/°C)	**1a**[b] % ee	**1b**[b] % ee
14 (*S*)[c]	52 (0)	55 (10)	54 (20)	56 (20)	−55	−82
15 (*S*)[c]	37 (0)	35 (20)	45 (0)	46 (20)	−56	−66
16 (*R*)[c]	67 (0)	65 (0)	66 (0)	66 (20)	∼0	
17 (*R*)[c]	84 (−5)	86 (−5)		86 (0)	∼0	
18 (*S*)[c]	29 (0)			42 (20)	−61	−84
19 (*S*)[c]	37 (0)	33 (0)	50 (10)	49 (27)		

[a] Reactions were carried out with 1.25 equiv of Ph_2SiH_2 in the presence of 1% of rhodium(I) complexes **7a−d** prepared from **5a−d**. [b] Reactions were carried out with 1.2 equiv of Ph_2SiH_2 in the presence of 2% of catalyst prepared *in-situ* from $[Rh(COD)Cl]_2$ and ligand **1a** or **1b** (ratio 1:5) starting at 0 °C and allowing the reaction mixture to warm to 20 °C.[8] [c] All ee values refer to the given absolute configuration of the respective product alcohol.

Scheme 6



According to Ridd,[17] the existence of only two selection steps may already give rise to the occurence of two points of inversion in the corresponding Eyring diagram. Consequently, one might consider the fact that the Eyring plots resulting from the asymmetric hydrosilylation cannot be simply described by two linear functions to be consistent with one of the above mentioned mechanisms. But, as the transitional region between the inversion temperatures usually ranges over about 100 °C, according to the calculations carried out by Ridd, we assume the rather abrupt changes in the behavior of the plots in the high-temperature region to be caused by at least one additional partial step influencing the overall enantioselectivity. Apparently, at the stage of the catalytic intermediates **D** and **D′**, diastereodifferentiating β-hydride elimination leading to competitive formation of the silylenol ether $\mathbf{P_{el}}$[14] (Scheme 6) forms a further relevant step wthin the selection mechanism, for the lower conversions at elevated temperatures coincide with the observed irregularities in the high-temperature region of the Eyring plots.

Influence of the Ligand Backbone on Asymmetric Induction. On the basis of the above findings which already disclosed the general characteristics of the temperature dependence of the enantioselective rhodium catalyzed hydrosilylation of ketones by diphenylsilane, the optimization of the further systems comprising ketones **14−19** as substrates and complexes **7a−d**, **10**, and **13** as catalysts required only a few measurements (3−5 runs). The enantioselectivities achieved with the L-tartaric acid derived ligands **4a−d** and **1a,b** are summarized in Table 2. As expected, in all cases the inversion temperature (T_i) could be localized in the mid-temperature region between −10 and 30 °C. Therefore, one may assume the results reported by Seebach,[8] which were obtained with the TADDOL-derived ligands **1a**,**b** at reaction temperatures between 0 and 20 °C, to reflect at least approximately the enantioselectivities attainable at the point of inversion of the respective systems.

Concerning the asymmetric inductions achievable at optimized reaction temperatures, comparison of the results obtained with **4a**,**b** as well as with **4c**,**d** clearly reveal the influence of the alkoxy substituent of the diacetal moiety to be negligible. However, with regard to the inversion temperatures, a significant trend becomes apparent as the majority of the points of inversion found for the ethyl acetals **4b**,**d** is shifted to slightly higher temperatures as compared with the methyl acetals **4a**,**c**. If we look at Figures 1−3, this phenomenon turns out to be valid in the whole temperature region investigated. Indeed, the curves measured for a certain ketone with **7a**,**b** as catalyst are characterized by an almost identical profile, but the plots of **7b** are shifted to higher temperatures. According to the Eyring formalism,[15] such a parallel shift of plots is caused exclusively by entropic effects. Thus, the difference between the plots of **7a** and **7b** illustrates the extent to which the entropic portion of the free conformation enthalpy of the phosphonite ligand is influenced by the additional number of degrees of freedom accrued from the ethyl groups in **7b**.

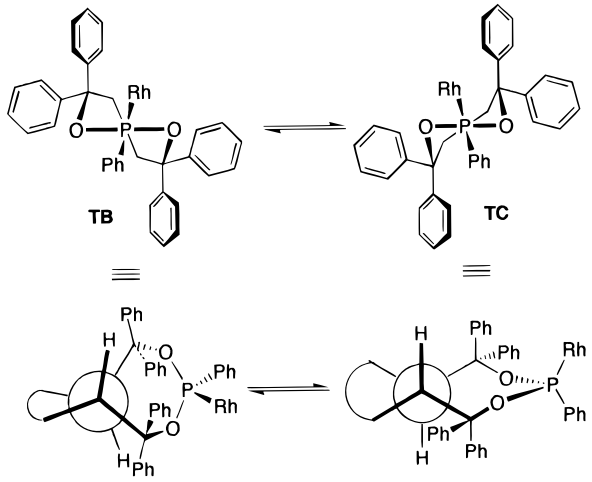
A much more dramatic interaction between structural features of the ligand and the stereochemical course of the hydrosilylation is displayed on replacement of the 1,4-dioxane backbone common to the phosphonites **4a−d** by the 1,3-dioxolane backbone present in **1a**,**b**. The large differences of the asymmetric induction, amounting up to 146% ee, indicate a quasi enantiomeric behavior of these two structural classes of ligands. In the case of the reduction of acetophenone (**14**) with catalysts derived from **4b** and **1a**, respectively, this phenomenon culminates in an exact reversal of the enantioselectivity. Furthermore whereas, in the presence of the 1,3-dioxolane **1a**, hydrosilylation of isobutyrophenone (**16**) and pivalophenone (**17**) proceeds with almost no enantioselection, application of the 1,4-dioxane-based catalysts **7a**,**b** leads to fairly good enantioselectivities. To the best of our knowledge, the ee value (86%) achieved in the hydrosilylation of pivalophenone (**17**) is the best ever observed in catalytical variants of the asymmetric reduction of this substrate.

Obviously, the conformational properties of the ligand backbone are efficiently transmitted to the annelated seven-membered phosphonite ring which may adopt two extremely different conformations[18] with a respective enantiomorphous arrangement of the *C*-aryl groups. A

(16) A comparable reversible *E*/*Z*-selective coordination of chiral boranes to ketones has been shown to be the first relevant selection step in the enantioselective hydroboration of ketones: Wiegers; A.; Scharf, H.-D. *Tetrahedron: Asymmetry* **1996**, *7*, 2303.

(17) (a) Hale, K. J.; Ridd, J.-H. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1601. (b) Hale, K. J.; Ridd, J.-H. *J. Chem. Soc., Chem. Commun.* **1995**, 357.

Scheme 7



schematic illustration of this conformational equilibrium is presented in Scheme 7. In the case of ligands of type **4**, the preferred chair conformation of the 1,4-dioxane backbone, implying an *anti-periplanar* orientation of the bridge head hydrogen atoms, supports the twist-chair conformation **TC** of the phosphonite ring. On the contrary, in compounds **1a**,**b** the same arrangement of the bridgehead substituents imposes a considerable strain upon the 1,3-dioxolane ring—a fact that is well-known from the protection of cyclic *trans*-1,2-diols as acetonides. Tapering of the dihedral angle between the substituents of the backbone provides a suitable expedient to reduce this strain. As depicted in the Newman projection (Scheme 7), such a distortion of the bridging C−C bond is accompanied by a favorization of the twist-boat conformation **TB** of the phosphonite ring. Although disregarding the complexly composed mechanism of the hydrosilylation and any debates on the validity of the Curtin−Hammett principle, this rather simple consideration relying on the equilibrium between two quasi enantiomeric conformers of the phosphonite ring offers a suitable rationalization to account for the observed strong influence of the ligand backbone on the extent as well as the direction of enantioselection.

At this point, it is worth mentioning that, on application of L-tartaric acid derivatives as source of chiral induction in the rhodium-catalyzed hydrogenation[20] as well as in the intramolecular [2 + 2] photodimerization,[9,21] the same tendency has already been observed. Again, in comparison with substrates bearing a fused 1,3-dioxolane backbone, those marked by a 1,4-dioxane backbone show a strikingly different potential in asymmetric syntheses that may even result in the reversed direction of stereoselectivity.

Table 3. Temperature Dependence of the Asymmetric Hydrosilylation of Acetophenone (14) in the Presence of Cyclobutane-Based Rhodium(I) Complexes 10 and 13

	T/°C				
	−25	−10	0	20	50
10: % ee[a]	35	25	17	−2	4
13: % ee[a]		11	53	15	

[a] All ee values refer to (*R*)-2-phenylethanol.

Furthermore, the results listed in Table 2 indicate that, as in the Ti−TADDOLate-catalyzed nucleophilic addition of dialkylzinc compounds to aldehydes,[22] replacement of the phenyl groups on the methanol groups of **5a,b** by 2-naphthyl substituents (**5c,d**) may lead to slightly improved enantioselectivities. Whether this effect originates from a shift of the conformational equilibrium of the ligands or from a more efficient enantiodifferentiation within a single conformation owing to the increased steric demand of the 2-naphthyl groups yet remains elusive.

Finally, we expanded our investigations on the application of the cyclobutane-based catalysts **10** and **13**. As exemplified by the hydrosilylation of acetophenone (**14**), the results presented in Table 3 confirm the already observed existence of points of inversion in the middle temperature range. Direct comparison of catalysts **10** and **13** discloses a reversed temperature dependent behavior, as is particularly evident from the enantioselectivities achieved at the respective inversion temperatures. Whereas with **10** ($T_i \sim 20$ °C) the formation of the (*S*)-configurated alcohol gains favor, with **13** ($T_i \sim 0$ °C) the point of inversion is marked by maximal (*R*)-selectivity. Moreover, the results obtained on employment of **10** reveal that the point of inversion does not necessarily have to coincide with the temperature at which the "best" selectivities can be attained. However, with regard to the very low level of enantioselection, such behavior is not very surprising.

Random tests with ketones **15**−**19** did not show any remarkable deviations from the trends established for the reduction of acetophenone (**14**), and ee values did not exceed 35%.[23] Accordingly, concerning their potential as catalysts in the asymmetric hydrosilylation, our results place the cyclobutane-based complexes **10** and **13** between the 1,4-dioxanes **7a**−**d** and catalysts derived from the 1,3-dioxolanes **1a,b**. With reference to the aforementioned conformational equilibrium of the seven-membered phosphonite ring, from the asymmetric inductions achieved with **10** as catalyst, it can be deduced that, in presence of the diphenyl-substituted cyclobutane backbone, a distinct preference for one of the conformers cannot be accomplished.[24]

Conclusions

We have elaborated a versatile access to a novel class of rhodium(I) complexes bearing monodentate chiral

(18) A similar conformational equilibrium of the seven-membered rhodium(I) chelate ring is also discussed to be a relevant factor determining the enantioselectivity of the catalytic asymmetric hydrogenation: (a) Glaser, R.; Geresh, S.; Twaik, M. *Isr. J. Chem.* **1980**, *20*, 102. (b) Brown, J. M.; Chaloner, P. A. *J. Am. Chem. Soc.* **1978**, *100*, 4321. (c) Brown, J. M.; Chaloner, P. A.; Glaser, R.; Geresh, S. *Tetrahedron* **1980**, *36*, 815. (d) Pavlov, V. A.; Bagatur'yants, A. A.; Kazanskii, V. B.; Klabunovskii, E. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 508.

(19) (a) Curtin, D. Y. *Rec. Chem. Prog.* **1954**, *15*, 11. (b) Seeman, J. I.; Farone, W. A. *J. Org. Chem.* **1978**, *43*, 1854. (c) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

(20) Berens, U.; Selke, R. *Tetrahedron: Asymmetry* **1996**, *7*, 2055.

(21) Green, B. S.; Hagler, A. T.; Rabinsohn, Y.; Rejtö, M. *Isr. J. Chem.* **1976/77**, *15*, 124.

(22) (a) Seebach, D.; Behrendt, L.; Felix, D. *Angew. Chem.* **1991**, *103*, 991; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1008. (b) Seebach, D.; Beck, A. K.; Schmidt, B.; Wang, Y. M. *Tetrahedron* **1994**, *50*, 4363.

(23) Haag, D. Dissertation, RWTH Aachen, 1997.

(24) This rank is paralleled by an appropriate change of the NMR coupling constants between the bridgehead protons: **5b**, 10.4 Hz; **10**, 9.2 Hz; **1a**, 8.5 Hz (last value taken from: Seebach, D.; Hayakawa, M.; Sakaki, J.; Schweizer, B. W. *Tetrahedron* **1993**, *49*, 1711).

phosphonite ligands. These complexes proved to be highly active catalysts in the asymmetric hydrosilylation of ketones, thus permitting a detailed examination of this reaction.

Evaluation of the temperature dependent measurements according to the Eyring formalism disclosed a nonlinear relationship between ln *P* (*P* = ratio of the enantiomeric product alcohols) and the reciprocal of temperature marked by the occurrence of points of inversion. As the corresponding Eyring plots cannot be simply described by two linear functions, we conclude that the stereochemical outcome is controlled by more than two relevant partial steps within the selection mechanism.[12] From a more practical point of view, the existence of points of inversion in the mid-temperature region from −5 to 30 °C is of considerable interest, since, for any system related to those treated in this paper, the optimal reaction temperature with respect to the enantioselectivity is usually expected to lie in this range.

Furthermore, by comparison of **7a**−**d** and **10** with catalysts derived from **1a,b**,[8] we have demonstrated the structural properties of the ligand backbone to have a pronounced influence on the conformational equilibrium of the seven-membered phosphonite ring which may adopt two extremely different conformations with a respective enantiomorphous arrangement of the *C*-aryl groups. As is apparent especially from the hydrosilylation of acetophenone (**14**) and pivalophenone (**17**), concerning the direction of chiral induction as well as the substrate specificity, this effect may be efficiently exploited to achieve complementarity within a single class of ligands all possessing the same absolute configuration in their backbone.

Experimental Section

General Comments. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. THF was dried by the sodium−benzophenone method immediately prior to use. Dry toluene was obtained by distillation from sodium. TLC was conducted with plates precoated with Kieselgel 60 F_{254}. Detection was first by UV (254 nm) and then charring with a solution of 1.0 g of vanillin in 250:25:10 methanol−acetic acid−sulfuric acid. After extraction of aqueous solutions the combined organic layers were dried over $MgSO_4$. Evaporation of solvents was accomplished with a rotary evaporator. Melting points (Pyrex capillary) are uncorrected. GC analyses of the enantiomeric ratios were performed on a Hewlett-Packard HP 5890 series II plus equipped with a permethylated cyclodextrin capillary column (FS-CYCLODEX-β-I/P, 25 m × 0.25 mm; carrier gas H_2), a flame ionization detector, and a HP 3396 series II integrator. All chromatograms obtained were compared with those of authentic references of educts and products (racemic). The absolute configurations of the product alcohols obtained on hydrosilylation were assigned by comparing the optical rotation with the reported value.[25] All reaction temperatures were kept constant by means of cryostats (below room temperature) or electronically controlled heating baths.

(2*R*,3*R*,5*R*,6*R*)-2,3-Bis(hydroxydiphenylmethyl)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxane (3a). A solution of 1.20 mol of phenylmagnesium bromide in 375 mL of THF was prepared from 29.2 g of Mg turnings and 126 mL of bromobenzene (188 g). To the resulting slightly turbid solution was added a solution of 43.8 g of dimethyl ester **2a**[10] (0.150 mol) in 300 mL of THF at a rate maintaining gentle reflux. Afterward, the reaction mixture was heated at reflux for 3 h. Then, the mixture was diluted with 400 mL of THF and hydrolyzed by careful addition of a saturated NH_4Cl solution (∼650 mL). The phases were separated, and the aqueous layer was extracted four times with 250 mL of ether. After the combined organic phase was dried, filtered, and evaporated, the resulting reddish-brown viscous residue was heated under vacuum (0.05 mmHg), finally up to a temperature of 100 °C. The residue, a brown glass, was dissolved in a minimum of ethyl acetate, and hexane was added until the solution became turbid. After standing at −24 °C overnight, the product crystallized to give 58.2 g of diol **3a** as a 1:1 clathrate with ethyl acetate (62% based on **2a**). (In some cases it may be necessary to purify the crude product roughly by column chromatography on 500 g of silica gel with 4:1 hexane−ethyl acetate.) Removal of ethyl acetate, which may cause trouble in further conversions of diol **3a**, was accomplished without any loss of material by recrystallization from ether to furnish the corresponding 1:1 clathrate of diol **3a** with ether. For analytical purposes ethyl acetate was removed by azeotropic distillation with hexane. Mp: 105 °C. $[\alpha]^{20}_D$: +53.2 (c = 1.10, $CHCl_3$). IR (KBr): 3471, 3368, 3058, 2948, 2833, 1601, 1494, 1449, 1374, 1142, 1127, 1038, 916, 760, 744, 701 cm^{-1}. MS (70 eV): m/z (%) 391 (0.3) [M − H − $(MeCOOMe)_2$]$^+$, 373 (0.4), 325 (11.1), 269 (11.4), 209 (13.6), 183 (65.6) [Ph_2COH], 143 (37.4), 116 (20.6), 105 (100), 101 (72.0), 77 (32.2). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.94 (s, 6), 2.51 (s, 6), 4.32 (s, 2), 4.37 (s, 2, OH), 6.95−7.07 (m, 10), 7.25-7.39 (m, 6), 7.91 (m, 4). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 17.25, 47.77, 76.07, 79.51, 98.59, 126.92, 127.21, 127.25, 127.39, 127.81, 128.11, 142.96, 146.17. Anal. Calcd for $C_{34}H_{36}O_6$: C, 75.53; H, 6.71. Found: C, 75.35; H, 7.11.

(2*R*,3*R*,5*R*,6*R*)-2,3-Diethoxy-5,6-bis(hydroxydiphenylmethyl)-2,3-dimethyl-1,4-dioxane (3b). This compound was prepared in analogy to the procedure for **3a** from 1.60 mol of phenylmagnesium bromide (38.9 g of Mg turnings and 168 mL of bromobenzene (251 g) in 500 mL of THF) and a solution of 69.7 g of diethyl ester **2b**[10] (0.200 mol) in 400 mL of THF. The crude product, a brown glass, was purified by crystallization from ether−pentane at −24 °C to yield 68.1 g of diol **3b** as a 1:1 clathrate with ether (53% based on **2b**). For analytical purposes ether was removed by azeotropic distillation with hexane. Mp: 198 °C. $[\alpha]^{20}_D$: +61.3 (c = 1.04, $CHCl_3$). IR (KBr): 3691, 3551, 3396, 3064, 2974, 2886, 1602, 1494, 1448, 1394, 1373, 1191, 1148, 1124, 1096, 1050, 1031, 954, 913, 756, 745, 698 cm^{-1}. MS (70 eV): m/z (%) 477 (1.2) [M − 2 EtO − H], 391 (3.3) [M − H − $(MeCOOEt)_2$]$^+$, 373 (3.4), 339 (33.5), 269 (48.8), 209 (35.5), 183 (99.6) [Ph_2COH], 157 (37.7), 144 (25.7), 115 (69.1), 105 (100), 101 (72.0), 87 (51.9), 77 (19.4). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.03 (t, 6, ^3J = 7.1 Hz), 1.04 (s, 6), 2.34, 2.93 (2 dq, 4, $|^2J|$ = 9.0 Hz), 4.47 (s, 2), 4.51 (s, 2, OH), 7.00−7.05 (m, 4), 7.09−7.14 (m, 6), 7.32−7.45 (m, 6), 8.02 (m, 4). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 15.16, 17.91, 55.21, 76.07, 79.43, 98.31, 126.81, 127.01, 127.13, 127.18, 127.72, 128.32, 142.87, 146.43. Anal. Calcd for $C_{36}H_{40}O_6$: C, 76.08; H, 7.09. Found: C, 75.79; H, 7.25.

(2*R*,3*R*,5*R*,6*R*)-2,3-Bis(hydroxybis(2-naphthyl)methyl)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxane (3c). This compound was prepared in analogy to the procedure for **3a** from 30.0 mmol of 2-naphthylmagnesium bromide (0.729 g of Mg turnings and 6.21 g of bromonaphthalene in 15 mL of THF) and a solution of 1.46 g of dimethyl ester **2a**[10] (5.00 mmol) in 10 mL of THF. The crude product was purified by column chromatography on 220 g of silica gel with 4:1 hexane−ethyl acetate to furnish 2.16 g of diol **3c** (58% based on **2a**) as a colorless solid. Mp: 155 °C. $[\alpha]^{20}_D$: +55.1 (c = 0.94, $CHCl_3$). IR (KBr): 3322, 3055, 2949, 2831, 1599, 1505, 1374, 1142, 1128, 1036, 895, 860, 820, 801, 757, 746 cm^{-1}. MS (SIMS: FAB − VE): m/z (%) 740 [M]$^-$ (100), 283 [Ar_2COH] (1.6). ^{1}H-

(25) Kagan, H. B. *Stereochemistry, Vol. 4, Absolute Configurations of 6000 Selected Compounds with One Asymmetric Carbon Atom*; Georg Thieme Publishers: Stuttgart, Germany, 1977.

NMR ($CDCl_3$, 300 MHz): δ 1.06 (s, 6), 2.63 (s, 6), 4.81 (s, 2), 4.95 (br s, 2, OH), 7.18−7.35 (m, 6), 7.42−7.57 (m, 10), 7.63 (m, 2), 7.90−7.99 (m, 6), 8.11 (m, 2), 8.72 ("s", 2). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 17.27, 48.01, 75.77, 79.97, 98.59, 125.49, 125.71, 125.79, 125.94, 126.29, 126.54, 126.59, 127.16, 127.26, 127.31, 127.55, 128.38, 128.85, 132.32, 132.49, 132.77, 133.16, 140.57, 143.38. Anal. Calcd for $C_{50}H_{44}O_6$: C, 81.06; H, 5.99. Found: C, 81.37; H, 5.71.

(2*R*,3*R*,5*R*,6*R*)-2,3-Diethoxy-5,6-bis(hydroxybis(2-naphthyl)methyl)-2,3-dimethyl-1,4-dioxane (3d). This compound was prepared in analogy to the procedure for **3a** from 30.0 mmol of 2-naphthylmagnesium bromide (0.729 g of Mg turnings and 6.21 g of bromonaphthalene in 15 mL of THF) and a solution of 1.74 g of diethyl ester **2b**[10] (5.00 mmol) in 10 mL of THF. The crude product was purified by column chromatography on 220 g of silica gel with 4:1 hexane−ethyl acetate and subsequent crystallization from ether−pentane at −24 °C to furnish 3.33 g of diol **3d** as a 1:1 clathrate with ether (79% based on **2b**). For analytical purposes ether was removed by azeotropic distillation with hexane. Mp: 224 °C. $[\alpha]^{20}_D$: +34.4 (c = 1.18, $CHCl_3$). IR (KBr): 3568, 3449, 3051, 2975, 2880, 1598, 1505, 1391, 1375, 1152, 1130, 1048, 1020, 960, 892, 859, 821, 803, 747 cm^{-1}. MS (70 eV): m/z (%) 676 (0.3) [M − 2EtOH], 591 (0.2) [M − H − $(MeCOOEt)_2$]$^+$, 439 (4.6), 309 (6.3), 295 (14.3), 283 (100) [Ar_2COH], 267 (11.3), 155 (94.2), 144 (20.0), 127 (32.3), 115 (49.6), 87 (45.2). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.99 (t, 6, ^3J = 7.1 Hz), 1.07 (s, 6), 2.28, 2.84 (2 dq, 4, $|^2J|$ = 8.9 Hz), 4.65 (br s, 2, OH), 4.88 (s, 2), 7.17 (m, 2), 7.24−7.36 (m, 4), 7.42 ("d", 2), 7.47−7.59 (m, 8), 7.65 (m, 2), 7.91−7.98 (m, 6), 8.22 (m, 2), 8.66 ("s", 2). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 15.36, 18.03, 55.52, 76.24, 79.87, 98.66, 125.52, 125.66, 125.72, 125.94, 126.02, 126.42, 126.80, 127.18, 127.30, 127.37, 127.57, 128.33, 128.93, 132.32, 132.53, 132.85, 133.18, 140.78, 143.88. Anal. Calcd for $C_{52}H_{48}O_6$: C, 81.22; H, 6.29. Found: C, 80.86; H, 6.49.

(1*R*,2*R*,3*S*,4*S*)-1,2-Bis(hydroxydiphenylmethyl)-3,4-diphenylcyclobutane (9). This compound was prepared in analogy to the procedure for **3a** from 16.0 mmol of phenylmagnesium bromide (0.388 g of Mg turnings and 2.51 g of bromobenzene in 8 mL of THF) and a solution of 0.993 g of diester **8**[10] (2.00 mmol) in 4 mL of THF. The crude product was purified by column chromatography on 100 g of silica gel with 4:1 hexane−ethyl acetate and subsequent crystallization from ether−pentane at −24 °C to furnish 1.14 g of diol **9** as a 1:1 clathrate with ether (88% based on **8**). For analytical purposes ether was removed by azeotropic distillation with hexane. Mp: 114 °C. $[\alpha]^{20}_D$: −27.2 (c = 0.49, $CHCl_3$). IR (KBr): 3376, 3058, 3026, 2960, 1601, 1494, 1446, 1031, 780, 763, 722, 699 cm^{-1}. MS (70 eV): m/z (%) 536 (0.01) [M − 2 H_2O]$^+$, 372 (59.8) [M − H_2O − Ph_2CO]$^+$, 281 (34.3), 205 (15.9), 192 (10.1), 183 (39.8) [Ph_2COH]$^+$, 167 (11.5), 105 (100), 91 (13.7), 77 (30.7). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 3.09 (half of AA′BB′ pattern, 2), 3.59 (half of AA′BB′ pattern, 2), 4.56 (br s, 2, OH), 6.41 (m, 4), 6.92−6.96 (m, 8), 7.00−7.09 (m, 10), 7.41−7.50 (m, 8). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 47.85, 48.34, 80.28, 126.30, 127.10, 127.25, 127.61, 127.71, 127.75, 127.79, 128.25, 129.06, 143.24, 144.64, 145.64. Anal. Calcd for $C_{42}H_{36}O_2$: C, 88.08; H, 6.34. Found: C, 87.85; H, 6.47.

(1*S*,2*S*,6*S*,7*S*)-Dibenzo-1,6-bis(hydroxydiphenylmethyl)-tricyclo[5.3.0.0^{2,6}]deca-3,8-diene (12). This compound was prepared in analogy to the procedure for **3a** from 16.0 mmol of phenylmagnesium bromide (0.388 g of Mg turnings and 2.51 g of bromobenzene in 10 mL of THF) and 1.04 g of diester **11**[10] (2.00 mmol). The crude product was purified by column chromatography on 100 g of silica gel with 4:1 hexane−ethyl acetate and subsequent crystallization from ether−pentane at −24 °C to furnish 1.08 g of diol **12** as a 1:1 clathrate with ether (81% based on **11**). For analytical purposes ether was removed by azeotropic distillation with hexane. Mp: 256 °C. $[\alpha]^{20}_D$: +26.6 (c = 0.56, $CHCl_3$). IR (KBr): 3288, 3066, 3021, 2974, 2930, 2870, 1599, 1493, 1482, 1444, 1115, 1007, 766, 748, 702 cm^{-1}. MS (70 eV): m/z (%) 396 (19.0) [M − H_2O − Ph_2CO]$^+$, 298 (41.8), 281 (23.6), 229 (45.9), 192 (47.2), 183 (71.5) [Ph_2COH]$^+$, 167 (38.9), 115 (23.5), 105 (100), 91 (4.8), 77 (34.6). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 2.44, 2.96 (2 d, 4, $|^2J|$ = 17.8 Hz), 5.09 (s, 2), 5.70 (br s, 2, OH), 6.15 (m, 2), 6.66 (m, 2), 6.85−6.94 (m, 8), 6.95−7.03 (m, 6), 7.36−7.42 (m, 6), 7.51−7.57 (m, 4). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 40.37, 53.09, 56.76, 85.04, 124.14, 125.37, 126.00, 126.54, 127.04, 127.22, 127.65, 127.78, 127.93, 128.36, 142.82, 144.79, 145.11, 146.10. Anal. Calcd for $C_{44}H_{36}O_2$: C, 88.56; H, 6.08. Found: C, 88.30; H, 6.17.

(1*R*,7*R*,9*R*,10*R*)-4-Boranato-9,10-dimethoxy-9,10-dimethyl-2,2,4,6,6-pentaphenyl-3,5,8,11-tetraoxa-4-phosphabicyclo[5.4.0]undecane (4a). The reaction was conducted under an Ar atmosphere in a flame-dried Schlenk flask fitted with a rubber septum. To a solution of 12.3 g of the 1:1 clathrate of diol **3a** (20.0 mmol) with ether in 80 mL of THF at 0 °C was added 27.5 mL of 1.6 M *n*-butyllithium (44.0 mmol) in hexane. After 10 min the reaction mixture was allowed to warm to room temperature and stirred for 2 h. Then the mixture was cooled to −70 °C again, and 4.12 g of dichlorophenylphosphane (23.0 mmol) was added slowly without allowing the temperature to rise. After the temperature was kept at −70 °C for an additional 1 h, the reaction mixture was again warmed to ambient temperature within 1 h and stirred for further 12 h. Then, the mixture was concentrated in vacuum. The obtained solid white residue was suspended in 100 mL of toluene, treated with 1.90 mL of borane−dimethyl sulfide complex (20.0 mmol), and stirred for 1 h. After careful destruction of the excess borane−dimethylsulfide complex by addition of 20 g of wet silica gel, the mixture was stirred for another 1 h, filtered, and evaporated to give 14.2 g of a solid white residue. The crude product was purified by column chromatography on 220 g of silica gel with 4:1 hexane−ethyl acetate and subsequent crystallization from ethyl acetate−hexane to furnish 8.19 g of borane−phosphonite adduct **4a** (62% based on **3a**) as colorless crystalls. Mp: 209 °C. $[\alpha]^{20}_D$: +36.1 (c = 1.00, $CHCl_3$). IR (KBr): 3056, 2993, 2945, 2895, 2834, 2440, 2406, 2332, 1496, 1448, 1375, 1195, 1144, 1128, 1099, 1034, 998, 945, 909, 873, 756, 745, 699 cm^{-1}. MS (70 eV): m/z (%) 660 (1.1) [M]$^+$, 433 (1.6) [M − $PhPBH_3$ − PhCO], 358 (8.2), 351 (7.8), 279 (4.1), 207 (4.3), 195 (29.6), 178 (6.2), 167 (40.0), 130 (8.6), 116 (100), 105 (13.7), 101 (28.3), 91 (5.5), 77 (3.4), 73 (7.8). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ −0.2 to 1.0 (br s, 3), 1.05, 1.07 (2 s, 6), 2.39, 2.76 (2 s, 6), 4.87, 5.33 (2 d, 2, ^3J = 10.4 Hz), 7.00 (m, 2), 7.11 (m, 1), 7.14−7.31 (m, 12), 7.35−7.41 (m, 4), 7.50 (m, 2), 7.71 (m, 2), 7.94 (m, 2). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 16.94, 17.01, 47.35, 47.97, 72.80 (d, $|^3J|_{P,C}$ = 2.5 Hz), 74.11, 88.23 (d, $|^2J|_{P,C}$ = 6.1 Hz), 88.46 (d, $|^2J|_{P,C}$ = 12.2 Hz), 98.51, 98.54, 126.80, 127.05, 127.13, 127.38 (d, $|^3J|_{P,C}$ = 5.5 Hz), 127.58, 127.89, 127.93, 128.07, 128.30, 128.45, 129.88, 130.80 (d, $|^2J|_{P,C}$ = 12.8 Hz), 131.30, 131.60 (d, $|^4J|_{P,C}$ = 2.4 Hz), 133.09 (d, $|^1J|_{P,C}$ = 73.2 Hz), 138.38, 138.74, 145.27 (d, $|^3J|_{P,C}$ = 6.7 Hz), 146.17 (d, $|^3J|_{P,C}$ = 7.4 Hz). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ 125.13. ^{11}B-NMR ($CDCl_3$, 160 MHz): δ −36.98. Anal. Calcd for $C_{40}H_{42}O_6BP$: C, 72.74; H, 6.41. Found: C, 72.58; H, 6.17.

(1*R*,7*R*,9*R*,10*R*)-4-Boranato-9,10-diethoxy-9,10-dimethyl-2,2,4,6,6-pentaphenyl-3,5,8,11-tetraoxa-4-phosphabicyclo-[5.4.0]undecane (4b). This compound was prepared in analogy to the procedure for **4a** from 12.9 g of the 1:1 clathrate of diol **3b** (20.0 mmol) with ether besides the same amounts of the remaining reagents. The crude product was purified by column chromatography on 220 g of silica gel with 3:1 hexane−ether to yield 8.40 g of borane−phosphonite adduct **4b** (61% based on **3b**) as a colorless solid. Mp: 191 °C. $[\alpha]^{20}_D$: +103.4 (c = 1.08, $CHCl_3$). IR (KBr): 3059, 2974, 2930, 2887, 2425, 2378, 2345, 1495, 1448, 1376, 1201, 1150, 1129, 1099, 1048, 1033, 1015, 998, 945, 914, 871, 754, 746, 699 cm^{-1}. MS (70 eV): m/z (%) 688 (1.1) [M]$^+$, 447 (1.2), 358 (8.0), 351 (7.1), 267 (4.3), 207 (2.6), 195 (6.8), 191 (4.9), 178 (3.5), 167 (29.3), 144 (100), 115 (22.2), 105 (9.4), 91 (6.3), 77 (2.8), 73 (1.1). ^{1}H-

NMR ($CDCl_3$, 500 MHz): δ −0.1 to 0.7 (br s, 3), 0.95 (t, 3, ^3J = 7.0 Hz), 1.08 (s, 3), 1.11 (t, 3, ^3J = 7.0 Hz), 1.13 (s, 3), 2.02, 2.17, 2.93, 2.99 (4 dq, 4, $|^2J|$ = 8.9 Hz), 5.03, 5.19 (2 d, 2, ^3J = 10.8 Hz), 6.88 (m, 2), 7.08 (m, 1), 7.16−7.25 (m, 12), 7.35−7.40 (m, 4), 7.54 (m, 2), 7.65 (m, 2), 8.00 (m, 2). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 15.20, 15.26, 17.63, 17.68, 55.37, 55.59, 74.53, 75.33, 88.19 (d, $|^2J|_{P,C}$ = 5.5 Hz), 88.46 (d, $|^2J|_{P,C}$ = 14.6 Hz), 98.67, 98.76, 126.84, 126.92, 127.24 (d, $|^3J|_{P,C}$ = 4.9 Hz), 127.61, 127.74, 127.83, 127.98, 128.11, 128.75, 130.33, 130.89 (d, $|^2J|_{P,C}$ = 12.2 Hz), 131.40, 132.03, 133.19 (d, $|^1J|_{P,C}$ = 68.9 Hz), 137.54, 146.23 (d, $|^3J|_{P,C}$ = 8.5 Hz), 147.26 (d, $|^3J|_{P,C}$ = 8.5 Hz). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ 123.23. ^{11}B-NMR ($CDCl_3$, 160 MHz): δ −36.83. Anal. Calcd for $C_{42}H_{46}O_6BP$: C, 73.26; H, 6.73. Found: C, 73.41; H, 6.97.

(1*R*,7*R*,9*R*,10*R*)-4-Boranato-9,10-dimethoxy-9,10-dimethyl-2,2,6,6-tetrakis(2-naphthyl)-4-phenyl-3,5,8,11-tetraoxa-4-phosphabicyclo[5.4.0]undecane (4c). This compound was prepared in analogy to the procedure for **4a** from 1.63 g of diol **3c** (2.20 mmol), 3.1 mL of 1.6 M *n*-butyllithium (4.96 mmol) in hexane, 0.453 g of dichlorophenylphosphane (2.53 mmol), and 0.167 g of borane−dimethyl sulfide complex (2.20 mmol). The crude product was purified by column chromatography on 100 g of silica gel with 6:1 hexane−ethyl acetate to yield 1.02 g of borane−phosphonite adduct **4c** (54% based on **3c**) as a colorless solid. Mp: 178 °C. $[\alpha]^{20}_D$: +109.8 (c = 1.09, $CHCl_3$). IR (KBr): 3055, 2991, 2945, 2832, 2412, 2385, 2343, 1599, 1506, 1437, 1375, 1273, 1164, 1143, 1120, 1080, 1022, 999, 946, 904, 861, 816, 799, 758, 745 cm^{-1}. MS (70 eV): m/z (%) 847 (0.2) $[M - BH_2]^+$, 706 (0.8), 574 (1.3), 558 (4.2), 437 (2.9), 406 (3.4), 295 (82.4), 280 (11.1), 267 (100), 252 (14.9), 155 (5.8), 139 (4.7), 133 (6.5), 115 (48.0), 101 (10.3), 77 (8.5). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.0 to 1.0 (br s, 3), 1.12, 1.15 (2 s, 6), 2.37, 2.80 (2 s, 6), 5.24, 5.74 (2 d, 2, ^3J = 10.6 Hz), 7.10 (m, 2), 7.25−7.83 (m, 27), 7.86 (m, 1), 7.94 (m, 1), 8.56 ("s", 1), 9.12 ("s", 1). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 17.02, 17.07, 47.58, 48.16, 73.30, 74.72, 88.48 (d, $|^2J|_{P,C}$ = 6.1 Hz), 89.07 (d, $|^2J|_{P,C}$ = 13.4 Hz), 98.69, 98.82, 125.72, 125.85, 126.10, 126.15, 126.24, 126.31, 126.42, 126.53, 126.61, 126.69, 127.24, 127.27, 127.31 (d, $|^3J|_{P,C}$ = 4.8 Hz), 127.34, 127.70, 127.85, 127.99, 128.15, 128.51, 128.68, 128.71, 128.88, 129.07, 129.69, 130.14, 130.87 (d, $|^2J|_{P,C}$ = 12.8 Hz), 131.72 (d, $|^4J|_{P,C}$ = 1.9 Hz), 132.25, 132.35, 132.43, 132.60, 132.68, 132.73, 132.92 (d, $|^1J|_{P,C}$ = 73.8 Hz), 133.01, 133.34, 135.38, 136.03, 142.30 (d, $|^3J|_{P,C}$ = 7.4 Hz), 143.32 (d, $|^3J|_{P,C}$ = 8.0 Hz). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ 126.44. Anal. Calcd for $C_{56}H_{50}O_6BP$: C, 78.14; H, 5.85. Found: C, 77.99; H, 5.82.

(1*R*,7*R*,9*R*,10*R*)-4-Boranato-9,10-diethoxy-9,10-dimethyl-2,2,6,6-tetrakis(2-naphthyl)-4-phenyl-3,5,8,11-tetraoxa-4-phosphabicyclo[5.4.0]undecane (4d). This compound was prepared in analogy to the procedure for **4a** from 1.83 g of diol **3d** (2.38 mmol), 3.3 mL of 1.6 M *n*-butyllithium (5.28 mmol) in hexane, 0.490 g of dichlorophenylphosphane (2.74 mmol), and 0.181 g of borane−dimethyl sulfide complex (2.38 mmol). The crude product was purified by column chromatography on 100 g of silica gel with 5:1 hexane−ether to yield 1.10 g of borane−phosphonite adduct **4d** (52% based on **3d**) as a colorless solid. Mp: 179 °C. $[\alpha]^{20}_D$: +220.6 (c = 0.96, $CHCl_3$). IR (KBr): 3057, 2972, 2928, 2866, 2428, 2383, 2346, 1599, 1506, 1438, 1377, 1273, 1186, 1148, 1120, 1077, 1046, 1020, 998, 946, 901, 816, 800, 758, 745 cm^{-1}. MS (SIMS: FAB + VE): m/z (%) 888 (3.7) $[M]^+$, 734 (1.1), 559 (6.2), 545 (4.2), 440 (6.3), 309 (8.5), 295 (100), 279 (6.6), 267 (27.2), 223 (94.8), 155 (7.2), 144 (47.7). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ −0.1 to 0.9 (br s, 3), 0.81, 1.03 (2 t, 6, ^3J = 7.1 Hz), 1.12, 1.18 (2 s, 3), 1.93, 2.06, 2.81, 2.88 (4 dq, 4, $|^2J|$ = 8.7 Hz), 5.43, 5.62 (2 d, 2, ^3J = 10.6 Hz), 6.99 (m, 2), 7.17−7.24 (m, 2), 7.29−7.85 (m, 25), 7.90 (m, 1), 7.93 (m, 1), 8.45 ("s", 1), 8.94 ("s", 1). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 15.36, 17.83, 55.64, 55.90, 74.93, 75.90, 88.46 (d, $|^2J|_{P,C}$ = 5.0 Hz), 88.86 (d, $|^2J|_{P,C}$ = 14.7 Hz), 99.06, 99.15, 125.72, 125.82, 125.87, 126.01, 126.10, 126.21, 126.37, 126.42, 126.54, 126.59, 126.67, 127.05, 127.26, 127.35 (d, $|^3J|_{P,C}$ = 4.9 Hz), 127.69, 127.78, 127.82, 128.48, 128.68, 129.05, 129.53, 130.15, 130.74, 130.93 (d, $|^2J|_{P,C}$ = 12.2 Hz), 131.49, 132.28, 132.35, 132.41, 132.50, 132.68, 132.71, 132.76 (d, $|^1J|_{P,C}$ = 73.2 Hz), 132.83, 133.53, 135.06, 135.31, 143.49 (d, $|^3J|_{P,C}$ = 8.6 Hz), 144.27 (d, $|^3J|_{P,C}$ = 8.5 Hz). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ 124.44. Anal. Calcd for $C_{58}H_{54}O_6BP$: C, 78.38; H, 6.12. Found: C, 78.04; H, 6.51.

(1*R*,7*R*,8*S*,9*S*)-4-Boranato-2,2,4,6,6,8,9-heptaphenyl-3,5-dioxa-4-phosphabicyclo[5.2.0]nonane (20). This compound was prepared in analogy to the procedure for **4a** from 883 mg of diol **9** (1.54 mmol), 2.2 mL of 1.6 M *n*-butyllithium (3.52 mmol) in hexane, 317 mg of dichlorophenylphosphane (1.77 mmol), and 117 mg of borane−dimethyl sulfide complex (1.54 mmol). The crude product was purified by column chromatography on 100 g of silica gel with 8:1 hexane−ethyl acetate to yield 540 mg of borane−phosphonite adduct **20** (51% based on **9**) as a colorless solid. Mp: 131 °C. $[\alpha]^{20}_D$: −109.8 (c = 0.89, $CHCl_3$). IR (KBr): 3060, 3027, 2960, 2931, 2387, 2345, 1600, 1494, 1447, 1385, 1030, 1004, 991, 966, 909, 752, 721, 698 cm^{-1}. MS (70 eV): m/z (%) 692 (0.9) $[M]^+$, 512 (1.0), 423 (7.6), 358 (11.0), 345 (2.6), 279 (2.5), 269 (100), 191 (25.0), 179 (4.5), 167 (18.3), 91 (10.6). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ −0.1 to 1.0 (br s, 3), 2.61, 2.76, 4.10, 4.30 (4 t, 4, ^3J = 9.1 Hz), 6.54 (m, 2), 6.78−6.85 (m, 6), 6.96 (m,1), 7.05−7.56 (m, 24), 7.66 (m, 2). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 47.23 (d, $|^3J|_{P,C}$ = 2.4 Hz), 47.71 (d, $|^3J|_{P,C}$ = 3.7 Hz), 48.73, 49.57, 90.75 (d, $|^2J|_{P,C}$ = 4.3 Hz), 92.34 (d, $|^2J|_{P,C}$ = 15.2 Hz), 126.92, 127.13, 127.60, 127.68, 127.78, 127.81, 127.90, 127.96, 128.03, 128.24, 128.51, 128.68, 130.57 (d, $|^2J|_{P,C}$ = 12.8 Hz), 131.59, 133.09 (d, $|^1J|_{P,C}$ = 69.6 Hz), 141.16, 141.21, 142.87, 142.99, 143.96 (d, $|^3J|_{P,C}$ = 7.3 Hz), 144.23 (d, $|^3J|_{P,C}$ = 8.5 Hz). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ 126.83. Anal. Calcd for $C_{48}H_{42}O_2BP$: C, 83.24; H, 6.11. Found: C, 82.96; H, 5.99.

(1*S*,7*S*,8*S*,12*S*)-Dibenzo-4-boranato-2,2,4,6,6-pentaphenyl-3,5-dioxa-4-phosphatetracyclo[5.4.4.0^{1,8}.0^{7,12}]pentadeca-9,13-diene (21). This compound was prepared in analogy to the procedure for **4a** from 998 mg of diol **12** (1.67 mmol), 2.4 mL of 1.6 M *n*-butyllithium (3.84 mmol) in hexane, 344 mg of dichlorophenylphosphane (1.92 mmol), and 127 mg of borane−dimethyl sulfide complex (1.67 mmol). The crude product was purified by column chromatography on 100 g of silica gel with 15:1 hexane−ethyl acetate to yield 405 mg of borane−phosphonite adduct **21** (34% based on **12**) as a colorless solid. Mp: 186 °C. $[\alpha]^{20}_D$: −71.0 (c = 1.13, $CHCl_3$). IR (KBr): 3059, 3022, 2929, 2851, 2384, 2345, 1742, 1600, 1484, 1445, 1117, 1078, 1011. 996, 963, 923, 771, 749, 729, 701 cm^{-1}. MS (SIMS: FAB − VE): m/z (%) 716 (5.8) $[M]^-$, 434 (41.5), 320 (52.9), 307 (5.8), 281 (9.9), 155 (100), 141 (23.2), 138 (28.6), 124 (18.8). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ −0.2 to 0.9 (br s, 3), 2.19, 2.25, 2.99, 3.22 (4 d, 4, $|^2J|$ = 17.8 Hz), 5.64, 5.81 (2 s, 2), 6.22 (m, 1), 6.55 (m, 1), 6.67 (m, 2), 6.78−7.07 (m, 9), 7.13−7.22 (m, 6), 7.27−7.44 (m, 10), 7.49 (m, 2), 7.74 (m, 2). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 41.45, 41.74, 53.78, 53.83, 55.75 (d, $|^3J|_{P,C}$ = 1.2 Hz), 55.95 (d, $|^3J|_{P,C}$ = 1.2 Hz), 94.44 (d, $|^2J|_{P,C}$ = 6.8 Hz), 95.77 (d, $|^2J|_{P,C}$ = 19.0 Hz), 123.87, 124.12, 125.53, 126.01, 126.12, 126.29, 127.05, 127.26, 127.31, 127.43, 127.49, 127.72, 127.78, 127.87, 127.95, 128.14, 128.23, 128.46, 128.82, 129.08, 130.35 (d, $|^2J|_{P,C}$ = 12.8 Hz), 130.83, 131.01, 134.23 (d, $|^1J|_{P,C}$ = 76.9 Hz), 139.65, 139.77, 140.88, 141.33, 143.67, 144.15 (d, $|^3J|_{P,C}$ = 7.9 Hz), 144.94 (d, $|^3J|_{P,C}$ = 7.9 Hz). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ 112.95. Anal. Calcd for $C_{50}H_{42}O_2BP$: C, 83.80; H, 5.91. Found: C, 83.48; H, 5.79.

(1*R*,7*R*,9*R*,10*R*)-9,10-Diethoxy-9,10-dimethyl-2,2,4,6,6-pentaphenyl-3,5,8,11-tetraoxa-4-phosphabicyclo[5.4.0]-undecane (5b). The whole procedure, workup included, was conducted under an Ar atmosphere. A solution of 2.06 g of borane−phosphonite adduct **4b** (3.00 mmol) and 0.370 g of DABCO (3.30 mmol) in 10 mL of toluene was heated at 50 °C for ∼4 h until TLC (4:1 hexane−ethyl acetate) indicated complete conversion. Then, the mixture was allowed to cool to ambient temperature and concentrated to ∼4 mL under

vacuum. The resulting solution was subjected to a filtration over 60 g of flame-dried silica gel with 3:1 hexane−ethyl acetate (previously degassed). The whole product was contained in the first 250 mL of the eluate. This fraction was evaporated under vacuum to furnish 1.94 g of phosphonite **5b** (96%, contaminated with ∼5% of tetrahydrofuran **6b**) as a colorless, foamy solid. (Further purification may be accomplished by column chromatography on flame-dried silica gel with 6:1 hexane−ethyl acetate to give in order of increasing polarity phosphonite **5b** and tetrahydrofuran **6b** along with fractions containing mixtures of both compounds.) Mp: 119 °C. $[\alpha]^{20}_D$: −7.8 (c = 0.92, $CHCl_3$). IR (KBr): 3057, 2972, 2938, 2881, 1599, 1493, 1446, 1375, 1192, 1148, 1129, 1098, 1049, 988, 953, 932, 910, 842, 818, 754, 745, 701 cm^{-1}. MS (70 eV): m/z (%) 550 (1.9) $[M - PhPO]^+$, 521 (13.7), 433 (5.2), 391 (3.7), 373 (18.9), 297 (60.5), 269 (27.2), 220 (17.7), 207 (7.0), 195 (16.1), 191 (16.8), 178 (4.4), 167 (42.9), 144 (10.4), 131 (4.4), 115 (13.0), 105 (100), 91 (6.9), 87 (33.2), 77 (12.8). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 0.70 (t, 3, $|^3J|$ = 7.1 Hz), 1.09, 1.10 (2 s, 6), 1.26 (t, 3, ^3J = 7.1 Hz), 1.99, 2.78, 2.82, 3.23 (4 dq, 4, $|^2J|$ = 8.9 Hz), 4.60 (d, 1, ^3J = 10.6 Hz), 5.32 (dd, 1, $|^4J|_{P,H}$ = 1.5 Hz), 7.00−7.41 (m, 19), 7.53−7.68 (m, 4), 8.09 (m, 2). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 15.14, 15.63, 17.95, 18.07, 55.26, 56.23, 73.79 (d, $|^3J|_{P,C}$ = 11.6 Hz), 75.62 (d, $|^3J|_{P,C}$ = 1.8 Hz), 84.72 (d, $|^2J|_{P,C}$ = 7.3 Hz), 85.33 (d, $|^2J|_{P,C}$ = 4.9 Hz), 98.14, 98.43, 126.60, 126.92, 127.13, 127.70, 127.83, 128.04, 128.09, 128.13, 128.17, 128.93 (d, $|^1J|_{P,C}$ = 38.4 Hz), 129.97, 130.07, 130.29, 130.39, 131.17, 131.21, 141.27 (d, $|^3J|_{P,C}$ = 19.0 Hz), 141.64 (d, $|^3J|_{P,C}$ = 27.5 Hz), 147.63 (d, $|^3J|_{P,C}$ = 4.3 Hz), 147.97 (d, $|^3J|_{P,C}$ = 4.9 Hz). Anal. Calcd for $C_{42}H_{43}O_6P$: C, 74.76; H, 6.42. Found: C, 75.06; H, 6.58.

(1*R*,3*R*,4*R*,6*R*)-3,4-Diethoxy-3,4-dimethyl-7,7,9,9-tetraphenyl-2,5,8-trioxabicyclo[4.3.0]nonane (6b). Mp: 151 °C. $[\alpha]^{20}_D$: −163.5 (c = 1.02, $CHCl_3$). IR (KBr): 3068, 2974, 2929, 2873, 1600, 1491, 1448, 1374, 1218, 1193, 1141, 1114, 1097, 1052, 1032, 978, 959, 935, 915, 883, 745, 699 cm^{-1}. MS (70 eV): m/z (%) 550 (1.5) $[M]^+$, 521 (20.5) $[M - Et]^+$, 505 (1.5) $[M - EtO]^+$, 433 (4.1), 391 (5.9), 373 (32.2), 297 (100), 269 (37.4), 220 (19.3), 207 (10.3), 195 (12.6), 191 (22.2), 178 (7.4), 167 (50.9), 152 (7.2), 115 (10.2), 105 (49.4), 87 (18.5), 77 (13.8). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.89 (t, 6, ^3J = 7.1 Hz), 1.30 (s, 6), 3.49, 3.58 (2 dq, 4, $|^2J|$ = 9.2 Hz), 4.62 (s, 2), 7.03−7.12 (m, 6), 7.22 (m, 2), 7.31 (m, 4), 7.41 (m, 4), 7.62 (m, 4). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 14.99, 18.87, 55.91, 73.69, 82.96, 100.47, 125.65, 126.29, 126.87, 127.05, 127.08, 127.98, 143.05, 146.29. Anal. Calcd for $C_{36}H_{38}O_5$: C, 76.08; H, 7.09. Found: C, 75.79; H, 7.25.

Rhodium(I) (1*R*,7*R*,9*R*,10*R*)-9,10-Dimethoxy-9,10-dimethyl-2,2,4,6,6-pentaphenyl-3,5,8,11-tetraoxa-4-phosphabicyclo[5.4.0]undecane 2,5-Norbornadiene Chloride (7a). The reaction was conducted under an Ar atmosphere in a flame-dried Schlenk flask with a rubber septum. A solution of 2.31 g of borane−phosphonite adduct **4a** (3.50 mmol) and 0.397 g of DABCO (3.54 mmol) in 10 mL of toluene was heated at 50 °C for ∼4 h until TLC (4:1 hexane−ethyl acetate) indicated complete conversion. Then, the mixture was allowed to cool to ambient temperature and treated with 0.761 g of bis(μ-chloro)bis[(2,5-norbornadiene)rhodium(I)] (1.65 mmol). After about a 0.25 h the reaction mixture was concentrated under vacuum and filtered over 100 g of silica gel. Small amounts of less polar impurities (tetrahydrofuran **6a**) were removed with 4:1 hexane−ethyl acetate. Finally, elution with 1:1 hexane−ethyl acetate furnished rhodium complex **7a** (∼2.9 g) as a rigid yellow oil, which crystallizes slowly upon standing for several days. This material was recrystallized from ether−pentane to give 2.73 g of complex **7a** (89% based on **4a**) as a yellow powder. Mp: 249 °C. $[\alpha]^{20}_D$: +67.3 (c = 1.05, $CHCl_3$), 92.9 (c = 0.56, $CHCl_3$). IR (KBr): 3056, 2993, 2947, 2834, 1618, 1600, 1494, 1446, 1438, 1375, 1309, 1207, 1178, 1142, 1130, 1031, 1008, 995, 973, 931, 914, 854, 744, 706, 699 cm^{-1}. MS (70 eV): m/z (%) 885 (0.9) $[M - nbd]^+$, 784 (1.9), 504 (1.5), 460 (3.39, 386 (2.9), 358 (5.3), 279 (5.6), 267 (7.3), 195 (25.4), 178 (6.3), 167 (39.8), 152 (8.3), 129 (5.4), 116 (67.7), 105 (12.1), 101 (24.1) 91 (79.5), 78 (16.8), 66 (21.0), 44 (100). NMR assignments were verified by COSY and NOE (ambient temperature; acquisition time, 1.834 s; relaxation delay, 0.000 s; mixing time, 0.500 s; pulse width, 90.0°) experiments. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 0.99, 1.11 (2 s, 6), 1.35, 1.42 (2 br "d", 2, $|^2J|$ = 8.2 Hz, nbd-CH_2), 2.33, 2.46 (2 s, 6), 2.60 (br m, 1, $|^3J|_{P,H}$ = 3.3 Hz, $|^2J|_{Rh,H}$ = 3.0 Hz, nbd-CH-5), 3.45 (br "s", 1, nbd-CH-4), 3.76 (br "s", 1, nbd-CH-1), 4.12 (br m, 1, $|^3J|_{P,H}$ = 3.5 Hz, $|^2J|_{Rh,H}$ = 3.2 Hz, nbd-CH-6), 4.79, 4.98 (2 d, 2, ^3J = 10.7 Hz, H-1, H-7), 5.03 (br m, 1, nbd-CH-3), 5.32 (br m, 1, $|^3J|_{P,H}$ = 1.5 Hz, $|^2J|_{Rh,H}$ = 3.2 Hz, nbd-CH-2), 6.72 (br "s", 2), 6.86 (m, 2), 6.95 (m, 1), 7.07−7.27 (m, 15), 7.70 (m, 1), 7.78 (br "s", 2), 8.38 (br "s", 2). ^{13}C-NMR ($CDCl_3$, 126 MHz): δ 16.81, 16.90, 47.33, 47.45, 50.07 (d, 12.0 Hz, nbd-CH-6, $|^1J|_{H,C}$ = 180.0 Hz), 50.19 (d, 2.1 Hz, nbd-CH-1, $|^1J|_{H,C}$ = 151.8 Hz), 50.68 (br s, nbd-CH-4, $|^1J|_{H,C}$ = 151.8 Hz), 51.20 (dd, 12.3 Hz, 4.5 Hz, nbd-CH-5, $|^1J|_{H,C}$ = 176.5 Hz), 63.12 (d, 4.6 Hz, nbd-CH_2-7, $|^1J|_{H,C}$ = 133.2 Hz), 75.01, 75.21, 84.57 (dd, 19.1 Hz, 3.8 Hz, nbd-CH-3, $|^1J|_{H,C}$ = 176.5 Hz), 86.20 (d, $|^2J|_{P,C}$ = 4.1 Hz), 86.68 (d, $|^2J|_{P,C}$ = 16.2 Hz), 89.98 (dd, 12.4 Hz, 5.3 Hz, nbd-CH-2, $|^1J|_{H,C}$ = 180.0 Hz), 99.25, 99.26, 126.44, 126.64, 127.06, 127.20, 127.50, 127.54, 127.64, 127.85 (br), 128.45, 128.60 (br), 130.11 (d, $|^4J|_{P,C}$ = 2.3 Hz), 130.54 (br), 136.80 (d, $|^3J|_{P,C}$ = 2.3 Hz), 137.57 (dd, $|^1J|_{P,C}$ = 48.2 Hz, $|^2J|_{Rh,C}$ = 4.1 Hz), 138.04 (d, $|^3J|_{P,C}$ = 4.1 Hz), 146.37 (d, $|^3J|_{P,C}$ = 6.3 Hz), 148.21 (d, $|^3J|_{P,C}$ = 7.7 Hz). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ 134.41 (d, $|^1J|_{Rh,P}$ = 245.5 Hz). ^{103}Rh-NMR ($CDCl_3$, 500 MHz): δ 668.0 (d). Anal. Calcd for $C_{47}H_{47}O_6ClPRh$: C, 64.35; H, 5.40. Found: C, 64.31; H, 5.47.

Rhodium(I) (1*R*,7*R*,9*R*,10*R*)-9,10-Diethoxy-9,10-dimethyl-2,2,4,6,6-pentaphenyl-3,5,8,11-tetraoxa-4-phosphabicyclo[5.4.0]undecane 2,5-Norbornadiene Chloride (7b). This compound was prepared in analogy to the procedure for complex **7a** from 2.30 g of borane−phosphonite adduct **4b** (3.31 mmol), 0.375 g of DABCO (3.34 mmol), and 0.719 g of bis(μ-chloro)bis[(2,5-norbornadiene)rhodium(I)] (1.56 mmol). Purification of the crude product was accomplished by column chromatography on 100 g of silica gel. After removal of less polar impurities (tetrahydrofuran **6b**) with 4:1 hexane−ethyl acetate, elution with 1:1 ethyl acetate−CH_2Cl_2 gave rhodium complex **7b** as a rigid yellow oil. Finally, crystallization from ethyl acetate−hexane furnished 2.64 g of complex **7b** (88% based on **4b**) as a yellow powder. Mp: 256 °C. $[\alpha]^{20}_D$: +75.3 (c = 1.08, $CHCl_3$), +122.9 (c = 0.49, $CHCl_3$). IR (KBr): 3056, 2996, 2971, 2931, 2893, 1655, 1494, 1446, 1374, 1307, 1201, 1181, 1148, 1128, 1101, 1046, 1029, 1006, 994, 977, 931, 910, 858, 753, 744, 707, 698 cm^{-1}. MS (70 eV): m/z (%) 813 (1.8) $[M - nbd]^+$, 812 (3.3), 497 (1.2), 460 (2.8), 386 (2.0), 362 (2.5), 358 (8.2), 293 (2.6), 270 (3.3), 267 (2.5), 207 (2.4), 195 (9.0), 178 (3.9), 167 (22.8), 165 (9.4), 152 (5.1), 144 (100), 115 (22.6), 105 (7.2), 91 (22.6), 87 (33.9), 77 (4.8), 66 (7.2), 44 (77.3). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.01 (s, 3), 1.038, 1.043 (2 t, 6, ^3J = 7.1 Hz), 1.12 (s, 3), 1.34, 1.43 (2 br "d", 2, $|^2J|$ = 8.4 Hz, nbd-CH_2), 1.80, 2.05 (2 dq, 2, $|^2J|$ = 8.9 Hz), 2.55 (br "s", 1, nbd-CH-5), 2.85, 2.94 (2 dq, 2), 3.46 (br "s", 1, nbd-CH-4), 3.76 (br "s", 1, nbd-CH-1), 4.12 (br "s", 1, nbd-CH-6), 4.83, 5.05 (2 d, 2, ^3J = 10.7 Hz), 5.06 (br "s", 1, nbd-CH-3), 5.31 (br "s", 1, nbd-CH-2), 5.71 (br "s", 2), 6.83 (m, 2), 6.96 (m, 1), 7.04−7.26 (m, 15), 7.68−7.90 (m, 3), 8.46 (br "s", 2). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 15.30, 15.47, 17.58, 17.68, 50.07 (d, 12.0 Hz, nbd-CH-6), 50.16 (br s, nbd-CH-1), 50.67 (br s, nbd-CH-4), 51.15 (dd, 12.8 Hz, 4.5 Hz, nbd-CH-5), 55.06, 55.23, 63.04 (d, 5.0 Hz, nbd-CH_2-7), 74.97, 75.26, 84.08 (dd, 18.9 Hz, 3.9 Hz, nbd-CH-3), 86.31 (d, $|^2J|_{P,C}$ = 3.7 Hz), 86.75 (d, $|^2J|_{P,C}$ = 17.1 Hz), 89.77 (dd, 12.8 Hz, 5.1 Hz, nbd-CH-2), 98.90, 126.24, 126.46, 126.90, 126.97, 127.14, 127.48, 127.62, 127.67 (br), 128.50, 128.97 (br), 130.03, 131.21 (br), 136.53 (d, $|^3J|_{P,C}$ = 2.1 Hz), 137.66 (dd, $|^1J|_{P,C}$ = 48.0 Hz, $|^2J|_{Rh,C}$ = 4.1 Hz), 137.74 (d, $|^3J|_{P,C}$ = 3.8 Hz), 146.47 (d, $|^3J|_{P,C}$ = 6.1 Hz), 148.19 (d, $|^3J|_{P,C}$ = 7.9 Hz). ^{31}P-

NMR ($CDCl_3$, 202 MHz): δ 134.40 (d, $|^1J|_{Rh,P} = 245.5$ Hz). Anal. Calcd for $C_{49}H_{51}O_6ClPRh$: C, 65.01; H, 5.68. Found: C, 65.04; H, 5.76.

Rhodium(I) (1*R*,7*R*,9*R*,10*R*)-9,10-Dimethoxy-9,10-dimethyl-4-phenyl-2,2,6,6-tetrakis(2-naphthyl)-3,5,8,11-tetraoxa-4-phosphabicyclo[5.4.0]undecane 2,5-Norbornadiene Chloride (7c). This compound was prepared in analogy to the procedure for complex **7a** from 689 mg of borane−phosphonite adduct **4c** (800 μmol), 91 mg of DABCO (811 μmol), and 176 mg of bis(μ-chloro)bis[(2,5-norbornadiene)-rhodium(I)] (382 μmol). Purification of the crude product was accomplished by column chromatography on 60 g of silica gel. After removal of less polar impurities with 4:1 hexane−ethyl acetate, elution with 1:1 hexane−ethyl acetate gave rhodium complex **7c** as a rigid yellow oil. Finally, crystallization from ether−pentane furnished 608 mg of complex **7c** (71% based on **4c**) as a yellow powder. Mp: 232 °C (with decomp). $[\alpha]^{20}_D$: +141.0 ($c = 0.58$, $CHCl_3$). IR (KBr): 3056, 2992, 2947, 2833, 1599, 1506, 1436, 1376, 1309, 1273, 1192, 1163, 1143, 1121, 1021, 996, 928, 902, 864, 815, 799, 774, 757, 744 cm^{-1}. MS (SIMS FAB; *m*/*z* (%)): +VE, 1042 (3.7) $[M - Cl]^+$, 950 (8.7) $[M - nbd - Cl]^+$, 809 (6.0), 695 (6.9), 371 (9.7), 367 (9.4), 295 (100), 279 (11.0), 267 (79.3), 252 (12.4), 115 (15.7), 101 (13.2); −VE, 1015 (1.2), 863 (4.6), 660 (4.1), 439 (4.4), 422 (4.3), 293 (4.1), 253 (17.4), 251 (15.2), 189 (7.0), 157 (100), 95 (4.9), 79 (24.5). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.05, 1.18 (2 s, 6), 1.19−1.34 (m, 2), 2.26 ("s", 1), 2.38, 2.50 (2 s, 6), 3.68 ("s", 1), 4.23 ("s", 2), 4.89 ("s", 1), 5.22 (d, 1, $^3J = 10.6$ Hz), 5.31 ("s", 1), 5.44 (d, 1), 6.30−9.35 (m, 33), all signals broadened. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 16.85, 16.95, 47.65, 47.76, 49.4−50.2 (m, nbd-CH-1,4,5,6), 63.48 (d, 4.5 Hz, nbd-CH_2), 75.18, 75.36, 84.9 (very br, nbd-CH), 86.43 (d, $|^2J|_{P,C} = 4.0$ Hz), 86.70 (d, $|^2J|_{P,C} = 16.5$ Hz), 90.0 (very br, nbd-CH), 99.38, 125.63, 125.76, 126.03, 126.16, 126.53, 126.71, 126.82, 127.10, 127.26, 127.30, 127.46, 127.80, 128.25, 128.79, 128.87, 130.41, 131.95, 132.16, 132.36, 132.51, 133.48, 134.46, 135.17, 137.12 ("d", $|^1J|_{P,C} = 48.9$ Hz), 144.99 (d, $|^3J|_{P,C} = 6.0$ Hz), all signals broadened. ^{31}P-NMR ($CDCl_3$, 202 MHz): δ 137.51 (d, $|^1J|_{Rh,P} = 244.3$ Hz). Anal. Calcd for $C_{63}H_{55}O_6ClPRh$: C, 70.23; H, 5.15. Found: C, 70.28; H, 5.52.

Rhodium(I) (1*R*,7*R*,9*R*,10*R*)-9,10-Diethoxy-9,10-dimethyl-4-phenyl-2,2,6,6-tetrakis(2-naphthyl)-3,5,8,11-tetraoxa-4-phosphabicyclo[5.4.0]undecane 2,5-Norbornadiene Chloride (7d). This compound was prepared in analogy to the procedure for complex **7a** from 889 mg of borane−phosphonite adduct **4d** (1.00 mmol), 114 mg of DABCO (1.02 mmol), and 217 mg of bis(μ-chloro)bis[(2,5-norbornadiene)rhodium(I)] (0.47 mmol). Purification of the crude product was accomplished by column chromatography on 60 g of silica gel. After removal of less polar impurities with 4:1 hexane−ethyl acetate, elution with 1:1 hexane−ethyl acetate gave rhodium complex **7d** as a rigid yellow oil. Finally, crystallization from ether−pentane furnished 917 mg of complex **7d** (83% based on **4d**) as a yellow powder. Mp: 229 °C (with decomp). $[\alpha]^{20}_D$: +140.8 ($c = 1.13$, $CHCl_3$). IR (KBr): 3057, 2972, 2945, 2926, 2895, 1630, 1600, 1507, 1438, 1376, 1309, 1273, 1186, 1148, 1129, 1104, 1046, 1020, 997, 944, 926, 867, 823, 800, 777, 759, 745 cm^{-1}. MS (SIMS FAB; *m*/*z* (%)): +VE, 1070 (61.9) $[M - Cl]^+$, 1013 (5.4) $[M - nbd]^+$, 978 (2.9) $[M - nbd - Cl]^+$, 695 (7.6), 491 (7.2), 371 (13.2), 367 (17.8), 295 (49.9), 267 (83.1), 252 (15.1), 195 (11.7), 144 (29.5), 115 (23.7), 87 (100); −VE, 1013 (3.7) $[M - nbd]^-$, 487 (3.8), 383 (5.7), 347 (52.3), 341 (8.3), 293 (13.8), 278 (22.0), 253 (5.7), 201 (8.3), 188 (100), 157 (20.4), 141 (39.2), 79 (21.2). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.89, 0.98 (2 t, 6, $^3J = 7.1$ Hz), 1.06, 1.17 (2 s, 6), 1.18−1.33 (m, 2), 1.60 (m, 1), 1.91 (m, 1), 2.21 ("s", 1), 2.71, 2.82 (2 dq, 2, $|^2J| = 8.7$ Hz), 3.68 ("s", 1), 4.05−4.39 (m, 2), 4.92 ("s", 1), 5.25 (d, 1, $^3J = 10.4$ Hz), 5.29 ("s", 1), 5.50 ("d", 1), 6.25−9.42 (m, 33), all signals broadened. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 15.69, 17.69, 17.84, 49.3−50.2 (m, nbd-CH-1,4,5,6), 55.29, 55.51, 63.47 (d, 4.5 Hz, nbd-CH_2), 75.78, 75.90, 83.7 (very br, nbd-CH), 86.51 (d, $|^2J|_{P,C} = 3.9$ Hz), 86.67 (d, $|^2J|_{P,C} = 17.8$ Hz), 89.4 (very br, nbd-CH), 99.33, 125.64, 125.78, 126.00, 126.13, 126.47, 127.07, 127.22, 128.14, 128.67, 129.10, 130.31, 131.98, 132.20, 132.37, 132.49, 132.62, 133.57, 134.43, 135.21, 137.02 (dd, $|^1J|_{P,C} = 49.1$ Hz, $|^2J|_{Rh,C} = 4.6$ Hz), 145.56 (d, $|^3J|_{P,C} = 6.5$ Hz), all signals broadened. ^{31}P-NMR ($CDCl_3$, 202 MHz): δ 137.46 (d, $|^1J|_{Rh,P} = 241.1$ Hz). Anal. Calcd for $C_{65}H_{59}O_6ClPRh$: C, 70.62; H, 5.38. Found: C, 70.48; H, 5.45.

Rhodium(I) (1*R*,7*R*,8*S*,9*S*)-2,2,4,6,6,8,9-Heptaphenyl-3,5-dioxa-4-phosphabicyclo[5.2.0]nonane 2,5-Norbornadiene Chloride (10). This compound was prepared in analogy to the procedure for complex **7a** from 365 mg of borane−phosphonite adduct **20** (527 μmol), 61 mg of DABCO (543 μmol), and 114 mg of bis(μ-chloro)bis[(2,5-norbornadiene)-rhodium(I)] (247 μmol). Purification of the crude product was accomplished by column chromatography on 60 g of silica gel. After removal of less polar impurities with 4:1 hexane−ethyl acetate, elution with 1:1 hexane−ethyl acetate gave rhodium complex **10** as a rigid yellow oil. Finally, crystallization from ether−pentane furnished 415 mg of complex **10** (87% based on **20**) as a yellow powder. Mp: 224 °C. $[\alpha]^{20}_D$: −151.3 ($c = 0.95$, $CHCl_3$). IR (KBr): 3059, 3025, 2999, 2966, 2923, 1600, 1493, 1446, 1385, 1310, 1199, 1107, 1040, 1029, 982, 939, 917, 905, 857, 839, 778, 744, 719, 698 cm^{-1}. MS (SIMS FAB; *m*/*z* (%)): +VE, 873 (27.5) $[M - Cl]^+$, 639 (3.3), 359 (26.8), 269 (75.6), 191 (25.9), 167 (100), 151 (97.4), 139 (72.7), 124 (23.5), 105 (7.2), 91 (29.9); −VE: 909 (0.6) $[M]^-$, 845 (7.4), 817 (5.3) $[M - nbd]^-$, 695 (5.7), 537 (4.3), 469 (7.9), 455 (14.0), 425 (8.6), 347 (34.5), 307 (14.2), 293 (13.8), 278 (17.5), 245 (13.4), 203 (10.9), 141 (100). ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 1.29, 1.38 (2 br "d", 2, $|^2J| = 7.9$ Hz), 2.40, 2.56 (2 t, 2, $^3J = 9.2$ Hz), 3.03, 3.28, 3.61, 3.74 (4 br "s", 4), 4.04 (t,1), 4.16 (br "t", 1), 4.96 (br "s", 1), 5.07 (br m, 1), 6.65−7.82 (m, 35). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 47.62, 48.57, 49.43, 49.55 (2 C), 50.41 (2 C), 51.65 (d, 12.8 Hz), 64.73, 88.81, 89.45 (d, 18.3 Hz), 90.47 (d, $|^2J|_{P,C} = 17.0$ Hz), 92.47 (d, 12.1 Hz), 126.76, 126.86, 127.08, 127.22, 127.30, 127.50, 127.65, 127.70, 127.80, 127.99, 128.06, 128.42, 128.54, 128.86, 129.46 (br), 130.20, 131.07, 131.30, 141.14, 141.56 (d, $|^1J|_{P,C} = 57.3$ Hz), 144.05, 144.39 (d, $|^3J|_{P,C} = 6.7$ Hz), 145.54 (d, $|^3J|_{P,C} = 7.9$ Hz). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ 137.82 (d, $|^1J|_{Rh,P} = 247.2$ Hz). Anal. Calcd for $C_{55}H_{47}O_2ClPRh$: C, 72.65; H, 5.21. Found: C, 72.29; H, 5.18.

Rhodium(I) (1*S*,7*S*,8*S*,12*S*)-Dibenzo-2,2,4,6,6-pentaphenyl-3,5-dioxa-4-phosphatetracyclo[5.4.4.0^{1,8}.0^{7,12}]pentadeca-9,13-diene 2,5-Norbornadiene Chloride (13). This compound was prepared in analogy to the procedure for complex **7a** from 370 mg of borane−phosphonite adduct **21** (516 μmol), 59 mg of DABCO (526 μmol), and 112 mg of bis(μ-chloro)bis-[(2,5-norbornadiene)rhodium(I)] (243 μmol). Purification of the crude product was accomplished by column chromatography on 60 g of silica gel. After removal of less polar impurities with 4:1 hexane−ethyl acetate, elution with 1:1 hexane−ethyl acetate gave rhodium complex **13** as a rigid yellow oil. Finally, crystallization from ether−pentane furnished 395 mg of complex **13** (82% based on **21**) as a yellow powder. Mp: 212 °C. Decomp pt: 216 °C. $[\alpha]^{20}_D$: −123.8 ($c = 0.89$, $CHCl_3$). IR (KBr): 3058, 3022, 2999, 2924, 2848, 1657, 1601, 1483, 1443, 1395, 1309, 1176, 1104, 1033, 1002. 977, 936, 917, 841, 771, 747, 727, 703 cm^{-1}. MS (SIMS FAB; *m*/*z* (%)): +VE, 805 (0.1) $[M - nbd - Cl]^+$, 561 (0.6), 433 (0.5), 313 (1.3), 281 (100), 265 (2.0), 215 (1.9), 203 (5.8), 167 (5.1); −VE, 867 (10.2) $[M - C_5H_6]^-$, 595 (11.7), 447 (4.6), 312 (6.4), 281 (100), 198 (7.3), 157 (12.5), 141 (74.2). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.33, 1.40 (2 br "d", 2, $|^2J| = 8.1$ Hz), 1.93, 2.14, 2.81, 3.07 (4 d, 4, $|^2J| = 17.7$ Hz), 3.00, 3.33, 3.72, 4.11 (4 br "s", 4), 4.81 (br "s", 1), 5.27 (br "s", 2), 5.81 (s, 1), 6.44−7.71 (m, 33). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 41.91, 42.20, 49.10 (d, 12.0 Hz), 50.00, 50.09, 51.48 (d, 12.9 Hz), 53.25, 53.82, 55.68, 56.31, 63.42, 84.32 (d, 17.1 Hz), 88.85 (d, 17.7 Hz), 91.92 (d, $|^2J|_{P,C} = 4.9$ Hz), 93.45 (d, $|^2J|_{P,C} = 22.0$ Hz), 123.78, 124.00, 125.88, 126.06,

126.94, 127.07, 127.16, 127.22, 127.38, 127.64, 127.82, 128.08, 128.40, 129.52, 129.99, 131.06 (br), 136.91 (dd, $|^1J|_{P,C}$ = 47.6 Hz, $|^2J|_{Rh,C}$ = 4.2 Hz), 137.12, 139.06 (d, $|^3J|_{P,C}$ = 3.7 Hz), 140.78, 140.86, 143.28, 143.57, 145.72 (d, $|^3J|_{P,C}$ = 6.1 Hz), 146.21 (d, $|^3J|_{P,C}$ = 8.6 Hz). ^{31}P-NMR ($CDCl_3$, 202 MHz): δ 123.99 (d, $|^1J|_{Rh,P}$ = 247.2 Hz). Anal. Calcd for $C_{57}H_{47}O_2ClPRh$: C, 73.35; H, 5.08. Found: C, 73.18; H, 5.22.

General Procedure for the Enantioselective Hydrosilylation of Ketones. All reactions were conducted under an Ar atmosphere in flame-dried Schlenk flasks fitted with a rubber septum. A solution of 20 μmol of the respective rhodium(I)−phosphonite complex **7a**−**d**, **10**, or **13** (1.0 mol %) and 461 mg of diphenylsilane (2.50 mmol) in 2 mL of toluene was stirred at ambient temperature for 5 min and then brought to the desired reaction temperature. After 10 min of temperation, a solution of 2.00 mmol of the respective ketone **14**−**19** in 0.5 mL of toluene was added slowly within 5 min. The reaction mixture was kept at the appropriate temperature for 16 h, or 40 h in the case of experiments carried out below 0 °C, and then poured on 15 mL of 6:1 acetone−10% aqueous HCl and stirred for 2 h. After neutralization with saturated $NaHCO_3$, the phases were separated, and the aqueous layer was extracted three times with 25 mL of CH_2Cl_2. The combined organic phase was dried, filtered, and concentrated under vacuum. To remove Rh- and Si-containing impurities, the resulting yellow residue was distilled with a Kugelrohr apparatus at reduced pressure. Generally the obtained distillate (alcohol and varying amounts of unconverted ketone) amounted to 90−98% of the mass of starting ketone. In the case of 1-phenylethanol, 1-(1′-naphthyl)ethanol, and 2,2-dimethyl-1-phenylpropanol enantiomeric ratios were determined by GC at this point. 1-Phenylpropanol, 2-methyl-1-phenylpropanol, and 1-cyclohexylethanol had to be converted into the corresponding acetates to achieve baseline separation of their enantiomers. For this purpose, the previously distilled alcohol was dissolved in 3.0 mL of ether, and 316 mg of pyridine (4.0 mmol) was added. This solution was treated with 236 mg of acetyl chloride (3.0 mmol) and stirred at ambient temperature for 3 h. Then, the mixture was poured on 5 mL of 1 M H_2SO_4 and 10 mL of ether, the phases were separated, and the aqueous layer was extracted twice with 10 mL of ether. The combined organic phase was washed with saturated $NaHCO_3$, dried, filtered, and evaporated in vacuum. Finally, the enantiomeric ratio was determined by GC.

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