Chiral Dibenzazepine-Based P-Alkene Ligands and Their Rhodium Complexes: Catalytic Asymmetric 1,4 Additions to Enones

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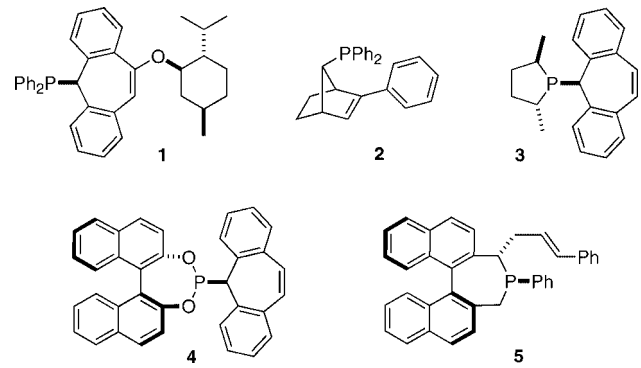
N-Dichlorophosphanyldibenzo[*b*,*f*]azepine (**6**) reacted with (−)-2,3-*O*-isopropylidene-D-threitol, (*R*)-taddol, (*R,R*)-diethyltartrate, (*R,R*)-diethyltartrate, (*S*)-binaphthol, α,α-diphenyl-L-prolinol, and (*S*)-proline to form the corresponding chiral P-alkene ligands **7**−**12**. These ligands were then used to synthesize dinuclear chloro-bridged Rh(I) complexes **13**−**18** with the general formula $[Rh(\mu\text{-}Cl)(P\text{-alkene})]_2$. It was shown by X-ray diffraction analyses that these P-alkenes indeed act as bidentate ligands for Rh(I). Furthermore, the crystal structures revealed a change in the hybridization state of the dibenzazepine N atom, passing from sp^2 in the free ligand to sp^3 when coordinated to Rh in a bidentate fashion, thus modifying the bite angle of the ligands. The Rh complexes **16** and **18**, bearing the (*S*)-binaphthol-derived ligand **10** and the α,α-diphenyl-L-prolinol-derived ligand **12**, respectively, were shown to be active and enantioselective catalysts for the 1,4 addition of arylboronic acids to enones. At 80 °C turnover numbers of up to 61 and enantiomeric excesses of up to 92% were observed.

Introduction

P-alkene ligands constitute a rather new entry in the development of efficient bidentate ligand systems for organometallic reactivity and catalysis. The success story of enantioselective catalysis in organic synthesis is largely based on the development of chiral phosphine ligands, whereas chiral olefin ligands have been introduced only recently.[1] The combination of these two ligand functionalities is straightforward, and the design of chiral phosphine-olefin ligands is thus of great interest. Grützmacher et al. used the chiral phosphine-olefin ligand **1** (see Table 1) for the Ir-catalyzed asymmetric (86% ee) imine hydrogenation,[2] while Hayashi showed ligand **2** to be highly enantioselective in Rh-catalyzed 1,4 additions of aryl boronic acids to α,β-unsaturated carbonyl compounds[3] and Pd-catalyzed allylic alkylations.[4] Other chiral P-alkene ligands such as **3** and **4** were described in a patent,[5] and **5** was recently shown to be good for up to 98% ee in conjugate addition reactions.[6] Furthermore, de Vries and Feringa showed that monodentate chiral phosphoramidites are highly versatile ligands,[7] and in relation to a technical application it was found that a mixed-ligand approach (chiral phosphoramidite plus triphenylphosphine) is beneficial in terms of activity and selectivity.[8] We anticipated that the dibenzo[*b*,*f*]azepin molecule could readily be incorporated[5] to form new chiral phosphoramidite-olefin ligands such as **10** (*vide infra*). Ligand **10** was used for the enantioselective formation of an allylic amine from an allylic alcohol with 70% ee,[9] and the crystal structure of a Pd complex bearing this ligand was briefly communicated by us[10] as part of a wider synthetic study.

Table 1



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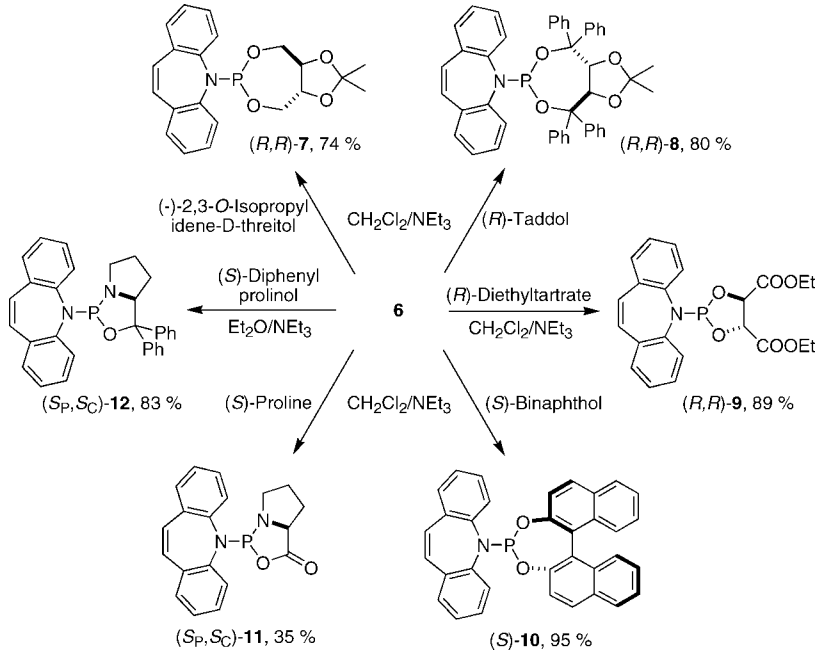
10.1021/om800793q CCC: $40.75
Publication on Web 11/16/2008

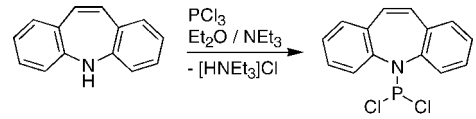
Scheme 1



Since the first report on the asymmetric Rh-BINAP-catalyzed 1,4 addition of boronic acids to enones by Hayashi et al.,[11] a variety of ligands were investigated for this transformation.[12] Chiral binol-based diphosphonites,[13] hemilabile amidomonophosphines,[14] and phosphoramidites[15] in combination with suitable Rh precursors all led to active and highly enantioselective catalyst systems, and more recently, chiral dienes[16] and bis-sulfoxides[17] were also demonstrated to be highly efficient ligands. Since the phosphoramidite and olefin functionalities, each on their own, were shown to be successful ligands for the Rh-catalyzed 1,4 addition of boronic acids to enones, we embarked on the synthesis of new bidentate chiral phosphoramidite-olefin ligands that can be viewed as a combination of Grützmacher's olefin bearing dibenz[*b*,*f*]azepine moiety[5] with Feringa's chiral phosphoramidite function. Furthermore, we disclose the synthesis and full characterization of dinuclear Rh complexes bearing these new ligands and their use as catalysts for conjugate addition reactions with up to 92% ee. We note that only in a few studies were isolated and characterized Rh complexes[3b,16f,17,21] used as catalysts for the title reaction.

Results and Discussion

1. Ligand Syntheses. Dibenz[*b*,*f*]azepine reacted with PCl_3 in diethyl ether to form dichloride **6** on a 10 g scale in excellent yield (eq 1). This reaction needs ca. 90 h at RT to go to completion. A large excess of dibenzazepine with respect to PCl_3 did not lead to bis- or tris-amide formation, probably due to steric hindrance.



6, 94 % (1)

Compound **6** reacted cleanly with six commercially available chiral auxiliaries as outlined in Scheme 1. These syntheses were carried out in the presence of a 3-fold excess of NEt_3, and the resulting ammonium chloride precipitate was quantitatively removed by filtration from the Et_2O solution. Yields of the isolated ligands **7**−**12** were good to excellent. During the synthesis of products **7**, **11**, and **12** the formation, in each case, of two isomers in varying ratios depending on reaction conditions was observed. Importantly, the pure isomers were obtained by selective crystallization, and the precise stereochemistry was determined in all cases.

Compound **6** reacted with (−)-2,3-*O*-isopropylidene-D-threitol in CH_2Cl_2 in the presence of NEt_3 to form one major isomer displaying a characteristic singlet at 139 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Recrystallization from CH_3CN solution afforded isomerically pure **7** in good yield and on a gram scale. In analogy with the structurally characterized ligands **8** and **10** (*vide infra*), **7** has a "twist" phospha-dioxa-cycloheptane ring conformation that connects to the dibenzazepine moiety through an axial P−N vector (see Scheme 2).[18]

We reasoned that in order to limit isomer formation, the analogous but sterically more hindered diol (*R*)-taddol should

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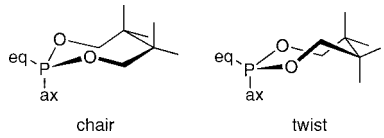
(18) This affirmation is based on an X-ray crystal structure analysis of complex $[PdCl_2(\mathbf{7})_2]$. The other, minor isomer of **7** is thought to be the equatorial variant. Dorta, R.; Briceño, A. Unpublished results.

Scheme 2



give good results. Indeed, the reaction of **6** with (*R*)-taddol in CH_2Cl_2 solution in the presence of NEt_3 afforded one sole isomer of compound **8**. In the $^{31}P\{^1H\}$ NMR spectrum a singlet at 136 ppm was observed, while the proton spectrum showed a large diastereotopic separation of the two methyl groups (resonating at 0.29 and 1.27 ppm). As can be seen in Figure 3, the N−P bond is axial with respect to the "twist" phospha-dioxa cycloheptane ring (see also the solid state structure of **10** in Figure 1). Reaction of diethyltartrate with **6** gave **9** in excellent yields and as one single isomer, and its $^{31}P\{^1H\}$ NMR spectrum is characterized by a singlet at 148 ppm. In this case the formation of the smaller, rigid, five-membered ring does not give rise to axial/equatorial isomerism. Binaphthol reacted with **6** on a multigram scale in CH_2Cl_2 in the presence of excess NEt_3 to afford the P-alkene **10**, which is characterized by a singlet at 139 ppm in the $^{31}P\{^1H\}$ NMR spectrum. We note that our protocol compares favorably with Carreira's:[7] It is high yielding and needs neither alkyllithium reagents nor a chromatographic purification step. The solid state structure of **10** is shown in Figure 1, and the crystal data and collection parameters are listed in Table 4. The structure of **10** reveals a "twist" phospha-dioxa seven-membered ring and, relative to it, the axial arrangement of the dibenzazepine remainder. The naphthyl groups are twisted, forming a C1−C10−C11−C12 torsion angle of 53.2°. The molecule displays an intramolecular hydrogen bond (C22···O2 3.037(8) Å) and a $\pi-\pi$ stacking interaction (3.555(8) Å) as outlined in Figure 1. The N atom adopts a nearly planar configuration with a maximum deviation of −0.014(8) Å from the C21/C34/P1 plane, and the C═C double bond shows the expected distance (1.34(2) Å). The dibenzazepine unit was found disordered over two sets of positions (see Supporting Information).

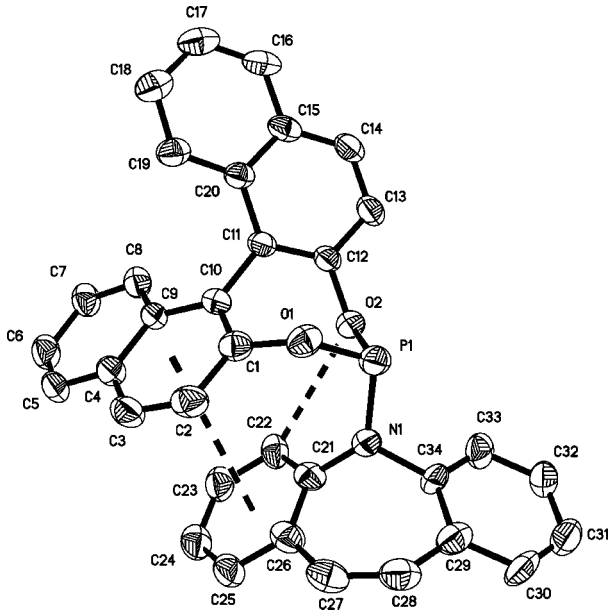


Figure 1. ORTEP view of ligand (*S*)-**10** (30% probability ellipsoids) showing $\pi-\pi$ stacking and H-bonding interactions. Selected bond lengths (Å) and angles (deg): P1−O1, 1.639(4); P1−O2, 1.654(3); P1−N1, 1.679(4); O2−C12, 1.392(5); O1−C1, 1.403(5), C27−C28, 1.34(2); C21−N1−P1, 129.4(7); C34−N1−P1, 112.4(7); C21−N1−C34, 118.2(10).

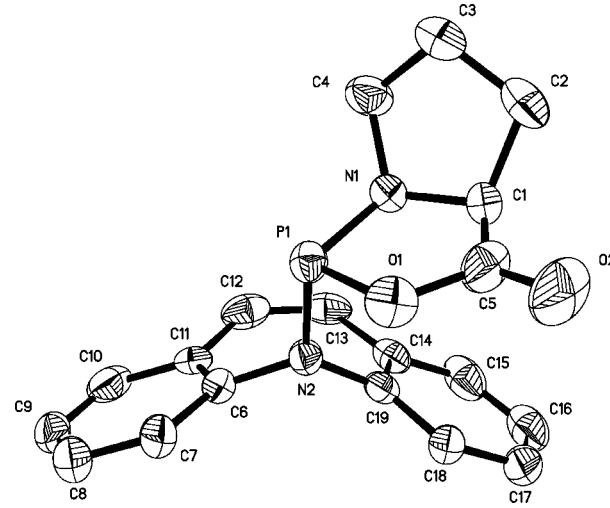


Figure 2. ORTEP view of ligand (S_P,S_C)-**11** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): P1−N1: 1.682(5); P1−N2, 1.691(4); P1−O1, 1.701(4); N1−C1, 1.439(7); N2−C6, 1.434(6); N2−C19, 1.423(6); C12−C13, 1.334(9); C5−O1, 1.336(8); C5−O2, 1.206(7); O1−P1−N1, 92.0(2); N2−P1−O1, 99.0(2); C6−N2−C19, 117.9(4); C19−N2−P1, 122.8(3); C6−N2−C19, 117.9(4).

The reaction of the inexpensive chiral modifier (*S*)-proline with **6** in CH_2Cl_2 solution in the presence of excess NEt_3 gave rise to two isomers of **11**, characterized by a major singlet at 138 ppm and a minor singlet at 134 ppm in the $^{31}P\{^1H\}$ NMR spectrum. In this case, the existence of two diastereoisomers is due to the steroegenicity of the P atom in **11**. This is equivalent to stating that the dibenzazepine moiety may be located *syn* or *anti* with respect to the proline ring.[19] The pure diastereoisomer resonating at 138 ppm was isolated by recrystallization from Et_2O. Single crystals suitable for an X-ray diffraction analysis were grown from a cold Et_2O solution, and the solid state structure revealed its absolute (S_P,S_C)-configuration (see Figure 2).[20] The five-membered ring formed by the N1/C1/O1/P1/C5 atoms is almost planar, with a maximum deviation of 0.0367 Å from the mean plane. The proline ring adopts an envelope conformation, and the flap atom C3 deviates from the mean plane by 0.166(6) Å. These rings make a dihedral angle of 129.5(2)°. Compared with the typical tetrahedral conformation of the proline N1 atom with a deviation of 0.365(6) Å with respect to the C1/C4/P1 plane, the N2 atom of the dibenzazepine moiety approaches a trigonal-planar conformation with a deviation of −0.137(5) Å with respect to the C6/C19/P2 plane (cf. structure of **10**). As in ligand **10**, the alkene distance lies in the expected range (1.334(9) Å). Ligand (S_P,S_C)-**11** turned out to be air sensitive, rapidly decomposing in humid air, thereby turning orange (which indicates the liberation of dibenzazepine).

The use of the more bulky auxiliary (*S*)-diphenylprolinol did not lead to any appreciable degree of diastereocontrol when the reaction with **6** was performed in CH_2Cl_2/NEt_3, affording a 1:1 diastereomeric mixture of ligand **12**. However, in Et_2O solution

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(20) It is theoretically possible that traces of the minor diastereomer co-crystallized and that such a crystal was picked by accident. However, the structural characterization of a Rh complex bearing the ligand diastereoisomer resonating at 138 ppm in the $^{31}P\{^1H\}$ NMR revealed the same (*S*,*S*) configuration, thus minimizing the probability of an accidental mix-up. Dorta, R.; Briceño, A. Unpublished results.

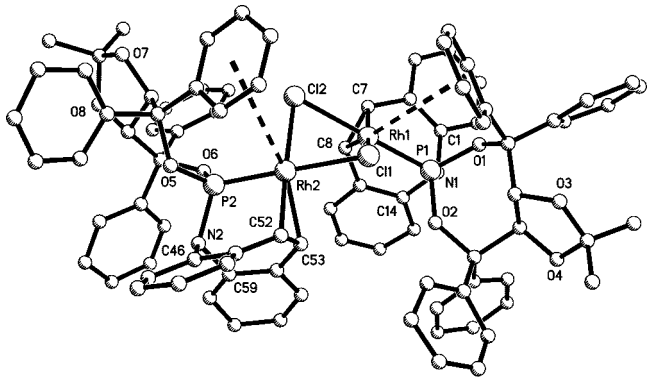


Figure 3. Ball and stick representation (for clarity) of *trans*-**14** showing different phenyl−Rh distances (see text). Selected bond lengths (Å) and angles (deg): Rh1−P1, 2.138(4); Rh1−Cl1, 2.388(3); Rh1−Cl2, 2.474(3); Rh2−P2 2.143(3); Rh2−Cl1, 2.455(3); Rh2−Cl2, 2.412(4); Rh1−C7, 2.119(14); Rh1−C8, 2.092(13); Rh2−C52, 2.122(15); Rh2−C53, 2.088(13); P1−O2, 1.605(9); P1−O1, 1.631(9); P1−N1 1.730(10); P2−O5, 1.590(9); P2−O6, 1.586(8); P2−N2, 1.721(11); N1−C1, 1.424(17); N1−C14, 1.465(19); C52−C53, 1.40(2); N2−C46, 1.470(16); N2−C59, 1.484(17); C7−C8, 1.42(2); C52−C53, 1.40(2).

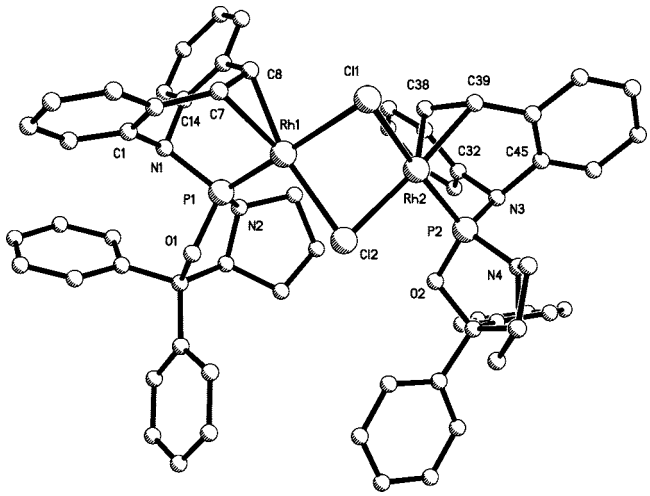
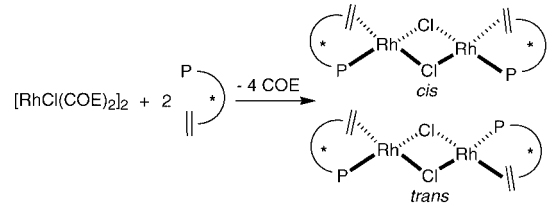


Figure 4. Ball and stick representation (for clarity) of *cis*-**18**. Selected bond lengths (Å) and angles (deg): Rh1−P1, 2.155(2); Rh1−Cl1, 2.501(2); Rh1−Cl2, 2.404(2); Rh1−C7, 2.112(8); Rh1−C8, 2.121(9); Rh2−P2, 2.148(2); Rh2−Cl1, 2.457(2); Rh2−Cl2, 2.411(2); Rh2−C38, 2.097(8); Rh2−C39, 2.160(8); P1−O1, 1.622(6); P1−N1, 1.720(7); P1−N2, 1.665(6); P2−O2, 1.603(6); P2−N3, 1.714(6); P2−N4, 1.659(7); C7−C8, 1.448(12); C38−C39, 1.462(12); P1−Rh1−Cl1, 170.79(9); P1−Rh1−Cl2, 97.65(9); P2−Rh2−Cl2, 95.10(8); P2−Rh2−Cl2, 170.79(9); O1−P1−N1, 104.3(3), O1−P1−N2, 97.5(3); N1−P1−N2, 101.7(3); O2−P2−N4, 96.3(3); O2−P2−N3, 102.3(3), N4−P2−N3, 104.1(3).

preferential formation (ca. 1:10) of the diastereoisomer resonating at 135 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum was observed, and slurrying the crude product in CH_3CN afforded the diastereomerically pure ligand in good yield. Ligand **12** is featured in the solid state structure of its Rh complex depicted in Figure 4, and its absolute configuration is thus S_P,S_C.

2. Complex Syntheses. Ligands **7**−**12** were then used to synthesize dinuclear Rh complexes, a class of compounds that was shown to efficiently catalyze the enantioselective 1,4 addition of carbon nucleophiles.[17,21] Two equivalents of ligands **7**−**12** reacted cleanly with $[RhCl(COE)_2]_2$ (COE = cyclooctene) in benzene or toluene solutions to afford complexes **13**−**18** in very high yields (Scheme 3). Slurrying and washing the products with pentane assured analytical and isomeric purity by removing the liberated cyclooctene.[22] The presence of a sole doublet in most of the $^{31}P\{^{1}H\}$ NMR spectra hinted at the preferred formation of single isomers with complete selectivity, and only one complex was obtained as a *cis/trans* mixture (complex **17**, *vide infra*).

Scheme 3



Ligand	Complex	Isolated Yield (%)	$^{31}P\{^{1}H\}$ NMR (J_{Rh-P})
7	**13**	92	150 ppm (293 Hz)
8	***trans*-14**	92 (98[a])	150/153 ppm (288 Hz)
9	**15**	95	178 ppm (298 Hz)
10	**16**	94	174 ppm (298 Hz)
11	***cis/trans*-17**	72	175/178 ppm (270/278 Hz)
12	***cis*-18**	96	180 ppm (265 Hz)

During the optimization of the synthesis of complex **13** we noticed the appearance of a byproduct of composition $[RhCl(\mathbf{7})_2]$[23] if care was not taken to *slowly* add ligand **7** to the Rh precursor. Somewhat surprisingly, complex **14**, bearing the taddol-derived ligand **8**, was accessible from both $[RhCl(COE)_2]_2$ and $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) precursors. Furthermore, the presence of two doublets centered at 150 and 153 ppm of the same intensity and with identical Rh−P coupling, irrespective of the method of synthesis used,[24] made the first hypothesis of a *cis/trans* mixture look doubtful. Single crystals suitable for an X-ray diffraction study were obtained from a chloroform solution of **14** that was layered with Et_2O. The molecular structure is displayed in Figure 3 and presents the expected $Rh_2(\mu\text{-}Cl)_2$ butterfly-shaped core with a dihedral angle of 117° and pseudo-square-planar coordination of the Rh centers. The P atoms are located *trans* within the dimeric structure. However, the two P atoms (and of course corresponding H atoms) are not related through a pseudo-C_2 axis, as is usually the case in such dimers, thus explaining their nonequivalency in the NMR spectra. The lack of symmetry is exemplified by the different distances of the two phenyl rings that cover the Rh atoms [Rh1−centroid (C19−C24) = 4.34 Å; Rh2−centroid (C67−C72) = 3.80 Å]. Interestingly, the bidentate coordination of the ligand produces a significant hybridization change of the N atoms, which departs from planar, as found in the free ligand, to tetrahedral. The N atoms displayed a deviation of 0.44(1) and 0.45(1) Å in relation to the P1/C1/C14 and P2/C46/C59 planes, respectively. The coordinated olefins showed an average bond distance of 1.41(2) Å. The

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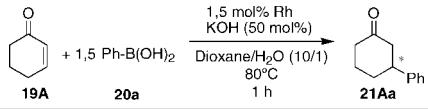
(22) Ligand **7** reacted with $[RhCl(COE)_2]_2$ in toluene-d_8 solution to afford compound **13** *in situ* in quantitative NMR yield as a 1:1 *cis/trans* mixture. The two isomers were characterized by two doublets centered at 151.5 ppm (J_{RhP} = 293 Hz) and 150.5 ppm (J_{RhP} = 291 Hz), along with ca. 3.5 equiv of free COE in the proton spectrum. After washing in pentane, one single isomer was isolated in 95% yield.

(23) This compound was prepared and characterized separately, manuscript in preparation.

(24) Running the reactions in THF, benzene, toluene, or chloroform with either $[RhCl(COE)_2]_2$ or $[RhCl(COD)]_2$ as starting materials invariably led to the observation of two doublets in a 1:1 ratio in the $^{31}P\{^{1}H\}$ NMR spectrum.

Table 2. Screening of Complexes 13−18 for the Catalytic 1,4 Addition



19A 20a 21Aa

	catalyst					
	13	**14**	**15**	**16**	**17**	**18**
yield (%)[a]	92	87	91	90	traces	52
ee (%)[b]	6	3	10	92	nd	50
configuration[c]	*R*	*S*	*S*	*R*	nd	*S*

[a] Isolated yields of **21Aa**. [b] Determined by HPLC analysis with Daicel's Chiralcel OD-H chiral column (for details see Experimental Part). [c] Configuration determined by comparison with reported data.

lengthening of the coordinated olefin when compared with the free ligands **10** and **11** (*vide supra*) is due to π back-bonding from the Rh(I) centers.[25] Complex **16**, bearing the binaphthol-derived ligand **10**, also formed in almost quantitative yield as a single isomer. The ^{1}H NMR spectrum showed a characteristic pair of broad doublets at 4.69 and 4.93 ppm (J = 9.0 Hz) attributed to the diastereotopic H atoms of the coordinated olefin function of the dibenzazepine substituent. While complexes **15** and **16** formed in excellent yields and as a single isomer,[26] the reaction of the proline-derived ligand **11** led to inseparable *cis*/*trans* mixtures of complex **17** under a variety of conditions. This could be due to the comparatively low steric bulk of the proline moiety and thus poor stereochemical control upon formation of dimer **17**. Finally, analogous to the synthesis of **14**, complex **18** was also accessible from the more convenient precursor $[RhCl(COD)]_2$ by displacement of the COD ligand. Good quality single crystals were grown from a $CDCl_3$ solution of the complex that was layered with Et_2O. Its solid state structure is depicted in Figure 4 and reveals the usual square-planar coordination of the Rh nuclei and the butterfly-shaped Rh_2Cl_2 core with a dihedral angle of 121°, being 5° wider than that observed in **14**. Again, the dibenzazepine N atoms are clearly tetrahedral, which appears to be typical for this class of ligands in their bidentate coordination mode. The relative *cis* orientation of the two ligand moieties, though, is rather unexpected. The ^{31}P{^{1}H} NMR spectrum showed a doublet at 180 ppm (J = 270 Hz), and we did not detect any long-range $^4J_{P-P}$ coupling.

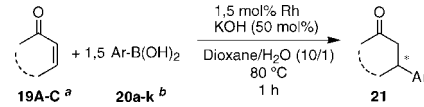
3. Catalysis. Complexes **13**−**18** were tested in the catalytic 1,4 additions of arylboronic acids to enones. It is important to note that only commercially available substrates without purification were used throughout this study, thus testing the robustness of the catalyst precursors toward common impurities. After optimization of the reaction conditions, a first screening of the complexes in the addition of phenylboronic acid (**20a**) to cyclohexenone (**19A**) revealed that the best dinuclear species in terms of activity and selectivity was complex **16** (see Table 2). The poor selectivity of complex **14** is somewhat surprising in view of the fact that ligand **8** contains the usually efficient chiral auxiliary taddol,[27] while the selectivity of complex **18** (bearing diphenylprolinol-derived ligand **12**) proved more promising. Complex **17**, bearing the proline-derived ligand **11**, did not catalyze the title reaction and the appearance of a black precipitate during catalysis was observed.

(25) (a) Dewar, M. J. S. *Bull. Chem. Soc. Fr.* **1951**, *18*, C71. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, *2939*.

(26) The determination of the *cis*/*trans* isomerism in complexes **13**, **15**, and **16** is the subject of ongoing efforts, and results will be published in due course.

(27) Seebach, D.; Beck, A. K.; Heckel, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 92.

Table 3. Substrate Screening with Complexes 16 and 18



19A-C [a] 20a-k [b] 21

entry	enone	boronic acid	catalyst	yield of **21** (%)[c]	ee (%)[d,e]
1	**19A**	**20b**	**16**	91 (**21Ab**)	88[ab]
2	**19A**	**20b**	**18**	47 (**21Ab**)	40
3	**19A**	**20c**	**16**	73 (**21Ac**)	77
4	**19A**	**20c**	**18**	69 (**21Ac**)	40
5	**19A**	**20d**	**16**	86 (**21Ad**)	84
6	**19A**	**20d**	**18**	50 (**21Ad**)	50
7	**19A**	**20e**	**16**	66 (**21Ae**)	79
8	**19A**	**20e**	**18**	42 (**21Ae**)	56
9	**19A**	**20f**	**16**	66 (**21Af**)	81
10	**19A**	**20f**	**18**	48 (**21Af**)	39
11	**19A**	**20g**	**16**	54 (**21Ag**)	86
12	**19A**	**20g**	**18**	40 (**21Ag**)	65
13	**19A**	**20h**	**16**	51 (**21Ah**)	86
14	**19A**	**20h**	**18**	35 (**21Ah**)	46
15	**19A**	**20i**	**16**	38 (**21Ai**)	81
16	**19A**	**20i**	**18**	28 (**21Ai**)	50
17	**19A**	**20j**	**16**	54 (**21Aj**)	86
18	**19A**	**20j**	**18**	30 (**21Aj**)	50
19	**19A**	**20k**	**16**	85 (**21Ak**)	72
20	**19A**	**20k**	**18**	47 (**21Ak**)	33
21	**19B**	**20a**	**16**	95 (**21Ba**)	65
22	**19B**	**20a**	**18**	65 (**21Ba**)	0
23	**19C**	**20a**	**16**	72 (**21Ca**)	72
24	**19C**	**20a**	**18**	34 (**21Ca**)	0

[a] **19A** = 2-cyclohexenone, **19B** = 2-cyclopentenone, **19C** = 3-octene-2-one. [b] Ar = Ph (**20a**), 2-$CH_3C_6H_4$ (**20b**), 3-$CH_3C_6H_4$ (**20c**), 4-$CH_3C_6H_4$ (**20d**), 3-$CH_3OC_6H_4$ (**20e**), 4-$CH_3OC_6H_4$ (**20f**), 3-FC_6H_4 (**20g**), 4-FC_6H_4 (**20h**), 3-ClC_6H_4 (**20i**), 4-ClC_6H_4 (**20j**), 1-naphthyl (**20k**). [c] Isolated yields. [d] Determined by HPLC analysis with Daicel Chiralcel OD-H, OJ-H, and OB chiral columns (for details see Experimental Part). [e] Entries 1−24 are expected to have the absolute configuration *S* for runs using **18** and *R* for those using **16** and **20** due to the enantioselective face attack of the enone following the configurations in Table 2.

We speculate that the presence of the phenylboronic acid nucleophile is incompatible with the ester function present in ligand **11**. When the temperature was lowered to 60 °C while maintaining the other variables fixed, reaction times tended to be longer without appreciable gains in yield or selectivity. The use of 3 mol % of Rh allowed the catalysis to be run at 50 °C with essentially quantitative yields (except for **17** and **18**), but selectivity remained at the same levels. Decreasing the amount of boronic acid led to lower yields under all conditions studied, while varying the amount of base in the range of 25−100 mol % did not change the reaction outcome.

Table 3 summarizes the results of 1,4 additions catalyzed by complexes **16** and **18** by combining various arylboronic acids and enones under the conditions employed in Table 2. In all reactions complex **16** turned out to be the more active and the more selective catalyst. With the smaller enone 2-cyclopentenone a maximum turnover number (TON) of 63 was achieved (entry 21) and the *ortho*-methyl-substituted variant of the nucleophile added with 88% enantioselectivity to 2-cyclohexenone (entry 1). Likewise, catalyst **18** was most active in the reaction of 2-cyclopentenone with phenylboronic acid (TON = 43, entry 22) and reached a selectivity of 65% ee when *meta*-fluorophenylboronic acid was reacted with 2-cyclohexenone (entry 12). Catalyst **16** proved also efficient in combination with an acyclic enone (entry 23). However, in the presence of **16** or **18**, cyclic esters such as 5,6-dihydro-2*H*-pyran-2-one or 4,5-dihydrofuran-2-one reacted only very sluggishly, if at all, with phenylboronic acid.

Conclusions

We disclosed a general synthetic protocol for the synthesis of six new chiral P-alkene ligands, **7**−**12**. Dichlorophosphanyldibenzoazepine **6** was shown to be an ideal precursor for the reaction with chiral diols, amino alcohols, and an amino acid in the presence of NEt_3, leading to ligands **7**−**12**. Most importantly, all ligands were obtained in isomerically pure form, and their absolute stereochemistries were determined. We note that in addition to the backbone chirality of the proline/prolinol auxiliary, ligands **11** and **12** feature sterogenic P atoms. Compounds **7**−**12** were shown to act as bidentate P-alkene ligands in chloro-bridged dinuclear Rh(I) complexes. The syntheses of complexes **13**−**18** are high yielding and give isomerically pure material (*cis* or *trans*) in five of six cases. A comparison of the X-ray crystal structures of the free versus the coordinated ligands revealed a certain flexibility in the hybridization state of the dibenzoazepine N atom, passing from sp^2 in the free ligand to sp^3 when coordinated to Rh in a bidentate fashion. This hybridization flexibility allows the ligands to adapt the P-alkene bite angle to the requirements of the coordination sphere of the Rh center. With the exception of **11**, all Rh complexes were excellent catalyst precursors in terms of activity for the conjugate addition of arylboronic acids to enones, and complexes **16** and **18** also showed medium to excellent enantioselectivity with up to 92% ee for catalyst **16**.

Experimental Part

All reactions were carried out under anaerobic and anhydrous conditions, using standard Schlenk and glovebox techniques unless otherwise stated. THF, Et_2O, and benzene were distilled from purple Na/Ph_2CO solutions, toluene from Na, pentane and C_6D_6 from Na/K alloy, CH_3CN and CH_2Cl_2 from CaH_2, and NEt_3 from from K. $CDCl_3$ was degassed with three freeze−pump−thaw cycles and then kept over activated molecular sieves (4 Å) in the glovebox. NMR spectra were recorded on a JEOL 400 MHz spectrometer, and elemental analyses were performed at IVIC and OCI.

***N*-Dichlorophosphanyldibenzo[*b*,*f*]azepine (6).** PCl_3 (18.54 g, 135.0 mmol) was rapidly added to an orange mixture of iminostilbene (13.04 g, 67.49 mmol) and NEt_3 (27.4 g, 271 mmol) in Et_2O (540 mL). This mixture was then stirred for 90 h at RT, during which time the color gradually turned pale yellow and large amounts of a white solid precipitated. Evaporation of the volatiles under HV afforded a pale yellow powder, which was extracted with toluene (3 × 80 mL). The resulting clear yellow solution was then pumped down to a beige solid, which was slurried in CH_3CN (30 mL) and then kept at 250 K overnight. The brownish mother liquor was siphoned off while still cold, and the residue washed with a fresh portion of CH_3CN (20 mL). Filtration of the cold slurry and HV drying yielded 18.72 g (94%) of an off-white powder. Anal. Found: C 54.30, H 3.51, N 4.59. Calcd for $C_{14}H_{10}Cl_2NP \cdot H_2O$: C 53.87, H 3.88, N 4.49. ^1H NMR (400 MHz, $CDCl_3$): δ 6.86 (s, br, 2H), 7.25−7.35 (m, 4H), 7.35−7.50 (m, 2H), 7.55−7.60 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 127.1−127.5 (m), 127.9, 129.3−129.7 (m), 131, 135.6−135.7 (m), 141.4−141.9 (m). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ 151 (s).

(3a*R*,8a*R*)-(−)-*N*-(2,2-Dimethyl-6-phospha-1,3,5,7-tetraoxabicyclo[3.5.0]decan-6-yl)dibenzo[*b*,*f*]azepine ((*R*,*R*)-7). NEt_3 (3.38 g, 33.4 mmol) was added to a lemon yellow solution of **6** (2.584 g, 8.784 mmol) in CH_2Cl_2 (100 mL). To this solution was then added dropwise over 40 min a solution of (−)-2,3-*O*-isopropylidene-D-threitol (1.425 g, 8.786 mmol) in CH_2Cl_2 (75 mL) under vigorous stirring. After stirring overnight the yellow solution was evaporated to a yellowish sticky solid that was redissolved in Et_2O (100 mL), affording a yellowish mother liquor and a white solid. The solid was separated by filtration over a medium-porosity frit and washed with fresh Et_2O (2 × 50 mL), giving 2.33 g of $NEt_3 \cdot HCl$ (96%). The combined ether phases were evaporated to dryness, redissolved in CH_3CN (15 g), and kept at 250 K overnight to afford an off-white precipitate. The yellow mother liquor was decanted off and the solid dried *in vacuo* (2.49 g, 74%). This material is usually sufficiently pure (ca. 95% according to ^{31}P NMR spectroscopy) for subsequent reactions. Recrystallization: 2.49 g was dissolved in a minimum amount of CH_3CN (12.1 g), stirred for 4 h at RT, and then left at 250 K for 24 h. This procedure ensures selective precipitation of the main contaminant as a small amount of a white solid, which was separated by cold filtration. The CH_3CN solution was then concentrated to about half its volume and left at 250 K to induce precipitation of the white product. Decantation of the cold mother liquor and HV drying of the solid afforded 2.21 g (66%). Anal. Found: C 65.40, H 5.89, N 3.68. Calcd for $C_{21}H_{22}PNO_4$: C 65.79, H 5.78, N 3.65. HR-MS: 406.12 [$M + Na^+$]. $[\alpha]_D^{25} = 9.7$ (*c* 1.485, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 3H), 1.38 (s, 3H), 3.55−3.70 (m, 1H), 3.75−3.95 (m, 2H), 3.95−4.10 (m, 1H), 4.10−4.25 (m, 2H), 6.79 (s, 2H), 7.10−7.45 (m, 8H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 139 (s). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 26.9, 64.1−64.3 (m), 79.6−80.0 (m), 111.0, 126.2−126.3 (m), 128.1 (d, $J = 7.7$ Hz), 128.2−128.3 (m), 129.0 (d, 7.7 Hz), 129.4, 131.3, 136.0, 136.2−136.2 (m), 143.3, 143.3, 143.5, 143.6.

(3a*R*,8a*R*)-(−)-*N*-(2,2-Dimethyl-6-phospha-1,3,5,7-tetraoxa-4,4,8,8-tetraphenylbicyclo[3.5.0]decan-6-yl)dibenzo[*b*,*f*]azepine ((*R*,*R*)-8). A solution of (*R*)-taddol (1.769 g, 3.790 mmol) in CH_2Cl_2 (38 mL) was added dropwise over 10 min to a vigorously stirred solution of **6** (1.115 g, 3.790 mmol) in CH_2Cl_2 (38 mL) and NEt_3 (2.14 g, 21.1 mmol). The resulting pale yellow clear solution was stirred overnight and then evaporated to dryness under HV, affording a pale yellow solid, which was extracted with toluene (2 × 40 mL, filtration over GF-M). The resulting yellowish toluene solution was pumped down to dryness to afford the pale yellow crude product. Washing with cold Et_2O (10 mL) and drying under HV yielded 2.08 g (80%) of a white solid. Anal. Found: C 78.29, H 5.74, N 2.10. Calcd for $C_{45}H_{38}O_4PN$: C 78.59, H 5.57, N 2.04. HR-MS: 710.24 [$M + Na^+$]. $[\alpha]_D^{25} = 130.4$ (*c* 1.040, $CHCl_3$). ^1H NMR (400 MHz, C_6D_6): δ 0.29 (s, 3H), 1.27 (s, 3H), 5.00−5.10 (m, 1H), 5.50−5.60 (m, 1H), 6.5 (s, 2H), 6.90−7.20 (m, 18H), 7.25−7.35 (m, 2H), 7.40−7.50 (m, 1H), 7.55−7.70 (m, 3H), 7.85−7.95 (m, 2H), 8.05−8.15 (m, 2H). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 136 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 25.2, 27.5, 82.0−83.5 (m), 111.8, 126.2, 126.4, 127.0−128.4 (m), 128.8−129.6 (m), 131.3, 131.4, 137.2, 137.3, 141.8, 142.3, 142.9, 143.0, 143.6, 146.7, 147.2.

(4*R*,5*R*)-*N*-(1,3-Dioxa-4,5-dicarboxyethylphosphonlanyl)dibenzo[*b*,*f*]azepine ((*R*,*R*)-9). A solution of (*R*,*R*)-diethyltartrate (0.643 g, 3.12 mmol) in CH_2Cl_2 (22 mL) was added dropwise over 10 min to a vigorously stirred solution of **6** (0.917 g, 3.12 mmol) in CH_2Cl_2 (22 mL) and NEt_3 (1.88 g, 18.6 mmol). The resulting pale yellow clear solution was stirred overnight and then evaporated to dryness under HV, affording a yellowish glassy solid, which was extracted with Et_2O (3 × 25 mL, filtration over cotton plugs). This yellowish extract was evaporated to dryness to afford the off-white product plus a yellow contaminant, which was effectively removed by washing with pentane (2 × 25 mL). Drying under HV yielded 1.18 g (89%) of a white fluffy solid. Anal. Found: C 60.41, H 5.71, N 3.30. Calcd for $C_{22}H_{22}PNO_6 \cdot 0.5H_2O$: C 60.55, H 5.31, N 3.21. $[\alpha]_D^{25} = 49.7$ (*c* 1.060, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 1.15−1.30 (m, 6H), 3.95−4.25 (m, 5H), 4.50−4.55 (m, 1H), 6.85 (s, 2H), 7.20−7.35 (m, 8H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 147 (s).

(S)-(+)-*N*-(3,5-Dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)-dibenz[*b*,*f*]azepine ((*S*)-10). A solution of (*S*)-binaphthol (3.178 g, 11.10 mmol) in CH_2Cl_2 (55 mL) was added dropwise over 30 min to a vigorously stirred solution of **6** (3.264 g, 11.10 mmol) in CH_2Cl_2 (110 mL) and NEt_3 (4.60 g) at 283 K.

The resulting pale yellow clear solution was stirred overnight at RT and then evaporated to dryness under HV, affording a pale yellow solid, which was extracted with toluene (3 × 50 mL, filtration over GF-M). The resulting lemon yellow toluene solution was evaporated to dryness to afford 5.46 g (95%) of an off-white powder. Anal. Found: C 80.31, H 4.31, N 2.81. Calcd for $C_{34}H_{22}NO_2P$: C 80.46, H 4.37, N 2.76. HR-MS: 530.13 [M + Na^+]. $[\alpha]_D^{25}$ = 320.0 (*c* 1.010, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 6.50−6.55 (m, 1H), 6.80−7.05 (m, 4H), 7.10−7.45 (m, 13H), 7.60−7.65 (m, 1H), 7.70−7.80 (m, 1H), 7.85−7.95 (m, 1H), 7.95−8.05 (m, 1H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 138 (s). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 121.2 (m), 121.5, 122.2, 124.4 (m), 124.9, 125.7, 126.1−126.3 (m), 126.8−126.9 (m), 127.2 (m), 128, 128.3−129.3 (m), 130.2−130.5 (m), 131.4−131.7 (m), 132.2, 132.9, 135.3, 136.5 (m), 142.6, 142.9, 143.1, 148.8, 150 (m).

(2*S*,5*S*)-(−)-*N*-(Aza-3-oxa-2-phosphabicyclo[3.3.0]octan-4-on-2-yl)dibenz[*b*,*f*]azepine ((*S*$_P$,*S*$_C$)-11). NEt_3 (4.56 g) was added to a solution of **6** (3.147 g, 10.70 mmol) in CH_2Cl_2 (100 mL), followed by solid (*S*)-proline (1.232 g, 10.70 mmol). The resulting yellow solution was stirred overnight and then evaporated to dryness, affording a yellow-white solid. The ammonium salt was separated by extracting the solid with Et_2O (2 × 100 mL, filtration over GF-M). Evaportation of the ether yielded 3.43 g of the crude, ammonium-free product. To obtain the (*R, S*) isomer, the crude yellowish solid was slurried five times for 12 h in Et_2O (10 mL), followed by cooling to 250 K and decanting of the ether washings while cold. This procedure yielded 1.25 g (35%) of a snow white powder containing >99% of the (*S,S*) diastereoisomer. Anal. Found: C 67.58 H 5.25 N 8.37. Calcd for $C_{19}H_{17}N_2O_2P$: C 67.85 H 5.09 N 8.33. HR-MS: 359.09 [M + Na^+]. $[\alpha]_D^{25}$ = 74.9 (*c* 1.135, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 1.35−1.50 (m, 1H), 1.65−1.80 (m, 1H), 1.80−2.00 (m, 2H), 2.85−3.10 (m, 2H), 3.40−3.55 (m, 1H), 6.81 (s, 2H), 7.15−7.40 (m, 8H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 138.3 (s).

(2*S*,5*S*)-(−)-*N*-(Aza-4,4-diphenyl-3-oxa-2-phosphabicyclo[3.3.0]-octan-2-yl)dibenz[*b*,*f*]azepine ((*S*$_P$,*S*$_C$)-12). At room temperature a precooled (250 K) solution of α,α-diphenyl-L-prolinol (1.666 g, 6.576 mmol) in Et_2O (28 mL) and *n*-pentane (16 mL) was rapidly added dropwise over 10 min to a turbid, cooled (250 K), and vigorously stirred solution of **6** (1.934 g, 6.576 mmol) in Et_2O (42 mL), *n*-pentane (16 mL), and NEt_3 (5.5 mL). The resulting white mixture was stirred at RT for 8 h, after which the white precipitate was separated by filtration over a glass frit (GF-M) and extracted with Et_2O (2 × 50 mL). The combined yellowish filtrates were evaporated to an off-white powder. The crude product was slurried overnight in CH_3CN (20 mL), affording a snow white solid and a yellow mother liquor. The solid was separated by filtration (GF-F) and dried *in vacuo*, yielding 2.40 g (77%) of a white fluffy solid. From the cooled mother liquor another crop of crystals precipitated (0.20 g, 6%). This procedure gives material with a diastereomeric purity of >98%. Anal. Found: C 79.15, H 5.66, N 5.68. Calcd for $C_{31}H_{27}PN_2O$: C 78.46, H 5.73, N 5.90. HR-MS: 497.18 [M + Na^+]. $[\alpha]_D^{25}$ = 243.1 (*c* 1.145, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 0.60−0.80 (m, 1H), 1.30−1.45 (m, 2H), 1.60−1.75 (m, 1H), 2.80−2.95 (m, 1H), 3.15−3.35 (m, 2H), 6.54 (d, 12 Hz, 1H), 6.65−6.80 (m, 1H), 6.72 (d, 12 Hz, 1H), 6.90−7.45 (m, 19H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 134.9 (s), traces of the 2*R*,5*S* diastereoisomer: 144.3 (s). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 26.4, 26.5, 45.7, 46.0, 68.4, 94.3, 94.4, 125.9, 125.9, 126.8, 127.0, 127.2, 127.5, 127.6, 127.7, 128.7, 128.8, 129.0, 129.1, 129.7, 130.8, 131.3, 136.7, 137.2, 143.0, 143.7, 143.8, 144.2, 144.4, 145.3.

[RhCl((*R*,*R*)-7)]$_2$ (13). A solution of (*R*,*R*)-**7** (216 mg, 0.563 mmol) in toluene (5.6 g) was added dropwise over 15 min to a vigorously stirred slurry of $[RhCl(COE)_2]_2$ (202 mg, 0.282 mmol) in toluene (2.8 g). The resulting orange-red solution was stirred for 2 h and evaporated to dryness. Then the solid was slurried in pentane (8 mL), separated by filtration, and dried *in vacuo* to afford a bright orange powder (270 mg, 92%). Anal. Found (calcd): C 48.32 (48.34), H 4.30 (4.25), N 4.62 (2.68). ^1H NMR (400 MHz, $CDCl_3$): δ 1.41 (s, 6H), 1.46 (s, 6H), 3.90−4.35 (m, br, 10H), 4.50−4.70 (br, 2H), 4.70−5.00 (m, br, 4H), 7.05−7.75 (m, br, 16H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 149.6 (d, *J* = 293 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 26.9, 27.0, 59.5−61.0 (m), 65.4 (d, 14 Hz), 67.3 (d, 14 Hz), 78.5, 78.6, 112.0, 127.5, 128.0, 128.2, 128.5, 129.3, 140.6−141.5 (m, br).

***trans*-[RhCl((*S*,*S*)-8)]$_2$ (*trans*-14), method A.** A clear, cool (273 K) solution of (*S,S*)-**8** (209.9 mg, 0.3028 mmol) in toluene (2.8 g) was added dropwise over 10 min to a vigorously stirred and cool (273 K) slurry of $[RhCl(COE)_2]_2$ (108.5 mg, 0.1512 mmol) in toluene (2.8 g). This afforded initially a clear red solution that gradually turned bright orange over 16 h under stirring. Then, the volatiles were evaporated *in vacuo*, and the orange-red glassy residue was slurried in pentane (6 mL) to afford a bright yellow, finely divided solid. Separation by filtration over a glass frit (F) and drying *in vacuo* afforded 230 mg (92%) of a yellow powder. Anal. Found: C 66.32, H 5.00, N 1.55. Calcd for $C_{90}H_{76}O_8P_2N_2Rh_2Cl_2 \cdot C_5H_{12}$: C 66.17, H 5.14, N 1.62. ^1H NMR (400 MHz, $CDCl_3$): δ 0.36 (s, br, 6H), 0.49 (s, 3H), 0.68 (s, 3H), 3.90−4.00 (m, 1H), 4.70−4.85 (m, 2H), 5.20−5.25 (m, 1H), 5.35−5.45 (m, 3H), 5.60−5.75 (m, 2H), 5.85−5.90 (m, 1H), 6.50−6.60 (m, 1H), 5.70−5.80 (m, 2H), 5.80−7.05 (m, 4H), 7.05−7.75 (m, 47H), the spectrum indicates the presence of 1.4 equiv of cocrystallized pentane. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 149.9 (d, *J* = 288 Hz), 152.8 (d, *J* = 288 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 14.1, 22.4, 26.6, 27.0, 27.4, 34.2, 53.0 (d, 15 Hz), 56.4 (d, 15 Hz), 60.0 (d, 17), 60.7 (d, 17), 80.6, 81.6, 87.0, 87.5, 90.4 (d, 20), 91.6 (d, 20), 115.3, 115.8, 126.0−132.0 (m), 139.5−144.0 (m). Crystals suitable for an X-ray diffraction experiment were grown from material (30 mg) that contained CH_2Cl_2 of cocrystallization, which was dissolved in $CDCl_3$ (0.6 mL) and layered with Et_2O in an NMR tube.

***trans*-[RhCl((*S*,*S*)-8)]$_2$ (*trans*-14), method B.** A yellowish solution of (*S,S*)-**8** (570 mg, 0.822 mmol) in THF (4.3 g) was added dropwise over 15 min to a vigorously stirred turbid solution of $[RhCl(COD)]_2$ (203 mg, 0.411 mmol) in THF (3.7 g). After stirring the red reaction mixture for 2 h the volatiles were evaporated *in vacuo*. The resulting orange solid was slurried in pentane (10 mL) overnight, separated by filtration (GB/F), and washed with a fresh portion of pentane (10 mL). Drying *in vacuo* yielded 665 mg (98%) of a yellow powder. NMR spectra were identical to the ones reported under method A.

[RhCl((*R*,*R*)-9)]$_2$ (15). A yellowish solution of (*R,R*)-**9** (222 mg, 0.519 mmol) in benzene (3.4 g) was added dropwise over 10 min to a vigorously stirred benzene (4.2 g) solution of $[RhCl(COE)_2]_2$ (186 mg, 0.259 mmol) to afford a bright red solution, which was stirred for 7 h. Evaporation of the volatiles, followed by washing in pentane, filtration over a cotton plug, and drying *in vacuo* afforded a very fine yellow powder (279 mg, 95%). Anal. Found: C 45.95, H 4.10, N 2.56. Calcd for $C_{44}H_{44}P_2N_2O_{12}Rh_2Cl_2 \cdot H_2O$: C 45.97, H 4.03, N 2.44. ^1H NMR (400 MHz, C_6D_6): δ 1.15−1.50 (br, 12H), 4.10−4.55 (br, 8H), 4.90−5.10 (br, 4H), 5.10−5.25 (br, 1H), 5.45−5.55 (br, 1H), 6.90−7.60 (br, 18H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 177.3 (d, *J* = 300 Hz).

[RhCl((*S*)-10)]$_2$ (16). A solution of (*S*)-**10** (288 mg, 0.568 mmol) in toluene (7.5 g) was added dropwise over 15 min to a vigorously stirred slurry of $[RhCl(COE)_2]_2$ (204 mg, 0.284 mmol) in toluene (6.5 g). The resulting clear red solution was stirred for 2.5 h and then concentrated to about one-third of its volume. Addition of pentane (20 mL) caused immediate precipitation of a yellow flocculating solid, which was separated by filtration and washed with another portion of pentane. Drying *in vacuo* yielded 345 mg (94%) of a red-orange powder. Anal. Found: C 64.06 H 3.85 N 2.12. Calcd for $C_{68}H_{44}N_2O_4P_2Rh_2Cl_2 \cdot 0.5C_7H_8$: C 64.19, H 3.62, N 2.09. ^1H NMR (400 MHz, $CDCl_3$): δ 4.69 (d, 9.0 Hz, 2H), 4.93

(d, 9.0 Hz, 2H), 7.00−7.65 (m, 32H), 7.90−8.10 (m, 8H). The spectrum indicated the presence of about 0.5 equiv of toluene of cocrystallization. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 174.4 (d, J = 298 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 59.8 (d, 14 Hz), 63.5 (d, 14 Hz), 121.8, 122.5, 122.8, 123.3, 125.2, 125.4, 126.1, 126.3, 127.3, 127.7, 127.8, 128.3, 128.3, 128.7, 128.8, 129.2, 129.6, 129.7, 130.3, 131.5, 131.8, 132.7, 132.9, 138.0, 140.6, 140.9, 141.6, 142.3, 147.2, 148.8, 149.0.

[RhCl((*S*,*S*)-11)]$_2$ (17). A precooled (250 K) solution of (*S*,*S*)-**11** (107.4 mg, 0.3193 mmol) in toluene (3.2 g) was added dropwise over 5 min to a vigorously stirred precooled (250 K) slurry of $[RhCl(COE)_2]_2$ (115.0 mg, 0.1603 mmol) in toluene (3.2 g), affording a clear orange-red solution that was kept stirring at RT for 3 h and then evaporated to dryness. The solid was washed and slurried in pentane (2 × 3 mL) and dried *in vacuo* to yield 110 mg (72%) of an orange powder. Anal. Found: C 48.15, H 3.97, N 5.67. Calcd for $C_{38}H_{34}N_4O_4P_2Rh_2Cl_2$: C 48.08, H 3.61, N 5.90. ^1H NMR (400 MHz, C_6D_6): mixture of 2 isomers, ratio ≅ 1:2, δ 0.90−1.15 (m, 2H), 1.15−1.70 (m, 5H), 1.80−2.30 (m, 3H), 3.60−4.10 (m, 4H), 4.91 (d, 8 Hz, 2H, major isomer), 5.33 (d, 7 Hz, 2H, minor isomer), 5.52 (d, 8 Hz, 2H, major isomer), 5.61 (d, 7 Hz, 2H, minor isomer), the system of 4 doublets integrates as 4H with respect to the rest of the spectrum, 6.60−7.55 (m, 16H). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 175.0 (d, 270 Hz), 177.9 (d, 278 Hz), isomeric ratio ≅ 1: 2.

***cis*-[RhCl((*S*,*S*)-12)]$_2$ (*cis*-18).** A solution of (*S*,*S*)-**12** (274.1 mg, 0.5776 mmol) in benzene (2.6 g) was added dropwise over 10 min to a vigorously stirred benzene (2.6 g) slurry of $[RhCl(COE)_2]_2$ (207.1 mg, 0.2886 mmol) to afford an clear orange solution, which was stirred for 80 min. Then the volatiles were evaporated *in vacuo*, the orange-red residue was washed and slurried in pentane (2 × 12 mL), and the solid was separated by filtration (glass fiber filter GF/B). HV drying yielded 339 mg (96%) of an orange powder. Anal. Found: C 60.77, H 4.60, N 4.22. Calcd for $C_{62}H_{54}P_2N_4O_2Rh_2Cl_2$: C 60.75, H 4.44, N 4.57. ^1H NMR (400 MHz, $CDCl_3$): δ 0.80−2.10 (m, 8H), 2.45−2.75 (br, 2H), 4.25−5.10 (m, br, 6H), 5.35−5.60 (br, 2H), 6.75−7.80 (m, 36H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 179.9 (d, 265 Hz). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 14.2, 22.4, 25.5, 31.5, 34.2, 47.8, 59.2, 62.2, 69.7, 91.0, 125.0−128.5 (m), 129.5, 130.0, 141.3, 142.0−143.5 (m), 144.8.

General Procedure for 1,4 Addition of Boronic Acids to Enones. Inside a glovebox the Rh precatalyst (0.0075 mmol of **13**−**18**) was weighed into a 20 mL vial, followed by arylboronic acid (1.5 mmol) and 2 mL of dioxane. The vial was fitted with a magnetic stirring bar, closed with a Teflon cap, and taken out of the glovebox. The degassed enone (1.0 mmol) was then added via syringe followed by degassed KOH (2.5 M in H_2O, 0.2 mL, 0.5 mmol). The reaction was stirred at 80 °C for 1 h, after which time it was diluted in Et_2O (20 mL), washed with water (10 mL), dried over $MgSO_4$, concentrated to a small volume, and submitted to column chromatography (silica gel, hexane/Et_2O eluent) to afford the pure product.

3-Phenylcyclohexanone (21Aa): eluted with hexane/Et_2O (9:1), obtained as a colorless oil. HPLC conditions: Chiralcel OD-H column (*n*-hexane/2-propanol, 98:2, 0.5 mL/min); t_R 24.3 min (major), 26.6 min (minor) for reactions with **14**, **15**, and **18** and t_R 24.3 min (minor), 26.6 min (major) for reactions with **13**, **16**, **19**, and **20**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.76−1.96 (m, 2H), 2.10−2.24 (m, 2H), 2.37−2.68 (m, 4H), 3.00−3.12 (m, 1H), 7.24−7.31 (m, 3H), 7.34−7.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.74 (s), 32.99 (s), 41.39 (s), 44.95 (s), 49.15 (s), 126.77 (s), 126.89 (s), 128.89 (s), 144.56 (s), 211.17 (s).

3-(2-Methylphenyl)cyclohexanone (21Ab): eluted with hexane/Et_2O (9:1), obtained as light yellow oil. HPLC conditions: Chiralcel OD-H column (*n*-hexane/2-propanol, 99.5:0.5, 0.5 mL/min); t_R 43.2 min (major), 48.0 min (minor) for **18** and t_R 43.2 min (minor), 48.0 min (major) for **16** and **20**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.77−1.96 (m, 2H), 2.02−2.09 (m, 1H), 2.17−2.26 (m, 1H), 2.37 (s, 3H), 2.40−2.60 (m, 4H), 3.21−3.31 (m, 1H), 7.15−7.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.46 (s), 26.00 (s), 32.23 (s), 40.52 (s), 41.50 (s), 48.55 (s), 125.28 (s), 126.63 (d, J = 4.4 Hz), 130.86 (s), 135.30 (s), 142.49 (s), 211.37 (s).

3-(3-Methylphenyl)cyclohexanone (21Ac): eluted with hexane/Et_2O (9:1), obtained as colorless oil. HPLC conditions: Chiralcel OJ-H column (*n*-hexane/2-propanol (99.5:0.5), 1.0 mL/min); t_R 24.7 min (major), 27.9 min (minor) for **18** and t_R 24.7 min (minor), 27.9 min (major) for **16**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.70−1.91 (m, 2H), 2.03−2.20 (m, 2H), 2.35 (s, 3H), 2.32−2.63 (m, 4H), 2.92−3.03 (m, 1H), 6.99 7.08 (m, 3H), 7.19−7.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.68 (s), 25.80 (s), 33.05 (s), 41.43 (s), 44.96 (s), 49.21 (s), 123.77 (s), 127.63 (d, J = 3.2 Hz), 128.79 (s), 138.49 (s), 144.57 (s), 211.28 (s).

3-(4-Methylphenyl)cyclohexanone (21Ad): eluted with hexane/Et_2O (9:1), obtained as a white solid. HPLC Cconditions: Chiralcel OD-H column (*n*-hexane/2-propanol, 99.9:0.1, 0.5 mL/min); t_R 113.0 min (major), 135.3 min (minor) for **18** and t_R 113.0 min (minor), 135.3 min (major) for **16** and **20**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.70−1.90 (m, 2H), 2.03−2.19 (m, 2H), 2.33 (s, 3H), 2.35−2.62 (m, 4H), 2.92−3.03 (m, 1H), 7.08 7.18 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.19 (s), 25.77 (s), 33.13 (s), 41.42 (s), 44.61 (s), 49.30 (s), 126.66 (s), 129.56 (s), 136.48 (s), 141.66 (s), 211.34 (s).

3-(3-Methoxylphenyl)cyclohexanone (21Ae): eluted with hexane/Et_2O (9:1), obtained as a light yellow oil. HPLC conditions: Chiralcel OJ-H column (*n*-hexane/2-propanol, 99:1, 1.0 mL/min); t_R 36.3 min (minor), 39.7 min (major) for **18** and t_R 36.3 min (major), 39.7 min (minor) for **16** and **20**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.74−1.96 (m, 2H), 2.02−2.21 (m, 2H), 2.37−2.68 (m, 4H), 2.96−3.08 (m, 1H), 3.84 (s, 3H), 6.78−6.87 (m, 3H), 7.25 7.32 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.71 (s), 32.89 (s), 41.38 (s), 44.95 (s), 49.11 (s), 55.39 (s), 111.85 (s), 112.90 (s), 119.09 (s), 129.87 (s), 146.23 (s), 160.04 (s), 211.08 (s).

3-(4-Methoxyphenyl)cyclohexanone (21Af): eluted with hexane/Et_2O (9:1), obtained as a light yellow oil. HPLC conditions: Chiralcel OJ-H column (*n*-hexane/2-propanol, 99:1, 1.0 mL/min); t_R 45.6 min (major), 49.0 min (minor) for **18** and t_R 45.6 min (minor), 49.0 min (major) for **16**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.67−1.88 (m, 2H), 2.00−2.19 (m, 2H), 2.30−2.62 (m, 4H), 2.91−3.02 (m, 1H), 3.79 (s, 3H), 6.83−6.90 (d, J = 8.7 Hz, 2H), 7.11−7.17 (d, J = 11.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.64 (s), 33.18 (s), 41.33 (s), 44.13 (s), 49.39 (s), 55.43 (s), 114.20 (s), 127.65 (s), 136.75 (s), 158.45 (s), 211.26 (s).

3-(3-Fluorophenyl)cyclohexanone (21Ag): eluted with hexane/Et_2O (9:1), obtained as a colorless oil. HPLC conditions: Chiralcel OJ-H column (*n*-hexane/2-propanol, 99:1, 0.5 mL/min); t_R 37.2 min (minor), 39.4 min (major) for **18** and t_R 37.2 min (major), 39.4 min (minor) for **16**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.74−1.94 (m, 2H), 2.05−2.25 (m, 2H), 2.35−2.67 (m, 4H), 2.98−3.10 (m, 1H), 6.91−7.05 (m, 3H), 7.27−7.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.56 (s), 32.77 (s), 41.29 (s), 44.55 (d, J = 1.4 Hz), 48.87 (s), 113.62 (d, J = 7.1 Hz), 113.83 (d, J = 6.8 Hz), 122.47 (d, J = 2.7 Hz), 130.35 (d, J = 8.3 Hz), 147.09 (d, J = 6.7 Hz), 162.22 (d, J = 245.9 Hz), 210.56 (s).

3-(4-Fluorophenyl)cyclohexanone (21Ah): eluted with hexane/Et_2O (9:1), obtained as a colorless solid. HPLC conditions: Chiralcel OJ-H column (*n*-hexane/2-propanol, 99.5:0.5, 1.0 mL/min); t_R 37.5 min (major), 43.5 min (minor) for **18** and t_R 37.5 min (minor), 43.5 min (major) for **16** and **20**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.70−1.88 (m, 2H), 2.00−2.21 (m, 2H), 2.31−2.61 (m, 4H), 2.94−3.05 (m, 1H), 6.97−7.04 (t, J = 8.7 Hz, 2H), 7.14−7.21 (dd, J = 5.3 and 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.59 (s), 32.10 (s), 41.30 (s), 44.19 (s), 49.26 (s), 115.63 (d, J = 21.2 Hz), 128.18 (d, J = 7.9 Hz), 140.25 (d, J = 3.2 Hz), 161.76 (d, J = 244.7 Hz), 210.81 (s).

Table 4. Crystal Data and Data Collection Parameters of 10, 11, 14, and 18

	10	11	14	18
formula	$C_{34}H_{22}NO_2P$	$C_{19}H_{17}N_2O_2P$	$C_{92}H_{79}Cl_7N_2O_8P_2Rh_2$	$C_{62}H_{54}Cl_2N_4O_2P_2Rh_2$
M (g mol^{-1})	507.50	336.32	1856.48	1225.75
cryst syst	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	12.074 (4)	8.8321 (17)	15.257 (2)	14.1831 (15)
b (Å)	7.705 (3)	9.7972 (17)	22.269 (4)	18.3783 (19)
c (Å)	14.042 (5)	20.158 (4)	25.817 (4)	20.1175 (18)
β (deg)	96.228 (9)			
V (Å^3)	1298.5 (8)	1744.3 (6)	8772 (2)	5243.9 (9)
Z	2	4	4	4
μ (mm^{-1})	0.14	0.17	0.68	0.84
D_c (g cm^{-3})	1.298	1.281	1.406	1.553
reflns collected	14 682	20 012	87 459	59 948
indep reflns, R_{int}	4533, 0.029	3345	15 904, 0.095	11 028, 0.087
GOF	1.13	1.14	1.04	1.08
R_1, wR_2 [$I > 2\sigma(I)$]	0.070, 0.179	0.081, 0.189	0.091, 0.268	0.055, 0.123
largest features in final diff map (max./min. e Å^{-3})	0.26, −0.24	0.198, −0.165	0.73, −0.89	0.59, −0.79

3-(3-Chlorophenyl)cyclohexanone (21Ai): eluted with hexane/Et_2O (9:1), obtained as a light yellow oil. HPLC conditions: Chiralcel OD-H column (*n*-hexane/2-propanol, 99.5:0.5, 0.5 mL/min); t_R 51.0 min (major), 59.5 min (minor) for **18** and t_R 51.0 min (minor), 59.5 min (major) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74−1.94 (m, 2H), 2.06−2.27 (m, 2H), 2.34−2.66 (m, 4H), 2.97−3.08 (m, 1H), 7.11−7.16 (m, 1H), 7.23−7.32 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.59 (s), 32.78 (s), 41.29 (s), 44.58 (s), 48.84 (s), 125.06 (s), 127.05 (d, J = 8.2 Hz), 130.17 (s), 134.70 (s), 146.52 (s), 210.45 (s).

3-(4-Chlorophenyl)cyclohexanone (21Aj): eluted with hexane/Et_2O (9:1), obtained as a white solid. HPLC conditions: Chiralcel OJ-H column (*n*-hexane/2-propanol, 99:1, 1.0 mL/min); t_R 25.3 min (major), 29.3 min (minor) for **18** and t_R 25.3 min (minor), 29.3 min (major) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70−1.88 (m, 2H), 2.00−2.10 (m, 1H), 2.10−2.20 (m, 1H), 2.31−2.60 (m, 4H), 2.92−3.04 (m, 1H), 7.12−7.17 (d, J = 8.3 Hz, 2H), 7.25−7.32 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.56 (s), 32.87 (s), 41.28 (s), 44.27 (s), 48.96 (s), 128.56 (d, J = 86.2 Hz), 132.55 (s), 142.96 (s), 210.63 (s).

3-(1-Naphthyl)cyclohexanone (21Ak). Eluted with hexane/Et_2O (9:1), obtained as a white solid. HPLC conditions: Chiralcel OD-H column (*n*-hexane/2-propanol, 95:5, 0.5 mL/min); t_R 42.8 min (minor), 62.5 min (major) for **18** and t_R 42.8 min (major), 62.5 min (minor) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86−2.08 (m, 2H), 2.15−2.30 (m, 2H), 2.41−2.82 (m, 4H), 3.81−3.92 (m, 1H), 7.38−7.57 (m, 4H), 7.73−7.79 (d, J = 8.1 Hz, 1H), 7.85−7.91 (d, J = 8.9 Hz, 1H), 8.01−8.07 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.80 (s), 32.53 (s), 39.61 (s), 41.66 (s), 48.79 (s), 122.78 (d, J = 27.1 Hz), 125.79 (d, J = 10.8 Hz), 126.42 (s), 127.47 (s), 129.38 (s), 131.13 (s), 134.20 (s), 140.27 (s), 211.38 (s).

3-Phenylcyclopentanone (21Ba): eluted with hexane/Et_2O (9:1), obtained as a colorless oil. HPLC conditions: Chiralcel OB column (*n*-hexane/2-propanol, 99.5:0.5, 1.0 mL/min); t_R 34.5 min (major), 39.3 min (minor) for **18** and t_R 34.5 min (minor), 39.3 min (major) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97−2.11 (m, 1H), 2.28−2.57 (m, 4H), 2.66−2.77 (m, 1H), 3.41−3.53 (m, 1H), 7.26−7.32 (m, 3H), 7.36−7.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.39 (s), 39.05 (s), 42.42 (s), 45.99 (s), 126.92 (s), 128.88 (s), 143.27 (s), 218.51 (s).

4-Phenyloctan-2-one (21Ca): eluted with hexane/Et_2O (9:1), obtained as a colorless oil. HPLC conditions: Chiralcel OD-H column (*n*-hexane/2-propanol, 98:2, 0.5 mL/min); t_R 11.8 min (minor), 12.9 min (major) for **18** and t_R 11.8 min (major), 12.9 min (minor) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81 (t, 3H, J = 7.2 Hz), 1.06−1.30 (m, 4H), 1.54−1.65 (m, 2H), 2.00 (s, 3H), 2.70 (d, 2H, J = 8.0 Hz), 3.05−3.15 (m, 1H), 7.15−7.30 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9 (s), 22.6 (s), 29.5 (s), 30.6 (s), 36.2 (s), 41.3 (s), 50.9 (s), 126.3 (s), 127.4 (s), 128.4 (s), 144.6 (s), 208.0 (s).

Crystal Structure Determination. Intensity data were recorded at room temperature on a Rigaku AFC-7S diffractometer using monochromated Mo(Kα) radiation (λ = 0.71073 Å). Experimental details on unit cell and intensity measurements can be found in the CIF files deposited with the CCDC numbers 694272 for **10**, 671271 for **11**, 694273 for **14**, and 694274 for **18**. Crystal data, intensity data collection parameters, and final refinement results are summarized in Table 4. An empirical absorption correction (multiscan) was applied to all the data using the CrystalClear crystallographic software package.[28] The structures were solved by direct methods and refined by full-matrix least-squares on F^2. The H atoms on C were placed in calculated positions using a riding atom model with fixed C−H distances [0.93 Å for C(sp^2), 0.96 Å for C(sp^3, CH_3), and 0.97 Å for C(sp^3, CH_2)]. All the H atoms were refined with isotropic displacement parameters set to 1.2U_{eq} for C(sp^2) and 1.5 for C(sp^3) of the attached atom. In structure **10** the iminostilbenyl unit was found disordered over two sets of positions, which were included by constraining the aromatic rings to be a regular hexagon. The occupational parameters were refined to 0.48:0.52. In structure **14** either dichloromethane or chloroform molecules were found disordered. For each molecule such disorder was modeled over two orientations with restraints in the C−Cl and Cl···Cl distances and complementary occupancies: 40:60 for dichloromethane and 42:58 for chloroform, respectively. These atoms were refined only with isotropic displacement parameters. All the refinement calculations were made using SHELXTL-NT.[29]

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) *SHELXTL-NT, Version 5.1*; Bruker AXS Inc.: Madison, WI, 1998.