C_2-BIPNOR: An Easily Accessible Homologue of BIPNOR for Asymmetric Catalysis

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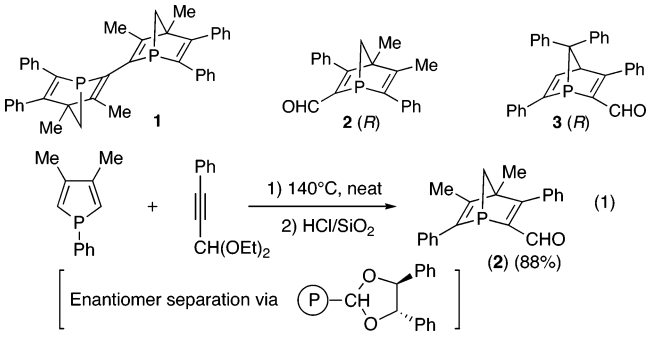
Under mild conditions at −78 °C, the McMurry coupling of the (*R*)-2-formyl-1-phosphanorbornadiene **2** yields the enantiopure (R_P, S_C, S_C, R_P) diol **4**, dubbed C_2-BIPNOR. In boiling THF, the same reaction leads to the *trans*-alkene **6**. C_2-BIPNOR is easier to prepare and to handle than BIPNOR while benefiting from the same configurational stability at phosphorus. It appears to have a wider range of catalytic applications than BIPNOR and, in one case (asymmetric Heck reaction), to be competitive with the best ligands proposed in the literature.

Introduction

The incorporation of phosphorus into ring systems has led to the synthesis of several chiral bis-phosphines of high interest as ligands for asymmetric catalysis. Among the well-known examples are the phospholane-based DuPHOS,[1] the phosphetane-based FerroTANE,[2,3] and the phosphanorbornane-based PennPhos.[4] The higher rigidity of these cyclic species by comparison with their noncyclic analogues probably plays a significant role in their enantioselective efficiency. Along the same line, it is tempting to incorporate phosphorus at the bridgehead of a bicyclic system. This leads to phosphines of even higher rigidity than the monocyclic species and, if phosphorus is the chiral center, prevents any loss of ligand enantiopurity during the catalytic process, by pyramidal inversion if some heating is required and by pseudorotation if protic media are used. With these ideas in mind, we developed, some time ago, the so-called BIPNOR (**1**),[5] whose enantioselective efficiency proved to be quite high in the rhodium-catalyzed asymmetric hydrogenation of functional alkenes[5] and asymmetric isomerization of cyclic dienes.[6] The full development of BIPNOR was unfortunately hampered by the low yield and complexity of its synthesis. While keeping the core structure of the two 1-phosphanorbornadiene chiral units, we decided to study the synthesis of BIPNOR homologues where the two phosphanorbornadiene units would be connected via a bridge instead of a direct C−C bond. Our prerequisite was, of course, to achieve higher yields and synthetic simplicity than in the case of BIPNOR. We report hereafter on the synthesis of a C_2-bridged homologue of BIPNOR that meets these requirements and on a preliminary evaluation of its efficiency as ligand in a selected number of asymmetric catalytic processes.

Results and Discussion

Some time ago, we described a simple and efficient access to enantiopure 1-phosphanorbornadiene-2-carboxaldehydes **2** and **3**[7] (eq 1).



It was tempting to study the reductive coupling of these aldehydes using the powerful McMurry reaction[8] in order to get C_2-bridged homologues of BIPNOR. When conducted at −78 °C in THF, the reductive coupling of **2** with the $TiCl_4$/Zn system exclusively leads to a single diastereomer of the diol **4** (Scheme 1).

When performing the coupling on *rac*-**2**, we have been able to get crystals of *rac*-**4**. The structure is shown in Figure 1. The crystals are constituted of a 50:50 mixture of (R_P, S_C, S_C, R_P) and (S_P, R_C, R_C, S_P) enantiomers. Hence, the absolute configurations of the carbons of the bridge of **4** is (*S*,*S*) as

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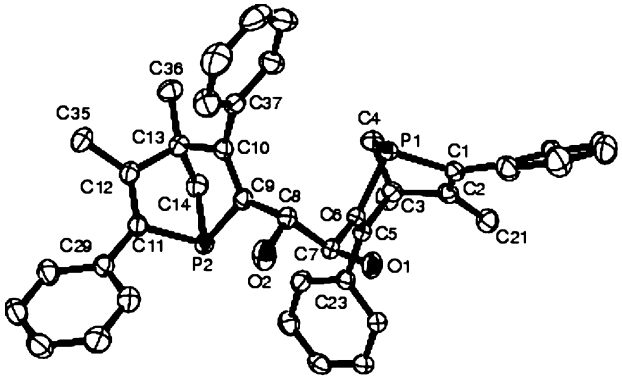


Figure 1. ORTEP drawing of *rac*-**4** showing the (R_P, S_C, S_C, R_P) configuration. Hydrogen atoms are omitted for clarity.

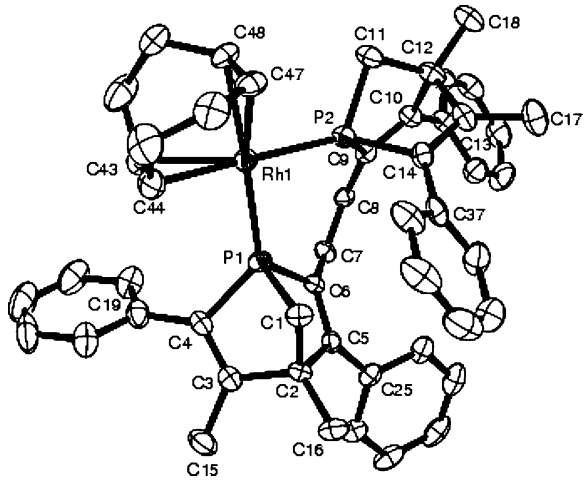
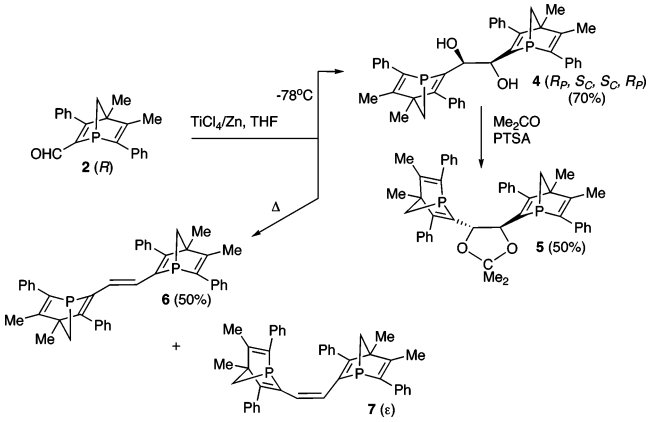
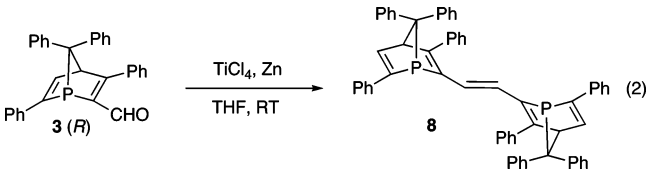


Figure 2. ORTEP drawing of [Rh(cod)(**7**)]$^+$ (**7Rh**). Hydrogen atoms are omitted for clarity.

Scheme 1

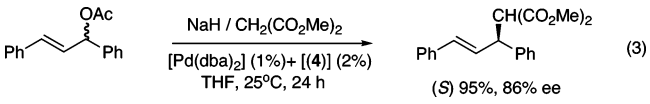


indicated in Scheme 1. The acetal **5** was also prepared in order to check the influence of additional rigidity on the enantioselectivity of the catalytic reactions. When performed in boiling THF, the coupling reaction goes one step further and mainly gives the *trans* olefin **6** together with a minute quantity of the *cis* olefin **7**. The two olefins cannot be separated, but the presence of a small quantity of **7** can be ascertained by its ^{31}P resonance 0.2 ppm upfield from the resonance of **6**. The structures of **6** and **7** have been established by X-ray analysis of a dinuclear palladium complex for **6** and a rhodium chelate for **7**. In Figure 2, we show the structure of **7Rh** as an example. The cationic rhodium center displays an almost perfect square planar geometry with a P−Rh−P bite angle of 90.13°. The structure confirms the (*R*)-configuration of the starting aldehyde. As a final synthetic note, the reductive coupling of **3** led only to the *trans* olefin **8**, which was not investigated further (eq 2). Obviously the huge steric bulk of the phosphanorbornadiene units prevents the formation of the *cis* olefin in this case.

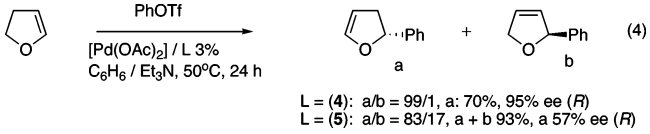


We performed a series of asymmetric hydrogenation experiments with **4** and **5**, which are collected in Table 1. For comparison, we also performed a test with the crystallographically characterized **7Rh**. In this case, with compound **a** as the substrate and under the same experimental conditions as in the first entry of Table 1, the conversion was quantitative and the (*R*) product was obtained with a 95% ee. From the data in Table 1, it is clear that the additional rigidity provided by the dioxolane ring in **5** has an adverse effect on the enantioselectivity of the reactions. We thus focused on **4**, named C_2-BIPNOR for convenience (*C_2*-bridged *bis*-*p*hospha*nor*bornadiene). When compared with BIPNOR,[5] it appears that C_2-BIPNOR does not reach the same level of enantioselectivity in the Rh-catalyzed asymmetric hydrogenation of functional alkenes. In the Ir-catalyzed asymmetric hydrogenation of imines, whereas BIPNOR is inefficient in terms of both activity and enantioselectivity, C_2-BIPNOR displays good activity and moderate enantioselectivities when compared with the other systems described in the literature.[9]

We also investigated the possible use of C_2-BIPNOR in some palladium-catalyzed reactions. Under standard conditions, the allylic alkylation of 1,3-diphenylprop-2-enyl acetate by dimethyl malonate gives the (*S*)-enantiomer in 95% yield and 86% ee (eq 3).



More exciting results were obtained in the asymmetric Heck reaction as shown in eq 4.



The results obtained with **4** can be compared with the best ones described recently in the literature,[10] in terms of both activity and enantioselectivity. Once again, the more rigid dioxolane **5** showed less selectivity and enantioselectivity than C_2-BIPNOR.

As a conclusion, C_2-BIPNOR (**4**) displays several advantages when compared to BIPNOR while retaining its configurational

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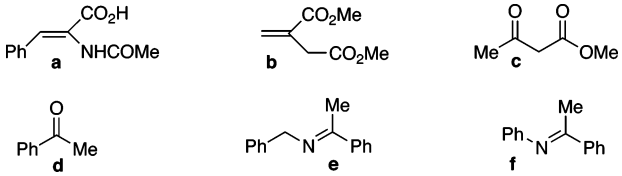
Table 1. Asymmetric Hydrogenation Experiments with 4 and 5 as Ligands[a]



			diol **4**		dioxolane **5**	
compound	catalyst	conditions	conversion, %	ee, %	conversion, %	ee, %
a	[Rh(cod)(L)]PF_6 1%	MeOH, H_2 3 atm, 25 °C, 30 min	100	>98 (*R*)	100	93 (*R*)
b	[Rh(cod)(L)]PF_6 1%	MeOH, H_2 3 atm, 25 °C, 30 min	100	88 (*S*)	100	43 (*S*)
c	[$RuBr_2$(L)]	MeOH, H_2 40 atm, 80 °C, 24 h	100	49 (*R*)		
c	[$RuCl_2$(cym)(L)] 0.5%	MeOH, H_2 10 atm, 50 °C, 24 h	100	70 (*R*)		
d	[$RuCl_2$(cym)(L)] 0.5%, TMEDA, tBuOK, diamine	MeOH, H_2 30 atm, 25 °C, 36 h	100	36 (*R*)		
e	[Ir(cod)(L)]PF_6 1%	MeOH, H_2 10 atm, 50 °C, 24 h	100	54 (*R*)		
f	[Ir(cod)(L)]PF_6 1%	MeOH, H_2 10 atm, 50 °C, 24 h	100	57 (*R*)		

[a] [Rh(cod)(**4**)]PF_6: δ^{31}P 31.6, J_{P-Rh} = 155 Hz; [Rh(cod)(**5**)]PF_6: δ^{31}P 33.3, J_{P-Rh} = 148.8 Hz; [$RuBr_2$(**4**)]: δ^{31}P 43.2; [$RuCl_2$(cym)(**4**)]: δ^{31}P 42.0; [Ir(cod)(**4**)]PF_6: δ^{31}P 22.7.

stability at phosphorus. It is both easier to prepare (40% overall yield from 3,4-dimethyl-1-phenylphosphole vs 10% for BIPNOR) and easier to store (indeed, we have kept it in the cold for several months without oxidation). It appears to have a wider range of applications than BIPNOR. Finally, in some cases (Heck), it is competitive with the best ligands proposed in the literature. A more thorough investigation of the catalytic potential of this ligand is thus warranted.

Experimental Section

General Experimental Methods. All reactions were performed under argon. The solvents were distilled using standard techniques. Chromatography was performed with SDS silica gel (60A 40−63 μm). Infrared (IR) spectra were recorded on a Perkin-Elmer 297; wavenumbers are indicated in cm^{-1} (in CH_2Cl_2). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance 300 spectrometer operating respectively at 300, 75, and 121.5 MHz. Mass spectra with electronic impact (EI) were obtained at 70 eV by the direct inlet method on a Hewlett-Packard (HP) 5989B coupled with a GC HP 5890. Commercial reagents were used as received.

McMurry Reagent. A dry argon-filled, three-necked, round-bottom flask was charged with dry THF (20 mL), titanium(IV) chloride (0.69 mL, 12 mmol), and Zn powder (0.81 g, 12 mmol). The mixture was refluxed for 1.5 h with stirring, during which the color of the reaction mixture changed from green yellow to black-green.

Diol 4. This mixture was cooled to −78 °C, and then a solution of aldehyde **2** (1.3 g, 4 mmol) in THF (10 mL) was added within 15 min. The cold bath was removed and stirring continued for 1 h. The reaction mixture was hydrolyzed with a saturated solution of $NaHCO_3$, extracted with CH_2Cl_2, washed twice with H_2O, and dried (Na_2SO_4). Removal of the solvent and subsequent column chromatography over silica gel (hexane/AcOEt, 80/20) yielded the diol **4** (1.0 g, 70%) as a pale yellow solid. Mp = 104 °C. ^{31}P NMR ($CDCl_3$): δ −19.9. ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 6H, CH_3); 1.96 (s, 6H, CH_3); 2.02 (m, 4H, CH_2); 4.65 (pseudo d, 2H, C*H*OH); 7.17−7.38 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 17.19 (*C*H_3); 21.94 (*C*H_3); 66.27 (*C*H_2); 72.24 (d, $^2J_{C-P}$ = 4.8 Hz, *C*^{4}); 74.84 (d, $^2J_{C-P}$ = 19.3 Hz, *C*HOH); 127.60−130.11 (Ph); 138.60; 140.48 (d, J_{C-P} = 21.4 Hz); 151.32 (d, J_{C-P} = 24.3 Hz); 154.02 (d, J_{C-P} = 30.8 Hz); 158.27; 166.97. Mass spectrum: *m*/*z* 638 (M^+, 50%); 620 ($M^+ - H_2O$, 100%). $[\alpha]^{25}_D$ −107 (*c* 1, $CDCl_3$).

Dioxolane 5. Diol **4** (0.64 g, 1 mmol) was refluxed in acetone (5 mL) with 20 mg of PTSA for 2 h. The mixture was neutralized with a saturated solution of $NaHCO_3$, extracted with CH_2Cl_2, and dried (Na_2SO_4). Removal of the solvent and subsequent column chromatography over silica gel (hexane/CH_2Cl_2, 80/20) yielded the dioxolane **5** (0.35 g, 50%) as a white solid. ^{31}P NMR ($CDCl_3$): δ −21.2. ^{1}H NMR ($CDCl_3$): δ 1.41 (s, 3H, CH_3); 1.42 (s, 6H, CH_3); 1.48 (s, 3H, CH_3); 2.04 (m, 4H, CH_2); 2.11 (s, 6H, CH_3); 4.88 (pseudo d, 2H, C*H*O); 6.99−7.45 (m, 20H, Ph). ^{13}C NMR ($CDCl_3$): δ 15.96 (*C*H_3); 20.73 (*C*H_3); 26.92 (*C*H3); 65.02 (*C*H_2); 71.21 (d, $^2J_{C-P}$ = 4.8 Hz, *C*^{4}); 78.80 (pseudo q, *C*HO); 109.5 [*C*(CH3)$_2$]; 125.3−128.2 (Ph); 136.57; 139.19 (d, J_{C-P} = 21.4 Hz); 149.64; 149.77 (d, J_{C-P} = 29.9 Hz); 156.30; 167.64. Mass spectrum: *m*/*z* 678 (M^+, 10%); 620 (M^+ − acetone, 100%). $[\alpha]^{25}_D$ −265 (*c* 1.3, CH_2Cl_2).

Alkene 6. The McMurry mixture was cooled to room temperature, and then a solution of aldehyde **2** (1.3 g, 4 mmol) in THF (10 mL) was added dropwise over 15 min. Then the reaction mixture was refluxed for 1 h. The solution was cooled to room temperature, hydrolyzed, extracted with CH_2Cl_2, washed twice with H_2O, and dried (Na_2SO_4). Column chromatography (hexane/AcOEt, 95/5) yielded the *trans* alkene **6** (0.63 g, 50%) as a yellow oil. ^{31}P NMR ($CDCl_3$): δ −23.5. ^{1}H NMR ($CDCl_3$): δ 1.39 (s, 6H, CH_3); 2.00 (s, 6H, CH_3); 2.02 (d, $^2J_{H-P}$ = 3.9 Hz, 4H, CH_2); 7.03−7.44 (m, 22H, C=C*H*, Ph). ^{13}C NMR ($CDCl_3$): δ 15.76 (*C*H_3); 20.68 (*C*H_3); 63.82 (*C*H_2); 71.12 (d, $^2J_{C-P}$ = 5.2 Hz, *C*^{4}); 125.89−128.70 (Ph); 129.04 (d, J_{C-P} = 17.4 Hz); 137.62; 138.99 (d, J_{C-P} = 21.1 Hz); 147.83 (d, J_{C-P} = 22.2 Hz); 151.71 (d, J_{C-P} = 26.0 Hz); 157.83; 161.45. Mass spectrum: *m*/*z* 604 (M^+, 100%); 589 ($M^+ - CH_3$, 10%); 489 ($M^+ - C_9H_7$, 15%); 417 ($M^+ - C_{12}H_{12}P$, 15%). $[\alpha]^{25}_D$ +533 (*c* 1.1, $CDCl_3$).

Palladium Complex of *trans*-Alkene 6Pd. *trans*-Alkene **6** (120 mg, 0.2 mmol) was added dropwise under dry nitrogen to a stirred solution of optically pure palladium complex [bis{μ-chloro[(*R*)-*N*,*N*-dimethyl(α-methylbenzyl)amino-2-*C*,*N*]palladium(II)}*] (58 mg, 0.1 mmol) in CH_2Cl_2 (2 mL). Stirring was continued for 30 min at room temperature and the solution concentrated. Diethyl ether (3 mL) was added to precipitate the yellow complex, which was crystallized in a biphasic solution of CH_2Cl_2/Et_2O to grow single crystals for X-ray analysis. ^{31}P NMR ($CDCl_3$): δ 35.7.

Rhodium Complex of *cis*-Alkene 7Rh. This complex was prepared by mixing 1 equiv of [Rh(cod)$_2$][PF_6] (54.0 mg) and 1 equiv of the mixture of *cis* (δ^{31}P = −22.0) and *trans* (δ^{31}P = −23.5) alkene (**6** + **7**) (64.0 mg) in CH_2Cl_2 (5 mL). Slow evaporation of the solvent gave suitable red single crystals of the *cis* complex. ^{31}P NMR ($CDCl_3$): δ 31.8 J_{Rh-P} = 150.0 Hz.

Rhodium-Catalyzed Hydrogenation. α-Acetamidocinnamic Acid. To a 0.2 M solution of 410 mg (2 mmol) of α-acetamidocinnamic acid in freshly degassed methanol was added 1 mol % of

catalyst precursor prepared by mixing 1 equiv of $[Rh(cod)_2][PF_6]$ (9.0 mg) and 1 equiv of diol **4** (12.8 mg). The solution was subsequently transferred with a syringe into a hydrogenation bomb, previously purged three times with hydrogen (7 atm), and stirred under 3 atm of hydrogen for 30 min. The pressure was released and the solvent was removed in vacuo. The conversion was determined from the ^{1}H NMR spectra of the crude product in DMSO-d_6. A small sample was converted into its methyl ester with trimethylsilyldiazomethane in hexane/2-propanol (90:10), and the enantiomeric excess was determined by HPLC analysis using a Daicel column Chiralcel OD at 254 nm (hexane/2-propanol, 90/10), 1 mL/ min; retention times: 9.7 min (*R*), 12.3 min (*S*). The absolute configuration was attributed by determination of the sign of the optical rotation of the product.

Dimethyl Itaconate. The same procedure as above was used from 320 mg of dimethyl itaconate. The conversion was determined from the ^{1}H NMR spectra of the crude product, and the enantiomeric excess was determined by HPLC analysis using a Daicel column Chiralcel OD at 215 nm (hexane/2-propanol, 98/2), 1 mL/ min; retention times: 9.0 min (*R*), 18.0 min (*S*). The absolute configuration was attributed by determination of the sign of the optical rotation of the product.

Ruthenium-Catalyzed Hydrogenation. Methyl Acetylacetate. Method A: The ruthenium catalyst was prepared as in ref 11 by reaction of $[Ru(cod)(2\text{-methylallyl})_2]$ (3.2 mg, 0.01 mmol) with diol **4** (7.7 mg, 0.012 mmol) in acetone (1 mL). Methanolic HBr (0.13 mL, 0.18 M, 0.024 mmol) was added to the solution, which was subsequently stirred for 30 min. The solvent was evaporated in vacuo. A solution of the substrate (120 mg, 1 mmol) in degassed methanol/H_2O (95/5) (10 mL) was added to the catalyst. The glass flask was placed under argon in a stainless steel autoclave, which was then purged and pressurized with H_2. The solution was stirred under 40 atm of H_2 (initial pressure) for 24 h at 80 °C. The conversion was determined from the ^{1}H NMR spectra after evaporation of the solvent in vacuo. Optical rotation was used to determine the absolute configuration, and the enantiomeric excess was determined by HPLC analysis using a Daicel column Chiralcel OD at 215 nm (hexane/2-propanol, 98/2), 1 mL/ min; retention times: 14.0 min (*R*), 24.0 min (*S*).

Method B: Diol **4** (7.7 mg, 0.012 mmol) and $[RuCl_2cym]_2$ (3.7 mg, 0.006 mmol) were dissolved in 1 mL of degassed anhydrous dichloromethane. The substrate (300 mg, 2.5 mmol) was dissolved in 25 mL of MeOH/H_2O (95/5). The catalyst and subtrate solutions were introduced by a syringe into a stainless steel autoclave. The mixture was degassed and the autoclave was pressurized at 10 atm (initial pressure). The mixture was vigorously stirred at 50 °C for 24 h.

Acetophenone. $[RuCl_2cym]_2$ (6.2 mg, 0.01 mmol) and diol **4** (14 mg, 0.022 mmol) were placed in a Schlenk flask under argon. Previously distilled TMEDA (1 mL) was added to the flask. The mixture was then heated at 110 °C for 1 h with stirring to give a brown solution. TMEDA was then removed under reduced pressure. (*S*,*S*)-1,2-Diphenylethylenediamine (DPEN) (5.5 mg, 0.026 mmol), 2-propanol (2 mL), and $(CH_3)_3COK$ (11.2 mg, 0.1 mmol) were added, and the mixture was stirred for 15 min at room temperature. Acetophenone (2.4 g, 20 mmol), 2-propanol (15 mL), and the catalyst solution were placed in a stainless steel autoclave. The mixture was degassed and hydrogen was introduced at a pressure of 30 atm. The mixture was vigorously stirred at 25 °C for 36 h. The yield was determined by NMR. After evaporation of the solvent under reduced pressure, the residue was passed through a short pad of silica gel (dichloromethane) and then distilled to give 1-phenylethanol. Optical rotation was used to determine the absolute configuration, and the enantiomeric excess was determined by HPLC analysis using a Daicel column Chiralcel OD at 254 nm (hexane/2-propanol, 99/1), 1 mL/ min; retention times: 14.0 min (*R*), 15.0 min (*S*).

Iridium-Catalyzed Hydrogenation. Benzylimine. To a 0.2 M solution of 400 mg (2 mmol) of benzylimine **e** in freshly degassed methanol (25 mL) was added 1 mol % of catalyst precursor prepared by mixing 1 equiv of $[Ir(cod)_2][PF_6]$ (12.2 mg) and 1 equiv of diol (12.8 mg). The solution was subsequently transferred by means of a syringe into a hydrogenation bomb, previously purged three times with 7 atm hydrogen, and stirred under 10 atm hydrogen (initial pressure) for 24 h at 50 °C. The pressure was released and the solvent was removed in vacuo. The conversion was determined from ^{1}H NMR spectra of the crude product. A small sample was filtered on a short column of silica gel, and the enantiomeric excess was determined by HPLC analysis using a Daicel column Chiralcel OD at 254 nm (hexane/2-propanol, 200/1), 1 mL/ min; retention times: 9.2 min (*R*), 10.5 min (*S*). The absolute configuration was attributed by determination of the sign of the optical rotation of the product.

Phenylimine. The same procedure as for **e** was used for **f** (370 mg). The enantiomeric excess was determined by HPLC analysis using a Daicel column Chiralcel OD at 254 nm (hexane/2-propanol, 90/10), 1 mL/ min; retention times: 6.9 min (*R*), 8.6 min (*S*). The absolute configuration was attributed by determination of the sign of the optical rotation of the product.

C−C Coupling with Palladium. Palladium-Catalyzed Allylic Substitution. Reaction of 1,3-Diphenylprop-2-enyl Acetate with $NaCH(CO_2Me)_2$ in THF. A mineral oil dispersion of NaH (60% NaH, 1.8×10^{-3} mol) was washed until free of oil with dry pentane (2×5 mL). The oil-free NaH was suspended in THF (4 mL) and cooled to 0 °C, and dimethyl malonate (0.23 mL, 1.2 equiv) was added dropwise to the stirred suspension. After the reaction was complete, the resulting solution was transferred into a 50 mL flask containing 1,3-diphenyl-2-propenyl acetate (250 mg, 1×10^{-3} mol) in 1 mL of THF and the catalytic precursor [prepared by mixing $Pd(dba)_2$ (5.8 mg, 0.01 mmol) and 2 equiv of **4** (13.0 mg, 0.02 mmol) in THF (2 mL)]. The solution was stirred at room temperature for 24 h. The reaction mixture was then worked up to give the product as a yellow oil (dilution in AcOH, extraction with Et_2O, and washing with brine). The conversion was calculated from the crude product by ^{1}H NMR. Chromatography using hexane/ethyl acetate (80/20) afforded the pure allylation product. Enantiomeric excess was determined by HPLC analysis of the purified material using a Daicel column chiralcel OD (200/1 hexane/2-propanol; 1 mL/min flow). t_R ((*R*)-1,3-diphenyl-2-propenyl dimethylmalonate) = 25.1 min. t_R ((*S*)-1,3-diphenyl-2-propenyl dimethylmalonate) = 27.7 min.

Heck Reaction. A mixture of $Pd(OAc)_2$ (8.7 mg, 0.04 mmol) and diol **4** (74.6 mg, 0.12 mmol) in degassed benzene was stirred at room temperature for 30 min before 2,3-dihydrofuran (0.5 mL, 6.62 mmol), phenyl triflate (0.22 mL, 1.36 mmol), and triethylamine (0.68 mL, 4.89 mmol) were added. This mixture was allowed to stir at 50 °C for 16 h. The reaction was monitored by GC. Upon completion, the mixture was diluted with diethyl ether and washed with water, dried, and evaporated. The crude product was purified by column chromatography (hexane/ethyl acetate, 10/1) to give the coupling product (2-phenyl-2,3-dihydrofuran, 70% yield). Enantiomeric excess was determined by HPLC analysis of the purified material using a Daicel column chiralcel OD at 254 nm (hexane/2-propanol, 99/1), 0.5 mL/min; retention times: 11.2 min (*R*), 12.0 min (*S*). The absolute configuration was attributed by determination of the sign of the optical rotation of the pure product.

X-ray Crystal Data. All data were collected on a KappaCCD diffractometer at 150.0(1) K with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å).

***rac*-4:** $C_{42}H_{40}O_2P_2$; $M = 638.68$ g/mol; triclinic; space group $P\bar{1}$; $a = 10.572(1)$ Å, $b = 13.172(1)$ Å, $c = 13.501(1)$ Å, $\alpha = 86.396(1)°$, $\beta = 67.056(1)°$, $\gamma = 87.169(1)°$, $V = 1727.3(2)$ Å^3; $Z = 2$; $D = 1.228$ g cm^{-3}; $\mu = 0.161$ cm^{-1}; $F(000) = 676$. Crystal dimensions $0.22 \times 0.10 \times 0.10$ mm. Total reflections collected

15 587 and 7955 with $I > 2\sigma(I)$. Goodness of fit on F^2 1.074; $R(I > 2\sigma(I)) = 0.0461$, wR2 = 0.1455(all data); maximum/minimum residual density 1.328(0.054)/−0.606(0.054) e Å^{-3}.

6Pd: $C_{64}H_{70}Cl_6N_2P_2Pd_2$: M = 1354.66 g/mol; orthorhombic; space group $P2_12_12_1$; a = 17.66(5) Å, b = 18.503(5) Å, c = 19.066(5) Å, V = 6230(3) Å^3; Z = 4; D = 1.444 g cm^{-3}; μ = 0.926 cm^{-1}; $F(000)$ = 2768. Crystal dimensions 0.20 × 0.16 × 0.16 mm. Total reflections collected 8497 and 6267 with $I > 2\sigma(I)$. Goodness of fit on F^2 1.034; $R(I > 2\sigma(I)) = 0.0601$, wR2 = 0.1694(all data); maximum/minimum residual density 0.805(0.108)/−0.920(0.108) e Å^{-3}.

7Rh: $C_{50}H_{50}F_6P_3Rh$: M = 960.72 g/mol; orthorhombic; space group $P2_12_12_1$; a = 12.737(5) Å, b = 16.766(5) Å, c = 20.593(5) Å, V = 4398(2) Å^3; Z = 4; D = 1.451 g cm^{-3}; μ = 0.558 cm^{-1}; $F(000)$ = 1976. Crystal dimensions 0.22 × 0.12 × 0.08 mm. Total reflections collected 9997 and 9101 with $I > 2\sigma(I)$. Goodness of fit on F^2 1.004; $R(I > 2\sigma(I)) = 0.0490$, wR2 = 0.1293(all data); maximum/minimum residual density 2.599(0.095)/−1.316(0.095) e Å^{-3}.

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Supporting Information Available: X-ray crystal structure analyses of ligand *rac*-**4** and complexes **6Pd** and **7Rh**. This material is available free of charge via the Internet at http://pubs.acs.org.

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