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Expanding the C_2-Symmetric Bicyclo[2.2.1]hepta-2,5-diene Ligand Family: Concise Synthesis and Catalytic Activity in Rhodium-Catalyzed Asymmetric Addition

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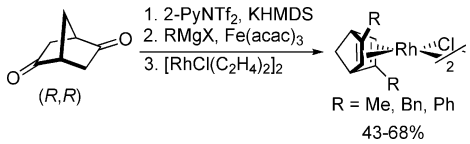

New C_2-symmetric bicyclo[2.2.1]hepta-2,5-dienes bearing methyl and phenyl substituents at the 2 and 5 positions were prepared enantiomerically pure through a two-step sequence starting from the readily available bicyclo[2.2.1]hepta-2,5-dione. Due to the instability or volatility of these dienes, their isolation was achieved through the formation of the corresponding stable $[RhCl(diene)]_2$ complexes. These chiral rhodium complexes displayed high activity and enantioselectivity (up to 99% ee) in the rhodium-catalyzed 1,4-addition and 1,2-addition of phenylboronic acid to cyclic enones and *N*-sulfonylimines, respectively.

The recent introduction of chiral diene ligands is a major landmark in the field of asymmetric catalysis.[1] Chiral diene ligands have displayed higher activity and enantioselectivities than chiral diphosphine ligands in a number of rhodium- and iridium-catalyzed reactions.[2−4] Of the several of chiral diene backbones explored by our group[2] and others,[3−5] 2,5-disubstituted [2.2.1] and [2.2.2] bicyclic olefins have emerged as privileged structures, forming stable rhodium complexes and displaying consistently high levels of enantiocontrol and activity. Chiral 2,5-disubstituted bicyclo[2.2.1]heptadienes (nbd*) are ideal scaffolds as they can be efficiently generated through the palladium-catalyzed asymmetric hydrosilylation of norbornadiene.[6] However, attempts to expand the nbd* substitution pattern to aromatic groups were foiled by the instability of the resulting 2,5-arylbicyclo[2.2.1]heptadienes (Ar-nbd*).[2a] These downfalls with the nbd* backbone led us to investigate the structurally similar 2,5-disubstituted bicyclo[2.2.2]octadiene (bod*) ligands of which we have recently reported the preparation.[2e] The major drawbacks from the synthesis of the chiral bod* ligands are the low yielding resolution of the key intermediate, bicyclo[2.2.2]octa-2,5-dione, or the need to separate the racemic ligand by chiral HPLC in the final step. Prompted by the spectacular results obtained with the 2,5-diphenylbicyclo[2.2.2]octadiene (Ph-bod*) ligand and the very similar levels of enantiocontrol between Bn-nbd* and Bn-bod*, we set out to reinvestigate the synthesis of 2,5-disubstituted bicyclo[2.2.1]heptadienes. We present herein a highly efficient two-step synthesis of the chiral methyl, benzyl, and phenyl disubstituted bicyclo[2.2.1]heptadienes, from the easily accessible chiral bicyclo[2.2.2]hepta-2,5-dione.[7,8] This novel route allows a rapid access to previously unattainable Me and Ph substituted bicyclo[2.2.1]hepta-2,5-dienes. The catalytic activity of the $[RhCl(nbd*)]_2$ complexes in the 1,4-addition of phenylboronic acid to cyclic enones and the 1,2-addition to *N*-sulfonylimines is presented.

Our previously disclosed synthetic route for Bn-nbd* involved the circuitous mono acetal protection of chiral diketone (*R*,*R*)-**1**. This route was chosen because the corresponding bistriflate **2** proved difficult to isolate.[7] Very recently, Van der Eycken et al. reported the synthesis of the racemic bistriflate **2** directly from the corresponding racemic diketone **1**, where the combination of a mild triflating agent ($PhNTf_2$), KHMDS, and low reaction temperature proved instrumental for the isolation of bistriflate **2** in good yield.[9] We were able to further refine these reaction conditions to obtain chiral bistriflate (*R*,*R*)-**2** reproducibly in over 85% isolated yield on a 10 mmol scale. Thus, a clean conversion of diketone (*R*,*R*)-**1** was obtained by slow addition of a toluene solution of KHMDS onto a mixture of (*R*,*R*)-**1** and 2-$PyNTf_2$ in THF (Scheme 1).[10] Bistriflate **2** was unstable and prone to rapid decomposition (formation of a black tar) if traces of acid were present, but this could be avoided by storing **2** over a small amount of anhydrous K_2CO_3.[11]

With convenient access to bistriflate (*R*,*R*)-**2**, we set forth to find optimal cross-coupling conditions with Grignard reagents. From literature precedents, we selected $NiCl_2$(dppe),[12] $PdCl_2$(dppf),[13] $Co(acac)_3$,[14] and $Fe(acac)_3$[15] as potential catalysts for

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(6) Uozumi, Y.; Lee, S.-Y.; Hayashi, T. *Tetrahedron Lett.* **1992**, *33*, 7185. The asymmetric hydrosilylation produces a chiral disilylnorbornane of >99% ee, which is converted into norbornanedione (**1**) by way of norbornanediol.

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(11) When stored over K_2CO_3, bistriflate (*R*,*R*)-**2** showed no sign of decomposition at R.T. for several weeks.

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SCHEME 1. Optimized Synthesis of Bistriflate (*R,R*)-2

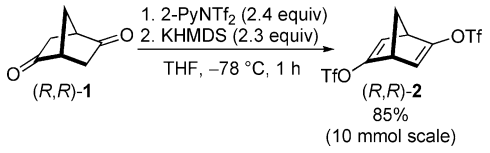
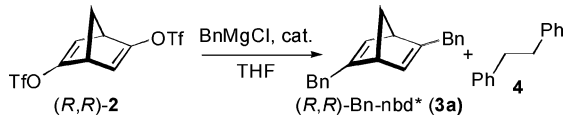


TABLE 1. Screening of Catalyst Systems for the Grignard Cross-Coupling of Bistriflate (*R,R*)-2 with BnMgCl[a]



entry	cat. (mol %)	*T* (°C)	*t* (h)[b]	**3a**/**4**[c]	yield (%)[d]
1	$NiCl_2$(dppe), 1	40	1	0.7	44
2	$PdCl_2$(dppf), 1	40	1	0.6	45
3	Co(acac)$_3$, 5[e]	0	0.25	0.6	28
4	Fe(acac)$_3$, 5[e]	0	0.25	13	98

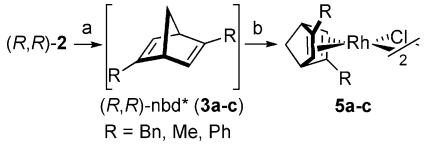
[a] To a mixture of bistriflate (*R,R*)-**2** (0.25 mmol, 1 equiv) and catalyst in THF (2.5 mL, 0.1 M) was added BnMgCl (1.0 mmol, 1 M in Et_2O, 4 equiv) at 0 °C, and the mixture was stirred at the indicated temperature. [b] Time for complete conversion of (*R,R*)-**2** (GC/MS). [c] Ratio of products determined by ^{1}H NMR. [d] Yield calculated from the mixture of (*R,R*)-**3a** and **4**. [e] NMP (1 equiv relative to BnMgCl) used as cosolvent. dppe: 1,2-bis(diphenylphosphino)ethane; dppf: 1,1′-bis(diphenylphosphino)ferrocene; NMP: *N*-methylpyrrolidinone.

the Grignard cross-coupling. As a model reaction, we chose the reaction of bistriflate (*R,R*)-**2** with four equivalents BnMgCl, which yields the stable and isolable (*R,R*)-Bn-nbd* diene. The results are depicted in Table 1.

The palladium- and nickel-catalyzed cross-coupling reactions (Table 1, entries 1 and 2) displayed very similar product profiles and proceeded swiftly to lead to complete conversion of the starting bistriflate (*R,R*)-**2** in less than 1 h (GC/MS analysis). These reactions were hampered by a significant amount of homocoupling product, 1,2-diphenylethane (**4**), which consumed the excess BnMgCl employed.[16] Use of a larger excess of BnMgCl (6 equiv) leads to a higher yield of diene (*R,R*)-**3a**, but the product is contaminated with several equivalents a **4**.[17] Gratifyingly, the iron-catalyzed reaction provided an almost quantitative yield of (*R,R*)-**3a** in less than 5 min with the end product being contaminated with only a minute amount of **4** (7 mol %) (Table 1, entry 4).

With efficient cross-coupling conditions in hand, we next turned our attention to the synthesis of Me-nbd* and Ph-nbd* ligands. Bistriflate (*R,R*)-**2** reacted smoothly with MeMgBr to yield (*R,R*)-2,5-dimethylbicyclo[2.2.1]heptadiene ((*R,R*)-Me-nbd*, **3b**) as a volatile compound which rendered its isolation in an analytically pure form exceedingly difficult.[18] In the case

TABLE 2. Iron-Catalyzed Cross-Coupling and Rhodium-Complexation Sequence[a]



entry	RMgX	product	yield (%)[b]
1	BnMgCl[c]	[RhCl((*R,R*)-Bn-nbd*)]$_2$ (**5a**)	80
2	MeMgBr[d]	[RhCl((*R,R*)-Me-nbd*)]$_2$ (**5b**)	50
3	PhMgBr[e]	[RhCl((*R,R*)-Ph-nbd*)]$_2$ (**5c**)	55

[a] Reagent and conditions: (a) (*R,R*)-**2** (1 equiv), RMgX (4 equiv), Fe(acac)$_3$ (5 mol %), THF/NMP (*N*-methylpyrrolidinone, 20/1, 0.1 M), 0 °C, 5 min; (b) [RhCl(C_2H_4)$_2$]$_2$ (0.5 equiv), toluene, 25 °C, 2 h. [b] Isolated yield over 2 steps. [c] 2 M in THF. [d] 1 M in Et_2O. [e] 3 M in Et_2O.

of the cross-coupling with PhMgBr, the reaction yielded the desired (*R,R*)-Ph-nbd* (**3c**) along with a significant amount of biphenyl due to the homocoupling of the Grignard reagent. Although GC/MS analysis of the crude reaction mixture was very clean, all attempts to obtain a pure sample of (*R,R*)-Ph-nbd* (**3c**) were frustrated by its decomposition in solution and its contamination by biphenyl. To circumvent the problem associated with the isolation of (*R,R*)-Me-nbd* (**3b**) and (*R,R*)-Ph-nbd* (**3c**), the crude dienes were reacted directly with 0.5 equivalents of [RhCl(C_2H_4)$_2$]$_2$ in toluene (Table 2). This led to the formation of the corresponding [RhCl(nbd*)]$_2$ (**5a**−**c**) complexes which could be isolated in analytically pure form by chromatography on silica gel.

To assess whether the Ph-nbd* decomposes when subjected to light or acid or both, a fresh sample of Ph-nbd* in C_6D_6 was shielded from light while another sample was stored over K_2CO_3. Two control samples were prepared; one was left in C_6D_6 under ambient conditions while the other was kept at −30 °C. The decomposition rates of the Ph-nbd* samples were monitored by ^{1}H NMR. The decomposition of the Ph-nbd* C_6D_6 solutions displayed roughly zero-order kinetics, 5.7×10^{-3} h^{-1} ($t_{1/2} \approx$ 75 h) and 6.6×10^{-3} h^{-1} ($t_{1/2} \approx 62$ h) for the sample stored over K_2CO_3 and the sample shielded from light, respectively. The control sample under ambient conditions decomposed only slightly faster (8.0×10^{-3} h^{-1}, $t_{1/2} \approx 54$ h), although complete decomposition of Ph-nbd* in $CDCl_3$ occurred in less than 24 h. The sample at −30 °C showed only a small amount of decomposition after 5 days. The origin of the instability of the Ph-nbd* is presumably due to the presence of a styrene moiety in a strained bicyclic[2.2.1] core, and this effectively lowers π^* of the alkene rendering it highly reactive and prone to radical and acid-catalyzed decomposition. Although it leads to inherent instability of the ligand, this property is key for increasing the stability of the corresponding [RhCl(Ph-nbd*)]$_2$ complex.

The rhodium dimer [RhCl(Ph-nbd*)]$_2$ (**5c**) proved to be remarkably stable and showed no sign of decomposition when its toluene solution was exposed to air for several weeks. Moreover, the melting point of **5c** was over 300 °C (in an air atmosphere) and the complex remained stable at this elevated temperature. This is in contrast with the [RhCl(Bn-nbd*)]$_2$ complex which slowly decomposed at its melting point (163−165 °C). The X-ray crystal structure of [RhCl((*R,R*)-Ph-nbd*)]$_2$ (**5c**) is depicted in Figure 1. Analysis of the key structural parameters of **5c** reveals a very close resemblance with the parent [RhCl((*S,S*)-Ph-bod*)]$_2$ dimer.[2e,f] Hence, the Rh−Cl bond distance 2.4001(6) (vs 2.405(3) Å for [RhCl(Ph-bod*)]$_2$), the alkene bond distance (C(1)−C(2)) 1.407(3) Å (vs. 1.42(1) Å for [RhCl(Ph-bod*)]$_2$), and the bite angle (C(2)−Rh(1)-C(4)) 67.64(9)° (vs. 67.8(3)° for [RhCl(Ph-bod*)]$_2$) are in close

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(16) In the GC/MS analysis of the reaction mixture, a significant amount of monocoupled product in which the triflate function has been reduced is observed.

(17) The separation of **4** from **3a** is difficult due to the low polarity of these compounds (R_f > 0.6 in pentane). Thus, minimizing the amount of **4** is necessary for obtaining Bn-nbd* with acceptable purity.

(18) The low molecular weight, 120 g/mol, and its branched structure contribute to making (*R,R*)-Me-nbd* a highly volatile compound.

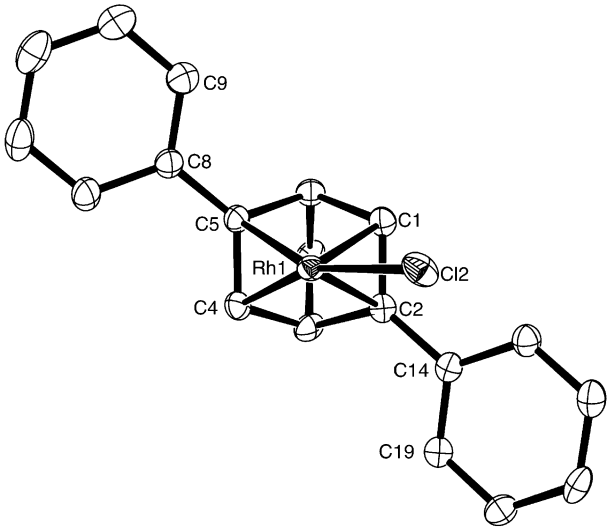
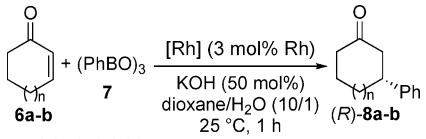


FIGURE 1. ORTEP illustration of [RhCl((*R*,*R*)-Ph-nbd*)]$_2$ (**5c**) with thermal ellipsoids at the 50% probability level (shown as a monomer for clarity). Selected bond distances (Å) and angles (°): Rh(1)−Cl(2), 2.4001(6); Rh(1)−C(1), 2.080(2); Rh(1)−C(2), 2.127(2); C(1)−C(2), 1.407(3); C(4)−C(5), 1.414(3); C(2)−Rh(1)−C(5), 81.94(8); C(1)−Rh(1)-C(4), 81.19(9); C(2)−Rh(1)−C(4), 67.64(9); C(1)−C(2)−C(4)−C(5), 1.1(2); C(1)−C(2)−C(14)−C(19), −179.7(2); C(4)−C(5)−C(8)−C(9), 166.4(2).

TABLE 3. Asymmetric 1,4-Addition of Phenylboronic Acid to Cyclic Enones Catalyzed by [RhCl(nbd*)]$_2$ (5a−c) Complexes[a]



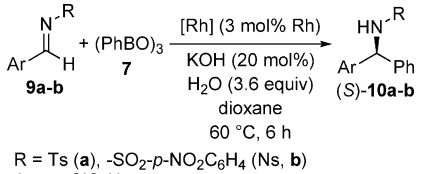
entry	**6**	[RhCl(nbd*)]$_2$	yield (%)[b]	% ee[c]
1	**6a**	[RhCl(Me-nbd*)]$_2$ (**5b**)	90 (**8a**)	95
2	**6a**	[RhCl(Bn-nbd*)]$_2$ (**5a**)	87 (**8a**)	96
3	**6a**	[RhCl(Ph-nbd*)]$_2$ (**5c**)	89 (**8a**)	97
4	**6b**	[RhCl(Me-nbd*)]$_2$ (**5b**)	86 (**8b**)	85
5	**6b**	[RhCl(Ph-nbd*)]$_2$ (**5c**)	92 (**8b**)	96

[a] The reaction was carried out with **6** (0.5 mmol, 1 equiv), **7** (0.2 mmol, 1.2 equiv B), [RhCl((nbd*)]$_2$ (**5**) (3 mol % Rh), and 1.5 M aq KOH (0.25 mmol, 0.17 mL, 0.5 equiv) in 1,4-dioxane (1.7 mL) at 25 °C for 1 h. [b] Isolated yield after silica gel chromatography. [c] Determined by HPLC analysis with a chiral stationary phase column (Chiracel OD−H for **8a** and Chiracel OB−H for **8b**).

agreement. The elongated alkene bond in **5c** reveals predominant back-bonding of the rhodium center onto the alkene. The small dihedral angle between the double bond and the plane of the phenyl group (−179.7(2)° and 166.4(2)° for C(1)−C(2)−C(14)−C(19) and C(4)−C(5)-C(8)−C(9), respectively) indicates conjugation of the π system; this effect further reinforces the back-bonding through delocalization and probably accounts for the higher stability of [RhCl(Ph-nbd*)]$_2$ (**5c**) over [RhCl(Bn-nbd*)]$_2$ (**5a**). The similarities between the solid-state structures of [RhCl(Ph-nbd*)]$_2$ (**5c**) and [RhCl(Ph-bod*)]$_2$ is somewhat surprising when one considers the large difference in stability between the free Ph-nbd* and Ph-bod* dienes.[19]

The catalytic activity of these new complexes in the 1,4-addition of phenylboronic acid to cyclic enones was evaluated (Table 3). The high level of enantiocontrol achieved by [RhCl((*R*,*R*)-Me-nbd*)]$_2$ (**5b**), 95% ee, (Table 3, entry 1) is truly impressive, given the small size of the Me-nbd* ligand with a molecular weight of only 120 g/mol and only two methyl groups effecting the enantiocontrol of the reaction. The increase of steric bulk of the substituents on the nbd* ligand (Table 3, entries 2 and 3) leads to incremental but marginal increase in enantioselectivity. The 1,4-addition to 2-cyclopentenone (**6b**), a much more demanding substrate, proved more telling of the difference of steric effects between (*R*,*R*)-Me-nbd* (85% ee) and (*R*,*R*)-Ph-nbd* (96% ee) (Table 3, entries 4 and 5); the latter is close to the enantioselectivity previously reported with the (*R*,*R*)-Ph-bod* ligand (99% ee).[2e]

TABLE 4. Asymmetric 1,2-Addition of Phenylboronic Acid to *N*-Sulfonylimine Catalyzed by [RhCl(nbd*)]$_2$ (5a−c)[a]



entry	**9**	[RhCl(nbd*)]$_2$	yield (%)[b]	% ee[c]
1	**9a**	[RhCl(Me-nbd*)]$_2$ (**5b**)	96 (**10a**)	89
2	**9a**	[RhCl(Bn-nbd*)]$_2$ (**5a**)	98 (**10a**)	92[d]
3	**9a**	[RhCl(Ph-nbd*)]$_2$ (**5c**)	96 (**10a**)	99
4	**9b**	[RhCl(Me-nbd*)]$_2$ (**5b**)	93 (**10b**)	82
5	**9b**	[RhCl(Bn-nbd*)]$_2$ (**5a**)	88 (**10b**)	81[e]
6	**9b**	[RhCl(Ph-nbd*)]$_2$ (**5c**)	92 (**10b**)	98

[a] The reaction was carried out with **9** (0.10 mmol, 1 equiv), **7** (0.12 mmol, 3.6 equiv B), [RhCl((nbd*)]$_2$ (**5**) (3 mol % Rh), and 3.1 M aq KOH (0.02 mmol, 6.5 μL, 0.2 equiv) in 1,4-dioxane 0.4 mL) at 60 °C for 6 h. [b] Isolated yield after silica gel chromatography. [c] Determined by HPLC analysis with a chiral stationary phase column (Chiracel OD−H). [d] Reported in ref 2c. [e] Reported in ref 2d.

To gain further insight into the reaction scope offered by the Me-nbd* and Ph-nbd* ligands, we investigated the rhodium-catalyzed 1,2-addition of phenylboronic acid to *N*-sulfonylimines. This reaction is much more sensitive to the size of the substituents on the diene and on the backbone-type.[2c,d] Both the 1,2-addition to *N*-tosyl and *N*-nosyl imines was investigated, the latter being more synthetically useful though more challenging.

The enantioselectivities observed with (*R*,*R*)-Me-nbd* and (*R*,*R*)-Bn-nbd* were quite similar for both imines **9a** and **9b** (Table 4, entries 1 vs 2 and 4 vs 5). It is remarkable that the (*R*,*R*)-Ph-nbd* ligand showed high enantiocontrol in the phenylation of the imines **9a** and **9b** (Table 4, entries 3 and 6). Particularly, the enantioselectivity of 98% ee observed for *N*-nosyl imine **9b** is striking because the closely related (*R*,*R*)-Ph-bod* ligand only gave 89% ee under the same reactions conditions.[2d] Thus, subtle steric and electronic differences in these ligands that are not revealed by comparison of structural features in the X-ray analysis bring about a significant effect on the enantioselection process.

In summary, two new rhodium complexes bearing chiral methyl and phenyl 2,5-disubstituted bicyclo[2.2.1]heptadiene ligands were synthesized and fully characterized. The synthesis is highly efficient, and the corresponding rhodium complexes ([RhCl(nbd*)]$_2$) can be isolated in 42−68% yield over three steps starting from the readily available (*R*,*R*)-2,5-norbornanedione. These new rhodium complexes displayed high levels of activity and enantioselectivities in the 1,4-addition and 1,2-addition of phenylboronic acid to cyclic enones and to aryl *N*-sulfonyl imines, respectively. The [RhCl(Ph-nbd*)]$_2$ complex performs exceptionally well in both reactions and leads to enantioselectivities that are similar or better than the parent [RhCl(Ph-bod*)]$_2$ complex.

Experimental Section

Preparation of Bistriflate (*R,R*)-2. To a solution diketone (*R,R*)-**1**[8] (1.24 g, 10 mmol, 1 equiv) and 2-PyNTf$_2$[10] (8.60 g, 24 mmol, 2.4 equiv) in dry THF (30 mL, 0.30 M) at −78 °C was slowly added KHMDS (44 mL, 0.50 M in toluene, 23 mmol, 2.3 equiv) affording a clear, light-red solution. Stirring was further continued for 1 h at −78 °C at which point the reaction turned light brown and turbid. The reaction was quenched with a sat. $NaHCO_3$ solution at this temperature. After warming to room temperature, the layers were separated and the aqueous layer was extracted twice with hexane. The combined organic layers were sequentially washed with 5% NaOH solution (until the aqueous layer remained colorless), water, and brine. The organic layer was dried over K_2CO_3. The crude product was purified by flash chromatography over silica gel (hexane/ethyl acetate 95/5) affording 3.30 g (8.5 mmol, 85%) of bistriflate (*R,R*)-**2** as a colorless oil. To avoid decomposition, the product was stored over K_2CO_3. Racemic bistriflate **2** has been reported in ref 9. ^{1}H NMR ($CDCl_3$): δ 2.60 (t, J = 1.8 Hz, 2H), 3.51 (m, 2H), 6.49 (dd (app. t), J = 2.4, 2.4 Hz, 2H) ppm; ^{13}C-{^{1}H} NMR ($CDCl_3$): 50.3 (CH), 73.1 (CH_2), 118.5 (q, J_{C-F} = 321 Hz, CF_3), 123.7 (CH), 168.2 (C) ppm; $[\alpha]^D_{25}$ +24 (*c* 0.35, $CHCl_3$).

Procedure for the Catalyst Screening for Cross-Coupling of Bistriflate (*R,R*)-2 with Benzylmagnesium Chloride (Table 1). To a solution of bistriflate (*R,R*)-**2** (97 mg, 0.25 mmol, 1 equiv), NMP (120 μL, Table 1, entries 3 and 4), and a catalyst (amount indicated in Table 1) in THF (2.5 mL, 0.1 M) at 0 °C was added the BnMgCl (1 mL, 1 mmol, 1.0 M in Et_2O, 4 equiv) under nitrogen. The reaction was stirred for the indicated time and temperature before being quenched by sat. NH_4Cl at 0 °C. The aqueous layer was extracted three times with hexane. The combined organic extracts were washed three times with water followed by a wash with brine and dried over $MgSO_4$. The crude product was passed through a plug of silica gel, eluted with hexane, and concentrated in vacuo. The crude product, consisting of (*R,R*)-Bn-nbd* (**3b**) and 1,2-diphenylethane (**4**), was analyzed by ^{1}H NMR and compared to the spectral data previously reported in ref 2a.

A Typical Procedure for the Preparation of [RhCl(nbd*)]$_2$ Complexes. Preparation of [RhCl((*R,R*)-Bn-nbd*)]$_2$ (5a) (Table 2, entry 1). A solution of BnMgCl (2 mL, 2 mmol, 1.0 M in Et_2O, 4 equiv) was added dropwise to a solution of bistriflate (*R,R*)-**2** (194 mg. 0.50 mmol), Fe(acac)$_3$, (8.8 mg, 5 mol %), and NMP (250 μL) in THF (5 mL, 0.1 M) at 0 °C under nitrogen. The initial clear, orange solution became pale yellow before turning dark brown toward the end of the addition. The reaction mixture was further stirred for 5 min at that temperature before being quenched by sat. NH_4Cl. The aqueous layer was extracted three times with hexane. The combined organic extracts were washed three times with water followed by a wash with brine and dried over K_2CO_3. The crude product was passed through a plug of silica gel and eluted with hexane. Crude (*R,R*)-Bn-nbd* (**3a**) was characterized by comparison of the spectral and analytical data with those reported in the literature.[2a] The crude product was dissolved in toluene (5 mL, 0.1 M), and [RhCl(C_2H_4)$_2$]$_2$ (97 mg, 0.25 mmol, 1 equiv) was added. The mixture was stirred under nitrogen for 2 h and the solvents were removed in vacuo. The product was purified by flash chromatography over silica gel (hexane/CH_2Cl_2, 1/1) to yield a 164 mg (0.20 mmol, 80%) of complex **5a** as a light-yellow crystalline solid. ^{1}H NMR ($CDCl_3$): δ 0.77 (s, 4H), 3.08 (d, J = 14.4 Hz, 4H), 3.51 (s, 4H), 3.76 (d, J = 14.4 Hz, 4H), 3.80 (s, 4H), 7.26 (d, J = 7.0 Hz, 4H), 7.34 (t, J = 7.5 Hz, 8H), 7.26 (d, J = 7.5 Hz, 8H). ^{13}C{^{1}H} NMR ($CDCl_3$): 40.6 (CH_2), 47.7 (d, J_{C-Rh} = 10.8 Hz, CH), 53.3 (d, J_{C-Rh} = 3.0 Hz, CH_2), 60.1 (d, J_{C-Rh} = 7.1 Hz, CH), 70.1 (d, J_{C-Rh} = 11.4 Hz, C), 126.4 (CH), 128.5 (CH), 129.1 (CH), 138.7 (C) ppm; $[\alpha]^D_{25}$ +56 (*c* 0.60, $CHCl_3$); mp = 163−165 °C (dec).

Preparation of [RhCl((*R,R*)-Me-nbd*)]$_2$ (5b). The reaction was run on 0.50 mmol of (*R,R*)-**2** using a MeMgCl (3 M in Et_2O) solution. Hexane was substituted for pentane. The residual solvent was carefully evaporated on a rotary evaporator to yield crude (*R,R*)-Me-nbd* (**3b**). ^{1}H NMR ($CDCl_3$): δ 1.76 (d, J = 1.8 Hz, 6H), 1.87 (t, J = 1.7 Hz, 2H), 3.02 (m, 2H), 6.06 (dd (app. t), J = 1.9, 2.0 Hz, 2H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$): 16.9 (CH_3), 54.9 (CH), 71.7 (CH_2), 132.5 (CH), 154.9 (C) ppm. Complex **5b** was isolated as an orange solid after flash chromatography (hexane/CH_2Cl_2, 60/40), 65 mg (0.13 mmol, 50%). ^{1}H NMR ($CDCl_3$): δ 1.22 (s, 2H), 1.73 (d, J = 11.0 Hz, 6H), 3.47 (d, J = 1.9 Hz, 2H), 3.55 (d, J = 1.5 Hz, 2H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$): 20.3 (d, J_{C-Rh} = 2 Hz, CH_3), 46.9 (d, J_{C-Rh} = 10.9 Hz, CH), 55.6 (d, J_{C-Rh} = 3.6 Hz, CH_2), 58.6 (d, J_{C-Rh} = 7.8 Hz, CH), 66.5 (d, J_{C-Rh} = 11.3 Hz, C) ppm; $[\alpha]^D_{25}$ −285 (*c* 0.6, $CHCl_3$); mp 137−139 °C; anal. calcd for $C_{18}H_{24}Cl_2Rh_2$: C, 41.81, H, 4.68; found C, 42.08, H, 4.55.

Preparation of [RhCl((*R,R*)-Ph-nbd*)]$_2$ (5c). The reaction was run on 0.50 mmol of (*R,R*)-**2** using a solution of PhMgBr (2.5 M in Et_2O) to yield crude Ph-nbd* (**3c**). ^{1}H NMR ($CDCl_3$): δ 2.31 (t, J = 1.4 Hz, 2H), 4.10 (t, J = 2.0 Hz, 2H), 7.06 (dd (app. t), J = 2.2, 2.1 Hz, 2H), 7.49−7.46 (m, 6H), 7.63−7.65 (m, 4H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$): 52.3 (CH), 69.7 (CH_2), 124.9 (CH), 127.3 (CH), 128.5 (CH), 134.6 (CH), 141.3 (C), 156.9 (C) ppm. Complex **5c** was isolated as a bright-red crystalline solid after flash chromatography (hexane/CH_2Cl_2, 60/40), 105 mg (0.14 mmol, 55%). ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 2H), 3.67 (d, J = 2.4 Hz, 2H), 4.21 (dd, J = 1.4, 1.7 Hz, 2H), 7.36−7.37 (m, 6H), 7.50−7.53 (m, 4H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$): 41.3 (d, J_{C-Rh} = 10.8 Hz, CH), 52.9 (d, J_{C-Rh} = 2.6 Hz, CH_2), 57.9 (d, J_{C-Rh} = 6.8 Hz, CH), 65.1 (d, J_{C-Rh} = 10.9 Hz, C), 127.2 (CH), 127.8 (CH), 128.2 (CH), 138.5 (C) ppm; $[\alpha]^D_{25}$ −52 (*c* 1.05, $CHCl_3$); mp > 300 °C; anal. calcd for $C_{38}H_{32}Cl_2Rh_2 \cdot H_2O$: C, 58.26, H, 4.37; found C, 58.63, H, 4.24.

Genral Procedure for the Asymmetric 1,4-Addtion of Phenylboronic Acid to Cyclic Enones (6). To a solution of [RhCl-(nbd*)]$_2$ (**5**) (3 mol % Rh) and phenylboroxine (**7**, 62 mg, 0.20 mmol, 1.2 equiv of boron) in 1.7 mL of 1,4-dioxane was added the cyclic enone **6** (0.50 mmol, 1 equiv) and KOH aq. (1.5 M, 0.17 mL, 0.25 mmol, 0.5 equiv). The solution was stirred at 25 °C for 1 h. The resulting mixture was passed through a short silica gel pad and eluted with Et_2O. Evaporation of the solvent followed by chromatography over silica gel (hexane/ethyl acetate = 95/5) gave (*R*)-3-phenylcycloalkanone **8** as a colorless oil. Compounds **8a**−**b** were fully characterized by comparison of the spectral and analytical data with those reported in the literature.[20]

General Procedure for the Asymmetric 1,2-Addition of Phenylboronic Acid to *N*-Sulfonyl Imines. To a solution of [RhCl-(nbd*)]$_2$ **5** (3 mol % Rh), phenylboroxine **7** (0.12 mmol, 1.2 equiv), and imine **9** (0.10 mmol, 1 equiv) in 1,4-dioxane (0.4 mL) was added KOH aq. (6.5 μL, 3.1 M, 0.2 equiv, H_2O: 1 equiv to boron) at room temperature. The resulting homogeneous solution was stirred for 6 h at 60 °C. The mixture was passed through a short silica gel pad and eluted with Et_2O. Evaporation of the solvent followed by chromatography over silica gel (hexane/ethyl acetate = 4/1) gave the arylated product **10**. Compounds **10a** and **10b** were fully characterized by comparison of their spectral and analytical data with those reported in the literature.[2c,d]

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Supporting Information Available: Experimental details for the acquisition and structure refinement for rhodium complex (*R,R*)-**5c**, the corresponding CIF file, and spectroscopic data for all new compounds are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Ph-bod* can be easily handled and stored indefinitely at room temperature.

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