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C_2-Symmetric bicyclo[3.3.1]nona-2,6-diene and bicyclo[3.3.2]deca-2,6-diene: new chiral diene ligands based on the 1,5-cyclooctadiene framework

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Abstract—As a new type of C_2-symmetric chiral diene ligands, which coordinate to a metal by their 1,5-cyclooctadiene framework, we prepared 2,6-disubstituted bicyclo[3.3.1]nona-2,6-diene (bnd*) and bicyclo[3.3.2]deca-2,6-diene (bdd*), and examined their catalytic activity and enantioselectivity for rhodium-catalyzed asymmetric 1,4-addition to α,β-unsaturated ketones and 1,2-addition to *N*-sulfonylimines. High enantioselectivity of the Ph-bnd* ligand was observed in the addition of phenylboroxine to *N*-tosylimine and *N*-4-nitrobenzenesulfonylimine of 4-chlorobenzaldehyde to give phenyl(4-chlorophenyl)methylamines in high enantiomeric excess (98–99% ee).

1. Introduction

Chiral dienes, as a new type of chiral ligand, have been gaining a prominent position in asymmetric reactions catalyzed by late transition metal complexes.[1] They have been demonstrated to be highly effective especially in rhodium-catalyzed aryl transfer reactions, where the chiral diene–rhodium catalysts showed higher catalytic activity and/or higher enantioselectivity than chiral phosphine–rhodium catalysts. One common feature of the chiral dienes reported to date is that they coordinate to a metal with their 1,4-cyclohexadiene moiety (Fig. 1). This common 1,4-cyclohexadiene framework is found in 2,5-dibenzylbicyclo[2.2.1]hepta-2,5-diene (Bn-nbd*),[2,3] which we reported as the first example of diene ligands in 2003, and in C_2-symmetric 2,5-disubstituted bicyclo[2.2.2]octa-2,5-dienes (e.g., Bn-bod* and Ph-bod*) which have been applied successfully to rhodium-catalyzed asymmetric additions of arylboron reagents to α,β-unsaturated ketones[4] and *N*-tosylarylimines,[5] and asymmetric arylative cyclization of alkynals.[6] Carreira's C_1-symmetric bicyclo[2.2.2]octa-2,5-dienes,[7,8] which were readily prepared from (−)-carvone, also have the 1,4-cyclohexadiene moiety as coordinating functionality. Very recently, we reported the preparation of 2,6-diphenylbicyclo[3.3.1]nona-2.6-diene (Ph-bnd*) and its application to rhodium-catalyzed asymmetric arylation of *N*-4-nitrobenzenesulfonylimines. This chiral diene is different from other 1,4-cyclohexadiene-based dienes because it coordinates to a metal through its 1,5-cyclooctadiene framework.[9] Herein we report in detail on the new chiral dienes whose diene framework is 1,5-cyclooctadiene, that is, 2,6-disubstituted bicyclo[3.3.1]nona-2,6-diene (bnd*) and its homologue bicyclo[3.3.2]deca-2,6-diene (bdd*). Structural features of their rhodium complexes and the results obtained for the rhodium-catalyzed asymmetric phenylation reactions are also described.

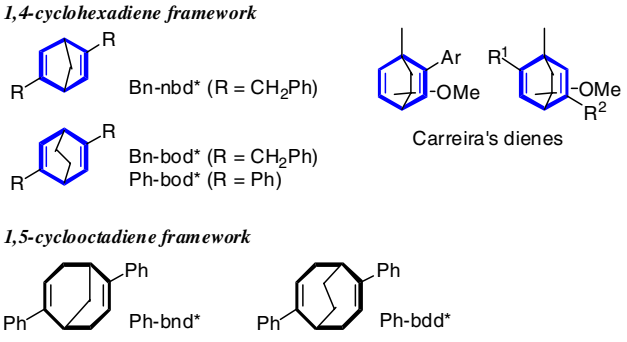

Figure 1. Chiral dienes.

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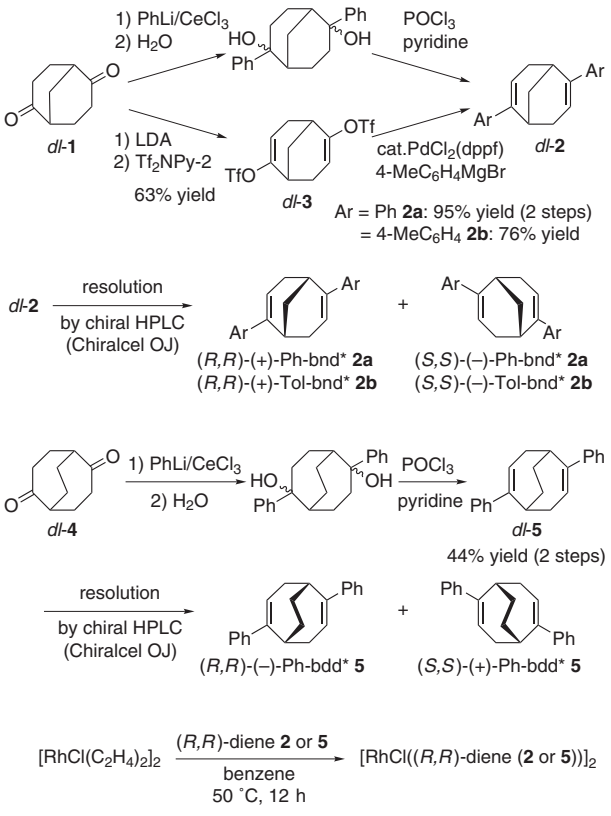
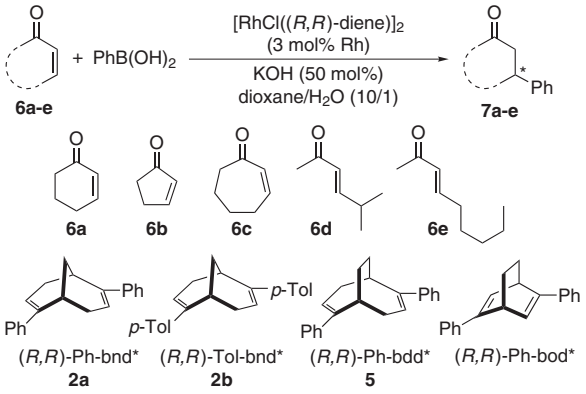
2. Results and discussion

Scheme 1 shows the synthetic pathways to the enantiomerically pure 2,6-disubstituted bicyclo[3.3.1]nona-2,6-diene (bnd*) and bicyclo[3.3.2]deca-2,6-diene (bdd*). Starting racemic diketone, bicyclo[3.3.1]nonane-2,6-dione *dl*-**1** was readily obtained through condensation of dimethyl malonate with paraformaldehyde according to the procedures reported by Schaefer.[10] Phenylation of two carbonyl groups in diketone *dl*-**1** with an excess (2.6 equiv) of a phenylcerium reagent generated from phenyllithium and cerium trichloride in THF gave a quantitative yield of the diol, dehydration of which with phosphorus oxychloride and pyridine gave racemic 2,6-diphenylbicyclo[3.3.1]nona-2,6-diene *dl*-**2a** (Ph-bnd) in 95% yield (two steps). Alternatively, racemic 2,6-disubstituted dienes **2** can be prepared by way of ditriflate *dl*-**3**, which is obtained by treatment of diketone **1** with lithium diisopropylamide (LDA) and *N*-(2-pyridyl)triflimide. Thus, for example, palladium-catalyzed Grignard cross-coupling of *dl*-**3** with 4-methylphenylmagnesium bromide in ether in the presence of $PdCl_2(dppf)$[11] provided 2,6-di(4-methylphenyl)bicyclo[3.3.1]nona-2,6-diene *dl*-**2b** (Tol-bnd). Another type of 2,6-disubstituted diene, 2,6-diphenylbicyclo[3.3.2]deca-2,6-diene *dl*-**5** (Ph-bdd), which is also expected to coordinate to a metal with its 1,5-cyclooctadiene moiety, was prepared, in a similar manner to Ph-bnd *dl*-**2a**, starting with bicyclo[3.3.2]decane-2,6-dione *dl*-**4**[12] by the addition of phenylcerium followed by dehydration of the resulting diol.

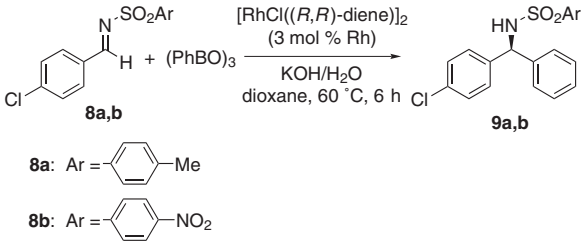


Scheme 1.

Resolution of the C_2-symmetric dienes *dl*-**2a**, **b**, and **5** thus obtained was efficiently carried out by use of a chiral stationary phase column (Chiralcel OJ) of a preparative size to give both enantiomers of these dienes in an enantiomerically pure form. The absolute configuration of (−)-Tol-bnd* **2b** was determined to be (*S*,*S*) by X-ray crystal analysis of its rhodium complex (vide infra). The other dienes, Ph-bnd* **2a** and Ph-bdd* **5**, were assigned to be (−)-(*S*,*S*) and (−)-(*R*,*R*), respectively, by consideration of the stereochemical reaction pathway[2–5] in the catalytic asymmetric phenylation reactions shown in Schemes 2 and 3.



Scheme 2.



Scheme 3.

Treatment of the enantiomerically pure dienes (*R*,*R*)-**2a**, **b**, and **5** with $[RhCl(C_2H_4)_2]_2$ in benzene at 50 °C for 12 h gave high yields of the corresponding diene–rhodium complexes. Figure 2 shows the ^1H NMR spectra of Ph-bnd* **2a** and its rhodium complex. On complexation of **2a** with rhodium, the olefinic proton H^3 at 5.97 ppm was largely shifted to a higher field (4.70 ppm). A lower field shift of the allylic protons H^4 and a higher field shift of the protons H^5 and H^9 were also observed on complexation. The chemical shifts and coupling constants of $[RhCl(Ph\text{-}bnd^*\ \mathbf{2a})]_2$ in ^{13}C NMR are shown in Figure 3. The couplings between rhodium and carbons at the olefin and ipso position on the phenyl group were observed by coordination to the rhodium. These observations support the idea that the chiral diene ligand **2a** forms a stable chelating complex with the rhodium.

The X-ray crystal structure of $[RhCl((S,S)\text{-}Tol\text{-}bnd^*\ \mathbf{2b})]_2$ is shown in Figure 4. The steric difference between

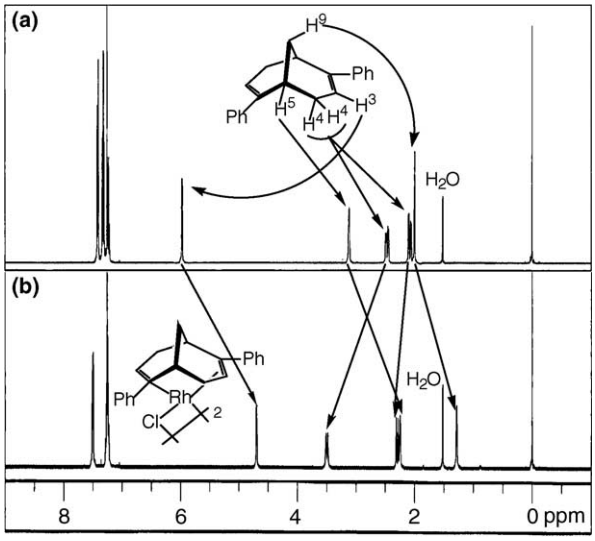


Figure 2. Comparison of the ^{1}H NMR spectra (at 500 MHz in $CDCl_3$) of Ph-bnd* **2a** (a) and its rhodium complex (b).

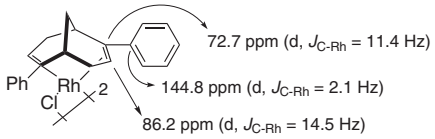


Figure 3. ^{13}C NMR spectra (at 125 MHz in $CDCl_3$) of [RhCl((*R*,*R*)-Ph-bnd* **2a**)]$_2$.

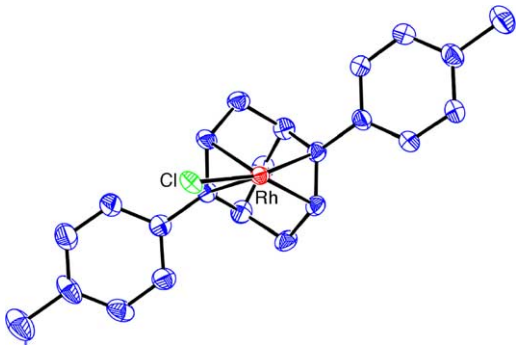


Figure 4. ORTEP illustration of [RhCl((*S*,*S*)-Tol-bnd* **2b**)]$_2$ with thermal ellipsoids drawn at the 50% probability level (shown as a monomer for clarity).

a bulky 4-methylphenyl group and a small hydrogen on the ligand is effectively dissecting the space in a C_2-fashion, thereby creating a very good chiral environment around the rhodium. Figure 5 shows the structure of the diene–rhodium moiety of this rhodium complex coordinated with Tol-bnd* **2b** and selected bond distances and angles around the rhodium atom. The data reported for [RhCl(Ph-bod*)]$_2$[4] are also shown for comparison. Two double bonds (Cα=Cβ and Cα′=Cβ′) of bnd* coordinated to the rhodium are not parallel to each other but twisted by 23°. As a result, the angles ∠Cα–Rh–Cα′ (87°) and ∠Cβ–Rh–Cβ′ (103°) are very

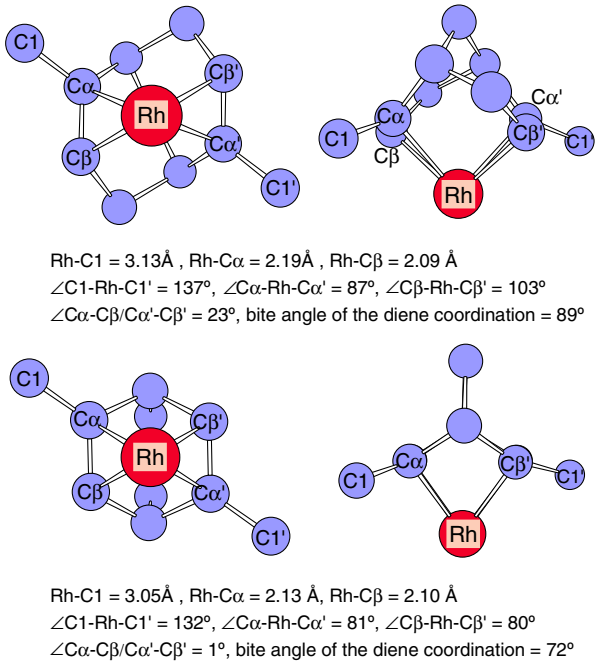


Figure 5. Selected bond distances and angles for [RhCl(Tol-bnd* **2b**)]$_2$ (upper) and [RhCl(Ph-bod*)]$_2$ (lower).

different to each other. This coordination manner is very different from non-substituted cyclooctadiene complexes such as [RhCl(cod)]$_2$[13] where the diene coordination is parallel. The twisted coordination of bnd* is probably caused by the torsion of the bridged backbone. Conversely, the 1,4-cyclohexadiene framework of the Ph-bod* complex is highly symmetric, the two double bonds coordinating to rhodium almost parallel (1°). The bite angle of the diene coordination in [RhCl(Tol-bnd*)]$_2$ is 89°, much larger than that (72°) in the bod* complex. The distance from rhodium to phenyl substituent on the olefin of Tol-bnd* (Rh–C1 = 3.13 Å) is slightly longer than that of [RhCl(Ph-bod*)]$_2$ (Rh–C1 = 3.05 Å).

The rhodium complexes coordinated with the chelating chiral dienes (*R*,*R*)-Ar-bnd* (Ar = Ph **2a** and Tol **2b**) and (*R*,*R*)-Ph-bdd* **5** were examined for their catalytic activity and enantioselectivity in the asymmetric 1,4-addition[14–16] of phenylboronic acid to α,β-unsaturated ketones **6** (Scheme 2). As a general procedure, to a solution containing a phenylboronic acid and a chiral diene–rhodium complex (3 mol%) in dioxane (1.0 mL) were added enone **6** (0.30 mmol) and 1.5 M aqueous KOH (0.10 mL), and the mixture stirred at 30–50 °C for 1–8 h. The 1,4-addition product **7** was isolated by a silica gel chromatography after filtration through a pad of silica gel. The results obtained are summarized in Table 1, which also contains the data reported using Ph-bod for comparison.[4] All the chiral diene complexes showed high catalytic activity, but unfortunately the enantioselectivity observed with Ar-bnd* **2a** and **b** and Ph-bdd* **5** was lower than that with Ph-bod* for all the α,β-unsaturated ketones examined. The enantioselectivity of not lower than 90% was observed only for two enones, 90% ee for cyclohexenone **6a** with Ph-bdd* **5**

Table 1. Asymmetric 1,4-addition of phenylboronic acid to enones **6** catalyzed by [RhCl((*R*,*R*)-diene)]$_2$[a]

Entry	6	Diene	Temp (°C)	Time (h)	Yield (%) of 7[b]	Ee[c] (%)
1	**6a**	Ph-bnd* **2a**	30	3	93 **7a**	83 (*R*)
2	**6a**	Tol-bnd* **2b**	30	3	97 **7a**	79 (*R*)
3	**6a**	Ph-bdd* **5**	30	3	98 **7a**	90 (*R*)
4[d]	**6a**	Ph-bod*	30	1	97 **7a**	96 (*R*)
5	**6b**	Ph-bnd* **2a**	50	6	86 **7b**	91 (*R*)
6	**6b**	Ph-bdd* **5**	50	8	98 **7b**	84 (*R*)
7[d]	**6b**	Ph-bod*	50	1	97 **7b**	99 (*R*)
8	**6c**	Ph-bnd* **2a**	50	6	83 **7c**	78 (*R*)
9	**6c**	Ph-bdd* **5**	50	3	90 **7c**	71 (*R*)
10[d]	**6c**	Ph-bod*	50	1	95 **7c**	92 (*R*)
11	**6d**	Ph-bnd* **2a**	50	6	88 **7d**	82 (*R*)
12	**6d**	Ph-bdd* **5**	50	3	86 **7d**	83 (*R*)
13[d]	**6d**	Ph-bod*	30	3	95 **7d**	85 (*R*)
14	**6e**	Ph-bnd* **2a**	50	6	86 **7e**	67 (*S*)
15	**6e**	Ph-bdd* **5**	50	3	85 **7e**	59 (*S*)
16[d]	**6e**	Ph-bod*	30	1	90 **7e**	83 (*S*)

[a] The reaction was carried out with enone **6a**–**e** (0.30 mmol), phenylboronic acid (0.60 mmol), [RhCl((*R*,*R*)-diene)]$_2$ (3 mol% Rh, diene = **2a**,**b**, or **5**), and 1.5 M aq KOH (0.10 mL) in dioxane (1.0 mL).
[b] Isolated yield after silica gel chromatography.
[c] Determined by HPLC analysis with chiral stationary phase columns: Chiralcel OD-H for **7a, c**–**e**; OB-H for **7b**.
[d] Reported in Ref. 4.

(entry 3) and 91% ee for cyclopentenone **6b** with Ph-bnd* **2a** (entry 5). In the phenylation of enones **6c** and **d**, the enantioselectivity was around 80% ee with both of the newly prepared dienes, bdd* and bnd*.

We have reported that the rhodium complexes of the diene ligands are much more active and enantioselective than those of the phosphorus ligands for the addition of arylboroxines to *N*-tosylimines[5] and *N*-4-nitrobenzenesulfonylimines.[9] The chiral dienes, Ph-bnd* **2a**, Ph-bdd* **5**, and Ph-bod*, were examined for their ability in the rhodium-catalyzed asymmetric addition of phenylboroxine to *N*-tosylimine **8a** and *N*-4-nitrobenzenesulfonylimine **8b** of 4-chlorobenzaldehyde giving diarylmethylamines **9** (Scheme 3). Ph-bnd* **2a** showed the highest enantioselectivity for both **8a** (99% ee) and **8b** (98% ee) (entries 1 and 4 in Table 2). The enantioselectivity of Ph-bod* is as high as that of Ph-bnd* **2a** for the phenylation of *N*-tosylimine **8a**, but it is not so high for *N*-4-nitrobenzenesulfonylimine **8b** (entries 3 and 6). Ph-bdd* **5** is also an enantioselective ligand for the phenylation of imines, although its enantioselectivity is a little lower than Ph-bnd* **2a** (entries 2 and 5).

3. Conclusions

As a new type of C_2-symmetric chiral diene ligands, we prepared 2,6-disubstituted bicyclo[3.3.1]nona-2,6-diene (bnd*) and bicyclo[3.3.2]deca-2,6-diene (bdd*), which coordinate to a metal by their 1,5-cyclooctadiene framework. Although their enantioselectivity in the rhodium-catalyzed asymmetric 1,4-addition to α,β-unsaturated ketones was not as high as that of bicyclo[2.2.2]octa-2,5-diene (bod*) ligands which we previously reported,[4] one of the bnd* ligand showed the highest enantioselectivity in the asymmetric addition of a phenylboron reagent to *N*-sulfonylimines.

4. Experimental

4.1. General

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under prepurified argon. NMR spectra were recorded at 500 MHz for ^{1}H, and 125 MHz for ^{13}C. Chemical shifts

Table 2. Asymmetric addition of phenylboroxine to imines **8** catalyzed by [RhCl((*R*,*R*)-diene)]$_2$[a]

Entry	Ar	Diene	Yield (%) of 9[b]	% Ee[c] (%)
1	4-MeC$_6$H$_4$ **8a**	Ph-bnd* **2a**	95 **9a**	99 (*S*)
2		Ph-bdd* **5**	88 **9a**	94 (*S*)
3[d]		Ph-bod*	96 **9a**	98 (*S*)
4[e]	4-NO$_2$C$_6$H$_4$ **8b**	Ph-bnd* **2a**	96 **9b**	98 (*S*)
5		Ph-bdd* **5**	99 **9b**	90 (*S*)
6[e]		Ph-bod*	96 **9b**	89 (*S*)

[a] The reaction was carried out in dioxane (1.0 mL) at 60 °C for 6 h with imine **8** (0.10 mmol) and 1.2 equiv of phenylboroxine in the presence of 20 mol% KOH, 1 equiv (with respect to boron) of H_2O, and 3 mol% Rh of [RhCl((*R*,*R*)-diene (**2a** or **5**))]$_2$.
[b] Isolated yield after silica gel chromatography.
[c] Determined by HPLC analysis with a chiral stationary phase column (Chiralcel OD-H).
[d] Reported in Ref. 5.
[e] Reported in Ref. 9.

are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^1H NMR and chloroform-*d* (δ 77.05) for ^{13}C NMR. Chiralcel OJ (2 cm$\varnothing \times$ 25 cm) was used for the separation of enantiomers of diene ligands **2** and **5**.

4.2. Materials

THF, benzene, and dioxane were distilled from sodium benzophenone-ketyl under nitrogen. Racemic bicyclo-[3.3.1]nonane-2,6-dione **1**,[10] racemic bicyclo[3.3.2]decane-2,6-dione **4**,[12] $[RhCl(C_2H_4)_2]_2$,[17] and $PdCl_2$(dppf)[11] were prepared according to the reported procedures.

4.3. (1*R*,5*R*)-2,6-Diphenylbicyclo[3.3.1]nona-2,6-diene (*R*,*R*)-2a

$CeCl_3 \cdot 7H_2O$ (969 mg, 2.6 mmol) was heated in vacuo at 140 °C for 2 h and cooled. THF (10 mL) was added and the suspension stirred for 1 h. To this suspension was added at −78 °C, phenyllithium in cyclohexane/Et_2O (2.5 mL, 1.05 M, 2.6 mmol) with stirring. After stirring was continued for 1 h, racemic bicyclo[3.3.1]nonane-2,6-dione (*dl*-**1**, 152 mg, 1.0 mmol) in THF (2.0 mL) was added, and the reaction mixture stirred at −78 °C for 6 h. Water was added to quench the reaction and the organic solvent removed in vacuo. The aqueous layer was extracted with ethyl acetate three times. The combined organic layers were dried over magnesium sulfate. Removal of the solvent gave the crude diol. To the crude diol were added pyridine (1.0 mL) and $POCl_3$ (927 mg, 6.0 mmol) at room temperature, and the mixture was heated to reflux for 12 h. After being cooled to room temperature, the reaction mixture was quenched with water, and extracted with Et_2O. The combined organic layers were washed with 2 M NaOH and water, and then dried over magnesium sulfate. Removal of the solvent gave the crude product, which was purified by preparative TLC (silica gel, hexane/Et_2O = 5/1) to give 259 mg (95% yield for two steps) of racemic 2,6-diphenylbicyclo[3.3.1]nona-2,6-diene *dl*-**2a**. ^1H NMR ($CDCl_3$): δ 2.00 (t, J = 3.1 Hz, 2H), 2.08 (dd, J = 18.1 and 5.1 Hz, 2H), 2.47 (dm, J = 18.1 Hz, 2H), 3.10–3.14 (m, 2H), 5.97 (dd, J = 5.1 and 2.4 Hz, 2H), 7.23 (t, J = 7.4 Hz, 2H), 7.32 (t, J = 7.4 Hz, 4H), 7.41 (d, J = 7.4 Hz, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.2, 29.8, 31.7, 122.6, 125.8, 126.6, 128.2, 140.2, 141.4. Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.47; H, 7.52. Enantiomerically pure (1*R*,5*R*)-2,6-diphenylbicyclo[3.3.1]nona-2,6-diene (*R*,*R*)-**2a** was obtained by separation of the racemic diene on Chiralcel OJ column with hexane/2-propanol = 2/1, flow = 12 mL/min, wavelength = 254 nm. $[\alpha]_D^{20} = +39$ (*c* 0.58, $CHCl_3$).

4.4. Preparation of [RhCl((*R*,*R*)-Ph-bnd* 2a)]$_2$

A suspension of $[RhCl(C_2H_4)_2]_2$ (117 mg, 0.60 mmol Rh) and (1*R*,5*R*)-2,6-diphenylbicyclo[3.3.1]nona-2,6-diene (*R*,*R*)-**2a** (136 mg, 0.50 mmol) in 15 mL of benzene was stirred at 50 °C for 12 h. After being cooled to room temperature, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by recrystallization (THF/hexane) to give 179 mg (87% yield) of [RhCl((*R*,*R*)-Ph-bnd* **2a**)]$_2$. ^1H NMR ($CDCl_3$): δ 1.28 (s, 4H), 2.24 (s, 4H), 2.29 (d, J = 15.1 Hz, 4H), 3.50 (dt, J = 15.1 and 3.7 Hz, 4H), 4.70 (d, J = 2.9 Hz, 4H), 7.22–7.29 (m, 12H), 7.50 (d, J = 7.2 Hz, 8H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 32.9, 34.6, 41.5, 72.7 (d, J = 11.4 Hz), 86.2 (d, J = 14.5 Hz), 126.5, 126.6, 127.8, 144.8 (d, J = 2.1 Hz). $[\alpha]_D^{20} = -998$ (*c* 0.06, $CHCl_3$).

4.5. 2,6-Bis(trifluoromethanesulfonyloxy)bicyclo[3.3.1]-nona-2,6-diene 3

LDA was generated by the dropwise addition of a 1.59 M solution of *n*-BuLi (7.1 mL, 13 mmol) in hexane to a solution of diisopropylamine (1.6 mL, 11 mmol) in 20 mL of THF at 0 °C. This solution was stirred for an additional 10 min before a solution of bicyclo[3.3.1]nonan-2,6-dione *dl*-**1** (610 mg, 4.0 mmol) in 17 mL of THF was slowly added at −78 °C. The resulting mixture was stirred at −78 °C for an additional hour, before a solution of *N*-(2-pyridyl)triflimide (4.0 g, 11 mmol) in 20 mL of THF was slowly added at −78 °C. This mixture was warmed to room temperature while being stirred for 41 h. Ice water was added to quench the reaction and the organic solvent removed under reduced pressure. The aqueous layer was extracted with Et_2O three times. The combined organic layers were washed with 10% NaOH and then dried over magnesium sulfate. Removal of the solvent gave the crude product, which was chromatographed on silica gel (ethyl acetate/hexane = 1/10) to give 1.0 g (63% yield) of ditriflate **3**. ^1H NMR ($CDCl_3$): δ 1.99 (t, J = 3.1 Hz, 2H), 2.42 (m, 4H), 2.76 (br, 2H), 5.77 (dd, J = 5.2 and 2.5 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 28.0, 29.3, 30.9, 116.0, 118.5 (q, J = 319 Hz), 149.8. Anal. Calcd for $C_{11}H_{10}F_6O_6S_2$: C, 31.73; H, 2.42. Found: C, 31.72; H, 2.33.

4.6. (1*R*,5*R*)-2,6-Di-(4-methylphenyl)bicyclo[3.3.1]nona-2,6-diene 2b

To a mixture of ditriflate **3** (416 mg, 1.00 mmol) and $PdCl_2$(dppf) (14.8 mg, 20 μmol) in 3.0 mL of Et_2O was added 4-methylphenylmagnesium bromide (2.1 mL, 1.4 M, 3.0 mmol) in Et_2O at room temperature, and the reaction mixture heated to reflux overnight. After being cooled to room temperature, the reaction mixture was quenched with water, and extracted with Et_2O. The combined organic layers were dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate/hexane = 1/10) to give 227 mg (76% yield) of racemic 2,6-di(4-methylphenyl)bicyclo[3.3.1]nona-2,6-diene (*dl*-**2b**). ^1H NMR ($CDCl_3$): δ 1.97 (t, J = 3.1 Hz, 2H), 2.05 (dd, J = 18.3 and 5.0 Hz, 2H), 2.33 (s, 6H), 2.44 (dd, J = 18.3 and 5.3 Hz, 2H), 3.08 (br, 2H), 5.92 (dd, J = 5.0 and 2.4 Hz, 2H), 7.12 (d, J = 8.1 Hz, 4H), 7.30 (d, J = 8.1 Hz, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 21.0, 29.3, 29.8, 31.7, 121.8, 125.7, 129.0, 136.2, 138.6, 139.9. Anal. Calcd for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 91.75; H, 8.15. Enantiomerically pure (1*R*,5*R*)-2,6-di(4-methylphenyl)bicyclo[3.3.1]nona-2,6-diene

(*R*,*R*)-**2b** was obtained by separation of the racemic diene on Chiralcel OJ column with hexane/2-propanol = 9/1, flow = 18 mL/min, wavelength = 254 nm. $[\alpha]_D^{20} = +43$ (*c* 0.25, $CHCl_3$).

4.7. Preparation of [RhCl((*R*,*R*)-Tol-bnd* 2b)]$_2$

In a similar manner to the preparation of [RhCl((*R*,*R*)-Ph-bnd* **2a**)]$_2$, treatment of (*R*,*R*)-Tol-bnd **2b** (47.9 mg, 0.16 mmol) with $[RhCl(C_2H_4)_2]_2$ (31.1 mg, 0.16 mmol Rh) in benzene at 50 °C for 12 h gave a quantitative yield of [RhCl((*R*,*R*)-Tol-bnd* **2b**)]$_2$. ^{1}H NMR ($CDCl_3$): δ 1.25 (br, 4H), 2.21 (br, 4H), 2.25 (d, *J* = 15.0 Hz, 4H), 2.29 (s, 12H), 3.42 (d, *J* = 15.0 Hz, 4H), 4.69 (br, 4H), 7.05 (d, *J* = 8.0 Hz, 8H), 7.37 (d, *J* = 8.0 Hz, 8H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.2, 32.9, 34.5, 41.2, 71.9 (d, *J* = 11.4 Hz), 86.0 (d, *J* = 13.9 Hz), 126.3, 128.5, 136.2, 141.6. Anal. Calcd for $C_{46}H_{48}Cl_2Rh_2$: C, 62.96; H, 5.51. Found: C, 63.26; H, 5.80. $[\alpha]_D^{20} = -907$ (*c* 0.19, $CHCl_3$).

4.8. X-ray crystal structure of [RhCl((*R*,*R*)-Tol-bnd* 2b)]$_2$

A yellow prism crystal ($0.60 \times 0.30 \times 0.10$ mm) of $C_{46}H_{44}Cl_2Rh_2$ was obtained by solvent evaporation from dichloromethane solution at room temperature. Crystallographic data for [RhCl((*S*,*S*)-Tol-bnd* **2b**)]$_2$ (at -150 ± 1 °C). F.W. = 873.57, monoclinic, C2 (#5), *a* = 28.87(2), *b* = 6.787(4), *c* = 12.232(9) Å, β = 113.30(3)°, *V* = 2201(2) Å^3, *Z* = 2, ρ_{calcd} = 1.32 g/cm^3, $2\theta_{max}$ = 55.0°, F_{000} = 880, μ(Mo-Kα) = 9.0 cm^{-1}. A total of 2726 reflections were collected. The final *R* values were *R* = 0.043 ($I > 2\theta(I)$), *R* = 0.044, R_w = 0.015 (all data). The maximum and minimum peaks on the final difference Fourier map corresponded to 2.87 and -2.99 e$^-$/Å^3, respectively. CCDC-262190 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

4.9. (1*R*,5*R*)-2,6-Diphenylbicyclo[3.3.2]deca-2,6-diene (*R*,*R*)-5

In a similar manner to the preparation of (*R*,*R*)-**2a**, racemic bicyclo[3.3.2]decane-2,6-dione *dl*-**4** (445 mg, 2.7 mmol) was treated with a phenylcerium reagent generated from phenyllithium in cyclohexane/Et_2O (7.8 mL, 0.90 M, 7.0 mmol) and cerium trichloride (1.73 g, 7.0 mmol) in THF followed by dehydration of the resulting diol with phosphoryl chloride (1.5 mL, 16 mmol) in pyridine gave 44% yield of racemic 2,6-diphenylbicyclo[3.3.2]deca-2,6-diene *dl*-**5**. ^{1}H NMR ($CDCl_3$): δ 1.97–2.08 (m, 2H), 2.22–2.31 (m, 2H), 2.37 (dt, *J* = 18.0 and 6.7 Hz, 2H), 2.56 (d, *J* = 18.0 Hz, 2H), 3.09 (t, *J* = 5.8 Hz, 2H), 5.78 (dd, *J* = 7.8 and 1.2 Hz, 2H), 7.18–7.23 (m, 2H), 7.25–7.33 (m 8H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 32.0, 32.2, 41.6, 126.5, 126.7, 127.1, 128.1, 145.1, 146.2. Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 91.98; H, 7.92. Enantiomerically pure (1*R*,5*R*)-2,6-diphenylbicyclo-[3.3.2]deca-2,6-diene (*R*,*R*)-**5** was obtained by separation of the racemic diene on Chiralcel OJ column with hexane/2-propanol = 2/1, flow = 8 mL/min, wavelength = 254 nm. $[\alpha]_D^{20} = -67$ (*c* 0.34, $CHCl_3$).

4.10. Preparation of [RhCl((*R*,*R*)-Ph-bdd* 5)]$_2$

In a similar manner to the preparation of [RhCl((*R*,*R*)-Ph-bnd* **2a**)]$_2$, treatment of (*R*,*R*)-Ph-bdd **5** (140 mg, 0.49 mmol) with $[RhCl(C_2H_4)_2]_2$ (114 mg, 0.59 mmol Rh) in benzene at 50 °C for 12 h gave a quantitative yield of [RhCl((*R*,*R*)-Ph-bdd* **5**)]$_2$. ^{1}H NMR ($CDCl_3$): δ 1.37–1.48 (m, 4H), 1.70–1.79 (m, 4H), 2.47 (d, *J* = 15.6 Hz, 4H), 2.93 (t, *J* = 7.4 Hz, 4H), 3.64 (ddd, *J* = 14.8, 8.1, and 6.7 Hz, 4H), 4.38 (d, *J* = 5.5 Hz, 4H), 7.20–7.24 (m, 12H), 7.44–7.54 (m, 8H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 27.4, 39.4, 45.8, 73.4 (d, *J* = 11.9 Hz), 93.2 (d, *J* = 14.4 Hz), 126.2, 126.5, 127.5, 149.2 (d, *J* = 1.6 Hz). $[\alpha]_D^{20} = -286$ (*c* 0.06, $CHCl_3$).

4.11. Rhodium-catalyzed asymmetric 1,4-addition of phenylboronic acid to enones

The reaction conditions and results are summarized in Table 1. A typical experimental procedure (entry 1 in Table 1) is shown below: To a solution of [RhCl((*R*,*R*)-Ph-bnd* **2a**)]$_2$ (3.7 mg, 9.0 μmol Rh) and phenylboronic acid (73.2 mg, 0.60 mmol) in 1.0 mL of dioxane was added 2-cyclohexenone **6a** (28.8 mg, 0.30 mmol) and aqueous KOH (0.10 mL, 1.5 M, 0.15 mmol). After stirring at 30 °C for 3 h, the mixture was passed through a short silica gel column (eluent: diethyl ether). Evaporation of the solvent followed by preparative TLC (silica gel, hexane/ethyl acetate = 3/1) gave 48.7 mg (93% yield) of (*R*)-**7a** in 83% ee. Products **7** obtained by the rhodium-catalyzed asymmetric 1,4-addition were fully characterized by comparison of their spectral and analytical data with those reported in the literature.[15a]

4.12. Rhodium-catalyzed asymmetric phenylation of imines with phenylboroxine

The reaction conditions and results are summarized in Table 2. A typical experimental procedure is shown below: To a solution of [RhCl((*R*,*R*)-Ph-bnd* **2a**)]$_2$ (1.2 mg, 1.5 μmol, 3 mol% Rh) in 1,4-dioxane (0.30 mL) was added aqueous KOH (6.5 μL, 3.1 M, 20 mol% KOH, H_2O: 1 equiv to boron) at room temperature and the solution was stirred for 5 min. This solution containing the catalyst was added to a solution of *N*-(4-chlorophenyl)methylidene-4-methybenzenesulfonamide **8a** (29.4 mg, 0.10 mmol) and phenylboroxine (37.4 mg, 0.12 mmol) in 1,4-dioxane (0.50 mL) at the same temperature. After being stirred at 60 °C for 6 h, the mixture was passed through a short silica gel column (pretreated with methanol, eluent: ethyl acetate). Evaporation of the solvent followed by silica gel chromatography (hexane/ethyl acetate = 2/1) gave 35.5 mg (95% yield) of (*S*)-**9a**[5,9] which is 99% ee.

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