Article

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Planar-Chiral Phosphine-Olefin Ligands Exploiting a (Cyclopentadienyl)manganese(I) Scaffold to Achieve High Robustness and High Enantioselectivity

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ABSTRACT: A series of 2-methyl-1,3-propenylene-bridged (η^5-diarylphosphinocyclopentadienyl)(phosphine)manganese(I) dicarbonyl complexes **2** have been developed as a new class of phosphine-olefin ligands based on a planar-chiral transition-metal scaffold, which show the better robustness as well as the higher enantioselectivity over phosphine-olefin ligands **1** that are with a planar-chiral (η^6-arene)chromium(0) framework. The practical enantiospecific and scalable synthesis of **2** has been established. Phosphine-olefin ligands **2** enable to construct the effective chiral environment around a transition-metal center upon coordination, and thus their rhodium(I) complexes exhibit excellent catalytic performances in the various asymmetric addition reactions of arylboron nucleophiles. Complex **2b**, which is with bis(3,5-dimethylphenyl)phosphino group on the cyclopentadienyl ring, is found to be a superior chiral ligand in the rhodium-catalyzed asymmetric 1,4-addition reactions of arylboronic acids to various cyclic/acyclic enones giving the corresponding arylation products in over 99% ee. On the other hand, **2c** and **2d**, which are with bis[3,5-bis(trifluoromethyl)phenyl]phosphino and bis(3,5-di-*tert*-buthyl-4-methoxyphenyl)phosphino groups respectively, are highly efficient chiral ligands in the rhodium-catalyzed asymmetric 1,2-addition reactions of the arylboron nucleophiles to imines or aldehydes showing up to 99.9% ee. The X-ray crystallographic studies of (*R*)-**2b** and [RhCl((*S**)-**2b**)]$_2$ reveal the absolute configuration of **2b** and its phosphine-olefin bidentate coordination to a rhodium(I) cation. Structural comparison with [RhCl((*R**)-**1b**)]$_2$ postulates the origins of the higher enantioselectivity of newly developed phosphine-olefin ligands **2**.

INTRODUCTION

Enantioselective reactions catalyzed by chiral transition-metal complexes are very powerful methods to supply various chiral building blocks in modern organic synthesis. The most common method for chiral modification of transition-metal catalysts is introduction of appropriate chiral ligands onto a metal center, and thus, design and synthesis of new chiral ligands, which could provide high activity and high enantioselectivity for the metal catalysts, has been a central subject in the development of asymmetric reactions.[1] Chiral phosphines are arguably the chiral ligands most extensively studied for transition-metal-catalyzed asymmetric reactions. Meanwhile, conceptually novel chiral dienes have been elaborated over the last decade and have demonstrated to be superior to traditional chiral phosphines in various rhodium- and iridium-catalyzed asymmetric reactions.[2] While chiral diene ligands enable to construct the effective chiral environment around the metal center, their coordination to a transition metal is generally weaker than that of phosphorus-based ligands, which diminish their applicability in transition-metal catalysis. Recently, chiral phosphine-olefin ligands have been emerged as a new promising class of ligands, whose structural motifs can be regarded as a hybrid of classical chiral phosphines and chiral dienes (Figure 1).[3] In 2012, we developed highly enantioselective kinetic resolution of various racemic planar-chiral (π-arene)chromium species by the molybdenum-catalyzed asymmetric ring-closing metathesis (ARCM). During the course of the studies, we unexpectedly recognized highly effective chiral phosphine-olefin ligand (*R*)-**1a** which was based on the planar-chiral (arene)chromium scaffold. Ligand (*R*)-**1a** showed very high enantioselectivity and reactivity in the rhodium-catalyzed asymmetric 1,4-addition reaction (the Hayashi-Miyaura conjugate addition reaction) of cyclohexenone with phenylboronic acid (99.5% ee, 98%).[4a] This result prompted us to investigate the further details of this unique phosphine-olefin ligand. After the extensive screening, we found out that planar-chiral ligand (*R*)-**1b**, which possesses a bis(3,5-dimethylphenyl)phosphino group on the η^6-arene ring, was superior to precedent (*R*)-**1a** in the rhodium-catalyzed reactions (Scheme 1).[4b] While planar-chiral

(arene)chromium-based ligands (*R*)-**1** showed the very high performance in the Hayashi-Miyaura reaction of the series of cyclic enones and related substrates, it was realized that (*R*)-**1** had some drawbacks: (i) instability of the ligands toward air-oxidation especially in a solution state, and (ii) insufficient enantioselectivities and reactivities in the reactions with acyclic enones. We thought that the former point was particularly critical for the practical application of the phosphine-olefin ligands, since the excessive fragility made handling of the compound difficult.

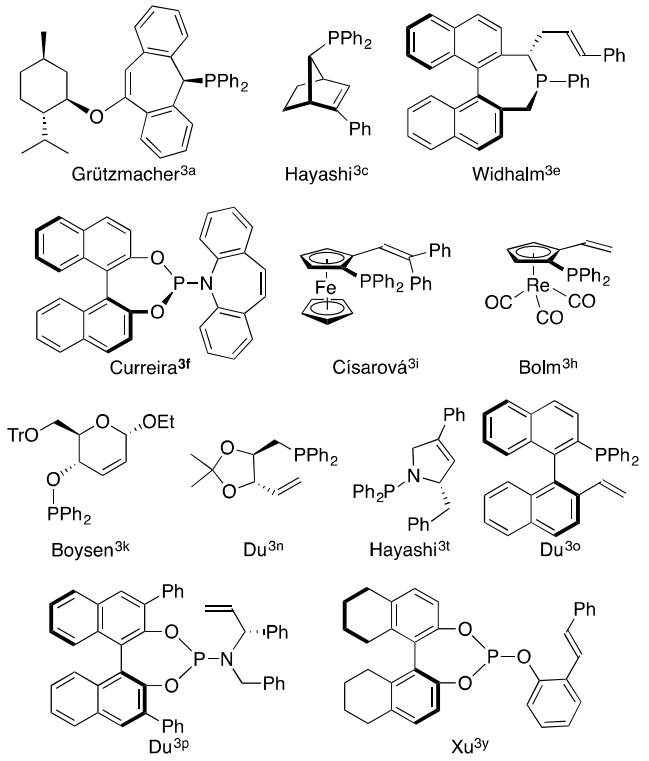
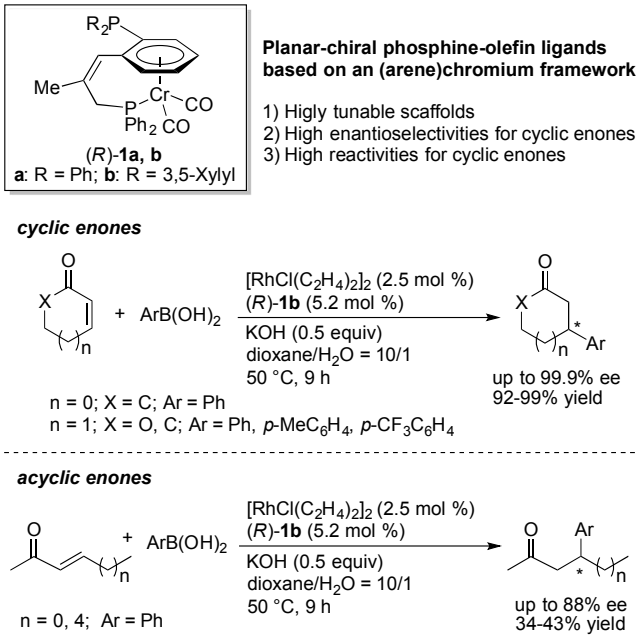


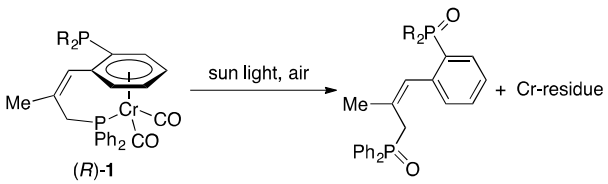
Figure 1. Structures of representative chiral phosphine-olefin ligands.

Scheme 1. Rhodium-Catalyzed Asymmetric 1,4-Addition Reactions Using Planar-Chiral (Arene)chromium-Based Phosphine-Olefin Ligand (*R*)-1.[4]



With the background mentioned above, we started the present studies with intention to improve the stability of the chiral ligands. The fragility of (arene)chromium-based phosphine-olefin ligands **1** is ascribed to the presence of the (arene)chromium substructure, since they suffer from the photo-induced oxidative degradation (Scheme 2).[5] We envisioned that the replacement of the (arene)chromium(0) moiety in **1** with an isoelectronic and more robust (cyclopentadienyl)manganese(I) moiety might be an answer to this problem. The enantiospecific and scalable synthesis of these (cyclopentadienyl)manganese(I)-based phosphine-olefin ligands **2** has been developed. Indeed, manganese complexes **2** show much better robustness than **1** as we expected. Furthermore, the introduction of the CpMn(I) framework in **2** gives us an extra (and more important) benefit: planar-chiral phosphine-olefin ligands **2** are far superior to (arene)Cr-based "first-generation" phosphine-olefin ligands **1** in terms of the enantioselectivities and catalytic activities in a wide range of rhodium-catalyzed asymmetric reactions. The Rh(I) catalysts coordinated with (*R* or *S*)-**2** are applicable to the asymmetric 1,4-arylation of not only cyclic but acyclic enones and the asymmetric 1,2-arylation of imines/aldehydes to give the corresponding addition products in >99% ee in many cases.

Scheme 2. Photo-Induced Oxidative Degradation of (π-Arene)chromium Complexes (*R*)-1.[5]



In this article, we would like to report the results of our studies on the innovative "second-generation" planar-chiral phosphine-olefin ligands, which are with an (η^5-cyclopentadienyl)manganese(I) framework.

RESULTS AND DISCUSSION

Design and Stereospecific Preparation of Planar-Chiral (Cyclopentadienyl)manganese(I)-Based Phosphine-Olefin Ligands 2. To retain the efficient chiral environment in (*R*)-**1**, the key structural motifs such as the bridging structure between the π-arene and the chromium-bound phosphine and a methyl group on the olefin unit should be adopted in a newly designed ligand.[4b] On the other hand, the photo/oxygen-sensitive (π-arene)chromium(0) moiety needed to be replaced with a robust component of an isoelectronic structure. From these perspectives, we designed "second-generation" planar-chiral phosphine-olefin ligands (*R*)-**2**, which are with a (η^5-cyclopentadienyl)manganese(I) scaffold as a new planar-chiral platform (Figure 2). While the partially ionic metal/π-ligand interaction in **2** (i.e., the coordination of an anionic cyclopentadienide to a manganese(I) cation in **2** and the coordination of an electronically neutral arene to a chromium(0) atom in **1**) may lead to the better stability of **2**, the different phosphine-olefin bite angles between **1** and **2**, which are originated from a five-membered Cp ligand in **2** and a six-membered π-arene ligand in **1**, may lead to the different reactivities and selectivities in the applied transition-metal-catalyzed asymmetric reactions.

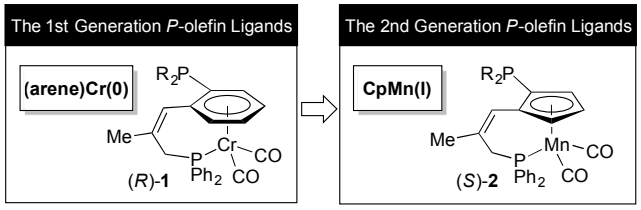
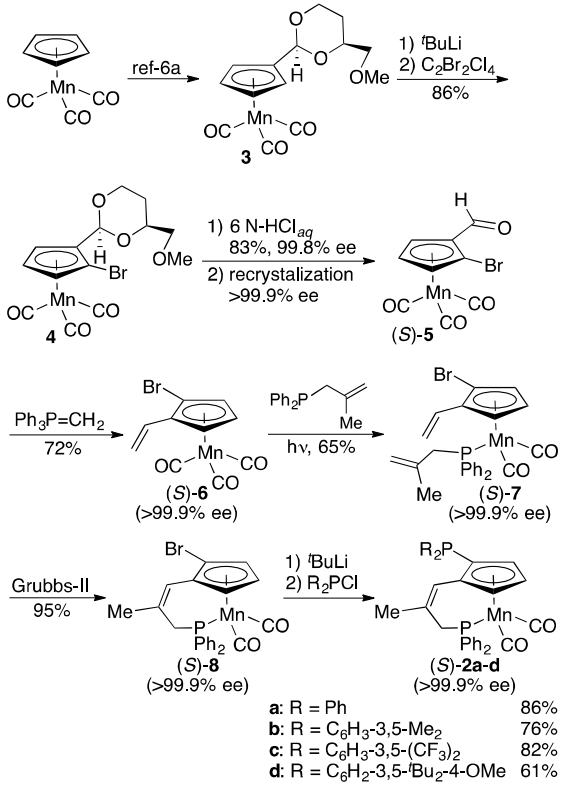


Figure 2. Design of second-generation phosphine-olefin ligands (*S*)-**2** based on the (cyclopentadienyl)manganese(I) framework.

It should be noted that the (*R*)/(*S*)-nomenclature rules commonly used for notating the absolute configuration of planar-chiral (η^5-cyclopentadienyl)metal complexes[6,7] are different from those used for the (*R*)/(*S*)-notation of (η^6-arene)metal complexes.[5c,7b] Consequently, the two planar-chiral compounds shown in Figure 2 have opposite (*R*)/(*S*)-descriptors to each other, although the relative orientations between the PR_2 group and the bridging olefin moiety are same in both (*R*)-**1** and (*S*)-**2**.

Scheme 3. Stereospecific Preparation of Planar-Chiral (Cyclopentadienyl)manganese(I)-Based Phosphine-Olefin Ligands.



The enantiospecific and multi-gram scale synthesis of the designed planar-chiral CpMn(I)-based phosphine-olefin ligands was achieved as outlined in Scheme 3. The key synthetic intermediate in the synthesis is enantiomerically pure 1-bromo-2-formylcymantrene (*S*)-**5**, which was prepared from Jaouen's chiral acetal **3**.[8a] The *ortho*-lithiation of **3** using ^{t}BuLi in ether at −78 °C took place with excellent diastereoselectivity as reported,[8a] and subsequent bromination with 1,2-dibromotetrachloroethane gave bromo-acetal **4** in 86% yield. After the hydrolysis of **4** with aqueous hydrochloric acid, 1-bromo-2-formylcymantrene **5** was obtained in 83% yield and 99.8% ee. The absolute configuration of the product was determined to be (*S*) by the analogy with the previous report.[8c] Recrystallization of the product from hexane/ethyl acetate afforded enantiomerically pure (*S*)-**5**. The Wittig methylenation of the formyl substituent and the photo-induced ligand exchange reaction with diphenylmethallylphosphine gave (cyclopentadienyl)(phosphine)manganese(I) complex (*S*)-**7** in good yield. The subsequent ruthenium-catalyzed ring-closing metathesis of (*S*)-**7** provided bridging bromide (*S*)-**8** in 95% yield. In the final step, a series of phosphine-olefin ligands (*S*)-**2a**-**d** with a respective diarylphosphino group on the cyclopentadienyl unit were obtained in good yields by the conventional lithiation/phosphanylation sequence. In the same way, the corresponding antipodes, (*R*)-**2a-d**, could be synthesized by using (*R*)-1,2,4-butanetriol as a chiral auxiliary in manganese complex **3**. The absolute configuration of (+)-**2b** was the confirmed as (*R*) by the single-crystal X-ray crystallography (see Figure 6 (a)).

Alternatively, (*S*)- and (*R*)-**8** were obtained by the enantiomeric resolution of preformed *rac*-**8** by HPLC with a

preparative chiral stationary phase column (Daicel Chiralcel OD).

Comparison of Air-Oxidation Tolerance between CpMn(I)- and (Arene)Cr(0)-Based Ligands.

The stability of the ligands is crucial for their practical applications in catalytic organic transformations. The photo-induced oxidative decomposition of (arene)Cr-based ligands **1** (see Scheme 2) results in high oxidation-state chromium residue, which may oxidize a transition-metal catalyst as well as a phosphine moiety of the ligand. Since these undesired side reactions directly affect lowering reactivities and enantioselectivities of the catalytic processes, the stability of the transition-metal-based ligands is pivotal for the further development of our planar-chiral phosphine-olefin ligands. The tolerance (or sensitivity) to air-oxidation of the CpMn(I)- and the (arene)Cr(0)-based phosphine-olefin ligands was monitored by the ^{31}P-NMR measurements (Figures 3 and 4). Phosphorus atoms **P^1** of the free phosphine moieties in both *rac*-**2b** and *rac*-**1b** were protected as the corresponding phosphine selenides, and the air-oxidation experiments were carried out for *rac*-**2b-Se** and *rac*-**1b-Se**. The ^{31}P-NMR spectra of *rac*-**2b-Se** showed the two signals at δ 27.9 and 93.5, which were assigned to **P^1** and **P^2** atoms, respectively. As we expected, the manganese compound was persistent in the air-oxidation, and the two spectra taken in 10 min and in 14 h after the NMR sample preparation are essentially identical and showed no traces of decomposition (Figure 3).

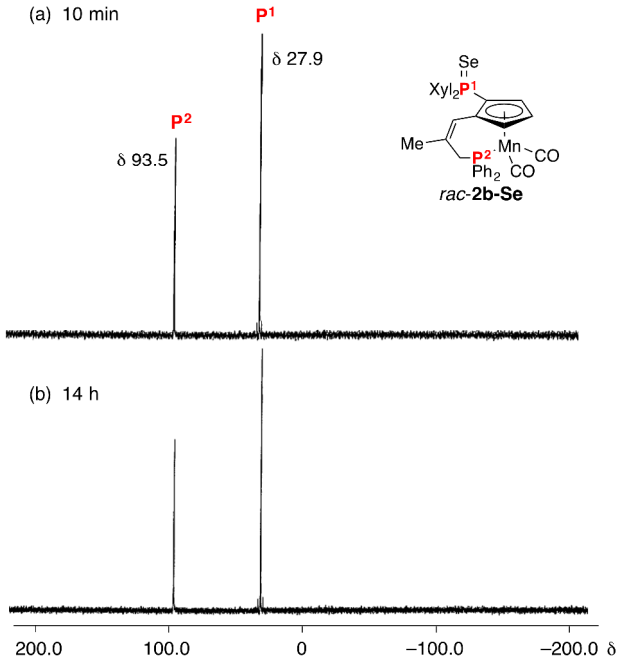


Figure 3. ^{31}P-NMR trace of *rac*-**2b-Se** solution in $CDCl_3$ prepared under air: (a) 10 min, and (b) 14 h after the sample preparation.

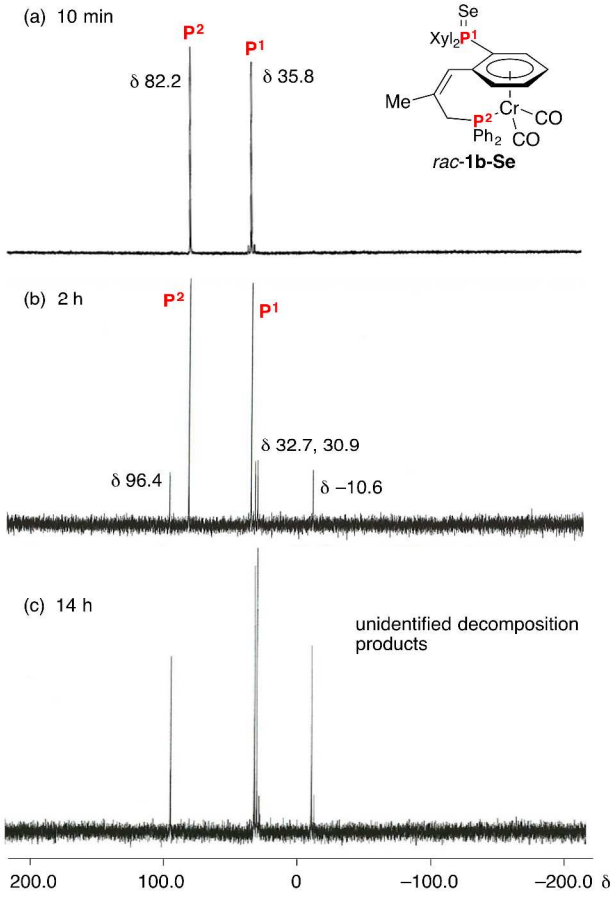


Figure 4. ^{31}P-NMR trace of *rac*-**1b-Se** solution in $CDCl_3$ prepared under air: (a) 10 min, (b) 2 h, and (c) 14 h after the sample preparation.

On the other hand, the ^{31}P-NMR spectra of (arene)Cr-based *rac*-**1b-Se** changed drastically over time (Figure 4). The freshly prepared sample of *rac*-**1b-Se** showed two resonances at δ 35.8 and 82.2, which were assigned to **P^1** and **P^2** atoms, respectively, in the ^{31}P-NMR spectrum (Figure 4, (a)). As time proceeded, the oxidative degradation of *rac*-**1b-Se** was detected in the ^{31}P-NMR spectra. In the NMR sample kept under air for 2 h, four new peaks emerged at δ −10.6, 30.9, 32.7, and 96.4 in addition to the original two signals (Figure 4, (b)). The decomposition was completed within 14 hours and the two signals from *rac*-**1b-Se** were disappeared (Figure 4, (c)). The decomposition process was also visibly observed: the clear orange solution of *rac*-**1b-Se** (Figure 5, (a)) turned into a heterogeneous mixture of a yellow supernatant and green precipitate during 15 hours (Figure 5, (b)). On the contrary, the clear yellow solution of manganese-based *rac*-**2b-Se** did not change at all under the same conditions.

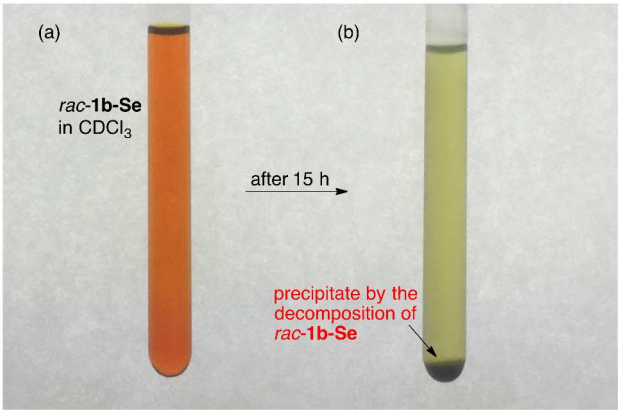
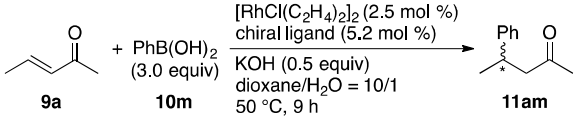


Figure 5. Photos of NMR sample tube containing a solution of *rac*-**1b-Se** in $CDCl_3$: (a) right after preparation, (b) kept for 15 h under air.

Application of Planar-Chiral CpMn(I)-Based Ligands to Rh-Catalyzed Asymmetric Reactions. A series of CpMn(I)-based planar-chiral ligands **2a-d**, the 2nd generation phosphine-olefin ligands, were applied to the various Rh-catalyzed asymmetric reactions. Firstly, the potential of **2** was evaluated on the asymmetric 1,4-addition reaction of phenylboronic acid (**10m**) to 3-penten-2-one (**9a**).[2,9] The asymmetric 1,4-addition reactions to acyclic enones are known to be difficult to control due to their conformational flexibility, however, a problematic reaction system was chosen as a benchmark test of **2a-d**. Indeed, as reported in 2014, the rhodium catalyst generated in situ from $[RhCl(C_2H_4)_2]_2$ and (*R*)-**1a** or (*S*)-**1b** promoted the asymmetric phenylation of **9a** in low yields with only 57% ee or 88% ee, respectively (Table 1, entries 1 and 2).[4b] Meanwhile, the enantioselectivity was improved to 92% ee by the use of (*R*)-**2a**, but the yield of the product (**11am**) was still low in 32% (entry 3). To our delight, both reactivity and enantioselectivity were markedly updated by the use of (*S*)-**2b** which is with a bis(3,5-dimethylphenyl)phosphino substituent on the cyclopentadienyl ring to give **11am** in 99% yield with 98% ee (entry 4). Electron deficient ligand (*R*)-**2c** also showed an excellent enantioselectivity (94% ee), but the yield was moderate (entry 5). The ligand (*R*)-**2d**, which is with an electron rich and bulky bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino group, showed the very low reactivity and enantioselectivity (entry 6).

Table 1. Rhodium-Catalyzed Asymmetric 1,4-Addition of Phenylboronic Acid (10m) to 3-Penten-2-one (9a)[a]



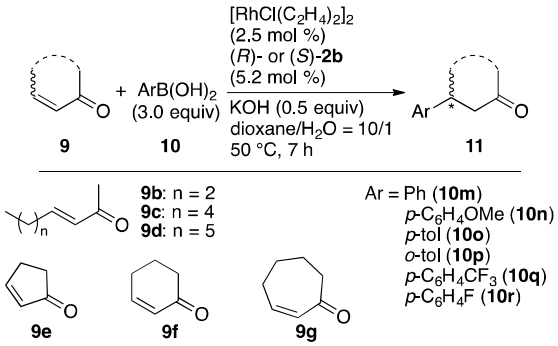
entry	chiral ligand	yield (%)[b]	% ee[c]
1[d]	(*R*)-**1a**	31 (**11am**)	57 (*S*)
2[d]	(*S*)-**1b**	34 (**11am**)	88 (*R*)
3	(*R*)-**2a**	32 (**11am**)	92 (*R*)
4	(*S*)-**2b**	99 (**11am**)	98 (*S*)
5	(*R*)-**2c**	60 (**11am**)	94 (*R*)
6	(*R*)-**2d**	43 (**11am**)	32 (*R*)

[a] The reaction was carried out in dioxane/H_2O (10/1) in the presence of the rhodium catalyst (5 mol %) generated in situ from $[RhCl(C_2H_4)_2]_2$ and the chiral ligand. [b] Isolated yield by silica gel chromatography. [c] Determined by chiral HPLC analysis. [d] Taken from ref-4b. The reaction mixture was stirred for 24 h.

The results in Table 1 indicated the superiority of CpMn(I)-based ligands **2** over (arene)Cr(0)-based homologues **1** in the Rh-catalyzed asymmetric 1,4-addition reactions (see, entries 1 *vs* 3; entries 2 *vs* 4). With the more promising ligand system in hands, the additional application of **2b** was examined and the results are summarized in Table 2. The Rh/**2b** catalytic system was effective in the 1,4-addition to the longer acyclic enones as well. The addition of **10m** to 3-hepten-2-one (**9b**) took place smoothly to give the addition product **11bm** in 92% yield and 99% ee (entry 1). When 3-nonen-2-one (**9c**) was used as a substrate, phenyl-addition product **11cm** was obtained in a remarkable level of enantioselectivity of 99.8% ee in 77% yield (entry 2). The yields of the addition products gradually decreased as elongation of the alkyl chain in the acyclic enone, however, the high enantioselectivity was retained in the phenylation of 3-decen-2-one (**9d**) with 99.7% ee (entry 3). The low yield (43%) in the reaction of **9d** (entry 3) can be ascribed to competitive hydrolysis of phenylboronic acid **10m**.[9a] With the longer alkyl chain in **9d**, the phenylrhodation to **9b** (insertion of **9b** to the Rh-Ph intermediate)[9b] becomes slower, while **10m** is hydrolyzed by a side reaction. Indeed, the reaction in entry 3 showed complete consumption of **10m** within 48 h even with a substantial amount of unreacted **9d**.[10]

Furthermore, CpMn-based ligand **2b** showed the near-perfect performance in the asymmetric 1,4-addition to a series of cyclic enones (entries 4-10). In addition, various arylboronic acids **10** were applied in the 1,4-addition to **9f** showing the enantioselectivities of over 99.2% ee with nearly quantitative yields regardless of the nature of the aryl substituents in **10** (entries 5-9).

Table 2. Rhodium-Catalyzed Asymmetric 1,4-Addition of Arylboronic Acids (10) to Enones (9)[a]



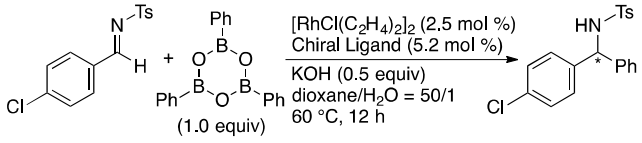
entry	sub-strate	ArB(OH)$_2$	**2b**	yield (%)[b]	% ee[c]
1	**9b**	**10m**	(*S*)	92 (**11bm**)	98.9

					(*S*)
2[d]	**9c**	**10m**	(*S*)	77 (**11cm**)	99.8 (*S*)
3[e]	**9d**	**10m**	(*S*)	43 (**11dm**)	99.7 (*S*)
4	**9e**	**10m**	(*R*)	99 (**11em**)	99.6 (*S*)
5	**9f**	**10n**	(*S*)	99 (**11fn**)	99.8 (*R*)
6	**9f**	**10o**	(*S*)	99 (**11fo**)	99.9 (*R*)
7	**9f**	**10p**	(*R*)	99 (**11fp**)	99.9 (*S*)
8	**9f**	**10q**	(*R*)	99 (**11fq**)	99.2 (*S*)
9	**9f**	**10r**	(*R*)	99 (**11fr**)	99.6 (*S*)
10	**9g**	**10m**	(*R*)	99 (**11gm**)	99.9 (*S*)

[a] The reaction was carried out in dioxane/H_2O (10/1) in the presence of the rhodium catalyst (5 mol %) generated in situ from $[RhCl(C_2H_4)_2]_2$ and **2b**. [b] Isolated yield by silica gel chromatography. [c] Determined by chiral HPLC analysis. [d] The reaction mixture was stirred for 24 h. [e] The reaction mixture was stirred for 48 h.

Newly developed CpMn(I)-based ligands **2** were also tested in the rhodium-catalyzed asymmetric 1,2-addition of phenylboroxine to *p*-chlorobenzaldehyde *N*-tosylimine (Table 3).[11] For this reaction, (*S*)-**2c** and (*S*)-**2d** were found to be the most promising ligands showing very high enantioselectivities in 99.6% ee and 99.2% ee, respectively, although the yield of the desired addition product with (*S*)-**2c** was moderate (entries 5 and 6).

Table 3. Rhodium-Catalyzed Asymmetric 1,2-Addition of Phenylboroxine to *p*-Chlorobenzaldehyde *N*-Tosylimine[a]

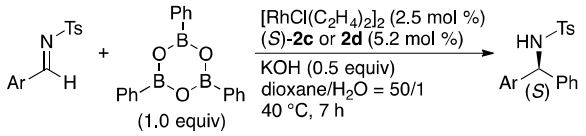


entry	chiral ligand	yield (%)[b]	% ee[c]
1[d]	(*R*)-**1a**	94	88 (*S*)
2[d]	(*S*)-**1b**	98	93 (*R*)
3	(*S*)-**2a**	64	85 (*S*)
4	(*S*)-**2b**	99	94 (*S*)
5	(*S*)-**2c**	62	99.6 (*S*)
6	(*S*)-**2d**	92	99.2 (*S*)

[a] The reaction was carried out in dioxane/H_2O (50/1) in the presence of the rhodium catalyst (5 mol %) generated in situ from $[RhCl(C_2H_4)_2]_2$ and the chiral ligand. [b] Isolated yield by silica gel chromatography. [c] Determined by chiral HPLC analysis. [d] Taken from ref-4b.

After the initial screening experiments shown in Table 3, applicability of both (*S*)-**2c** and (*S*)-**2d** was further examined in the 1,2-addition of phenylboroxine to the other imine substrates (Table 4). The phenylation of *p*-methoxybenzaldehyde *N*-tosylimine proceeded quantitatively with very high enantioselectivities using either of (*S*)-**2c** or (*S*)-**2d** (entries 1 and 2). It is worth mentioning that the ligand (*S*)-**2c** afforded the desired product in extremely high enantioselectivity of 99.9% ee. The similar trend in high reactivities and selectivities was observed in the reaction of *o*-methoxybenzaldehyde *N*-tosylimine (entries 3 and 4). The activity of [Rh]/(*S*)-**2c** catalysis was slightly diminished compared to that of [Rh]/(*S*)-**2d** for the reaction of the *N*-tosylimine having an electron withdrawing substituent, although the enantioselectivities were still very high (entries 5 and 6). The lower activity of (*S*)-**2c** shown in entry 5 is correlated with the reactivity toward electron deficient *p*-chlorobenzaldehyde *N*-tosylimine (Table 3, entry 5). To our delight, both ligands were also applicable in the asymmetric reaction of the imine substrates having a heteroarene substituent, and the addition products were obtained in >99.7% ee (entries 7-10). All in all, both (*S*)-**2c** and **2d** are equally reactive and highly enantioselective in the rhodium-catalyzed asymmetric 1,2-addition reactions giving the addition products over 99.0% ee in all cases.

Table 4. Rhodium-Catalyzed Asymmetric 1,2-Addition of Phenylboroxine to Arylaldehyde *N*-Tosylimines[a]



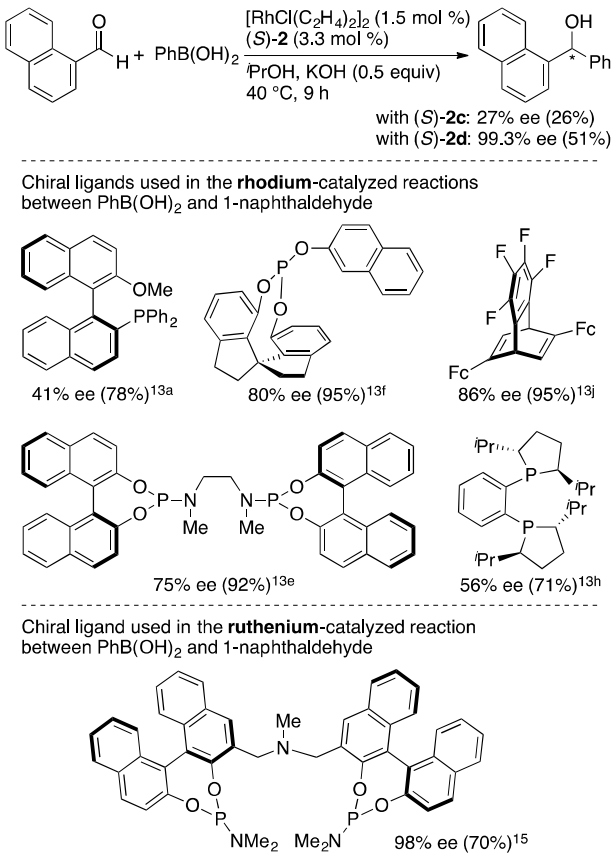
entry	Ar in tosylimine	(*S*)-**2**	yield (%)[b]	% ee[c]
1	*p*-C_6H_4OMe	**2c**	99	99.9 (*S*)
2		**2d**	99	99.6 (*S*)
3	*o*-C_6H_4OMe	**2c**	99	99.9 (*S*)
4		**2d**	99	99.0 (*S*)
5	*p*-$C_6H_4CF_3$	**2c**	88	99.8 (*S*)
6		**2d**	96	99.6 (*S*)
7	2-furyl	**2c**	99	99.8 (*S*)
8		**2d**	97	99.8 (*S*)
9	2-thienyl	**2c**	99	99.9 (*S*)
10		**2d**	89	99.7 (*S*)

[a] The reaction was carried out in dioxane/H_2O (50/1) in the presence of the rhodium catalyst (5 mol %) generated in situ from $[RhCl(C_2H_4)_2]_2$ and (*R*)-**2**. [b] Isolated yield by silica gel chromatography. [c] Determined by chiral HPLC analysis.

Optically active chiral diarylmethanols are important synthetic intermediates as key building blocks for various biologically active compounds. A straightforward method of preparing these compounds is an asymmetric nucleophilic addition of an aryl nucleophile to an appropriate arylaldehyde. The reactions between an arylzinc reagent and an arylaldehyde have been studied in the presence of a chiral Lewis-base with fair success.[12] The transition-

metal-catalyzed variants of these asymmetric reactions have been developed as well. To our best knowledge, the first example of the transition-metal-catalyzed reaction was reported by Miyaura and co-workers in 1998 using a rhodium catalyst and phenylboronic acid as a nucleophile.[13a] Since then, rhodium catalysts coordinated with a chiral ligand have played central roles in the asymmetric reactions.[13] As summarized in Scheme 4, however, the rhodium-catalyzed reactions clearly need further improvement in terms of enantioselectivities. Whereas (*S*)-**2c** and (*S*)-**2d** showed the excellent performance in the rhodium-catalyzed 1,2-addition to the imines (Tables 3 and 4), next we turned our attention to their application in the related 1,2-addition of phenylboronic acid to 1-naphthaldehyde. Although the rhodium catalyst generated from $[RhCl(C_2H_4)_2]_2$ and (*S*)-**2c** showed poor results (27% ee and 26% yield), Rh/(*S*)-**2d** catalyst afforded the desired diarylmethanol in excellent enantioselectivity of 99.3% ee in 51% yield (Scheme 4, top). For this reaction, the clear difference in enantioselectivities was observed between (*S*)-**2c** and (*S*)-**2d**. The asymmetric reaction between phenylboronic acid and 1-naphthaldehyde was also reported using nickel[14] or ruthenium[15] catalysts. And, the ruthenium catalyst showed the highest enantioselectivity so far with 98% ee (Scheme 4, bottom).[15] It should be mentioned that the Rh/(*S*)-**2d** catalyst outperformed the ruthenium catalyst as well in the 1,2-addition reaction in terms of the enantioselectivity. The results shown in Scheme 4 displayed the great potential of phosphine-olefin ligands **2** in transition-metal-catalyzed asymmetric reactions.

Scheme 4. Rhodium-Catalyzed Asymmetric 1,2-Addition of Phenylboronic Acid to 1-Naphthaldehyde.



Consideration of Structural Difference between 2b and 1b. Single crystals of (+)-**2b** suitable for X-ray crystallography were grown from the chloroform solution as orange prisms. The crystal structure of (+)-**2b** is shown in Figure 6 (a) (see the Supporting Information for details), which revealed the absolute configuration of dextrorotatory **2b** ($[\alpha]_D^{26}$ +135.1 (*c* 0.5, $CHCl_3$)) to be (*R*). The configurations of the other CpMn-based phosphine-olefin ligands **2** are determined by analogy.

The single-crystal X-ray analysis of the homologous bis(3,5-dimethylphenyl)phosphino-derivative of the (arene)Cr(0)-based phosphine-olefin ligand, *rac*-**1b**, was also conducted for comparison, and its ball & stick drawings is shown in Figure 6 (b). Although both **2b** and **1b** display similar overall structures each other, the local substructures around the central metals (Mn in **2b**; Cr in **1b**) show a clear contrast between the two.[16] The metal (Cr)-phosphorus bond in **1b** (2.280(1) Å) is ca. 3% longer than that in **2b** (Mn(1)-P(2) = 2.209(1) Å), and the η^6-arene ligand in **1b** is larger than the η^5-cyclopentadienyl ligand in **2b**. Although arene(centroid)-Cr(1) distance (1.674 Å) in **1b** is considerably shorter than Cp(centroid)-Mn(1) distance in **2b** (1.773 Å), the chelate ring size in **2b** is smaller than that in **1b**. Consequently, Cp(centroid)-Mn(1)-P(2) angle in **1b** (121.88°) is much smaller than arene(centroid)-Cr(1)-P(2) angle in **1b** (124.68°).

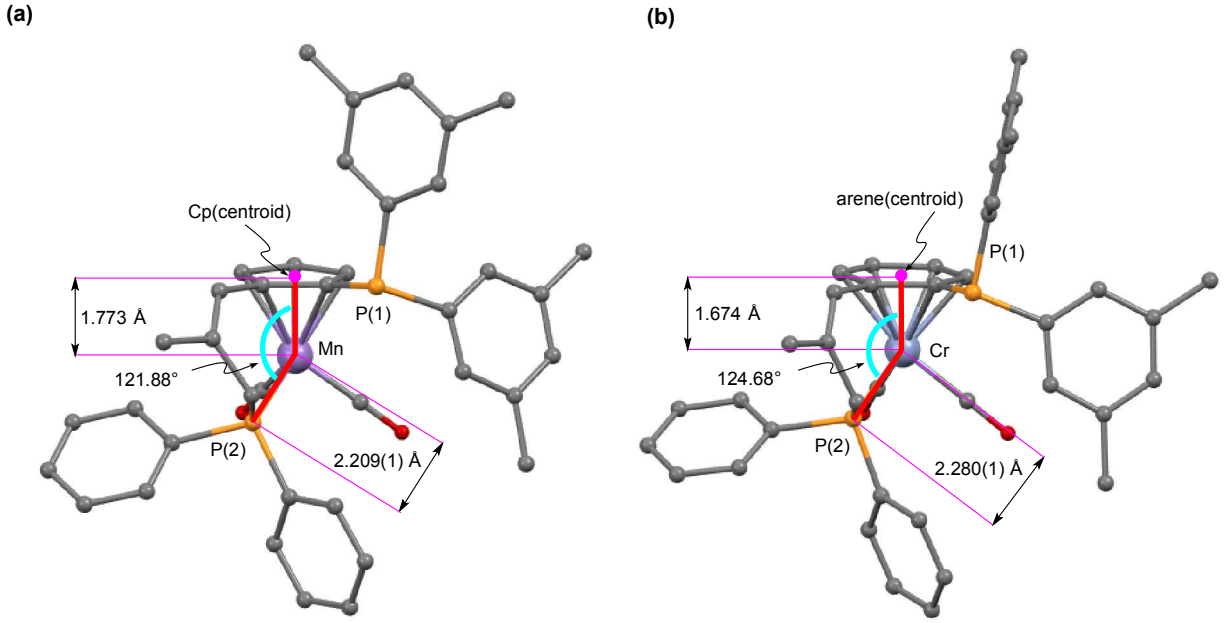


Figure 6. Ball & stick drawings of (a) (*R*)-**2b** and (b) *rac*-**1b** with selected atom numbering. All hydrogen atoms are omitted for clarity.

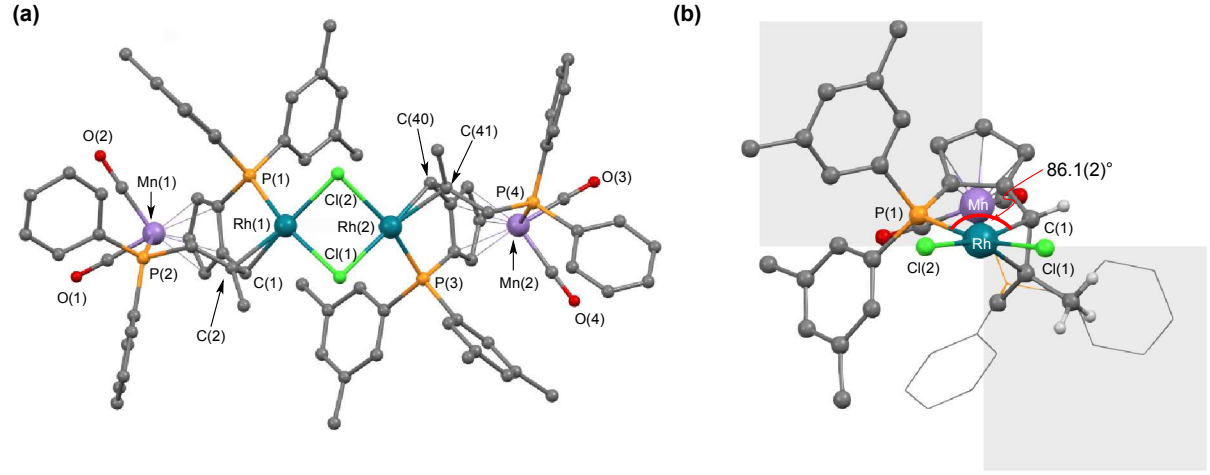


Figure 7. Ball & stick drawings of (a) [RhCl/(*S**)-**2b**]$_2$ ((*S**,*S**)-**12**) and (b) monomeric substructure of (*S**,*S**)-**12** with selected atom numbering. All hydrogen atoms and cocrystallized solvent molecules are omitted for clarity. Both xylyl groups on P(3) atom are disordered over two positions (one of the two observed P(3)-xylyl$_2$ groups is shown in (a). See Supporting Information for detail). A part of structure (b) is shown as a wireframe drawing for clarity.

Next, the coordination mode of phosphine-olefin ligand **2b** to a rhodium(I) center was examined by the X-ray crystallography. A (μ-Cl)$_2$-bridged dinuclear rhodium(I) complex with **2b**, [Rh(I)/**2b**]$_2$ (**12**), was prepared from [RhCl(CH$_2$=CH$_2$)$_2$]$_2$ and *rac*-**2b** (1 equiv. to Rh) nearly quantitatively. Whereas racemic **2b** was used for the preparation of **12**, the rhodium complex comprises of both (*R*,*R*)- and (*S*,*S*)-**12** enantiomers in the 1:1 molar ratio. Interestingly, complex **12** showed the strong preference for the formation of the homoenantiomeric dimer, and the corresponding mesomeric dimer, (*R*,*S*)-**12**, was not detected either in the solid state (by the X-ray crystallography) or in solution (by the NMR spectroscopy). Single-crystals of **12** were obtained as dark brown prisms by recrystallization from dichloromethane/hexane. Complex **12** cocrystallizes with two dichloromethane molecules per dimeric unit, and the ball and stick drawing of (*S**,*S**)-**12** is shown in Figure 7 (a) (see Supporting Information for details). The determined solid-state structure of (*S**,*S**)-**12** is pseudo-*C*$_2$-symmetric and consists of two similar but crystallographically independent [Rh(I)/(*S**)-**2b**] units. The crystal structure confirms the bidentate coordination of **2b** to the Rh(I) cation as a phosphine-olefin chelate. The bond lengths of the coordinating olefin moieties (C(1)-C(2) and C(40)-C(41)) in (*S**,*S**)-**12** are 1.423(8) and 1.41(2) Å, respectively, which are ca. 6% longer than that in free ligand (*R*)-**2b**.

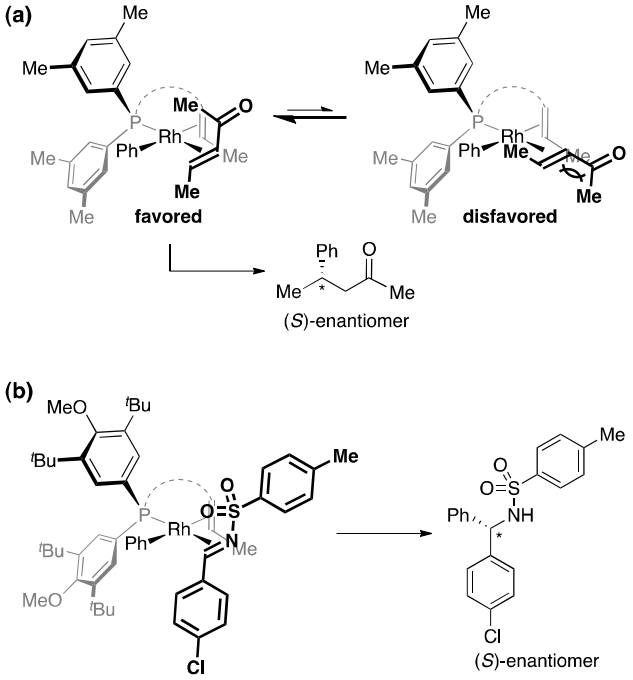
The X-ray single-crystal analysis of the Rh(I) complex coordinated with **1b**, [RhCl/(*R**)-**1b**]$_2$ ((*R**,*R**)-Sl**1**), was also examined for comparison (not shown in the main text,

see Supporting Information), which reveals the crystal structures of the two rhodium complexes are quite similar. The clear difference between the two structures is detected in the phosphine-rhodium-olefin bite angles (Figure 7 (b)). While the average bite angle in (S^*,S^*)-**12** is 86.1(2)° [P(1)-Rh(1)-C(1) = 86.5(2)°, P(3)-Rh(2)-C(40) = 85.7(2)°], that in (R^*,R^*)-SI**1** is 84.5(1)°. The two donor moieties (Xyl_2P-substituent and the olefin) in **2b** are arrayed on the five-membered CpMn scaffold. On the other hand, the structural core in **1b** is the six-membered (arene)Cr on which the two donors are arranged. Our previous studies revealed that the orientations of the two phosphorus-bound aryl groups as well as of the olefin-bound methyl group are primarily constructing the chiral environment around the rhodium center.[4b] The different bite angles between **2b** and **1b** should lead to the different orientations of the *Xyl*$_2$P- and the -CH=C*Me*- moieties in the Rh complexes,[17] which may be an origin of the better enantioselectivity of **2b**.

Consideration of Stereochemical Pathways in Rhodium-Catalyzed 1,4- and 1,2-Addition Reactions. On the basis of the results in Table 1 and the structural analyses mentioned above, the stereochemical pathway of the 1,4-addition reaction of phenylboronic acid (**10m**) to 3-pentene-2-one (**9a**) catalyzed by Rh/(*S*)-**2b** can be rationalized as shown in Scheme 5-(a). The phenylrhodium species has *trans*-relationship between the Rh-bound phenyl group and the olefin ligand,[3g] and **9a** coordinates to the rhodium center with its *si*-face at the *cis*-position of the olefin ligand to minimize the steric repulsion with coordinating (*S*)-**2b**. Subsequent insertion of **9a** to the Rh-Ph bond followed by hydrolysis gives the 1,4-adduct with (*S*)-configuration. On the other hand, coordination of **9a** to the rhodium center with the *re*-face was disfavored due to the steric repulsion between the acetyl tether in **9a** and the methyl group on the ligating olefin moiety in (*S*)-**2b**.

Likewise, the stereochemical pathway of the 1,2-addition of phenylboroxine to arylaldehyde imine can be rationalized in the similar way (Scheme 5-(b)). Thus, the imine approaches the rhodium with its *si*-face at the *cis*-position of the olefin ligand to give (*S*)-enantiomer of the phenylation product.

Scheme 5. Proposed Stereochemical Pathways for (a) Rh/(*S*)-2b-Catalyzed Enantioselective 1,4-Addition of Phenylboronic Acid to 3-Pentene-2-one and (b) Rh/(*S*)-2d-Catalyzed Enantioselective 1,2-Addition of Phenylboroxine to Arylaldehyde *N*-Tosylimine.



CONCLUSIONS

A new family of chiral phosphine-olefin bidentate ligands **2**, whose chirality is based on a planar-chiral (η^5-cyclopentadienyl)manganese(I) dicarbonyl scaffold, has been developed. Ligand **2** shows the better robustness as well as the higher enantioselectivity over homologous (η^6-arene)chromium(0)-based planar-chiral phosphine-olefin ligands **1**. We have developed the general and enantiospecific synthetic method of **2** that can be conducted in a macroscale with ease. Whereas the chelate coordination of **2** to a rhodium(I) cation constructs the effective chiral environment at the rhodium(I) center, the rhodium complexes of **2** display excellent catalytic performances in the various asymmetric reactions with arylboron nucleophiles. Ligand **2b**, which is with bis(3,5-dimethylphenyl)phosphino group on the cyclopentadienyl ring, shows very high enantioselectivity in the rhodium-catalyzed asymmetric 1,4-addition reactions of arylboronic acids to various cyclic and acyclic enones to give the corresponding arylation products in up to 99.9% ee. Ligands **2c** (with bis[3,5-bis(trifluoromethyl)phenyl]phosphino group) and **2d** (with bis(3,5-di-*tert*-buthyl-4-methoxyphenyl)phosphino group) are suited for the rhodium-catalyzed asymmetric 1,2-addition reactions of the arylboron nucleophiles to imines or aldehydes showing up to 99.9% ee selectivity.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, compound characterization data, and crystallographic data of (*R*)-**2b**, *rac*-**1b**, [RhCl/(S^*)-**2b**]$_2$ ((S^*,S^*)-**12**), [RhCl/(R^*)-**1b**]$_2$ ((R^*,R^*)-SI**1**) in CIF formats. This material is available free of charge via the Internet at http://pubs.acs.org.

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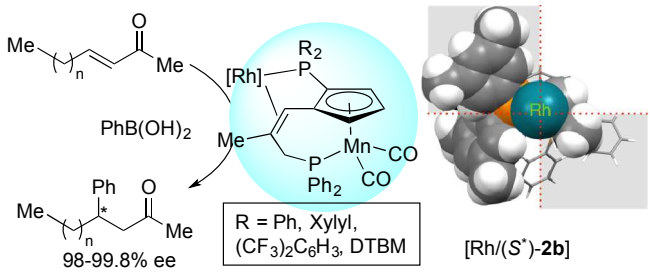
Me
O
Me
n
PhB(OH)2
[Rh]
R2
P
Me
P
Mn
CO
CO
Ph2
Ph
O
Me
*
Me
n
98-99.8% ee
R = Ph, Xylyl,
(CF3)2C6H3, DTBM
Rh
[Rh/(S*)-2b]