Article

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Kinetic Resolution of Planar-Chiral Ferrocenylphosphine Derivatives by Molybdenum-Catalyzed Asymmetric Ring-Closing Metathesis and Their Application in Asymmetric Catalysis

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Abstract. Highly enantioselective kinetic resolution of racemic planar-chiral metallocenylphosphine sulfides was realized by the molybdenum-catalyzed asymmetric ring-closing metathesis reaction with the k_{rel} values of up to 147. The enantiomerically enriched 1,4-but-2-enylene-bridged ferrocenylphosphine sulfides thus obtained could be purified to enantiomerically pure forms by the simple recrystallization from hot methanol, and subsequent reduction of the phosphine sulfides provided the corresponding planar-chiral phosphines with

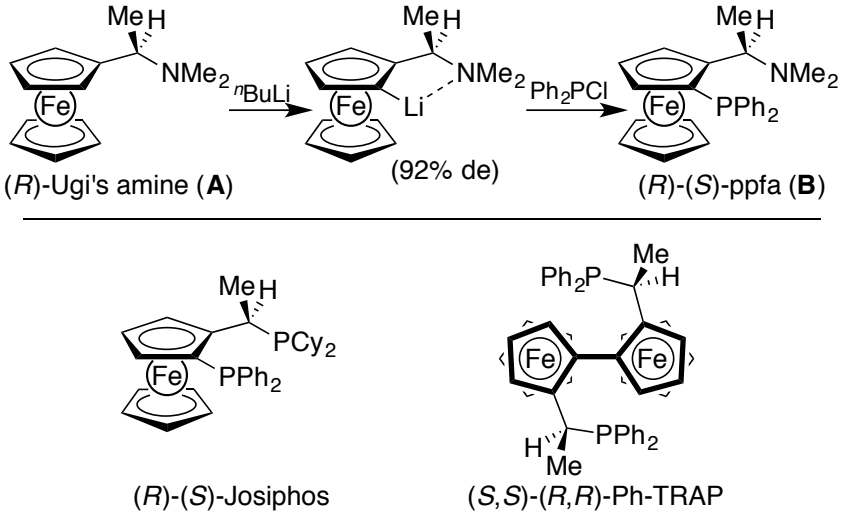
retention of the enantiomeric homogeneity. This is a rare example of preparing planar-chiral ferrocenylphosphines by catalytic asymmetric reactions. The single-enantiomeric planar-chiral ferrocenylphosphines were applied as chiral ligands in the rhodium-catalyzed asymmetric 1,4-addition reaction (the Hayashi-Miyaura conjugate addition reaction) of phenylboronic acid to 2-cyclohexenone to show excellent enantioselectivity and high yields. The NMR studies clarified that the butenylene-bridged ferrocenylphosphine coordinated to a rhodium(I) cation in a monodentate fashion and an interaction of the bridging olefin moiety to the rhodium atom was not detected.

Keywords. planar-chiral; metallocene; ring-closing metathesis; enantioselective; kinetic resolution; ferrocenylphosphine; molybdenum-alkylidene

Introduction

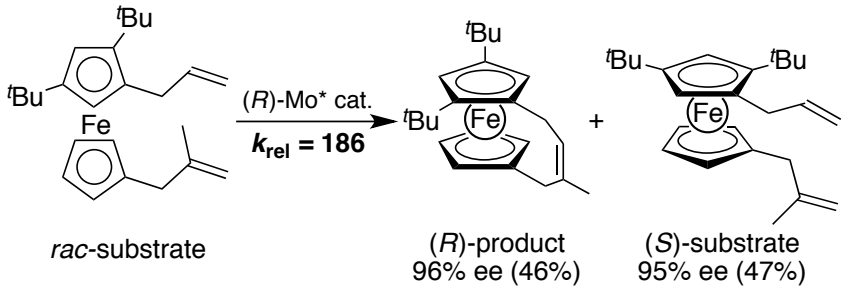
Chiral phosphines are arguably the most important chiral scaffolds in transition-metal-catalyzed asymmetric reactions.[1] Among various chiral phosphines reported so far, planar-chiral ferrocenylphosphines are one of the most successful classes of chiral ligands in transition-metal catalysis.[2] Since the first introduction of a planar-chiral ferrocenylphosphine as (*R*)-(*S*)-ppfa (**B** in Scheme 1) by Hayashi and Kumada in 1974,[3] numerous such ferrocenylphosphines have been developed with considerable success.[2] Surprisingly, however, their synthetic methods in optically active forms are rather limited. Standard methods of preparing enantiomerically enriched planar-chiral ferrocenes are based on diastereoselective metalation using preinstalled chiral directing groups[4] or external chiral bases,[5] and these strategies have been successfully utilized in the

preparation of planar-chiral ferrocenylphosphines.[3,6] A notable synthetic precursor to planar-chiral ferrocenylphosphines is (*R*)- or (*S*)-*N*,*N*-dimethyl-(1-ferrocenylethyl)amine (**A**; Scheme 1), which is known as "Ugi's amine".[4a,b] The 1-(dimethylamino)ethyl group in **A** is an effective chiral directing group at the *ortho*-lithiation of **A** to induce the ferrocene-based planar-chirality by the diastereoselective control. Trapping of the lithiated intermediate with Ph_2PCl provides **B** in 92% de.[3a] Various other planar-chiral ferrocenylphosphines, such as Josiphos[7] and TRAP,[8] can be derived from **A** as well. Although the diastereoselective directed *ortho*-lithiation protocols are highly effective for preparing planar-chiral ferrocene derivatives, these methods generally require stoichiometric chiral sources for inducing/controlling the planar chirality. Whereas catalytic asymmetric reactions of preparing scalemic planar-chiral ferrocenes are limited,[5d,9-11] examples of catalytic asymmetric syntheses of planar-chiral ferrocenylphosphines have been extremely rare.



Scheme 1. Ugi's Amine (**A**) and Representative Planar-Chiral Ferrocene-Based Phosphine Ligands Derived from **A**.

Recently, we have developed a protocol for the enantioselective kinetic resolution of racemic planar-chiral ferrocenes by the molybdenum-catalyzed asymmetric interannular ring-closing metathesis (ARCM; Scheme 2).[11a,b,12] Although our method is highly effective for the kinetic resolution of certain ferrocene substrates with the k_{rel} values of up to >500, the scope of the method described in our original reports was rather limited: (i) the substrates used were alkyl- or silylferrocenes and functionalized substrates were not examined; (ii) only a single molybdenum-alkylidene species was employed as a precatalyst, and effects of various other chiral ligands were unexplored.



Scheme 2. Kinetic Resolution of Racemic Planar-Chiral Ferrocene by Molybdenum-Catalyzed Asymmetric RCM.

In this article, we report the results of our studies on the application of the ARCM method to the enantioselective kinetic resolution of planar-chiral ferrocenyl- and ruthenocenylphosphine derivatives. After the extensive survey of various reaction conditions, including the screening of the molybdenum-alkylidene precatalysts, the planar-chiral metallocenylphosphine sulfides were obtained with excellent enantioselectivity of >90% ee. We also systematically investigated the

correlation between the structural motifs in the metallocene substrates and the enantioselectivity of the reactions to clarify the structural requirements of the substrates for the high enantioselectivity. The enantiomerically enriched ferrocene products could be purified into enantiomerically pure forms by the simple recrystallization, and subsequent their reduction afforded the corresponding ferrocenylphosphines. The obtained single-enantiomeric ferrocenylphosphines were applied in a couple of transition-metal-catalyzed asymmetric reactions as chiral ligands and found to be highly effective in the rhodium-catalyzed asymmetric 1,4-addition reaction (the Hayashi-Miyaura conjugate addition reaction)[13] of phenylboronic acid to 2-cyclohexenone. It should be emphasized that this is a rare example of *catalytic* asymmetric synthesis of planar-chiral ferrocenylphosphines and the phosphines obtained herewith are indeed functioning as effective chiral ligands in asymmetric catalysis.

Results and Discussion

Design and Preparation of Metallocenylphosphine Substrates for ARCM Kinetic Resolution. Our preliminary studies on the kinetic resolution of the racemic planar-chiral alkylferrocenes postulated that a couple of structural factors in the substrates were crucial to achieve the high enantioselectivity in the molybdenum-catalyzed ARCM: (i) steric discrimination of the two allylic groups with a methyl substituent at the 2-allylic position of one of the two allylic groups, and (ii) a bulky substituents at the position adjacent to the unsubstituted (i.e., the more reactive) allyl group (Figure 1).[11a,b] We assumed that an $Ar_2P(=E)$- group might work as a proper bulky substituent required in the effective ARCM kinetic resolution. And thus, metallocenes **1** were designed as potential "good" substrates for the present kinetic resolution study. In addition to **1a-g** that fulfill the two structural requirements mentioned above, **1h** and **1i**

were also prepared for comparison although these two were expected to be "poor" substrates for the kinetic resolution reaction (see, Schemes 3 and 4).

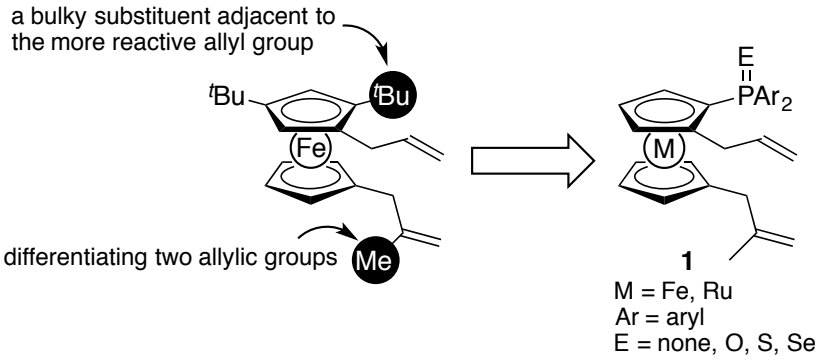
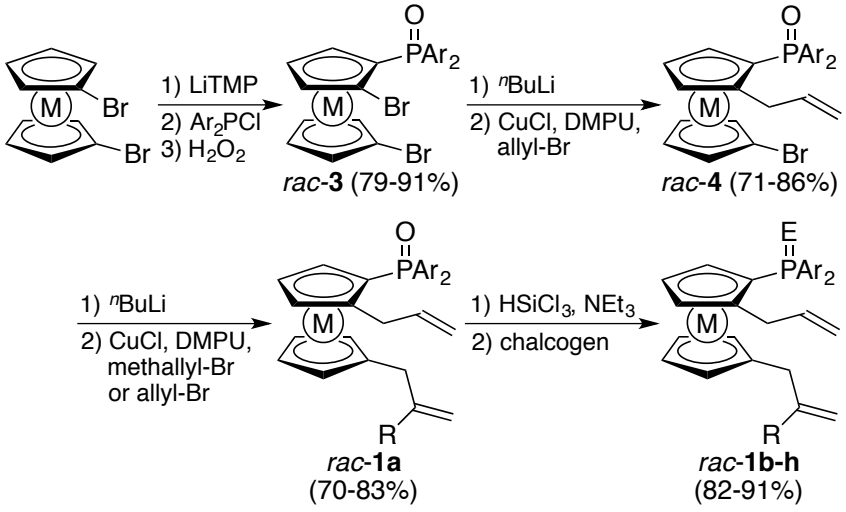


Figure 1. Design of planar-chiral ferrocenylphosphine derivatives as substrates for molybdenum-catalyzed ARCM kinetic resolution.

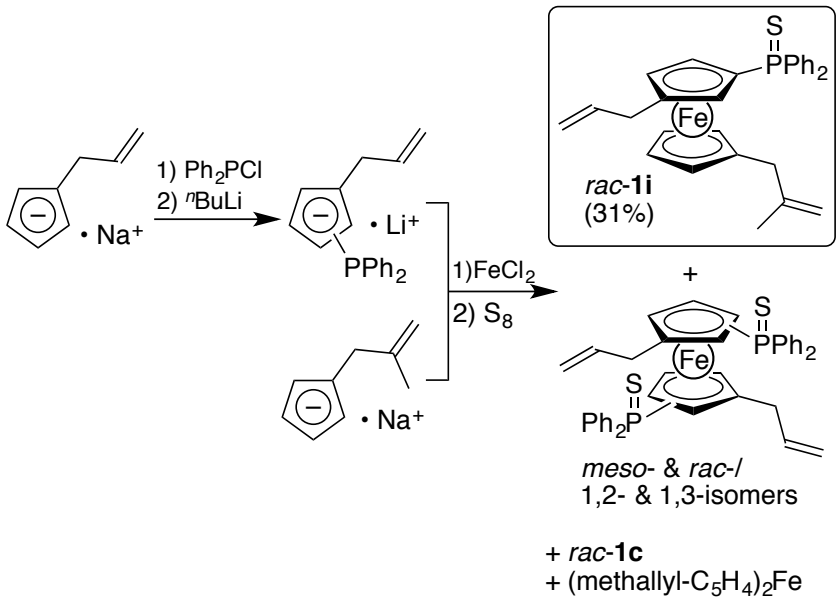
Preparation of **1a-h** was achieved by the regioselective and stepwise introduction of the three substituents starting with 1,1'-dibromoferrocene/ruthenocene[14] as outlined in Scheme 3. First, a diarylphosphino group [aryl = Ph, -C_6H_3-3,5-Me_2 (Xyl), -C_6H_2-3,5-$^t Bu_2$-4-OMe (DTBM)] was introduced to the dibromometallocene core by regioselective *ortho*-lithiation using lithium tetramethylpiperidide[15] followed by quenching the lithiated species with diarylchlorophosphine, and subsequent oxidation with H_2O_2 gave **3** in 79-91% yields. The lithium-bromine exchange on **3** using one equivalent of butyllithium took place at the bromide adjacent to the diarylphosphinyl group selectively, probably the Lewis basic phosphinyl group worked as a directing group, and a following reaction with allyl bromide in the presence of CuCl gave **4** in 71-86% yields. The remaining bromide in **4** was replaced with methallyl (or allyl) group in the same way. The obtained phosphine oxides were reduced to the corresponding phosphines with

trichlorosilane/triethylamine and subsequently derivatized to phosphine chalcogenides as needed to furnish desired substrates **1a-h** selectively.



Scheme 3. Preparation of ARCM Kinetic Resolution Substrates *rac*-**1a-h**.

On the other hand, substrate **1i** was prepared by an unstylish manner (Scheme 4). A reaction of $FeCl_2$ with a mixture of Na^+(methallyl-C_5H_4)$^-$ and Li^+[1,2- and 1,3-allyl(Ph_2P)C_5H_3]$^-$ followed by a treatment with S_8 afforded a mixture of several ferrocene derivatives, of which careful chromatographic separation provided pure *rac*-**1i** albeit in low yield (31%).



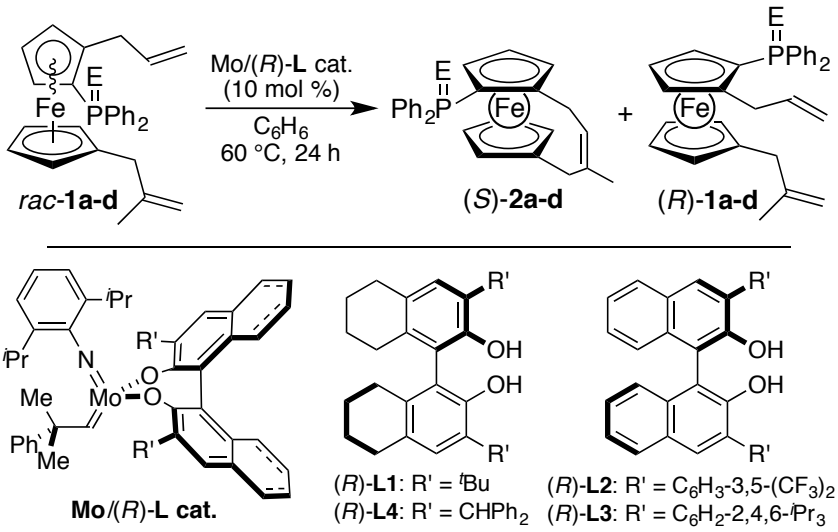
Scheme 4. Preparation of Substrate *rac*-**1i**.

Molybdenum-Catalyzed ARCM Kinetic Resolution of Racemic Planar-Chiral Ferrocenylphosphine Derivatives 1. The prepared substrates **1** were subjected to the kinetic resolution studies under various conditions in the presence of a molybdenum-alkylidene precatalyst which was generated in situ from the molybdenum precursor [(pyrrolyl)$_2$Mo(=CHCMe$_2$Ph)(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)] and an appropriate axially chiral binaphthol derivative as reported by Hoveyda and Schrock.[16] At the outset, a proper choice of the P=E moieties in *rac*-**1** was determined for substrates *rac*-**1a-d** (Table 1; entries 1-4). The RCM reactions were carried out in benzene at 60 °C in the presence of the Mo-alkylidene precatalyst (10 mol %) generated with (*R*)-**L1**.[16,17a] Under these conditions, phosphine oxide *rac*-**1a** was inert and desired cyclized species **2a** was not obtained at all (entry 1). On the other hand, phosphine *rac*-**1b** and phosphine sulfide *rac*-**1c** afforded the corresponding cyclized products **2b** (6%) and **2c** (17%), respectively, but their yields were far from satisfactory (entries 2 and 3). It was rationalized that Lewis basic **1a** and **1b** poisoned the Lewis acidic molybdenum-alkylidene

species. Phosphine selenide *rac*-**1d** was unstable under the RCM conditions, and the reaction of *rac*-**1d** with the Mo/(*R*)-**L1** precatalyst gave a mixture of various uncharacterized species (entry 4).

Next, screening of chiral biaryloxide ligands in the molybdenum catalysts was examined for the ARCM reactions of *rac*-**1c**. Most of the chiral ligands examined, (*R*)-**L1-3**,[17a-c] were found to be inactive or nearly inactive (Table 1; entries 3, 5 and 6), however, the Mo-alkylidene species generated with (*R*)-**L4**[17d] showed reasonable catalytic activity and enantioselectivity to give cyclized (*S*)-**2c** in 62% yield and 53% ee together with recovered (*R*)-**1c** of 97%ee in 31% yield (entry 7). The k_{rel} value ([rate of fast-reacting enantiomer]/[rate of slow-reacting enantiomer]; selectivity factor) for this reaction is estimated to be 13.[18] Lowering the temperature improved the selectivity; the reaction at 23 °C showed excellent enantioselectivity with the k_{rel} value of 65 giving (*S*)-**2c** of 88% ee in 52% yield and (*R*)-**1c** of 97% ee in 43% yield (entry 8).

Table 1. Molybdenum-Catalyzed ARCM Kinetic Resolution of Planar-Chiral Metallocenylphosphine Derivatives: Optimization of Reaction Conditions[a]



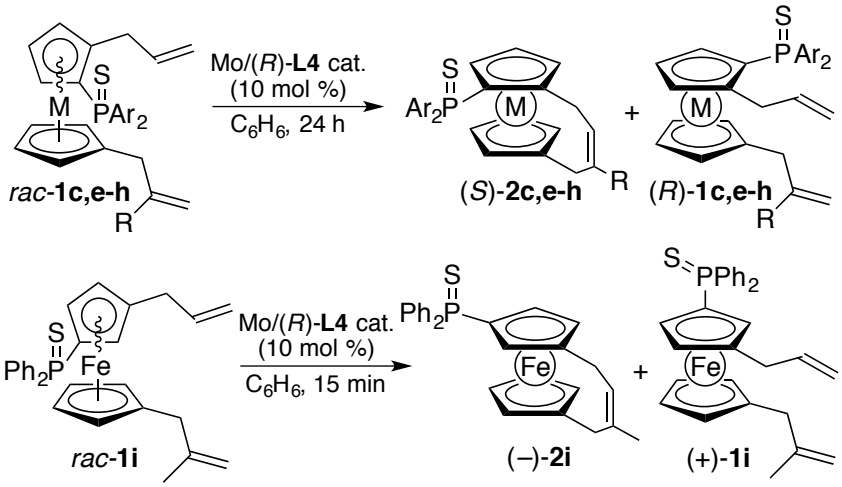
entry	substrate	chiral **L**	cyclized **2**[b,d]	recovered **1**[c,d]	k_{rel}[e]
1	*rac*-**1a**	(*R*)-**L1**	— (0%)	— (>90%)	—
2	*rac*-**1b**	(*R*)-**L1**	75% ee (6%)	5% ee (88%)	7.0
3	*rac*-**1c**	(*R*)-**L1**	85% ee (17%)	21% ee (76%)	15
4	*rac*-**1d**	(*R*)-**L1**	messy		—
5	*rac*-**1c**	(*R*)-**L2**	— (0%)	— (>90%)	—
6	*rac*-**1c**	(*R*)-**L3**	<1% ee (8%)	n.d. (90%)	—
7	*rac*-**1c**	(*R*)-**L4**	53% ee (62%)	97% ee (31%)	13
8[f]	*rac*-**1c**	(*R*)-**L4**	88% ee (52%)	97% ee (43%)	65

[a] The reaction was carried out using **1** (0.16 mmol) in benzene at 60 °C for 24 h in the presence of an appropriate metathesis catalyst generated in situ (10 mol %) unless otherwise noted. [b] Enantiomeric excess was determined by chiral HPLC (see Supporting Information for detail). [c] Enantiomeric excess of recovered **1** was determined after conversion into **2** by a reaction with the Grubbs-II catalyst. [d] Isolated yield in parentheses. [e] Calculated based on a first-order equation (ref. 18). [f] At 23 °C.

After the optimization studies, Mo/(*R*)-**L4** precatalyst was applied to the other phosphine sulfide substrates (Table 2). The substrate *rac*-**1e**, which has a bis(3,5-xylyl)thiophosphinyl substituent in place of the $Ph_2P(=S)$- group in **1a**, was also resolved as above. The enantioselectivity and the reaction efficiency of kinetic resolution of *rac*-**1e** was still high with

the k_{rel} value of 62 (entry 2). With a much bulkier thiophosphinyl group in *rac*-**1f**, the ARCM reaction needed to be conducted at higher temperature (40 °C). However, the selectivity was still excellent with k_{rel} = 43 (entry 3). The reaction of ruthenocenylphosphine sulfide *rac*-**1g** was also conducted at 40 °C to show the highest selectivity with the k_{rel} factor of 147, and the ARCM product (**2g**) and the recovered substrate (**1g**) were obtained in 96% ee and 89% ee, respectively (entry 4). Enantioselectivity of the ARCM kinetic resolution was strongly dependent on the structures of the allylic groups in the substrates. Introduction of C_5H_4-allyl in place of C_5H_4-methallyl in *rac*-**1h** diminishes enantioselectivity of the asymmetric reaction. With two unsubstituted allyl groups in it, the RCM of *rac*-**1h** was very rapid and completed within an hour. For this reason, the kinetic resolution of *rac*-**1h** was conducted at 23 °C for 5 min with lower catalyst loading. The reaction with Mo/(*R*)-**L4** afforded cyclized product **2h** in 16% ee and recovered **1h** in 7% ee. The selectivity factor for the reaction is only 1.5 (entry 5). The relative orientation between the diarylthiophosphiyl group and the allyl substituent in **1** is also crucial for the high enantioselectivity of the kinetic resolution process (vide infra). While *rac*-**1c** showed the excellent selectivity (entry 1), the ARCM reaction of *rac*-**1i**, that is with a 1,3-substituted cyclopentadienide, was much less selective with the k_{rel} value of less than 1.1 (entry 6).

Table 2. Molybdenum-Catalyzed ARCM Kinetic Resolution of Planar-Chiral Metallocenylphosphine Sulfides[a]



entry	substrate	temp.	cyclized **2**[b,d]	recovered **1**[c,d]	k_{rel}[e]
1[f]	*rac*-**1c**	23 °C	88% ee (52%)	97% ee (43%)	65
2	*rac*-**1e**	23 °C	90% ee (53%)	92% ee (45%)	62
3	*rac*-**1f**	40 °C	89% ee (48%)	81% ee (47%)	43
4	*rac*-**1g**	40 °C	96% ee (48%)	89% ee (49%)	147
5[g]	*rac*-**1h**	23 °C	16% ee (29%)	7% ee (64%)	1.5
6[h]	*rac*-**1i**	23 °C	3% ee (30%)	1% ee (49%)	<1.1

[a] The reaction was carried out using **1** (0.16 mmol) in benzene for 24 h in the presence of Mo/(*R*)-**L4** precatalyst generated in situ (10 mol %) unless otherwise noted. [b] Enantiomeric excess was determined by chiral HPLC (see Supporting Information for detail). [c] Enantiomeric excess of recovered **1** was determined after conversion into **2** by a reaction with the Grubbs-II catalyst. [d] Isolated yield in parentheses. [e] Calculated based on a first-order equation (ref. 18). [f] Same with entry 8 in Table 1. [g] With 5 mol % catalyst loading for 5 min. [h] For 15 min.

Determination of Absolute Configuration of (–)-2e. Single crystals of (–)-**2e** suitable for X-ray crystallography were grown from the hot methanol solution as orange prisms. The crystal structure of (–)-**2e** is shown in Figure 2 with the selected bond lengths and angles (see the Supporting Information for details), which revealed that the absolute configuration of levorotatory **2e** ($[\alpha]_D^{22}$ = –1.75 (*c* = 1.76, $CHCl_3$) for the sample of 94% *ee*) was (*S*). The

configurations of the other ARCM kinetic resolution products were deduced by analogy. The iron atom in **2e** located at the center of the two η^5-ligands: the distance from Fe(1) to the least-squares planes of η^5-C(6-10) and η^5-C(11-15) are 1.636(9) Å and 1.642(9) Å, respectively. The two η^5-ligands are slightly tilted due to the bridging moiety and the dihedral angle between the two η^5-C_5 planes is 6.06(10)°, which is within the range of those found in the analogous [4]ferrocenophanes.[11a-c,19]

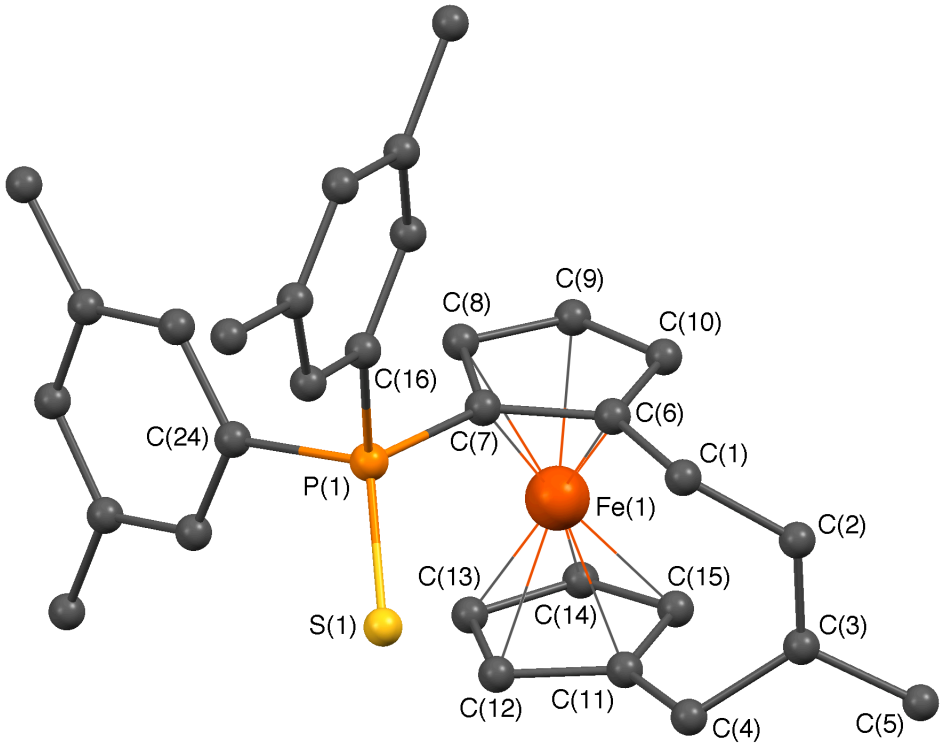
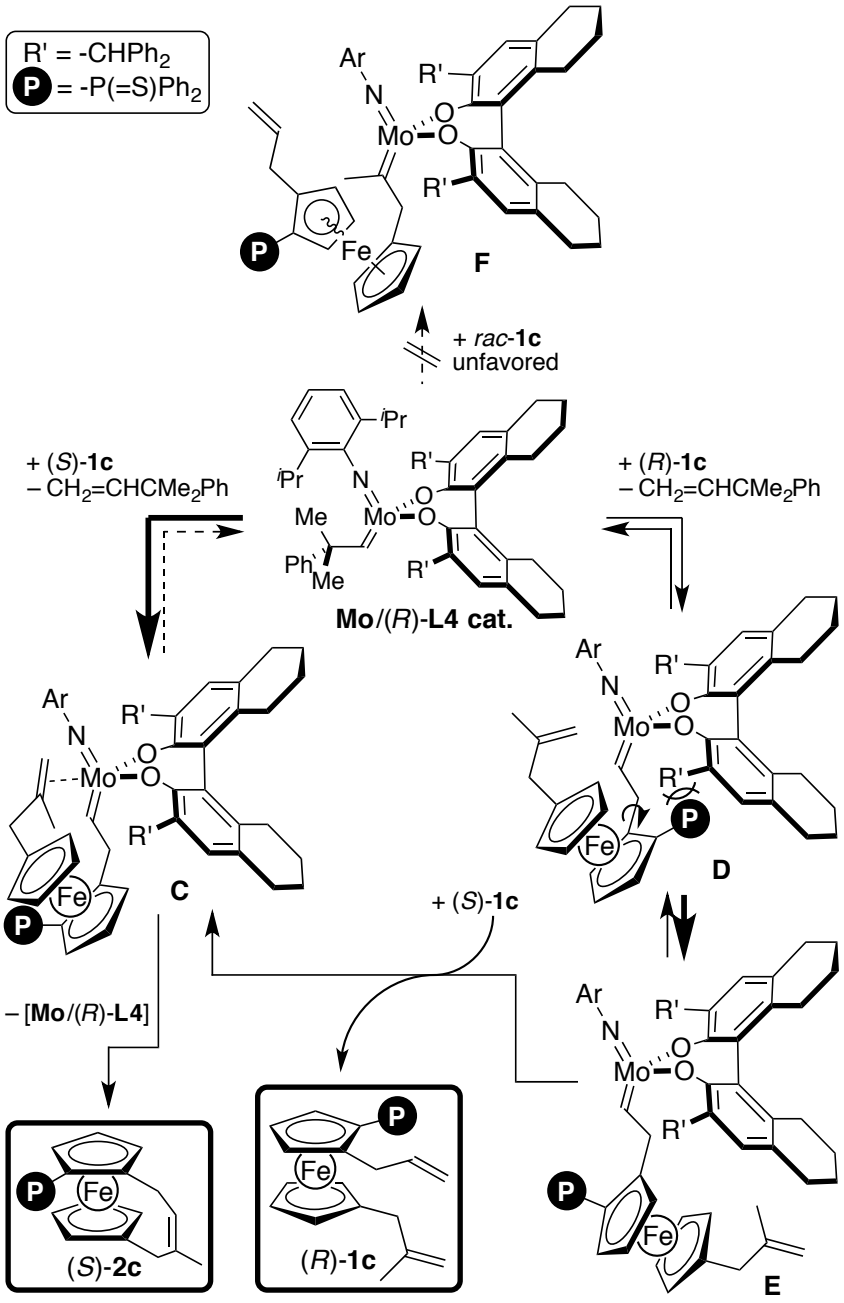


Figure 2. Ball-and-stick drawing of (*S*)-(–)-**2e**. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C(6)-C(1) = 1.52(1), C(1)-C(2) = 1.50(1), C(2)-C(3) = 1.33(1), C(3)-C(4) = 1.51(1), C(4)-C(11) = 1.49(1), Fe(1)-least-squares plane$_{C(6-10)}$ = 1.636(9), Fe(1)-least-squares plane$_{C(11-15)}$ = 1.642(9); dihedral angle between the two Cp planes = 6.06(10).

Consideration of Stereochemical Pathways of Molybdenum-Catalyzed ARCM Kinetic Resolution of 1. Plausible reaction pathways of the Mo-catalyzed ARCM kinetic resolution of *rac*-**1c** are illustrated in Scheme 5. Whereas a less substituted olefin is more reactive than a more substituted one in olefin metathesis, the initial reactions between Mo/(*R*)-**L4** and (*S*)- or (*R*)-**1c** take place at the parent allyl group to form intermediates **C** or **D**, respectively, and the formation of intermediate **F** is unlikely. The methallylic olefin in **C** is able to take a position proximal to the molybdenum center, and thus **C** gives (*S*)-**2c** smoothly by the intramolecular second metathesis. On the other hand, epimeric **D** is forced to take non-productive conformation in **E** due to the steric repulsion between the diphenylthiophosphinyl substituent in the ferrocene moiety and the diphenylmethyl group in the chiral biaryloxide ligand. Subsequent intermolecular metathesis between **E** and (*S*)-**1c** liberates (*R*)-**1c** intact together with intermediate **C**.

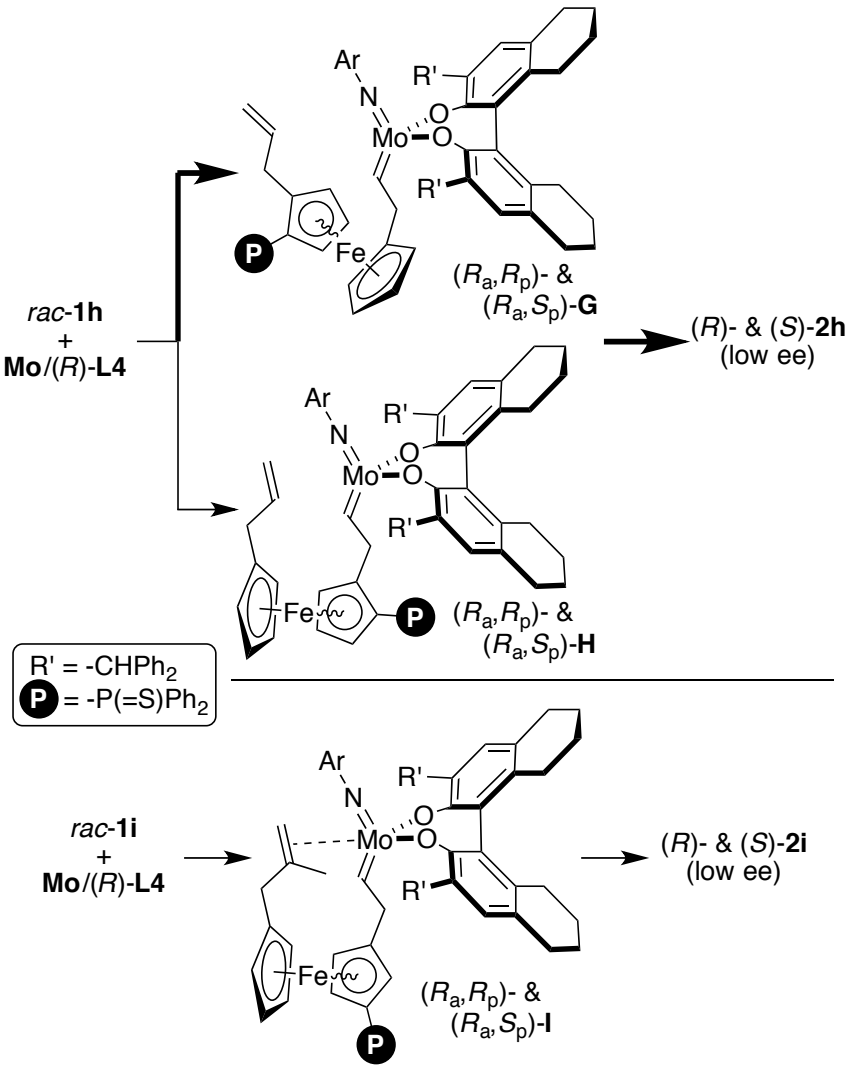


Scheme 5. Plausible Stereochemical Pathways of ARCM Kinetic Resolution of *rac*-**1c** Catalyzed by Mo/(*R*)-**L4**.

While *rac*-**1c** and *rac*-**1e-g** were resolved efficiently in the same way by the Mo-catalyzed ARCM, the kinetic resolution of *rac*-**1h** and *rac*-**1i** were much less selective (see Table 2).

Substrate *rac*-**1h** possesses two parent allyl groups instead of the allyl/methallyl combination in *rac*-**1c**, and thus the RCM reaction of *rac*-**1h** may be initiated at both allyl substituents. That is, two intermediates **G** and **H** are involved in the ARCM of *rac*-**1h**. Intermediate **G** is favored over **H**, because **G** is sterically less congested. Whereas the C_5H_4-bound allyl group in *rac*-**1h** is remote from the planar-chiral environment regulated by η^5-$C_5H_3(P(=S)Ph_2)$(allyl), the formation of diastereomeric **G** is less selective. Following ring-closure step, which is an intramolecular process, proceeds smoothly in both (R_a,R_p)- and (R_a,S_p)-**G** to give **2h** with the low enantioselectivity (Scheme 6, top).

On the other hand, the low enantioselectivity in the kinetic resolution of *rac*-**1i**, which is with a 1,3-substituted cyclopentadienide, can be rationalized as lack of the crucial steric interaction in intermediate **I**. Since the thiophosphinyl group in **I** is remote from the chiral Mo[(*R*)-biaryloxide] core, no effective diastereomeric interaction is operated in **I** (cf., the steric interaction in **D**) leading to the low enantioselectivity of the kinetic resolution process (Scheme 6, bottom).

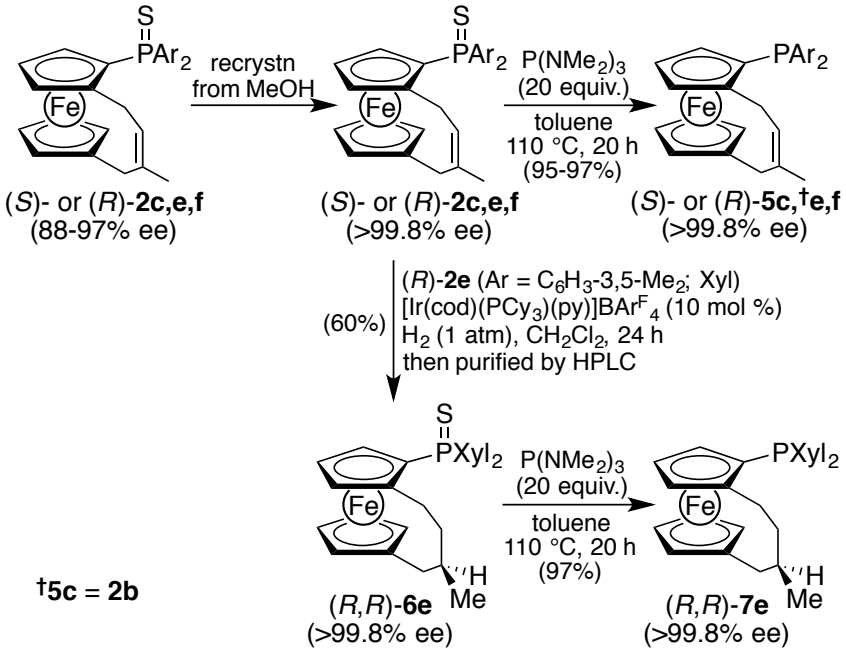


Scheme 6. Plausible Pathways of ARCM Kinetic Resolution of *rac*-**1h** and *rac*-**1i** Catalyzed by Mo/(*R*)-**L4**.

Preparation of Enantiomerically Pure Planar-Chiral Ferrocenylphosphines 5 and Hydrogenated Derivative 7. Enantiomerically enriched planar-chiral ferrocenylphosphine sulfides (*R*)- or (*S*)-**2c**, **2e**, and **2f** obtained by the Mo-catalyzed kinetic resolution could be further purified by recrystallization from hot methanol to give the respective planar-chiral compounds in essentially enantiomerically pure form (>99.8% ee). Reduction of single-

enantiomeric phosphine sulfides **2** was achieved by treating with excess $P(NMe_2)_3$ to give the corresponding ferrocenylphosphines **5** quantitatively.[20-22] The enantiopurity of the phosphine sulfides was retained during the reduction, and phosphines **5** were also single-enantiomeric (Scheme 7).

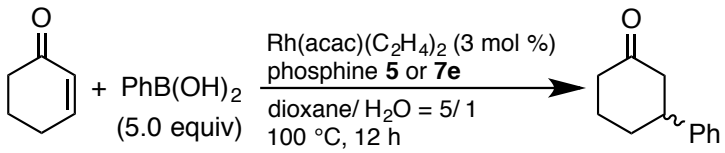
Dextrorotatory (*R*)-**2e** was hydrogenated under 1 atom of H_2 in the presence of the modified Crabtree's catalyst, $[Ir(cod)(PCy_3)(py)]BAr^F_{4,}$[23] to give a diastereomeric mixture of (R_c,R_p)- and (S_c,R_p)-**6e** in a 94/6 ratio. The minor diastereomer was removed by HPLC purification, and purified (R_c,R_p)-**6e** was reduced as above to give the corresponding ferrocenylphosphine (R_c,R_p)-**7e** as a single stereoisomer (Scheme 7).



Scheme 7. Preparation of Enantiomerically Pure Planar-Chiral Ferrocenylphosphines **5c**, **e**, **f**, and **7e**.

Application of Planar-Chiral Ferrocenylphosphines 5 and 7 to Rh- and Pd-Catalyzed Asymmetric Reactions. The synthetic utility of the planar-chiral ferrocenylphosphines as chiral ligands was examined in two transition-metal-catalyzed asymmetric reactions. The first one is the rhodium-catalyzed asymmetric 1,4-addition reaction (the Hayashi-Miyaura conjugate addition reaction) of phenylboronic acid to 2-cyclohexenone (Table 3).[13,24] A rhodium catalyst generated in situ from Rh(acac)$(C_2H_4)_2$ and (*R*)-**5c** (2 equiv. to Rh) showed excellent performance in the reaction and (*S*)-3-phenylcyclohexanone was obtained in 94% ee and 89% yield (entry 1). Phosphine (*R*)-**5e** was as effective as (*R*)-**5c** in the Rh-catalyzed reaction giving the desired product in 94% ee (entry 2). A catalyst generated from an equimolar mixture of Rh(acac)$(C_2H_4)_2$ and (*R*)-**5e** retained the high catalytic activity as well as the high enantioselectivity as above (entry 3). On the other hand, phosphine (*R*)-**5f**, which is with a bulky bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino group, showed slightly lower enantioselectivity (entry 4). Ligand (*R*)-**7e** possesses a saturated bridging tether but is otherwise isostructural to (*R*)-**5e**. Indeed, the effect of the saturated bridging tether is minimal and the rhodium species coordinated with (*R*)-**7e** showed nearly identical activity and selectivity with those of the Rh/(*R*)-**5e** species (entries 2 and 5).

Table 3. Rhodium-Catalyzed Asymmetric 1,4-Addition of Phenylboronic Acid to 2-Cyclohexenone[a]

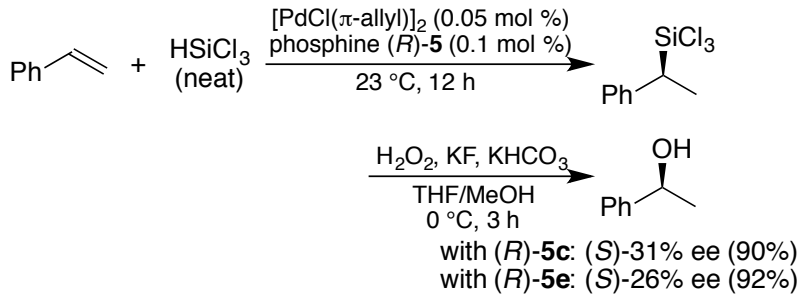


entry	chiral ligand	ligand/Rh	yield (%)[b]	% ee[c]

1	(*R*)-**5c**	2	89	94 (*S*)
2	(*R*)-**5e**	2	99	94 (*S*)
3	(*S*)-**5e**	1	93	95(*R*)
4	(*R*)-**5f**	2	89	87 (*S*)
5	(*R*)-**7e**	2	88	94 (*S*)

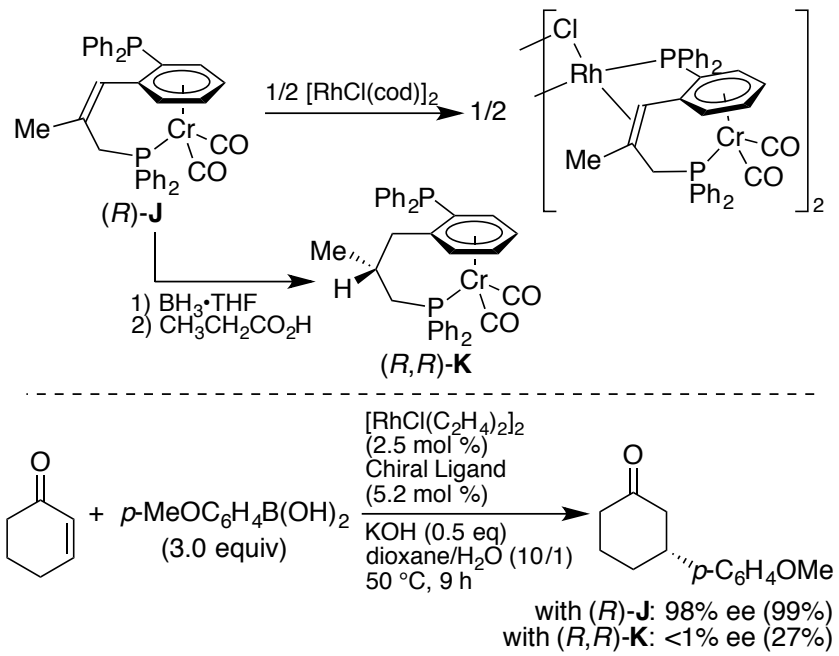
[a] The reaction was carried out using 2-cyclohexenone (0.156 mmol) in dioxane/H_2O (5/1) in the presence of the rhodium catalyst (3 mol %) generated in situ from Rh(acac)$(C_2H_4)_2$ and the chiral ligand. [b] Isolated yield by silica gel chromatography. [c] Determined by chiral HPLC analysis.

The second reaction examined was the palladium-catalyzed asymmetric hydrosilylation,[25] and the applicability of (*R*)-**5c** and (*R*)-**5e** was explored for the reaction between styrene and trichlorosilane (Scheme 8). A palladium complex generated in situ from $[PdCl(\pi\text{-allyl})]_2$ and the equimolar ferrocenylphosphine ligand catalyzed the reaction smoothly to provide the desired hydrosilylation product, whose yield and enantiomeric purity were determined after converting it into 1-phenylethanol by the Tamao-Flemming oxidation.[26] In both cases, the enantioselectivity was moderate with around 30% ee, however, these results clearly indicate that the applications of the ferrocenylphosphine ligands **5** are not limited to the Rh(I)-catalyzed reaction, and the ligands might be applicable to various transition-metal-catalyzed asymmetric reactions.



Scheme 8. Palladium-Catalyzed Asymmetric Hydrosilylation of Styrene with Trichlorosilane.

Coordination mode of ferrocenylphosphines 5 to Rh(I). We recently disclosed that planar-chiral (π-arene)chromium-based phosphine **J** was an exceptionally effective chiral ligand in various transition-metal-catalyzed asymmetric reactions.[27] Phosphine **J** coordinates to a Rh(I) cation in a bidentate fashion with the phosphine and the olefin donors, and the chelate coordination plays an important role for the high enantioselectivity (Scheme 9).[24] Whereas ferrocenylphosphines **5** possess a phosphine/olefin substructure somewhat similar to that in **J**, initially its coordination to a Rh(I) cation was postulated to be bidentate as in the case with **J**. However, the results of the Rh-catalyzed 1,4-addition reaction summarized in Table 3 indicated that ferrocenylphosphines **5** might behave as monodentate ligands upon the coordination to a Rh(I) cation since **7e**, which has no olefin substructure in it, showed nearly identical catalytic activity and enantioselectivity with those of **5e** (Table 3, entries 2 and 5). These are clear contrast to the difference between **J** and **K** in the Rh-catalyzed reaction. Ligand **K** possesses the saturated bridging tether but is otherwise isostructural to **J**. Due to the absence of an olefinic donor moiety, **K** is unable to coordinate to a Rh(I) atom in the bidentate fashion. The outcome of this structural change is drastic and the rhodium species coordinated with **K** showed virtually no enantioselectivity in the Rh-catalyzed 1,4-addition reaction giving a nearly racemic product.



Scheme 9. (π-Arene)chromium-Based Planar-Chiral Phosphine Ligands and Their Application in the Rh-Catalyzed 1,4-Addition of *p*-$MeOC_6H_4B(OH)_2$ to Cyclohexenone.[27b]

With the above-mentioned considerations in mind, the coordination mode of **5c** to a Rh(I) cation was examined by the NMR experiments. A reaction of (*R*)-**5c** (^{31}P-NMR: δ –20.9) and a half equivalent of $[RhCl(cod)]_2$ in C_6D_6 at room temperature afforded a new rhodium species **8** quantitatively in the time of mixing (Figure 3, top). Upon the coordination to the Rh(I) cation, the ^{31}P-NMR resonance for the free phosphine in (*R*)-**5c** was shifted downfield to δ 18.3 in **8** with the large P-Rh coupling ($J_{P\text{-}Rh}$ = 147.3 Hz), which indicated the direct ligation at the Ph_2P-(η^5-C_5) moiety to the rhodium atom. In the ^{1}H-NMR spectra, the olefinic H atom in (*R*)-**5c** was detected at δ 5.66, which was slightly shifted downfield to δ 5.92 upon the coordination to Rh(I) in **8** (Figure 3, bottom). This chemical shift is within the normal range for free olefinic hydrogens. All these NMR observations clearly indicate that ferrocenylphosphine (*R*)-**5c** behaves as a simple monodentate phosphine, not as a *P*-olefin bidentate ligand, in **8**. In accordance with these, the

signals assignable for the η^2-coordinating cyclooctadiene were detected in the ^{1}H-NMR spectrum of **8**: δ 5.84 (br, free -CH=CH-, 2H), 3.06 (br, Rh-η^2-CH=CH, 1H), 2.86 (br, Rh-η^2-CH=CH, 1H). The MS measurement revealed complex **8** to be dimeric, and the structure with the two μ-Cl ligands is proposed as shown in Figure 3.

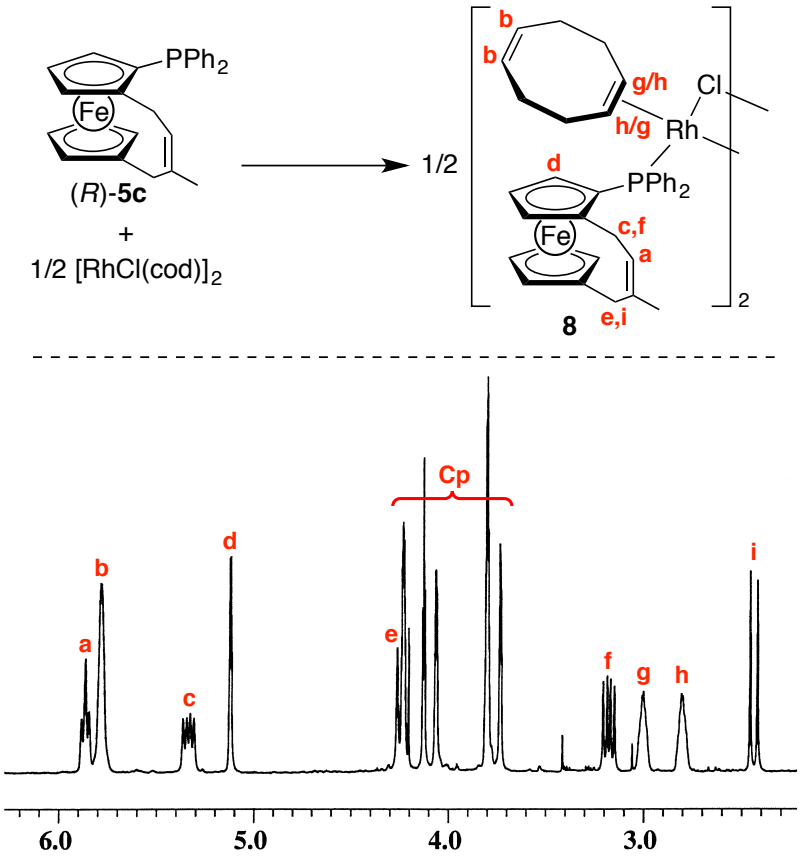


Figure 3. Formation of complex **8** and its ^{1}H-NMR spectrum in the olefinic/Cp/allylic region at 400 MHz in C_6D_6.

Conclusions

Highly enantioselective kinetic resolution of racemic planar-chiral metallocenylphosphine sulfides was realized by the molybdenum-catalyzed asymmetric ring-closing metathesis reaction. Recrystallization of the obtained enantiomerically enriched 1,4-but-2-enylene-bridged ferrocenylphosphine sulfides afforded the single-enantiomeric products, and subsequent their reduction provided the corresponding ferrocenylphosphines. Whereas no racemization was associated with the reduction process, the ferrocenylphosphines thus obtained were also single-enatiomeric. The enantiomerically pure planar-chiral ferrocenylphosphines were applied as chiral ligands in the rhodium-catalyzed asymmetric 1,4-addition reaction of phenylboronic acid to 2-cyclohexenone to show excellent enantioselectivity and high yields. The NMR studies clarified that the butenylene-bridged ferrocenylphosphine coordinated to a rhodium(I) cation in a monodentate fashion and an interaction of the bridging olefin moiety to the rhodium atom was not detected.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, compound characterization data, and crystallographic data of ferrocenylphosphine sulfide (*S*)-(–)-**2e** (CIF file). This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Börner, A. Ed. *Phosphorus Ligands in Asymmetric Catalysis*; Wiley-VCH: Weinheim, 2008.

(2) Reviews of planar-chiral ferrocenylphosphine ligands: (a) Hayashi, T. In *Ferrocenes*; Togni, A.; Hayashi, T., Eds.; VCH: Weinheim, 1995; p. 105-142. (b) Togni, A. In *Metallocenes*; Togni, A.; Halterman, R. L., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2, p. 685-721. (c) Colacot, T. J. *Chem. Rev.* **2003**, *103*, 3101-3118. (d) Barbaro, P.; Bianchini, C.; Giambastiani, G.; Parisel, S. L. *Coord. Chem. Rev.* **2004**, *248*, 2131-2150. (e) Arrayás, R. G.; Adrio, J.; Carretero, J. C. *Angew. Chem. Int. Ed.* **2006**, *45*, 7674-7715. (f) Fu, G. C. *Acc. Chem. Res.* **2006**, *39*, 853-860. (g) Ganter, C. In *Phosphorus Ligands in Asymmetric Catalysis*; Börner, A. Ed.; Wiley-VCH: Weinheim, 2008; p. 393-407. (h) Dai, L.-X.; Hou, X.-L., Eds. *Chiral Ferrocenes in Asymmetric Catalysis*; Wiley-VCH: Weinheim, 2010.

(3) (a) Hayashi, T.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett*. **1974**, 4405-4408. (b) Hayashi, T.; Tajika, M.; Tamao, K.; Kumada, M. *J. Am. Chem. Soc*. **1976**, *98*, 3718-3719. (c) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn*. **1980**, *53*, 1138-1151.

(4) (a) Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc*. **1970**, *92*, 5389-5393. (b) Battelle, L. F.; Bau, R.; Gokel, G. W.; Oyakawa, R. T.; Ugi, I. K. *J. Am. Chem. Soc*. **1973**, *95*, 482-486. (c) Riant, O.; Samuel, O.; Kagan, H. B. *J. Am. Chem. Soc*. **1993**, *115*, 5835-5836. (d) Rebière, F.; Riant, O.; Ricard, L.; Kagan, H. B. *Angew. Chem. Int. Ed. Engl*. **1993**, *32*, 568-570. (e) Richards, C. J.; Damalidis, T.; Hibbs, D. E.; Hursthouse, M. B. *Synlett* **1995**, 74-76. (f) Enders, D.; Peters, R.; Lochtman, R.; Raabe, G. *Angew. Chem. Int. Ed*. **1999**, *38*, 2421-2423.

(5) (a) Tsukazaki, M.; Tinkl, M.; Roglans, A.; Chapell, B. J.; Taylor, N. J.; Snieckus, V. *J. Am. Chem. Soc*. **1996**, *118*, 685-686. (b) Nishibayashi, Y.; Arikawa, Y.; Ohe, K.; Uemura, S. *J. Org. Chem*. **1996**, *61*, 1172-1174. (c) Laufer, R. S.; Veith, U.; Taylor, N. J.; Snieckus, V. *Org. Lett*. **2000**, *2*, 629-631. (d) Genet, C.; Canipa, S. J.; O'Brien, P.; Taylor, S. *J. Am. Chem. Soc*. **2006**, *128*, 9336-9337.

(6) (a) Pedersen, H. L.; Johannsen, M. *J. Org. Chem*. **2002**, *67*, 7982-7994. (b) Jensen, J. F.; Johannsen, M. *Org. Lett*. **2003**, *5*, 3025-3028. (c) Jensen, J. F.; Søtofte, I.; Sørensen, H. O.; Johannsen, M. *J. Org. Chem*. **2003**, *68*, 1258-1265.

(7) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Lanbert, H.; Tijani, A. *J. Am. Chem. Soc*. **1994**, *116*, 4062-4066.

(8) (a) Sawamura, M; Hamashima, H.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 8295-8296. (b) Sawamura, M.; Kuwano, R.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9602-9603. (c) Sawamura, M.; Sudoh, M.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3309-3310.

(9) (a) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965-994. (b) Wagner, G.; Herrmann, R. In *Ferrocenes*; Togni, A.; Hayashi, T., Eds.; VCH: Weinheim, 1995; p. 173-218. (c) Togni, A. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1475-1477. (d) Richards, C. J.; Locke, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377-2407. (e) Štěpnička, P.; Lamač, M. In *Ferrocenes*; Štěpnička, P., Ed.; Wiley: Chichester, 2008; p. 237-277. (e) Ogasawara, M.; Watanabe, S. *Synthesis* **2009**, 1761-1785. (f) Alba, A.-N. R.; Rios, R. *Molecules* **2009**, *14*, 4747-4757. (g) Arae, S.; Ogasawara, M. *J. Synth. Org. Chem., Jpn.* **2012**, *70*, 593-605. (h) Schaarschmidt, D.; Lang, H. *Organometallics* **2013**, *32*, 5668-5704. (i) Arae, S.; Ogasawara, M. *Tetrahedron Lett.* **2015**, *56*, 1751-1761.

(10) (a) Siegel, S.; Schmalz, H.-G. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2456-2458. (b) Bueno, A.; Rosol, M.; García, J.; Moyano, A. *Adv. Synth. Catal.* **2006**, *348*, 2590-2596. (c) Mercier, A.; Yeo, W. C.; Chou, J.; Chaudhuri, P. D.; Bernardinelli, G.; Kündig, E. P. *Chem. Commun.* **2009**, 5227-5229. (d) Alba, A.-N.; Gómez-Sal, P.; Rios, R.; Moyano, A. *Tetrahedron: Asymmetry* **2009**, *20*, 1314-1318. (e) Mercier, A.; Urbaneja, X.; Yeo, W. C.; Chaudhuri, P. D.; Cumming, G. R.; House, D.; Bernardinelli, G.; Kündig, E. P. *Chem. Eur. J.* **2010**, *16*, 6285-6299. (f) Gao, D.-W.; Shi, Y.-C.; Gu, Q.; Zhao, Z.-L.; You, S.-L. *J. Am. Chem. Soc.* **2013**, *135*, 86-89. (g) Pi, C.; Li, Y.; Cui, X.; Zhang, H.; Han, Y.; Wu, Y. *Chem. Sci.* **2013**, *4*, 2675-2679. (h) Wagschal, S.; Mercier, A.; Kündig, E. P. *Organometallics* **2013**, *32*, 7133-7140. (i) Akiyama, M.; Akagawa, K.; Seino, H.; Kudo, K. *Chem. Commun.* **2014**, *50*, 7893-7896. (j) Deng, R.; Huang, Y.; Ma, X.; Li, G.; Zhu, R.; Wang, B.; Kang, Y.-B.; Gu, Z. *J. Am. Chem. Soc.* **2014**, *136*, 4472-4475. (k) Gao, D.-W.; Yin, Q.; Gu, Q.; You, S.-L. *J. Am. Chem. Soc.* **2014**, *136*, 4841-

4844. (l) Shibata, T.; Shizuno, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 5410-5413. (m) Shibata, T.; Shizuno, T.; Sasaki, T. *Chem. Commun.* **2015**, *51*, 7802-7804. (n) Zhang, Q.-W.; An, K.; Liu, L-C.; Yue, Y.; He, W. *Angew. Chem. Int. Ed.* **2015**, *54*, 6918-6921. (o) Gao, D.-W.; Zheng, C.; Gu, Q.; You, S.-L. *Organometallics* **2015**, *34*, 4618-4625.

(11) (a) Ogasawara, M.; Watanabe, S.; Fan, L.; Nakajima, K.; Takahashi, T. *Organometallics* **2006**, *25*, 5201-5203. (b) Ogasawara, M.; Watanabe, S.; Nakajima, K.; Takahashi, T. *Pure Appl. Chem.* **2008**, *80*, 1109-1113. (c) Ogasawara, M.; Watanabe, S.; Nakajima, K.; Takahashi, T. *J. Am. Chem. Soc.* **2010**, *132*, 2136-2137. (d) Ogasawara, M.; Arae, S.; Watanabe, S.; Nakajima, K.; Takahashi, T. *Chem. Eur. J.* **2013**, *19*, 4151-4154. (e) Arae, S.; Nakajima, K.; Takahashi, T.; Ogasawara, M. *Organometallics* **2015**, *34*, 1197-1202.

(12) Reviews of asymmetric olefin metathesis: (a) Hoveyda, A. H.; Schrock, R. R. *Chem. Eur. J.* **2001**, *7*, 945-950. (b) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2003**, *42*, 4592-4633. (c) Hoveyda, A. H. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; Vol. 2, p. 128-150. (d) Hoveyda, A. H.; Schrock, R. R. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H., Eds.; Springer-Verlag: Berlin, 2004; Supplement 1, p. 207-233. (e) Klare, H. F. T.; Oestreich, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 2085-2089. (f) Hoveyda, A. H.; Malcolmson, S. J.; Meek, S. J.; Zhugralin, A. R. *Angew. Chem. Int. Ed.* **2010**, *49*, 34-44. (g) Collins, S. K. In *Science of Synthesis, Stereoselective Synthesis*; de Vries, J. G.; Molander, G. A.; Evans, P. A., Eds.; Georg Thieme Verlag: Stuttgart, 2011; Vol. 1, p. 819-871. (h) Hoveyda, A. H. *J. Org. Chem.* **2014**, *79*, 4763-4792. See also: (i) Hoveyda, A. H.; Zhugralin, A. R. *Nature* **2007**, *450*, 243-251.

(13) (a) Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc.* **1998**, *120*, 5579-5580. (b) Hayashi, T.; Takahashi, M.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc.* **2002**, *124*, 5052-5028. For reviews, see: (c) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829-2844. (d) Hayashi, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 13-21. (e) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169-196. (f) Hayashi, T. In *Modern Rhodium-Catalyzed Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, 2005, p. 55-77.

(14) (a) Dog, T.-Y.; Lai, L.-L. *J. Organomet. Chem.* **1996**, *509*, 131-134. (b) Shafir, A.; Power, M. P.; Whitener, G. D.; Arnold, J. *Organometallics* **2000**, *19*, 3978-3982. (c) Habata, Y.; Akabori, S.; Sato, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3540-3546.

(15) (a) Butler, I. R.; Müssig, S.; Plath, M. *Inorg. Chem. Commun.* **1999**, *2*, 424-427. (b) Butler, I. R. *Inorg. Chem. Commun.* **2008**, *11*, 15-19. (c) Butler, I. R. *Eur. J. Inorg. Chem.* **2012**, 4387-4406.

(16) Hock, A. S.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 16373-16375.

(17) (a) Aeilts, S. L.; Cefalo, D. R.; Bonitatebus, Jr., P. J.; Houser, J. H.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem. Int. Ed.* **2001**, *40*, 1452-1456. (b) Singh, R.; Czekelius, C.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *Organometallics* **2007**, *26*, 2528-2539. (c) Zhu, S. S.; Cefalo, D. R.; La, D. S.; Jamieson, J. Y.; Davis, W. M.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 8251-8259. (d) Schrock, R. R.; Jamieson, J. Y.; Dolman, S. J.; Miller, S. A.; Bonitatebus, Jr., P. J.; Hoveyda, A. H. *Organometallics* **2002**, *21*, 409-417.

(18) (a) Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1988**, *18*, 249-330. (b) Vedejs, E.; Jure, M. *Angew. Chem. Int. Ed.* **2005**, *44*, 3974-4001.

(19) (a) Ogasawara, M.; Nagano, T.; Hayashi, T. *J. Am. Chem. Soc.* **2002**, *124*, 9068-9069. (b) Ogasawara, M.; Nagano, T.; Hayashi, T. *J. Am. Chem. Soc.* **2002**, *124*, 12626 [correction to ref. 19a]. (c) Ogasawara, M.; Nagano, T.; Hayashi, T. *Organometallics* **2003**, *22*, 1174-1176. (d) Ogasawara, M.; Watanabe, S.; Nakajima, K.; Takahashi, T. *Organometallics* **2008**, *27*, 6565-6569. (e) Ogasawara, M.; Wu, W.-Y.; Arae, S.; Nakajima, K.; Takahashi, T. *Organometallics* **2013**, *32*, 6593-6598.

(20) Olah, G. A.; Berrier, A.; Ohannesian, L. *New J. Chem.* **1986**, *10*, 253-257.

(21) For examples of related planar-chiral ferrocenophane-phosphines, see: (a) Sturm, T.; Weissensteiner,W.; Spindler, F.; Mereiter, K.; López-Agenjo, A. M.; Manzano, B. R.; Jalón, F. A. *Organometallics* **2002**, *21*, 1766-1774. (b) Liptau, P.; Seki, T.; Kehr, G.; Abele, A.; Fröhlich, R.; Erker, G.; Grimme, S. *Organometallics* **2003**, *22*, 2226-2232. (c) Šebesta, R.; Almassy, A.; Císařová, I.; Toma, Š. *Tetrahedron: Asymmetry* **2006**, *17*, 2531-2537. (d) Voituriez, A.; Panossian, A.; Fleury-Brégeot, N.; Retailleau, P.; Marinetti, A. *J. Am. Chem. Soc.* **2008**, *130*, 14030-14031.

(22) For examples of related planar-chiral alkenylferrocenylphosphines, see: (a) Štěpnička, P.; Císařová, I. *Inorg. Chem.* **2006**, *45*, 8785-8798. (b) Stemmler, R. T.; Bolm, C. *Synlett* **2007**, *9*, 1365-1370. (c) Štěpnička, P.; Lamač, M.; Císařová, I. *J. Organomet. Chem.* **2008**, *693*, 446-456. (d) Csizmadiová, J.; Mečiarová, M.; Rakovský, E.; Horváth, B.; Šebesta, R. *Eur. J. Org. Chem.* **2011**, 6110-6116.

(23) Wüstenberg, B.; Pfaltz, A. *Adv. Synth. Catal.* **2008**, *350*, 174-178.

(24) The optimized conditions for the Rh-catalyzed asymmetric 1,4-addition reaction of arylboronic acid to 2-cyclohexenone using chiral ligand **5** or **7e** in Table 3 are different from those using chiral ligand **J** or **K** shown in Scheme 9. These are probably due to the difference of the coordination modes between **5**/**7e** and **J**/**K**. In both cases, however, the catalytically active species should be analogous Rh-OH species generated in situ. See, ref-13b.

(25) (a) Hayashi, T. *Acc. Chem. Res.* **2000**, *33*, 354-362. (b) Yamamoto, K.; Hayashi, T. In *Transition Metals for Organic Synthesis (II)*; Beller, M.; Bolm, C., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 2, p. 167-191. (c) Hayashi, T.; Yamasaki, K. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H.; Mingos, D. M. P., Eds.; Elsevier: Oxford, 2007; Vol. 10, p. 815-838. (d) Gibson, S. E.; Rudd, M. *Adv. Synth. Catal.* **2007**, *349*, 781-795. (e) Han, J. W.; Hayashi, T. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed., 3rd ed.; Wiley- VCH: New York, 2009; p. 771-798. (f) Han, J. W.; Hayashi, T. In *Stereoselective Synthesis 1: Stereoselective Reactions of Carbon–Carbon Double Bonds*; de Vries, J. G., Ed.; George Thieme: Stuttgart, 2011; p. 923-939. (g) Han, J. W.; Hayashi, T. *Tetrahedron: Asymmetry* **2014**, *25*, 479-484.

(26) (a) Tamao, K. In *Advances in Silicon Chemistry*; Larson, G. L., Ed.; JAI Press: London, 1996; p. 1-62. (b) Tamao, K. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, 1985; p. 231-242.

(27) (a) Ogasawara, M.; Wu, W.-Y.; Arae, S.; Watanabe, S.; Morita, T.; Takahashi, T.; Kamikawa, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 2951-2955. (b) Ogasawara, M.; Tseng, Y.-Y.; Arae, S.; Morita, T.; Nakaya, T.; Wu, W.-Y.; Takahashi, T.; Kamikawa, K. *J. Am. Chem. Soc.* **2014**, *136*, 9377-9384.

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