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Synthesis of Chiral Ferrocenyl Imidazolium Salts and Their Rhodium(I) and Iridium(I) Complexes

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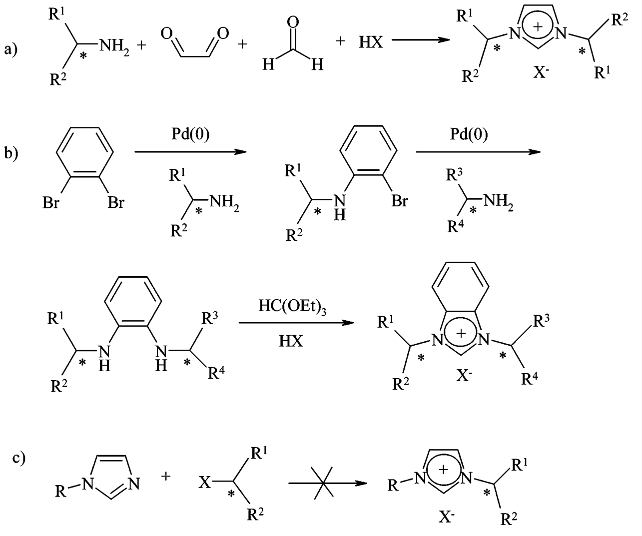
Chiral ferrocenyl imidazolium salts were obtained from optically pure ferrocenyl alcohols or acetates by substitution with retention of configurations. Their rhodium and iridium complexes were synthesized and applied to asymmetric hydrogenations. The benzimidazolylidene−iridium complex showed up to 52.6% ee in the transfer hydrogenation of 4′-methylacetophenone.

Introduction

Recently, N-heterocyclic carbene (NHC) ligands have become universal ligands in organometallic and inorganic chemistry.[1] Owing to their specific coordination chemistry, NHCs stabilize and activate metal centers and sometimes can replace organophosphanes.[2] NHCs have a much higher trans effect than N- or P-donors and are more tightly bound to the metal.[3] Many catalytic reactions of N-heterocyclic carbene−Pd, −Ni, −Rh, −Ir, −Cu, and −Ru complexes have been reported.[4] Asymmetric NHC−metal complex-catalyzed reactions such as hydrosilylation, 1,4-conjugated addition, cross-coupling, and olefin metathesis have also been reported.[5−8] Most reported chiral NHCs are C_2-symmetric. Non-C_2-symmetric carbenes whose α-carbons of the nitrogen of the imidazolium core have a chiral center have not been reported except for chiral triazoliums.[5a,b] Various non-C_2-symmetric, monodentate ligands showed high enantioselectivities, and in some cases, they showed better enantioselectivities than C_2-symmetric ones.[9] Thus, it will be useful to synthesize C_1-symmetric, chiral carbene ligands for asymmetric catalysis.

Scheme 1. Synthetic Methods for Chiral Imidazolium Salts



Chiral imidazolium salts are synthesized from chiral amines according to the method shown in Scheme 1a.[7,10] However, this method is not suitable for substituting two different groups for the two nitrogens. Scheme 1b shows an example of differently substituted imidazoliums.[11] Scheme 1c can be considered a good method. This route might be a simple way to obtain a differently substituted chiral imidazolium salt. However, there had been no previous reports on the substitution with retention or inversion of the configuration to an optically

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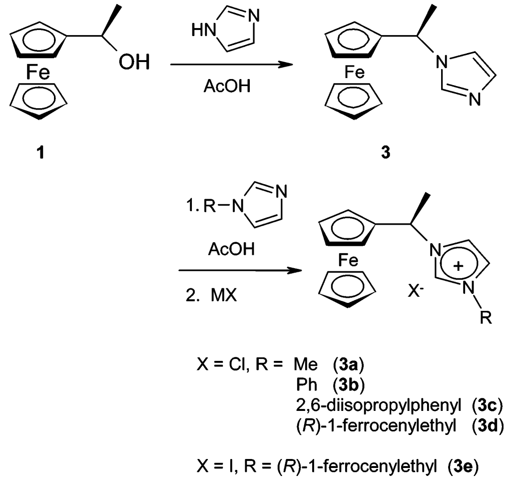
Scheme 2. Synthesis of the Chiral Ferrocenyl Imidazolium Salts



pure imidazolium salt when we initiated this study.[12] While we were studying the synthesis of C_2-symmetric chiral ferrocenyl NHC, a paper describing the same methodology as ours had been reported by Togni and Broggini.[12f] Ferrocenyl alcohols such as **1** are known to be substituted with other heteroatoms with retention of configurations.[13] We thought that the synthesis of chiral ferrocenyl imidazolium salts whose two nitrogens were differently substituted would be possible, and this will expand the scope of the synthesis of various chiral imidazolium salts.

Results and Discussion

Synthesis. It is well known[13] that chiral ferrocenyl alcohols such as **1** can preserve their chirality when their alcohol groups are substituted with other functional groups. (*R*)-Ferrocenyl ethanol (**1**) was obtained in a high yield and with a very high optical purity (>95% ee) by the oxazaborolidine-mediated reduction of acetyl ferrocene.[14] We recently reported[15] on the preparation of ortho-functionalized chiral ferrocenyl imidazolium salts. New chiral imidazolium salts having no planar chirality were synthesized by the same method as the synthesis of the ortho-functionalized ones. Treatment of **1** with imidazole in acetic acid at 60 °C for 6 h resulted in the substitution of the hydroxy group with imidazole. A basic workup yielded a chiral ferrocenyl imidazole **3** (Scheme 2). Reaction of **1** with 1-substituted imidazole instead of imidazole gave an imidazolium salt with the hydroxide as a counteranion.

Scheme 3. Synthesis of the Imidazolin-2-thiones

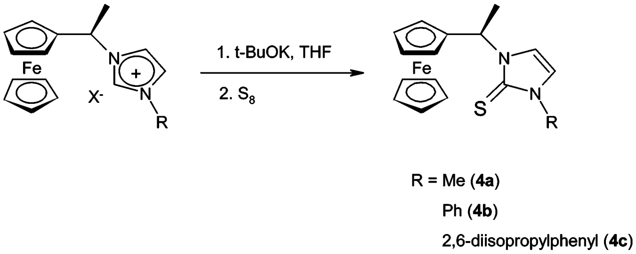


Table 1. Synthesis of Chiral Imidazolium Salts

imidazolium salt	temp (°C)	yield (%)	ee (%)
3a	60	72	76.1
	25	74	92.9
3b	25	95	91.5
	25[a]	70	97.5
3c	60	55	3.9
	25	95	87.1
3d	25	72	-
3e	25	62	-
3f	25	82	1.8
	25[b]	88	91.7

[a] **1a** used. [b] **2a** used.

Compounds **3a** and **3c** were obtained by the same method at 60 °C. The counteranion could be exchanged with a less basic acetate ion in the acetic acid solution. Addition of excess LiCl or NaI to the reaction mixture resulted in anion exchange to give a halide ion as a counteranion. Thus, compounds **3d** and **3e** having the same cation structure with different counteranions were obtained just by changing halide sources. To determine the optical purity of the new imidazolium salts, the imidazolium salts were converted to imidazole-2-thiones to facilitate the determination of the enantiomeric excess by HPLC.

Treatment of **3a** and **3c** with t-BuOK followed by addition of sulfur led to compounds **4a** and **4c** (Scheme 3). The enantiomeric excesses of **4a**–**c** were determined by studying their imidazole-2-thione derivatives. When the salts were produced at 60 °C, low to moderate ee values were obtained: 76% ee of **4a** and 3.9% ee of **4c** were obtained. The ortho-functionalized chiral ferrocenylamines were converted to the imidazolium salts by the same method with a complete retention of the configurations. In the case of ortho-substituted ferrocenyl alcohols and amines, it is expected that the rotation barriers for the intermediate cations are higher than those of non-ortho-substituted ones. Thus, it may be difficult for the racemization to occur even at a high reaction temperature. However, the newly synthesized imidazolium salts in this study have no ortho-substituent and the rotation barriers may be low. To test a racemization of the ferrocenyl ethanol **1** at 60 °C in acetic acid, **1** was heated at 60 °C for 6 h in acetic acid. After workup, **1** was obtained with a 6.3% ee. Thus, the racemization occurred during the substitution. Therefore, the substitution reaction was carried out at low temperature to raise the ee values. As shown in Table 1, high ee values with moderate yields were obtained at room temperature: the ee values of **4a** were promoted to 92.9%. For **4c**, the ee value was dramatically increased from 3.9% to 87.1%. As expected, the enantiospecificities were highly dependent upon the reaction temperature. The steric effect also influenced the ee

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(12) Ferrocenyl imidazoliums that have no chiral centers and the catalytic reactions of their metal complexes were reported: (a) Bildstein, B.; Malaun, M.; Kopacka, H.; Wurst, K.; Mitterböck, M.; Ongania, K.-H.; Opromolla, G.; Zanello, P. *Organometallics* **1999**, *18*, 4325. (b) Bildstein, B. *J. Organomet. Chem.* **2001**, *617–618*, 28. (c) Thomas, J.-L.; Howarth, J.; Hanlon, K.; Mcguirk, D. *Tetrahedron Lett.* **2001**, *41*, 413. (d) Jackstell, R.; Frisch, A.; Beller, M.; Röttger, D.; Malaun, M.; Bildstein, B. *J. Mol. Catal. A: Chem.* **2002**, *185*, 105. A planar chiral ferrocenyl carbene was synthesized: (e) Bolm, C.; Kesselgruber, M.; Raabe, G. *Organometallics* **2002**, *21*, 707. (f) Broggini, D.; Togni, A. *Helv. Chim. Acta* **2002**, *85*, 2518.

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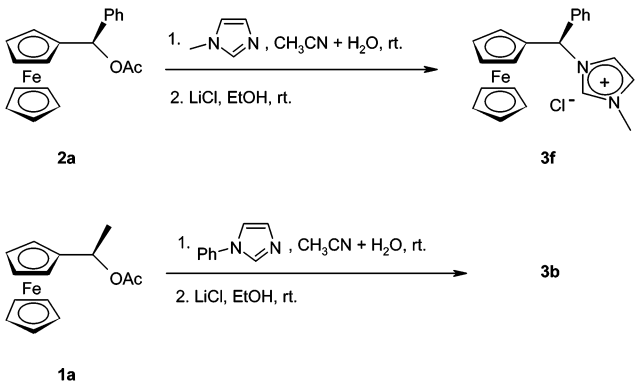
Scheme 4. Substitution of the Chiral Ferrocenyl Acetates

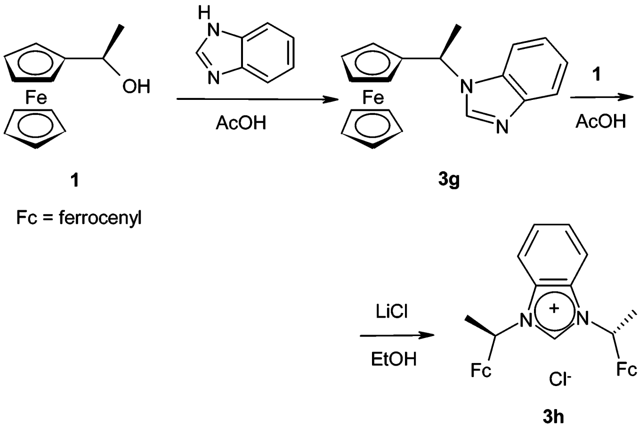


values: substitution with 2,6-diisopropylphenyl imidazole yielded the lowest ee value. Interestingly, phenylimidazole-substituted salt **4b** was synthesized at ambient temperature with 91.5% ee.

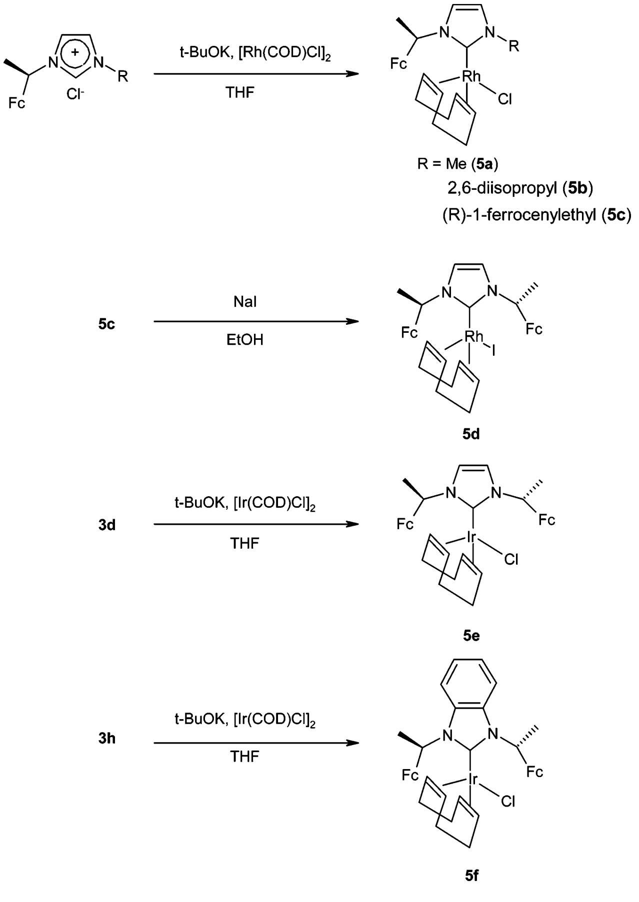
We applied the above method to other chiral ferrocenyl alcohols. Treatment of ferrocenyl benzyl alcohol **2** with 1-methylimidazole in acetic acid at ambient temperature yielded **3f** in 82% yield with a poor ee value (1.8%). Thus, the above procedure was not suitable for the ferrocenyl alcohol bearing a phenyl group as an α-substituent. While we searched for other methodologies, we found that aryl-substituted chiral ferrocenyl acetates such as **2a** were substituted by amines in a mixture of water and acetonitrile with a complete retention of configuration.[9b] Thus, we investigated a substitution of **2a** with 1-methylimidazole in a mixture of water and acetonitrile at ambient temperature. As expected, high yields (88%) and high ee (91.7%) values for **3f** were obtained (Scheme 4). When this method was applied to **1a**, a high ee (97.5%) value for **3b** was obtained. In the same way, C_2-symmetric imidazolium salts, **3d** and **3e**, were also synthesized. The diastereomeric purity of the C_2-symmetric imidazolium salt can be determined by the inspection of the ^{1}H NMR spectrum. The methyl protons of C_2-symmetric- and meso-imidazolium salts **3d** were split about 1.8 Hz in the NMR spectrum. Recrystallization of **3d** and **3e** gave crystalline solids whose NMR spectra showed no diastereomeric peaks. Compound **3g** was also synthesized in 56% yield with 95% ee from **1**. Compound **3h** bearing two chiral ferrocenylethyl units was synthesized in 48% yield by the reaction of **3g** with **1** (Scheme 5).

To obtain rhodium complexes **5a**−**c**, ferrocenyl imidazolium salts such as **3a**, **3c**, and **3d** were treated with t-BuOK and [Rh(COD)Cl]$_2$ in THF (Scheme 6). When a rhodium chloride such as **5c** was treated with NaI, the rhodium iodide compound **5d** was obtained. In the same way, iridium complexes were also synthesized. Reaction of **3d** with t-BuOK followed by the addition of [Ir(COD)-Cl]$_2$ yielded iridium complex **5e**. Compound **5f** was obtained from **3h**.

Scheme 5. Substitution with Benzimidazole



Scheme 6. Synthesis of Rh(I)− and Ir(I)−Carbene Complexes



Compounds **5a** and **5b**, whose imidazolylidene moieties are C_1-symmetric, have axial chirality on the Rh−C(carbene) bonds. According to an NMR study, the ratios of diastereomers were 2:1 for both **5a** and **5b**. The sizes of the two substituents of the imidazolylidenes of **5a** and **5b** are markedly different, but their diastereomeric ratios are the same. These mixtures could not be separated by column chromatography or recrystallization. Thus, the configuration of the major diastereomers could not be determined. We envision that in the major diastereomer, the larger ferrocene may face the smaller Cl, and the smaller methyl may face the larger COD (Figure 1). Like **5a** and **5b**, some rhodium carbene complexes exist as diastereomeric mixtures.[5a,b,12e]

Molecular Structures of 4a, 5c, 5d, 5e, and 5f. The geometry of **4a** along with the atomic numbering scheme used is depicted in Figure 2. The X-ray diffraction study shows the retention of the configuration. The C=S(exo) thioketonic bond distance value (1.675(4) Å) is in agreement with the average value of 1.671 Å for the Csp^2=S bond distance type in the structural fragment (X)$_2$−C=

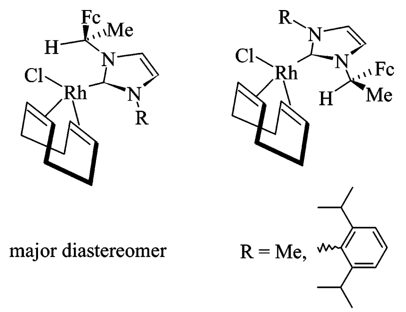


Figure 1. Hypothetical conformations of **5a** and **5b**.

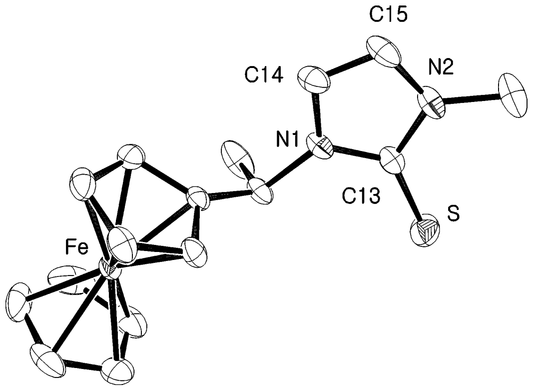


Figure 2. ORTEP drawing of **4a**. Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å): C13−S 1.675(4), C13−N1 1.367(4), C13−N2 1.363(4).

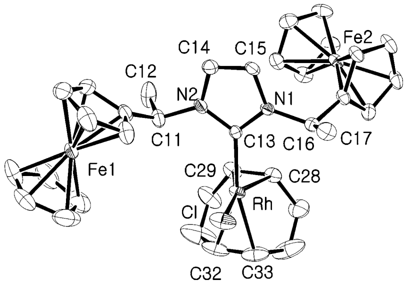


Figure 3. ORTEP drawing of **5c**. Thermal ellipsoids are shown at 30% probability.

S, where X = C, N, O, and S, and the C−N endocyclic distances (1.364(4) and 1.367(4) Å) are close to the C−N bond in the general structural fragment Car−Nsp^2 (1.371 Å).[16]

The geometries of **5c**, **5d**, **5e**, and **5f** along with their atomic numbering schemes used are depicted in Figures 3−6, and bond distances and angles are given in Tables 2 and 3. These four structures show common features. Owing to the steric congestion, two ferrocenyl groups are directed outward from the metals and are located at the opposite sites of the imidazolylidene plane from each other. The metal−C(COD) bond distances for the COD vinyl carbons trans to the carbenes are longer than those trans to the halogens: av 2.207 and 2.123 Å for **5**−**3**, av 2.229 and 2.137 Å for **5d**, av 2.167 and 2.101 Å for **5e**, and av 2.199 and 2.120 Å for **5** and **6**. The C═C bond lengths of COD trans to the carbenes are shorter than those trans to the halogens: 1.338(12) and 1.407(9) Å for **5c**, 1.332(19) and 1.406(16) Å for **5d**, 1.340(20) and 1.377(17) Å for **5e**, and 1.396(15) and 1.447(15) Å for **5f**. These mean that the metal−(C═C) interactions trans to carbenes are weaker because of the weak π-accepting power of the carbenes.[17] These observations were also reported for other chiral carbene−metal complexes.[10] Dihedral angles between the carbene ligand plane and M−X (M = Rh, Ir; X = Cl, I) are as follows: **5c**, 86.4(2)°; **5d**, 87.1(3)°; **5e**, 88.0(4)°; **5f**, 83.1(3)°.

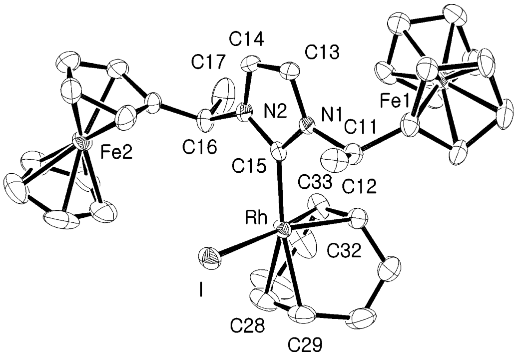


Figure 4. ORTEP drawing of **5d**. Thermal ellipsoids are shown at 30% probability.

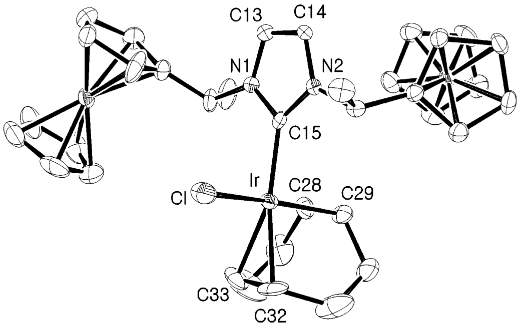


Figure 5. ORTEP drawing of **5e**. Thermal ellipsoids are shown at 30% probability.

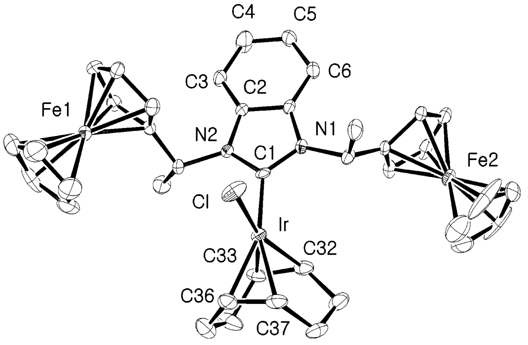


Figure 6. ORTEP drawing of **5f**. Thermal ellipsoids are shown at 30% probability.

Catalytic Reactions. Catalytic hydrosilylation reactions using NHC−Rh(I) complexes are well known.[5] We first employed **5a** as a catalyst in the hydrosilylation of 4′-methyl acetophenone using Ph_2SiH_2 as a silylating agent. Under standard conditions, i.e., at ambient temperature in THF for 3 days, the corresponding racemic product was obtained in 55% yield. Instead of improving the reactivity and enantioselectivity of the rhodium N-heterocyclic carbene complexes in the hydrosilylation, we decided to search for other reactions. There are many examples of transfer hydrogenations

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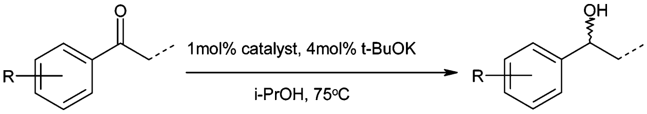
Table 2. X-ray Data for 4a and 5c−f

	4a	5c	5d	5e	5f
empirical formula	$C_{16}H_{18}FeN_2S$	$C_{35}H_{40}N_2ClFe_2Rh$	$C_{35}H_{40}N_2IFe_2Rh$	$C_{35}H_{40}N_2ClFe_2Ir$	$C_{39}H_{42}N_2ClFe_2Ir$
fw	326.2	738.8	830.2	828.0	878.1
cryst syst	orthorombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1$
a, Å	10.1670(10)	10.331(1)	10.0810(1)	10.292(1)	12.041(1)
b, Å	11.7260(10)	12.012(1)	12.3180(1)	12.049(1)	11.425(1)
c, Å	13.0010(10)	13.652(1)	14.0720(1)	13.640(1)	12.495(1)
β, deg		111.799(1)	110.679(2)	111.669(1)	94.5670(1)
volume, Å^3	1550.0(2)	1573.0(2)	1634.8(2)	1571.9(2)	1713.5(2)
Z, *D*(calcd), Mg/m^3	4, 1.398	2, 1.560	2, 1.686	2, 1.749	2, 1.702
no. of reflns collected	3549	6395	6502	6294	7133
no. of unique reflns	3549	6395	6502	6294	7133
no. of refined params	183	372	372	373	408
R1 ($I > 2\sigma(I)$)	R1 = 0.0329	R1 = 0.0354	R1 = 0.0382	R1 = 0.0516	R1 = 0.0368
R1 (all data)	wR2 = 0.0910	wR2 = 0.0911	wR2 = 0.0964	wR2 = 0.1262	wR2 = 0.0995
flack param	0.03(2)	0.02(2)	0.02(4)	0.00	0.025(9)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 5c−f

5c		5d		5e		5f	
Rh−C13	2.036(5)	Rh−C15	2.035(9)	Ir−C15	2.031(12)	Ir−C1	2.033(7)
Rh−Cl	2.3759(14)	Rh−I	2.6639(9)	Ir−Cl	2.344(3)	Ir−Cl	2.365(2)
Rh−C29	2.123(6)	Rh−C33	2.146(10)	Ir−C28	2.120(11)	Ir−C32	2.103(9)
Rh−C28	2.104(5)	Rh−C32	2.128(11)	Ir−C29	2.081(13)	Ir−C33	2.137(11)
Rh−C32	2.208(7)	Rh−C28	2.226(12)	Ir−C33	2.180(13)	Ir−C36	2.183(8)
Rh−C33	2.207(6)	Rh−C29	2.232(11)	Ir−C32	2.153(11)	Ir−C37	2.216(9)
C28−C29	1.407(9)	C32−C33	1.406(16)	C28−C29	1.377(17)	C32−C33	1.447(15)
C32−C33	1.338(12)	C28−C29	1.332(19)	C32−C33	1.340(20)	C36−C37	1.396(15)
C13−Rh−C29	92.7(2)	C15−Rh−C33	93.4(4)	C15−Ir−C28	92.6(4)	C1−Ir−C32	93.0(4)
C13−Rh−C28	93.9(2)	C15−Rh−C32	93.5(4)	C15−Ir−C29	93.2(5)	C1−Ir−C33	94.8(5)
C13−Rh−Cl	89.03(13)	C15−Rh−I	88.4(2)	C15−Ir−Cl	89.1(3)	C1−Ir−Cl	87.9(4)
C13−Rh−C32	159.3(3)	C15−Rh−C28	160.5(5)	C15−Ir−C33	157.7(6)	C1−Ir−C36	159.6(4)
C13−Rh−C33	165.4(3)	C15−Rh−C29	164.7(5)	C15−Ir−C32	166.1(6)	C1−Ir−C37	163.4(4)
Cl−Rh−C29	165.22(19)	I−Rh−C33	165.9(3)	Cl−Ir−C28	164.7(3)	Cl−Ir−C32	158.3(3)
Cl−Rh−C28	155.61(19)	I−Rh−C32	155.4(3)	Cl−Ir−C29	156.8(4)	Cl−Ir−C33	161.5(3)
Cl−Rh−C32	92.1(2)	I−Rh−C28	92.0(4)	Cl−Ir−C33	92.2(4)	Cl−Ir−C36	90.0(4)
Cl−Rh−C33	89.46(19)	I−Rh−C29	89.9(3)	Cl−Ir−C32	90.0(3)	Cl−Ir−C37	92.1(3)

Table 4. Catalytic Asymmetric Transfer Hydrogenation



substrate	catalyst	yield (%)	ee (%)[b]
4′-methyl acetophenone	**5a**	>99	6.4 (*R*)
	5b	>99	racemic
	5c	>99	6.7 (*R*)
	5e[a]	>99	14 (*S*)
	5f[a]	98	52.6 (*S*)
propiophenone	**5a**	>99	2.6 (*R*)
	5b	>99	1.6 (*R*)
	5c	>99	1.9 (*R*)
	5e[a]	>99	22.1 (*R*)
	5f[a]	98	32.0 (*S*)
3′-methoxy acetophenone	**5a**	>99	racemic
	5b	>99	racemic
	5c	>99	2.1 (*R*)
	5e[a]	>99	5.8 (*S*)
4′-chloro acetophenone	**5a**	5.8	racemic
	5b	4.8	5.9 (*R*)
	5c	8.7	9.2 (*R*)

[a] 0.2 mol % catalyst was used. [b] Determined by HPLC.

using Rh(I)−phosphine and Rh(I)−amine complexes as catalysts.[18] Thus, we investigated the use of our rhodium complexes in the transfer hydrogenations (Table 4). Four phenones were reduced using 1 mol % of the catalyst and 4 mol % of t-BuOK in i-PrOH. The reaction did not proceed at low temperatures, but the reaction proceeded at 75 °C to yield the corresponding product quantitatively except for 4′-chloro acetophenone. The low reactivity of 4′-chloroacetophenone may be due to the electron-withdrawing effect of the chloro group. The relatively low reactivity of our carbene complexes may be due to the stronger σ-donation of the carbene ligands than those of amines and phosphines. The high electron density on the metal makes the metal center less reactive toward ketones. These trends could be seen in other NHC-ligated catalysts.[19] Generally, very poor ee values were obtained. The iridium complexes **5e** and **5f** showed better enantioselectivity than the rhodium complexes. The highest (52.6%) ee value was obtained when 4′-methylacetophenone was used as a substrate and **5f** as a catalyst. The steric bulk of the benzimidazole moiety might result in beneficial effects on the high enantioselectivity. Interestingly, the enantioselections of the catalysts **5e** and **5f** were different when propiophenone was used as a substrate: **5e** gave an *R*-configurated product, but **5f** gave an *S*-configurated one. NHC−Ir(I),[17] −Ir(III),[20] −Rh(III),[21] and −Ru(II)[22] complexes have been applied to transfer hydrogenation reactions, but this is the first example of NHC−Ir(I) and

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−Rh(I) complex-catalyzed asymmetric versions of the transfer hydrogenation reaction.

It has been known[19b] that iridium complexes with an N-heterocyclic carbene and a pyridine catalyze transfer hydrogenations and also catalyze hydrogenations of alkenes. Thus, we employed our chiral N-heterocyclic carbene complexes to the hydrogenation of dimethyl itaconate, a typical substrate for an asymmetric hydrogenation. We screened the optimal reaction conditions. Complex **5c** was chosen as a catalyst, and 0.5 mol % of the catalyst was used in the reaction. However, at 55 °C under 1 atm, no reaction was observed after 12 h. At room temperature under 10 atm, a hydrogenated product was obtained in 23% yield. The reaction was completed at 55 °C under 10 atm within 12 h. Compounds **5b** and **5e** were also used as catalysts in the reaction. Catalysts **5b** and **5c** yielded almost racemic products, and **5e** gave 8.7% ee.

Conclusion

We synthesized chiral ferrocenyl imidazolium salts by substitution with retention of configurations. The method described yielded very high enantioselectivities. These salts were converted to N-heterocyclic carbenes that were complexed with rhodium(I) and iridium(I). The complexes were applied to transfer hydrogenation of ketones and hydrogenation of dimethyl itaconate. The Ir complex of the chiral ferrocenyl benzimidazolylidene showed moderate enantioselectivities.

Experimental Section

General Procedures. All reactions were conducted under nitrogen using standard Schlenk-type flasks. Workup procedures were done in air. All solvents were dried and distilled according to the standard methods before use. Reagents were purchased from Aldrich Chemical Co. and Strem Chemical Co. and were used as received. (*R*)-1-Ferrocenyl ethanol (**1**), (*R*)-1-ferrocenyl ethyl acetate (**1a**), (*R*)-ferrocenyl benzyl alcohol (**2**), (*R*)-ferrocenyl benzyl acetate (**2a**), 1-(2,6-diisopropylphenyl)imidazole, and 1-(4-*tert*-butylphenyl)imidazole were synthesized according to the literature methods.[9b,14,23,24]

Synthesis of 1-[(*R*)-1-Ferrocenylethyl]imidazole (3). Method A. (*R*)-1-Ferrocenyl ethanol (**1**) (1.0 g) and imidazole (0.41 g) were dissolved in 5 mL of acetic acid and stirred at 60 °C for 6 h. Volatiles were evaporated. NaOH solution and ethyl acetate were added, and the layers were separated. The organic layer was collected and evaporated. Flash column chromatography (ether/MeOH, 5:1) gave 0.74 g (60% yield, 64% ee) of pure **3**.

Method B. 1 (0.31 g, 1.3 mmol) and imidazole (0.12 g, 1.3 equiv) were dissolved in 3 mL of acetic acid and stirred overnight. Basic workup and subsequent flash column chromatography gave **3** (44% yield, 94.5% ee). ^{1}H NMR (CDCl$_3$): δ 7.49 (br s, 1 H), 7.02 (br s, 1 H), 6.92 (s, 1 H), 5.17 (q, J = 7.0 Hz, 1 H), 4.18 (m, 3 H), 4.15 (s, 5 H), 4.08 (m, 1 H), 1.80 (d, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (CDCl$_3$): δ 135.62, 128.56, 117.29, 88.84, 68.88, 68.58, 68.06, 67.62, 65.90, 52.87, 22.23 ppm. HRMS (M$^+$): calcd 280.0663, obsd 280.0663. IR (CH$_2$Cl$_2$, ν): 3053, 2986, 2685, 2521, 2410, 2305, 2155, 2125, 2054, 1603, 1551, 1421, 1260 cm^{-1}. Anal. Calcd for $C_{15}H_{16}FeN_2$: C, 64.31; H, 5.76; N, 10.00. Found: C, 64.13; H, 5.99; N, 9.89. $[\alpha]^{27}_{D}$ −67.8 (*c* 0.85, MeOH).

Synthesis of 1-[(*R*)-1-Ferrocenylethyl]benzimidazole (3g). 1 (0.26 g, 1.13 mmol) and benzimidazole (0.17 g, 1.4 mmol) were dissolved in 3 mL of acetic acid and stirred overnight. Basic workup and subsequent flash column chromatography eluting with ethyl acetate gave 0.21 g (56% yield, 95.0% ee) of **3g**. ^{1}H NMR (CDCl$_3$): δ 7.80 (s, 1 H), 7.79 (m, 1 H), 7.43 (m, 1 H), 7.27 (m, 2 H), 5.51 (q, J = 7.0 Hz, 1 H), 4.36 (m, 1 H), 4.26 (m, 1 H), 4.21 (m, 1 H), 4.20 (s, 5 H), 4.15 (m, 1 H), 1.92 (d, J = 6.9 Hz, 1 H) ppm. ^{13}C NMR (CDCl$_3$): δ 143.65, 141.16, 133.04, 122.50, 121.92, 120.24, 110.05, 87.53, 68.87, 68.04, 66.27, 51.25, 20.63 ppm. HRMS (M$^+$): calcd 330.0819, obsd 330.0820. IR (KBr, ν): 3093, 3050, 2995, 2980, 1936, 1608, 1480, 1459, 1278, 1218, 1193, 745, 501, 466 cm^{-1}. Anal. Calcd for $C_{19}H_{18}FeN_2$: C, 69.11; H, 5.49; N, 8.48. Found: C, 69.05; H, 5.58; N, 8.49. $[\alpha]^{27}_{D}$ −158.7 (*c* 0.78, MeOH).

General Methods for the Synthesis of the Imidazolium Salts. Method A. 1 (0.30 g, 1.3 mmol) and 1-methylimidazole (0.15 mL, 1.9 mmol) were dissolved in 3 mL of acetic acid and stirred for 5 h at 60 °C. Volatiles were evaporated, and a solution of LiCl (0.17 g, 4.0 mmol) in EtOH (5 mL) was added. After the solution had been stirred for 2 h, the solvent was evaporated. CH$_2$Cl$_2$ was added to the solution, and the solution was filtered through Celite. After column chromatography (CH$_2$Cl$_2$/MeOH, 10:1), recrystallization from CH$_2$Cl$_2$/ether afforded 0.31 g (72% yield, 76.1% ee) of **3a**.

Method B. 1 and 1-methylimidazole in acetic acid were stirred for 12 h at ambient temperature and treated with LiCl as in method A.

Method C. 1a (0.11 g, 0.40 mmol) and 1-phenylimidazole (0.07 mL, 1.3 equiv) were added in a mixed solvent of CH$_3$CN (5 mL) and H$_2$O (5 mL) and stirred overnight at ambient temperature. Volatiles were evaporated, and a solution of LiCl (64 mg, 1.5 mmol) in 5 mL of ethanol was added. After the solution had been stirred for 2 h, the solvent was evaporated. The solution was dissolved in CH$_2$Cl$_2$ and filtered through Celite. Flash column chromatography (CH$_2$Cl$_2$/MeOH, 10:1) and subsequent recrystallization from CH$_2$Cl$_2$/ether afforded 0.11 g (70%) of **3b**.

1-Methyl-3-[(*R*)-1-ferrocenylethyl]imidazolium Chloride (3a). Method A: 72% yield; 76% ee. Method B: 74% yield; 92.9% ee. ^{1}H NMR (CDCl$_3$): δ 10.90 (s, 1 H), 7.13 (s, 1 H), 6.99 (s, 1 H), 5.81 (q, J = 6.7 Hz, 1 H), 4.36 (s, 1 H), 4.32 (s, 1 H), 4.27 (s, 1 H), 4.24 (s, 1 H), 4.22 (s, 5 H), 4.06 (s, 3 H), 1.96 (d, J = 6.7 Hz, 3 H) ppm. ^{13}C NMR (acetone-d_6): δ 135.29, 123.67, 120.77, 86.19, 69.29, 69.13, 68.79, 68.23, 66.09, 56.88, 35.42, 20.11 ppm. IR (KBr): ν 3113, 3001, 2910, 2784, 2773, 1539, 1437, 1299, 1210, 794, 554, 520, 410 cm^{-1}. HRMS (M$^+$): calcd 295.0898, obsd 295.0893; $[\alpha]^{30}_{D}$ −63.2 (*c* 1.2, MeOH).

1-Phenyl-3-[(*R*)-1-ferrocenylethyl]imidazolium Chloride (3b). Method B: 95% yield; 91.5% ee. Method C: 70% yield; 97.5% ee. ^{1}H NMR (CDCl$_3$): δ 11.69 (s, 1 H), 7.79 (d, J = 7.87 Hz, 2 H), 7.61−7.48 (m, 3 H), 7.41 (s, 1 H), 7.13 (s, 1 H), 6.36 (q, J = 6.0 Hz, 1 H), 4.54 (s, 1 H), 4.42 (s, 1 H), 4.29 (m, 7 H), 2.08 (d, J = 6.0 Hz, 3 H) ppm. ^{13}C NMR (CDCl$_3$): δ 135.5, 134.9, 130.9, 130.4, 122.0, 121.1, 120.9, 85.7, 70.1, 69.8, 69.5, 69.4, 66.4, 57.5, 21.8 ppm. IR (KBr): ν 3154, 5091, 2830, 2684, 2520, 2410, 2306, 2156, 2125, 2053, 1600, 1550, 1421, 424, 408 cm^{-1}. Anal. Calcd for $C_{21}H_{25}ClFeN_2O_2$ (**3b**·2H$_2$O): C, 58.83; H, 5.88; N, 6.53. Found: C, 59.16; H, 6.45; N, 6.73. HRMS (M$^+$): calcd 357.1054, obsd 357.1054; $[\alpha]^{26}_{D}$ −81.9 (*c* 0.80, MeOH).

1-(2,6-Diisopropylphenyl)-3-[(*R*)-1-ferrocenylethyl]imidazolium Chloride (3c). Method A: 55% yield; 4% ee. Method B: 95% yield; 87.1% ee. ^{1}H NMR (CDCl$_3$): δ 10.46 (s, 1 H), 7.64 (s, 1 H), 7.52 (m, 1 H), 7.28 (d, J = 8.4 Hz, 2 H), 7.03 (s, 1 H), 6.73 (q, J = 5.7 Hz, 1 H), 4.58 (s, 1 H), 4.38 (s, 1 H), 4.32−4.29 (m, 7 H), 3.49 (s, 3 H), 2.21 (m, 2 H), 2.08 (d, J = 5.5 Hz, 3 H), 1.24 (d, J = 6.9 Hz, 3 H), 1.21 (d, J = 6.9 Hz, 3 H), 1.14 (d, J = 6.8 Hz, 3 H), 1.11 (d, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (CDCl$_3$): δ 164.81, 147.83, 147.80, 134.95, 132.88, 131.21, 125.28, 119.53, 115.73, 88.92, 75.79, 70.09, 69.93,

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69.83, 69.51, 69.31, 69.19, 68.83, 68.76, 68.56, 67.04, 56.47, 53.33, 29.24, 29.19, 25.08, 25.05, 24.05, 20.75, 20.17 ppm. IR (KBr): ν 3157, 3127, 3092, 2963, 2930, 2868, 1662, 1630, 1560, 1549, 1471, 1414, 1398, 1333, 1197, 1104, 819, 808, 502, 480 cm^{-1}. Anal. Calcd for $C_{54}H_{68}Cl_2Fe_2N_4O$[(**3c**)$_2$·H_2O]: C, 66.74; H, 7.05; N, 5.77. Found: C, 66.45; H, 7.09; N, 5.69. $[\alpha]^{30}_D$ −64.2 (*c* 1.0, MeOH).

1,3-Bis[(*R*)-1-ferrocenylethyl]imidazolium chloride (3d). Method B. 3 (94.5% ee) was used. Yield: 72%. ^{1}H NMR ($CDCl_3$): δ 11.33 (s, 1 H), 6.79 (s, 2 H), 5.90 (q, J = 6.9 Hz, 1 H), 4.36 (m, 2 H), 4.33 (m, 2 H), 4.23 (m, 14 H), 1.96 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ 136.49, 118.85, 118.66, 85.55, 70.19, 69.76, 68.99, 68.93, 68.49, 68.33, 65.96, 56.81, 21.75, 21.66 ppm. HRMS (M^+) calcd 493.1030, obsd 493.1030. IR (KBr): ν 3389, 3093, 2937, 1708, 1614, 1546, 1469, 1431, 1397, 1377, 1240, 1200, 817, 749, 499, 481 cm^{-1}. Anal. Calcd for $C_{27}H_{31}ClFe_2N_2O$ (**3d**·$2H_2O$): C, 57.43; H, 5.89; N, 4.96. Found: C, 57.57; H, 5.83; N, 4.90. $[\alpha]^{27}_D$ −99.79 (*c* 1.4, MeOH).

1,3-Bis[(*R*)-1-ferrocenylethyl]imidazolium iodide (3e). Method B. 3 (94.5% ee) and NaI were used. Yield: 62%. ^{1}H NMR ($CDCl_3$): δ 10.53 (s, 1 H), 6.85 (s, 2 H), 5.91 (q, J = 6.9 Hz, 2 H), 4.40 (m, 2 H), 4.34 (m, 1 H), 4.25 (m, 14 H), 1.97 (d, J = 6.9 Hz, 6 H) ppm. ^{13}C NMR (acetone-d_6): δ 120.92, 87.15, 69.46, 68.82, 68.56, 68.46, 66.75, 56.80, 20.71 ppm. HRMS (M^+): calcd 493.1030, obsd 493.1030. IR (KBr): ν 3435, 3063, 2987, 2930, 1544, 1306, 1239, 1145, 1104, 816, 512, 482 cm^{-1}. Anal. Calcd for $C_{27}H_{29}Fe_2IN_2$: C, 52.29; H, 4.71; N, 4.52. Found: C, 52.28; H, 4.70; N, 4.50. $[\alpha]^{25}_D$ −85.24 (*c* 0.67, MeOH).

1-Methyl-3-[(*R*)-ferrocenylbenzyl]imidazolium Chloride (3f). Method B: **2** was used. Yield: 82% (1.8% ee). Method C: Yield: 88% (91.7% ee). ^{1}H NMR ($CDCl_3$): δ 10.49 (s, 1 H), 7.44 (m, 5 H), 7.05 (s, 1 H), 7.00 (s, 1 H), 5.31 (s, 1 H), 4.35−4.23 (m, 3 H), 4.09 (m, 9 H) ppm. ^{13}C NMR ($CDCl_3$): δ 135.2, 127.1, 126.9, 125.9, 121.7, 118.8, 81.5, 67.7, 67.5, 66.8, 66.5, 63.8, 62.4, 35.1, 13.2 ppm. IR (KBr): ν 3089, 2960, 2927, 2871, 2827, 1637, 1469, 1407, 1359, 1278, 821, 736, 505, 480 cm^{-1}. HRMS (M^+): calcd 357.1054, obsd 357.1052. $[\alpha]^{25}_D$ 15.7 (*c* 0.67, MeOH).

1,3-Bis[(*R*)-1-ferrocenylehyl]benzimidazolium Chloride (3g). Method B. 3f (95.0% ee) and LiCl were used. Yield: 48%. ^{1}H NMR ($CDCl_3$): δ 11.77 (s, 1 H), 7.55 (m, 2 H), 7.39 (m, 2 H), 6.28 (q, J = 6.9 Hz, 1 H), 4.64 (s, 2 H), 4.32 (s, 2 H), 4.26 (s, 5 H), 4.19 (s, 2 H), 2.16 (d, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ 130.40, 126.62, 115.07, 84.74, 69.94, 69.58, 69.13, 68.77, 68.30, 68.06, 67.64, 66.34, 66.16, 66.00, 65.50, 57.98, 14.95 ppm. HRMS (M^+): calcd 543.1186, obsd 543.1187. IR (KBr, ν): 3419, 3094, 2979, 1627, 1546, 1240, 1105, 818, 749, 500, 482 cm^{-1}. Anal. Calcd for $C_{32}H_{35}ClFe_2N_2O_1$ (**3g**·MeOH): C, 62.93; H, 5.40; N, 4.84. Found: C, 63.23; H, 5.49; N, 4.62. $[\alpha]^{12}_D$ −205.4 (*c* 0.8, MeOH).

Synthesis of 1-Methyl-3-[(*R*)-ferrocenylethyl]imidazole-2-thione (4a). To a solution of **3a** (0.71 g, 2.15 mmol) in 15 mL of THF was added t-BuOK (0.34 g, 3.0 mmol), and the mixture was stirred for 1 h. Sulfur (0.13 g, 4.0 mmol) was added to the reaction mixture. After 2 h saturated ammonium chloride solution and ether were added and the layers were separated. Collected organic phase was evaporated, and flash column chromatography (hexane/ether; v/v, 1:2) afforded 0.16 g of **4a** (23% yield). Single crystals suitable for X-ray diffraction study were grown by slow evaporation of a solution of **4a** in diethyl ether and hexane. ^{1}H NMR ($CDCl_3$): δ 6.54 (d, J = 2.4 Hz, 1 H), 6.43 (d, J = 2.5 Hz, 1 H), 5.95 (q, J = 6.9 Hz, 1 H), 4.29 (m, 1 H), 4.27 (m, 1 H), 4.21 (s, 5 H), 4.19 (m, 1 H), 4.17 (m, 1 H), 3.60 (s, 3 H), 2.17 (s, 3 H), 1.70 (d, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ 161.23, 117.99, 114.30, 88.02, 69.40, 69.29, 69.02, 68.22, 66.32, 52.96, 35.23, 19.75 ppm. HRMS (M^+): calcd 326.0540, obsd 326.0540. IR (KBr, ν): 3154, 3126, 3090, 3068, 2980, 2929, 1448, 1407, 1347, 1307, 1271, 1241, 1213, 1139, 1102, 831, 710, 674, 499, 465 cm^{-1}. Anal. Calcd for $C_{16}H_{18}FeN_2S$: C, 58.91; H, 5.56; N, 8.59; S, 9.83. Found: C, 58.83; H, 5.66; N, 8.42; S, 9.86. $[\alpha]^{30}_D$ −137.9 (*c* 1.0, CH_2Cl_2).

1-Phenyl-3-[(*R*)-ferrocenylethyl]imidazole-2-thione (4b). Yield: 19%. ^{1}H NMR ($CDCl_3$): δ 7.57 (m, 2 H), 7.48 (m, 2 H), 7.41 (m, 1 H), 6.74 (d, J = 2.4 Hz, 1 H), 6.56 (d, J = 2.6 Hz, 1 H), 6.05 (q, J = 6.9 Hz, 1 H), 4.35 (m, 2 H), 4.22 (m, 7 H), 1.77 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ 162.03, 138.69, 129.43, 128.67, 126.59, 118.14, 115.19, 87.98, 69.49, 69.43, 69.24, 68.32, 66.43, 53.10, 19.68 ppm. HRMS (M^+): calcd 388.0697, obsd 388.0697. IR (KBr, ν): 3127, 3099, 2978, 1711, 1593, 1417, 1395, 1300, 1251, 1105, 825, 762, 706, 690, 508, 484 cm^{-1}. Anal. Calcd for $C_{21}H_{20}FeN_2S$: C, 64.96; H, 5.19; N, 7.21; S, 8.26. Found: C, 65.32; H, 5.40; N, 6.93; S, 8.07. $[\alpha]^{30}_D$ −99.79 (*c* 0.65, CH_2Cl_2).

1-(2,6-Diisopropylphenyl)-3-[(*R*)-1-ferrocenylethyl]imidazole-2-thione (4c). Yield: 37%. ^{1}H NMR ($CDCl_3$): δ 7.44 (t, J = 7.7 Hz, 1 H), 7.26 (m, 2 H), 6.63 (d, J = 2.5 Hz, 1 H), 6.54 (d, J = 2.4 Hz, 1 H), 6.07 (q, J = 6.9 Hz, 1 H), 4.35 (m, 1 H), 4.22 (m, 7 H), 2.48 (m, 2 H), 1.76 (d, J = 6.9 Hz, 3 H), 1.28 (d, J = 6.8 Hz, 3 H), 1.27 (d, J = 6.8 Hz, 3 H), 1.10 (d, J = 6.8 Hz, 3 H), 1.06 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ 163.81, 146.95, 146.90, 134.06, 130.39, 124.51, 118.75, 114.89, 88.31, 69.49, 69.38, 68.88, 68.25, 66.52, 53.04, 29.07, 29.00, 24.85, 23.83, 23.80, 19.93 ppm. HRMS (M^+): calcd 472.1636, obsd 472.1636. IR (KBr, ν): 3158, 3132, 3089, 2965, 2928, 2867, 2189, 1713, 1557, 1472, 1416, 1393, 1334, 1303, 923, 821, 735, 724 cm^{-1}. Anal. Calcd for $C_{27}H_{32}FeN_2S$: C, 68.64; H, 6.83; N, 5.93; S, 6.79. Found: C, 68.31; H, 6.88; N, 5.85; S, 6.64. $[\alpha]^{28}_D$ −120.6 (*c* 2.0, CH_2Cl_2).

1-Methyl-3-[(*R*)-ferrocenylbenzyl]imidazole-2-thione (4d). Yield: 67%. ^{1}H NMR ($CDCl_3$): δ 7.34−7.25 (m, 5 H), 6.62 (d, J = 2.5 Hz, 1 H), 6.60 (d, J = 2.5 Hz, 1 H), 4.24 (m, 1 H), 4.21 (m, 2 H), 4.14 (s, 5 H), 4.03 (m, 1 H), 3.61 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ 162.70, 139.65, 128.69, 128.68, 128.14, 117.74, 115.99, 87.19, 69.64, 69.57, 69.29, 68.52, 68.40, 61.05, 35.46 ppm. HRMS (M^+): calcd 388.0697, obsd 388.0697. IR (KBr, ν): 3162, 3134, 3099, 3063, 3029, 2939, 1711, 1649, 1564, 1540, 1446, 1404, 1216, 825, 743, 716, 700, 677, 509 cm^{-1}. Anal. Calcd for $C_{21}H_{20}FeN_2S$: C, 64.96; H, 5.19; N, 7.21; S, 8.26. Found: C, 65.17; H, 5.33; N, 7.11; S, 8.24. $[\alpha]^{25}_D$ −85.24 (*c* 1.1, CH_2Cl_2).

Methyl-3-[(*R*)-ferrocenyethyl]benzimidazole-2-thione (4e). Yield: 24.6%. ^{1}H NMR ($CDCl_3$): δ 7.12 (m, 2 H), 7.01 (m, 2 H), 6.72 (q, J = 7.1 Hz, 1 H), 4.51 (m, 1 H), 4.25 (s, 1 H), 4.23 (m, 1 H), 4.19 (m, 1 H), 4.12 (m, 1 H), 3.80 (s, 3 H), 1.81 (d, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ 169.35, 133.15, 130.41, 122.77, 122.69, 111.55, 109.18, 87.10, 69.65, 69.58, 69.39, 67.75, 67.15, 52.73, 31.86, 17.30 ppm. HRMS (M^+): calcd 376.0697, obsd 376.0697. IR (KBr, ν): 3066, 2967, 2928, 1482, 1428, 1402, 1377, 1350, 1338, 1316, 1288, 1232, 1103, 832, 806, 737 cm^{-1}. Anal. Calcd for $C_{20}H_{20}FeN_2S$: C, 63.84; H, 5.36; N, 7.44; S, 8.52. Found: C, 63.86; H, 5.22; N, 7.11; S, 8.66. $[\alpha]^{15}_D$ −243.5 (*c* 1.0, CH_2Cl_2).

Synthesis of Chloro(η^4-1,5-cyclooctadienyl){1-methyl-3-[(*R*)-1-ferrocenylethyl] imidazol-2-ylidene}rhodium(I) (5a). 3a (0.14 g, 0.42 mmol), t-BuOK (67 mg, 0.60 mmol), and $[Rh(COD)Cl]_2$ (99 mg, 0.20 mmol) were dissolved in 5 mL of THF and stirred overnight. After volatiles had been evaporated, the product was purified by flash column chromatography (hexane/ether, 4:1). Recrystallization from CH_2Cl_2/hexane afforded 0.10 g (43% yield) of a crystalline product with 2:1 diastereomeric mixtures. ^{1}H NMR ($CDCl_3$): δ 6.91 (q, J = 7.2 Hz, 0.33 H), 6.70 (d, J = 1.7 Hz, 1 H), 6.61 (t, J = 1.7 Hz, 1 H), 6.55 (q, J = 6.8 Hz, 0.66 H), 5.08−5.00 (m, 2 H), 4.96 (m, 0.33 H), 4.34 (m, 0.66 H), 4.29−4.11 (m, 8 H), 4.04 (s, 2 H), 4.03 (s, 1 H), 3.56−3.30 (m, 2 H), 2.53−2.29 (m, 4 H), 2.08−1.89 (m, 4 H), 1.84 (d, J = 6.9 Hz, 2 H), 1.83 (d, J = 7.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ 181.50, 180.82, 122.75, 122.40, 117.96, 117.59, 98.99, 98.92, 98.83, 98.78, 98.38, 88.52, 88.46, 71.12, 69.96, 69.53, 69.45, 69.23, 69.04, 68.58, 68.40, 68.25, 67.92, 67.72, 67.60, 67.23, 66.94, 66.75, 65.98, 56.29, 56.19, 38.10, 34.30, 33.72, 33.21, 32.72, 30.36, 29.80, 29.00, 28.51, 22.51, 21.05 ppm. HRMS (M$^+$): calcd 540.0502, obsd 540.0503. IR (KBr, ν): 3153, 3119, 3093, 2987, 2930, 2871, 2825, 1737, 1715, 1563, 1444, 1395, 1236, 1208, 821, 727 cm^{-1}. Anal. Calcd for $C_{24}H_{30}ClFeN_2Rh$: C, 53.31; H, 5.59; N, 5.18. Found: C, 53.37; H, 5.59; N, 5.19. $[\alpha]^{27}_{D}$ −116.3 (*c* 1.05, CH_2Cl_2).

Chloro(η^4-1,5-cyclooctadienyl){1-(2,6-diisopropylphenyl)-3-[(*R*)-1-ferrocenylethyl] imidazol-2-ylidene}rhodium(I) (5b). Yield: 74% yield with 2:1 diastereomeric mixtures. ^{1}H NMR ($CDCl_3$): δ 7.45 (m, 2 H), 7.18 (m, 1 H), 7.15 (q, J = 7.0 Hz, 0.33 H), 6.91 (d, J = 2.0 Hz, 0.66 H), 6.90 (q, J = 6.9 Hz, 0.66 H), 6.75 (d, J = 1.9 Hz, 0.33 H), 5.02−4.91 (m, 1.33 H), 4.90−4.81(m, 1 H), 4.38 (s, 0.33 H), 4.30−4.21 (m, 7.66 H), 4.20 (m, 0.66 H), 3.61−3.41 (m, 2 H), 3.92 (m, 1 H), 2.50−2.38 (m, 1 H), 2.31−2.14 (m, 1 H), 2.06 (d, J = 6.9 Hz, 2 H), 1.96 (d, J = 7.0 Hz, 1 H), 2.01−1.89 (m, 2 H), 1.82−1.70 (m, 2 H), 1.54 (d, J = 6.8 Hz, 4 H), 1.51−1.42 (m, 2 H), 1.10 (d, J = 6.8 Hz, 4 H), 1.05 (d, J = 6.7 Hz, 2 H), 0.97 (d, J = 6.9 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 181.79, 181.11, 148.36, 148.25, 145.80, 145.64, 136.26, 136.03, 130.06, 129.93, 125.28, 124.84, 124.78, 124.35, 123.45, 118.07, 117.6297.66, 97.57, 97.22, 97.12, 97.01, 96.91, 90.50, 87.86, 71.66, 69.79, 69.67, 69.47, 69.30, 68.14, 68.06, 67.96, 67.84, 67.74, 67.65, 66.61, 66.58, 57.23, 56.47, 34.48, 31.94, 29.38, 28.72, 28.63, 28.57, 27.06, 26.84, 26.47, 24.06, 23.30, 23.15, 21.70 05 ppm. HRMS (M$^+$): calcd 686.1597, obsd 686.1598. IR (KBr, ν): 3162, 3091, 2965, 2929, 2870, 2830, 1590, 1465, 1392, 1292, 1198, 1103, 957, 833, 804, 730, 703, 510, 483 cm^{-1}. Anal. Calcd for $C_{35}H_{44}ClFeN_2Rh$: C, 61.20; H, 6.46; N, 4.08. Found: C, 61.32; H, 6.46; N, 4.03. $[\alpha]^{27}_{D}$ −162.5 (*c* 1.0, CH_2Cl_2).

Chloro(η^4-1,5-cyclooctadienyl){1,3-bis[(*R*)-1-ferrocenylethyl]imidazol-2-ylidene}rhodium(I) (5c). Yield: 34%. Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a solution of **5c** in CH_2Cl_2 and hexane. ^{1}H NMR ($CDCl_3$): δ 6.88 (q, J = 7.0 Hz, 1 H), 6.55 (d, J = 2.0 Hz, 1 H), 6.53 (d, J = 2.1 Hz, 1 H), 6.44 (q, J = 6.8 Hz, 1 H), 5.26 (m, 1 H), 5.07 (m, 1 H), 4.99 (m, 1 H), 4.29 (m, 2 H), 4.25−4.16 (m, 13 H), 4.12 (m, 2 H), 3.64 (m, 1 H), 3.41 (m, 1 H), 2.64−2.48 (m, 4 H), 2.19−1.94 (m, 4 H), 1.85 (d, J = 6.7 Hz, 3 H), 1.80 (d, J = 7.1 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ 179.12 117.89, 117.30, 97.86, 88.51, 88.07, 70.82, 69.55, 69.12, 69.02, 68.88, 68.40, 67.93, 67.74, 67.13, 66.80, 66.71, 65.63, 55.98, 33.75, 32.59, 30.92, 29.69, 28.49, 22.09, 20.76 ppm. HRMS (M$^+$): calcd 738.0634, obsd 738.0636. IR (KBr, ν): 3154, 3122, 3091, 3072, 2966, 2928, 2869, 2832, 1561, 1524, 1466, 1449, 1421, 1409, 1396, 1372, 1207, 1177, 1104, 822, 724, 483 cm^{-1}. Anal. Calcd for $C_{35}H_{40}ClFe_2N_2Rh$: C, 56.90; H, 5.46; N, 3.79. Found: C, 56.80; H, 5.48; N, 3.79. $[\alpha]^{27}_{D}$ −81.1 (*c* 0.95, CH_2Cl_2).

Iodo(η^4-1,5-cyclooctadienyl){1,3-bis[(*R*)-1-ferrocenylethyl]imidazol-2-ylidene}rhodium(I) (5d). A solution of **5c** (0.10 g, 0.14 mmol) in 5 mL of CH_2Cl_2 and a solution of NaI (0.10 g, 5 equiv) in 5 mL of ethanol were mixed and stirred for 2 h. Volatiles were evaporated, and the product was purified by flash column chromatography (hexane/ether, 2:1) to yield 0.11 g (93%) of **5d**. Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a solution of **5d** in CH_2Cl_2 and hexane. ^{1}H NMR ($CDCl_3$): δ 6.64 (d, J = 2.1 Hz, 1 H), 6.61 (q, J = 6.9 Hz, 1 H), 6.56 (d, J = 2.0 Hz, 1 H), 6.30 (q, J = 6.7 Hz, 1 H), 5.39 (m, 1 H), 5.27 (m, 1 H), 5.06 (m, 1 H), 4.27 (m, 1 H), 4.25−4.18 (m, 14 H), 4.14 (m, 1 H), 4.11 (m, 1 H), 3.79 (m, 1 H), 3.64 (m, 1 H), 2.51−2.32 (m, 4 H), 2.12−1.91 (m, 4 H), 1.84 (d, J = 6.8 Hz, 3 H), 1.80 (d, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ 178.35, 177.69, 118.03, 96.16, 96.07, 95.80, 88.98, 88.05, 72.05, 71.86, 71.27, 70.52, 69.36, 69.13, 68.98, 68.83, 67.65, 67.59, 67.09, 66.92, 66.12, 55.41, 55.37, 32.93, 31.98, 30.12, 29.32, 21.87, 21.34 ppm. HRMS (M$^+$): calcd 829.9990, obsd 829.9991. IR (KBr, ν): 3120, 3083, 2989, 2929, 2912, 2870, 2816, 1675, 1542, 1519, 1455, 1415, 1361, 1302, 1272, 1235, 1204, 1178, 1105, 999, 822, 721, 693, 484 cm^{-1}. Anal. Calcd for $C_{35}H_{40}Fe_2IN_2Rh$: C, 50.64; H, 4.86; N, 3.37. Found: C, 50.71; H, 4.91; N, 3.35. $[\alpha]^{27}_{D}$ −178.3 (*c* 1.05, CH_2Cl_2).

Chloro(η^4-1,5-cyclooctadienyl){1,3-bis[(*R*)-1-ferrocenylethyl]imidazol-2-ylidene}iridium(I) (5e). $[Ir(COD)Cl]_2$ was used instead of $[Rh(COD)Cl]_2$. Yield: 65%. Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a solution of **5e** in CH_2Cl_2 and hexane. ^{1}H NMR ($CDCl_3$): δ 6.67 (q, J = 7.0 Hz, 1 H), 6.54 (d, J = 2.1 Hz, 1 H), 6.53 (d, J = 2.1 Hz, 1 H), 6.25 (q, J = 6.8 Hz, 1 H), 4.89 (m, 1 H), 4.84 (m, 1 H), 4.65 (m, 1 H), 4.31 (m, 1 H), 4.26 (m, 1 H), 4.22−4.18 (m, 13 H), 4.11 (m, 1 H), 4.09 (m, 1 H), 3.28 (m, 1 H), 3.06 (m, 1 H), 2.38−2.26 (m, 4 H), 1.91−1.69 (m, 4 H), 1.78 (d, J = 7.0 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ 188.55, 133.34, 133.10, 121.54, 112.25, 112.01, 86.78, 86.33, 85.88, 85.56, 76.59, 69.75, 69.48, 69.38, 69.18, 67.41, 66.92, 66.50, 56.62, 52.07, 51.63, 34.26, 33.62, 29.38, 18.52, 18.28 ppm. HRMS (M$^+$): calcd 828.1204, obsd 828.1204. IR (KBr, ν): 3089, 2973, 2959, 2926, 2871, 2827, 1470, 1407, 1360, 1278, 1104, 1070, 997, 820, 736, 504, 481 cm^{-1}. Anal. Calcd for $C_{35}H_{40}ClFe_2IrN_2$: C, 50.77; H, 4.87; N, 3.38. Found: C, 50.85; H, 4.90; N, 3.36. $[\alpha]^{27}_{D}$ −309.8 (*c* 0.55, CH_2Cl_2).

Chloro(η^4-1,5-cyclooctadienyl){1,3-bis[(*R*)-1-ferrocenylethyl]benzimidazol-2-ylidene}iridium(I) (5f). Yield: 61%. Single crystals suitable for X-ray diffraction study were obtained by slow evaporation of a solution of **5f** in CH_2Cl_2 and hexane. ^{1}H NMR ($CDCl_3$): δ 7.44 (q, J = 7.2 Hz, 1H), 7.04 (m, 1 H), 6.93 (m, 2 H), 6.81 (m, 2 H), 4.99 (m, 1 H), 4.96 (m, 1 H), 4.81 (m, 1 H), 4.59 (s, 1 H), 4.46 (s, 1 H), 4.29 (s, 5 H), 4.27 (s, 5 H), 4.26 (m, 1 H), 4.20 (m, 2 H), 4.10 (m, 2 H), 3.52 (m, 1 H), 3.29 (m, 1 H), 2.50−2.28 (m, 4 H), 2.01 (d, J = 7.1 Hz, 3 H), 1.93 (d, J = 7.0 Hz, 3 H), 2.00−1.81 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ 188.58, 133.37, 121.51, 112.25, 112.02, 86.77, 86.33, 85.89, 85.56, 71.34, 69.76, 69.50, 69.39, 69.19, 6763, 66.93, 66.51, 56.62, 52.09, 51.64, 34.27, 33.63, 29.85, 29.39, 18.53, 18.29 ppm. HRMS (M$^+$): calcd 878.1361, obsd 878.1361. IR (KBr, ν): 3089, 2973, 2926, 2871, 2827, 1470, 1407, 1360, 1278, 1104, 1071, 997, 819, 736, 503, 481 cm^{-1}. Anal. Calcd for $C_{39}H_{42}ClFe_2IrN_2$: C, 53.34; H, 4.82; N, 3.19. Found: C, 53.54; H, 4.89; N, 3.12. $[\alpha]^{12}_{D}$ −502.0 (*c* 0.80, CH_2Cl_2).

Catalytic Asymmetric Transfer Hydrogenation. Rh or Ir catalyst (1 mol %), t-BuOK (4 mol %), and substrate (2 mmol) were added in 5 mL of 2-propanol and heated at 75 °C for 12 h. After the solvent was evaporated, the product was purified by column chromatography. Enantiomeric excesses were determined by HPLC with Chiralcel OD-H. Absolute configurations were determined by comparing the optical rotations with the reported values.[25]

Catalytic Hydrogenation for Dimethyl Itaconate. Dimethyl itaconate (2.0 mmol) and a catalyst (0.5 mol %) were added to a high-pressure reactor. MeOH (4 mL) was added, and the solution was purged with hydrogen. Ten atm of hydrogen was charged. The solution was stirred at 55 °C for 12 h. The pressure was released, and the solvent was evaporated. The product was filtered through a short pad of silica. Conversion was measured by NMR, and the ee values were determined by HPLC with a Chiralcel OD-H column according to the literature method.[26]

Determination of the Enantiomeric Excess for the Ferrocenyl Imidazole-2-thiones by HPLC. 4a: Chiralpak-AD, *n*-hexane/2-propanol = 90:10, 0.6 mL/min, UV 254 nm; t_R = 13.0 min, t_S = 17.6 min.

4b: Chiralpak-AD, *n*-hexane/2-propanol = 88:12, 0.8 mL/min, UV 254 nm; t_R = 16.5 min, t_S = 26.8min.

4c: Chiralpak-AD, *n*-hexane/2-propanol = 96:4, 0.6 mL/min, UV 254 nm; t_R = 11.4 min, t_S = 16.0 min.

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4d: Chiralpak-AD, *n*-hexane/2-propanol = 93:7, 0.7 mL/min, UV 254 nm; $t_R = 16.6$ min, $t_S = 22.2$ min.

4e: Chiralpak-AD, *n*-hexane/2-propanol = 97:3, 0.5 mL/min, UV 254 nm; $t_R = 19.9$ min, $t_S = 24.4$ min.

Structure Determinations of 4a, 5c, 5d, 5e, and 5f by X-ray Diffraction Study. X-ray data for single crystals were collected on an Enraf-Nonius CCD single-crystal X-ray diffractometer at room temperature using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) and refined against all F^2 data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were treated as idealized contributions.

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Supporting Information Available: Tables of crystal data and structure refinement details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **4a** and **5c**−**f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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