Novel Chiral Ligands, Diferrocenyl Dichalcogenides and Their Derivatives, for Rhodium- and Iridium-Catalyzed Asymmetric Hydrosilylation

Yoshiaki Nishibayashi,† Kyohei Segawa,† Jai Deo Singh,† Shin-ichi Fukuzawa,‡ Kouichi Ohe,† and Sakae Uemura*,†

Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan, and Faculty of Science and Engineering, Chuo University, Bunkyo-ku, Tokyo 112, Japan

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As chiral ligands for transition metal complex-catalyzed asymmetric reactions, a variety of novel chiral ferrocenyl chalcogen compounds, which possess planar chirality due to the 1,2-unsymmetrically disubstituted ferrocene structure, have been prepared from chiral ferrocenes. There are seven diferrocenyl dichalcogenides (**4**−**10**), nine alkyl or aryl ferrocenyl chalcogenides (**11**−**19**), two bis(ferrocenylseleno)alkanes (**20** and **21**), two 1-(phenylchalcogeno)-1-[2-(diphenylphosphino)ferrocenyl]ethanes (**22** and **24**), and two 1-(phenylchalcogeno)-1-[1′,2-bis(diphenylphosphino)ferrocenyl]ethanes (**23** and **25**). 2,3-*O*,*O*′-Isopropylidene-2,3-dihydroxy-1,4-bis(phenylchalcogeno)butanes (**26**−**28**) are also synthesized. The Rh(I) complex-catalyzed hydrosilylation of ketones with diphenylsilane in the presence of these chiral ligands including the reported [*R*,*S*;*R*,*S*]-bis[2-[1-(dimethylamino)ethyl]ferrocenyl] dichalcogenides (**1**−**3**), followed by hydrolysis with dilute HCl, affords the corresponding chiral alcohols (*R*-configuration) in moderate to quantitative yield with up to 88% enantiomeric excess (ee). Similar treatment of acetophenone in the presence of diferrocenyl dichalcogenides (**1**, **2**, **3**, and **10**) and a catalytic amount of Ir(I) complex gives chiral 1-phenylethanol of the opposite configuration (*S*) compared with the Rh case in high yield with up to 23% ee. The new complex prepared from a cationic rhodium compound and the diferrocenyl diselenide (**2**) shows an activity for asymmetric hydrosilylation of acetophenone to afford 1-phenylethanol in 60% chemical yield with 60% ee. Asymmetric hydrosilylation of imines and asymmetric hydrogenation of an enamide also proceed smoothly using the Rh(I)−diselenide (**2**) catalytic system to give the corresponding *sec*-amines and amide with up to 53% and 69% ee, respectively. A catalytic cycle involving the formation of tetracoordinated rhodium(I)−dichalcogenide complex (two Se and two N atoms to one Rh) followed by oxidative addition of the Si−H bond to Rh(I) and carbonyl addition to the produced rhodium(III) hydride complex is proposed for hydrosilylation of ketones.

Introduction

In transition metal-catalyzed asymmetric reactions, optically active phosphine compounds have been known to be effective chiral ligands.[1] Thus, Kagan et al. and Knowles et al. found that 2,3-*O*,*O*′-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP) acted as an effective ligand for rhodium-catalyzed asymmetric hydrogenation of enamides,[2] while Noyori and Takaya et al. developed the utility of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) in various types of asymmetric reactions catalyzed by transition metal complexes.[3] On the other hand, Hayashi et al. introduced the ferrocenylphosphines as chiral ligands for those catalytic reactions,[4,5] the phosphines posssessing a characteristic nature in that structural modification can be readily made by introduction of a desired functional group on the ferrocene ring to match a variety of asymmetric reactions: i.e., rhodium-catalyzed hydrogenation,[6] palladium-catalyzed allylic substitution reactions,[7] and gold- or silver-catalyzed aldol-type reactions of isocyano carboxylates.[8]

We are currently interested in the preparation of optically active [*R*,*S*;*R*,*S*]- and [*S*,*R*;*S*,*R*]-bis[2-[1-(dimethylamino)ethyl]ferrocenyl] dichalcogenides [abbreviated as (*R*,*S*)- and (*S*,*R*)-(Fc*E)$_2$; E = S, Se, and Te] and their stoichiometric use for asymmetric selenoxide elimination,[9ab] [2,3]sigmatropic rearrangement,[9a,b] and nucleophilic ring-opening of *meso*-epoxides,[9c] in which

† Kyoto University.
‡ Chuo University.
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(1) For an example : Brunner, H.; Zettlmeier, W. *Handbook of Enantioselective Catalysis with Transition Metal Compounds*; VCH: Weinheim, Germany, 1993.
(2) (a) Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, *94*, 6429. (b) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. *J. Chem. Soc., Chem. Commun.* **1972**, 10. (c) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Backman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946.
(3) For examples: (a) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (b) Takaya, H.; Ohta, T.; Noyori, R. *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; Chapter 1.
(4) 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.
(5) Sawamura, M.; Ito, Y. *Chem. Rev.* **1992**, *92*, 867.
(6) (a) Hayashi, T.; Kawamura, N.; Ito, Y. *J. Am. Chem. Soc.* **1987**, *109*, 7876. (b) Hayashi, T.; Kawamura, N.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 5969.
(7) For an example: Hayashi, T. *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; Chapter 7.1.
(8) For an example: Sawamura, M.; Ito, Y. *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; Chapter 7.2.

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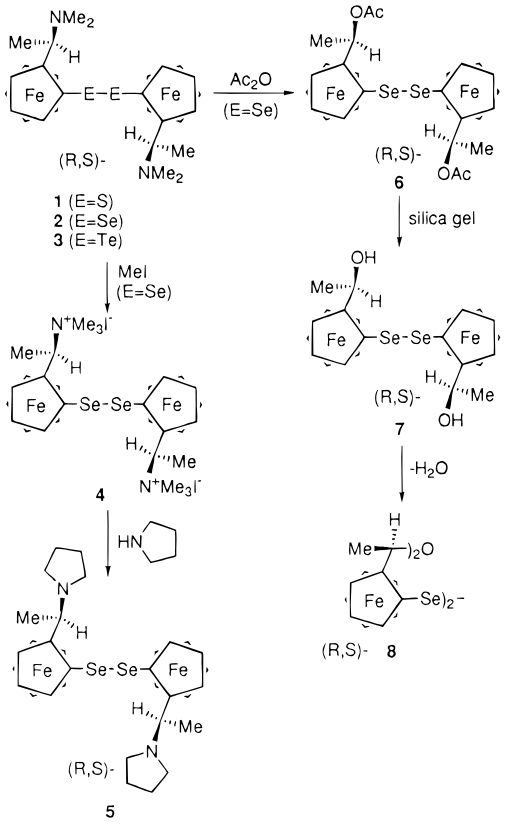
Scheme 1



the planar chirality of ferrocenes played a most important role for the stereoselection. As a next step, we envisaged to use these chiral dichalcogenides as ligands for catalytic asymmetric reactions. When hydrosilylation of acetophenone with diphenylsilane followed by acid hydrolysis was attempted in the presence of a catalytic amount of $[Rh(COD)Cl]_2$ and $(Fc^*Se)_2$ in benzene at 25 °C, a nearly quantitative yield of 1-phenylethanol with modest enantiomeric excess (ee) was obtained. The result was somewhat unexpected because it has been known that many organochalcogen compounds interacted with transition metal salts to afford stable coordination compounds which might be unsuitable for transition metal-catalyzed reactions.[10] It prompted us to examine such asymmetric reactions in more detail by designing and preparing various types of chiral diferrocenyl dichalcogenides and chalcogenogroup containing ferrocenes. We report here the results of Rh(I)- and Ir(I)-catalyzed asymmetric hydrosilylation of ketones, imines, and an enamide using $(Fc^*E)_2$ and other related compounds as chiral ligands.[11]

Results and Discussion

Synthesis of Chiral Diferrocenyl Dichalcogenides. A variety of diferrocenyl diselenides could be derived from the previously reported [*R,S*;*R,S*]-bis[2-[1-(dimethylamino)ethyl]ferrocenyl] diselenide (**2**) [**1** for (R,S)-$(Fc^*S)_2$ and **3** for (R,S)-$(Fc^*Te)_2$][9] by several transformations. Treatment of **2** with methyl iodide afforded its ammonium salt **4** which was transformed to compound **5** in 35% overall isolated yield with complete retention of configuration by the reaction with pyrrolidine (Scheme 1).[4,12] Treatment of **2** with an excess of acetic anhydride at room temperature afforded the optically pure acetate **6** of the same configuration[4] in 62% isolated yield which was then hydrolyzed to the alcohol **7** by treatment with silica gel in 60% isolated yield. Interestingly, a slow recrystallization of **7** from dichloromethane at room temperature afforded a single crystal of the diselenide having a nine-membered ring **8** and its structure was fully characterized by X-ray crystallography (Figure 1).[13] Its absolute configuration was clarified to be *R,S* where the configuration around the chiral carbon is *R*, showing complete retention at this carbon during the transformation from **2** to **6**, **7**, and **8**.

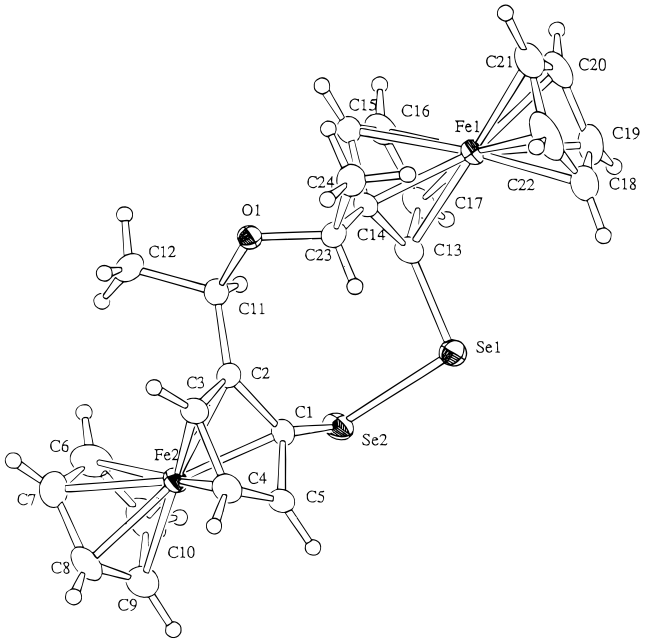


Figure 1. Crystal structure of **8**.

Next, we envisaged preparing novel dichalcogenides having a chiral sulfoxide moiety on the ferrocene ring which might show activity as chiral ligands different from **2**−**8**. Treatment of (*R*)-ferrocenyl *p*-tolyl sulfoxide, which can be prepared easily by the Anderson method,[14] with lithium diisopropylamide (LDA) at −78 °C, followed by addition of elemental sulfur and air oxidation, afforded an enantiomeric mixture of bis[2-(*p*-tolylsulfinyl)ferrocenyl] disulfide which consisted mainly of the (*R,S*)-isomer in accordance with the reported high diastereoselective lithiation (>99% de)[14] of the ferrocene (Scheme 2). By purification via column chromatography on SiO_2, pure (*R,R*)-disulfide **9** was obtained in 23% isolated yield. The corresponding pure

(9) (a) Nishibayashi, Y.; Singh, J. D.; Uemura, S.; Fukuzawa, S. *Tetrahedron Lett.* **1994**, *35*, 3115. (b) Nishibayashi, Y.; Singh, J. D.; Fukuzawa, S.; Uemura, S. *J. Org. Chem.* **1995**, *60*, 4114. (c) Nishibayashi, Y.; Singh, J. D.; Fukuzawa, S.; Uemura, S. *J. Chem. Soc., Perkin Trans. 1*, in press.

(10) For examples (a) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365. (b) Gysling, H. J. *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1, p 679.

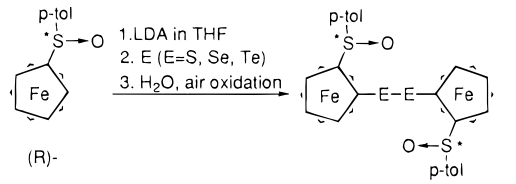
(11) Preliminary communication: Nishibayashi, Y.; Singh, J. D.; Segawa, K.; Fukuzawa, S.; Uemura, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1375.

(12) Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5396. Marquarding, D.; Burghard, H.; Ugi, I.; Urban, R.; Klusacek, H. *J. Chem. Res. (S)* **1977**, 82.

(13) The sulfur analogue of **8** was also formed and similarly fully characterized.

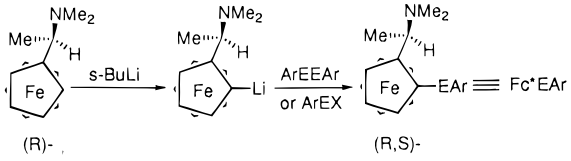
(14) Rebiere, F.; Riant, O.; Ricard, L.; Kagan, H. B. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 568.

Scheme 2



9 : (R,R)-(Fs*S)$_2$
10 : (R,S)-(Fs*Se)$_2$

Scheme 3



11 : E=S, Ar=Ph
12 : E=Se, Ar=Ph
13 : E=Te, Ar=Ph
14 : E=Se, Ar=2,4,6-(i-Pr)$_3$C$_6$H$_2$

(*R,S*)-diselenide **10** was similarly prepared in 20% isolated yield, while the attempts for preparation and isolation of the corresponding pure ditelluride were unsuccessful.

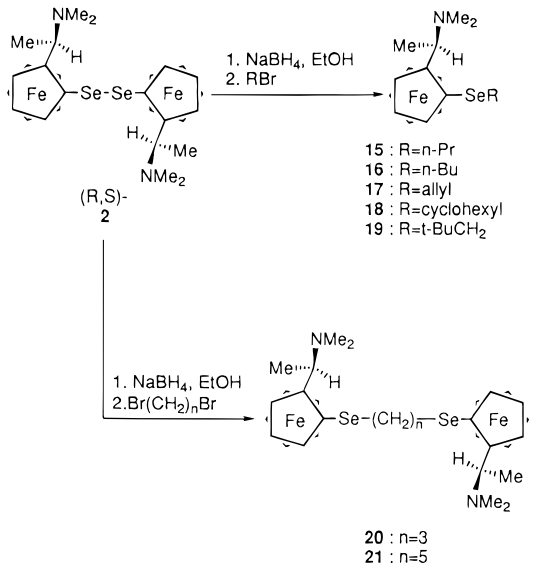
Synthesis of Chiral Aryl and Alkyl Ferrocenyl Chalcogenides. Treatment of (*R*)-[1-(dimethylamino)-ethyl]ferrocene with *sec*-butyllithium followed by reaction with diphenyl disulfide afforded an enantiomeric mixture of [1-(dimethylamino)ethyl]ferrocenyl phenyl sulfide which consisted mainly of the (*R,S*)-isomer, and purification with column chromatography on SiO_2 gave (*R,S*)-sulfide **11** in pure form in 42% isolated yield (Scheme 3). Similarly, other chiral aryl ferrocenyl chalcogenides such as (*R,S*)-ferrocenyl phenyl selenide (**12**) and telluride (**13**) and (*R,S*)-ferrocenyl 2,4,6-triisopropylphenyl selenide (**14**) were prepared by reaction with the corresponding diphenyl dichalcogenides and 2,4,6-triisopropylphenylselenenyl bromide and isolated in 56%, 51%, and 34% yields, respectively. Attempts to prepare the (*R,S*)-ferrocenyl 2,4,6-tri-*tert*-butylphenyl selenide were unsuccessful.

On the other hand, novel (*R,S*)-alkyl ferrocenyl selenides (**15**−**19**) were prepared by the reaction of chiral ferrocenyl selenide anion derived from **2** with the corresponding alkyl halides in 38−82% isolated yield (Scheme 4). However, the expected selenides were not produced in the case of R = *i*-Pr and *t*-Bu. When the anion derived from **2** was reacted with 1,3-dibromopropane (n = 3) and 1,5-dibromopentane (n = 5), [*R,S;R,S*]-alkanes possessing two ferrocenylselenium moieties such as **20** and **21** were produced both in 55% isolated yield (Scheme 4). With 1,4-dibromobutane (n = 4), however, the corresponding compound was not produced in accordance with the reported result[15] using phenyl selenide anion ($PhSe^-$) where the internal quaternization is much faster than nucleophilic attack of the anion upon another bromide.

Synthesis of Chiral Ferrocenylphosphines Possessing a Chalcogeno Moiety on the Side Chain of the Ferrocene. Recent reports by Togni et al. for the preparation of chiral ferrocenylphosphines possessing a different type of phosphine on the side chain of

(15) Singh, A. K.; Srivastava, V. *J. Coord. Chem.* **1992**, *27*, 237.

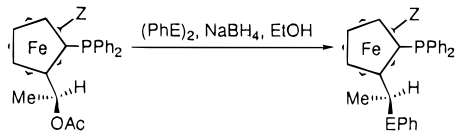
Scheme 4



15 : R=n-Pr
16 : R=n-Bu
17 : R=allyl
18 : R=cyclohexyl
19 : R=t-BuCH$_2$

20 : n=3
21 : n=5

Scheme 5



PPFOAc(Z=H)
BPPFOAc(Z=PPh$_2$)

22 : E=S, Z=H
23 : E=S, Z=PPh$_2$
24 : E=Se, Z=H
25 : E=Se, Z=PPh$_2$

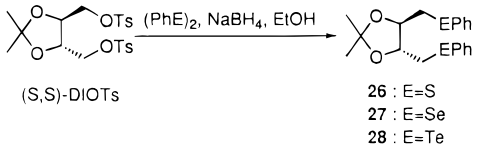
ferrocene ring[16] promoted us to attempt the introduction of a chalcogeno moiety into the side chain of ferrocenylphosphines. As it has been known that the nucleophilic substitution of an acetoxy group on chiral 1-[2-(diphenylphosphino)ferrocenyl]ethyl acetate (PPFOAc) and 1-[1′,2-bis(diphenylphosphino)ferrocenyl]ethyl acetate (BPPFOAc) occurred easily with retention of configuration,[4] these acetates were allowed to react with benzenethiolate anion and phenyl selenide anion in refluxing ethanol. As a result, the corresponding (*S,R*)-sulfides (**22** and **23**) and (*S,R*)-selenides (**24** and **25**) were produced in 74−99% yield (Scheme 5), the configuration at the secondary carbon being believed to be that shown in the scheme. Attempts to prepare similar tellurium compounds were unsuccessful probably because of the air-instability of products having tellurium at the benzylic position.[17]

Synthesis of Chiral Bis(chalcogenides). DIOP [2,3-*O,O*′-isopropylidene-1,4-bis(diphenylphosphino)-2,3-butanediol], prepared by Kagan et al., was the first effective ligand for transition metal-catalyzed asymmetric reactions.[2a] The C_2 symmetrical structure in DIOP and four phenyl groups on the two phosphines played an important role in enantioselective reactions. In connection with this compound, we envisaged to prepare similar compounds having a phenylchalcogeno moiety in place of the diphenylphosphino moiety and

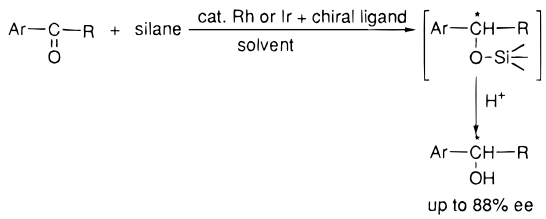
(16) (a) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062. (b) Breutel, C.; Pregosin, P. S.; Salzmann, R.; Togni, A. *J. Am. Chem. Soc.* **1994**, *116*, 4067.

(17) (a) Ferreira, J. T. B.; Oliveira, A. R. M.; Comasseto, J. V. *Tetrahedron Lett.* **1992**, *33*, 915. (b) Nishibayashi, Y.; Chiba, T,; Singh, J. D.; Uemura S.; Fukuzawa, S. *J. Organomet. Chem.* **1994**, *473*, 205.

Scheme 6



Scheme 7



succeeded in the preparation of novel (*S,S*)-bis(sulfide) (**26**), bis(selenide) (**27**) and bis(telluride) (**28**) (Scheme 6) in very high yields (72−97%) by treatment of (*S,S*)-2,3-*O,O′*-isopropylidene-1,4-bis(tosyloxy)-2,3-butanediol with the corresponding phenyl chalcogenide anions.

Rhodium-Catalyzed Asymmetric Hydrosilylation of Ketones Using Various Chiral Chalcogenides as Ligands. Rhodium(I)-catalyzed enantioselective asymmetric hydrosilylation of ketones developed by Kagan et al.,[18] Brunner et al.,[19] and Nishiyama et al.[20] has been an important asymmetric reaction because of the utility of optically pure alcohols in organic synthesis.[21] Therefore, in the first place, we chose Rh(I)-catalyzed asymmetric hydrosilylation in order to examine the effectiveness of newly prepared chiral chalcogeno compounds, although the possibility existed that the reaction would not occur because of the formation of a too stable complex between Rh(I) complex and the chalcogeno compounds.[10]

The reaction was generally carried out as follows. The catalyst was prepared *in situ* by stirring the rhodium complex, $[Rh(COD)Cl]_2$ or $[Rh(COD)_2]BF_4$, and a chiral chalcogeno compound in a suitable solvent at room temperature for 1 h under N_2. Ketone and then arylsilane were added dropwise at 0 or 25 °C, and the mixture was stirred for an appropriate time at that temperature and then quenched with methanol and dilute HCl to afford the corresponding chiral alcohol (Scheme 7). Chemical yields were determined by GLC, while the ee value and the configuration were determined by HPLC using Daicel Chiralcel OJ, OD, OB, and OF columns. First, we searched for an optimum condition for hydrosilylation by using acetophenone as the substrate and the selenide **2** as the chiral ligand. The yield of chiral 1-phenylethanol and its ee value obtained under various conditions are summarized in Table 1. As a result, the optimum condition was found to be the use of tetrahydrofuran (THF), $[Rh(COD)Cl]_2$, and diphenylsilane at 0 °C with a rhodium/**2** ratio of 1. When the reaction was carried out at 25 °C, the product yield was higher in all solvents, but the ee value was always lower (runs 6 and 7, runs 8 and 9, runs 12 and 13). Either at −20 or +40 °C the reaction hardly occurred. As to the silane, diphenylsilane (85% ee, run 13) and α-naphthylphenylsilane (82% ee, run 17) showed similar activities, followed by dimethylphenylsilane (73% ee, run 18), phenylsilane (∼0% ee, run 19), and triphenylsilane (no reaction, run 20) roughly in accordance with the tendency observed in the case of chiral phosphines,[22] while it has been reported that, in the case of DIOP ligand, the reaction using α-naphthylphenylsilane afforded a higher selectivity than diphenylsilane.[18,23] As to the rhodium catalyst, the neutral complex $[Rh(COD)Cl]_2$ was more effective than the cationic complex $[Rh(COD)_2]BF_4$ (runs 13 and 16). Next, the effectiveness of a variety of chiral dichalcogenide ligands (**1**−**10**) was examined under the above optimum conditions, and typical results are also shown in Table 1. Although it has been known that the presence of an hydroxy group on a side chain of ferrocenylphosphine compounds has a remarkable effect upon enantioselective hydrogenation of ketones,[22] ligand **7** (run 25) did not act well in our case. The ligand possessing a morpholinoethyl moiety **5** (run 23), as well as ligands possessing *p*-tolylsulfinyl moieties **9** and **10** (runs 26 and 27), were not effective, while ligands **1** and **3** showed moderate activity (31−50% ee, runs 21 and 22). These results show that the presence of a (dimethylamino)ethyl moiety on the ferrocene ring is most important for highly enantioselective hydrosilylations when diferrocenyl dichalcogenides are employed as chiral ligands.

Similar hydrosilylation of acetophenone was then carried out in THF at 0 °C using various newly prepared chiral alkyl or aryl ferrocenyl chalcogenides and chalcogeno-group containing ferrocenes (**11**−**28**) in place of diferrocenyl dichalcogenides. The reaction proceeded smoothly to give chiral 1-phenylethanol using any ligands except for **28**, but unfortunately the enantioselectivity was always modest to low. Typical results are shown in Table 2. Among the chalcogeno ethers (**11**−**13**), the seleno ether **12** gave the best ee as in the case of dichalcogenide series, but in the series of seleno ethers (**12** and **14**−**19**), no characteristic tendency for enantioselectivity was observed. Although we anticipated high enantioselectivity of the product from the reaction using chiral ligands **22**−**28**, the result was disappointing and, especially in the case of **26**−**28**, the product was nearly the racemate in sharp contrast to the previously reported DIOP case.[18,23]

As the ligand **2** was found to be most effective for enantioselective hydrosilylation of acetophenone, the reactions of a variety of alkyl aryl ketones with diphenylsilane were then examined in THF at 0 °C using $[Rh(COD)Cl]_2$−**2** as a catalyst. The product yield or the reaction rate was much affected by the nature of alkyl and aryl groups of the ketone (Scheme 7, Table 3). As expected, this decreased as the bulkiness of the alkyl group increased: Me (31%) > Et (14%) > *t*-Bu (5%). Replacement of methyl by trifluoromethyl stopped the reaction completely. For aryl groups, the introduction

(18) Dumont, W.; Poulin, J. C.; Dang, T.-P.; Kagan, H. B. *J. Am. Chem. Soc.* **1973**, *95*, 8295.

(19) (a) Brunner, H.; Becker, R.; Riepl, G. *Organometallics* **1984**, *3*, 1354. (b) Brunner, H.; Oberman, U. *Chem. Ber.* **1989**, *122*, 499. (c) Brunner, H.; Brandl, P. *Tetrahedron Asymmetry* **1991**, 931.

(20) (a) Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics* **1991**, *10*, 500. (b) Nishiyama, H.; Yamaguchi, S.; Kondo, M.; Nakamura, T.; Itoh, K. *J. Org. Chem.* **1992**, *57*, 4306.

(21) The transition metal-catalyzed asymmetric hydrosilylation of ketones has been well studied. For an example: Brunner, H.; Nishiyama, H.; Itoh, K. *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; Chapter 6.

(22) (a) Hayashi, T.; Katsumura, A.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* **1979**, 425. (b) Hayashi, T.; Mise, T.; Kumada, M. *Tetrahedron Lett.* **1976**, 4531.

(23) Ojima, I.; Kogure, T.; Kumagai, M. *J. Org. Chem.* **1977**, *42*, 1671.

Table 1. Asymmetric Hydrosilylation of Acetophenone Catalyzed by Rh(I)−(2−10)[a]

run	solvent	catalysts	ligand	ratio of Rh(I)/ligand	silane	temp (°C)	time (h)	1-phenylethanol GLC yield (%)	1-phenylethanol ee (%)[b]	1-phenylethanol config[c]
1	*d*	$[Rh(COD)Cl]_2$	2	1	Ph_2SiH_2	25	1	73	12	*R*
2	*d*	$[Rh(COD)Cl]_2$	2	1	Ph_2SiH_2	0	26	60	9	*R*
3	benzene	$[Rh(COD)Cl]_2$	2	1	Ph_2SiH_2	25	12	100	21	*S*
4	benzene	$[Rh(COD)Cl]_2$[e]	2	2	Ph_2SiH_2	25	5	60	15	*R*
5	benzene	$[Rh(COD)Cl]_2$[f]	2	0.2	Ph_2SiH_2	25	12	64	11	*S*
6	Et_2O	$[Rh(COD)Cl]_2$	2	1	Ph_2SiH_2	25	2	71	8	*R*
7	Et_2O	$[Rh(COD)Cl]_2$	2	1	Ph_2SiH_2	0	24	37	47	*R*
8	DME	$[Rh(COD)Cl]_2$	2	1	Ph_2SiH_2	25	3	100	∼0	
9	DME	$[Rh(COD)Cl]_2$	2	1	Ph_2SiH_2	0	26	31	27	*R*
10	CH_2Cl_2	$[Rh(COD)Cl]_2$	2	1	Ph_2SiH_2	25	12	100	6	*S*
11	CH_3CN	$[Rh(COD)Cl]_2$	2	1	Ph_2SiH_2	25	20	43	∼0	
12	THF	$[Rh(COD)Cl]_2$	2	1	Ph_2SiH_2	25	48	70	11	*R*
13	THF	$[Rh(COD)Cl]_2$	2	1	Ph_2SiH_2	0	48	31	85	*R*
14	THF	$[Rh(COD)Cl]_2$[e]	2	2	Ph_2SiH_2	0	48	45	25	*R*
15	THF	$[Rh(COD)_2]BF_4$	2	1	Ph_2SiH_2	25	48	62	33	*R*
16	THF	$[Rh(COD)_2]BF_4$	2	1	Ph_2SiH_2	0	48	47	9	*R*
17	THF	$[Rh(COD)Cl]_2$	2	1	α-NapPhSiH$_2$	0	40	65	82	*R*
18	THF	$[Rh(COD)Cl]_2$	2	1	$PhMe_2SiH$	0	72	48	73	*R*
19	THF	$[Rh(COD)Cl]_2$	2	1	$PhSiH_3$	0	36	82	∼0	
20	THF	$[Rh(COD)Cl]_2$	2	1	Ph_3SiH	0	72	0		
21	THF	$[Rh(COD)Cl]_2$	1	1	Ph_2SiH_2	0	72	46	31	*R*
22	THF	$[Rh(COD)Cl]_2$	3	1	Ph_2SiH_2	0	72	67	50	*R*
23	THF	$[Rh(COD)Cl]_2$	5	1	Ph_2SiH_2	0	72	37	31	*R*
24	THF	$[Rh(COD)Cl]_2$	6	1	Ph_2SiH_2	0	72	50	12	*R*
25	THF	$[Rh(COD)Cl]_2$	7	1	Ph_2SiH_2	0	20	90	5	*R*
26	THF	$[Rh(COD)Cl]_2$	9	1	Ph_2SiH_2	25	94	81	0	
27	THF	$[Rh(COD)Cl]_2$	10	1	Ph_2SiH_2	25	190	36	26	*R*
28	Et_2O	$[Rh(COD)Cl]_2$	10	1	Ph_2SiH_2	25	290	52	11	*R*
29	THF	$[Rh(COD)_2]BF_4$	10	1	Ph_2SiH_2	25	190	0		
30	THF	$[Rh(COD)Cl]_2$	10	1	α-NapPhSiH$_2$	25	190	18	22	*R*
31	THF	$[Rh(COD)Cl]_2$	10	1	Ph_2SiH_2	0	190	0		
32	THF	$[Rh(COD)Cl]_2$[e]	10	2	Ph_2SiH_2	25	190	84	8	*R*

[a] All the reactions were carried out by using acetophenone (1.0 mmol) and diphenylsilane (1.5 mmol) in the solvent (4 mL) in the presence of $[Rh(COD)Cl]_2$ (2.5 mol %) or $[Rh(COD)_2]BF_4$ (5 mol %) and **2**−**10** (5 mol %) unless otherwise stated. [b] Determined by HPLC using a Daicel Chiralcel OB column. [c] By optical rotation. [d] Without solvent. [e] $[Rh(COD)Cl]_2$, 5 mol %. [f] $[Rh(COD)Cl]_2$, 0.5 mol %.

Table 2. Asymmetric Hydrosilylation of Acetophenone Catalyzed by Rh(I)−(11−28)[a]

catalyst	ligand	ratio of Rh(I)/ligand	(*R*)-1-phenylethanol GLC yield (%)	(*R*)-1-phenylethanol ee (%)[b]
$[Rh(COD)Cl]_2$	**11**	0.5	51	16
$[Rh(COD)Cl]_2$	**12**	0.5	26	40
$[Rh(COD)Cl]_2$	**12**	1	41	11
$[Rh(COD)_2]BF_4$	**12**	1[c]	77	∼0
$[Rh(COD)_2]BF_4$	**12**	0.5	62	18
$[Rh(COD)Cl]_2$	**13**	0.5	30	18
$[Rh(COD)Cl]_2$	**14**	0.5	73	8
$[Rh(COD)Cl]_2$	**15**	0.5	81	16
$[Rh(COD)Cl]_2$	**16**	0.5	36	12
$[Rh(COD)Cl]_2$	**17**	0.5	25	35
$[Rh(COD)Cl]_2$	**18**	0.5	51	∼0
$[Rh(COD)Cl]_2$	**19**	0.5	39	36
$[Rh(COD)Cl]_2$	**20**	1	52	33
$[Rh(COD)Cl]_2$	**21**	1	44	40
$[Rh(COD)_2]BF_4$	**22**	1[c]	65	31
$[Rh(COD)Cl]_2$	**23**	1	53	13
$[Rh(COD)_2]BF_4$	**23**	1[c]	73	27
$[Rh(COD)_2]BF_4$	**24**	1[c]	50	32
$[Rh(COD)_2]BF_4$	**25**	1[c]	73	24
$[Rh(COD)Cl]_2$	**25**	1	53	20
$[Rh(COD)Cl]_2$	**26**	1	35	5
$[Rh(COD)Cl]_2$	**27**	1	83	∼0
$[Rh(COD)Cl]_2$	**28**	1	0	

[a] All the reactions were carried out by using acetophenone (1.0 mmol) and diphenylsilane (1.5 mmol) in THF (4 mL) at 0 °C for 20 h in the presence of Rh(I) complex (0.5 mol %) and ligand (1.0 or 2.0 mol %) unless otherwise stated. [b] See footnote *a* of Table 1. [c] Rh(I) (1.0 mol %) and ligand (1.0 mol %) were used.

Table 3. Asymmetric Hydrosilylation of Alkyl Aryl Ketones Catalyzed by Rh(I)−2[a]

ketone Ar	ketone R	time (h)	alcohol (*R*) GLC yield (%)	alcohol (*R*) ee (%)[b]
Ph	Me	24	31	85
Ph	Et	70	14	58
Ph	CH_2Cl	120	85	88[c]
Ph	CO_2Me	25	31	60
Ph	*t*-Bu	240	5	85
indanone		240	5	42
p-$NO_2C_6H_4$	Me	72	45	76[d]
p-ClC_6H_4	Me	72	41	74[c]
2-thienyl	Me	96	100	78

[a] All the reactions were carried out using alkyl aryl ketones (1.0 mmol) and diphenylsilane (1.5 mmol) in THF (4 mL) at 0 °C in the presence of $[Rh(COD)Cl]_2$ (2.5 mol %) and **2** (5 mol %). [b] See a footnote of Table 1. [c] The absolute configuration of the product is *S*. [d] The absolute configuration was not determined.

of an electron-withdrawing group, such as NO_2 and Cl, or the use of thienyl group increased the product yield, while the introduction of an electron-releasing group such as *p*-Me or *p*-MeO or the use of a bulky group such as naphthyl inhibited the reaction completely. Reasonably high ee values were obtained in many cases, and the highest ee (88% ee) was obtained from α-chloroacetophenone. It is worth noting that the ee value of the product from the α-keto ester was lower than that from acetophenone in this case, as it has been reported that, in similar reactions using chiral phosphine ligands, the result was completely reversed due to secondary coordination of the carbonyl oxygen of the ester to rhodium giving good enantioselective surroundings. Hydrosilylation using **10** in place of **2** as a ligand was nearly unsuccessful, and only the α-keto ester afforded the expected compound in 46% yield (26% ee) by reaction at 0 °C for 120 h; almost no reaction occurred

Table 4. Asymmetric Hydrosilylation of Acetophenone Catalyzed by Ir(I)−(1−3 or 10)[a]

reacn condition			1-phenylethanol		
ligand	temp (°C)	time (h)	GLC yield (%)	ee (%)[b]	config[b]
1	15	20	82	15	*R*
1	0	144	43	13	*R*
2	40	4	100	∼0	
2	15	15	100	23	*S*
2	0	24	55	18	*S*
2	−20	24	40	∼0	
3	15	20	90	∼0	
3	0	144	81	22	*R*
10	25	120	98	11	*R*

[a] All the reactions were carried out by using acetophenone (1.0 mmol) and diphenylsilane (1.5 mmol) in THF (4 mL) in the presence of $[Ir(COD)Cl]_2$ (2.5 mol %) and **1**−**3** or **10** (5 mol %). [b] See footnotes of Table 1.

with methyl 2-thienyl ketone, α-chloroacetophenone, *p*-nitroacetophenone, and *p*-chloroacetophenone.

Iridium-Catalyzed Asymmetric Hydrosilylation of Acetophenone Using Chiral Diferrocenyl Dichalcogenides as Ligands. Compared to rhodium-catalyzed asymmetric reactions, the study of iridium-catalyzed ones is still limited, and highly enantioselective results were obtained in only several cases such as transfer hydrogenation[24] and hydrogenation.[25] We applied the previously described Rh(I)-catalyzed hydrosilylation system to an iridium(I) complex using acetophenone as a substrate and diferrocenyl dichalcogenides (**1**−**3** and **10**) as chiral ligands. The results are shown in Table 4. Hydrosilylation proceeded smoothly to give 1-phenylethanol in good yield, but the enantioselectivity was generally low. It is noteworthy that 1-phenylethanol of the opposite configuration (*S*) was obtained when the diselenide **2** was used. Although the formation of 1-phenylethanol of opposite configuration has been observed between the Rh(I)- and Ir(I)-complex-catalyzed hydrosilylations of acetophenone using chiral aminophosphines as ligands,[26] it is difficult to explain in our system why the configuration of the product using **1** and **3** was different from that using **2** in spite of a very similar structure of **1**−**3**.

Rhodium-Catalyzed Asymmetric Hydrosilylation of Imines Using 2 as a Chiral Ligand. Asymmetric hydrosilylation of imines affords synthetically useful chiral *sec*-amines, but the study on this subject is still quite limited and the observed enantioselectivity thus far is low.[27] We applied our Rh(I)−**2** catalytic system to two imines in various solvents (Scheme 8, Table 5). In all cases, the reaction proceeded smoothly and the conversion of imines to the hydrosilylated products was almost 100%, but the isolated yield of the corresponding amines after acid hydrolysis in a pure form was low because of difficulty in their separation from **2**. A good result was obtained from *N*-phenyl-1-phenylpropanimine (**29**) (up to 53% ee), but the reaction with *N*-benzyl analogue (**30**) gave low selectivity (up to 11% ee).

Scheme 8

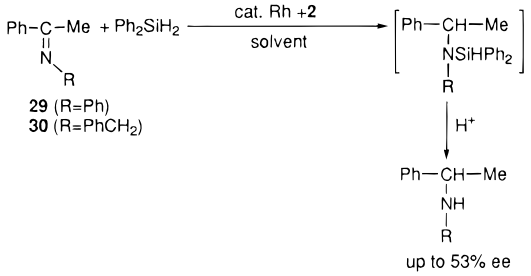
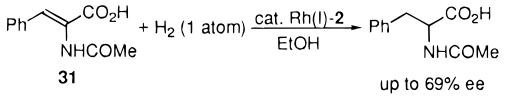


Table 5. Asymmetric Hydrosilylation of Imines Catalyzed by Rh(I)−2[a]

				amine	
imine R	solvent	temp (°C)	time (h)	yield (%)[b]	ee (%)[c]
Ph	benzene	25	24	54	∼0
Ph	Et_2O	25	24	27	∼0
Ph	Et_2O	0	140	28	53
Ph	THF	25	24	28	0
Ph	THF	0	140	37	18
$PhCH_2$	Et_2O	0	45	52	11
$PhCH_2$	THF	0	45	47	7

[a] All the reactions were carried out using imines (1.0 mmol) and diphenylsilane (1.5 mmol) in solvent (4 mL) at 0 °C in the presence of $[Rh(COD)Cl]_2$ (2.5 mol %) and **2** (5 mol %). [b] Isolated yield in a pure form. [c] The absolute configuration of the product was not determined.

Scheme 9



Rhodium-Catalyzed Asymmetric Hydrogenation of an Enamide Using 2 as a Chiral Ligand. In order to find another utility of **2** as a chiral ligand, asymmetric hydrogenation of an enamide, α-acetamidocinnamic acid (**31**), was carried out under 1 atm hydrogen in the presence of a Rh(I) complex (Scheme 9), as highly enantioselective hydrogenation of the enamide has been reported in many cases.[3b] In the presence of 5 mol % $[Rh(COD)Cl]_2$−**2** complex, **31** was hydrogenated in dry ethanol at room temperature to give the hydrogenated product in 49% yield (50 h) and its ee value was 69% as determined by the optical rotation. The result was not satisfactory, but it was shown that **2** could also act as a chiral ligand for asymmetric hydrogenation.

Preparation of a Complex between Cationic Rhodium(I) Compound and 2 and a Plausible Scheme for Hydrosilylation. In order to study the reaction scheme of this catalytic hydrosilylation, we have tried to confirm the *in situ* formation of the complex between $[Rh(COD)Cl]_2$ and **2** or to isolate it, if possible. However, ^{1}H-NMR determination of the mixture of the two compounds in THF-d_8 under argon did not give any information on complex formation, and attempts to isolate it after reaction of the two compounds in THF at room temperature for 20 h resulted in a complete recovery of **2**. The latter fact also suggests that oxidative addition of **2** to Rh(I) does not occur under our conditions in contrast to the so far known facile oxidative addition of diphenyl diselenide or diphenyl disulfide to low-valent Rh compounds.[28]

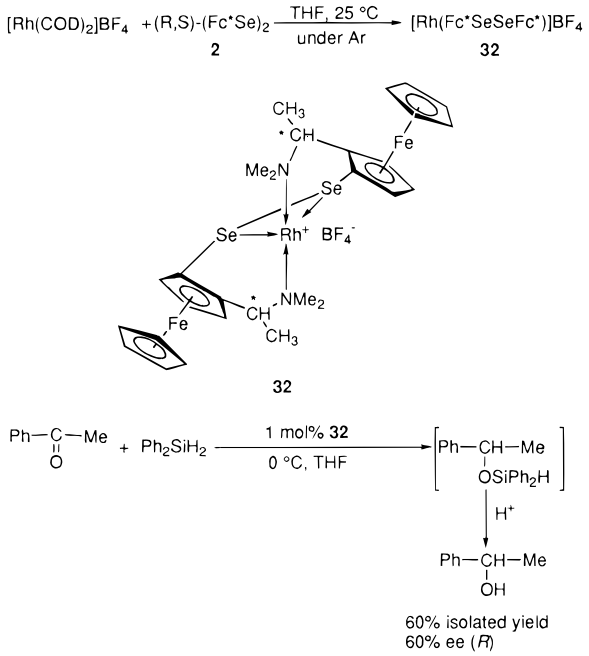
(24) (a) Zassinovich, G.; Bettella, R.; Mestroni, G.; Bresciani-Pahor, N.; Geremia, S.; Randaccio, L. *J. Organomet. Chem.* **1989**, *370*, 187. (b) Müller, D.; Umbricht, G.; Weber, B.; Pfaltz, A. *Helv. Chim. Acta* **1991**, 74, 232.

(25) Mashima, K.; Akutagawa, T.; Zhang, X.; Takaya, H.; Taketomi, T.; Kumobayashi, H.; Akutagawa, S. *J. Organomet. Chem.* **1992**, *428*, 213.

(26) Kinting, A.; Kreuzfeld, H. J.; Abicht, H. P. *J. Organomet. Chem.* **1989**, *370*, 343.

(27) (a) Langlois, N.; Dang, T. P.; Kagan, H. B. *Tetrahedron Lett.* **1973**, 4865. (b) Kagan, H. B.; Langlois, N.; Dang, T. P. *J. Organomet. Chem.* **1975**, *90*, 353. (c) Becker, R.; Brunner, H.; Mahboobi, S.; Wiegrebe, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 995.

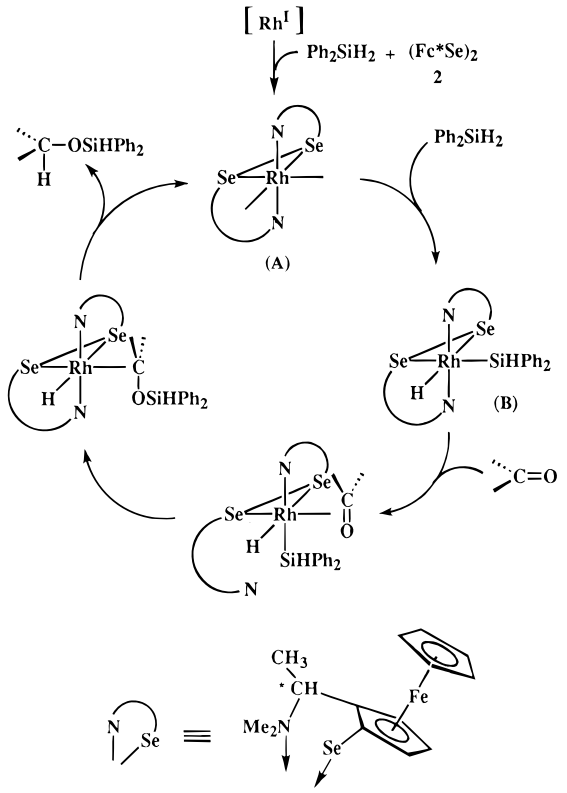
Scheme 10



On the other hand, we succeeded in isolation of the complex between a cationic rhodium compound ([Rh(COD)$_2$]BF$_4$) and **2** by mixing them in THF at 25 °C. The new complex, isolated in 53% yield, was insoluble in $CHCl_3$ and THF but soluble in acetone. Proton-NMR analysis in acetone-d_6 did not show any peaks due to COD and showed all downfield shifted protons of the complex compared with those of **2** itself, which was especially prominent for the singlet methyl resonance of the $-NMe_2$ group. Although a single crystal of the complex was not available for X-ray structural determination, we presumed it to be a 1:1 complex between Rh and diselenide where two Se and two N are coordinated to Rh from the results of the ^{1}H-NMR analysis together with CH analytical data. It may also be possible that the complex was formed by oxidative addition of the Se−Se bond to a Rh(I) to afford a Rh(III) complex such as [(Fc*Se)Rh(SeFc*)]BF$_4$, which would give the same CH analysis and similar ^{1}H-NMR data. Therefore, we examined the utility of this new complex for asymmetric hydrosilylation. If it were a Rh(III) complex, the possibility for oxidative addition of an Si−H bond to it should be quite low and no reaction is expected to occur. Hydrosilylation of acetophenone in the presence of 1 mol % of this complex under the previously described conditions, however, proceeded smoothly to give (*R*)-1-phenylethanol in 60% isolated yield with 60% ee (Scheme 10). This fact shows that the complex may have the structure shown in **32** where **2** coordinates to Rh(I) as a tetradentate ligand.

By considering these results, we propose Scheme 11 as a catalytic cycle for the Rh(I) complex catalyzed hydrosilylation of ketones using **2** as a chiral ligand. Under the catalytic conditions, COD of the Rh(I) complex might be hydrosilylated and removed from the rhodium to generate the catalytically active species (A), where **2** coordinates to the rhodium giving a tetracoordinated Rh(I) complex, on which oxidative addition of

Scheme 11



Si−H bond of arylsilane occurs. Subsequent coordination of a carbonyl group to the rhodium, formation of a C−Rh bond, and reductive elimination from Rh furnish the hydrosilylated compound. The key step for stereoselection seems to be the coordination of a carbonyl group to the rhodium of Rh(III)−**2** complex B, which may have a more suitable rigid structure for stereoselection than any complexes having other newly prepared dichalcogenides and monochalcogenides as chiral ligands.

In conclusion, many novel chiral diferrocenyl dichalcogenides and chalcogeno-group containing ferrocenes have been prepared. These compounds acted as chiral ligands for Rh(I)- and Ir(I)-catalyzed asymmetric hydrosilylation of ketones and imines and asymmetric hydrogenation of an enamide to give the corresponding products with moderate to good ee, with [*R,S;R,S*]-bis[2-[1-(dimethylamino)ethyl]ferrocenyl] diselenide (**2**) being the most effective ligand.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GSX-270 (270 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are reported in δ units downfield from the internal reference Me_4Si. The coupling constants (J) are in hertz (Hz). Melting points were determined on a Yanaco MP-S3 micro melting point apparatus and uncorrected. Optical rotations were measured on a JASCO DIP-360. GLC analyses were performed on a Hitachi 163 instrument (1 m × 3 mm stainless steel column packed with 20% EGSS on Shimalite) and a Shimadzu GC-14A instrument (25 m HiCap-CBP-10-S25 capillary column) with flame-ionization detectors and N_2 as carrier gas. Column chromatography on Al_2O_3 was performed with ICN Alumina N, Akt. I (hexane and hexane/ethyl acetate as eluents). Column chromatography on SiO_2 was performed with Wakogel C-300 (hexane and hexane/ethyl acetate as eluents). Elemental analyses were performed at

(28) (a) Collman, J. P.; Rothrock, R. K.; Sen, J. P.; Tullius, T. D.; Hodgson, K. O. *Inorg. Chem.* **1976**, *15*, 2947. (b) Collman, J. P.; Rothrock, R. K.; Stark, R. A. *Inorg. Chem.* **1977**, *16*, 437.

the Microanalytical Center of Kyoto University. All solvents were distilled from CaH_2 or $LiAlH_4$ and stored over 4 Å molecular sieves under nitrogen. (*R*)-(+)-*N*,*N*-Dimethyl-(1-ferrocenyl)ethylamine and the (*S*)-(−)-*N*,*N*-dimethyl-(1-ferrocenylethyl)amine were prepared easily by the reported method on a large scale.[29] (*R*,*S*)-Diferrocenyl diselenide (**2**), (*R*,*S*)-diferrocenyl disulfide (**1**), and (*R*,*S*)-diferrocenyl ditelluride (**3**) were prepared by the reported method, respectively.[9] (*R*)-Ferrocenyl *p*-tolyl sulfoxide was prepared by the reported method in a large scale.[14] (*S*,*R*)-BPPFOAc was a commercial reagent, while (*S*,*R*)-PPFOAc was prepared by the reported method from (*S*,*R*)-*N*,*N*-dimethyl-[1-[2-(diphenylphosphino)-ferrocenyl]ethyl]amine and acetic anhydride.[4] (*2S*,*3S*)-(−)-1,4-Di-*O*-tosyl-2,3-*O*,*O*′-isopropylidene-L-threitol (DIOTs) was a commercial reagent.

Preparation of Diselenide 5 (Scheme 1). To a solution of **2** (670 mg, 1.0 mmol) in acetonitrile (6 mL) was added 10 mL of methyl iodide, and the mixture was stirred at room temperature for 4 h during which time the solution turned from heterogeneous to homogeneous. The solvent was then evaporated completely to leave a viscous oil of the ammonium salt of **4**. To this compound, acetonitrile (6 mL) and pyrrolidine (5.0 g, 70 mmol) were added, and the mixture was stirred at room temperature for 48 h to give a yellow heterogeneous mixture. After the solvent was removed under reduced pressure, the residue was treated with brine (100 mL) and then extracted with CH_2Cl_2 (50 mL × 3). The extract was dried over $MgSO_4$ and evaporated to leave an orange solid of (*R*,*S*)-**5** which was purified by column chromatography on alumina with CH_2Cl_2 as an eluent: yield 260 mg, 0.35 mmol (35% based on **2**); mp 63−65 °C. ^{1}H-NMR δ 4.04−4.45 (6H, m), 4.10 (10H, s), 3.70 (2H, q, J = 6.48 Hz), 2.64 (4H, m), 2.50 (4H, m), 1.58−1.76 (8H, m), 1.53 (6H, d, J = 6.48 Hz); ^{13}C-NMR δ 75.4 (d), 73.0 (s), 70.0 (s), 69.9 (d), 69.5 (d), 68.3 (d), 55.0 (d), 51.0 (t), 23.3 (t), 20.4 (q). Anal. Calcd for $C_{32}H_{40}N_2Fe_2Se_2$: C, 53.21; H, 5.58; N, 3.88. Found: C, 53.29; H, 5.55; N, 3.51.

Preparation of Diselenide 6. Under nitrogen, a mixture of **2** (677 mg, 1.01 mmol) and acetic anhydride (2.0 mL) was stirred at room temperature for 10 h. The mixture was treated with saturated Na_2CO_3 (100 mL) and then extracted with CH_2Cl_2 (50 mL × 3). The extract was dried over $MgSO_4$ and evaporated to leave a black oil of a mixture of **6** and *N*,*N*-dimethylacetamide. After recrystallization from ethanol, the (R,S)-diferrocenyl diselenide (**6**) (mp 155−156 °C) was isolated as a red solid in 62% yield (440 mg, 0.63 mmol): ^{1}H-NMR δ 6.02 (2H, q, J = 6.48 Hz), 4.49 (2H, t, J = 1.89 Hz), 4.37 (4H, t, J = 1.89 Hz), 4.09 (10H, s), 2.11 (6H, s), 1.63 (6H, d, J = 6.48 Hz); ^{13}C-NMR δ 170.1 (s), 89.5 (s), 76.8 (d), 74.7 (s), 70.1 (d), 70.0 (d), 68.8 (d), 68.6 (d), 21.7 (q), 18.5 (q). Anal. Calcd for $C_{28}H_{30}O_4Fe_2Se_2$: C, 48.03; H, 4.32. Found: C, 48.22; H, 4.28.

Preparation of Diselenide 7. A mixture of **6** (677 mg, 1.01 mmol) and silica gel (1.0 g) in CH_2Cl_2 (10 mL) was stirred at room temperature for 10 h. Silica gel was removed by a short alumina column, and evaporation of solvent from the eluent afforded an almost pure **7**. After recrystallization from *n*-hexane and CH_2Cl_2, the (*R*,*S*)-diferrocenyl diselenide (**7**) (mp 224−225 °C (dec)) was isolated as a yellow solid in 61% yield (373 mg, 0.61 mmol): ^{1}H-NMR δ 4.46 (4H, m), 4.36 (2H, t, J = 2.43 Hz), 4.10 (10H, s), 4.10 (2H, q, J = 6.75 Hz), 1.55 (2H, br), 1.48 (6H, d, J = 6.75 Hz); ^{13}C-NMR δ 94.9 (s), 74.4 (s), 74.0 (d), 70.1 (d), 70.0 (d), 68.8 (d), 66.4 (d), 24.0 (q). Anal. Calcd for $C_{24}H_{26}O_2Fe_2Se_2$: C, 46.79; H, 4.25. Found: C, 46.80; H, 3.88.

X-ray Structural Determination of Diselenide 8 (Figure 1). A single crystal of (*R*,*S*)-**8** was obtained from **7** recrystallized carefully and slowly from CH_2Cl_2 at room temperature. Data for **8** (an orange crystal; mp >250 °C) of formula $C_{24}H_{24}OFe_2Se_2$ were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) and a 12 kW rotating anode generator. Crystal data for **8** are as follows: monoclinic, space group $P2_1$ (No. 4); a = 7.363(3), b = 9.326(2), c = 15.826(2) Å; V = 1085.5(4) Å^3; Z = 2; D_{calcd} = 1.83 g cm^{-3}; μ(Mo Kα) = 47.02 cm^{-1}; total of 3589 reflections within 2θ = 60.0°. The final R value was 0.047 (R_w = 0.055). The structure was solved by direct methods (SHELXS86). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were geometrically calculated or taken from a difference Fourier map. Selected bond distances and angles for **8** are shown in Table 6. The final non-H atomic parameters are summarized in Table 7.

Table 6. Selected Bond Distances (Å) and Angles (deg) for 8

Bond Distances			
Se(1)−Se(2)	2.354(1)	Se(2)−C(1)	1.869(8)
Se(1)−C(13)	1.904(10)	O(1)−C(23)	1.44(1)
O(1)−C(11)	1.46(1)		
Bond Angles			
Se(1)−Se(2)−C(1)	101.2(3)	O(1)−C(23)−C(14)	108.0(7)
Se(2)−Se(1)−C(13)	99.3(3)	C(11)−O(1)−C(23)	117.2(7)

Table 7. Atomic Coordinates for 8

atom	x	y	z	B_{eq} (Å^2)
Se(1)	0.7542(1)	0.1658	−0.15657(6)	3.10(2)
Se(2)	0.9900(1)	0.0164(1)	−0.20017(6)	3.35(2)
Fe(1)	0.7757(2)	0.5189(2)	−0.09504(8)	2.68(3)
Fe(2)	1.1941(2)	-0.0179(2)	−0.38636(8)	2.59(3)
O(1)	1.0674(9)	0.4330(7)	−0.3266(4)	2.9(1)
C(1)	0.890(1)	0.336(1)	−0.1329(6)	2.8(2)
C(2)	0.928(1)	0.4450(9)	−0.1921(6)	2.5(2)
C(3)	1.026(1)	0.557(1)	−0.1464(7)	3.4(2)
C(4)	1.048(1)	0.510(1)	−0.0591(7)	4.1(2)
C(5)	0.962(1)	0.374(1)	−0.0503(6)	3.6(2)
C(6)	0.662(2)	0.647(2)	−0.0077(8)	5.3(3)
C(7)	0.579(2)	0.514(2)	−0.0090(8)	5.2(3)
C(8)	0.501(1)	0.488(2)	−0.0865(9)	4.9(3)
C(9)	0.533(2)	0.605(2)	−0.1395(9)	6.3(4)
C(10)	0.640(2)	0.708(1)	−0.088(1)	5.9(4)
C(11)	0.893(1)	0.439(1)	−0.2883(6)	2.8(2)
C(12)	0.807(1)	0.577(1)	−0.3243(6)	3.5(2)
C(13)	0.993(1)	0.0613(10)	−0.3152(5)	2.5(2)
C(14)	1.094(1)	0.178(1)	−0.3530(5)	2.6(2)
C(15)	1.077(1)	0.159(1)	−0.4440(6)	3.0(2)
C(16)	0.968(1)	0.029(1)	−0.4608(6)	3.3(2)
C(17)	0.915(1)	-0.026(1)	−0.3827(6)	2.7(2)
C(18)	1.335(2)	-0.163(2)	−0.4543(9)	5.2(3)
C(19)	1.446(1)	-0.042(2)	−0.432(1)	5.7(4)
C(20)	1.456(1)	-0.036(2)	−0.340(1)	6.1(4)
C(21)	1.358(2)	-0.151(2)	−0.3140(9)	5.4(3)
C(22)	1.283(1)	-0.228(1)	−0.3825(9)	4.5(3)
C(23)	1.180(1)	0.306(1)	−0.3088(6)	2.8(2)
C(24)	1.368(1)	0.344(1)	−0.3394(8)	4.3(3)

Preparation of Diselenide 10 (Scheme 2). After lithiation of (*R*)-ferrocenyl *p*-tolyl sulfoxide (1.23 g, 3.8 mmol) in tetrahydrofuran (THF) (40 mL) with lithium diisopropylamide (4.2 mmol) in dry heptane/THF/ethylbenzene (2.1 mL) at −78 °C under N_2, selenium powder (0.34 g, 4.3 mmol) was added portionwise and the resulting mixture was stirred at −78 °C for 10 min and then at room temperature for 1 h. The mixture was poured into water (10 mL), and then air was bubbled through the solution at room temperature for 9 h. An almost pure sample of (*R*,*S*)-bis[2-(*p*-tolylsulfinyl)ferrocenyl] diselenide [(Fs*Se)$_2$] (**10**) was isolated in 20% yield (0.31 g, 0.39 mmol) by column chromatography on SiO_2 with *n*-hexane and ethyl acetate as eluents. Recrystallization from *n*-hexane and CH_2Cl_2 afforded a pure **10** as an orange solid (mp 189−191 °C): ^{1}H-NMR δ 7.80 (4H, d, J = 7.97 Hz), 7.39 (4H, d, J = 7.97 Hz), 4.51 (2H, m), 4.37 (2H, m), 4.15 (10H, s), 4.06 (2H, m), 2.47 (6H, s); ^{13}C-NMR δ 141.4 (s), 140.4 (s), 129.5 (d), 125.6 (d), 97.9 (s), 78.6 (d), 75.2 (s), 71.3 (d), 71.0 (d), 70.4 (d), 21.5 (q). Anal. Calcd for $C_{34}H_{30}O_2Fe_2S_2Se_2$: C, 50.77; H, 3.76. Found: C, 50.44; H, 3.79. $[\alpha]^{25}_D$: +160 (c 0.12, $CHCl_3$).

(29) Gokel, G.; Ugi, I. *J. Chem. Educ.* **1972**, *49*, 82.

(*R,R*)-Diferrocenyl Disulfide (9). Similarly, (*R,R*)-bis[2-(*p*-tolylsulfinyl)ferrocenyl] disulfide [(Fs*S)$_2$] (**9**) (mp >250 °C) was prepared as a yellow solid in 23% isolated yield from (*R*)-ferrocenyl *p*-tolyl sulfoxide: ^{1}H-NMR δ 7.81 (4H, d, J = 7.97 Hz), 7.40 (4H, d, J = 7.97 Hz), 4.46 (2H, m), 4.38 (2H, m), 4.13 (10H, s), 4.10 (2H, m), 2.47 (6H, s); ^{13}C-NMR δ 141.4 (s), 140.4 (s), 129.5 (d), 125.6 (d), 97.4 (s), 84.0 (s), 77.2 (d), 71.2 (d), 70.8 (d), 70.4 (d), 21.5 (q). Anal. Calcd for $C_{34}H_{30}O_2Fe_2S_4$: C, 57.47; H, 4.26. Found: C, 57.17; H, 4.41. $[\alpha]^{25}_D$: +180 (*c* 0.12, $CHCl_3$).

(*R,S*)-Ferrocenyl phenyl sulfide (**11**) and (*R,S*)-ferrocenyl phenyl selenide (**12**) are known compounds which were prepared by the reported method.[30]

(*R,S*)-Ferrocenyl Phenyl Telluride (13) (Scheme 3). After lithiation of commercial (*R*)-(+)-*N,N*-dimethyl-(1-ferrocenylethyl)amine (526 mg, 2.05 mmol) with *sec*-BuLi (cyclohexane solution, 2.24 mmol) in dry diethyl ether (10 mL) at 0 °C under N_2, diphenyl ditelluride (836 mg, 2.05 mmol) was added portionwise and the resulting mixture was stirred at 0 °C for 2 h and then at room temperature for 4 h. The mixture was treated with saturated Na_2CO_3 (100 mL) and then extracted with CH_2Cl_2 (50 mL × 3). The extract was dried over $MgSO_4$ and evaporated to leave a black oil of crude (*R,S*)-**13** which was purified by column chromatography on active alumina with *n*-hexane and ethyl acetate as eluents giving a black oil (483 mg, 1.05 mmol) in 51% yield: ^{1}H-NMR δ 4.25 (1H, m), 4.21 (1H, t, J = 2.43 Hz), 4.12 (1H, m), 4.01 (5H, s), 3.98 (1H, q, J = 7.02 Hz), 2.04 (6H, s), 1.29 (3H, d, J = 7.02 Hz); ^{13}C-NMR δ 138.2 (d), 128.7 (d), 127.3 (d), 117.7 (s), 93.8 (s), 75.0 (s), 70.2 (s), 68.7 (d), 67.6 (d), 59.0 (d), 39.5 (q), 11.0 (q). Anal. Calcd for $C_{20}H_{23}NFeTe$: C, 52.12; H, 5.03; N, 3.04. Found: C, 52.49; H, 5.18; N, 2.91.

(*R,S*)-Ferrocenyl 2,4,6-Triisopropylphenyl Selenide (14). Similarly, the selenide **14** was prepared from (*R*)-(+)-*N,N*-dimethyl(1-ferrocenylethyl)amine and (2,4,6-triisopropylphenyl)selenenyl bromide as a red oil:[31] ^{1}H-NMR δ 6.98 (2H, s), 4.15 (1H, m), 4.10 (5H, s), 4.03−4.08 (2H, m), 3.96 (2H, quint, J = 6.75 Hz), 3.64 (1H, q, J = 6.48 Hz), 2.87 (1H, quint, J = 6.75 Hz), 2.02 (6H, s), 1.51 (3H, d, J = 6.48 Hz), 1.14−1.25 (18H, m); ^{13}C-NMR δ 152.7 (s), 149.5 (s), 128.5 (s), 121.6 (d), 77.2 (s), 71.8 (d), 70.3 (d), 66.6 (d), 57.4 (d), 41.3 (q), 34.2 (d), 34.0 (d), 24.6 (q), 24.4 (q), 24.0 (q), 16.7 (q). Anal. Calcd for $C_{29}H_{41}NFeSe$: C, 64.69; H, 7.68 N, 2.60. Found: C, 64.65; H, 7.65; N, 2.47. Yield: 34%.

Preparation of Chiral Alkyl Ferrocenyl Selenides (15−21)(Scheme 4). A typical experimental procedure for the preparation of these selenides is as follows. In a two-necked 50 mL round bottom flask containing a magnetic stirring bar were placed (*R,S*)-(Fc*Se)$_2$ (**2**) (107 mg, 0.32 mmol) and $NaBH_4$ (25 mg, 0.65 mmol) under nitrogen. Dry ethanol (5 mL) was added to the flask at 0 °C, and the mixture became homogeneous after stirring for 0.5 h at room temperature. An ethanol (1 mL) solution of *n*-propyl bromide (60 mg, 0.49 mmol) was then added to the resulting solution, and the mixture was stirred at the reflux temperature (bath temperature 100 °C) for 5 h. The mixture was treated with brine (100 mL) and then extracted with CH_2Cl_2 (50 mL × 3). The extract was dried over $MgSO_4$ and evaporated to leave a yellow solid of (*R,S*)-2-[1-(dimethylamino)ethyl]ferrocenyl propyl selenide (**15**), which was purified by column chromatography on alumina with hexane/ethyl acetate (9/1) as an eluent to give pure **15** as an orange oil: 84 mg, 0.22 mmol (69% yield based on **2**); ^{1}H-NMR δ 4.32 (1H, t, J = 2.16 Hz), 4.18 (2H, m), 4.09 (5H, s), 3.92 (1H, q, J = 7.02 Hz), 2.74−2.83 (1H, m), 2.54−2.64 (1H, m), 2.11 (6H, s), 1.64 (2H, six, J = 7.29 Hz), 1.37 (3H, d, J = 7.02 Hz), 0.96 (3H, t, J = 7.29 Hz); ^{13}C-NMR δ 93.6 (s), 74.7 (d), 73.1 (s), 69.9 (d), 67.5 (d), 56.9 (d), 40.3 (q), 31.5 (t), 23.6 (t), 14.6 (q), 12.7 (q). Anal. Calcd for $C_{17}H_{25}NFeSe$: C, 53.99; H, 6.66; N, 3.70. Found: C, 54.20; H, 6.71; N, 3.62.

Spectroscopic and analytical data and isolated yield of other selenides (*R,S*)-**16**−**21** are as follows.

16: an orange oil; ^{1}H-NMR δ 4.32 (1H, t, J = 2.16 Hz), 4.18 (2H, m), 4.09 (5H, s), 3.92 (1H, q, J = 7.02 Hz), 2.74−2.83 (1H, m), 2.54−2.64 (1H, m), 2.11 (6H, s), 1.64 (2H, m), 1.36 (3H, d, J = 7.02 Hz), 1.35 (2H, m), 0.88 (3H, t, J = 7.29 Hz); ^{13}C-NMR δ 93.7 (s), 74.7 (d), 73.1 (s), 69.9 (d), 67.5 (d), 56.9 (d), 40.3 (q), 32.5 (t), 29.0 (t), 23.0 (t), 13.6 (q), 12.6 (q). Anal. Calcd for $C_{18}H_{27}NFeSe$: C, 55.12; H, 6.94; N, 3.06. Found: C, 55.24; H, 7.13; N, 3.41. Yield: 82%.

17: a red oil; ^{1}H-NMR δ 5.08−5.98 (1H, m), 4.86−4.90 (2H, m), 4.32 (1H, t, J = 2.16 Hz), 4.20 (2H, m), 4.09 (5H, s), 3.96 (1H, q, J = 7.02 Hz), 3.47−3.52 (1H, m), 3.27−3.29 (1H, m), 2.12 (6H, s), 1.34 (3H, d, J = 7.02 Hz); ^{13}C-NMR δ 135.6 (d), 115.9 (t), 94.2 (s), 75.4 (d), 72.4 (s), 69.8 (d), 69.6 (d), 67.7 (d), 56.9 (d), 40.1 (q), 31.8 (t), 11.5 (q). Anal. Calcd for $C_{17}H_{23}NFeSe$: C, 54.28; H, 6.16; N, 3.72. Found: C, 54.58; H, 6.26; N, 3.37. Yield: 47%.

18: a red oil; ^{1}H-NMR δ 4.32 (1H, t, J = 2.16 Hz), 4.20 (2H, m), 4.09 (5H, s), 3.96 (1H, q, J = 7.02 Hz), 3.15 (1H, m), 2.12 (6H, s), 1.2−2.0 (10H, m), 1.36 (3H, d, J = 7.02 Hz); ^{13}C-NMR δ 76.1 (d), 71.8 (s), 70.0 (d), 69.8 (s), 68.0 (d), 67.8 (d), 57.2 (d), 43.6 (d), 40.1 (q), 34.8 (t), 33.7 (t), 25.9 (t), 12.8 (q). Anal. Calcd for $C_{20}H_{29}NFeSe$: C, 57.43; H, 6.99; N, 3.35. Found: C, 57.18; H, 6.64; N, 3.38. Yield: 38%.

19: a red oil; ^{1}H-NMR δ 4.32 (1H, t, J = 2.16 Hz), 4.20 (2H, m), 4.09 (5H, s), 3.93 (1H, q, J = 7.02 Hz), 2.76 (2H, m), 2.12 (6H, s), 1.38 (3H, d, J = 7.02 Hz), 1.01 (9H, s); ^{13}C-NMR δ 76.5 (s), 74.4 (d), 69.9 (d), 68.2 (s), 67.3 (d), 56.8 (d), 47.5 (s), 46.1 (t), 40.4 (q), 29.6 (q), 12.8 (q). Anal. Calcd for $C_{19}H_{29}NFeSe$: C, 56.17; H, 7.20; N, 3.45. Found: C, 56.02; H, 7.15; N, 3.70. Yield: 43%.

20: [*R,S*;*R,S*], an orange oil; ^{1}H-NMR δ 4.32 (2H, t, J = 2.16 Hz), 4.18 (4H, m), 4.09 (10H, s), 3.91 (2H, q, J = 7.02 Hz), 2.82−2.89 (2H, m), 2.57−2.67 (2H, m), 2.10 (12H, s), 1.90 (2H, t, J = 7.56 Hz), 1.35 (6H, d, J = 7.02 Hz); ^{13}C-NMR δ 94.2 (s), 77.5 (d), 75.3 (d), 72.9 (s), 70.2 (d), 67.8 (d), 57.2 (d), 40.5 (q), 31.0 (t), 29.2 (t), 12.3 (q). Anal. Calcd for $C_{31}H_{42}N_2Fe_2Se_2$: C, 52.27; H, 5.94; N, 3.93. Found: C, 52.52; H, 6.13; N, 3.55. Yield: 55%.

21: [*R,S*;*R,S*], an orange oil; ^{1}H-NMR δ 4.32 (2H, t, J = 2.16 Hz), 4.18 (4H, m), 4.08 (10H, s), 3.91 (2H, q, J = 7.02 Hz), 2.73−2.80 (2H, m), 2.55−2.63 (2H, m), 2.10 (12H, s), 1.63 (2H, m), 1.40 (4H, m), 1.36 (6H, d, J = 7.02 Hz); ^{13}C-NMR δ 94.0 (s), 77.5 (d), 75.1 (d), 73.1 (s), 70.2 (d), 67.8 (d), 57.2 (d), 40.6 (q), 30.4 (t), 30.2 (t), 29.3 (t), 12.6 (q). Anal. Calcd for $C_{33}H_{46}N_2Fe_2Se_2$: C, 53.54; H, 6.26; N, 3.78. Found: C, 53.15; H, 6.23; N, 3.44. Yield: 55%.

Preparation of Chiral Ferrocenylphosphines Possessing a Chalcogeno Moiety on the Side Chain of Ferrocene (22−25) (Scheme 5). A typical experimental procedure for the preparation of (*S,R*)-**22** is as follows. In a two-necked 50 mL round bottom flask containing a magnetic stirring bar were placed diphenyl disulfide (51.2 mg, 0.23 mmol) and $NaBH_4$ (53 mg, 1.40 mmol) under nitrogen. Ethanol (4 mL) was added to the flask at 0 °C, and the mixture became homogeneous after stirring for 0.5 h at room temperature. An ethanol (2 mL) solution of (*S,R*)-PPFOAc (200 mg, 0.45 mmol) was then added to the resulting solution, and the mixture was stirred at the reflux temperature (bath temperature 100 °C) for 4 h. The mixture was treated with brine (100 mL) and then extracted with CH_2Cl_2 (50 mL × 3). The extract was dried over $MgSO_4$ and evaporated to leave a yellow solid of (*S,R*)-**22**, which was recrystallized from EtOH (mp 76−78 °C): 230 mg, 0.45 mmol (100% yield based on PPFOAc); ^{1}H-NMR δ 7.61−7.68 (2H, m), 7.37−7.41 (3H, m), 7.18−7.30 (10H, m), 4.53 (1H, m), 4.36 (2H, m), 4.02 (1H, m), 3.92 (5H, s), 1.69

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(31) (2,4,6-Triisopropylphenyl)selenenyl bromide was prepared from bis(2,4,6-triisopropylphenyl) diselenide and bromine in CCl_4: Bochmann, M; Webb, K. J.; Hursthouse, M. B.; Mazid, M. *J. Chem. Soc., Dalton Trans.* **1991**, 2317.

(3H, d, J = 6.48 Hz). Anal. Calcd for $C_{30}H_{27}FePS$: C, 71.15; H, 5.37. Found: C, 71.18; H, 5.31.

Similarly, other (*S,R*)-ferrocenylphosphines (**23**−**25**) were prepared from (*S,R*)-PPFOAc or (*S,R*)-BPPFOAc and the corresponding diphenyl dichalcogenide, respectively.

23: a yellow solid; mp 119−121 °C; ^{1}H-NMR δ 7.53−7.59 (2H, m), 7.16−7.42 (23H, m), 4.46 (1H, m), 3.45−4.38 (7H, m), 1.55 (3H, d, J = 6.48 Hz). Anal. Calcd for $C_{42}H_{37}FeP_2S$: C, 72.94; H, 5.39. Found: C, 72.77; H, 5.07. Yield: 81%.

24: An orange oil; ^{1}H-NMR δ 7.61−7.68 (2H, m), 7.28−7.41 (3H, m), 7.16−7.29 (10H, m), 4.65 (1H, m), 4.35 (2H, m), 4.05 (1H, m), 3.90 (5H, s), 1.81 (3H, d, J = 6.48 Hz). Anal. Calcd for $C_{30}H_{27}FePSe$: C, 65.12; H, 4.92. Found: C, 65.34; H, 5.01. Yield: 100%.

25: a yellow solid; mp 73−75 °C; ^{1}H-NMR δ 7.52−7.59 (2H, m), 7.17−7.38 (23H, m), 4.56 (1H, m), 3.42−4.38 (7H, m), 1.67 (3H, d, J = 6.48 Hz). Anal. Calcd for $C_{42}H_{37}FeP_2Se$: C, 68.31; H, 5.05. Found: C, 67.97; H, 5.06. Yield: 74%.

Preparation of Bis(chalcogenides) (26−28) (Scheme 6). A typical experimental procedure for the preparation of (*S,S*)-**26** is as follows. In a two-necked 50 mL round bottom flask containing a magnetic stirring bar were placed diphenyl disulfide (144 mg, 0.66 mmol) and $NaBH_4$ (84 mg, 2.22 mmol) under nitrogen. Ethanol (15 mL) was added to the flask at 0 °C, and the mixture became homogeneous after stirring for 0.5 h at room temperature. An ethanol (5 mL) solution of (*S,S*)-DIOTs (300 mg, 0.64 mmol) was then added to the resulting solution, and the mixture was stirred at the reflux temperature (bath temperature 100 °C) for 5 h. The mixture was treated with brine (100 mL) and then extracted with CH_2Cl_2 (50 mL × 3). The extract was dried over $MgSO_4$ and evaporated to leave a colorless oil of **26**, which was purified by column chromatography on silica gel with hexane/ethyl acetate (9/1) as an eluent: 216 mg, 0.62 mmol (97% yield based on DIOTs); ^{1}H-NMR δ 7.17−7.39 (10H, m), 4.07 (2H, m), 3.21 (4H, m), 1.41 (6H, s); ^{13}C-NMR δ 135.5 (s), 129.4 (d), 129.0 (d), 126.3 (d), 110.0 (s), 79.0 (d), 37.0 (t), 27.3 (q). Anal. Calcd for $C_{19}H_{22}O_2S_2$: C, 65.86; H, 6.40. Found: C, 65.90; H, 6.37.

27: (*S,S*), a colorless oil; ^{1}H-NMR δ 7.47−7.52 (4H, m), 7.22−7.27 (6H, m), 4.08 (2H, m), 3.17 (4H, m), 1.40 (6H, s); ^{13}C-NMR δ 132.7 (d), 129.9 (s), 129.2 (d), 127.1 (d), 109.5 (s), 80.1 (d), 30.5 (t), 27.4 (q). Anal. Calcd for $C_{19}H_{22}O_2Se_2$: C, 51.83; H, 5.04. Found: C, 52.10; H, 5.25. Yield: 91%.

28: (*S,S*), a yellow oil; ^{1}H-NMR δ 7.69−7.73 (4H, m), 7.15−7.30 (6H, m), 4.03 (2H, m), 3.15 (4H, m), 1.34 (6H, s); ^{13}C-NMR δ 138.4 (d), 129.2 (d), 127.7 (d), 111.8 (s), 108.9 (s), 81.6 (d), 27.5 (q), 11.6 (t). Anal. Calcd for $C_{19}H_{22}O_2Te_2$: C, 42.45; H, 4.13. Found: C, 42.72; H, 4.11. Yield: 72%.

General Procedure for Rhodium- or Iridium-Catalyzed Asymmetric Hydrosilylation of Ketones Using Various Chiral Chalcogenides as Ligands. In a 20-mL flask were placed a metal complex and a chiral ligand under argon. Anhydrous THF (3.0 mL) was added by a syringe through a septum, and then the mixture was magnetically stirred at room temperature for 1 h. After addition of ketone (1.0 mmol) in anhydrous THF (1.0 mL) by a syringe, the reaction flask was dipped in a thermoregulated bath at 0 °C. Silane (1.5 mmol) was then added slowly by a syringe. For the workup, methanol (1 mL) was added slowly to the reaction mixture at 0 °C. After gas evolution ceased, 1 N HCl(aq) (5 mL) was added to the reaction mixture, which was stirred for 1 h at room temperature. The mixture was extracted with brine (50 mL) and diethyl ether (50 mL × 3) and dried over anhydrous $MgSO_4$. The extract was concentrated under reduced pressure by an aspirator. After the residue was distilled under reduced pressure by use of a Kugelrohr, the corresponding alcohol was obtained in a pure form. The ee values of the alcohols were determined by HPLC using Daicel Chiralcel OJ, OD, OB, and OF columns. The configuration of the alcohols was determined by the reported optical rotation.[32]

General Procedure for Rhodium-Catalyzed Asymmetric Hydrosilylation of Imines Using 2 as a Chiral Ligand. The reaction was carried out by a method similar to that described in the previous section. In this case only the purification method of the product was different. Purification was carried out by TLC because at high temperature (distillation) the product decomposed in many cases. The ee value of the product was determined by HPLC using Daicel Chiralcel OJ, OD, OB, and OF columns.

General Procedure for Rhodium-Catalyzed Asymmetric Hydrogenation of α-Acetamidocinnamic Acid Using 2 as a Chiral Ligand. In a 20-mL flask were placed a metal complex and a chiral ligand under argon. Anhydrous EtOH (3.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 1 h. This solution was added by a syringe to another flask containing α-acetamidocinnamic acid (1.0 mmol) under 1 atm of hydrogen pressure. After being stirred for a suitable time, the reaction mixture was slowly added to 0.5 N NaOH(aq) (30 mL) and extracted with diethyl ether (50 mL × 3). To the water layer, 1 N HCl(aq) was added until the solution became acidic, and then it was extracted with diethyl ether (50 mL × 3) and dried over anhydrous $MgSO_4$. The extract was concentrated under reduced pressure by an aspirator to leave an almost pure hydrogenated product (49% yield). The ee value and the configuration were determined by optical rotation in methanol.[33]

Preparation of 32. In a 20-mL flask was placed the cationic rhodium compound ($[Rh(COD)_2]BF_4$) (21 mg, 0.052 mmol) and (*R,S*)-$(Fc^*Se)_2$ (**2**) (35 mg, 0.051 mmol) under argon. Anhydrous THF (2.0 mL) was added, and then the resulting solution was magnetically stirred at room temperature for 20 h during which time the color of the solution turned from pale orange to red. When diethyl ether (5 mL) was added to the solution, **32** was precipitated as a brown solid, which was collected by filtration and dried under atmospheric pressure: 24 mg, 53% isolated yield based on **2**, mp 185−187 °C (dec); ^{1}H-NMR (acetone-d_6) δ 4.92 (2H, m), 4.84 (2H, q, J = 7.02 Hz), 4.79 (2H, m), 4.64 (2H, m), 4.30 (10H, s), 3.00 (12H, s, $-NMe_2$), 1.99 (6H, d, J = 7.02 Hz). Anal. Calcd for $C_{28}H_{36}BF_4Fe_2N_2RhSe_2$: C, 39.11; H, 4.22; N, 3.26. Found: C, 38.98; H, 4.60; N, 2.73. [For comparison, **2**: ^{1}H-NMR (acetone-d_6) δ 4.47 (2H, m), 4.30 (4H, m), 4.08 (10H, s), 3.93 (2H, q, J = 7.02 Hz), 2.14 (12H, s, $-NMe_2$), 1.35 (6H, d, J = 7.02 Hz).]

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Supporting Information Available: Text describing X-ray procedures and tables of crystal structure data, hydrogen positional and *B* parameters, anisotropic thermal parameters, and complete bond distances and angles for **8** (26 pages). Ordering information is given on any current masthead page.

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