Synthesis and structure of novel chiral oxazolinylferrocenes and oxazolinylferrocenylphosphines, and their rhodium(I) -complexes

Yoshiaki Nishibayashi [a,1], Kyohei Segawa [a], Yasuyoshi Arikawa [a], Kouichi Ohe [a], Masanobu Hidai [b], Sakae Uemura [a,*]

[a] *Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan*
[b] *Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Tokyo 113, Japan*

Abstract

A variety of chiral oxazolinylferrocenes are prepared from either ferrocenecarboxylic acid or cyanoferrocene and chiral β-amino alcohols. Highly diastereoselective *ortho*-lithiation (84 ~ 99% de) of the oxazolinylferrocenes is accomplished with *sec*-butyllithium and the treatment of the lithiated compounds with an electrophile such as MeI, Ph_2PCl or $(PhSe)_2$ gives the corresponding *ortho*-substituted oxazolinylferrocenes. The molecular structure of (S,S)-[2-(4'-isopropyloxazolin-2'-yl)ferrocenyl]diphenylphosphine (10), (S,S)-2-phenyl-seleno-1-(4'-isopropyloxazolinyl)ferrocene (17), (S,R)-3-methyl-1-diphenylphosphino-2-(4'-isopropyloxazolinyl)ferrocene (18), and (S,S,S)-[2-(4',5'-diphenyloxazolin-2'-yl)ferrocenyl]diphenylphosphine ((S,S,S)-DIPOF; 21) has been fully characterized by X-ray crystallography. In connection with their usefulness as chiral ligands for Rh(I)-catalyzed asymmetric hydrosilylation of ketones, the square planar transition metal complexes having oxazolinylferrocenylphosphines, such as [Rh(COD)(P–N)]BF_4 and Rh(CO)(P–N)Cl (P–N = 10 or 21), are prepared by treatment of [Rh(COD)$_2$]BF_4 and [Rh(CO)$_2$Cl]$_2$ with 10 and 21, respectively, and all structures have been characterized spectroscopically and further confirmed by X-ray crystallography. © 1997 Elsevier Science S.A.

Keywords: Ferrocene; Phosphine; Oxazoline; Rhodium; Crystal structure

1. Introduction

Molecular design of a chiral ligand for the transition metal-catalyzed asymmetric reaction is essential for obtaining the highly enantiomerically pure compounds and many efforts in preparing efficient ligands have been continuing [1–3], one of which is the chiral ferrocenylphosphines [4–7]. The ferrocenes with a chiral auxiliary possess a characteristic nature in that a structural modification can be readily made by introduction of a desired functional group on the ferrocene ring to give a suitable and efficient ligand for a variety of asymmetric reactions such as rhodium-catalyzed hydrogenation [8–10] and hydrosilylation [11], palladium-catalyzed allylic substitution [12,13], Grignard cross-coupling reactions [12,13], and gold- or silver-catalyzed

aldol-type reaction of isocyanocarboxylates [14]. On the other hand, we have been interested in the preparation of optically active [R,S; R,S]- and [S,R; S,R]-bis[2-[1-(dimethylamino)ethyl]ferrocenyl] dichalcogenides (S, Se, and Te as chalcogen atoms) and their stoichiometric use for various asymmetric reactions such as selenoxide elimination [15,16], [2,3]sigmatropic rearrangement [15–19], oxyselenation and selenocyclization of alkenes [20,21], and nucleophilic ring-opening of meso-epoxides [22]. Further, we revealed that these chiral dichalcogenides act as chiral ligands for Rh(I)- and Ir(I)-catalyzed asymmetric hydrosilylation of ketones and imines and asymmetric hydrogenation of an enamide with moderate to good enantioselectivity [23,24]. On these backgrounds, we envisaged to design a new type chiral ligand, oxazolinylferrocene-phosphine hybrid ligand, because Pfaltz [25], Lloyd-Jones and Pfaltz [26], Loiseleur et al. [27] and Grant and Meyers [28] have succeeded in some transition metal-catalyzed enantioselective reactions using chiral oxazolines and related compounds. Actually, we found that some of the oxazolinyl-
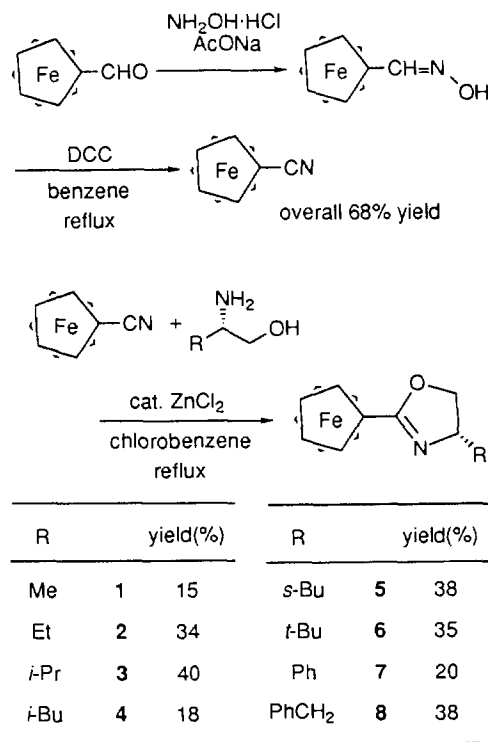
---

ferrocenylphosphines worked as effective chiral ligands for the Rh(I)-catalyzed asymmetric hydrosilylation of a variety of simple ketones lacking secondary coordinating functional group, a chiral [2-(4',5'-diphenyloxazolin-2'-yl)ferrocenyl] diphenylphosphine (abbreviated as DIPOF) being the best (up to 91% ee). [2] We present here the details on the synthesis of a variety of novel chiral oxazolinylferrocenes, oxazolinylferrocenylphosphines, and their rhodium-complexes as well as structural elucidation of some of them by X-ray crystallography. It is worth noting that the lithiation of the chiral oxazolinylferrocenes, especially with sec-BuLi, proceeds highly diastereoselectively, enabling us to prepare the corresponding chiral ortho-substituted oxazolinylferrocenes facilely and in good yields.

2. Results and discussion

2.1. Synthesis and highly diastereoselective ortho-lithiation of chiral oxazolinylferrocenes

First, the chiral oxazolinylferrocenes (1–8) were prepared by treatment of cyanoferrocene, which was obtained easily from the ferrocenecarbaldehyde by a literature method [31] (68% overall isolated yield), with the corresponding chiral β-amino alcohols in the presence of a catalytic amount of $ZnCl_2$ [32,33] and readily purified and isolated in an enantiomerically pure form by column chromatography (SiO_2) in 15–40% yields (Scheme 1). Deprotonation of the oxazolinylferrocenes by 1.1 equivalents of sec-BuLi (in cyclohexane) at −78°C for 2 h followed by quenching with electrophiles such as methyl iodide, chlorodiphenylphosphine and diphenyl diselenide led to the corresponding ortho-substituted oxazolinylferrocenes (9–17) in 51–77% isolated yields (Scheme 2, Table 1). [3] The unreacted oxazolinylferrocenes were recovered in 15–30% and there were no side-products. In almost all cases, the diastereoselectivity of the produced ferrocenes was revealed to be quite high by ^{1}H NMR determination of the crude products as shown in Table 1. Quite recently, a similar highly diastereoselective ortho-lithiation of chiral oxazolinylferrocenes has been independently reported by Richards et al. [35], Richards and Mulvaney [36], Sammakia et al. [37] and Samakia and Latham [38,39]. Similar phenomenon was also observed in chiral bis(oxazolinyl)ferrocenes [40–43]. The major di-

Scheme 1.

R		yield(%)	R		yield(%)
Me	1	15	s-Bu	5	38
Et	2	34	t-Bu	6	35
i-Pr	3	40	Ph	7	20
i-Bu	4	18	PhCH₂	8	38

astereoisomer of each of 9–17 was isolated in an optically pure form and confirmed by ^{1}H NMR after recrystallization from ethanol. The molecular structure of (S,S)-[2-(4'-isopropyloxazolin-2'-yl)ferrocenyl]diphenylphosphine (10) and (S,S)-2-phenylseleno-1-(4'-isopropyloxazolinyl)ferrocene (17), where the former (S) indicates the configuration at the oxazoline ring carbon and
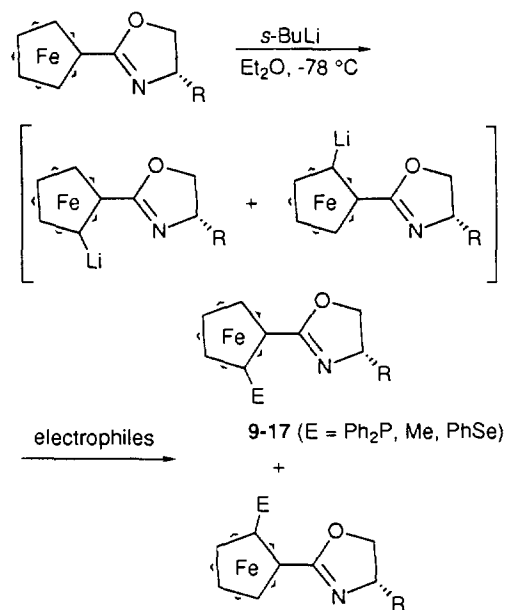
Scheme 2.

---

[2] The absolute configuration of 1-phenylethanol obtained from acetophenone using 14 as a chiral ligand was erroneously assigned as (S) in the report of Ref. [29]. However, it was actually (R) as reported in Ref. [30]).

[3] ortho-Lithiation of oxazolinylferrocenes having no stereogenic center has been reported ([34]).

Table 1
Diastereoselectivity in lithiation of (S)-oxazolynylferrocenes

R	Electrophiles	Major diastereomer	Yield (%)[a]	de (%)
Et	Ph$_2$PCl	**9**	58	68
i-Pr	Ph$_2$PCl	**10**	77	95
i-Bu	Ph$_2$PCl	**11**	63	48
s-Bu	Ph$_2$PCl	**12**	58	92
t-Bu	Ph$_2$PCl	**13**	51	84
Ph	Ph$_2$PCl	**14**	55	> 99
PhCH$_2$	Ph$_2$PCl	**15**	56	87
i-Pr	MeI	**16**	64	95
i-Pr	(PhSe)$_2$	**17**	54	95

[a]Total yield of diastereomers.

the latter (S) the configuration at the ferrocene planar chirality, were fully characterized by X-ray crystallography as shown in Figs. 1 and 2, respectively. The selected bond lengths and the bond angles of **10** and **17** are summarized in Tables 2 and 3, respectively. The second ortho-lithiation was accomplished by treatment of the isolated **16** with sec-BuLi and the quenching with Ph$_2$PCl as an electrophile resulted in the formation

Table 2
Selected bond distances (Å) and angles (°) for **10**

Bond distances			
P–C(2)	1.834(3)	C(14)–C(16)	1.520(7)
P–C(17)	1.842(3)	Fe–C(1)	2.027(3)
P–C(23)	1.828(4)	Fe–C(2)	2.037(3)
N–C(11)	1.253(4)	Fe–C(3)	2.051(4)
N–C(12)	1.478(4)	Fe–C(4)	2.049(4)
O–C(11)	1.363(4)	Fe–C(5)	2.043(3)
O–C(13)	1.441(4)	Fe–C(6)	2.020(5)
C(1)–C(2)	1.438(4)	Fe–C(7)	2.030(4)
C(1)–C(11)	1.468(4)	Fe–C(8)	2.044(4)
C(12)–C(13)	1.514(5)	Fe–C(9)	2.038(4)
C(12)–C(14)	1.521(5)	Fe–C(10)	2.030(4)
C(14)–C(15)	1.509(7)		

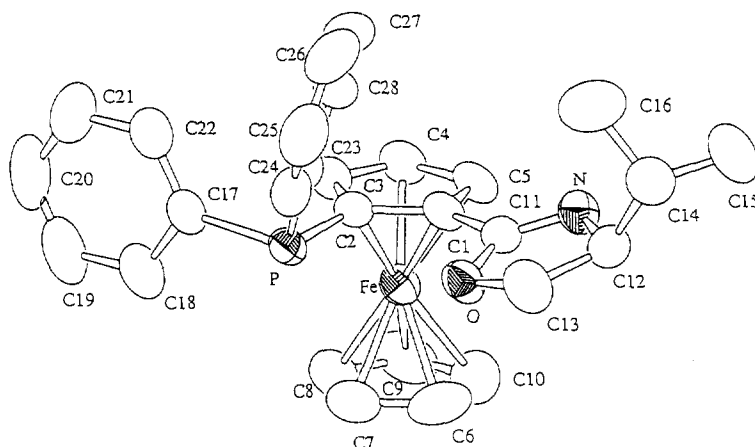| Bond angles			
C(2)–P–C(17)	98.8(1)	C(11)–N–C(12)	106.4(3)
C(2)–P–C(23)	100.8(2)	N–C(11)–C(1)	125.3(3)
C(17)–P–C(23)	102.9(2)	N–C(12)–C(13)	104.0(3)
P–C(2)–C(1)	126.0(2)	N–C(12)–C(14)	112.1(3)
C(11)–O–C(13)	104.5(3)	N–C(11)–O	119.2(3)
O–C(11)–C(1)	115.4(3)	C(2)–C(1)–C(11)	127.6(3)
O–C(13)–C(12)	105.2(3)	C(13)–C(12)–C(14)	115.4(4)

Fig. 1. Crystal structure of **10**, showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.
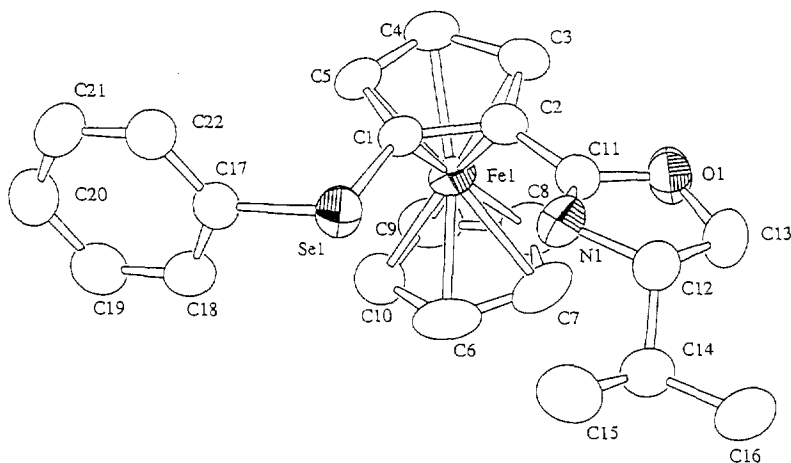

Fig. 2. Crystal structure of **17**, showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.
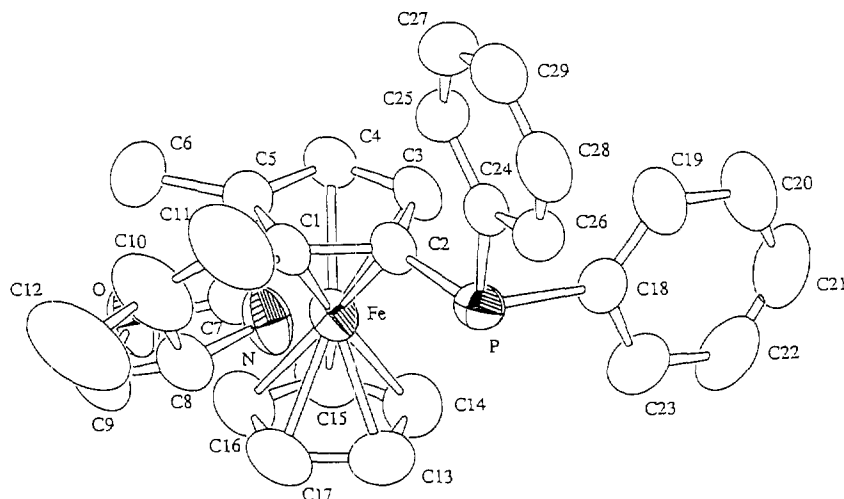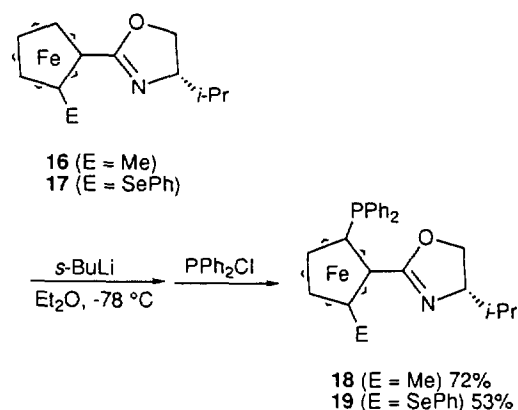
Fig. 3. Crystal structure of **18**, showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.

of (S,R)-3-methyl-1-diphenylphosphino-2-(4′-isopropyl)oxazolinyl-ferrocene (**18**). A similar treatment of **17** afforded (S,S)-1-phenylseleno-3-diphenylphosphino-2-(4′-isopropyloxazolinyl)ferrocene (**19**), in which the relative configuration of diphenylphosphinyl and oxazolinyl moieties in ferrocene ring was (R) (Scheme 3). The molecular structure of (S,R)-oxazolinylferrocenylphosphine (**18**) was also fully characterized by X-ray crystallography as shown in Fig. 3 which indicated clearly (R)-configuration at the ferrocene planar chirality. The selected bond lengths and the bond angles of **18** are summarized in Table 4.

Next, we envisaged preparing the oxazolinylferrocenylphosphines containing substituents on both carbons 4 and 5 of oxazoline ring. We employed the method starting from ferrocenecarbonyl chloride as

16 (E = Me)
17 (E = SePh)

18 (E = Me) 72%
19 (E = SePh) 53%

Scheme 3.

shown in Scheme 4. By this method, (S,S)-(4,5-diphenyloxazolin-2-yl)ferrocene (**20**) was prepared in 36% yield from (1R,2S)-(−)-2-amino-1,2-diphenylethanol. Deprotonation of **20** by 1.1 equivalents of sec-BuLi (in cyclohexane) at −78°C for 2 h followed by quenching with Ph₂PCl resulted in formation of a mixture of the corresponding diastereomeric [2-(4′,5′-diphenyloxazolin-2′-yl)ferrocenyl]diphenylphosphines (**21** and **22**). Each was abbreviated as (S,S,S)-DIPOF (**21**) and (S,S,R)-DIPOF (**22**), respectively (Scheme 4). [4] In this case, the diastereoselectivity of ortho-lithiation was low (**21**/**22** = 65/35). The molecular structure of **21**, separated in a pure form by column chromatography as a yellow solid in 44% yield, was fully characterized by X-ray crystallography as shown in Fig. 4 which indicated (S)-configuration around the ferrocene axis. The

Table 3
Selected bond distances (Å) and angles (°) for **17**

Bond distances			
Se–C(1)	1.906(4)	C(14)–C(16)	1.524(7)
Se–C(17)	1.928(4)	Fe–C(1)	2.056(4)
N–C(11)	1.258(7)	Fe–C(2)	2.026(4)
N–C(12)	1.484(5)	Fe–C(3)	2.040(4)
O–C(11)	1.359(6)	Fe–C(4)	2.056(4)
O–C(13)	1.443(6)	Fe–C(5)	2.056(4)
C(1)–C(2)	1.431(6)	Fe–C(6)	2.030(5)
C(2)–C(11)	1.462(6)	Fe–C(7)	2.033(4)
C(12)–C(13)	1.536(8)	Fe–C(8)	2.042(6)
C(12)–C(14)	1.535(7)	Fe–C(9)	2.047(5)
C(14)–C(15)	1.520(10)	Fe–C(10)	2.046(5)
Bond angles			
C(1)–Se–C(17)	96.2(2)	N–C(11)–C(2)	125.7(4)
Se–C(1)–C(2)	125.3(3)	N–C(12)–C(13)	103.7(4)
C(11)–O–C(13)	105.1(4)	N–C(12)–C(14)	111.8(4)
O–C(11)–C(2)	114.8(4)	N–C(11)–O	119.5(4)
O–C(13)–C(12)	104.8(4)	C(1)–C(2)–C(11)	125.0(4)
C(11)–N–C(12)	106.5(4)	C(13)–C(12)–C(14)	113.9(4)

---

[4] Here the 1st (S) indicates the configuration of oxazoline ring 4′-carbon, the 2nd (S) the configuration of oxazoline ring 5′-carbon, and the 3rd (S) or (R) the configuration around the ferrocene axis.

Table 4
Selected bond distances (Å) and angles (°) for **18**

Bond distances			
P–C(2)	1.817(4)	C(10)–C(12)	1.520(8)
P–C(18)	1.857(4)	C(5)–C(6)	1.512(6)
P–C(24)	1.832(4)	Fe–C(1)	2.023(4)
N–C(7)	1.232(5)	Fe–C(2)	2.048(4)
N–C(8)	1.476(5)	Fe–C(3)	2.048(4)
O–C(7)	1.354(5)	Fe–C(4)	2.050(4)
O–C(9)	1.462(5)	Fe–C(5)	2.044(4)
C(1)–C(2)	1.458(5)	Fe–C(13)	2.027(5)
C(1)–C(7)	1.471(5)	Fe–C(14)	2.026(5)
C(8)–C(9)	1.494(7)	Fe–C(15)	2.052(4)
C(8)–C(10)	1.551(7)	Fe–C(16)	2.052(4)
C(10)–C(11)	1.40(1)	Fe–C(17)	2.050(5)
Bond angles			
C(2)–P–C(18)	98.5(2)	C(7)–N–C(8)	107.7(4)
C(2)–P–C(24)	101.3(2)	N–C(7)–C(1)	125.4(4)
C(18)–P–C(24)	101.2(2)	N–C(8)–C(9)	103.5(4)
P–C(2)–(1)	126.6(3)	N–C(8)–C(10)	112.6(4)
C(7)–O–C(9)	104.7(3)	N–C(7)–O	118.1(3)
O–C(7)–C(1)	116.5(3)	C(2)–C(1)–C(7)	122.3(4)
O–C(9)–C(8)	104.1(4)	C(9)–C(8)–C(10)	112.1(5)

Table 5
Selected bond distances (Å) and angles (°) for **21**

Bond distances			
P–C(2)	1.83(2)	C(13)–C(20)	1.47(2)
P–C(26)	1.83(2)	Fe–C(1)	2.07(2)
P–C(32)	1.86(2)	Fe–C(2)	2.05(2)
N–C(11)	1.25(2)	Fe–C(3)	2.06(2)
N–C(12)	1.44(2)	Fe–C(4)	2.06(2)
O–C(11)	1.39(3)	Fe–C(5)	2.13(2)
O–C(13)	1.48(2)	Fe–C(6)	2.05(2)
C(1)–C(2)	1.39(3)	Fe–C(7)	2.05(3)
C(1)–C(11)	1.44(3)	Fe–C(8)	2.02(2)
C(12)–C(13)	1.53(3)	Fe–C(9)	2.10(3)
C(12)–C(14)	1.53(2)	Fe–C(10)	2.05(2)
Bond angles			
C(2)–P–C(26)	101(1)	C(11)–N–C(12)	108(2)
C(2)–P–C(32)	101(1)	N–C(11)–C(1)	131(2)
C(26)–P–C(32)	99(1)	N–C(12)–C(13)	106(1)
P–C(2)–C(1)	127(2)	N–C(12)–C(14)	114(1)
C(11)–O–C(13)	106(1)	N–C(11)–O	115(2)
O–C(11)–C(1)	112(2)	C(2)–C(1)–C(11)	124(2)
O–C(13)–C(12)	100(1)	C(12)–C(13)–C(20)	115(1)
O–C(13)–C(20)	110(1)	C(13)–C(12)–C(14)	114(1)

selected bond lengths and bond angles of **21** are summarized in Table 5. Similarly (R,R,R)-DIPOF (**23**), the enantiomer of **21**, was prepared in 28% yield in a pure form starting from ($1S,2R$)-(+)-2-amino-1,2-diphenylethanol also as a yellow solid.

From X-ray results of **10** and **17**, it is apparent that the diphenylphosphino group as well as the phenylseleno group is introduced to the ferrocene ring to give the (S)-configuration products in accordance with several recent reports by the other groups [35–43]. This

stereochemical outcome can be explained by assuming that the aggregate of butyllithium approaches to the oxazoline in such a way to avoid the interaction with the substituent on the oxazoline ring and to make a lithium–nitrogen chelation as also postulated by Richards et al. [35], Richards and Mulvaney [36] and Sammakia and Latham [38,39] (Scheme 5). Especially, Sammakia and Latham [39] reported highly diastereoselective lithiation of the constrained oxazolinylferrocene containing a linking oxazolinyl moiety to the other
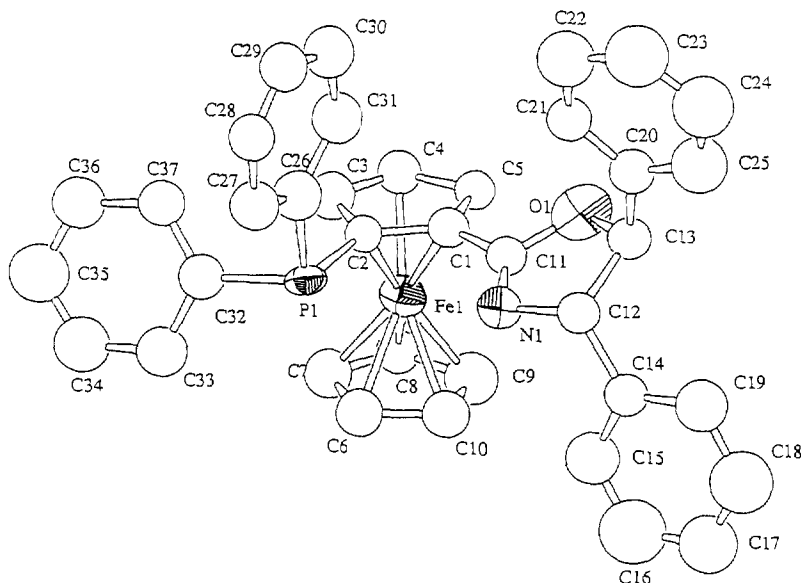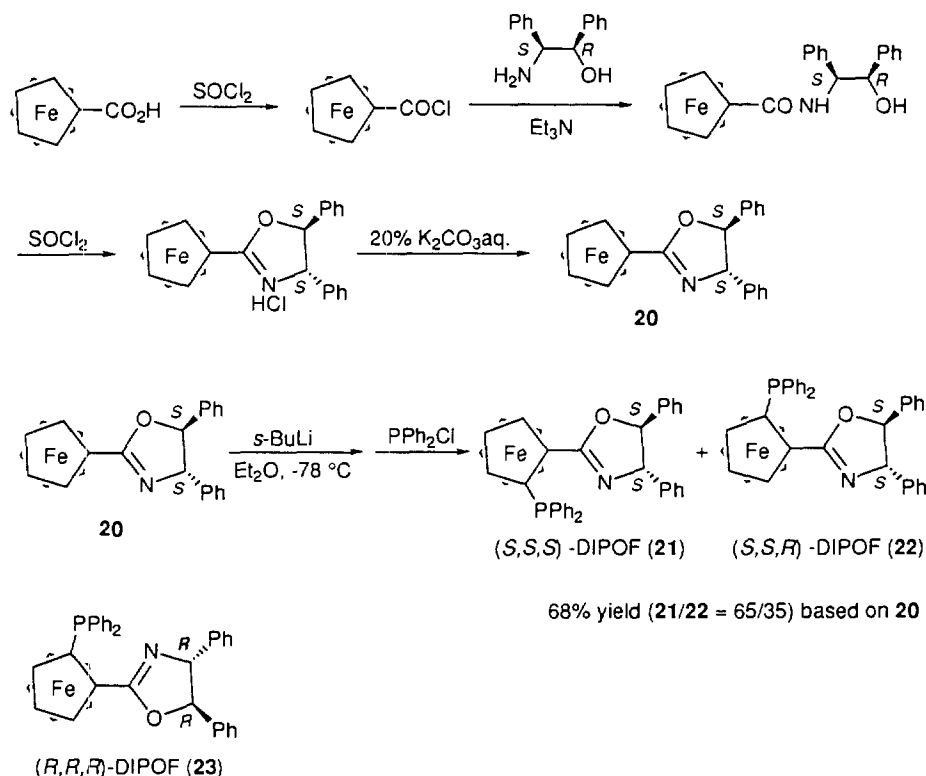

Fig. 4. Crystal structure of **21**, showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.
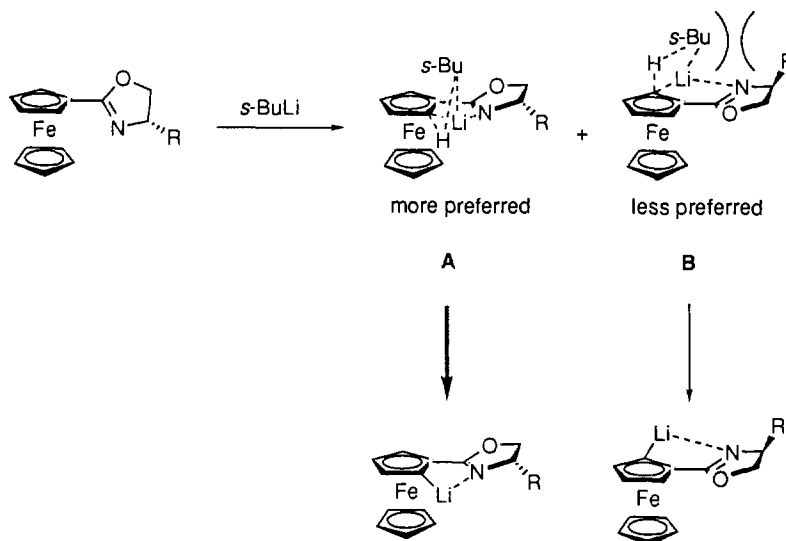
Scheme 4.

cyclopentadienyl ring, where the lithiation clearly proceeded via lithium–nitrogen chelation. The lithium–nitrogen chelation and the sterically less demanding approach of sec-BuLi lead to the preferable formation of A to B to provide a high diastereoselectivity. [5] In the case of 7, the lithiation proceeded with high diastereoselectivity (> 99% de), being consistent with the above assumption. On the other hand, in the case of 20, the diastereoselectivity of lithiation was low (30% de) (Scheme 6). The details are not yet known. Although the probability should be quite low, the pathway of the lithiation via lithium–oxygen chelation such as the structure C leading to the other diastereoisomer might not be completely excluded (Scheme 6) [38,39].
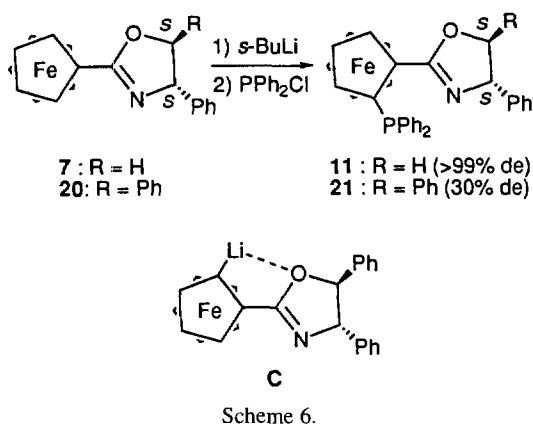

2.2. Preparation of the rhodium complexes of chiral oxazolinylferrocenylphosphines

As we have already shown, the above-described chiral phosphines worked as effective ligands for Rh-catalyzed asymmetric hydrosilylation of ketones [30]. In order to obtain some information for these catalytic reactions, we decided to prepare and investigate the structure of the several rhodium complexes of chiral oxazolinylferrocenylphosphines.

At first, the cationic complexes were prepared from [Rh(COD)$_2$]BF$_4$ and the chiral oxazolinylferrocenylphosphine (10 or 21). Treatment of 10 with [Rh(COD)$_2$]BF$_4$ in acetone at room temperature for 1 h afforded a cationic rhodium complex [Rh(COD)(10)]BF$_4$ (24) in 90% yield (Scheme 7). The structure of 24 was identified by ^{1}H and ^{31}P NMR. The ^{31}P{^{1}H} NMR showed a doublet peak at δ 23.3 ppm due to ^{103}Rh–^{31}P coupling ($J = 154$ Hz). The molecular structure of 24 was unambiguously confirmed by X-ray analysis. The structure is shown in Fig. 5, and the bond lengths and angles are summarized in Table 6. The bond lengths of Rh(1)–N(1) and Rh(1)–P(1) are 2.11(1) and 2.289(3) Å, respectively, which are reasonable compared with the reported values of some rhodium–oxazoline com-

more preferred   less preferred

A   B

Scheme 5.

7 : R = H
20: R = Ph

11 : R = H (>99% de)
21 : R = Ph (30% de)

C

Scheme 6.

plexes [6,7] and rhodium–ferrocenylphosphine complexes. [8] The geometry around the rhodium is square planar with cis-coordination of the nitrogen and the phosphorus atoms of 10. The P(1)–Rh(1)–N(1) angle is 90.3(3)°. The torsion angle of Rh(1)–P(1)–C(1)–C(2) is 18(1)°, and the rhodium atom of 24 exists above from the plane of the substituted cyclopentadienyl ring of ferrocene.

Next, in order to know any difference between 10 and DIPOF (21) in the structure of their cationic rhodium complexes, we also prepared a cationic rhodium complex [Rh(COD)(21)]BF$_4$ (25) from [Rh(COD)$_2$]BF$_4$ and DIPOF (21) by a similar method in 75% yield (Scheme

7). The structure of 25 was identified by ^{1}H and ^{31}P NMR and unambiguously confirmed by X-ray analysis. The structure is shown in Fig. 6, and the bond lengths and angles are summarized in Table 7. The bond lengths of Rh–N and Rh–P are 2.172(10) and 2.279(4) Å, respectively, which are almost the same with those in 24. However, the P(1)–Rh(1)–N(1) angle is 85.6(3)°, the value of which is smaller than that observed in 24. Further, the torsion angle of Rh(1)–P(1)–C(1)–C(2) is −42.3(10)°, the value of which is very different from that observed in 24. The environment around the rhodium atom of 25 is quite different from that of 24 and more crowded (compare Fig. 6 with Fig. 5). The position of the rhodium atom of 25 is closer to the iron, which might provide a better structure to recognize the approaching ketones in the asymmetric hydrosilylation [30], further study to clarify the details on its mechanism are now in progress.

The neutral rhodium complexes of 10 and 21 were next prepared by a similar method. Reaction of 10 with
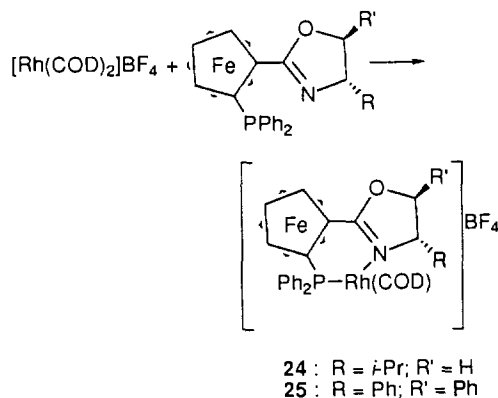
^{6} The bond lengths of Rh–N in N,N-bis[2-((4S)-(methyl)-1,3-oxazolinyl)]methane-bis(η^2-ethene)rhodium(I) have been reported to be 2.056(8) and 2.060(6) Å ([44]).

^{7} The bond lengths of Rh–N in [(S,S)-ip-pybox]RhCl$_3$ have been reported to be 2.003(17), 2.069(19) and 2.083(17) Å ([45]).

^{8} The bond length of Rh–P in [(PPFA)Rh(NBD)]PF$_6$ has been reported to be 2.28(1) Å ([46]).

24 : R = i-Pr; R' = H
25 : R = Ph; R' = Ph

Scheme 7.

Table 6
Selected bond distances (Å) and angles (°) for **24**

Bond distances

P–C(1)	1.79(1)	C(12)–C(13)	1.53(2)
P–C(17)	1.83(1)	C(12)–C(14)	1.58(2)
P–C(23)	1.82(1)	C(14)–C(15)	1.50(2)
N–C(11)	1.28(2)	C(14)–C(16)	1.59(3)
N–C(12)	1.49(2)	Fe–C(1)	2.06(1)
O–C(11)	1.35(1)	Fe–C(2)	2.03(1)
O–C(13)	1.44(2)	Fe–C(3)	2.04(1)
Rh–P	2.289(3)	Fe–C(4)	2.04(1)
Rh–N	2.11(1)	Fe–C(5)	2.07(1)
Rh–C(29)	2.13(1)	Fe–C(6)	2.04(2)
Rh–C(30)	2.14(1)	Fe–C(7)	2.06(1)
Rh–C(35)	2.26(1)	Fe–C(8)	2.04(1)
Rh–C(36)	2.19(1)	Fe–C(9)	2.03(1)
C(1)–C(2)	1.44(2)	Fe–C(10)	2.05(1)
C(2)–C(11)	1.45(2)		

Bond angles

C(1)–P–C(17)	101.9(6)	C(11)–N–C(12)	105(1)
C(1)–P–C(23)	108.3(6)	N–C(11)–C(2)	127(1)
C(17)–P–C(23)	106.5(6)	N–C(12)–C(13)	104(1)
P–C(1)–C(2)	124.3(9)	N–C(12)–C(14)	110(1)
C(11)–O–C(13)	107(1)	N–C(11)–O	117(1)
O–C(11)–C(2)	114(1)	C(1)–C(2)–C(11)	125(1)
O–C(13)–C(12)	102(1)	C(13)–C(12)–C(14)	117(1)
Rh–P–C(1)	110.8(4)	P–Rh–N	90.3(3)
Rh–P–C(17)	113.9(4)	P–Rh–C(29)	90.5(4)
Rh–P–C(23)	114.5(5)	P–Rh–C(30)	92.5(4)
Rh–N–C(11)	130.8(9)	P–Rh–C(35)	167.0(4)
Rh–N–C(12)	123.8(9)	P–Rh–C(36)	156.1(5)
N–Rh–C(29)	159.5(5)	N–Rh–C(35)	94.0(5)
N–Rh–C(30)	162.6(5)	N–Rh–C(36)	90.5(5)

Table 7
Selected bond distances (Å) and angles (°) for **25**

Bond distances

P–C(1)	1.80(1)	C(2)–C(11)	1.46(2)
P–C(26)	1.79(1)	C(12)–C(13)	1.53(2)
P–C(32)	1.82(1)	C(12)–C(14)	1.49(2)
N–C(11)	1.27(2)	C(13)–C(20)	1.55(2)
N–C(12)	1.50(1)	Fe–C(1)	2.04(1)
O–C(11)	1.35(1)	Fe–C(2)	2.02(1)
O–C(13)	1.43(1)	Fe–C(3)	2.04(1)
Rh–P	2.279(4)	Fe–C(4)	2.05(1)
Rh–N	2.172(10)	Fe–C(5)	2.07(1)
Rh–C(38)	2.23(1)	Fe–C(6)	2.04(2)
Rh–C(39)	2.24(1)	Fe–C(7)	2.04(2)
Rh–C(42)	2.14(1)	Fe–C(8)	2.01(2)
Rh–C(43)	2.14(1)	Fe–C(9)	2.03(2)
C(1)–C(2)	1.47(2)	Fe–C(10)	2.03(2)

Bond angles

|			
C(1)–P–C(26)	106.1(6)	C(11)–N–C(12)	125.9(9)
C(1)–P–C(32)	105.8(6)	N–C(11)–C(2)	129(1)
C(26)–P–C(32)	102.2(6)	N–C(12)–C(13)	102(1)
P–C(1)–C(2)	118.7(9)	N–C(12)–C(14)	112(1)
C(11)–O–C(13)	106.0(10)	N–C(11)–O	118(1)
O–C(11)–C(2)	111(1)	C(1)–C(2)–C(11)	123(1)
O–C(13)–C(12)	105(1)	C(13)–C(12)–C(14)	108(1)
O–C(13)–C(20)	109(1)	C(12)–C(13)–C(20)	116(1)
Rh–P–C(1)	108.0(4)	P–Rh–N	85.6(3)
Rh–P–C(26)	110.4(5)	P–Rh–C(38)	163.9(5)
Rh–P–C(32)	123.1(5)	P–Rh–C(39)	160.8(4)
Rh–N–C(11)	125.9(9)	P–Rh–C(42)	90.1(3)
Rh–N–C(12)	127.2(8)	P–Rh–C(43)	94.6(4)
N–Rh–C(38)	95.6(4)	N–Rh–C(42)	155.5(5)
N–Rh–C(39)	96.2(4)	N–Rh–C(43)	165.2(5)
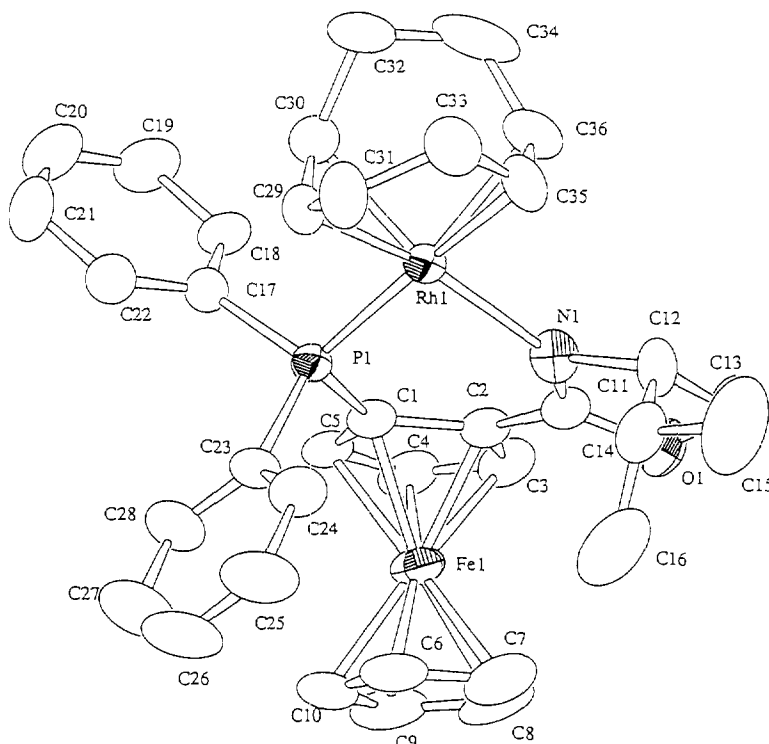
Fig. 5. Crystal structure of **24**, showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.
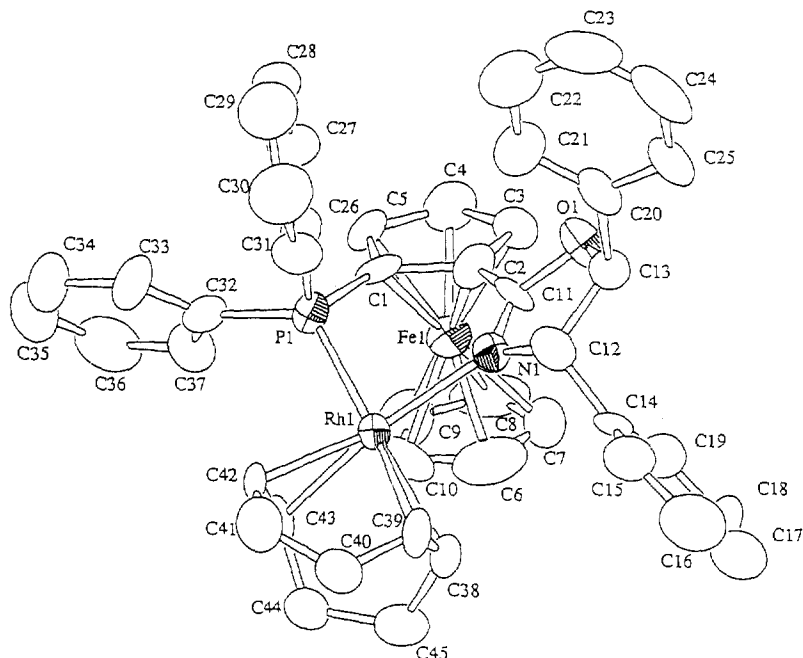
Fig. 6. Crystal structure of **25**, showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.

[Rh(CO)$_2$Cl]$_2$ in THF at room temperature for 14 h produced [Rh(CO)Cl(**10**)] (**26**) in 85% yield (Scheme 8). The structure of **26** was identified by ^{1}H and ^{31}P NMR and confirmed unambiguously by X-ray analysis. The structure is shown in Fig. 7, and the bond lengths and angles are summarized in Table 8. The geometry around the rhodium is square planar with *cis*-coordination of the nitrogen and the phosphine atoms of **10** and

with the chlorine atom in *trans* position to the phosphine. The ^{31}P{^{1}H} NMR showed a doublet peak at δ 34.5 ppm due to ^{103}Rh–^{31}P coupling ($J = 175$ Hz). The *trans* effect of chlorine to phosphine affords the larger coupling constant than that observed in **24**. Moreover, the distance between Rh and P of this neutral complex **26** is shorter (2.211(1) Å) than that of the corresponding cationic complex **24**. The P(1)–Rh(1)–N(1) angle is
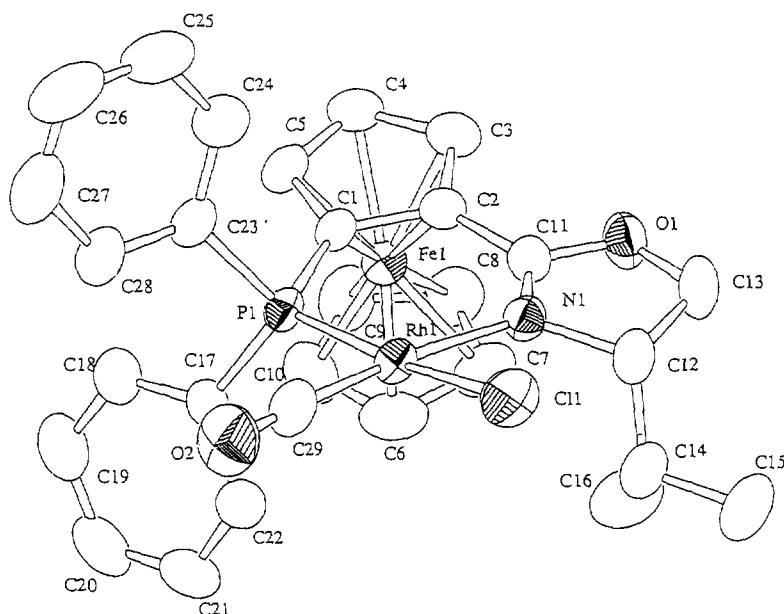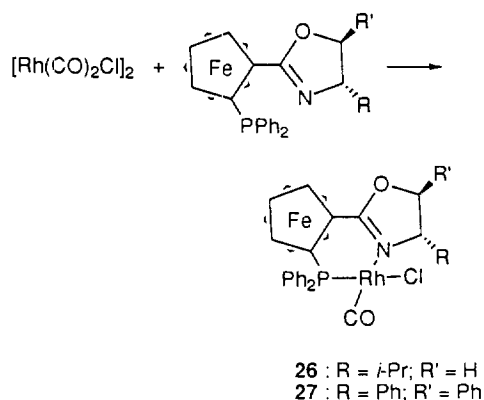

Fig. 7. Crystal structure of **26**, showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.

26 : R = i-Pr; R' = H
27 : R = Ph; R' = Ph

Scheme 8.

Table 8
Selected bond distances (Å) and angles (°) for **26**

Bond distances			
P–C(1)	1.804(4)	C(12)–C(13)	1.520(6)
P–C(17)	1.818(4)	C(12)–C(14)	1.516(7)
P–C(23)	1.828(4)	C(14)–C(15)	1.514(7)
N–C(11)	1.291(5)	C(14)–C(16)	1.508(8)
N–C(12)	1.493(5)	Fe–C(1)	2.039(4)
O(1)–C(11)	1.340(4)	Fe–C(2)	2.028(4)
O(1)–C(13)	1.460(5)	Fe–C(3)	2.039(4)
Rh–P	2.211(1)	Fe–C(4)	2.049(5)
Rh–N	2.105(3)	Fe–C(5)	2.044(4)
Rh–C(29)	1.811(4)	Fe–C(6)	2.035(5)
Rh–Cl	2.4025(9)	Fe–C(7)	2.049(5)
C(1)–C(2)	1.445(5)	Fe–C(8)	2.050(4)
C(2)–C(11)	1.451(5)	Fe–C(9)	2.052(4)
		Fe–C(10)	2.035(4)

Bond angles			
C(1)–P–C(17)	105.5(2)	C(11)–N–C(12)	107.1(3)
C(1)–P–C(23)	101.8(2)	N–C(11)–C(2)	128.3(3)
C(17)–P–C(23)	105.3(2)	N–C(12)–C(13)	102.9(3)
P–C(1)–C(2)	124.4(2)	N–C(12)–C(14)	111.0(3)
C(11)–O(1)–C(13)	106.3(3)	N–C(11)–O(1)	117.1(3)
O(1)–C(11)–C(2)	114.6(3)	C(1)–C(2)–C(11)	126.6(3)
O(1)–C(13)–C(12)	104.2(3)	C(13)–C(12)–C(14)	116.4(4)
Rh–P–C(1)	113.2(1)	N–Rh–Cl	91.06(9)
Rh–P–C(17)	119.4(1)	P–Rh–N	93.81(9)
Rh–P–C(23)	109.9(1)	P–Rh–C(29)	87.4(1)
Rh–N–C(11)	130.7(3)	P–Rh–Cl	170.10(5)
Rh–N–C(12)	122.3(2)	Cl–Rh–C(29)	88.3(1)
N–Rh–C(29)	176.3(2)	Rh–C(29)–O(2)	177.7(4)

93.81(9)°. The torsion angle of Rh(1)–P(1)–C(1)–C(2) is 4.9(4)°, which is smaller than that observed in the cationic complex **24**. A neutral rhodium complex **27**, prepared similarly from [Rh(CO)$_2$Cl]$_2$ and DIPOF (**21**) (Scheme 8) was identified by ^{1}H and ^{31}P NMR and its structure was unambiguously confirmed by X-ray analysis (Fig. 8). The bond lengths and angles are summarized in Table 9. The bond lengths of Rh–N and Rh–P are 2.110(3) and 2.220(1) Å, respectively, which are almost the same with those of **26**. Moreover, the P(1)–Rh(1)–N(1) angle is 93.5(1)°, being almost identical with those of **26**. The torsion angle of Rh(1)–P(1)–C(1)–C(2) is 2.9(4)°, which is slightly smaller than that of **26**. In contrast to the cases of **24** and **25** (Figs. 5 and 6), the environment around the rhodium in **27** is similar to that of **26**, as revealed by a comparison of the structures of **26** and **27** shown in Figs. 7 and 8.

In conclusion, we could prepare a variety of novel chiral oxazolinylferrocenes and find a highly diastereos-

elective *ortho*-lithiation of the ferrocenes leading to the corresponding *ortho*-substituted (Me, Ph$_2$P, PhSe) oxazolinylferrocenes, the structure of some of which being fully characterized by X-ray crystallography. Further,
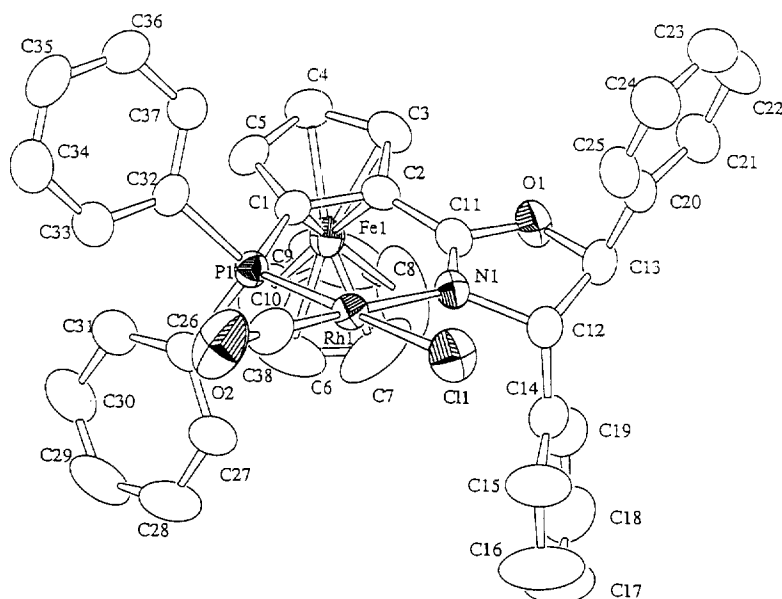

Fig. 8. Crystal structure of **27**, showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Table 9
Selected bond distances (Å) and angles (°) for **27**

Bond distances			
P–C(1)	1.794(4)	C(12)–C(14)	1.529(6)
P–C(26)	1.810(4)	C(13)–C(20)	1.509(6)
P–C(32)	1.826(4)	Fe–C(1)	2.036(4)
N–C(11)	1.282(5)	Fe–C(2)	2.024(4)
N–C(12)	1.512(5)	Fe–C(3)	2.036(5)
O–C(11)	1.349(5)	Fe–C(4)	2.035(5)
O–C(13)	1.492(4)	Fe–C(5)	2.035(5)
Rh–P	2.220(1)	Fe–C(6)	1.993(7)
Rh–N	2.110(3)	Fe–C(7)	1.981(9)
Rh–C(38)	1.780(1)	Fe–C(8)	1.993(7)
C(1)–C(2)	1.425(5)	Fe–C(9)	2.016(6)
C(2)–C(11)	1.473(6)	Fe–C(10)	2.007(6)
C(12)–C(13)	1.519(6)		

Bond angles			
C(1)–P–C(26)	105.6(2)	C(11)–N–C(12)	105.2(3)
C(1)–P–C(32)	105.8(6)	N–C(11)–C(2)	114.2(4)
C(26)–P–C(32)	103.4(2)	N–C(12)–C(13)	102.7(4)
P–C(1)–C(2)	124.6(3)	N–C(12)–C(14)	110.3(3)
C(11)–O–C(13)	104.4(4)	N–C(11)–O	118.5(4)
O–C(11)–C(2)	114.2(4)	C(1)–C(2)–C(11)	126.9(4)
O–C(13)–C(12)	102.3(4)	C(13)–C(12)–C(14)	114.6(4)
O–C(13)–C(20)	106.8(4)	C(12)–C(13)–C(20)	118.9(4)
Rh–P–C(1)	112.4(1)	P–Rh–N	93.5(1)
Rh–P–C(26)	116.4(2)	P–Rh–C(38)	88.8(2)
Rh–P–C(32)	115.8(1)	N–Rh–C(38)	177.4(2)
Rh–N–C(11)	129.5(3)		
Rh–N–C(12)	125.0(3)		

some cationic and neutral rhodium complexes having the novel oxazolinylferrocenylphosphines as ligands have been prepared and their structures have been clarified unambiguously by X-ray crystallography.

3. Experimental

^{1}H (270 MHz) and ^{13}C NMR (67.9 MHz) spectra were recorded on a JEOL GSX-270 spectrometer as solutions in CDCl$_3$. Chemical shifts were reported in δ units downfield from the internal reference Me$_4$Si. ^{31}P NMR spectra (109 MHz) was recorded on a JEOL JNM-EX-270 spectrometer as solutions in CDCl$_3$. Chemical shifts were reported in δ units downfield from the internal reference PPh$_3$. The coupling constants (J) were in hertz (Hz). Melting points were determined on a Yanaco MP-S3 micro melting point apparatus and are 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% PEG on Shimalite) and a Shimadzu GC-14A instrument (25-m Hi-Cap-CBP-10-S25 capillary column) with flame-ionization detectors and nitrogen as carrier gas. Column chromatographies on SiO$_2$ were performed with Wakogel

C-300 or Wakogel FC-40 (hexane and hexane/ethyl acetate as eluents). Elemental analyses were performed at Microanalytical Center of Kyoto University. All the solvents were distilled from CaH$_2$ or LiAlH$_4$ and stored over molecular sieves 4 Å under nitrogen. Cyanoferrocene was prepared from the ferrocenecarbaldehyde by the reported method [31]. Chiral amino alcohols except for commercial (1R,2S)- and (1S,2R)-2-amino-1,2-diphenylethanol (Aldrich Chemical) were obtained from the corresponding amino acids by reduction following the literature method [47].

3.1. Preparation of (S)-(4-isopropyloxazolin-2-yl)ferrocene (3)

In a 200 ml two-necked round-bottomed flask, zinc chloride (53 mg, 0.39 mmol), (L)-valinol (507 mg, 4.91 mmol) and cyanoferrocene (1.00 g, 4.74 mmol) were placed under nitrogen and then chlorobenzene (10 ml) was added to the flask. The reaction mixture was heated at reflux temperature for 72 h. The mixture was treated with brine (100 ml) and extracted with CH$_2$Cl$_2$ (50 ml × 3). The extract was dried over MgSO$_4$ and evaporated to leave a black solid. The crude product was purified by column chromatography on SiO$_2$ with hexane and ethyl acetate as eluents to afford pure compound **3** as a red solid: 570 mg, 1.92 mmol (40% yield based on cyanoferrocene), mp 61–62°C. ^{1}H NMR δ 0.93 (3H, d, $J = 6.75$ Hz), 1.01 (3H, d, $J = 6.75$ Hz), 1.85 (1H, sept., $J = 6.75$ Hz), 4.04 (2H, m), 4.19 (5H, s), 4.29 (1H, m), 4.32 (2H, m), 4.73 (1H, m), 4.77 (1H, m). ^{13}C NMR δ 17.8 (q), 18.9 (q), 32.3 (d), 69.0 (d), 69.0 (d), 69.3 (t), 69.5 (d), 70.1 (d), 70.1 (d), 70.6 (s), 72.3 (d), 165.7 (s). Anal. Found: C, 64.71; H, 6.51; N, 4.95. C$_{16}$H$_{19}$FeNO Calc.: C, 64.67; H, 6.44; N, 4.71%.

Similarly, other chiral oxazolinyferrocenes (**1**, **2**, **4–8**) were prepared. The physical, spectroscopic and analytical data are as follows.

3.1.1. (S)-(4-methyloxazolin-2-yl)ferrocene (1)

A red solid, mp 79–80°C. ^{1}H NMR δ 1.32 (3H, d, $J = 6.29$ Hz), 3.86 (1H, t, $J = 8.10$ Hz), 4.19 (5H, s), 4.22 (1H, m), 4.34 (2H, m), 4.21 (1H, dd, $J = 8.10$ and 9.00 Hz), 4.75 (2H, m). ^{13}C NMR δ 21.9 (q), 61.8 (d), 69.0 (d), 69.0 (d), 69.7 (d), 70.3 (d), 73.7 (t), 165.0 (s). Anal. Found: C, 62.46; H, 5.49; N, 5.36. C$_{14}$H$_{15}$FeNO Calc.: C, 62.48; H, 5.62; N, 5.21%. Yield, 15%.

3.1.2. (S)-(4-ethyloxazolin-2-yl)ferrocene (2)

An orange solid, mp 47–48°C. ^{1}H NMR δ 0.99 (3H, t, $J = 7.29$ Hz), 1.55 (1H, m), 1.73 (1H, m), 3.97 (1H, t, $J = 8.10$ Hz), 4.11 (1H, m), 4.19 (5H, s), 4.33 (2H, m), 4.37 (1H, dd, $J = 8.10$ and 9.00 Hz), 4.75 (2H, m). ^{13}C NMR δ 10.1 (q), 28.8 (t), 67.7 (d), 69.0 (d), 69.0

(d), 69.6 (d), 70.2 (d), 71.6 (t), 165.8 (s). Anal. Found: C, 63.79; H, 6.11; N, 4.97. $C_{15}H_{17}FeNO$ Calc.: C, 63.63; H, 6.05; N, 4.95%. Yield, 34%.

3.1.3. (S)-(4-isobutyloxazolin-2-yl)ferrocene (4)

A yellow solid, mp 61–62°C. ^1H NMR δ 0.95 (3H, d, $J = 6.75$ Hz), 0.99 (3H, d, $J = 6.75$ Hz), 1.34 (1H, m), 1.72 (2H, m), 3.91 (1H, t, $J = 8.10$ Hz), 4.18 (5H, s), 4.33 (2H, m), 4.39 (1H, m), 4.74 (2H, m). ^{13}C NMR δ 22.9 (q), 23.5 (q), 25.8 (d), 46.1 (t), 65.0 (d), 68.9 (d), 69.1(d), 69.7 (d), 70.3 (d), 72.7 (t), 77.5 (s), 165.6 (s). Anal. Found: C, 65.40; H, 6.85; N, 4.59. $C_{17}H_{21}FeNO$ Calc.: C, 65.61; H, 6.80; N, 4.50%. Yield, 37%.

3.1.4. (S)-(4-sec-butyloxazolin-2-yl)ferrocene (5)

A red solid, mp 58–59°C. ^1H NMR δ 0.87 (3H, d, $J = 6.75$ Hz), 0.96 (3H, t, $J = 7.29$ Hz), 1.23 (1H, m), 1.52 (1H, m), 1.73 (1H, m), 4.12 (2H, m), 4.19 (5H, s), 4.27 (1H, m), 4.32 (2H, m), 4.73 (1H, m), 4.76 (1H, m). ^{13}C NMR δ 11.8 (q), 14.1 (q), 26.3 (t), 36.7 (d), 68.7 (t), 68.9 (d), 69.5 (d), 70.1 (d), 70.1 (d), 70.6 (s), 70.8 (d), 165.6 (s). Anal. Found: C, 65.86; H, 6.96; N, 4.57. $C_{17}H_{21}FeNO$ Calc.: C, 65.61; H, 6.80; N, 4.50%. Yield, 38%.

3.1.5. (S)-(4-t-butyloxazolin-2-yl)ferrocene (6)

An orange solid, mp 127–128°C. ^1H NMR δ 0.96 (9H, s), 3.89 (1H, dd, $J = 7.32$ and 9.76 Hz), 4.16 (1H, t, $J = 7.32$ Hz), 4.19 (5H, s), 4.22 (1H, m), 4.32 (2H, m), 4.70 (1H, m), 4.77 (1H, m). ^{13}C NMR δ 26.2 (q), 33.9 (s), 68.3 (t), 69.0 (d), 69.0 (d), 69.5 (d), 70.0 (d), 70.1 (d), 70.8 (s), 76.1 (d), 165.8 (s). Anal. Found: C, 65.66; H, 6.86; N, 4.58. $C_{17}H_{21}FeNO$ Calc.: C, 65.61; H, 6.80; N, 4.50%. Yield, 35%.

3.1.6. (S)-(4-phenyloxazolin-2-yl)ferrocene (7)

A red solid, mp 75–76°C. ^1H NMR δ 4.20 (1H, t, $J = 8.10$ Hz), 4.25 (5H, s), 4.38 (2H, m), 4.70 (1H, dd, $J = 8.10$ and 9.99 Hz), 4.82 (1H, m), 4.86 (1H, m), 5.23 (1H, dd, $J = 8.10$ and 9.99 Hz), 7.2–7.4 (5H, m). 13C NMR δ 69.2 (d), 69.7 (d), 70.0 (d), 70.4 (d), 70.5 (d), 74.5 (t), 126.7 (d), 127.5 (d), 128.7 (d), 142.7 (s), 167.4 (s). Anal. Found: C, 68.86; H, 5.20; N, 4.38. $C_{19}H_{17}FeNO$ Calc.: C, 68.90; H, 5.17; N, 4.23%. Yield, 20%.

3.1.7. (S)-(4-benzyloxazolin-2-yl)ferrocene (8)

A red solid, mp 97–98°C. ^1H NMR δ 2.69 (1H, dd, $J = 9.1$ and 13.5 Hz), 3.22 (1H, dd, $J = 4.7$ and 13.5 Hz), 4.10 (1H, m), 4.17 (5H, s), 4.24 (1H, t, $J = 8.10$ Hz), 4.35 (2H, m), 4.44 (1H, m), 4.75 (2H, m), 7.2–7.4 (5H, m). ^{13}C NMR δ 41.8 (t), 67.7 (d), 69.0 (d), 69.6 (d), 70.3 (d), 71.3 (t), 126.5 (d), 126.5 (d), 128.6 (d), 129.3 (d), 138.0 (s), 166.6 (s). Anal. Found: C, 69.62; H, 5.41; N, 4.14. $C_{20}H_{19}FeNO$ Calc.: C, 69.58; H, 5.55; N, 4.06%. Yield, 38%.

3.2. Preparation of (S,S)-(4,5-diphenyloxazolin-2-yl)ferrocene (20)

The compound **20** was prepared from ferrocenecarboxylic acid and $(1R,2S)$-(–)-2-amino-1,2-diphenylethanol as follows.

Ferrocenecarboxylic acid. Commercial t-BuLi (120 ml of 1.64 N pentane solution; 196 mmol) was slowly added to THF solution (100 ml) of ferrocene (35 g, 188 mmol) at 0°C with stirring under nitrogen. After 30 min, dry ice (5 g) was added portionwise to the solution and the mixture left at room temperature for 1 h. The reaction mixture was added to the 5 N aqueous NaOH (200 ml) and then extracted with CH_2Cl_2 (200 ml × 3). The conc. HCl was added to the water layer until a yellow solid did not appear. The yellow solid of ferrocenecarboxylic acid was filtered and dried at 100°C for 20 h: 17.3 g, 75.2 mmol (40% yield). It was used for the following reaction without any further purification.

Ferrocenecarbonyl chloride [48]. To a suspension of ferrocenecarboxylic acid (5.41 g, 29.1 mmol) in petroleum ether (150 ml), thionyl chloride (10 ml, 137 mmol) in petroleum ether (50 ml) was added dropwise at room temperature. The resulting mixture was stirred at 50°C for 2 h. The produced tarry black solid was removed by filtration and dry toluene (50 ml) was added to the filtrate. The solvent was evaporated at reduced pressure and the oily residue was extracted with pentane (100 ml × 5). Evaporation of n-pentane left ferrocenecarbonyl chloride as a red oil: 3.90 g, 15.7 mmol (54% yield). ^1H NMR δ 4.34 (5H, s), 4.64 (2H, m), 4.92 (2H, m). It was used for the following reaction without any further purification.

To a cooled suspension of (–)-2-amino-1,2-diphenylethanol (1.00 g, 4.69 mmol) in dry CH_2Cl_2 (50 ml) were slowly added with ferrocenecarbonyl chloride (1.20 g, 4.84 mmol) and dry triethylamine (2.40 g, 23.7 mmol) in dry CH_2Cl_2 (30 ml). The resulting solution was stirred at room temperature for 24 h, treated with brine (100 ml) and extracted with CH_2Cl_2 (100 ml × 3). The extract was dried over $MgSO_4$ and evaporated to leave a yellow solid of an amide. The crude product was purified by column chromatography on SiO_2 with $CHCl_3$ as an eluent: 1.45 g, 3.56 mmol (76% yield based on (–)-2-amino-1,2-diphenylethanol. ^1H NMR δ 1.2 (1H, br.), 4.11 (5H, s), 4.35 (2H, m), 4.63 (1H, m), 4.67 (1H, m), 5.14 (1H, d, $J = 4.6$ Hz), 5.44 (1H, dd, $J = 4.6$ and 7.8 Hz), 6.35 (1H, d, $J = 7.8$ Hz), 7.1–7.4 (10H, m).

This amide (840 mg, 1.98 mmol) was suspended in dry CH_2Cl_2 (60 ml) to which thionyl chloride (240 mg, 2.02 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise at -20°C. After stirring at -20°C for 1 h and at 0°C for 1 h, cold 20% aqueous K_2CO_3 (200 ml) was added and the solution was stirred at room temperature for 30 min and then extracted with CH_2Cl_2 (100 ml × 3). The

extract was dried over $MgSO_4$ and evaporated to leave a red oil which was purified by column chromatography on SiO_2 with hexane and ethyl acetate as eluents to give a yellow solid of pure **20**: 287 mg, 0.71 mmol (36% yield based on the amide), mp 33–35°C. ^1H NMR δ 4.29 (5H, s), 4.42 (2H, t, $J = 2.2$ Hz), 4.92 (2H, m), 5.08 (1H, d, $J = 7.8$ Hz), 5.31 (1H, d, $J = 7.8$ Hz), 7.2–7.4 (10H, m). ^{13}C NMR δ 68.9 (d), 69.7 (d), 70.0 (s), 70.6 (d), 78.9 (d), 88.5 (d), 125.7 (d), 126.7 (d), 127.7 (d), 128.4 (d), 128.8 (d), 128.9 (d), 140.6 (s), 142.3 (s), 166.9 (s). Anal. Found: C, 73.70; H, 4.87; N, 3.18. $C_{25}H_{21}FeNO$ Calc.: C, 73.72; H, 5.20; N, 3.44%.

3.3. Preparation and structure of (S,S)-[2-(4'-isopropyloxazolin-2'-yl)ferrocenyl]diphenylphosphine (10) and related compounds

After lithiation of chiral (4-isopropyloxazolin-2-yl)ferrocene (**3**) (240 mg, 0.81 mmol) with *sec*-BuLi (1.01 mmol) in dry diethyl ether (10 ml) at −78°C for 2 h under nitrogen, chlorodiphenylphosphine (193 mg, 0.87 mmol) in dry diethyl ether (1 ml) was added at −78°C. The mixture was warmed up to room temperature and then heated at reflux temperature for 3 h. It was treated with brine (100 ml) and extracted with CH_2Cl_2 (50 ml × 3). The extract was dried over $MgSO_4$ and evaporated to leave a yellow solid of **10**. The crude product was purified by column chromatography on SiO_2 with hexane and ethyl acetate as eluents: 300 mg, 0.62 mmol (77% yield based on **3**). The optical purity of the lithiated oxazolinylferrocene was determined by integrals of two peaks in ^1H NMR for the substituted cyclopentadienyl ring protons (10–15 Hz separation) and for methyl protons of isopropyl group of oxazoline (10–20 Hz separation). The optically pure **10** (1.37 g, 2.85 mmol) was isolated from the diastereomeric mixture (95% de) (1.56 g, 3.24 mmol) by one recrystallization from dry ethanol (20 ml) under nitrogen. An orange solid, mp 164–165°C (> 99% de). ^1H NMR δ 0.68 (3H, d, $J = 6.75$ Hz), 0.82 (3H, d, $J = 6.75$ Hz), 1.66 (1H, sept., $J = 6.75$ Hz), 3.60 (1H, m), 3.67 (1H, t, $J = 8.10$ Hz), 3.85 (1H, m), 4.22 (5H, s), 4.26 (1H, m), 4.37 (1H, m), 4.98 (1H, m), 7.2–7.5 (10H, m). ^{13}C NMR δ 17.5 (q), 18.7 (q), 32.1(d), 69.6 (t), 70.6 (d), 72.0 (d), 72.1 (d), 73.9 (d), 73.9 (s), 77.2 (s), 127.9 (d), 127.9 (d), 128.0 (d), 128.1 (d), 128.2 (d), 128.9 (d), 132.3 (d), 132.6 (d), 134.7 (d), 135.0 (d), 138.1 (s), 139.6 (s), 165.6 (s). Anal. Found: C, 69.68; H, 5.81; N, 2.79. $C_{28}H_{28}FeNOP$ Calc.: C, 69.87; H, 5.86; N, 2.91%.

Similarly, other chiral (oxazolinylferrocenyl)diphenylphosphines (**9, 11–15**) were prepared. The physical, spectroscopic and analytical data are as follows.

3.3.1. (S,S)-[2-(4'-ethyloxazolin-2'-yl)ferrocenyl]diphenylphosphine (9)

A yellow solid, mp 79–80°C (68% de). As diastereomers; ^1H NMR δ a major product: 0.77 (3H, t,

$J = 7.32$ Hz), 1.36 (2H, m), 3.52 (1H, t, $J = 8.10$ Hz), 3.62 (1H, m), 4.00 (1H, m), 4.22 (5H, s), 4.36 (2H, m), 5.00 (1H, m), 7.2–7.5 (10H, m); a minor product: 0.68 (3H, t, $J = 7.32$ Hz), 4.21 (5H, s). ^{13}C NMR δ 9.6, 28.1, 67.4, 70.6, 70.9, 71.2, 71.9, 72.1, 73.9, 78.0, 127.9, 128.0, 128.1, 128.1, 128.3, 129.0, 132.2, 132.5, 134.7, 165.0. ^{31}P NMR δ 17.1. Anal. Found: C, 69.12; H, 5.63; N, 2.88. $C_{27}H_{26}FeNOP$ Calc.: C, 69.39; H, 5.61; N, 3.00%. Yield, 58% (as diastereomers).

3.3.2. (S,S)-[2-(4'-isobutyloxazolin-2'-yl)ferrocenyl]diphenylphosphine (11)

A brown oil (48% de). As diastereomers; ^1H NMR δ a major product: 0.85 (3H, d, $J = 6.75$ Hz), 0.88 (3H, d, $J = 6.75$ Hz), 1.06 (1H, m), 1.50 (2H, m), 3.42 (1H, t, $J = 8.10$ Hz), 3.61 (1H, m), 4.03 (1H, m), 4.22 (5H, s), 4.36 (2H, m), 4.98 (1H, m), 7.2–7.5 (10H, m); a minor product: 4.21 (5H, s), 4.96 (1H, m). ^{13}C NMR δ 22.5, 22.8, 23.0, 25.4, 45.3, 64.8, 70.8, 72.1, 73.0, 73.9, 74.0, 78.3, 127.8, 127.9, 128.0, 128.1, 128.1, 128.3, 129.0, 132.2, 132.5, 134.7, 135.0, 135.2, 142.0, 165.0. Anal. Found: C, 70.01; H, 6.24; N, 2.74. $C_{29}H_{30}FeNOP$ Calc.: C, 70.31; H, 6.10; N, 2.83%. Yield, 63% (as diastereomers).

3.3.3. (S,S)-[2-(4'-sec-butyloxazolin-2'-yl)ferrocenyl]diphenylphosphine (12)

A red solid, mp 137–138°C (> 99% de). ^1H NMR δ 0.58 (3H, d, $J = 6.75$ Hz), 0.85 (3H, t, $J = 7.29$ Hz), 1.06 (1H, m), 1.30 (1H, m), 1.53 (1H, m), 3.61 (1H, m), 3.67 (1H, t, $J = 8.10$ Hz), 3.99 (1H, m), 4.22 (5H, s), 4.24 (1H, m), 4.37 (1H, m), 4.98 (1H, m), 7.2–7.5 (10H, m). ^{13}C NMR δ 11.7 (q), 13.7 (q), 25.9 (t), 38.4 (d), 69.0 (t), 70.6 (d), 70.7 (d), 72.1(d), 72.1(d), 73.8 (d), 73.8 (d), 77.2 (s), 77.9 (s), 127.9 (d), 128.0 (d), 128.0 (d), 128.1 (d), 128.2 (d), 128.9 (d), 132.3 (d), 132.6 (d), 134.7 (d), 135.0 (d), 138.0 (s), 139.5 (s), 165.0 (s). Anal. Found: C, 70.26; H, 6.08; N, 2.77. $C_{29}H_{30}FeNOP$ Calc.: C, 70.31; H, 6.10; N, 2.82%. Yield, 58% (as diastereomers).

3.3.4. (S,S)-[2-(4'-t-butyloxazolin-2'-yl)ferrocenyl]diphenylphosphine (13)

An orange solid, mp 127–128°C (> 99% de). ^1H NMR δ 0.77 (9H, s), 3.61 (1H, m), 3.73 (1H, dd, $J = 7.32$ and 9.76 Hz), 3.87 (1H, t, $J = 7.32$ Hz), 4.19 (1H, m), 4.21 (5H, s), 4.35 (1H, m), 4.95 (1H, m), 7.2–7.6 (10H, m). ^{13}C NMR δ 25.7 (q), 33.5 (s), 68.4 (t), 70.6 (d), 70.7 (d), 72.1(d), 73.8 (d), 73.8 (s), 76.0 (d), 78.5 (s), 127.8 (d), 127.9 (d), 128.0 (d), 128.1(d), 128.2 (d), 128.8 (d), 132.3 (d), 132.6 (d), 134.7 (d), 135.0 (d), 138.5 (s), 139.6 (s), 164.5 (s). Anal. Found: C, 70.34; H, 5.98; N, 2.66. $C_{29}H_{30}FeNOP$ Calc.: C, 70.31; H, 6.10; N, 2.82%. Yield, 51% (as diastereomers).

3.3.5. (S,S)-[2-(4'-phenyloxazolin-2'-yl)ferrocenyl]diphenylphosphine (14)

A yellow solid, mp 184–185°C (dec.) (> 99% de). ^{1}H NMR δ 3.67 (1H, m), 3.81 (1H, t, $J = 8.10$ Hz), 4.27 (5H, s), 4.41 (1H, m), 4.67 (1H, dd, $J = 8.10$ and 9.99 Hz), 5.03 (1H, m), 5.08 (1H, dd, $J = 8.10$ and 9.99 Hz), 6.9–7.5 (15H, m). ^{13}C NMR δ 69.9 (d), 70.8 (d), 71.0 (d), 72.4 (d), 74.0 (d), 74.0 (d), 74.5 (s), 74.9 (t), 78.9 (s), 126.8 (d), 127.4 (d), 128.1 (d), 128.1 (d), 128.2 (d), 128.3 (d), 128.6 (d), 129.0 (d), 132.5 (d), 132.8 (d), 134.6 (d), 134.9 (d), 137.7 (s), 139.3 (s), 142.4 (d), 167.0 (s). Anal. Found: C, 71.99; H, 5.06; N, 2.68. $C_{31}H_{26}FeNOP$ calc.: C, 72.25; H, 5.09; N, 2.72%. Yield, 55%.

3.3.6. (S,S)-[2-(4'-benzyloxazolin-2'-yl)ferrocenyl]diphenylphosphine (15)

An orange solid, mp 62–63°C (87% de). As diastereomers; ^{1}H NMR δ a major product: 2.34 (1H, dd, $J = 9.1$ and 13.5 Hz), 3.09 (1H, dd, $J = 4.7$ and 13.5 Hz), 3.62 (1H, t, $J = 7.56$ Hz), 3.69 (1H, m), 4.13 (1H, m), 4.20 (5H, s), 4.30 (1H, m), 4.39 (1H, m), 4.98 (1H, m), 7.1–7.5 (15H, m); a minor product: 4.16 (5H, s), 4.94 (1H, m). ^{13}C NMR δ 41.7, 67.6, 70.7, 70.8, 71.7, 78.0, 126.4, 127.9, 128.0, 128.1, 129.0, 129.2, 129.5, 132.6, 134.8, 135.1, 138.2, 148.1, 167.3. Anal. Found: C, 72.66; H, 5.37; N, 2.59. $C_{32}H_{28}FeNOP$ Calc.: C, 72.60; H, 5.33; N, 2.65%. Yield, 56% (as diastereomers).

Similarly, compounds 16 and 17 were prepared by the addition of methyl iodide and diphenyl diselenide in place of chlorodiphenylphosphine, respectively. The physical, spectroscopic and analytical data are as follows.

3.3.7. (S,S)-1-methyl-2-(4'-isopropyloxazolinyl)ferrocene (16)

An orange solid, mp 42–43°C (95% de). As diastereomers; ^{1}H NMR δ a major product: 0.97 (3H, d, $J = 6.75$ Hz), 1.03 (3H, d, $J = 6.75$ Hz), 1.84 (1H, sept., $J = 6.75$ Hz), 2.28 (3H, s), 4.01 (1H, t, $J = 8.10$ Hz), 4.04 (1H, m), 4.10 (5H, s), 4.16 (1H, m), 4.25 (1H, m), 4.26 (1H, m), 4.61 (1H, m); a minor product: 2.25 (3H, s), 4.65 (1H, m). ^{13}C NMR δ 14.8 (q), 18.0 (q), 18.8 (q), 32.6 (d), 67.8 (d), 68.9 (t), 69.3 (d), 70.1 (d), 72.2 (d), 72.4 (d), 77.2 (s), 85.3 (s), 165.7 (s). Anal. Found: C, 65.75; H, 6.94; N, 4.57. $C_{17}H_{21}FeNO$ Calc.: C, 65.61; H, 6.80; N, 4.50%. Yield, 64% (as diastereomers).

3.3.8. (S,S)-2-(phenylseleno)-1-(4'-isopropyloxazolinyl)ferrocene (17)

An orange solid, mp 98–99°C (> 99% de). ^{1}H NMR δ 0.94 (3H, d, $J = 6.75$ Hz), 1.02 (3H, d, $J = 6.75$ Hz), 1.80 (1H, sept., $J = 6.75$ Hz), 4.02 (1H, m), 4.07 (1H, m), 4.11 (1H, m), 4.20 (5H, s), 4.27 (1H, m), 4.31 (1H,

m), 4.77 (1H, m), 7.2–7.3 (3H, m), 7.5–7.6 (2H, m). ^{13}C NMR δ 18.1 (q), 18.7 (q), 32.5 (d), 69.6 (d), 69.7 (t), 70.1(d), 71.3 (d), 72.4 (d), 73.8 (d), 78.5 (s), 127.4 (d), 129.0 (d), 131.3 (s), 133.9 (d), 164.9 (s). Anal. Found: C, 58.43; H, 5.19; N, 3.03. $C_{22}H_{23}FeNOSe$ Calc.: C, 58.43; H, 5.13; N, 3.10%. Yield, 54% (as diastereomers).

3.3.9. (S,R)-1-diphenylphosphino-3-methyl-2-(4'-isopropyloxazolinyl)ferrocene (18)

After lithiation of a diastereomeric mixture of 16 (157 mg, 0.50 mmol) with sec-BuLi (0.63 mmol) in dry diethyl ether (4 ml) at −78°C for 3 h under nitrogen, chlorodiphenylphosphine (134 mg, 0.61 mmol) in dry diethyl ether (1 ml) was added at −78°C. The mixture was warmed up to room temperature and then heated at reflux temperature for 27 h. It was treated with brine (100 ml) and extracted with CH_2Cl_2 (50 ml × 3). The extract was dried over $MgSO_4$ and evaporated to leave a yellow solid of 18 which was purified by column chromatography on SiO_2 with hexane and ethyl acetate as eluents; 179 mg, 0.36 mmol (72% yield based on 16). The optically pure 18 was obtained by one recrystallization from dry ethanol under nitrogen. An orange solid, mp 155–156°C (> 99% de). ^{1}H NMR δ 0.79 (6H, d, $J = 6.75$ Hz), 1.61 (1H, sept., $J = 6.75$ Hz), 2.29 (3H, s), 3.47 (1H, m), 3.83 (2H, m), 4.01 (1H, m), 4.13 (5H, s), 4.29 (1H, m), 7.1–7.5 (10H, m). ^{13}C NMR δ 14.8, 15.3, 18.0, 18.1, 18.2, 18.3, 32.4, 32.6, 69.1, 69.3, 71.4, 71.8, 71.9, 72.1, 72.8, 127.7, 127.9, 128.0, 128.0, 128.1, 128.8, 130.9, 131.1, 131.3, 131.5, 132.2, 132.4, 134.9, 135.2, 165.7. Anal. Found: C, 70.30; H, 6.11; N, 2.85. $C_{29}H_{30}FeNOP$ Calc.: C, 70.31; H, 6.10; N, 2.83%.

3.3.10. (S,S)-1-diphenylphosphino-2-(4'-isopropyloxazolinyl)-3-(phenylseleno)ferrocene (19)

Similarly, 19 was prepared from optically pure 17. The phosphine 10 was also found as a by-product. A yellow solid, mp 138–139°C (> 99% de). ^{1}H NMR δ 0.83 (6H, d, $J = 6.75$ Hz), 1.62 (1H, sept., $J = 6.75$ Hz), 3.54 (1H, m), 3.85–4.07 (4H, m), 4.19 (5H, s), 7.2–7.7 (15H, m). ^{13}C NMR δ 18.0 (q), 18.5 (q), 32.6 (d), 70.2 (d), 71.9 (d), 72.6 (d), 72.7 (d), 83.7 (s), 127.9 (d), 127.9 (d), 128.0 (d), 128.1 (d), 128.2 (d), 129.0 (d), 129.1 (d), 132.2 (d), 132.5 (d), 134.8 (d), 135.0 (d), 135.2 (d), 164.3 (s). Anal. Found: C, 64.47; H, 5.35; N, 2.21. $C_{34}H_{32}FeNOPSe$ Calc.: C, 64.17; H, 5.07; N, 2.20%. Yield, 53%.

3.4. Preparation and structure of (S,S,S)- and (S,S,R)-[2-(4',5'-diphenyloxazolin-2'-yl)ferrocenyl]diphenylphosphine (DIPOF) (21 and 22) and related compounds

After lithiation of 20 (163 mg, 0.40 mmol) with sec-BuLi (0.42 mmol) in dry diethyl ether (3 ml) at

−78°C for 3 h under nitrogen, chlorodiphenylphosphine (110 mg, 0.50 mmol) in dry diethyl ether (1 ml) was added at −78°C. The mixture was warmed up to room temperature and then heated at reflux temperature for 5 h. It was treated with brine (100 ml) and extracted with CH_2Cl_2 (50 ml × 3). The extract was dried over $MgSO_4$ and evaporated to leave a yellow solid which was purified by column chromatography on SiO_2 with hexane and ethyl acetate as eluents. The yellow solid eluted first (10% ethyl acetate/hexane as an eluent) was (S,S,R)-[2-(4′,5′-diphenyloxazolin-2′-yl)ferrocenyl] diphenylphosphine (22) [56 mg, 0.094 mmol (24% yield based on 20)] and the yellow solid eluted next (30% ethyl acetate/hexane as an eluent) was (S,S,S)-[2-(4′,5′-diphenyloxazolin-2′-yl)ferrocenyl]diphenylphosphine (21) [105 mg, 0.18 mmol (44% yield based on 20)]. The physical, spectroscopic and analytical data are as follows.

3.4.1. (S,S,S)-[2-(4′,5′-diphenyloxazolin-2′-yl)ferrocenyl]diphenylphosphine (21)

A yellow solid, mp 78–79°C (> 99% de). ^{1}H NMR δ 3.71 (1H, m), 4.29 (5H, s), 4.43 (1H, t, J = 2.7 Hz), 4.93 (1H, d, J = 7.70 Hz), 4.97 (1H, d, J = 7.70 Hz), 5.08 (1H, m), 7.0–7.5 (20H, m). ^{13}C NMR δ 70.9, 72.4, 74.1, 77.2, 88.6, 125.7, 126.9, 127.5, 128.0, 128.1, 128.3, 128.6, 128.8, 129.0, 132.9, 134.7, 140.8, 142.2, 165.0. Anal. Found: C, 75.35; H, 5.02; N, 2.19. $C_{37}H_{30}FeNOP$ Calc.: C, 75.14; H, 5.11; N, 2.37%.

3.4.2. (S,S,R)-[2-(4′,5′-diphenyloxazolin-2′-yl)ferrocenyl]diphenylphosphine (22)

A yellow solid, mp 124–128°C (> 99% de). ^{1}H NMR δ 3.72 (1H, m), 4.32 (5H, s), 4.46 (1H, t, J = 2.7 Hz), 5.08 (1H, d, J = 7.70 Hz), 5.13 (1H, m), 5.19 (1H, d, J = 7.70 Hz), 6.8–7.6 (20H, m). ^{13}C NMR δ 70.9, 71.0, 73.1, 74.6, 74.6, 77.2, 78.5, 88.5, 125.6, 126.3, 127.1, 128.1, 128.2, 128.3, 128.4, 128.5, 128.8, 129.0, 132.6, 132.9, 134.9, 135.2, 140.7, 142.5, 165.0. Anal. Found: C, 75.04; H, 5.03; N, 2.41. $C_{37}H_{30}FeNOP$ Calc.: C, 75.14; H, 5.11; N, 2.37%.

3.4.3. (R,R,R)-[2-(4′,5′-diphenyloxazolin-2′-yl)ferrocenyl]diphenylphosphine (DIPOF) (23)

(R,R,R)-DIPOF (23) was prepared from (1S,2R)-(+)-2-amino-1,2-diphenylethanol and isolated in a pure form by the same way as in the case of (S,S,S)- and (S,S,R)-DIPOF (21 and 22). A yellow solid, mp 78–79°C (> 99% de). Anal. Found: C, 74.87; H, 5.37; N, 2.37. $C_{37}H_{30}FeNOP$ Calc.: C, 75.14; H, 5.11; N, 2.37%.

3.5. Preparation of cationic rhodium complexes (24 and 25)

Preparation of [Rh(COD)(10)]BF$_4$ (24) and [Rh(COD)(21)]BF$_4$ (25) was carried out by the follow-

ing method. The typical procedure of [Rh(COD)(10)]BF$_4$ (24) was as follows. In a 20-ml round-bottomed flask was placed [Rh(COD)$_2$]BF$_4$ (41 mg, 0.10 mmol) and a chiral oxazolinylferrocenylphosphine (10) (50 mg, 0.10 mmol) under nitrogen. Anhydrous acetone (2 ml) was added, and then the resulting solution was magnetically stirred at room temperature for 1 h. When diethyl ether (20 ml) was added to the solution, 24 was precipitated as an orange solid which was collected by filtration and dried under vacuum: 70 mg (90% yield based on 10). ^{1}H NMR δ 0.90 (3H, d, J = 7.33 Hz), 1.11 (3H, d, J = 7.33 Hz), 1.8–2.8 (8H, m), 2.76 (1H, sept., J = 7.33 Hz), 3.45 (2H, m), 3.73 (5H, s), 3.96 (2H, m), 4.45 (1H, m), 4.61 (1H, m), 4.82 (1H, m), 5.12 (1H, m), 5.24 (1H, m), 5.48 (1H, m), 7.0–8.2 (10H, m). ^{31}P NMR δ 23.2 (d, J_{Rh-P} = 154 Hz). Anal. Found: C, 55.34; H, 5.16; N, 1.77. $C_{36}H_{40}BF_4FeNOPRh$ Calc.: C, 55.49; H, 5.17; N, 1.80%.

3.5.1. [Rh(COD)(21)]BF$_4$ (25)

An orange solid; 75% isolated yield. ^{1}H NMR δ 1.7–2.8 (10H, m), 3.43 (1H, m), 3.75 (1H, m), 4.01 (5H, s), 4.89 (1H, m), 4.99 (1H, m), 5.12 (1H, m), 5.37 (1H, m), 5.44 (1H, m), 7.0–8.2 (20H, m). ^{31}P NMR δ 22.2 (d, J_{Rh-P} = 154 Hz). Anal. Found: C, 60.51; H, 4.89; N, 1.65. $C_{45}H_{42}BF_4FeNOPRh$ Calc.: C, 60.77; H, 4.76; N, 1.58%.

3.6. Preparation of neutral rhodium complexes (26 and 27)

In a 20-ml round-bottomed flask was placed [Rh(CO)$_2$Cl]$_2$ (19 mg, 0.10 mmol). and a chiral oxazolinylferrocenylphosphine (10) (50 mg, 0.10 mmol) under nitrogen. Anhydrous THF (2 ml) was added, and then the resulting solution was magnetically stirred at room temperature for 20 h. When n-hexane (20 ml) was added to the solution, 26 was precipitated as an orange solid, which was collected by filtration and dried under vacuum: 55 mg, 85% isolated yield based on 10. ^{1}H NMR δ 0.87 (3H, d, J = 7.33 Hz), 0.97 (3H, d, J = 7.33 Hz), 2.72 (1H, sept., J = 7.33 Hz), 3.69 (5H, s), 4.20 (1H, t, J = 10.8 Hz), 4.32 (1H, dd, J = 10.8 and 2.44 Hz), 4.51 (1H, m), 4.64 (1H, t, J = 2.44 Hz), 4.95 (1H, m), 5.15 (1H, m), 7.0–8.2 (10H, m). ^{31}P NMR δ 34.2 (d, J_{Rh-P} = 175 Hz). Anal. Found: C, 54.03; H, 4.51; N, 2.08. $C_{29}H_{28}ClFeNO_2PRh$ Calc.: C, 53.78; H, 4.36; N, 2.16%.

3.6.1. [Rh(CO)Cl(21)] (27)

An orange solid; 80% yield. ^{1}H NMR δ 3.85 (5H, s), 4.67 (1H, m), 4.79 (1H, m), 5.15 (1H, m), 5.53 (1H, m), 6.59 (1H, m), 7.20–8.34 (20H, m). ^{31}P NMR δ 31.2 (d, J_{Rh-P} = 171 Hz). Anal. Found: C, 59.57; H, 4.26; N, 2.08. $C_{38}H_{30}ClFeNO_2PRh$ Calc.: C, 60.23; H, 3.99; N, 1.85%.

Table 10
Crystallographic data for **10, 17, 18, 21** and **24–27**

	10	17	18	21	24	25	26	27
Formula	$C_{28}H_{28}FeNOP$	$C_{22}H_{23}FeNOSe$	$C_{29}H_{30}FeNOP$	$C_{37}H_{30}FeNOP$	$C_{36}H_{40}BF_4FeNOPRh$	$C_{45}H_{42}BF_4FeNOPRh$	$C_{29}H_{28}ClFeNO_2PRh$	$C_{38}H_{30}ClFeNO_2PRh$
Formula weight	481.36	452.24	495.39	591.47	779.25	889.36	647.73	726.87
Crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$
Crystal color	orange	red	orange	orange	orange	orange	orange	orange
a (Å)	10.918(2)	7.479(2)	13.920(3)	10.95(1)	12.988(2)	19.157(2)	10.732(3)	15.304(10)
b (Å)	23.589(3)	7.781(3)	17.157(5)	33.302(8)	24.038(2)	20.646(2)	11.664(3)	20.414(7)
c (Å)	9.285(3)	16.875(1)	10.515(3)	8.14(1)	10.910(2)	9.829(2)	10.944(3)	10.439(6)
β (°)		93.30(2)					92.73(2)	
V (Å³)	2391(1)	980.4(4)	2511.2(9)	2968(5)	3406.1(6)	3887.8(9)	1368.5(6)	3261(2)
Z	4	2	4	4	4	4	2	4
D_{cal} (g cm⁻³)	1.337	1.532	1.170	1.323	1.519	1.519	1.572	1.48
$F(000)$	1008	460	924	1232	1592	1816	656	1476
μ_{cal} (cm⁻¹)	7.17	26.35	6.77	5.92	10.08	8.94	13.14	10.65
Max. 2θ (°)	55	60	60	55	55	55	55	55
No. of reflections	3137	3270	4111	3477	4395	4999	3475	4209
No. of data used ($I > 3\sigma(I)$)	2321	2694	2864	861	2847	2179	3135	3780
No. of params refined	406	258	329	216	456	539	353	506
Reflection/parameter ratio	5.72	10.44	8.71	3.99	6.24	4.04	8.88	7.47
R	0.029	0.034	0.042	0.071	0.051	0.047	0.026	0.027
R_w	0.030	0.045	0.048	0.063	0.064	0.041	0.032	0.035
Goodness of fit	1.29	2.10	2.05	1.63	2.41	1.23	1.68	1.78
Maximum residuals (e Å⁻³)	0.19	0.53	0.45	0.36	0.92	0.48	0.95	0.61

3.7. Crystallography

Single crystals suitable for X-ray analysis were prepared by recrystallization from EtOH (**10, 17, 18** and **21**), acetone–diethyl ether (**24** and **25**), CH_2Cl_2-hexane (**26**) or CH_2Cl_2-diethyl ether (**27**). Diffraction data were collected on a Rigaku AFC-7R four-circle automated diffractomator with Mo-Kα ($\lambda = 0.71069$ Å) radiation and a graphite monochromator at 23°C using the $\omega - 2\theta$ scan technique. No significant decay was observed for three standard reflections which were monitored every 150 reflections. Details of the X-ray diffraction study are summarized in Table 10. [9]

For all structure analysis and refinement, computations were performed using TEXSAN [10] crystallographic software package of Molecular Structure. Neutral atom scattering factors were taken from Ref. [49]. Anomalous dispersion effects were included in F_{calc} [50]; the values for $\Delta f'$ and $\Delta f''$ were those of Ref. [51]. The structure was solved by the direct methods (**10, 17, 21** and **27**) or the Patterson methods (**18, 24, 25** and **26**). Full-matrix least squares refinement (on F), except for **21**, was employed with anisotropic thermal parameters for all non-hydrogen atoms. In the case of **21**, only iron, phosphorus, nitrogen and oxygen atoms were refined anisotropically, and all carbon atoms were refined isotropically. Hydrogen atoms were included but not refined. The weighing scheme $\omega = 1/\sigma^2(F_0)$, with $\sigma(F_0)$ from counting statistics gave satisfactory agreement analyses.

Acknowledgements

References

[1] For review, I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993.

[2] For review, R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley, New York, 1994.

[3] For review, H. Brunner, W. Zettimeier, Handbook of Enantioselective Catalysis with Transition Metal Compounds, VCH, Weinheim, 1993.

[4] A. Togni, T. Hayashi (Eds.), Ferrocenes, VCH, Weinheim, 1995, and references therein.

[5] A. Togni, Angew. Chem., Int. Ed. Engl. 35 (1996) 1475, and references therein.

[6] T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto, M. Kumada, Bull. Chem. Soc. Jpn. 53 (1980) 1138.

[7] M. Sawamura, Y. Ito, Chem. Rev. 92 (1992) 857, and references therein.

[8] T. Hayashi, N. Kawamura, Y. Ito, J. Am. Chem. Soc. 109 (1987) 7876.

[9] T. Hayashi, N. Kawamura, Y. Ito, Tetrahedron Lett. 29 (1988) 5969.

[10] A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, J. Am. Chem. Soc. 116 (1994) 4062.

[11] T. Hayashi, C. Hayashi, Y. Uozumi, Tetrahedron: Asymm. 6 (1995) 2503.

[12] T. Hayashi, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, Chap. 7.1, VCH, New York, 1993, p. 325, and references therein.

[13] A. Togni, U. Bruckhardt, V. Gramlich, P.S. Pregosin, R. Salzmann, J. Am. Chem. Soc. 118 (1996) 1031, and references therein.

[14] M. Sawamura, Y. Ito, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, Chap. 7.2, VCH, New York, 1993, p. 367, and references therein.

[15] Y. Nishibayashi, J.D. Singh, S. Uemura, S. Fukuzawa, Tetrahedron Lett. 35 (1994) 3115.

[16] Y. Nishibayashi, J.D. Singh, S. Fukuzawa, S. Uemura, J. Org. Chem. 60 (1995) 4114.

[17] T. Chiba, Y. Nishibayashi, J.D. Singh, K. Ohe, S. Uemura, Tetrahedron Lett. 36 (1995) 1519.

[18] Y. Nishibayashi, T. Chiba, K. Ohe, S. Uemura, J. Chem. Soc., Chem. Commun. (1995) 1243.

[19] Y. Nishibayashi, S.K. Srivastava, K. Ohe, S. Uemura, Tetrahedron Lett. 37 (1995) 6725.

[20] S. Fukuzawa, Y. Kasugahara, S. Uemura, Tetrahedron Lett. 35 (1994) 9403.

[21] Y. Nishibayashi, S.K. Srivastava, H. Takada, S. Fukuzawa, S. Uemura, J. Chem. Soc., Chem. Commun. (1995) 2321.

[22] Y. Nishibayashi, J.D. Singh, S. Fukuzawa, S. Uemura, J. Chem. Soc., Perkin Trans. 1 (1995) 2871.

[23] Y. Nishibayashi, J.D. Singh, K. Segawa, S. Fukuzawa, S. Uemura, J. Chem. Soc., Chem. Commun. (1994) 1375.

[24] Y. Nishibayashi, J.D. Singh, K. Segawa, S. Fukuzawa, K. Ohe, S. Uemura, Organometallics 15 (1996) 370.

[25] A. Pfaltz, Acc. Chem. Res. 26 (1993) 339, and references therein, for a review.

[26] G.C. Lloyd-Jones, A. Pfaltz, Angew. Chem., Int. Ed. Engl. 34 (1995) 462.

[27] O. Loiseleur, P. Meier, A. Pfaltz, Angew. Chem., Int. Ed. Engl. 35 (1996) 200.

[28] T.G. Grant, A.I. Meyers, Tetrahedron 50 (1994) 2297, and references therein.

[29] Preliminary communication: Y. Nishibayashi, S. Uemura, Synlett. (1995) 79.

[30] Y. Nishibayashi, K. Segawa, K. Ohe, S. Uemura, Organometallics 14 (1995) 5486.

[31] G.D. Broadhead, J.M. Qsgerby, P.L. Pauson, J. Chem. Soc. (1958) 650.

[32] H. Witte, W. Seeliger, Justus Liebigs Ann. Chem. 68 (1974) 996.

[9] The author has deposited atomic coordinates, thermal parameters, bond distances, and angles for the X-ray structure of **10, 17, 18, 21, 24, 25, 26** and **27** with the Cambridge Crystallographic Data Center. These data can be obtained, on request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

[10] TEXSAN: Crystal Structure Analysis Package, Molecular Structure, 1985 and 1992.

[33] C. Bolm, K. Weickhardt, M. Zehnder, T. Ranff, Chem. Ber. 124 (1991) 1173.

[34] G. Schmitt, P. Klein, W. Eberts, J. Organomet. Chem. 234 (1982) 63.

[35] C.J. Richards, T. Damalidis, D.E. Hibbs, M.B. Hursthouse, Synlett. (1995) 74.

[36] C.J. Richards, A.W. Mulvaney, Tetrahedron: Asymm. 7 (1996) 1419.

[37] T. Sammakia, H.A. Latham, D.R. Schaad, J. Org. Chem. 60 (1995) 10.

[38] T. Sammakia, H.A. Latham, J. Org. Chem. 60 (1995) 6002.

[39] T. Sammakia, H.A. Latham, J. Org. Chem. 61 (1996) 1629.

[40] J. Park, S. Lee, K.H. Aim, C.-W. Cho, Tetrahedron Lett. 36 (1995) 7263.

[41] K.H. Ahm, C.-W. Cho, H.-H. Beak, J. Park, S. Lee, J. Org. Chem. 61 (1996) 4937.

[42] W. Zhang, Y. Adachi, T. Hirao, I. Ikeda, Tetrahedron: Asymm. 7 (1996) 451.

[43] W. Zhang, T. Hirao, I. Ikeda, Tetrahedron Lett. 37 (1996) 4545.

[44] J.M. Brown, P.J. Guiry, D.W. Price, M.B. Hursthouse, S. Karalulov, Tetrahedron: Asymm. 5 (1994) 561.

[45] H. Nishiyama, M. Kondo, T. Nakamura, K. Itoh, Organometallics 10 (1991) 500.

[46] W.R. Cullen, F.W.B. Einstein, C.-H. Huang, A.C. Willis, E.-S. Yeh, J. Am. Chem. Soc. 102 (1980) 988.

[47] M.J. McKennon, A.I. Meyers, K. Drauz, M. Schwarm, J. Org. Chem. 58 (1993) 3568.

[48] T. Katada, M. Nishida, S. Kato, M. Mizuta, J. Organomet. Chem. 129 (1977) 189.

[49] D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, Vol. IV, The Kynoch Press, Birmingham, England, 1974, Table 2.2A.

[50] J.A. Ibers, W.C. Hamilton, Acta Crystallogr. 17 (1964) 781.

[51] D.C. Creagh, J.H. Hubbell, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, Vol. C, Kluwer Academic Publishers, Boston, 1992, Tables 4.2, 4.3, pp. 200–206.