Journal of Organometallic Chemistry, 370 (1989) 129–139
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09618

Asymmetric synthesis catalyzed by chiral ferrocenylphosphine-transition metal complexes

VII *. New chiral ferrocenylphosphines with C_2 symmetry

Tamio Hayashi *, Akihiro Yamamoto, Masahiro Hojo, Kohei Kishi, Yoshihiko Ito *
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606 (Japan)

Eriko Nishioka, Hitoshi Miura, and Kazunori Yanagi *
Takatsuki Research Laboratory, Sumitomo Chemical Co., Ltd., 2-10-1 Tsukahara, Takatsuki, Osaka 569 (Japan)

(Received October 21st, 1988)

Abstract

A new chiral ferrocenylphosphine ligand, 2,2′-bis[1-(*N,N*-dimethylamino)ethyl]-1,1′-bis(diphenylphosphino)ferrocene (**2**), which has C_2 symmetry and a functional group on the side chain, was prepared by ortho-lithiation and phosphination of 1,1′-bis[1-(*N,N*-dimethylamino)ethyl]ferrocene followed by optical resolution; recrystallization of the diammonium salt with tartaric acid. An X-ray diffraction study of $PdCl_2[(+)\text{-}\mathbf{2}]$ showed that the complex has square-planar geometry with two cis chlorine and two phosphorus atoms and ligand (+)-**2** has an (*S*) configuration on the 1-dimethylaminoethyl side chain and (*R*) ferrocene planar chirality.

Introduction

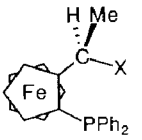
We have prepared optically active ferrocenylphosphine ligands starting with *N,N*-dimethyl-1-ferrocenylethylamine [1] and used them successfully for various types of asymmetric reactions catalyzed by chiral transition metal complexes [2,3]. The ferrocenylphosphines are unique in that the structure can be readily modified by introduction of a desired functional group onto the side chain according to the demand of the reaction type. It has been demonstrated that ferrocenylphosphines, PPF-X and BPPF-X ($X = NMe_2$ (PPFA and BPPFA), OH, $NMeCH_2CH_2NR_2$,

---

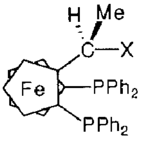
* For part VI see Ref. 3a.

0022-328X/89/$03.50 © 1989 Elsevier Sequoia S.A.

$NMeCH(OH_2OH)_2$, etc.), are superior to other chiral phosphine ligands for the catalytic asymmetric reactions [2,3].

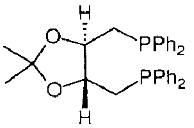


(*R*)-(*S*)-PPF-X

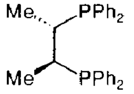


(*R*)-(*S*)-BPPF-X

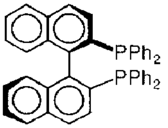
On the other hand, several efficient chiral bisphosphine ligands with C_2 symmetry have been reported [4]. Good examples are (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [DIOP] [5], (*S*,*S*)-2,3-bis(diphenylphosphino)butane [chiraphos] [6], and 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl [BINAP] [7]. Their efficiency could be partially explained on the basis of a reduced number of reaction intermediates in the presence of the C_2-symmetric ligand. Here we describe (i) the preparation of the new optically active ferrocenylphosphine ligands which have both the C_2 symmetry and the functionality at the same time, and (ii) the crystal structure of a palladium complex containing the C_2 ferrocenylphosphine ligand.



(-)-DIOP



(*S*,*S*)-chiraphos

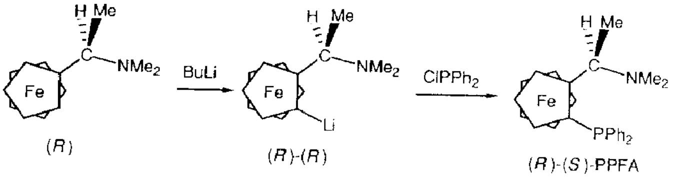


(*R*)-BINAP

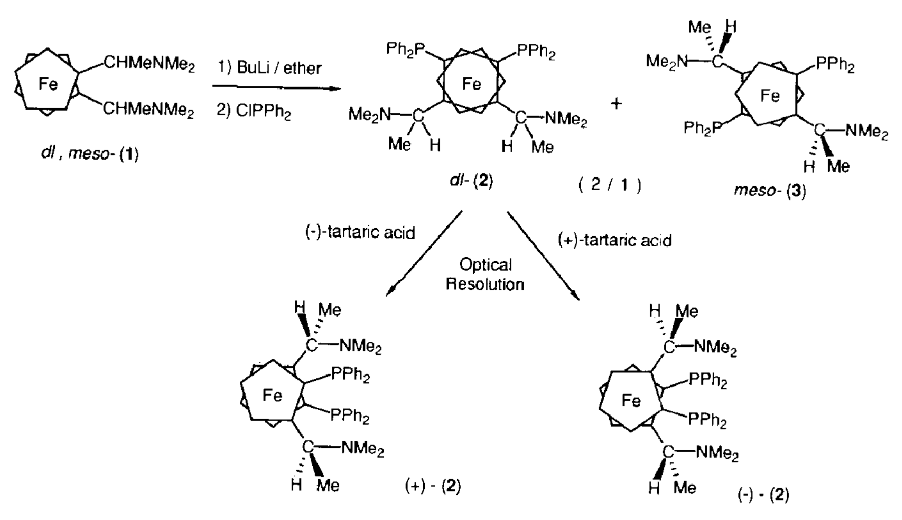
Results and discussion

Preparation of optically active C_2-symmetric ferrocenylphosphines

It has been reported by Ugi and coworkers that ortho-lithiation of (*R*)-*N*,*N*-dimethyl-1-ferrocenylethylamine proceeds with high stereoselectivity to give preferentially (*R*)-*N*,*N*-dimethyl-1-[(*R*)-2-lithioferrocenyl]ethylamine [8]. We have prepared ferrocenylphosphine (*R*)-(*S*)-PPFA by treatment of the lithiated ferrocene with chlorodiphenylphosphine [1] (Scheme 1). The first plan for the preparation of an optically active C_2-symmetric ferrocenylphosphine was to lithiate optically resolved 1,1′-bis[1-(*N*,*N*-dimethylamino)ethyl]ferrocene (**1**), the lithiation being expected to proceed stereoselectively on both of the cyclopentadienyl rings, but attempts to resolve diamine **1** were unsuccessful.



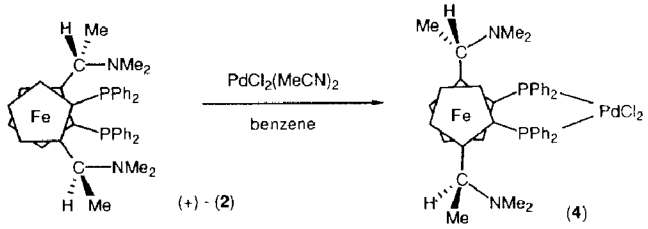
Scheme 1



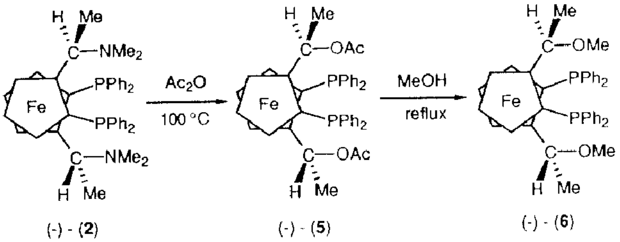
Scheme 2

We have successfully prepared an optically active C_2-symmetric ferrocenylphosphine by resolution of the racemic phosphine obtained by the ortholithiation and diphenylphosphination of racemic **1**. Thus, diamine **1**, which was prepared from 6-(dimethylamino)fulvene [9] as a mixture of *dl* and *meso* isomers, was lithiated with 3 equiv of butyllithium in ether by the procedure described [8] for the lithiation of *N*,*N*-dimethyl-1-ferrocenylethylamine. Treatment of the resulting dilithiated ferrocene with an excess of chlorodiphenylphosphine gave ferrocenylbisphosphine in 60% yield, which was shown by ^{1}H NMR spectroscopy to consist of two isomers in a ratio of 2 : 1 (Scheme 2). The configurations of ferrocene planar chirality on the two cyclopentadienyl rings of both of the isomers are expected to be related to the chiral carbon center on the 1-(dimethylamino)ethyl side chain since the ortho-lithiation assisted by the amino group is highly stereoselective [8]. The central carbon chirality (*S*) and (*R*) of the 1-(dimethylamino)ethyl group should afford selectively the planar chirality (*R*) and (*S*), respectively, in the ferrocenylbisphosphines. The major product was found to be the *dl* isomer, 2,2′-bis[($R^\star$)-1-(*N*,*N*-dimethylamino)ethyl]-($S^\star$)-($S^\star$)-1,1′-bis(diphenylphosphino)ferrocene (**2**) and the minor, the *meso* isomer **3** since the former could be optically resolved (vide infra). Stereoisomers with other combinations of planar and central elements of chirality were not detected by ^{1}H NMR spectroscopy. The optical resolution of *dl*-**2**, which was isolated by silica gel column chromatography of mixture of *dl*-**2** and *meso*-**3**, was readily made by fractional crystallization of its ditartrate salt. Both antipodes were obtained with 82% of the theoretical recovery. The ditartrate (–)-**2**/(+)-tartaric acid crystallized preferentially from methanol. The crystallization was repeated twice and optically pure (–)-**2** ($[\alpha]_D^{25}$ $-457°$ (*c* 0.54, chloroform)) was obtained. The (+)-rich **2** was recovered from the mother liquor and its ditartrate with (–)-tartaric acid was crystallized from methanol to give (+)-**2** ($[\alpha]_D^{25}$ $+450°$ (*c* 0.54, chloroform)).

The optically active C_2-symmetric ferrocenylphosphine (+)-**2** was converted to the palladium complex **4** by reaction with $PdCl_2(MeCN)_2$ in benzene (Scheme 3). The X-ray diffraction study of **4** indicated that the absolute configuration of the



Scheme 3



Scheme 4

1-dimethylaminoethyl side chain is (S) and that of the ferrocene planar chirality is (R) on both cyclopentadienyl rings of $(+)$-**2**.

The dimethylamino group on the side chain of $(-)$-2 was replaced with an acetoxy group by reaction with acetic anhydride at 100 °C, and then with a methoxy group by treatment of the diacetate $(-)$-**5** in refluxing methanol (Scheme 4). The substitution reactions are regarded as proceeding with retention of configuration, such as in the substitution at the ferrocenylmethyl position of 1-ferrocenylethyl system [10] and of ferrocenylphosphines, PPF-X and BPPF-X [1].

The C_2 ferrocenylphosphines, **2**, **6**, and several other phosphines derived from **2**, have been found to be effective ligands for transition metal-catalyzed asymmetric reactions, which will be described elsewhere.

Structure of the palladium complex 4

The structure of **4** was deduced from an X-ray diffraction study. Fractional coordinates, bond lengths, and bond angles are listed in Tables 1, 2, and 3, respectively. A stereoscopic view and the atom numbering scheme of the complex are illustrated in Figures 1 and 2, respectively. Ligand $(+)$-**2** takes an (S) configuration for the amine-substituted C(35) and C(39) atoms and an (R) configuration for both of the asymmetrically substituted cyclopentadienyl rings. Palladium complex **4** exhibits square planar geometry with two cis chlorine and two phosphorus atoms, and the nitrogen atoms are not bound to palladium. The average distances of two Pd–P and two Pd–Cl bonds are 2.310(1) and 2.340(1) Å, respectively. Noteworthy is the large P–Pd–P angle of **4**. It has been reported that palladium complexes bearing the 1,1′-bis(diphenylphosphino)ferrocene (dppf) skeleton, i.e., $PdCl_2$(dppf) [11,12] and $PdCl_2$(BPPFA) (BPPFA = *N,N*-dimethyl-1-[1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine) [13], have large P–Pd–P angles compared with bisphosphine-palladium complexes $PdCl_2[Ph_2P(CH_2)_nPPh_2]$ ($n = 2$ and 3) [14]. The value of 103.43(5)° for **4** is much larger than the values for the bisphosphine-palladium

(continued on p. 135)

Table 1

Fractional coordinates and equivalent isotropic temperature factors for $PdCl_2[(+)\text{-}2]$ (standard deviations of the least significant figures are given in parentheses)

Atom	*x*	*y*	*z*	B_{eq} [a]
Pd	0.85383(3)	0.5	0.91383(3)	2.360(6)
Fe	0.80844(5)	0.51066(6)	1.51733(6)	2.42(1)
Cl(1)	0.7544(1)	0.5113(2)	1.0761(1)	4.50(3)
Cl(2)	0.9943(1)	0.5241(1)	1.0638(1)	3.76(3)
P(1)	0.7092(1)	0.4635(1)	0.7822(1)	3.12(3)
P(2)	0.97539(9)	0.5007(1)	0.7807(1)	2.29(2)
N(1)	0.5052(5)	0.3989(6)	0.5026(7)	5.9(2)
N(2)	1.1288(4)	0.5757(4)	0.5030(4)	3.1(1)
C(1)	0.6986(4)	0.5140(5)	0.6268(5)	3.2(1)
C(2)	0.6595(4)	0.4859(5)	0.4982(5)	3.3(1)
C(3)	0.6791(5)	0.5593(5)	0.4173(6)	3.8(1)
C(4)	0.7281(5)	0.6314(5)	0.4883(7)	4.4(1)
C(5)	0.7395(5)	0.6047(5)	0.6174(6)	3.5(1)
C(6)	0.9420(4)	0.4798(4)	0.6148(4)	2.3(1)
C(7)	0.8868(4)	0.3974(4)	0.5772(5)	2.5(1)
C(8)	0.8688(4)	0.3958(4)	0.4445(5)	2.9(1)
C(9)	0.9111(4)	0.4773(4)	0.3978(5)	2.7(1)
C(10)	0.9581(4)	0.5283(4)	0.5005(5)	2.5(1)
C(11)	0.5917(5)	0.4979(8)	0.8370(6)	5.1(2)
C(12)	0.5450(7)	0.5763(8)	0.7948(9)	8.4(2)
C(13)	0.4563(9)	0.603(1)	0.832(1)	12.4(4)
C(14)	0.4166(7)	0.553(1)	0.920(1)	11.4(4)
C(15)	0.4615(6)	0.468(1)	0.9669(8)	9.4(4)
C(16)	0.5488(6)	0.4417(8)	0.9208(8)	6.7(2)
C(17)	0.7016(5)	0.3354(5)	0.7807(6)	3.8(1)
C(18)	0.7830(6)	0.2859(5)	0.8283(6)	4.1(1)
C(19)	0.7764(7)	0.1881(6)	0.8352(7)	5.2(2)
C(20)	0.6892(7)	0.1469(6)	0.7950(8)	6.0(2)
C(21)	0.6064(7)	0.1966(7)	0.753(1)	7.0(3)
C(22)	0.6120(6)	0.2913(7)	0.7398(9)	5.6(2)
C(23)	1.0708(4)	0.4105(4)	0.8126(5)	2.7(1)
C(24)	1.1497(5)	0.4094(5)	0.7390(6)	3.7(1)
C(25)	1.2207(5)	0.3399(6)	0.7572(7)	4.4(2)
C(26)	1.2126(6)	0.2720(5)	0.8450(8)	5.1(2)
C(27)	1.1339(6)	0.2720(5)	0.9143(7)	4.6(2)
C(28)	1.0642(5)	0.3437(4)	0.9013(6)	3.5(1)
C(29)	1.0361(4)	0.6119(4)	0.8000(5)	2.7(1)
C(30)	1.1391(5)	0.6223(5)	0.8329(7)	4.2(1)
C(31)	1.1792(6)	0.7088(6)	0.8536(7)	4.9(2)
C(32)	1.1219(6)	0.7874(5)	0.8392(6)	4.6(2)
C(33)	1.0201(6)	0.7764(5)	0.8071(7)	4.7(2)
C(34)	0.9784(5)	0.6892(5)	0.7892(7)	4.0(1)
C(35)	0.6033(5)	0.3983(6)	0.4563(7)	4.6(2)
C(36)	0.4440(6)	0.4757(9)	0.466(1)	8.9(3)
C(37)	0.5995(7)	0.3831(9)	0.3145(8)	7.9(3)
C(38)	0.4497(7)	0.314(1)	0.473(1)	9.4(3)
C(39)	1.0249(4)	0.6099(4)	0.4891(5)	2.5(1)
C(40)	1.2031(5)	0.6478(6)	0.5186(7)	4.5(2)
C(41)	0.9929(5)	0.6639(5)	0.3667(6)	3.5(1)
C(42)	1.1496(4)	0.5104(6)	0.4056(7)	4.5(1)

[a] $B_{eq} = \frac{4}{3}\Sigma_i \Sigma_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 2

Bond distances (Å) of $PdCl_2$[(+)-**2**] (standard deviations of the least significant figures are given in parentheses)

Pd–Cl(1)	2.331(1)	C(6)–C(7)	1.440(7)
Pd–Cl(2)	2.348(1)	C(6)–C(10)	1.453(7)
Pd–P(1)	2.317(1)	C(7)–C(8)	1.412(7)
Pd–P(2)	2.302(1)	C(8)–C(9)	1.432(8)
Fe–C(1)	2.000(5)	C(9)–C(10)	1.409(7)
Fe–C(2)	2.022(5)	C(10)–C(39)	1.503(8)
Fe–C(3)	2.053(6)	C(11)–C(12)	1.35(1)
Fe–C(4)	2.064(7)	C(11)–C(16)	1.39(1)
Fe–C(5)	2.032(7)	C(12)–C(13)	1.37(2)
Fe–C(6)	2.012(5)	C(13)–C(14)	1.35(2)
Fe–C(7)	2.016(6)	C(14)–C(15)	1.43(2)
Fe–C(8)	2.054(6)	C(15)–C(16)	1.39(1)
Fe–C(9)	2.056(5)	C(17)–C(18)	1.36(1)
Fe–C(10)	2.061(5)	C(17)–C(22)	1.39(2)
P(1)–C(1)	1.809(6)	C(18)–C(19)	1.43(1)
P(1)–C(11)	1.825(8)	C(19)–C(20)	1.34(1)
P(1)–C(17)	1.865(8)	C(20)–C(21)	1.36(1)
P(2)–C(6)	1.803(5)	C(21)–C(22)	1.39(1)
P(2)–C(23)	1.837(6)	C(23)–C(24)	1.401(9)
P(2)–C(29)	1.811(6)	C(23)–C(28)	1.369(9)
N(1)–C(35)	1.47(1)	C(24)–C(25)	1.39(2)
N(1)–C(36)	1.41(1)	C(25)–C(26)	1.38(1)
N(1)–C(38)	1.45(2)	C(26)–C(27)	1.37(1)
N(2)–C(39)	1.474(7)	C(27)–C(28)	1.40(1)
N(2)–C(40)	1.444(9)	C(29)–C(30)	1.394(9)
N(2)–C(42)	1.464(9)	C(29)–C(34)	1.363(9)
C(1)–C(2)	1.471(7)	C(30)–C(31)	1.38(1)
C(1)–C(5)	1.437(9)	C(31)–C(32)	1.38(2)
C(2)–C(3)	1.420(9)	C(32)–C(33)	1.38(1)
C(2)–C(35)	1.52(2)	C(33)–C(34)	1.40(1)
C(3)–C(4)	1.41(1)	C(35)–C(37)	1.53(1)
C(4)–C(5)	1.43(1)	C(39)–C(41)	1.543(8)

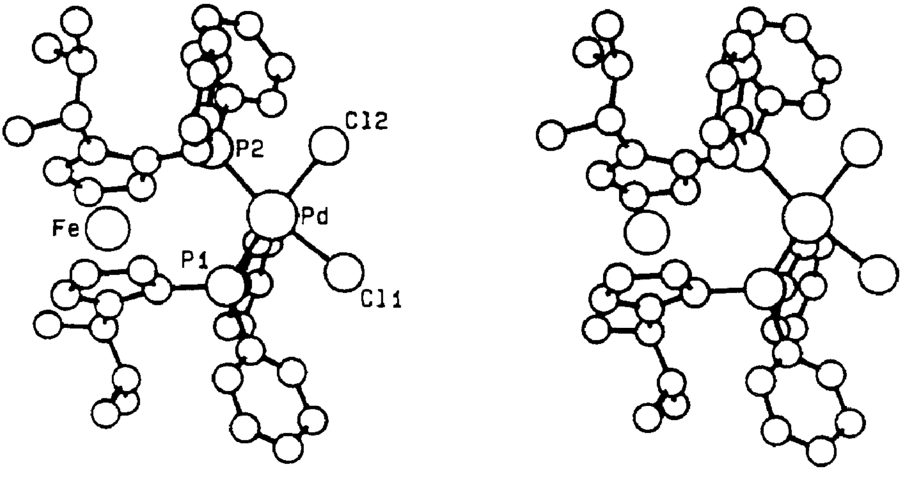


Fig. 1. Stereoscopic view of $PdCl_2$[(+)-**2**] (**4**).

Table 3

Bond angles (°) of PdCl$_2$[(+)−2] (standard deviations of the least significant figures are given in parentheses)

Cl(1)–Pd–Cl(2)	88.13(6)	Cl(2)–Pd–P(1)	173.19(6)
Cl(1)–Pd–P(1)	87.29(5)	Cl(2)–Pd–P(2)	81.35(5)
Cl(1)–Pd–P(2)	169.13(6)	P(1)–Pd–P(2)	103.43(5)
C(1)–P(1)–C(11)	102.4(4)	C(7)–C(8)–C(9)	108.2(5)
C(1)–P(1)–C(17)	113.6(3)	C(8)–C(9)–C(10)	108.8(4)
C(11)–P(1)–C(17)	103.2(4)	C(6)–C(10)–C(9)	107.7(5)
C(6)–P(2)–C(23)	98.3(2)	C(6)–C(10)–C(39)	127.3(4)
C(6)–P(2)–C(29)	108.4(2)	C(9)–C(10)–C(39)	124.5(5)
C(23)–P(2)–C(29)	108.8(3)	P(1)–C(11)–C(12)	120.6(7)
C(35)–N(1)–C(36)	115.4(8)	P(1)–C(11)–C(16)	119.6(8)
C(35)–N(1)–C(38)	112.4(8)	C(12)–C(11)–C(16)	119.8(8)
C(36)–N(1)–C(38)	110.0(7)	C(11)–C(12)–C(13)	122(2)
C(39)–N(2)–C(40)	113.7(6)	C(12)–C(13)–C(14)	120(1)
C(39)–N(2)–C(42)	114.3(4)	C(13)–C(14)–C(15)	121(2)
C(40)–N(2)–C(42)	111.2(5)	C(14)–C(15)–C(16)	117(2)
P(1)–C(1)–C(2)	136.7(5)	C(11)–C(16)–C(15)	120(2)
P(1)–C(1)–C(5)	116.8(4)	P(1)–C(17)–C(18)	119.1(5)
C(2)–C(1)–C(5)	106.5(6)	P(1)–C(17)–C(22)	120.6(6)
C(1)–C(2)–C(3)	106.9(5)	C(18)–C(17)–C(22)	120.3(7)
C(1)–C(2)–C(35)	128.0(6)	C(17)–C(18)–C(19)	119.7(7)
C(3)–C(2)–C(35)	125.0(5)	C(18)–C(19)–C(20)	119.1(8)
C(2)–C(3)–C(4)	109.9(6)	C(19)–C(20)–C(21)	121.2(9)
C(3)–C(4)–C(5)	107.9(7)	C(20)–C(21)–C(22)	120.6(9)
C(1)–C(5)–C(4)	108.9(5)	C(17)–C(22)–C(21)	118.8(8)
P(2)–C(6)–C(7)	118.2(4)	P(2)–C(23)–C(24)	117.7(5)
P(2)–C(6)–C(10)	134.7(4)	P(2)–C(23)–C(28)	122.0(5)
C(7)–C(6)–C(10)	107.1(5)	C(24)–C(23)–C(28)	120.2(6)
C(6)–C(7)–C(8)	108.2(5)	C(23)–C(24)–C(25)	119.2(6)
C(24)–C(25)–C(26)	120.3(7)	C(31)–C(32)–C(33)	117.2(7)
C(25)–C(26)–C(27)	120.3(7)	C(32)–C(33)–C(34)	120.7(7)
C(26)–C(27)–C(28)	120.1(7)	C(29)–C(34)–C(33)	121.7(7)
C(23)–C(28)–C(27)	119.8(6)	N(1)–C(35)–C(2)	109.3(6)
P(2)–C(29)–C(30)	123.0(5)	N(1)–C(35)–C(37)	114.8(6)
P(2)–C(29)–C(34)	118.9(5)	C(2)–C(35)–C(37)	111.5(8)
C(30)–C(29)–C(34)	118.0(7)	N(2)–C(39)–C(10)	107.2(4)
C(29)–C(30)–C(31)	119.7(7)	N(2)–C(39)–C(41)	114.6(5)
C(30)–C(31)–C(32)	122.6(7)	C(10)–C(39)–C(41)	111.4(4)

complexes and is the largest of those in the ferrocenylphosphine-palladium complexes.

The two cyclopentadienyl rings are almost planar, but deviate slightly from being parallel. The dihedral angle between the normals to each plane is 7(1)°. It should be noted that the location of (1-dimethylamino)ethyl side chain of ligand **2** is quite different from that of BPPFA in PdCl$_2$(BPPFA). Thus, the side chain on the BPPFA is directed toward the PdCl$_2$ moiety [13], while both of the side chains on the C_2 ligand **2** are located apart from the palladium (Figs. 3 and 4). The difference results from an opposite direction of twist by each of the cyclopentadienyl rings from the conformation in which the two diphenylphosphino groups on the cyclopentadienyl rings are in an eclipsed position. The cyclopentadienyl rings on ligand **2**

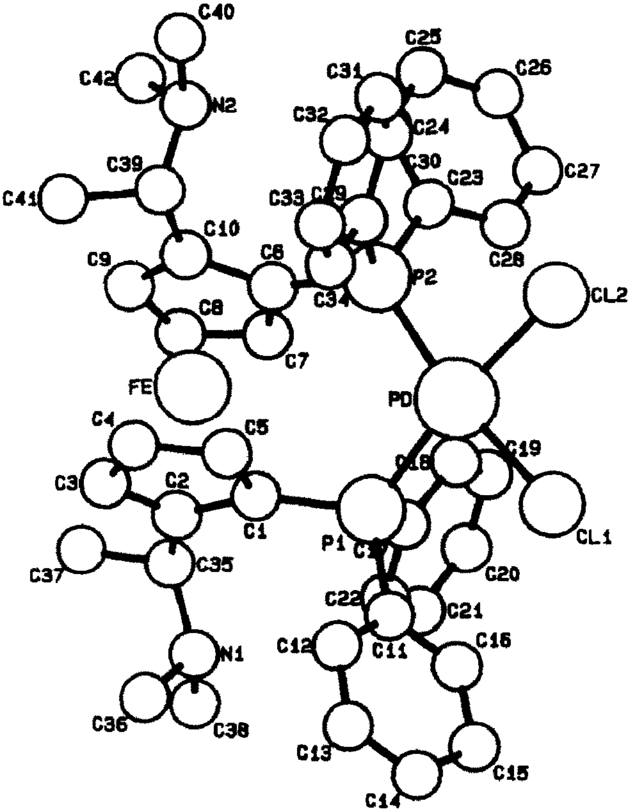


Fig. 2. Atom numbering scheme for $PdCl_2[(+)\text{-}2]$ (4).

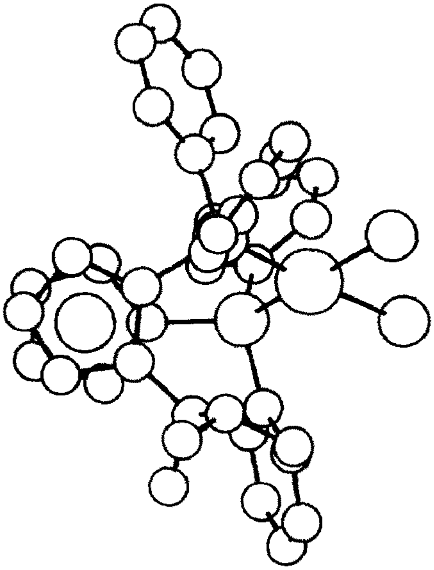


Fig. 3. View of $PdCl_2[(S)\text{-}(R)\text{-BPPFA}]$ down the ferrocene axis.

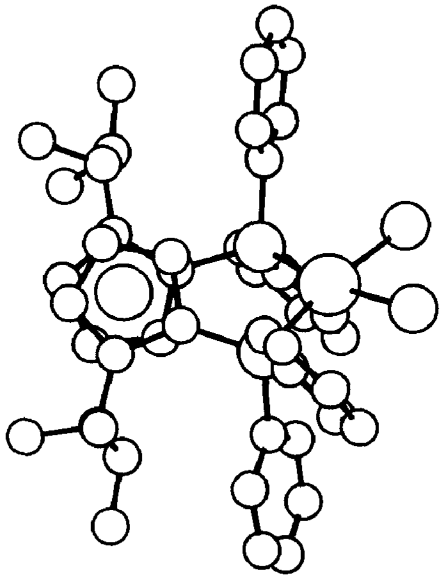


Fig. 4. View of $PdCl_2[(+)\text{-}\mathbf{2}]$ (4) down the ferrocene axis.

are twisted clockwise by about 50° while those on BPPFA are twisted anti-clockwise by about 30°, though both **2** and BPPFA shown in Figures 3 and 4 have the same ferrocene planar chirality (R). These differences in conformation are probably related to the steric demands by the diphenylphosphino groups coordinating to palladium. The dimethylaminoethyl side chain on BPPFA can be accommodated close to the palladium, which distorts the orientation of four phenyl rings from C_2 symmetry [13]. It is clear that the two side chains on **2** cannot be accommodated there at the same time and hence a conformation in which the side chains are repelled far from the palladium is adopted.

Experimental

2,2′-Bis[(R)-1-(N,N-dimethylamino)ethyl]-(S)-(S)-1,1′-bis(diphenylphosphino)ferrocene-(−)-(2) and its enantiomer (+)-(2)

To a solution of 23.2 g (70.7 mmol) of **1** in 200 ml of dry ether was added during 1 h at room temperature 0.21 mol of butyllithium in hexane. The mixture was stirred for 2.5 h and a solution of 55.2 g (0.25 mol) of chlorodiphenylphosphine in 100 ml of ether was added under gentle reflux during 2 h. After 5 h reflux, 400 ml of aqueous sodium bicarbonate was added at 0°C. The resulting organic layer and benzene extracts from the aqueous layer were combined, washed with water, dried over anhydrous sodium sulfate, and stripped of solvent. Addition of methanol to the residue precipitated the ferrocenylbisphosphines (29.5 g, 60%) as orange crystals. ^1H NMR data showed that the precipitates consisted of *dl*-**2** and *meso* isomer **3** in a ratio of 2 to 1. The isomers **2** and **3** were separated by silica gel column chromatography (ethyl acetate as eluent) to give 15.7 g of pure *dl*-**2**. ^1H NMR ($CDCl_3$). *dl*-**2**: δ 1.25 (d, J 6.5 Hz, 6H), 1.70 (s, 12H), 3.05 (m, 2H), 4.06 (dq, J 3 and 6.5 Hz, 2H), 4.14 (m, 2H), 4.32 (m, 2H), 6.80–7.46 (m, 20H). *meso*-**3**: δ 0.51 (d, J 6 Hz, 6H), 1.64 (s, 12H), 3.74 (m, 2H), 3.90 (m, 2H), 3.66–4.10 (m, 2H), 4.34 (m, 2H), 6.82–7.87 (m, 20H).

A mixture of 15.7 g (22.5 mmol) of *dl*-**2** and 6.75 g (45 mmol) of (+)-tartaric acid in 500 ml of methanol was warmed to 60 °C until the crystals had dissolved to give a clear orange solution within about 10 min. The solution was concentrated to 200 ml by a slow stream of nitrogen while it was kept at 60 °C and allowed to be cooled slowly to room temperature. The orange needles that formed were collected on a filter and washed with cold ethanol. Saturated sodium carbonate solution was added to the crystals, and the mixture was extracted with ether. The ether extracts were washed with saturated sodium carbonate solution and water, dried over anhydrous sodium sulfate, and stripped of solvent to give 7.82 g (11.2 mmol) of partially resolved (−)-**2**. The partially resolved (−)-**2** and 3.37 g (22.4 mmol) of (+)-tartaric acid were dissolved in 500 ml of methanol at 60 °C. The solution was concentrated to 200 ml and cooled to room temperature. The ditartrate salts obtained were treated with aqueous sodium carbonate to give 6.39 g (82%) of optically pure (−)-**2**: $[\alpha]_D^{25}$ −457° (*c* 0.54, chloroform); m.p. 199–200 °C; Anal. Found: C, 72.15; H, 6.71; N, 4.03. $C_{42}H_{46}FeN_2P_2$ calc: C, 72.41; H, 6.66; N, 4.02%. Treatment of the mother liquor of the first crystallization with aqueous sodium carbonate gave 7.75 g (11.1 mmol) of (+)-rich **2**. Formation of ditartrate with (−)-tartaric acid and recrystallization from methanol twice, similar to that described above gave (+)-**2**-di(−)-tartrate. Optically pure (+)-**2** (6.41 g, 82%) was released ($[\alpha]_D^{25}$ +450° (*c* 0.54, chloroform)).

$PdCl_2$[(+)-2] (4)

To a suspension of 149 mg (0.574 mmol) of dichlorobis(acetonitrile)palladium(II) in 6 ml of benzene was added with stirring a solution of 401 mg (0.574 mmol) of (+)-**2** in 6 ml of benzene. After the mixture had been stirred at room temperature for 12 h, the reddish brown precipitate that formed, was collected by filtration, washed with benzene, and dried in vacuo to give 502 mg (100%) of the palladium complex **4**: m.p. 205–208 °C (decomp); Anal. Found: C, 57.09; H, 5.24; N, 3.15; Cl, 8.11. $C_{42}H_{46}N_2Cl_2FeP_2Pd$ calc: C, 57.72; H, 5.31; N, 3.21; Cl 8.11%. A sample suitable for the X-ray diffraction study was obtained by recrystallization from dichloromethane and ether.

2.2′-Bis[(R)-1-acetoxyethyl]-(S)-(S)-1,1′-bis(diphenylphosphino)ferrocene-(−)-(5)

A mixture of 4.00 g (5.74 mmol) of (−)-**2** and 7.0 ml of acetic anhydride was sealed in a glass tube and heated at 100 °C for 1.5 h. Acetic anhydride was removed under reduced pressure, and the residue was chromatographed on silica gel (hexane/ethyl acetate = 5/1) to give 3.69 g (88%) of diacetate (−)-**5**; $[\alpha]_D^{25}$ −400° (*c* 0.58, chloroform); m.p. 168–171 °C. ^1H NMR ($CDCl_3$) δ 1.18 (s, 6H), 1.64 (d, *J* 6.5 Hz, 6H), 3.11 (m, 2H), 4.41 (m, 2H), 4.57 (m, 2H), 6.07 (dq, *J* 3.0 and 6.5 Hz, 2H), 6.86–7.43 (m, 20H). Anal. Found: C, 69.45; H, 5.51. $C_{42}H_{40}FeO_4P_2$ calc: C, 69.43; H, 5.55%.

2,2′-Bis[(R)-1-methoxyethyl]-(S)-(S)-1,1′-bis(diphenylphosphino)ferrocene(−)-(6)

A solution of 201 mg (0.277 mmol) of diacetate (−)-**5** in 11 ml of dry methanol was refluxed for 7 h. Methanol was evaporated, and the residue was chromatographed (TLC) on silica gel (hexane/ethyl acetate = 2/1) to give 169 mg (91%) of (−)-**6**: $[\alpha]_D^{25}$ −438° (*c* 0.63, chloroform); m.p. 137–139 °C. ^1H NMR ($CDCl_3$) δ

1.59 (d, J 6.4 Hz, 6H), 2.92 (s, 6H), 3.02 (m, 2H), 4.33 (m, 2H), 4.47 (m, 2H), 4.53 (dq, J 3.0 and 6.4 Hz, 2H), 7.01–7.40 (m, 20H). Anal. Found: C, 71.53; H, 5.95. $C_{40}H_{40}FeO_2P_2$ calc: C, 71.65; H, 6.01%.

X-Ray diffraction study of the palladium complex 4

A reddish brown crystal (0.45 × 0.37 × 0.10 mm) was used for the study. Crystal data: $C_{42}H_{46}Cl_2FeN_2P_2Pd$, $MW = 873.95$; monoclinic space group $P2_1$, a 13.460(2), b 14.540(5), c 10.713(2) Å, β 97.25(1)°, V 2079.9 Å^3; $Z = 2$; $D_{calcd} = 1.395$ g cm^{-3}; μ 10.10 cm^{-1}.

A total of 4946 reflections with $2\theta < 55°$ were collected on an Enraf–Nonius CAD 4 diffractometer using graphite-monochromated Mo-K_α radiation (λ 0.71073 Å). Structure was solved by heavy atom method using SHELX-86 and refined by full-matrix least squares. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were not included in the calculation. The final R and R_w factors were 0.032 and 0.044, respectively, for 3739 observed reflections ($I > 3\sigma(I)$). The absolute configuration of the complex $PdCl_2[(+)$-**2**] was determined to be (S) on the 1-dimethylaminoethyl side chain and (R) on ferrocene planar chirality. The enantiomeric structure gave R and R_w values of 0.034 and 0.046 and so was rejected on the basis of the significance test [15]. All crystallographic calculations were performed on a micro VAX II using the SDP program system. Fractional coordinates, bond lengths, and bond angles are listed in Tables 1, 2, and 3, respectively. Supplementary material providing additional crystallographic details is available from the authors.

References

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

2 (a) T. Hayashi, and M. Kumada, Acc. Chem. Res., 15 (1982) 395; (b) T. Hayashi, Pure Appl. Chem., 60 (1988) 7 and references cited therein.

3 (a) T. Hayashi, K. Hayashizaki, T. Kiyoi, and Y. Ito, J. Am. Chem. Soc., 110 (1988) 8153; (b) T. Hayashi, K. Kanehira, T. Hagihara, and M. Kumada, J. Org. Chem., 53 (1988) 113; (c) T. Hayashi, N. Kawamura, Y. Ito, J. Am. Chem. Soc., 109 (1987) 7876; (d) T. Hayashi, M. Konishi, Y. Okamoto, K. Kabeta, and M. Kumada, J. Org. Chem., 51 (1986) 3772; (e) Y. Ito, M. Sawamura, and T. Hayashi, J. Am. Chem. Soc., 108 (1986) 6405; (f) T. Hayashi, A. Yamamoto, T. Hagihara, Y. Ito, Tetrahedron Lett., 27 (1986) 191.

4 H.B. Kagan in J.D. Morrison (Ed.), Asymmetric Synthesis, Academic Press, New York, 1985, Vol. 5, p. 1.

5 H.B. Kagan and T.P. Dang, J. Am. Chem. Soc., 94 (1972) 6429.

6 M.D. Fryzuk and B. Bosnich, J. Am. Chem. Soc., 99 (1977) 6262.

7 H. Takaya, K. Mashima, K. Koyano, M. Yagi, H. Kumobayashi, T. Taketomi, S. Akutagawa, and R. Noyori, J. Org. Chem., 51 (1986) 629.

8 D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, and I. Ugi, J. Am. Chem. Soc., 92 (1970) 5389.

9 G.R. Knox, J.D. Munro, P.L. Pauson, G.H. Smith, and W.E. Watts, J. Chem. Soc., (1961) 4619.

10 G.W. Gokel, D. Marquarding, and I. Ugi, J. Org. Chem., 37 (1972) 3052.

11 T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, and K. Hirotsu, J. Am. Chem. Soc., 106 (1984) 158.

12 I.R. Butler, W.R. Cullen, T.J. Kim, S.J. Rettig, and J. Trotter, Organometallics, 4 (1985) 972.

13 T. Hayashi, M. Kumada, T. Higuchi, and K. Hirotsu, J. Organomet. Chem., 334 (1987) 195.

14 W.L. Steffen and G.L. Plenik, Inorg. Chem., 15 (1976) 2432.

15 W.C. Hamilton, Acta Cryst., 18 (1965) 502.