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Asymmetric synthesis catalyzed by chiral ferrocenylphosphine-transition metal complexes

IV *. Crystal structure of dichloro[*N*,*N*-dimethyl-1-[1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine]palladium(II) ($PdCl_2$[BPPFA])

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Abstract

An X-ray diffraction study of $PdCl_2$(BPPFA) (BPPFA = racemic ($S^\star$)-*N*,*N*-dimethyl-1-[($R^\star$)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine was carried out. The palladium-BPPFA complex has square-planar geometry with two *cis* chlorine and two phosphorus atoms, and the nitrogen atom which is not bound to palladium. The orientation of the four phenyl groups around the phosphorus atoms is nearly the same as that in its achiral analogue, $PdCl_2$(dppf) (dppf = 1,1′-bis(diphenylphosphino)ferrocene). The aminoalkyl side chain on the cyclopentadienyl ring is responsible for fixing the chiral conformation of the palladium-ferrocenylbisphosphine chelate.

Introduction

We have prepared various types of optically active ferrocenylphosphines [1] and shown that they are effective ligands for several asymmetric reactions catalyzed by transition metal complexes [2]. The ferrocenylphosphines are unique chiral ligands in that structural modifications can be readily made by the introduction of a desired

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* For part III see Ref. 15.

functional group into the side chain depending on the reaction type. The functional group to be introduced is expected to be attracted to the functional group on the prochiral substrate in the diastereomeric transition states to bring about high stereoselectivity [2].

Crystal structure analysis of chiral phosphine transition metal complexes has proved to be a useful tool in the elucidation of the mechanism of stereocontrol in catalytic asymmetric reactions, especially in rhodium-catalyzed hydrogenation of enamide precursors of amino acids [3]. Cullen and coworkers have reported [4] the structure of a chiral ferrocenylmonophosphine (PPFA)-rhodium complex in connection with their study of the asymmetric hydrogenation and have shown that the ligand chelates to the metal through the phosphorus and nitrogen atoms. Here we report the crystal structure of dichloro[($S^\star$)-*N*,*N*-dimethyl-1-[($R^\star$)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine]palladium(II) [$PdCl_2$(BPPFA)] (**1**), which is an effective catalyst for asymmetric Grignard cross-coupling [5]. This work is the first example of crystal structure analysis of chiral ferrocenylphosphine complexes containing two phosphorus atoms. It is expected to provide significant and general information regarding the function of a chiral ligand in the catalytic asymmetric reactions using ferrocenylbisphosphine ligands with functional groups on the side chain, which have been effective not only for the cross-coupling but also for several other catalytic asymmetric reactions [6–9].

Experimental

Preparation of dichloro[($S^\star$)-N,N-dimethyl-1-[($R^\star$)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine]palladium(II) [$PdCl_2$(BPPFA)] (1)

To a suspension of 259 mg (1.0 mmol) of dichlorobis(acetonitrile)palladium(II) in 9 ml of benzene was added with stirring a solution of 626 mg (1.0 mmol) of BPPFA [1] in 9 ml of benzene. After 4 h at room temperature, the reddish brown precipitate which had formed was collected by filtration, washed with benzene, and dried in vacuo to give a quantitative yield of crude **1**. A sample for the X-ray analysis was obtained by recrystallization from chloroform. Attempts to recrystallize an optically active BPPFA-palladium complex failed.

X-Ray analysis of 1

A brown crystal (0.26 × 0.12 × 0.30 mm) grown from chloroform was used for diffraction work. Crystal data: $C_{38}H_{37}NP_2FePdCl_2$, $M_r = 803.7$, triclinic space group $P\bar{1}$. On the basis of 54 reflections, the following unit cell parameters were obtained: a 16.206(9), b 11.372(5), c 10.914(8) Å, α 66.61(4), β 69.14(6), γ 78.62(5)°, V 1722(2) Å^3, D_{calc} (for $Z = 2$) 1.550 g cm^{-3}, and μ(Mo-K_α) 12.2 cm^{-1}.

Data were collected on an automated Philips PW1100 four circle diffractometer with graphite-monochromated Mo-K_α radiation (0.7107 Å). A total of 4367 reflections were obtained for a 2θ range of 3–45°, of which 3532 have $I > 3\sigma(I)$ and were judged observed. Three reflections, monitored every 180 min, showed neither systematic nor significant deviations from their initial intensities. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was applied. The structure was solved by direct methods. Block-diagonal least-squares refinements with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms converged to a residual value

R of 0.023. Neutral atomic scattering factors of Cromer and Waber were used for all atoms [10].

The Pd, Fe, Cl, and P atoms were corrected for the real part of the anomalous dispersion. Supplementary material (fractional coordinates, bond distances, bond angles including hydrogen atoms and observed and calculated structure factors) is available from the authors.

Results and discussion

Structure of 1

The structure of **1** was deduced from an X-ray diffraction study. Fractional coordinates, bond lengths, and bond angles, except for H atoms, are listed in Tables 1, 2, and 3, respectively. A view of the complex normal to the plane (I) consisting of two P and two Cl atoms around the central Pd atom is shown in Fig. 1 and another view along plane I is given in Fig. 2. Plane I is planar within 0.07 Å. Since the deviation of the Pd atom from the plane I is only 0.09 Å, it could also be regarded as being in plane I. The environment of the Pd atom is thus described as a square

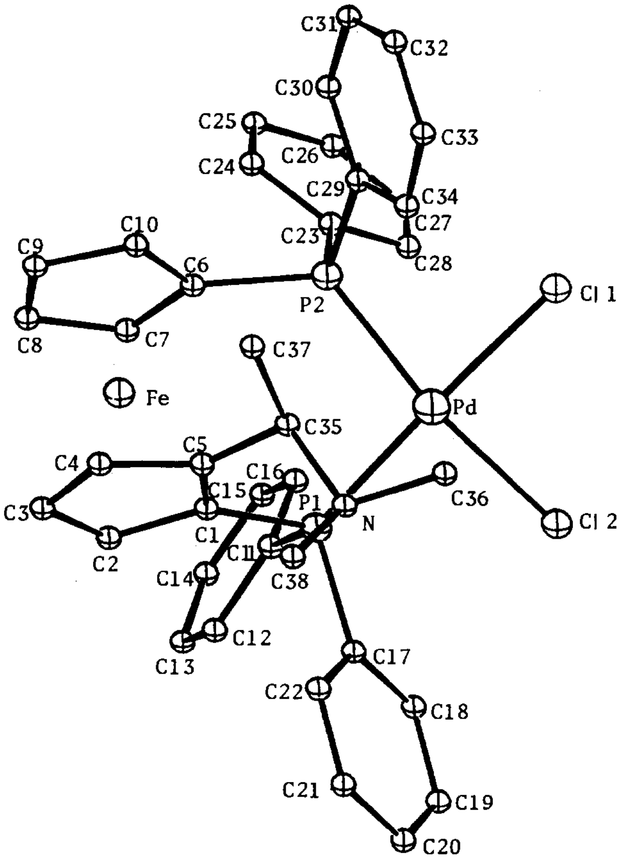


Fig. 1. Molecular structure and atom numbering scheme for $PdCl_2$(BPPFA) (**1**).

Table 1

Fractional coordinates and temperature factors for $PdCl_2$(BPPFA) (**1**) (standard deviations of the least significant figures are given in parentheses)

Atom	x	y	z	B_{eq} or B [a]
Pd	0.75338(2)	0.92247(3)	0.81220(3)	2.44(1)
Fe	0.75583(3)	0.52061(5)	0.8717(1)	2.98(2)
P(1)	0.8477(1)	0.7517(1)	0.8919(1)	2.44(3)
P(2)	0.6982(1)	0.8362(1)	0.7015(1)	2.56(3)
Cl(1)	0.6633(1)	1.1052(1)	0.7284(1)	4.22(4)
Cl(2)	0.8105(1)	1.0448(1)	0.8881(1)	3.98(4)
N	0.6547(2)	0.6593(4)	1.2277(4)	5.5(2)
C(1)	0.8080(2)	0.5926(3)	0.9656(4)	2.8(1)
C(2)	0.8615(2)	0.4811(3)	0.9434(4)	3.3(1)
C(3)	0.8076(3)	0.3764(4)	1.0149(4)	3.9(1)
C(4)	0.7218(3)	0.4178(4)	1.0841(4)	4.0(1)
C(5)	0.7201(2)	0.5521(3)	1.0561(4)	3.2(1)
C(6)	0.7182(2)	0.6684(3)	0.7189(4)	2.9(1)
C(7)	0.8012(2)	0.6077(4)	0.6600(4)	3.4(1)
C(8)	0.7873(3)	0.4776(4)	0.6936(5)	4.5(2)
C(9)	0.6979(3)	0.4570(4)	0.7704(5)	4.7(2)
C(10)	0.6539(3)	0.5733(4)	0.7863(4)	3.9(2)
C(11)	0.9469(2)	0.7525(3)	0.7431(4)	2.7(1)
C(12)	1.0244(2)	0.6770(3)	0.7623(4)	3.3(1)
C(13)	1.0982(3)	0.6823(4)	0.6463(5)	4.2(2)
C(14)	1.0975(3)	0.7608(4)	0.5129(4)	4.1(2)
C(15)	1.0226(3)	0.8358(4)	0.4941(4)	4.1(2)
C(16)	0.9476(2)	0.8332(4)	0.6086(4)	3.3(1)
C(17)	0.8956(2)	0.7467(3)	1.0235(3)	2.7(1)
C(18)	0.9596(2)	0.8316(4)	0.9890(4)	3.3(1)
C(19)	0.9965(2)	0.8216(4)	1.0889(4)	3.8(2)
C(20)	0.9722(3)	0.7309(4)	1.2213(4)	4.1(2)
C(21)	0.9102(3)	0.6471(4)	1.2555(4)	4.0(2)
C(22)	0.8717(2)	0.6561(3)	1.1568(4)	3.3(1)
C(23)	0.7422(2)	0.9121(3)	0.5107(4)	2.7(1)
C(24)	0.7390(3)	0.8517(4)	0.4252(4)	3.4(1)
C(25)	0.7722(3)	0.9084(4)	0.2804(4)	3.7(1)
C(26)	0.8120(5)	1.0217(4)	0.2223(4)	4.1(1)
C(27)	0.8175(3)	1.0803(4)	0.3051(4)	4.2(2)
C(28)	0.7817(3)	1.0277(4)	0.4498(4)	3.6(1)
C(29)	0.5775(2)	0.8555(3)	0.7490(4)	3.2(1)
C(30)	0.5338(3)	0.8541(4)	0.6606(5)	4.4(2)
C(31)	0.4411(3)	0.8589(5)	0.7061(5)	5.4(2)
C(32)	0.3945(3)	0.8658(5)	0.8349(5)	5.6(2)
C(33)	0.4369(3)	0.8692(4)	0.9210(5)	4.9(2)
C(34)	0.5284(4)	0.8661(4)	0.8775(4)	4.0(2)
C(35)	0.6421(2)	0.6326(4)	1.1154(4)	3.9(1)
C(36)	0.5966(4)	0.7680(7)	1.2540(8)	8.5(3)
C(37)	0.5533(3)	0.5782(5)	1.1527(5)	5.4(2)
C(38)	0.6474(4)	0.5488(8)	1.3551(6)	8.4(3)

[a] B_{eq} is given by the expression $4/3\Sigma_i\Sigma_j B_{ij}\cdot a_i\cdot a_j$.

planar with two *cis* chlorine and two phosphorus atoms. The geometry around the central Pd atom is almost equal to that of $PdCl_2$(dppf) [11,12], where dppf stands for 1,1′-bis(diphenylphosphino)ferrocene, an achiral ferrocenylbisphosphine ligand

Table 2

Bond distances (Å) of PdCl$_2$(BPPFA) (1) (standard deviations of the least significant figure of each distance is given in parentheses)

Pd–P(1)	2.302(1)	C(12)–C(13)	1.388(5)
Pd–P(2)	2.296(1)	C(13)–C(14)	1.376(6)
Pd–Cl(1)	2.351(1)	C(14)–C(15)	1.369(6)
Pd–Cl(2)	2.334(1)	C(15)–C(16)	1.394(5)
Fe–C(1)	1.998(5)	C(17)–C(18)	1.406(6)
Fe–C(2)	2.030(5)	C(17)–C(22)	1.376(4)
Fe–C(3)	2.048(4)	C(18)–C(19)	1.378(7)
Fe–C(4)	2.058(4)	C(19)–C(20)	1.371(5)
Fe–C(5)	2.043(4)	C(20)–C(21)	1.372(7)
Fe–C(6)	2.018(3)	C(21)–C(22)	1.389(7)
Fe–C(7)	2.030(3)	C(23)–C(24)	1.379(7)
Fe–C(8)	2.056(5)	C(23)–C(28)	1.383(5)
Fe–C(9)	2.065(6)	C(24)–C(25)	1.388(5)
Fe–C(10)	2.054(5)	C(25)–C(26)	1.366(6)
N–C(35)	1.462(8)	C(26)–C(27)	1.352(8)
N–C(36)	1.458(9)	C(27)–C(28)	1.386(5)
N–C(38)	1.442(7)	C(29)–C(30)	1.391(7)
C(1)–C(2)	1.441(5)	C(29)–C(34)	1.383(6)
C(1)–C(5)	1.455(5)	C(30)–C(31)	1.402(6)
C(2)–C(3)	1.406(5)	C(31)–C(32)	1.364(8)
C(3)–C(4)	1.414(5)	C(32)–C(33)	1.362(9)
C(4)–C(5)	1.430(6)	C(33)–C(34)	1.385(6)
C(5)–C(35)	1.512(5)	C(35)–C(37)	1.534(7)
C(6)–C(7)	1.438(5)	P(1)–C(1)	1.808(4)
C(6)–C(10)	1.437(6)	P(1)–C(11)	1.832(3)
C(7)–C(8)	1.420(6)	P(1)–C(17)	1.839(5)
C(8)–C(9)	1.403(6)	P(2)–C(6)	1.815(4)
C(9)–C(10)	1.418(6)	P(2)–C(23)	1.830(3)
C(11)–C(12)	1.405(5)	P(2)–C(29)	1.829(4)
C(11)–C(16)	1.386(5)		

lacking the aminoalkyl side chain. The average distances of two Pd–P bonds and the two Pd–Cl bonds are 2.299(1) and 2.343(1) Å, respectively. The relations between the large P–Pd–P angle (98.79(4)°), the small Cl–Pd–Cl angle (87.83(4)°) and the long Pd–P and the short Pd–Cl distances in the present complex are similar to those of the palladium-dppf complex [11]. The two cyclopentadienyl rings, which are nearly parallel (deviation of 4.7°) to each other, are in a staggered conformation with a twist angle of 30°. The dihedral angles between plane I and each cyclopentadienyl plane are 66 and 62°. The non-bonded distances P(1)–P(2), Cl(1)–Cl(2), Pd–N, and Pd–C(35) are 3.491(1), 3.249(2), 4.246(4), and 3.809(4) Å, respectively.

Interpretation of structure 1

The cyclopentadienyl and phenyl groups on the phosphorus atoms in BPPFA are arranged around the metal in a manner similar to that in the dppf complex, whose structure has been previously reported [11]. Thus, the palladium-BPPFA complex exhibits square-planar geometry with two *cis* chlorine and two phosphorus atoms, and the nitrogen atom which is not bound to palladium. The two cyclopentadienyl rings are planar and in a staggered conformation. The ferrocene moiety is not

(Continued on p. 202)

Table 3

Bond angles (°) of PdCl$_2$(BPPFA) (1) (standard deviations of the least significant figure of each angle is given in parentheses)

P(1)–Pd–P(2)	98.79(4)	C(1)–P(1)–C(11)	106.3(2)
P(1)–Pd–Cl(1)	176.55(4)	C(1)–P(1)–C(17)	101.6(2)
P(1)–Pd–Cl(2)	89.16(4)	C(11)–P(1)–C(17)	101.7(2)
P(2)–Pd–Cl(1)	84.00(4)	Pd–P(2)–C(6)	123.0(2)
P(2)–Pd–Cl(2)	169.34(3)	Pd–P(2)–C(23)	110.8(1)
Cl(1)–Pd–Cl(2)	87.83(4)	Pd–P(2)–C(29)	112.7(2)
C(1)–Fe–C(2)	41.9(2)	C(6)–P(2)–C(23)	99.9(2)
C(1)–Fe–C(3)	69.2(2)	C(6)–P(2)–C(29)	101.3(2)
C(1)–Fe–C(4)	69.5(2)	C(23)–P(2)–C(29)	107.5(2)
C(1)–Fe–C(5)	42.2(1)	C(35)–N–C(36)	111.3(5)
C(1)–Fe–C(6)	108.1(2)	C(35)–N–C(38)	113.7(5)
C(1)–Fe–C(7)	110.6(2)	C(36)–N–C(38)	111.7(5)
C(1)–Fe–C(8)	140.9(2)	Fe–C(1)–P(1)	125.1(2)
C(1)–Fe–C(9)	176.5(1)	Fe–C(1)–C(2)	70.2(3)
C(1)–Fe–C(10)	136.4(2)	Fe–C(1)–C(5)	70.5(3)
C(2)–Fe–C(3)	40.3(2)	P(1)–C(1)–C(2)	124.3(2)
C(2)–Fe–C(4)	68.5(2)	P(1)–C(1)–C(5)	128.0(3)
C(2)–Fe–C(5)	70.1(2)	C(2)–C(1)–C(5)	107.7(3)
C(2)–Fe–C(6)	134.1(1)	Fe–C(2)–C(1)	67.9(2)
C(2)–Fe–C(7)	107.1(2)	Fe–C(2)–C(3)	70.5(3)
C(2)–Fe–C(8)	110.9(2)	C(1)–C(2)–C(3)	107.7(3)
C(2)–Fe–C(9)	141.3(2)	Fe–C(3)–C(2)	69.1(2)
C(2)–Fe–C(10)	175.4(1)	Fe–C(3)–C(4)	70.2(2)
C(3)–Fe–C(4)	40.3(2)	C(2)–C(3)–C(4)	109.3(4)
C(3)–Fe–C(5)	68.8(2)	Fe–C(4)–C(3)	69.5(2)
C(3)–Fe–C(6)	173.8(1)	Fe–C(4)–C(5)	69.0(2)
C(3)–Fe–C(7)	133.4(2)	C(3)–C(4)–C(5)	108.3(3)
C(3)–Fe–C(8)	109.3(2)	Fe–C(5)–C(1)	67.3(2)
C(3)–Fe–C(9)	114.1(2)	Fe–C(5)–C(4)	70.2(3)
C(3)–Fe–C(10)	144.2(2)	Fe–C(5)–C(35)	129.2(3)
C(4)–Fe–C(5)	40.8(2)	C(1)–C(5)–C(4)	106.5(3)
C(4)–Fe–C(6)	144.8(1)	C(1)–C(5)–C(35)	127.7(4)
C(4)–Fe–C(7)	173.6(2)	C(4)–C(5)–C(35)	125.7(3)
C(4)–Fe–C(8)	135.6(2)	Fe–C(6)–P(2)	127.4(3)
C(4)–Fe–C(9)	112.3(2)	Fe–C(6)–C(7)	69.6(2)
C(4)–Fe–C(10)	115.7(2)	Fe–C(6)–C(10)	70.7(2)
C(5)–Fe–C(6)	113.2(2)	P(2)–C(6)–C(7)	125.9(3)
C(5)–Fe–C(7)	143.1(2)	P(2)–C(6)–C(10)	126.9(3)
C(5)–Fe–C(8)	176.1(2)	C(7)–C(6)–C(10)	107.1(3)
C(5)–Fe–C(9)	137.3(2)	Fe–C(7)–C(6)	68.8(2)
C(5)–Fe–C(10)	111.4(2)	Fe–C(7)–C(8)	70.6(2)
C(6)–Fe–C(7)	41.6(1)	C(6)–C(7)–C(8)	107.8(3)
C(6)–Fe–C(8)	69.1(2)	Fe–C(8)–C(7)	68.7(3)
C(6)–Fe–C(9)	68.7(2)	Fe–C(8)–C(9)	70.5(3)
C(6)–Fe–C(10)	41.3(2)	C(7)–C(8)–C(9)	108.5(4)
C(7)–Fe–C(8)	40.7(2)	Fe–C(9)–C(8)	69.7(3)
C(7)–Fe–C(9)	68.0(2)	Fe–C(9)–C(10)	69.4(3)
C(7)–Fe–C(10)	69.0(2)	C(8)–C(9)–C(10)	108.9(4)
C(8)–Fe–C(9)	39.8(2)	Fe–C(10)–C(6)	68.0(2)
C(8)–Fe–C(10)	67.9(2)	Fe–C(10)–C(9)	70.3(3)
C(9)–Fe–C(10)	40.3(2)	C(6)–C(10)–C(9)	107.7(3)
Pd–P(1)–C(1)	117.5(1)	P(1)–C(11)–C(12)	121.6(3)
Pd–P(1)–C(11)	107.7(1)	P(1)–C(11)–C(16)	119.7(3)
Pd–P(1)–C(17)	120.2(1)	C(12)–C(11)–C(16)	118.7(3)

Table 3 (continued)

C(11)-C(12)-C(13)	119.4(3)	C(23)-C(24)-C(25)	120.3(4)
C(12)-C(13)-C(14)	121.4(4)	C(24)-C(25)-C(26)	119.8(5)
C(13)-C(14)-C(15)	119.3(3)	C(25)-C(26)-C(27)	120.3(3)
C(14)-C(15)-C(16)	120.6(4)	C(26)-C(27)-C(28)	120.7(4)
C(11)-C(16)-C(15)	120.5(3)	C(23)-C(28)-C(27)	119.8(5)
P(1)-C(17)-C(18)	121.0(2)	P(2)-C(29)-C(30)	121.0(3)
P(1)-C(17)-C(22)	120.3(3)	P(2)-C(29)-C(34)	119.6(4)
C(18)-C(17)-C(22)	118.7(4)	C(30)-C(29)-C(34)	119.3(4)
C(17)-C(18)-C(19)	119.3(3)	C(29)-C(30)-C(31)	119.1(4)
C(18)-C(19)-C(20)	121.5(4)	C(30)-C(31)-C(32)	120.4(6)
C(19)-C(20)-C(21)	119.6(5)	C(31)-C(32)-C(33)	120.8(4)
C(20)-C(21)-C(22)	119.8(3)	C(32)-C(33)-C(34)	119.8(4)
C(17)-C(22)-C(21)	121.1(4)	C(29)-C(34)-C(33)	120.6(5)
P(2)-C(23)-C(24)	119.9(3)	N-C(35)-C(5)	111.1(4)
P(2)-C(23)-C(28)	121.2(4)	N-C(35)-C(37)	114.9(3)
C(24)-C(23)-C(28)	118.9(3)	C(5)-C(35)-C(37)	112.4(4)

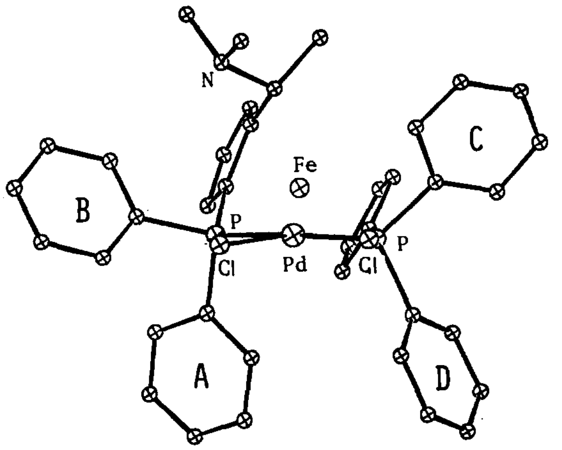
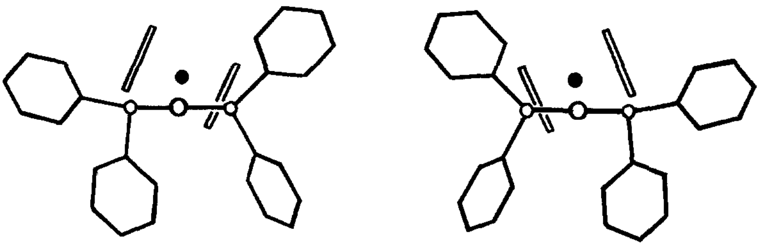
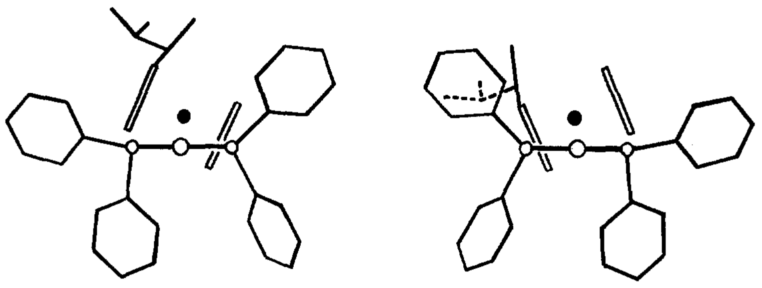


Fig. 2. View of 1 along the square plane.



(2) (3)

Fig. 3. Schematic structure of $PdCl_2(dppf)$.



(4) (5)

Fig. 4. Schematic structure of $PdCl_2$(BPPFA) (1).

parallel to the [$PdCl_2P_2$] plane. When observed along the square plane (Fig. 2), one of the cyclopentadienyl rings lies above the plane, and the other is bisected by the plane. The dimethylaminoethyl group of the ring above the plane is attached to the ring at the upper carbon. Of the four phenyl rings, the ring which is in an axial position in the bidentate ligand-palladium system (ring A) is furthest from the metal, and thus exposes its face to palladium, and offers a chiral pocket which allows a bulky substituent (on a substrate) to coordinate. Ring B which is equatorial, protrudes toward the space where the catalytic reaction takes place. The other two phenyl rings, C and D, are located above and below the plane with minor axial–equatorial distortion.

The orientation of the four phenyl groups in $PdCl_2$(dppf) [11] is nearly the same as that in the BPPFA complex. The crystal structure of the dppf complex (schematic structure **2** in Fig. 3) is chiral, but it should have its enantiomeric conformation (**3**) present in an equal number since the ligand is achiral and the complexes does not have net asymmetry. In the case of BPPFA complex, the conformation (schematic structure **4** in Fig. 4) shown in the crystal structure is expected to be frozen so that the alkyl side chain is directed toward the upper open space. Another conformation (**5**), which is not enantiomeric to **4** because of the presence of a substituent on the cyclopentadienyl ring, is unfavorable owing to steric hindrance between the alkyl side-chain and one of the phenyl groups. Thus the alkyl side-chain can fix the conformation of the ferrocene moiety and consequently the orientation of phenyl rings which must play a leading role in controlling the stereochemistry in asymmetric reactions by chiral ferrocenylphosphine-transition metal catalysts. The relationship between the dppf complex and the BPPFA complex is similar to that between dppe (1,2-bis(diphenylphoshino)ethane) complex and chiraphos (2,3-bis(diphenylphosphino)butane) or prophos (1,2-bis(diphenylphoshino)propane) complex which has been studied to rationalize the rhodium-catalyzed asymmetric hydrogenation of olefins [3,13,14]. The favored orientation of diphenylphosphino groups on a chiraphos or prophos complex has been shown to be caused by the equatorial conformation of the methyl group(s) in the five-membered chelate ring.

The 1-(dimethylamino)ethyl group attached to the cyclopentadienyl ring is located directly above the [$PdCl_2P_2$] plane (Fig. 1), though the amino group is not coordinating to palladium, as evidenced by the large separation (4.246 Å) of the palladium and nitrogen atoms. We have shown that chiral ferrocenylphosphine ligands containing an appropriate functional group on the side chain are very effective for several asymmetric reactions catalyzed by transition metal complexes, e.g., rhodium-catalyzed hydrogenation [6,7], nickel- or palladium-catalyzed Grignard cross-coupling [5,15], palladium-catalyzed allylation [8], and gold-catalyzed aldol reaction of isocyanoacetate [9], and have suggested that the high stereoselectivity is ascribed largely to attractive interactions between functional groups on the ferrocene side chain and on the substrate. The catalytic reactions must take place on that side of the metal which is opposite the phosphine ligands. The direction of the side chain, which is shown to face the reaction site in the crystal, supports the stereocontrol by attractive interactions occurring when a prochiral substrate approaches the catalyst center that bears a functionalized ferrocenylphosphine ligand.

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