Optically active (2-aminomethylferrocenyl)phosphines with the phosphorus chiral center

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The reaction of an enantiomeric planar-chiral palladium derivative of dimethylaminomethylferrocene with PhMePLi in THF at room temperature afforded a 1.5 : 1.0 mixture of diastereomeric aminophosphines containing the phosphorus asymmetrical center along with a chiral plane. The absolute configuration of the phosphorus atom was determined based on the X-ray diffraction data for the complex of the minor diastereomer with PdI_2. The presence of the (*S*)-chiral plane in the initial palladium compound favors the predominant formation of the product with the (*S*)-configuration of the phosphorus center.

Key words: ferrocene, aminophosphines, asymmetrical phosphorus atom, optical activity.

It is known that some heteroatomic ferrocene derivatives can be successfully used as ligands in catalytic processes. Complexes of divalent transition metals with 1,1′-bis(diphenylphosphino)ferrocene are the most universal catalysts.[1] However, the last-mentioned ligand is achiral and hence it cannot be used for enantioselective synthesis. Optically active 1,2-homoannular 2-aminoalkyl-1-diarylphosphino- and 2-aminoalkyl-1-hydroxyalkylferrocenes, which contain at least one α-carbon asymmetrical center along with a chiral plane, are used in the asymmetric synthesis. In the case of aminophosphines, the chiral plane makes the major contribution to the enantioselectivity of the catalytic processes, but the presence of the asymmetrical center in the side chain may also have a substantial effect on the efficiency of the inducing ligand.[2]

The aim of the present work was to synthesize the previously unknown planar-chiral (2-aminomethylferrocenyl)phosphines, which contain the phosphorus asymmetrical center, in the optically active form.

Results and Discussion

The enantiomeric palladium derivative of dimethylaminomethylferrocene (**1**)[3] was used as the starting compound. The previously reported reaction of palladium metallacycles with lithium phosphides, which results in their demetallation with the introduction of the di(organyl)phosphino group, is an alternative approach to the synthesis of aminoalkylferrocenylphosphines,[4] which are generally prepared by the reactions of 2-lithiated aminoalkylferrocenes with R_2PCl.[5]

In the present work, the above-mentioned reaction was used for introducing a substituent containing the chiral phosphorus atom. For this purpose, we performed the reaction of compound **1** with MePhPLi, which was prepared by treatment of $MePh_2P$ with metallic lithium.*[6] It is believed that the initial stage of the reaction involves the exchange of the halogen atom for the phosphide anion followed by reductive elimination of palladium accompanied by the formation of a product with the ferrocene—phosphorus bond, which can be obtained as a mixture of two diastereomers **2** and **3** (Scheme 1).

The reaction of dimer **1** with MePhPLi was carried out in THF in the presence of two equivalents of the initial phosphine at room temperature for 3 h. It should be noted that products **2** and **3** are more sensitive to atmospheric oxygen than their diphenylphosphine analog. A strictly inert atmosphere is particularly necessary for the treatment of the mixture after completion of the reaction because under the above-described conditions, palladium is eliminated, most likely, in the form of low-valent phosphine complexes, which are known as efficient catalysts of oxidation of tertiary phosphines with atmospheric oxygen.[7]

It seems likely that oxidation of phosphines that formed initially is of little importance and hence the operations may be also performed with oxides. Actually, the stereochemistry of oxidation of phosphines, *viz.*, the retention of the configuration, is known,[8] and $HSiCl_3$

* PhLi, which is formed simultaneously, is generally decomposed with Bu^tCl to avoid side reactions. However, under the conditions of the reaction used, PhLi is inert with respect to Pd derivative **1**, which is evident from our numerous experiments, and a product of a combination of these reagents, if it ever forms, occurs in only trace amounts. Hence, the above-mentioned treatment is not necessary.

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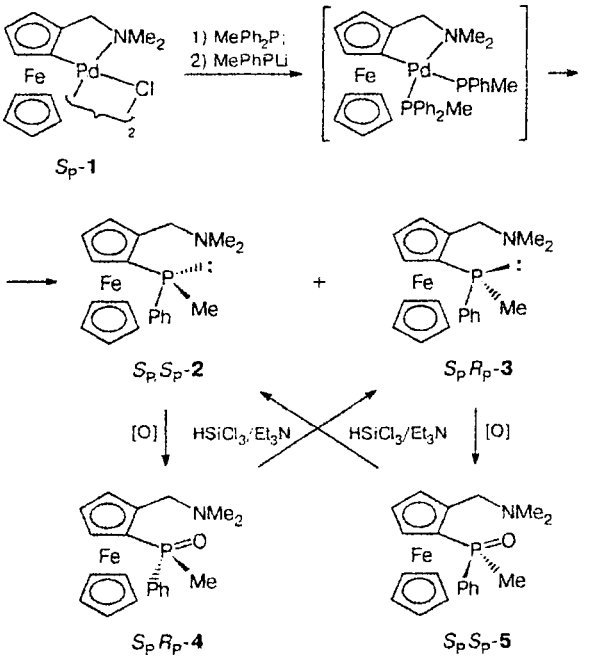
Scheme 1



has long been known as an excellent reagent for reduction of oxides. Under the action of this reagent in the presence of triethylamine, phosphines are obtained in high yields with an insignificant degree of racemization.[9] In the case of diastereomers, the latter fact is of no importance because epimerization at the phosphorus atom may lead only to a change in the ratio of diastereomers, while the optical activity persists. Reduction under the above-mentioned conditions proceeds with complete inversion of the configuration, *i.e.*, correlation with the initial stereochemistry of the chiral phosphorus center in molecules **2** and **3** is possible.

This approach was tested, and the mixture was worked up in air after completion of the reaction. Aminophosphines **2** and **3** were not detected even in trace amounts and only oxides **4** and **5** were found, which were characterized by ^{31}P and ^{1}H NMR spectroscopy and mass spectrometry. However, the procedure for the separation of compounds **4** and **5** from organic phosphine oxides, which are similar in solubility and chromatographic properties, appeared to be laborious and was accompanied by large losses. We failed to obtain analytically pure specimens, which, in turn, did not allow us to determine the optical rotation of diastereomers **4** and **5**. At the same time, the performance of all stages of the reaction under an inert atmosphere provided a possibility of synthesizing aminophosphines **2** and **3**. The latter are readily soluble in aliphatic hydrocarbons and they remained in solution when a fourfold volume of hexane was added to the reaction mixture to precipitate palladium complexes. We succeeded in purifying diastereomers **2** and **3** and in performing their selective separation by chromatography on a column with silica gel.

Aminophosphines **2** and **3** were obtained in a ratio of ~1.5 : 1.0 in a total yield of ~52%. These compounds are stable in pure form upon storage under an argon atmosphere and in a hexane solution. In a hexane solution, some fast operations, for example, measurements of the optical rotation, can be performed in air without visible oxidation of aminophosphines. In chloroform under analogous conditions, oxides are formed virtually immediately. If partial oxidation does occur in the course of some operations with aminophosphine **2** or **3**, the aminophosphine can be extracted with hexane and the remaining oxide can be reduced with $HSiCl_3$ in the presence of Et_3N. As follows from the data of ^{1}H NMR spectroscopy of the products, aminophosphines **3** and **2** are formed from oxides **4** and **5**, respectively, (see Scheme 1), *i.e.*, this reaction proceeds with complete inversion of the configuration,* which is in agreement with the published data.[9]

The maximum optical rotation $[\alpha]_D$ with respect to 100% optical purity is 292° and 116° for diastereomers **2** and **3**, respectively. The ^{31}P and ^{1}H NMR spectra of compounds **2** and **3** are consistent with the structures assigned as regards both the positions and the character of the signals. A comparison of the ^{1}H NMR spectra shows the relative deshielding of the protons of the nonsubstituted cyclopentadienyl ring in diastereomer **3** compared to those in diastereomer **2** (δ 4.14 and 3.91, respectively), the shielding of the protons of the *N*-methyl groups (δ 1.91 and 2.16, respectively), and, what is most important, the substantially larger difference between the chemical shifts of the diastereotopic methylene protons ($\Delta\delta$ = 0.18 and 0.72, respectively). Undoubtedly, the observed parameters are associated with the effect of the phenyl group, which exhibits strong magnetic anisotropy, and agree well with the predominant conformation of the phenyl group in molecule **3**. This conformation follows from the structure of **3** established by X-ray analysis. In going from phosphines **2** and **3** to their oxides **4** and **5**, the ^{1}H NMR spectra change only slightly and the diastereomers remain recognizable, which corresponds to the retention of the configuration upon oxidation of phosphines. Only the value of the spin-spin coupling constant of the phosphorus nucleus with the protons of the methyl group attached to the phosphorus atom increases (actually, an increase is always observed in these cases), the signals of these protons are shifted downfield (at δ 1.49 and 1.99 for **2** and **4**, respectively, and at δ 1.54 and 1.82 for **3** and **5**, respectively), and the protons of the *N*-methyl groups in molecule **4** are more shielded than those in molecule **5** (at δ 2.17 and 1.77, respectively).

* The case in hand is the actual inversion of the configuration because, according to the IUPAC rules, the stereochemical descriptor of the initial oxides and the aminophosphines prepared under the above-mentioned conditions remains the same.

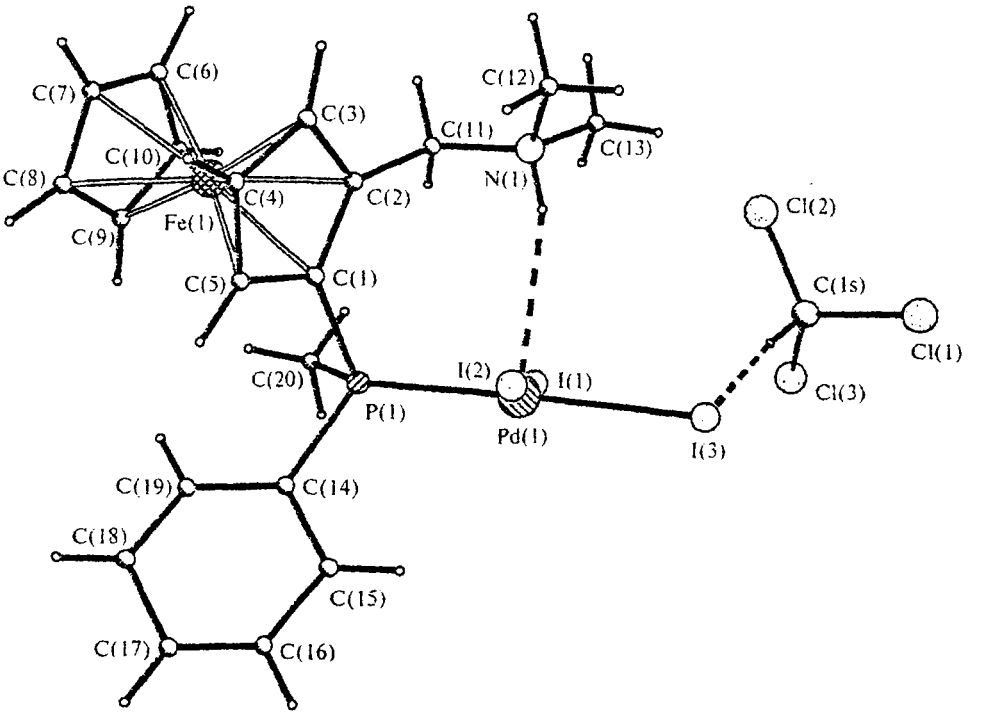


Fig. 1. Molecular structure and the character of the hydrogen bonds in the structure of **6**.

With the aim of performing direct determination of the absolute configurations of the phosphorus atoms in diastereomers **2** and **3** (which exist as viscous oils) by X-ray analysis, these compounds were treated with PdI_2 to convert them into solid crystalline chelate complexes. Crystals suitable for X-ray study were obtained for the complex of the minor diastereomer **3** upon storage of its solution in $CDCl_3$ in a tube after the ^1H NMR spectrum was recorded. It appeared that the composition and the structure of this complex (**6**) slightly differ from those expected. Thus, an open structure with the protonated dimethylamino group and the phosphorus atom coordinated by the PdI_3^- anion (Fig. 1) was established instead of the six-membered chelate with the N—PdI_2—P fragment. The structure of **6** consists of the bipolar complex (1-MePhP-2-$Me_2HN^+CH_2C_5H_3FeC_5H_5$)$PdI_3^-$ molecules and $CHCl_3$ molecules of solvation,* which are linked *via* I(3)...H(1s)—C(1s) hydrogen bonds (the parameters of the hydrogen bond are as follows: I(3)...H(1s), 2.80(2) Å; I(3)...C(1s), 3.754(8) Å; the I(3)—H(1s)—C(1s) angle is 164.1(6)°). The Pd atom, three I atoms, and the P atom of the phosphine ligand form a planar-square polyhedron (the average deviation of the atoms from the PdI_3P plane is 0.09 Å). The Pd—I bond lengths are nonequivalent. The longest bond (Pd(1)—I(3), 2.647(2) Å) is in the *trans* position with respect to the Pd(1)—P(1) bond, whose length is typical of bonds with phosphine ligands (2.273(4) Å; the mean values of the Pd—P distances in the Pd—PMe_3 and Pd—$PPhMe_2$ groups are 2.287 and 2.293 Å, respectively[10]). This elongation may be associated with the *trans*-effect of the phosphine ligand and with the involvement of the I(3) atom in hydrogen bonding. The remaining two Pd—I bonds (Pd(1)—I(1), 2.629(2) Å; and Pd(1)—I(2), 2.607(2) Å) are substantially shorter.

The Cp ring is virtually orthogonal to the $CH_2N^+HMe_2$ fragment (the C(1)—C(2)—C(11)—N(1) torsion angle is 92(2)°). Apparently, this orientation results from the interaction between the palladium atom and the hydrogen atom of the protonated amino group (Pd(1)...H, 2.64 Å; Pd(1)...N(1), 3.466 Å; the Pd(1)—H "bond" forms an angle of 13° with the coordination PdI_3P plane), which is analogous to the known agostic Pd...H—C interaction[11] observed, for example, in the complexes $(PPhMe_2)_2PdI_2$[12] (Pd...H, 2.8 Å) and (1-methylcytosine)$_2PdCl_2$[13] (Pd...H, 2.66 Å). The P(1)—C(1), P(1)—C(14), and P(1)—C(20) bond lengths (1.82(2), 1.80(2), and 1.84(2) Å, respectively) are equal within the experimental error and agree with the mean length of the bonds between the four-coordinate P atom and the C(Alk) or C(Ar) atoms (1.80 Å).[10]

Hence, treatment of diastereomers **2** and **3** with palladium(II) iodide is accompanied by the opening of the chelate ring under the action of HI, which can be

* Strictly speaking, it is deuterochloroform, but the hydrogen isotopes cannot be distinguished by X-ray diffraction analysis and hereinafter deuterium is changed to hydrogen for convenience.

formed, for example, as a result of decomposition of PdI_2 followed by the reaction of I_2, which was liberated, with traces of water. This is indicative of instability of the six-membered metallacycle with the bidentate N,P-ligand. The stereochemistry of the phosphorus atom in the initial phosphine **3** can be determined from the above-described structure because the Pd—P coordination bond persists. The absolute configuration of the phosphorus center (*R*) was determined using the refinement of Flack's parameter based on the X-ray diffraction data. In aminophosphine **2**, which was predominantly formed, the phosphorus atom has the (*S*)-configuration, which is kinetically more favorable in the case of the (*S*)-configuration of the chiral plane in the initial dimer **1**.

Experimental

The ^1H and ^{31}P NMR spectra were recorded on a Bruker WP-200 SY instrument (200.13 MHz) in $CDCl_3$; the ^{31}P chemical shifts (δ) were measured relative to an 85% H_3PO_4 solution. The mass spectra were obtained on a Kratos MS-890 instrument. The optical rotation was measured on an EPO-1 polarimeter. The solvents were purified according to standard procedures. All operations associated with the synthesis, isolation, and identification of aminophosphines were carried out under an argon atmosphere; THF was distilled over sodium benzophenone ketyl immediately before use.

2-*N*,*N*-Dimethylaminomethylferrocenylmethylphenylphosphine oxides (4 and 5). Diphenylmethylphosphine (0.5 mL, 2.687 mmol) and finely divided lithium (108 mg, an excess) were stirred in THF (5 mL) for 3.5 h. The solution of lithium methylphenylphosphide was filtered from an excess of lithium and then a solution prepared from complex **1** (0.8485 g, 2.21 mmol) ($[\alpha]_D$ +463°, *ee* 70%) and diphenylmethylphosphine (0.82 mL, 4.42 mmol) in THF (10 mL) was added dropwise to the filtrate. The reaction mixture was kept under an argon atmosphere overnight. Then water, ethylenediamine (to convert palladium complexes into the water-soluble form), and benzene were added, and the organic layer was separated, washed with water, and chromatographed on a column with silica gel. Diphenylmethylphosphine oxide and dimemethylaminomethylferrocene were eluted with 1 : 1 benzene—ethyl acetate and 10 : 1 benzene—Et_3N mixtures, respectively. Compounds **4** and **5** (R_f 0.37 and 0.22, respectively) were eluted with a 3 : 1 benzene—Et_3N mixture. After additional separation on Silufol plates, oxides **4** and **5** were obtained in yields of 117.5 and 81 mg, respectively. The total yield was 23.6%. **Diastereomer 4.** ^1H NMR ($CDCl_3$), δ: 1.99 (d, 3 H, CH_3P, $^2J_{PH}$ = 13.78 Hz); 2.17 (s, 6 H, $N(CH_3)_2$); 2.89 and 4.06 (AB system, 2 H, $C\underline{H}_2N(CH_3)_2$, ^2J = 12.73 Hz); 4.17 (s, 5 H, C_5H_5); 3.97, 4.22, and 4.34 (all br.s, 3 H, C_5H_3); 7.46—7.89 (m, 5 H, C_6H_5P). ^{31}P NMR ($CDCl_3$), δ: +31.37. MS, *m/z*: 381 $[M]^+$. **Diastereomer 5.** ^1H NMR ($CDCl_3$), δ: 1.77 (s, 6 H, $N(CH_3)_2$); 1.82 (d, 3 H, CH_3P, $^2J_{PH}$ = 13.77 Hz); 3.29 and 3.47 (AB system, 2 H, $C\underline{H}_2N(CH_3)_2$, ^2J = 13.17 Hz); 4.27 (s, 5 H, C_5H_5); 4.14, 4.34, and 4.50 (all br.s, 3 H, C_5H_3); 7.30—7.63 (m, 5 H, C_6H_5P). ^{31}P NMR ($CDCl_3$), δ: +30.79. MS, *m/z*: 381 $[M]^+$.

2-*N*,*N*-Dimethylaminomethyl-1-methylphenylphosphinoferrocenes (2 and 3). Diphenylmethylphosphine (0.3 mL, 1.612 mmol) and finely divided lithium (80 mg, an excess) were stirred in anhydrous THF (2 mL) for 80 min. The solution of lithium methylphenylphosphide was filtered from an excess of lithium. Then freshly distilled Bu^{t}Cl (0.14 mL, 1.29 mmol) was added to the filtrate to decompose phenyl-

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic factors ($U_{eq}/Å^2$; isotropic ($U_{iso}/Å^2$) for H atoms) in the crystal of **6**

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}
Pd(1)	7680(1)	7406(1)	1385(1)	35(1)
Fe(1)	3340(3)	3718(2)	1474(1)	50(1)
I(1)	8984(2)	6770(1)	705(1)	57(1)
I(2)	6108(2)	8179(1)	2005(1)	63(1)
I(3)	8456(2)	9940(1)	1275(1)	63(1)
P(1)	6985(5)	5271(4)	1534(2)	41(1)
N(1)	4053(22)	7808(14)	977(5)	62(5)
C(1)	4916(20)	5160(16)	1594(5)	34(4)
C(2)	3769(20)	5667(16)	1355(5)	37(4)
C(3)	2339(25)	5564(19)	1570(6)	54(5)
C(4)	2638(22)	4920(22)	1933(6)	62(6)
C(5)	4216(22)	4663(19)	1964(5)	47(5)
C(6)	2138(46)	2639(30)	1090(11)	117(12)
C(7)	1730(28)	2316(27)	1442(13)	109(12)
C(8)	3017(39)	1780(21)	1626(6)	81(8)
C(9)	4186(34)	1888(22)	1341(10)	92(9)
C(10)	3648(49)	2430(29)	994(8)	105(12)
C(11)	3927(28)	6335(17)	971(5)	55(5)
C(12)	2765(27)	8469(18)	1171(7)	81(8)
C(13)	4413(29)	8360(22)	575(6)	84(8)
C(14)	7825(23)	4576(20)	1979(6)	56(6)
C(15)	8633(25)	5378(21)	2251(5)	61(6)
C(16)	9189(24)	4767(28)	2587(6)	76(7)
C(17)	8894(32)	3516(28)	2702(7)	100(11)
C(18)	8047(30)	2669(23)	2408(7)	88(8)
C(19)	7557(27)	3183(20)	2071(7)	72(7)
C(20)	7397(23)	3999(17)	1152(5)	55(5)
C(1s)	1029(44)	645(27)	185(6)	111(11)
Cl(1)	1035(16)	2341(11)	223(2)	162(4)
Cl(2)	2587(10)	18(11)	−62(2)	125(3)
Cl(3)	712(9)	83(11)	−36(2)	116(3)
HN	4888(22)	7993(14)	1130(5)	74
H(3A)	1329(25)	5850(19)	1473(6)	65
H(4A)	1864(22)	4683(22)	2133(6)	74
H(5A)	4748(22)	4244(19)	2189(5)	56
H(6A)	1420(46)	3055(30)	902(11)	140
H(7A)	691(28)	2365(27)	1553(13)	131
H(8A)	3084(39)	1382(21)	1892(6)	97
H(9A)	5253(34)	1615(22)	1386(10)	111
H(10A)	4183(49)	2582(29)	741(8)	126
H(11A)	3047(28)	6098(17)	809(5)	66
H(11B)	4831(28)	5980(17)	840(5)	66
H(12A)	2916(27)	9421(18)	1165(7)	121
H(12B)	2698(27)	8175(18)	1443(7)	121
H(12C)	1831(27)	8248(18)	1034(7)	121
H(13A)	5269(29)	7884(22)	463(6)	125
H(13B)	4667(29)	9292(22)	598(6)	125
H(13C)	3535(29)	8259(22)	404(6)	125
H(15A)	8786(25)	6286(21)	2204(5)	73
H(16A)	9829(24)	5272(28)	2750(6)	91
H(17A)	9195(32)	3191(28)	2949(7)	120
H(18A)	7867(30)	1771(23)	2463(7)	106
H(19A)	7031(27)	2646(20)	1891(7)	87
H(20A)	6987(23)	4287(17)	900(5)	83
H(20B)	6931(23)	3165(17)	1226(5)	83
H(20C)	8487(23)	3881(17)	1128(5)	83
H(1s)	−1060(44)	286(27)	456(6)	133

Table 2. Bond lengths (d) and bond angles (ω) in complex **6**

Bond	d/Å	Bond	d/Å	Bond	d/Å
Pd(1)—P(1)	2.273(4)	P(1)—C(14)	1.80(2)	C(6)—C(10)	1.37(5)
Pd(1)—I(1)	2.629(2)	P(1)—C(1)	1.82(2)	C(7)—C(8)	1.39(4)
Pd(1)—I(2)	2.607(2)	P(1)—C(20)	1.84(2)	C(8)—C(9)	1.40(3)
Pd(1)—I(3)	2.647(2)	N(1)—C(12)	1.46(3)	C(9)—C(10)	1.37(4)
Fe(1)—C(6)	1.98(3)	N(1)—C(11)	1.48(2)	C(14)—C(15)	1.40(3)
Fe(1)—C(7)	1.99(2)	N(1)—C(13)	1.49(2)	C(14)—C(19)	1.44(3)
Fe(1)—C(8)	2.02(2)	C(1)—C(2)	1.38(2)	C(15)—C(16)	1.37(3)
Fe(1)—C(9)	2.02(2)	C(1)—C(5)	1.47(3)	C(16)—C(17)	1.33(3)
Fe(1)—C(2)	2.02(2)	C(2)—C(3)	1.44(3)	C(17)—C(18)	1.50(4)
Fe(1)—C(1)	2.03(2)	C(2)—C(11)	1.46(2)	C(18)—C(19)	1.31(3)
Fe(1)—C(4)	2.05(2)	C(3)—C(4)	1.40(3)	C(1s)—Cl(1)	1.70(3)
Fe(1)—C(5)	2.04(2)	C(4)—C(5)	1.40(3)	C(1s)—Cl(2)	1.71(3)
Fe(1)—C(3)	2.07(2)	C(6)—C(7)	1.28(4)	C(1s)—Cl(3)	1.78(4)
Fe(1)—C(10)	2.08(3)				

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
P(1)—Pd(1)—I(2)	87.87(13)	C(6)—Fe(1)—C(3)	111.3(12)	C(1)—C(2)—C(11)	128(2)
P(1)—Pd(1)—I(1)	94.54(13)	C(7)—Fe(1)—C(3)	109.9(10)	C(3)—C(2)—C(11)	124(2)
I(2)—Pd(1)—I(1)	172.58(7)	C(8)—Fe(1)—C(3)	139.2(11)	C(4)—C(3)—C(2)	108(2)
P(1)—Pd(1)—I(3)	175.27(14)	C(9)—Fe(1)—C(3)	175.0(10)	C(5)—C(4)—C(3)	109(2)
I(2)—Pd(1)—I(3)	87.84(6)	C(2)—Fe(1)—C(10)	114.7(9)	C(4)—C(5)—C(1)	106(2)
I(1)—Pd(1)—I(3)	89.95(6)	C(1)—Fe(1)—C(10)	120.3(11)	C(7)—C(6)—C(10)	117(4)
C(6)—Fe(1)—C(2)	119.5(12)	C(4)—Fe(1)—C(10)	170.0(13)	C(6)—C(7)—C(8)	107(3)
C(7)—Fe(1)—C(2)	143.0(11)	C(5)—Fe(1)—C(10)	149.5(14)	C(7)—C(8)—C(9)	105(2)
C(8)—Fe(1)—C(2)	175.9(9)	C(3)—Fe(1)—C(10)	136.7(12)	C(10)—C(9)—C(8)	111(3)
C(9)—Fe(1)—C(2)	139.5(10)	C(14)—P(1)—C(1)	106.7(9)	C(6)—C(10)—C(9)	101(3)
C(6)—Fe(1)—C(1)	150.7(13)	C(14)—P(1)—C(20)	103.5(9)	C(2)—C(11)—N(1)	117(2)
C(7)—Fe(1)—C(1)	171.6(13)	C(1)—P(1)—C(20)	103.2(9)	C(15)—C(14)—C(19)	119(2)
C(8)—Fe(1)—C(1)	136.4(10)	C(14)—P(1)—Pd(1)	115.8(7)	C(15)—C(14)—P(1)	121.5(14)
C(9)—Fe(1)—C(1)	116.1(9)	C(1)—P(1)—Pd(1)	110.2(6)	C(19)—C(14)—P(1)	119(2)
C(6)—Fe(1)—C(4)	130.7(13)	C(20)—P(1)—Pd(1)	116.3(6)	C(16)—C(15)—C(14)	117(2)
C(7)—Fe(1)—C(4)	104.1(11)	C(12)—N(1)—C(11)	114(2)	C(17)—C(16)—C(15)	126(3)
C(8)—Fe(1)—C(4)	109.3(9)	C(12)—N(1)—C(13)	114(2)	C(16)—C(17)—C(18)	116(2)
C(9)—Fe(1)—C(4)	143.7(12)	C(11)—N(1)—C(13)	112(2)	C(19)—C(18)—C(17)	121(2)
C(6)—Fe(1)—C(5)	166.6(13)	C(2)—C(1)—C(5)	108(2)	C(18)—C(19)—C(14)	121(2)
C(7)—Fe(1)—C(5)	129.3(13)	C(2)—C(1)—P(1)	129.2(13)	Cl(1)—C(1s)—Cl(2)	114(2)
C(8)—Fe(1)—C(5)	106.9(8)	C(5)—C(1)—P(1)	121.7(13)	Cl(1)—C(1s)—Cl(3)	110(2)
C(9)—Fe(1)—C(5)	117.3(11)	C(1)—C(2)—C(3)	107.9(14)	Cl(2)—C(1s)—Cl(3)	111(13)

lithium and the mixture was stirred for 40 min. A mixture of complex **1** (0.2214 g, 0.576 mmol) ($[\alpha]_D$ −592.6°, CH_2Cl_2, *ee* 89%) and diphenylmethylphosphine (0.2 mL, 1.075 mmol) in THF (4 mL) was added dropwise to the reaction mixture. After 3 h, anhydrous hexane (25 mL) was added and an abundant brick-red precipitate was formed. The solution was decanted into a column with silica gel and successively eluted with petroleum ether and a 5 : 1 petroleum ether—Et_3N mixture. Aminophosphines **2** and **3** and dimethylaminomethylferrocene were obtained in yields of 65.13, 44.98, and 30.49 mg, respectively (the total yield of the phosphines was 52.3%). **Diastereomer 2.** Found (%): C, 65.74; H, 6.96; P, 8.24. $C_{20}H_{24}FeNP$. Calculated (%): C, 65.77; H, 6.62; P, 8.48. ^1H NMR ($CDCl_3$), δ: 1.49 (d, 3 H, CH_3P, $^2J_{PH}$ = 3.78 Hz); 2.16 (s, 6 H, $N(CH_3)_2$); 3.06 and 3.78 (AB system, 2 H, $C\underline{H}_2N(CH_3)_2$, ^2J = 12.80 Hz); 3.91 (s, 5 H, C_5H_5); 3.72, 4.11, and 4.30 (all br.s, 3 H, C_5H_3); 7.40—7.78 (m, 5 H, C_6H_5P). ^{31}P NMR ($CDCl_3$), δ: −43.42. $[\alpha]_D$ −261° (*c* 0.18, *n*-hexane). **Diastereomer 3.** Found (%): C, 65.39; H, 6.46; P, 8.15. $C_{20}H_{24}FeNP$. Calculated (%): C, 65.77; H, 6.62; P, 8.48. ^1H NMR ($CDCl_3$), δ: 1.57 (d, 3 H, CH_3P, $^2J_{PH}$ = 3.61 Hz); 1.91 (s, 6 H, $N(CH_3)_2$); 3.36 and 3.54 (AB system, 2 H, $C\underline{H}_2N(CH_3)_2$, ^2J = 12 Hz); 4.14 (s, 5 H, C_5H_5); 4.30, 4.35, and 4.49 (all br.s, 3 H, C_5H_3); 7.15—7.40 (m, 5 H, C_6H_5P). ^{31}P NMR ($CDCl_3$), δ: −46.14. $[\alpha]_D$ −101° (*c* 0.312, *n*-hexane).

Reduction of 2-*N*,*N*-dimethylaminomethylferrocenylmethylphenylphosphine oxides 4 and 5. $HSiCl_3$ (0.3 mL, 2.97 mmol) was added to a solution of a mixture (210 mg) containing $MePh_2PO$ (76 mg), aminophosphine oxide **4** (80.4 mg), and aminophosphine oxide **5** (53.6 mg) in anhydrous benzene (3.5 mL) and Et_3N (0.4 mL) and the reaction mixture was refluxed for 1.5 h. After cooling to 0 °C, benzene and a 30% aqueous solution of NaOH (7.5 mL) were added. The organic layer was separated, washed with water, concentrated, and chromatographed on Silufol plates first in a 3 : 1 benzene—ether mixture and then in a 3 : 1 hexane—Et_3N mixture. Aminophosphines were washed off from the plates with ether. The ethereal solution was concentrated and the residue was dried in a desiccator over P_2O_5 and paraffin. Aminophosphines **2** and **3** were obtained in yields of 12.2 and 40.4 mg, respectively (the total yield was 39.2%).

Reaction of aminophosphine 3 with PdI_2. PdI_2 (55 mg, 153 mmol) was added to a solution of phosphine **3** (24 mg, 66 mmol) in benzene (0.5 mL) and stirred for 1 h. The precipitate was filtered off and extracted successively with benzene and CH_2Cl_2. The resulting solution was concentrated and dried. Complex **6** was obtained in a yield of 40 mg. ^1H NMR ($CDCl_3$), δ: 2.54 (d, 3 H, CH_3P, $^2J_{PH}$ = 11.54 Hz); 2.30—3.77 (br.s, 6 H, $N(CH_3)_2$); 2.94 and 3.62 (AB system, 2 H, $C\underline{H}_2N(CH_3)_2$, ^2J = 12.6 Hz); 4.41 (br.s, 7 H), 4.17 (m, 1 H) (C_5H_5, C_5H_3); 7.33—7.75 (m, 5 H, C_6H_5P). ^{31}P NMR ($CDCl_3$), δ: +3.80. Storage of the solution at room temperature afforded crystals, which were studied by X-ray analysis. Found (%): C, 26.26; H, 2.56; N, 1.48. $C_{20}H_{25}FeI_3NPPd \cdot CDCl_3$. Calculated (%): C, 25.90; H+D, 2.79; N, 1.44.

X-ray diffraction study of the product of the reaction of aminophosphine 3 with PdI_2 (complex 6). Dark-cherry crystals of **6**, $(1\text{-}MePhP\text{-}2\text{-}Me_2N^+HCH_2C_5H_3FeC_5H_5)PdI_3^- \cdot CDCl_3$, are orthorhombic, at 20 °C a = 8.709(2) Å, b = 9.991(2) Å, c = 33.573(7) Å, V = 2921 Å^3, d_{calc} = 2.212 g cm^{-3}, space group $P2_12_12_1$, Z = 4.

The experimental intensities of 3617 reflections were measured on a four-circle automated Syntex P21 diffractometer (Mo-Kα radiation, graphite monochromator) in the range of $2° < \theta < 27°$ at 20 °C. A total of 3539 independent reflections, which were obtained by merging equivalent reflections, were used in subsequent calculations (absorption was ignored, μ = 46.23 cm^{-1}). The structure was solved by direct methods. All nonhydrogen atoms were refined by the full-matrix least-squares method based on F^2_{hkl} with anisotropic thermal parameters. The positions of the hydrogen atoms were located from difference electron density syntheses. At the final stage, the hydrogen atoms were placed in geometrically calculated positions and refined using the riding model with fixed isotropic factors U_{iso}, which were equal to $1.5U_{eq}$ and $1.2U_{eq}$, where U_{eq} are the equivalent factors of the carbon (nitrogen) atoms to which the corresponding hydrogen atoms are attached in the CH_2 and CH_3 ($NHMe_2$) groups and in the Cp rings, respectively. The absolute configuration was determined using the refinement of Flack's parameter (x = 0.15(8)). The final values of the R factors were as follows: wR_2 = 0.1537 (based on F^2_{hkl} for all 3497 reflections), R_1 = 0.0553 (based on F_{hkl} for 1546 reflections with $I > \sigma(I)$). All calculations were carried out using the SHELXTL PLUS 5 program package.[14] The atomic coordinates are given in Table 1. The bond lengths and bond angles are listed in Table 2.

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