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First enantiopure phosphapalladacycle with planar chirality. X-Ray study of the racemic dimer and (S_{pl},$S_C S_N$)-diastereomer of its prolinate derivative

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Abstract

The first *P*,*C*-cyclopalladated complex with planar chirality was prepared by direct cyclopalladation of prochiral di-*tert*-butyl(ferrocenylmethyl)phosphine. Resolution of the racemic dimer was achieved through separation of its diastereomeric (*S*)-prolinate derivatives. The palladacycle structure was confirmed by the ^{1}H NMR spectra of the dimer and its triphenylphosphine adduct and an X-ray diffraction study of the racemic dimeric complex. The absolute configuration of the planar chirality was determined by an X-ray diffraction investigation of one of two diastereomers of the (*S*)-prolinate derivative.

1. Introduction

The high efficiency of transition metal coordination complexes bearing ligands with planar chirality in processes of chiral recognition (mainly in enantioselective catalysis) is well recognized.[1–6] The cyclometallated planar chiral complexes are much less investigated in this respect. Some of their representatives have attracted some interest as chiral synthones,[7–10] and were tested later as reagents for resolution[11] and enantioselective catalysts.[12–14] However, among the reported optically active cyclopalladated compounds, systems with planar chirality are presented only by the derivatives of N-donor ligands, such as 1-ferrocenylethylamines,[7,8,10,11,15–17] ferrocenylimines[18–22] and -hydrazones;[23–27] some homochiral derivatives of related metallocenes are also known.[9,28] To the best of our knowledge, planar chiral phosphorus analogues of these complexes have not been described to date. Moreover, the number of known enantiopure

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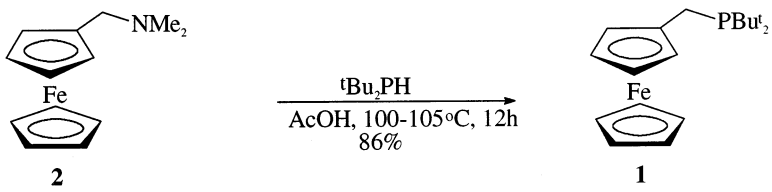
phosphapalladacycles is very restricted: one pincher complex of the P,C,P-type[29] containing only C-stereocenters in the side chains and the first P-chiral cyclopalladated complex have been described only recently.[30]

We report here our results on the preparation of the first enantiopure phosphapalladacycle with planar chirality as the sole source of its optical activity.

2. Results and discussion

2.1. Phosphine ligand synthesis

Di-*tert*-butyl(ferrocenylmethyl)phosphine **1** was prepared in high yield by direct substitution of the NMe_2 group of the easily available[31] tertiary amine **2** with the *tert*-Bu_2P group by reaction with the secondary phosphine (Scheme 1). As might be expected, this reaction of nucleophilic substitution involving a less stable primary carbocationic intermediate required prolonged heating (12 h) and provided a somewhat lower yield (86%) compared with those for the related process in the case of the α-Me substituted analogue (4 h, 95%[32]), which proceeds via secondary (more stable) intermediate carbocation.

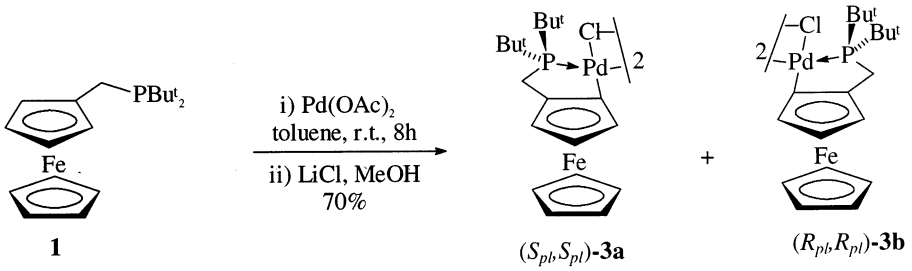


Scheme 1.

Previously, and before our recent research,[32] this route was used only for ferrocenyldiphosphines synthesis from the corresponding aminophosphines.[33] This work presents the first example of the preparation of novel non-functionalized monodentate ferrocenylmethylphosphine via the simple one-pot procedure. Methods reported previously are more tedious and usually based on multistep procedures. They include interaction of quaternary *N*,*N*,*N*-trimethyl(ferrocenylmethyl)ammonium salts with secondary[34] or tertiary phosphine,[35–38] or lithium phosphide attack on the chloromethyl derivative of ferrocene.[39] Moreover, only four monodentate phosphines of the type $FcCH_2PR^1R^2$ (where $R^1=R^2=CH_2OH$,[36,37] Ph,[35,38] or H;[40] and $R^1=H$, $R^2=CH_2OH$[36,37]) are currently known, with two further compounds derived from the first one.

2.2. Cyclopalladation reaction and phosphapalladacycle structure in solution

Racemic μ-chloro-bridged dimer **3** was prepared in a moderate yield of 70% by direct intramolecular cyclopalladation of phosphine **1** with palladium(II) acetate in toluene at room temperature, followed by anion metathesis (Scheme 2).

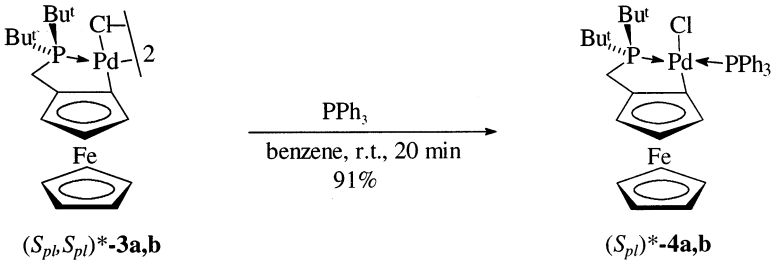


Scheme 2.

Apparently, a somewhat decreased yield of dimer **3** compared to that achieved for the α-Me substituted analogue (93%[32]) is due to the less pronounced steric stimulation of intramolecular palladation in the case of α-non-substituted ligand **1** (cf.[41,42]).

The C–H bond activation in prochiral ferrocenylmethylphosphine **1** generates planar chirality. As a result, cyclopalladated dimer **3** consists of the mixture of four species that are distinguished not only by the relative disposition of the donor atoms inside of the binuclear species (*syn* or *anti*), but also by the configuration of the planar chirality for two palladacycles linked by μ-chloro bridges, (S_{pl},S_{pl})-**3a**/(R_{pl},R_{pl})-**3b** and (S_{pl},R_{pl})-**3c**. The ratio of *anti*- and *syn*-racemic and *anti*- and *syn-meso*-isomers was estimated as ca. 6:2:2:1 from the ^{31}P NMR data taking into account the spectral pattern of enantiopure dimer (S_{pl},S_{pl})-**3a** and known preference for the *anti*-configuration typical for other cyclopalladated dimeric complexes.[43–48]

To confirm the phosphapalladacycle formation, dimer **3** was converted into its mononuclear phosphane derivative **4** by μ-chloro bridge cleavage with the triphenylphosphine ligand (Scheme 3).



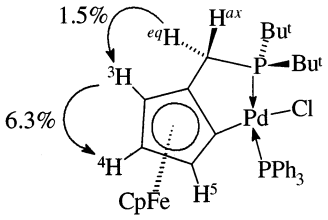
Scheme 3.

The ^{1}H NMR spectrum of isolated adduct **4** (measured in the presence of a slight excess of PPh_3[†]) is in complete agreement with the proposed structure; it contains the set of signals

[†] Necessary to suppress dissociation of triphenylphosphine ligand caused by the strong *trans*-influence of palladacycle P-donor atom and some steric effects; in the absence of excess PPh_3 the signals of dimer **3** were observed.

expected for the 1,2-disubstituted ferrocene moiety and the palladacycle side chain (see Section 4).

The assignment of the palladated cyclopentadienyl ring signals was performed using homonuclear decoupling and NOE experiments (Fig. 1). As the starting point, the enhancement of the C^3H proton of the palladated C_5H_3 ring (δ 4.235 ppm) under irradiation of the *pseudo*-equatorial α-CH proton (1.5%) was used. An unexpected feature of the ferrocenylene part of the spectra, a distinct spin–spin coupling of the C^4H proton with the phosphorus nuclei ($^5J_{HP}$ 0.5 Hz) over five bonds should be mentioned.



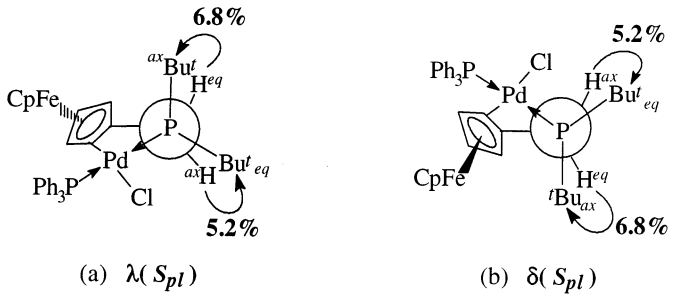
(S_{pl})-**4a**

Figure 1. NOE basis for the assignments of proton signals of palladated cyclopentadienyl ring in the ^1H NMR spectra of phosphane adduct **4**

The spectra of both isolated adduct **4** and that generated in situ from crude dimer **3** reveal only one set of signals, which suggests its existence as one geometric isomer. The *trans*-P,P-geometry of this complex may be inferred from a large value of the $^2J_{PP}$ constant equal to 398 Hz,[49] a high-field position (δ 3.097 ppm) and ^1H–^{31}P spin-spin coupling (J_{HP} 3 Hz) observed for the C^5H proton of the palladated cyclopentadienyl ring. This configuration is in line with the known general trend of phosphanes for *trans*-coordination with regard to the phosphorus atom of the *P,C*-palladacycles;[41,50–53] a few rare examples of *cis*/*trans* isomer mixtures (with predominance of the latter) have been reported for P-adducts of cyclopalladated phosphines[30,54] and only cyclopalladated phosphites form exclusively *cis*-adducts with P-donor ligands with the $^2J_{PP}$ constant values in the range 48–56 Hz.[55,56]

The ^1H NMR data for phosphane adduct **4** are indicative of the non-planar conformation of the phosphapalladacycle. Two diastereotopic α-CH protons are drastically different in the efficiency of their spin–spin coupling with two ^{31}P nuclei. The high-field signal (δ 2.544 ppm, ddd) reveals rather large spin–spin coupling constants with the ^{31}P nuclei of both phosphapalladacycle and PPh_3 ligand ($^2J_{HP}$ 12.6 and $^4J_{HP}$ 4.4 Hz, respectively) that points out its *quasi*-equatorial orientation.[57] In contrast, the low-field signal (δ 2.978 ppm, dd) belonging to another α-CH proton reveals only a rather weak coupling with the adjacent ^{31}P nucleus of the palladacycle ($^2J_{HP}$ 5.7 Hz), and no detectable spin–spin coupling with the distant PPh_3 ligand (J_{HP} <0.5 Hz) is observed, that is in accordance with *quasi*-axial orientation of this α-C–H bond.[57]

However, NOE experiments have demonstrated a rather flattened conformation of the palladacycle (probably, time-averaged). Thus, the irradiation of the *pseudo*-axial or *pseudo*-equatorial α-CH proton results in the distinct response of only one of two *tert*-Bu groups (Fig. 2), while in the case of pronounced palladacycle puckering for both λ(S_{pl}) and δ(S_{pl}) conformations the noticeable enhancement of the second *tert*-Bu group should be expected under the irradiation of the *pseudo*-equatorial α-CH proton. This property is similar to that found for the α-Me substituted analogue.[32]



(a) $\lambda(S_{pl})$ (b) $\delta(S_{pl})$

Figure 2. The NOE data in support of the flattened structure of the ferrocene-derived (S_{pl})-phosphapalladacycle in adduct **4** for λ (a) and δ (b) conformation

2.3. Crystal structure of racemic dimer **3**

The unambiguous confirmation of phosphapalladacycle structure was obtained from an X-ray diffraction study of racemic dimer **3**. Its molecular structure and numbering scheme are presented in Fig. 3 and selected bond lengths and angles are given in Table 1. Complex **3** exists in crystal as a racemate; the unit cell contains three pairs of centrosymmetrically related enantiomers of the dimeric complex of (S_{pl},S_{pl}) and (R_{pl},R_{pl}) configuration.

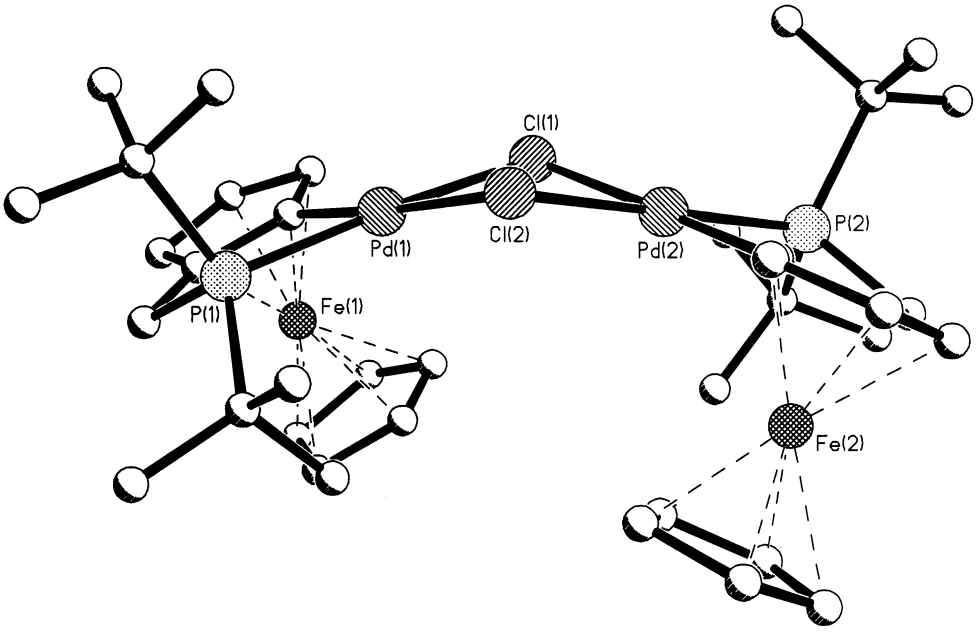


Figure 3. Molecular structure of racemic dimer **3** given for (R_{pl},R_{pl})-enantiomer in the projection illustrating the considerable bend of the central {Pd_2Cl_2} four-membered ring. Hydrogen atoms are omitted for clarity

In common with most structurally characterised dimeric cyclopalladated complexes of the C,P-[43–47] and C,N-type,[48] dimer **3** reveals an *anti*-arrangement of two phosphorus and two donor carbon atoms. The dimer consists of two crystallographically independent halves with minor differences in their structural parameters. The considerable bend of the central four-mem-

Table 1
Selected bond lengths (Å) and bond angles (°) for racemic dimer **3**

Bond lengths			
Pd(1)–C(6)	1.989(5)	P(1)–C(12)	1.868(8)
Pd(1)–P(1)	2.245(2)	P(1)–C(16)	1.873(9)
Pd(1)–Cl(1)	2.426(2)	P(2)–C(31)	1.860(8)
Pd(1)–Cl(2)	2.445(2)	P(2)–C(36)	1.884(10)
Pd(2)–C(26)	1.981(7)	P(2)–C(32)	1.897(6)
Pd(2)–P(2)	2.245(2)	C(6)–C(7)	1.381(10)
Pd(2)–Cl(2)	2.404(2)	C(6)–C(10)	1.438(10)
Pd(2)–Cl(1)	2.445(2)	C(7)–C(8)	1.445(9)
Fe(1)–C(2)	2.017(10)	C(7)–C(11)	1.515(10)
Fe(1)–C(10)	2.034(8)	C(8)–C(9)	1.390(12)
Fe(1)–C(9)	2.043(8)	C(9)–C(10)	1.426(11)
Fe(1)–C(7)	2.039(7)	C(12)–C(15)	1.507(14)
Fe(1)–C(1)	2.037(11)	C(12)–C(13)	1.538(12)
Fe(1)–C(4)	2.044(8)	C(12)–C(14)	1.553(10)
Fe(1)–C(3)	2.033(10)	C(16)–C(17)	1.528(14)
Fe(1)–C(5)	2.048(8)	C(16)–C(19)	1.542(14)
Fe(1)–C(8)	2.059(8)	C(16)–C(18)	1.549(10)
Fe(1)–C(6)	2.062(5)	C(26)–C(27)	1.411(12)
Fe(2)–C(25)	2.027(7)	C(26)–C(30)	1.448(10)
Fe(2)–C(30)	2.028(7)	C(27)–C(28)	1.437(11)
Fe(2)–C(29)	2.031(7)	C(27)–C(31)	1.507(11)
Fe(2)–C(24)	2.046(7)	C(28)–C(29)	1.412(14)
Fe(2)–C(23)	2.064(10)	C(29)–C(30)	1.428(13)
Fe(2)–C(27)	2.046(9)	C(32)–C(35)	1.512(13)
Fe(2)–C(28)	2.043(9)	C(32)–C(34)	1.526(12)
Fe(2)–C(26)	2.058(8)	C(32)–C(33)	1.559(12)
Fe(2)–C(21)	2.073(10)	C(36)–C(39)	1.52(2)
Fe(2)–C(22)	2.079(10)	C(36)–C(37)	1.53(2)
P(1)–C(11)	1.861(5)	C(36)–C(38)	1.536(11)
Bond angles			
C(6)–Pd(1)–P(1)	80.5(2)	C(7)–C(11)–P(1)	103.6(4)
C(6)–Pd(1)–Cl(1)	94.3(2)	C(15)–C(12)–C(13)	110.1(8)
P(1)–Pd(1)–Cl(1)	173.27(5)	C(15)–C(12)–C(14)	107.4(8)
C(6)–Pd(1)–Cl(2)	176.0(2)	C(13)–C(12)–C(14)	110.1(6)
P(1)–Pd(1)–Cl(2)	101.63(6)	C(15)–C(12)–P(1)	107.3(5)
Cl(1)–Pd(1)–Cl(2)	83.88(6)	C(13)–C(12)–P(1)	113.3(7)
C(26)–Pd(2)–P(2)	80.9(2)	C(14)–C(12)–P(1)	108.4(6)
C(26)–Pd(2)–Cl(2)	93.3(2)	C(17)–C(16)–C(19)	108.1(9)
P(2)–Pd(2)–Cl(2)	174.06(5)	C(17)–C(16)–C(18)	109.7(6)
C(26)–Pd(2)–Cl(1)	177.6(2)	C(19)–C(16)–C(18)	107.8(8)
P(2)–Pd(2)–Cl(1)	101.46(6)	C(17)–C(16)–P(1)	114.4(7)
Cl(2)–Pd(2)–Cl(1)	84.36(6)	C(19)–C(16)–P(1)	105.6(6)
Pd(1)–Cl(1)–Pd(2)	91.69(6)	C(18)–C(16)–P(1)	111.0(6)
Pd(2)–Cl(2)–Pd(1)	92.23(5)	C(27)–C(26)–Pd(2)	123.8(4)
C(11)–P(1)–C(12)	105.1(3)	C(30)–C(26)–Pd(2)	129.3(6)
C(11)–P(1)–C(16)	103.9(3)	Pd(2)–C(26)–Fe(2)	124.8(3)
C(12)–P(1)–C(16)	113.9(4)	C(26)–C(27)–C(31)	120.3(6)
C(11)–P(1)–Pd(1)	106.7(2)	C(28)–C(27)–C(31)	130.0(8)
C(12)–P(1)–Pd(1)	111.9(3)	C(31)–C(27)–Fe(2)	128.2(5)

Table 1 (*Continued*)

C(16)–P(1)–Pd(1)	114.4(3)	C(27)–C(31)–P(2)	103.9(6)
C(31)–P(2)–C(36)	106.2(4)	C(35)–C(32)–C(34)	110.0(9)
C(31)–P(2)–C(32)	103.4(3)	C(35)–C(32)–C(33)	109.8(7)
C(36)–P(2)–C(32)	113.6(4)	C(34)–C(32)–C(33)	109.4(8)
C(31)–P(2)–Pd(2)	106.2(3)	C(35)–C(32)–P(2)	113.3(6)
C(36)–P(2)–Pd(2)	109.8(3)	C(34)–C(32)–P(2)	103.9(5)
C(32)–P(2)–Pd(2)	116.6(3)	C(33)–C(32)–P(2)	110.2(5)
C(7)–C(6)-Pd(1)	124.4(5)	C(39)–C(36)-C(37)	110.2(11)
C(10)–C(6)–Pd(1)	127.7(6)	C(39)–C(36)–C(38)	109.5(8)
Pd(1)–C(6)–Fe(1)	124.5(4)	C(37)–C(36)–C(38)	108.9(8)
C(6)–C(7)–C(11)	120.8(5)	C(39)–C(36)–P(2)	113.5(7)
C(8)–C(7)–C(11)	129.6(6)	C(37)–C(36)–P(2)	108.6(7)
C(11)–C(7)–Fe(1)	129.7(5)	C(38)–C(36)–P(2)	106.0(6)

bered cycle $\{Pd_2(\mu\text{-}Cl)_2\}$ along the Cl(1)···Cl(2) axis equal to 28.8° (see Fig. 1) is in drastic contrast to a strictly planar configuration of this fragment in all other reported halide-bridged dimeric complexes of the C,P-type with *anti*-disposition of two palladacycles.[44–46] Moreover, this value is far beyond the range of values (0–16.3°) for the cyclopalladated *anti*-dimers of the C,N-type described previously.[48] Only in the case of the sterically very congested C,P-dimer of *syn*-configuration has a similar (but smaller) bend of 22.5° been observed.[58] The maximum distortion of the central four-membered cycle $\{Pd_2(\mu\text{-}Cl)_2\}$ along the Cl(1)···Cl(2) axis equal to 47.3° was found for the dimeric cyclopalladated derivative of *N*,*N*-dimethyl-1-(ferrocenyl)ethylamine of the *syn*-configuration.[17] It should be mentioned that the angle between the planes of two palladacycles is increased to 47.5°. The true reason of such strong distorsion of the structure of dimer **3** is unclear taking into account a rather distant arrangement of the bulky ferrocenyl moieties and *tert*-Bu_2P groups in the frame of a dimer of *anti*-configuration. It seems reasonable to suppose that it is caused by packing effects in crystal.

Both palladium atoms in complex **3** are in a nearly square-planar coordination with a slight tetrahedral distortion of 5.8–1.3°[‡] that is around the low limit of the range 3.6–14.9° reported previously for mono- and binuclear derivatives of five-membered phosphapalladacycles.[30] The length of the Pd–P bond (2.245 Å) in dimer **3** falls in the range of values reported for related cyclopalladated complexes with the Pd-PBu^t_2 moiety (2.219–2.354 Å[44,59–61]); the Pd–C bond in dimer **3** (1.989–1.981 Å) is slightly shortened compared to the Pd–C(sp^2, Ph) bonds in related *ortho*-palladated phosphines (2.009–2.036 Å[58,62,63]). The difference between the lengths of the Pd–Cl bonds *trans*-disposed to the C- (2.445 Å) and P-donor atoms of the palladacycle (2.426–2.404 Å) in dimer **3** structure is in accordance with the *trans*-influences of these atoms; their values are close to that reported previously for related dimeric complexes of the C,P-type (2.437–2.487 and 2.389–2.429 Å, respectively[44,46,58,64]).

In complex **3**, both five-membered phosphapalladacycles annulated with ferrocenylene moiety have the chiral envelope-like conformation with the bend along the Pd···C(α) bond of 21.1–23.4°. In accordance with the ^{1}H NMR data (see Section 2.2), the orientation of two α-methylene hydrogen atoms inside each palladacycle is different. One C–H bond is located in the vicinity of the axial position and another bond is arranged *pseudo*-equatorially; these α-C–H bonds form torsion angles of 14.5–17.4 and 56.6–54.6° with the normal to the mean coordina-

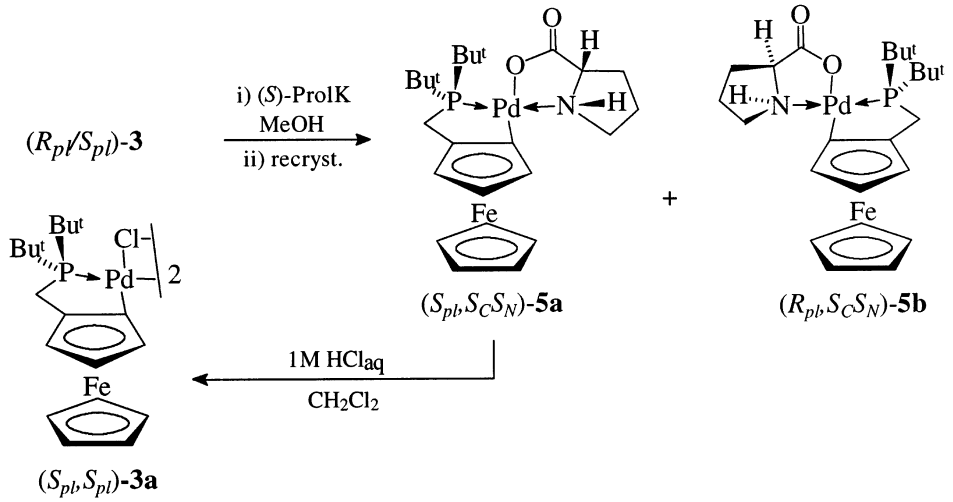
[‡] Here, and later on, two values cited correspond to Pd(1) and Pd(2) containing halves of dimeric molecule.

tion plane (mcpl), respectively. The difference between the positions of two PBu^t groups inside each palladacycle is not so pronounced: the torsion angles with the normal to the mcpl equal to 25.9–17.2 and 43.4–50.9° for *pseudo*-axial and *pseudo*-equatorial P–C(Bu^t) bonds, respectively.

The palladacycle twist in the dimer **3** structure is small, with average intrachelate torsion angles of 13.3–14.3°, which is near the lower limit of the range (11.5–29.2°) reported previously for cyclopalladated arylphosphines.[30] This feature is rather typical for the ferrocenyl-derived palladacycles: for example, the values of 6.4–10.5° were calculated for palladacycles of the C,N-type derived from the tertiary ferrocenylmethylamine non-substituted in the α-position.[65,66]

2.4. Phosphapalladacycle resolution

The resolution of racemic dimeric complex **3** was performed using (*S*)-prolinate as a chiral auxiliary ligand (Scheme 4). Both $(-)_D$-(S_{pl},$S_C$$S_N$)-**5a** and $(+)_D$-(R_{pl},$S_C$$S_N$)-**5b** diastereomers of this mononuclear adduct were isolated diastereomerically pure (>98% *de* according to the ^{31}P NMR data) in yields of 45 and 14%, respectively, by combining extraction and fractional crystallization of starting **5a**,**b** mixture (see Section 4). Moderate or low yields obtained in the separation of the diastereomers $(-)_D$-**5a** and $(+)_D$-**5b**, respectively, are caused by partial decomposition of the prolinate derivatives in solution.



Scheme 4.

The ^1H and ^{31}P NMR spectra of both complexes, $(-)_D$-**5a** and $(+)_D$-**5b**, contain only one signal or one set of signals, respectively, and the same spectra of starting diastereomers **5a**,**b** mixture (before their separation and any purification) presents a superposition of the spectral patterns of these diastereomers and does not reveal any additional signals. In addition to unambiguous confirmation of the complete diastereomeric purity of complexes $(-)_D$-**5a** and $(+)_D$-**5b** (within the accuracy of NMR spectral analysis), the absence of signal doubling is indicative of the regioselective chelation of non-symmetrical amino acidate ligand with ferrocene-derived phosphapalladacycle in the form of only one geometric isomer, presumably with the *trans*(P,N)-configuration (confirmed by an X-ray study of **5a**). This regioselectivity is in contrast to the behavior of cyclopalladated di-*ortho*-tolyl-*tert*-butylphosphine, which forms both *cis*- and *trans*-isomers with both triphenylphosphine and prolinate ligands.[30]

The possibility of enantiopure dimer (S_P,S_P)-**3a** and (R_P,R_P)-**3b** isolation from individual (*S*)-prolinate diastereomers (S_{pl},$S_C S_N$)-**5a** and (R_{pl},$S_C S_N$)-**5b**, respectively, was demonstrated for one of them. The high-yield conversion of more easily available diastereomer (S_{pl},$S_C S_N$)-**5a** into the enantiopure dimer (S_P,S_P)-**3a** was performed by protonation of the auxiliary amino acidate ligand with dilute HCl in a two-phase solvent system (Scheme 4).

2.5. Crystal structure of (S)-prolinate derivative **5a**

The absolute configuration of the planar chirality in the dimer $(-)_D$-**3a** was determined by an X-ray single crystal diffractometry of its precursor (*S*)-prolinate derivative (S_P,$S_C S_N$)-**5a** which crystallized as the mono dichloromethane solvate. The molecular structure of this diastereomer and the numbering scheme are presented in Fig. 4; selected bond lengths and angles are given in Table 2. The (S_{pl})-configuration of the 1,2-disubstituted ferrocene derivative is confirmed independently using coordinated ($S_C S_N$)-prolinate ligand as a reference point and on the basis of the anomalous X-ray scattering method with the Flack parameter 0.03(7).

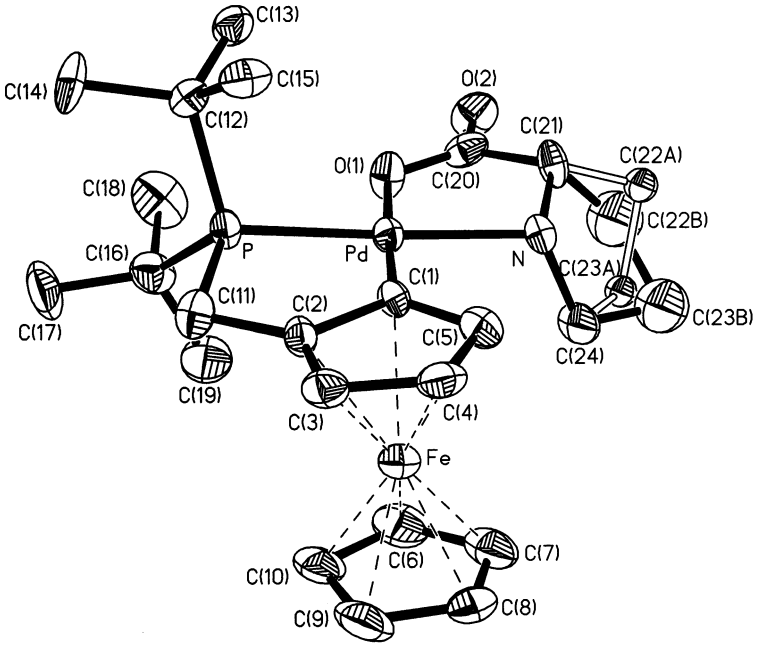


Figure 4. Molecular structure of (S_{pl},$S_C S_N$)-diastereomer of prolinate adduct **5a**. Hydrogen atoms and solvent CH_2Cl_2 molecules are omitted for clarity. Displacement ellipsoids are shown at 40% probability level

The main structural parameters of the palladacycle in mononuclear derivative **5a** are close to that found for starting dimer **3** (cf. Table 1 and Section 2.3). The only difference is the less pronounced palladacycle puckering, with the bend along the Pd···C(α) line of 18.6° and the average intrachelate torsion angle of 11.7°.

The geometric parameters of the prolinate moiety of the diastereomer **5a** are mainly in the range of the values typical for the other (*S*)-prolinate complexes of palladium(II),[30,67–71] including those containing cyclopalladated ligands of the C,N-[69–71] and C,P-type.[30] The Pd–N and Pd–O bond lengths in compound **5a** (2.140 and 2.103 Å, respectively) are in accordance with large *trans*-influence of the PBu^t_2 group and the (sp^2)-carbon atom of the palladacycle. The

Table 2
Selected bond lengths (Å) and bond angles (°) for (*S*)-prolinate derivative (S_{pl},$S_C$$S_N$)-**5a** (mono dichloromethane solvate)

Bond lengths			
Pd–C(1)	1.979(11)	C(3)–C(4)	1.40(2)
Pd–O(1)	2.103(9)	C(4)–C(5)	1.42(2)
Pd–N	2.140(9)	C(12)–C(13)	1.52(2)
Pd–P	2.240(3)	C(12)–C(15)	1.53(2)
Fe–C(3)	2.016(12)	C(12)–C(14)	1.55(2)
Fe–C(4)	2.028(12)	C(16)–C(17)	1.53(2)
Fe–C(5)	2.031(11)	C(16)–C(19)	1.55(2)
Fe–C(2)	2.040(12)	C(16)–C(18)	1.57(2)
Fe–C(1)	2.093(11)	C(20)–C(21)	1.50(2)
P–C(11)	1.815(13)	C(21)–C(22A)	1.49(2)
P–C(16)	1.873(13)	C(21)–C(22B)	1.52(2)
P–C(12)	1.881(12)	C(22A)–C(23A)	1.57(3)
O(1)–C(20)	1.28(2)	C(23A)–C(24)	1.53(2)
O(2)–C(20)	1.24(2)	C(22B)–C(23B)	1.57(3)
N–C(24)	1.45(2)	C(23B)–C(24)	1.48(2)
N–C(21)	1.47(2)	C(30)–Cl(4)	1.63(2)
C(1)–C(5)	1.42(2)	C(30)–Cl(3)	1.68(2)
C(1)–C(2)	1.44(2)	C(30)–Cl(1)	1.685(14)
C(2)–C(3)	1.39(2)	C(30)–Cl(2)	1.72(2)
C(2)–C(11)	1.53(2)		
Bond angles			
C(1)–Pd–O(1)	178.0(4)	C(13)–C(12)–C(14)	112.1(11)
C(1)–Pd–N	98.1(4)	C(15)–C(12)–C(14)	110.0(11)
O(1)–Pd–N	79.9(4)	C(13)–C(12)–P	109.4(8)
C(1)–Pd–P	81.9(3)	C(15)–C(12)–P	105.0(8)
O(1)–Pd–P	100.1(2)	C(14)–C(12)–P	113.3(9)
N–Pd–P	177.5(3)	C(17)–C(16)–C(19)	114.6(13)
C(11)–P–C(16)	105.7(6)	C(17)–C(16)–C(18)	108.6(13)
C(11)–P–C(12)	104.8(6)	C(19)–C(16)–C(18)	105.8(13)
C(16)–P–C(12)	114.1(6)	C(17)–C(16)–P	113.3(11)
C(11)–P–Pd	107.4(4)	C(19)–C(16)–P	105.1(10)
C(16)–P–Pd	115.0(5)	C(18)–C(16)–P	109.1(9)
C(12)–P–Pd	109.1(4)	O(2)–C(20)–O(1)	122.8(14)
C(20)–O(1)–Pd	114.4(8)	O(2)–C(20)–C(21)	117.8(12)
C(24)–N–C(21)	107.4(10)	O(1)–C(20)–C(21)	119.4(11)
C(24)–N–Pd	116.3(8)	N–C(21)–C(22A)	109(2)
C(21)–N–Pd	108.0(7)	N–C(21)–C(20)	112.4(10)
C(5)–C(1)–C(2)	104.9(10)	C(22A)–C(21)–C(20)	120(2)
C(5)–C(1)–Pd	132.3(9)	N–C(21)–C(22B)	100(2)
C(2)–C(1)–Pd	122.8(8)	C(20)–C(21)–C(22B)	105(2)
C(5)–C(1)–Fe	67.5(6)	C(21)–C(22A)–C(23A)	93(2)
C(2)–C(1)–Fe	67.6(6)	C(24)–C(23A)–C(22A)	109(2)
Pd–C(1)–Fe	126.5(6)	C(21)–C(22B)–C(23B)	113(2)
C(3)–C(2)–C(1)	110.5(10)	C(24)–C(23B)–C(22B)	92(2)
C(3)–C(2)–C(11)	130.3(10)	N–C(24)–C(23B)	111(2)
C(1)–C(2)–C(11)	119.1(10)	N–C(24)–C(23A)	102.0(14)
C(4)–C(5)–C(1)	108.5(11)	Cl(4)–C(30)–Cl(1)	122(2)
C(2)–C(11)–P	105.6(8)	Cl(3)–C(30)–Cl(1)	113.1(14)
C(13)–C(12)–C(15)	106.6(11)	Cl(1)–C(30)–Cl(2)	115.1(13)

structure of adduct **5a** in the crystal is characterized by disorder of the ethylene fragment ($C^{22}H_2C^{23}H_2$) of the pyrrolidine ring of prolinate ligand between two positions. Probably, this is caused by some unfavourable steric interactions with the ferrocenyl moiety resulting in the more flexible behaviour of the pyrrolidine ring. In line with this feature is an increase of the pyrrolidine ring puckering with the average intraring angles of 29.0 and 26.7° (for two positions) compared to 4.3–21.7° range for the other reported prolinate complexes. This phenomenon may be responsible for the line broadening observed for the signals of palladium-bonded prolinate ligand in the ^{1}H NMR spectra of complex **5a** (see Section 4).

3. Conclusion

Thus, the resolution of the racemic phosphapalladacycles of planar chirality was performed by the standard procedure of the diastereomeric (*S*)-prolinate derivatives separation. The most valuable feature of this new kind of palladacycles is its ability to regioselectively bond unsymmetric ligands, that seems to be a valuable property for their further use as stereoselectors.

4. Experimental

4.1. General

The ^{1}H and ^{31}P NMR spectra were recorded with a Varian VXR-400 spectrometer operating at the frequencies 400 and 161.9 MHz for ^{1}H and ^{31}P nuclei, respectively, using TMS as internal standard for protons and H_3PO_4 as an external reference for the ^{31}P nuclei. The assignment of signals was based on the homonuclear decoupling and NOE experiments. Optical rotations were measured with a VNIEKI-Prodmush AI-EPO polarimeter in 0.25 and 1.0 dm cells at 20°C. All manipulations with the free phosphines were carried out under dry purified argon in carefully desoxygenated solvents using Schlenk technique.

Solvents and starting reagents were purified as described previously.[57] *N*,*N*-Dimethylaminomethylferrocene was prepared by the known method[31] and purified by means of short dry column chromatography[72,73] on neutral Al_2O_3 (*h* 8 cm, *d* 1.5 cm) using benzene and benzene:acetone mixtures (in the ratios from 20:1 up to 1:10) as eluents.

4.2. *Di*-tert-*butyl(ferrocenylmethyl)phosphine* ***1*** *synthesis*

The solution of *N*,*N*-dimethylaminomethylferrocene (0.5610 g, 2.31 mmol) and Bu^t_2PH[74] (0.7770 g, 5.30 mmol, 1 mL) in glacial AcOH (6 mL) was heated at 100–105°C in the Schlenk tube under argon with the ^{31}P NMR control of reaction course. After 12 h the constant ca. 2:3 ratio of product **1** (δ 44.087 ppm) and starting secondary phosphine (δ 16.659 ppm) was achieved, that corresponds to a conversion of amine **2** into phosphine **1** of 86%. Then the solvent and volatile admixtures were removed by heating in vacuo (40°C/1 mmHg) and crude tertiary phosphine **1** was used for cyclopalladation without additional purification.

^{31}P NMR (AcOH/$CDCl_3$ 4:1 mixture): δ 44.09 ppm (s). ^{1}H NMR ($CDCl_3$): δ 1.096 (d, 18H, $^3J_{HP}$ 11.2 Hz, Bu^t), 2.587 (d, 2H, $^2J_{HP}$ 2.6 Hz, α-CH_2), 4.077 (s, 5H, C_5H_5 ring), 4.006 (m, 2H, C_5H_4-ring), 4.166 (m, 2H, C_5H_4-ring).

4.3. Preparation of the racemic cyclopalladated complexes

4.3.1. Di-μ-chloro-bis[2-(di-tert-butylphosphinomethyl)ferrocenyl-C,P]dipalladium(II) **3**

A solution of $Pd(OAc)_2$ (0.4075 g, 1.81 mmol) in anhydrous toluene (20 mL) was added to crude phosphine **1** (0.6250 g, 1.81 mmol) under argon in a Schlenk tube. The reaction mixture was stirred at rt for 8 h, evaporated in vacuo to dryness, and then treated by solution of LiCl (0.1535 g, 3.62 mmol) in anhydrous MeOH (15 mL). After stirring for 2 h at rt, the precipitate was filtered, washed with cold hexane (10 mL), dried in vacuo and purified by short dry column chromatography[72,73] on Silpearl (*h* 1 cm, *d* 5 cm) using benzene and benzene/acetone 10:1 mixture as eluents. Chromatographically pure racemic dimer **3** was obtained in the yield of 70% (0.6124 g, 0.631 mmol) as an orange amorphous powder. After precipitation from dichloromethane by hexane and drying in vacuo (0.01 mmHg): mp (dec.) 191–193°C; R_f 0.67 (Silufol, benzene/hexane 4:1). Anal. calcd for $C_{38}H_{56}Cl_2Fe_2P_2Pd_2$: C, 47.04; H, 5.82. Found: C, 46.91; H, 6.08.

^{31}P NMR ($CDCl_3$, four singlet signals in ca. 1:1.9:1.6:5.5 ratio from high to low fields); for racemic (R_{pl},R_{pl}/S_{pl},S_{pl})-isomer (**3a**,**b**): δ 101.14 (*syn*-form) and 102.12 (*anti*-form); for *meso* (R_{pl},S_{pl})-isomer (**3c**): δ 100.52 (*syn*-form) and 101.44 (*anti*-form). ^1H NMR ($CDCl_3$); for major (R_{pl},R_{pl}/S_{pl},S_{pl})-*anti*-isomer (**3a**,**b**): δ 1.266 (d, 9H, $^3J_{HP}$ 13.8 Hz, Bu^t), 1.638 (d, 9H, $^3J_{HP}$ 14.0 Hz, Bu^t), 2.402 (dd, 1H, $^2J_{HH}$ 16.5 Hz, $^2J_{HP}$ 12.4 Hz, α-CH^{eq}), 2.941 (dd, 1H, $^2J_{HH}$ 16.5 Hz, $^2J_{HP}$ 5.6 Hz, α-CH^{ax}), 3.968 (m, 1H, C^{4}H of palladated Cp-ring), 4.162 (m, 1H, C^{5}H of palladated Cp-ring), 4.225 (s, 5H, C_5H_5-ring), 4.297 (m, 1H, C^{3}H of palladated Cp-ring); for three minor isomers: δ 1.282, 1.313, 1.241 (d, 9H, $^3J_{HP}$ 13.8 Hz, Bu^t), 1.546, 1.607, 1.572 (d, 9H, $^3J_{HP}$ 14.0 Hz, Bu^t), 2.392 (dd, 1H, $^2J_{HH}$ 16.4 Hz, $^2J_{HP}$ 12.4 Hz, α-CH^{eq}), 2.922 (m, 1H, $^2J_{HH}$ 16.5 Hz, $^2J_{HP}$ 5.7 Hz, α-CH^{ax}), 3.995, 4.007, 4.027 (m, 1H, C^{4}H), 4.249, 4.183, 4.260 (s, 5H, C_5H_5), 4.392, 4.491, 4.441 (m, 1H, C^{3}H); the rest signals of minor isomers are hidden under the signals of major isomer.

4.3.2. Chloro[2-(di-tert-butylphosphinomethyl)ferrocenyl-C,P](triphenylphosphine)palladium(II) **4**

The suspension of dimer **3** (0.0501 g, 0.052 mmol) and a slight excess of PPh_3 (0.0284 g, 0.1081 mmol) in anhydrous benzene (2 mL) was stirred at rt for 20 min to give a homogeneous solution. It was evaporated in vacuo to dryness and purified by short dry column chromatography[72,73] on Silpearl (*h* 3 cm, *d* 2.5 cm) using hexane and benzene:acetone 10:1 mixture as eluents to afford the chromatographically pure adduct **4** in a yield of 91% (0.0706 g, 0.094 mmol) as an orange amorphous powder. After recrystallization from a dichloromethane/hexane mixture: mp 112–115°C; R_f 0.58 (Silufol, benzene/acetone/hexane 10:1:1). Anal. calcd for $C_{37}H_{43}ClFeP_2Pd$: C, 59.46; H, 5.80. Found: C, 59.64; H, 5.95.

^{31}P NMR ($CDCl_3$, in the presence of 10% excess of free PPh_3): δ 24.68 (d, $^2J_{PP}$ 398 Hz, ^{31}P of PPh_3), 89.14 (d, $^2J_{PP}$ 398 Hz, ^{31}P of palladacycle), −8.073 (s, free PPh_3). ^1H NMR ($CDCl_3$, in the presence of 10% excess of PPh_3): δ 1.418 (d, 9H, $^3J_{HP}$ 13.1 Hz, Bu$^t_{ax}$), 1.633 (d, 9H, $^3J_{HP}$ 13.8 Hz, Bu$^t_{eq}$), 2.544 (ddd, 1H, $^2J_{HH}$ 16.8 Hz, $^2J_{HP}$ 12.6 Hz, $^4J_{HP}$ 4.4 Hz, α-CH^{eq}), 2.978 (dd, 1H, $^2J_{HH}$ 16.8 Hz, $^2J_{HP}$ 5.7 Hz, α-CH^{ax}); 3.097 (ddd, 1H, $^3J_{H(5)H(4)}$ 2.5 Hz, $^4J_{H(5)H(3)}$ 0.8 Hz, J_{HP} 3.0 Hz, C^{5}H), 3.634 (s, 5H, C_5H_5-ring), 3.771 (ddd, 1H, $^3J_{H(4)H(5)}$ 2.5 Hz, $^3J_{H(4)H(3)}$ 2.3 Hz, J_{HP} 0.5 Hz, C^{4}H), 4.235 (dd, 1H, $^3J_{H(3)H(4)}$ 2.3 Hz, $^4J_{H(3)H(5)}$ 0.8 Hz, C^{3}H); 7.2–7.4 (m, *meta*-H and *para*-H of Pd-bonded PPh_3 and all H of free PPh_3), 7.747 (m, 6H, $^3J_{HP}$ 10.7 Hz, *ortho*-H of Pd-bonded PPh_3).

4.4. Racemic dimer **3** resolution

4.4.1. Diastereomeric (S)-prolinate complexes **5a**,**b**—preparation

A slight excess of potassium (*S*)-prolinate (0.1011 g, 0.6592 mmol) was added to a suspension of racemic dimer **3** (0.3050 g, 0.3144 mmol) in anhydrous MeOH (25 mL) and the reaction mixture was stirred for 3 h at rt. The homogeneous solution was evaporated to dryness in vacuo, the residue was extracted with dichloromethane (3×20 mL), the combined organic layers were evaporated to dryness in vacuo, dried over $CaCl_2$ in vacuo (5 mmHg) to give diastereomeric complexes **5a**,**b** mixture as a light-orange amorphous powder in the yield of 96% (0.3412 g, 0.6052 mmol). R_f 0.48 (Silufol, dichloromethane/ethanol/hexane mixture in 10:1:1 ratio),[§] mp (dec.) 204–206°C; $[\alpha]_D^{20}$ +42 (*c* 0.25, dichloromethane). Anal. calcd for $C_{24}H_{36}FeNO_2PPd{\cdot}0.5CH_2Cl_2$: C, 48.53; H, 6.15; N, 2.31. Found: C, 48.68; H, 6.10; N, 1.83.

^{31}P NMR ($MeOH/CDCl_3$ mixture in 3:1 ratio; two signals in the ratio of ca. 1:1); for (S_{pl},$S_C S_N$)-**5a**: δ 98.78 (s); for (R_{pl},$S_C S_N$)-**5b**: δ 99.20 (s). ^1H NMR ($CDCl_3$); for (S_{pl},$S_C S_N$)-**5a**: δ 1.211 (d, 9H, $^3J_{HP}$ 13.6 Hz, Bu^t), 1.537 (d, 9H, $^3J_{HP}$ 14.1 Hz, Bu^t), 2.380 (dd, 1H, $^2J_{HH}$ 16.6 Hz, $^2J_{HP}$ 12.2 Hz, α-CH^{eq}),¶ 2.820 (dd, 1H, $^2J_{HH}$ 16.6 Hz, $^2J_{HP}$ 5.8 Hz, α-CH^{ax}), 3.653 (br.m, 1H, CH of palladated Cp-ring); 4.066 (s, 5H, C_5H_5-ring), 4.273 (m, 1H, CH of palladated Cp-ring); one of CH of palladated Cp-ring is hidden under Cp-ring signal; for (R_{pl},$S_C S_N$)-**5b**: δ 1.226 (d, 9H, $^3J_{HP}$ 13.6 Hz, Bu^t), 1.508 (d, 9H, $^3J_{HP}$ 14.1 Hz, Bu^t), 2.380 (dd, 1H, $^2J_{HH}$ 16.6 Hz, $^2J_{HP}$ 12.2 Hz, α-CH^{eq}),¶ 2.803 (dd, 1H, $^2J_{HH}$ 16.6 Hz, $^2J_{HP}$ 5.8 Hz, α-CH^{ax}), 3.764 (br.m, 1H, CH of palladated Cp-ring); 4.103 (s, 5H, C_5H_5-ring), 4.266 (m, 1H, CH of palladated Cp-ring); one of CH of palladated Cp-ring is hidden under Cp-ring signal; protons of prolinate ligand for both diastereomers are presented by a series of broad overlapped multiplets at δ 1.75–2.54 and 3.23–3.60 ppm.

4.4.2. Diastereomeric (S)-prolinate complexes **5a**,**b**—separation

Version 1. The mixture of diastereomeric complexes **5a**,**b** in 1:1 ratio (0.1000 g, 0.1773 mmol) was dissolved in dichloromethane (6 mL) and treated with hexane (6 mL) to give the precipitate (0.0430 g, 0.0763 mmol) enriched with diastereomer $(-)_D$-**5a** (56% *de* according to $[\alpha]_D^{20}$ −59 (*c* 0.25, dichloromethane)). After slow evaporation on air of the solution of this precipitate in a dichloromethane/benzene/hexane mixture in 7:1:1 ratio, diastereomerically pure complex $(-)_D$-**5a** was isolated as light-orange coloured needle-like crystals in a yield of 45% (0.0223 g, 0.0395 mmol) and of >98% *de* (^{31}P NMR data). After drying in vacuo (7 mmHg): mp (dec.) 185–187°C; $[\alpha]_D^{20}$ −105 (*c* 0.25, dichloromethane). Anal. calcd for $C_{24}H_{36}FeNO_2PPd{\cdot}0.5CH_2Cl_2$: C, 48.53; H, 6.15; N, 2.31. Found: C, 48.60; H, 6.11; N, 1.98.

The diastereomeric mixture remaining in the first mother liquor (0.0552 g, 0.0979 mmol) was enriched with isomer $(+)_D$-**5b** (64% *de* according to $[\alpha]_D^{20}$ +122 (*c* 0.25, dichloromethane)). It was slowly recrystallized on air from a benzene/dichloromethane mixture in 3:2 ratio to give diastereomer $(+)_D$-**5b** as dark-red coloured blocks. After drying in vacuo (7 mmHg) it was obtained in a yield of 38% (0.0190 g, 0.0337 mmol) and 94% *de*. Mp (dec.) 173–176°C; $[\alpha]_D^{20}$ +179 (*c* 0.25, dichloromethane).

[§] Partial decomposition of prolinate complexes on silica was observed resulting in formation of dimer **1** (R_f 0.95).

¶ Signals of equatorial methylene proton for both diastereomers are overlapped.

Version 2. The mixture of diastereomeric complexes **5a**,**b** in 1:1 ratio (0.3400 g, 0.6031 mmol) was extracted with anhydrous benzene under stirring (2×6 mL) to give the insoluble precipitate (0.0808 g, 0.1418 mmol) enriched with diastereomer $(-)_D$-**5a** (89% *de* according to ^{31}P NMR data). Its slow recrystallization on air from a dichloromethane/benzene mixture in 5:1 ratio gave pure diastereomer complex $(-)_D$-**5a** as light-orange coloured needle-like crystals in a yield of 38% (0.0650 g, 0.1152 mmol) and >98% *de* (^{31}P NMR data); $[\alpha]_D^{20}$ −105 (*c* 0.25, dichloromethane).

The combined benzene extracts were evaporated to give the diastereomeric mixture (0.2521 g, 0.4471 mmol) enriched with isomer $(+)_D$-**5b** (56% *de* according to $[\alpha]_D^{20}$ +107 (*c* 0.25, dichloromethane)). It was slowly recrystallized on air from a benzene/dichloromethane mixture in ca. 3:2 ratio in isolated system using hexane diffusion, to give diastereomer $(+)_D$-**5b** as dark-red blocks in a yield of 14% (0.0243 g, 0.0431 mmol) and >98% *de* (^{31}P NMR data); $[\alpha]_D^{20}$ +190 (*c* 0.25, dichloromethane).

For diastereomer $(-)_D$-(S_{pl},$S_C$$S_N$)-**5a**: ^{31}P NMR (MeOH/$CDCl_3$ 3:1 mixture): δ 98.91 (s). ^{1}H NMR ($CDCl_3$/CH_2Cl_2 mixture in ca. 5:1 ratio): δ 1.211 (d, 9H, $^3J_{HP}$ 13.6 Hz, Bu^t), 1.538 (d, 9H, $^3J_{HP}$ 14.1 Hz, Bu^t), 2.383 (dd, 1H, $^2J_{HH}$ 16.6 Hz, $^2J_{HP}$ 12.2 Hz, α-CH^{eq}), 2.820 (dd, 1H, $^2J_{HH}$ 16.6 Hz, $^2J_{HP}$ 5.8 Hz, α-CH^{ax}), 3.638 (br.t, 1H, $^3J_{HH}$ 2.3 Hz, CH of palladated Cp-ring); 4.069 (s, 5H, C_5H_5-ring), 4.08 (m, 1H, CH of palladated Cp-ring), 4.275 (d, 1H, $^3J_{HH}$ 2.3 Hz, CH of palladated Cp-ring); protons of prolinate ligand are presented by a series of broad overlapped multiplets in interval δ 1.85–3.80 ppm.

For diastereomer $(+)_D$-(R_{pl},$S_C$$S_N$)-**5b**: ^{31}P NMR (MeOH/$CDCl_3$ 3:1 mixture): δ 99.31 (s). ^{1}H NMR ($CDCl_3$): δ 1.227 (d, 9H, $^3J_{HP}$ 13.6 Hz, Bu^t), 1.509 (d, 9H, $^3J_{HP}$ 14.1 Hz, Bu^t), 2.381 (dd, 1H, $^2J_{HH}$ 16.6 Hz, $^2J_{HP}$ 12.2 Hz, α-CH^{eq}), 2.802 (dd, 1H, $^2J_{HH}$ 16.6 Hz, $^2J_{HP}$ 5.8 Hz, α-CH^{ax}), 3.763 (br.m, 1H, CH of palladated Cp-ring); 4.104 (s, 5H, C_5H_5-ring), 4.269 (m, 1H, CH of palladated Cp-ring); one of CH of palladated Cp-ring is hidden under Cp-ring signal; protons of the prolinate ligand are presented by series of broad overlapped multiplets at δ 1.77–3.44 ppm.

*4.4.3. Enantiopure dimer $(-)_D$-(S_{pl},S_{pl})-**3a**—isolation*

The solution of individual diastereomer (S_{pl},$S_C$$S_N$)-**5a** (0.0650 g, 0.1152 mmol) in dichloromethane (6 mL) was treated with aqueous 1N HCl (5 mL) under vigorous shaking during ca. 5 min. The organic layer was separated and the protonation procedure was repeated once more with an additional volume of aqueous 1N HCl (5 mL). The combined organic layers were washed with water (3×5 mL), dried over Na_2SO_4, and concentrated in vacuo to dryness. The residue was dried in vacuo (7 mmHg) over $CaCl_2$/paraffine to obtain dimer $(-)_D$-(S_{pl},S_{pl})-**3a** as an amorphous orange powder in a yield of 98% (0.0543 g, 0.0559 mmol) and of >98% *ee* (^{31}P NMR data for (*S*)-prolinate precursor). Mp (dec.) 179–181°C; $[\alpha]_D^{20}$ −488 (*c* 0.25, dichloromethane). R_f 0.66 (Silufol, benzene/hexane 4:1).

^{31}P NMR ($CDCl_3$, two singlet signals in ca. 1:2.6 ratio from high to low fields): δ 101.15 (*syn*-isomer) and 102.12 (*anti*-isomer). ^{1}H NMR ($CDCl_3$, two sets of signals of *syn*/*anti* isomers in ca. 1:2.5 ratio); for major *anti*-isomer: δ 1.260 (d, $^3J_{HP}$ 13.9 Hz, Bu^t), 1.632 (d, $^3J_{HP}$ 14.3 Hz, Bu^t), 2.408 (dd, 1H, $^2J_{HH}$ 16.7 Hz, $^2J_{HP}$ 12.3 Hz, α-CH^{eq}), 2.952 (dd, 1H, $^2J_{HH}$ 16.7 Hz, $^2J_{HP}$ 5.2 Hz, α-CH^{ax}), 3.970 (t, 1H, $^3J_{H(4)H(3)}$ 2.4 Hz, $^3J_{H(4)H(5)}$ 2.3 Hz, C^{4}H of palladated Cp-ring), 4.155 (br.m, 1H, C^{5}H of palladated Cp-ring), 4.219 (s, 5H, C_5H_5-ring), 4.291 (br.m, 1H, $^3J_{HH}$ 2.4 Hz, $^2J_{HP}$ 1.8 Hz, C^{3}H of palladated Cp-ring); for minor *syn*-isomer: δ 1.276 (d, 9H, $^3J_{HP}$ 13.9 Hz, Bu^t), 1.540 (d, 9H, $^3J_{HP}$ 13.9 Hz, Bu^t), 2.398 (dd, 1H, $^2J_{HH}$ 16.4 Hz, $^2J_{HP}$ 12.3 Hz, α-CH^{eq}), 2.920 (dd, 1H, $^2J_{HH}$ 16.4 Hz, $^2J_{HP}$ 5.0 Hz, α-CH^{ax}), 4.022 (t, 1H, $^3J_{HH}$ 2.2 Hz, C^{4}H of palladated

Table 3
Crystal data, data collection, structure solution and refinement parameters for the racemic dimer **3** and (*S*)-prolinate adduct (S_{p1},$S_C S_N$)-**5a** (mono-dichloromethane solvate)

Compound	**3**	**5a**·CH_2Cl_2[a]
Empirical formula	$C_{38}H_{56}Cl_2Fe_2P_2Pd_2$	$C_{25}H_{38}Cl_2FeNO_2PPd$
Formula weight	970.16	648.68
Colour, habit	Red, block	Yellow, needle
Crystal size (mm)	$0.3\times0.2\times0.2$	$0.5\times0.1\times0.1$
Crystal system	Trigonal	Orthorhombic
Space group	$R\bar{3}$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	20.2642(7)	10.992(5)
b (Å)	20.2642(7)	10.843(4)
c (Å)	20.2642(7)	24.048(6)
α (°)	111.304(7)	90
β (°)	111.304(7)	90
γ (°)	111.304(7)	90
Volume (Å^3)	5931.4(4)	2866(2)
Z	6	4
D_{calcd} (g cm^{-3})	1.630	1.503
Absorption coefficient (mm^{-1})	1.856	1.397
F(000)	2952	1328
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Temperature (K)	293	293
Radiation (λ, Å)	Graphite monochromated Mo-Kα (0.71073)	Graphite monochromated Mo-Kα (0.71073)
Scan mode	ω	ω
Scan width (°)	$0.7+0.35\tan(\theta)$	$0.9+0.35\tan(\theta)$
Scan rate (°/min)	Variable	Variable
θ Range (°)	5.60–24.97	2.04–24.97
Index ranges (°)	$-22\le h\le20,\ -22\le k\le20,\ -24\le l\le0$	$-2\le h\le13,\ -2\le k\le12,\ -3\le l\le28$
No. reflections collected	8713	4791
No. independent reflections	4476 [$R_{int}=0.0676$]	4026 [$R_{int}=0.0469$]
Solution method	Direct methods (SHELX-86)[75]	Direct methods (SHELX-86)[75]
Refinement method	Full-matrix least-squares on F^2 (SHELX-93)[76]	Full-matrix least-squares on F^2 (SHELX-93)[76]
Hydrogen treatment	All H atoms were placed in calculated positions and refined using a riding model	All H atoms were placed in calculated positions and refined using a riding model
Data/restraints/parameters	3988/0/429	3619/9/295
Goodness-of-fit on F^2	0.975	1.015
Final R indices [$I<2\sigma(I)$]	$R_1=0.0362$, $wR_2=0.0739$	$R_1=0.0535$, $wR_2=0.1362$
R indices (all data)	$R_1=0.0886$, $wR_2=0.0896$	$R_1=0.1250$, $wR_2=0.1666$
Extinction coefficient	0.0003(2)	
Largest difference peak and hole (e Å^{-3})	0.553 and −0.451	0.813 and −0.783

[a] For **5a** structure: empirical absorption correction (Ψ scan) was applied with min. and max. transmission of 0.6500 and 0.9479; absolute structure parameter 0.03(7).

Cp-ring), 4.243 (s, 5H, C_5H_5-ring), 4.485 (br.m, 1H, C^3H of palladated Cp-ring); the signal of C^5H of palladated Cp-ring is hidden under the signal of the same proton of major isomer (δ ca. 4.16, m, 1H).

*4.5. X-ray diffraction study of dimeric complex **3** and (S)-prolinate derivative **5a***

Suitable single crystals of dimer **3** and mononuclear adduct **5a** were grown from dichloromethane/hexane and dichloromethane/benzene/hexane mixtures, respectively. Crystal data, data collection, structure solution and refinement parameters are listed in Table 3.

The experimental intensities were corrected for Lorentz and polarization effects.[77] All non-hydrogen atoms in both structures (except the components of disordered groups in adduct **5a**) were refined in the anisotropic approximation. Hydrogen atoms were placed in calculated positions and refined using a riding model.

5. Supplementary materials

Crystallographic data (excluding structure factors) for the structures **3** and **5a** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

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