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Resolution of a cyclopalladated ferrocenylketimine

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The cyclopalladated ferrocenylketimine, $[\{Pd[(\eta^5\text{-}C_5H_5)Fe\{\eta^5\text{-}C_5H_3C(CH_3){=}N(C_6H_4CH_3\text{-}4)\}](\mu\text{-}Cl)\}_2]$ **1** was resolved into optically active diastereomers by using (*S*)-leucine as chiral auxiliary. The new optically active (*S*)-leucinato complexes of Pd^{II} containing ferrocenylketimine could be converted into optically active dimers with the same absolute configurations in the ferrocene moiety. The structure of the chiral dimer (R_p,R_p)-**1** was determined by X-ray diffraction, on the basis of which the absolute configurations of all the optically active compounds studied were ascertained.

Introduction

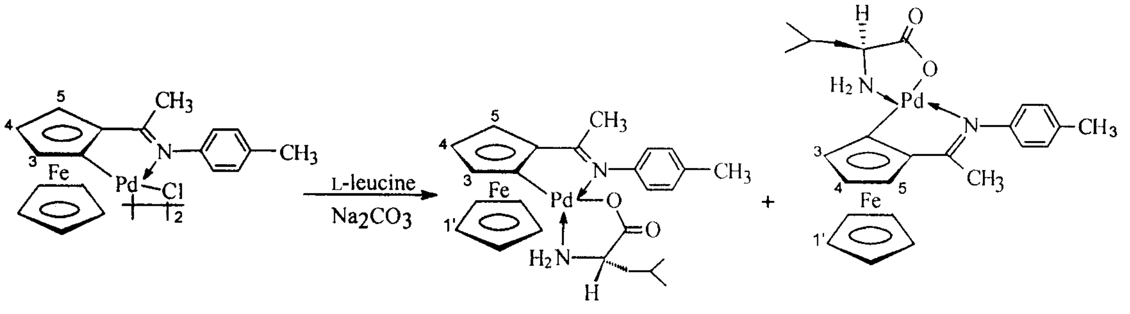
Cyclometallated compounds are important intermediates for synthesizing *ortho*-disubstituted aromatic compounds as well as heterocycles.[1] Chiral cyclopalladated compounds are valuable reagents for asymmetric reaction, resolution, the determination of enantiomeric excess and absolute configuration of chiral substrates.[2] On the other hand, optically active ferrocene derivatives are of increasing importance in the synthesis of chiral ligands used in asymmetric catalysis and asymmetric synthesis.[3] Therefore much effort has gone into developing practical methodologies for asymmetric synthesis and resolution of cyclopalladated ferrocene derivatives, such as: (*a*) enantiopure ferrocenes were mainly obtained by resolution methods with a chiral amino acid;[4] (*b*) Sokolov *et al.*[5] have developed useful methods to afford the planar chiral cyclopalladated ferrocene derivatives in the presence of the salts of optically active amino acids as nucleophilic catalysts. However most of the documented researches involving optically active cyclopalladated ferrocene derivatives have focused on 1-ferrocenyl-*N*,*N*-dimethylethylamine and its analogues; there have been few reports on other ligands.[6] Although the cyclopalladation reaction of ferrocenylimines has been extensively studied,[7] the cyclopalladated ferrocenylimines have not been resolved. In this paper will be reported the resolution and structure of a cyclopalladated ferrocenylketimine.

Results and discussion

A useful candidate for this study was the complex **1** prepared by the published method.[7a] Reaction of complex **1** with Na_2CO_3 and (*S*)-leucine gave the (*S*)-leucinato complex of Pd^{II} containing ferrocenylketimine as a solid in 84% yield (Scheme 1). The diastereomers **2** shown in Scheme 1 were assumed to be the *trans*-N, N form, similar to *ortho*-palladated complexes.[4,8]

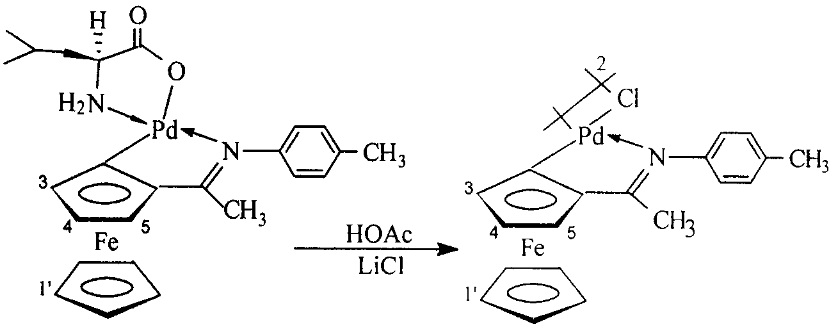
It was found that diastereomers **2** could be resolved both by chromatography and fractional crystallization techniques and the former was a most efficient method. Their isolation was easily achieved by chromatography of the reaction mixture on a silica gel plate developed with CH_2Cl_2–CH_3COCH_3 (1 : 1), since the diastereomer (+)-**2** exhibited a higher R_f value than that of the diastereomer (−)-**2**. Both of the compounds were characterized by elemental analysis, IR and ^1H NMR spectra. The infrared spectra of the imine showed a band at 1561 cm^{-1}. Other IR bands were found at *ca.* 1000 and 1100 cm^{-1}, which indicated an unsubstituted cyclopentadienyl ring.[7a] The IR features of the pair of diastereomers **2** were very similar. The ^1H NMR spectrum of (+)-**2** showed signals of H-3 at δ 4.66 (d), H-4 at δ 4.37 (t) and that of H-5 at δ 4.60 (d), while the other (−)-**2**, showed peaks at δ 4.72 (d), 4.38 (t) and 4.61 (d), respectively. The signal of H-3 was used as an indication of complete separation of the diastereomers.

The complex (+)-$[Pd\{C_5H_5FeC_5H_3C(CH_3){=}N(C_6H_4CH_3\text{-}4)\}(S\text{-}LeuO)]$ (+)-**2** was mixed with LiCl in acetic acid and stirred at room temperature for 10 min, giving (+)-**1** (Scheme 2) with the same absolute configuration of the ferrocene moiety, which was confirmed by CD spectra. The CD spectra of the pair of diastereomers **2** are shown in Fig. 1 together with the CD spectrum of (+)-**1**. The CD spectra of the diastereomers **2** were nearly enantiomeric to each other and the CD spectrum of (+)-**1** was similar to that of (+)-**2**, which indicated that compound (+)-**1** had the same absolute configuration in the ferrocene moiety as that of (+)-**2**. The chiral dimer (+)-**1** was air stable, soluble in dicholoromethane, acetone, and other common organic solvents. Moreover, it underwent a bridge-splitting reaction with PPh_3 to produce quantitatively the



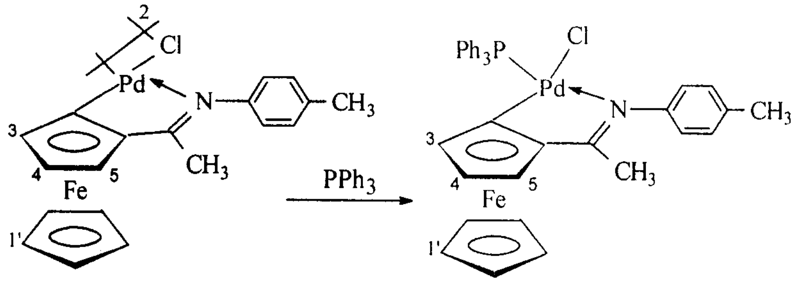
1 (S_p,S_c)-**2** (R_p,S_c)-**2**

Scheme 1



(R_p,S_c)-(+)-**2** (R_p,R_p)-(+)-**1**

Scheme 2



(R_p,R_p)-(+)-**1** (R_p)-(+)-**3**

Scheme 3

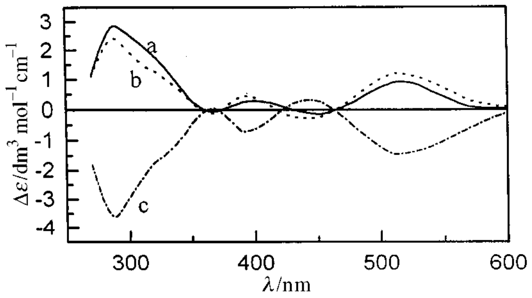


Fig. 1 The CD spectra of methanol solutions of (a) complexes (R_p,R_p)-**1**, (b) (R_p,S_c)-**2** and (c) (S_p,S_c)-**2**.

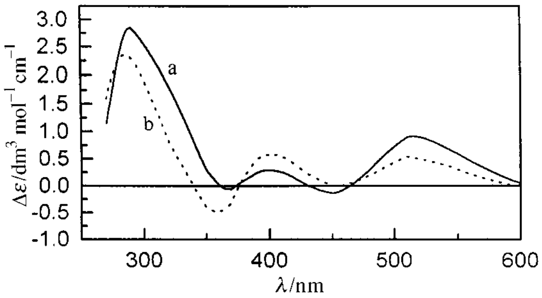


Fig. 2 The CD spectra of methanol solutions of complexes (a) (R_p,R_p)-**1** and (b) (R_p)-**3**.

Table 1 Selected bond distances (Å) for complex (R_p,R_p)-**1**

Pd(1)–Cl(1)	2.328(3)	Pd(1)–Cl(2)	2.470(3)
Pd(1)–N(1)	2.071(8)	Pd(1)–C(1)	1.969(9)
Pd(2)–Cl(1)	2.490(3)	Pd(2)–Cl(2)	2.321(3)
Pd(2)–N(2)	2.091(9)	Pd(2)–C(20)	1.96(1)
Fe(1)–C(1)	2.04(1)	Fe(1)–C(2)	2.02(1)
Fe(1)–C(3)	2.06(1)	Fe(1)–C(4)	2.04(1)
Fe(1)–C(5)	2.06(1)	Fe(1)–C(6)	2.04(1)
Fe(1)–C(7)	2.04(1)	Fe(1)–C(8)	2.04(1)
Fe(1)–C(9)	2.08(1)	Fe(1)–C(10)	2.03(2)
Fe(2)–C(20)	2.02(1)	Fe(2)–C(21)	2.06(1)
Fe(2)–C(22)	2.05(1)	Fe(2)–C(23)	2.03(1)
Fe(2)–C(24)	2.04(1)	Fe(2)–C(25)	2.06(2)
Fe(2)–C(26)	2.09(1)	Fe(2)–C(27)	2.04(2)
Fe(2)–C(28)	2.08(1)	Fe(2)–C(29)	2.05(2)
N(1)–C(11)	1.30(1)	N(1)–C(13)	1.43(1)
N(2)–C(30)	1.30(1)	N(2)–C(32)	1.42(1)
C(1)–C(2)	1.40(2)	C(1)–C(5)	1.43(1)
C(2)–C(3)	1.42(2)	C(2)–C(11)	1.48(2)
C(3)–C(4)	1.44(2)	C(4)–C(5)	1.42(1)
C(6)–C(7)	1.34(2)	C(6)–C(10)	1.41(3)
C(7)–C(8)	1.36(2)	C(8)–C(9)	1.38(3)
C(9)–C(10)	1.48(3)	C(20)–C(21)	1.40(2)
C(20)–C(24)	1.42(2)	C(21)–C(22)	1.44(2)
C(21)–C(30)	1.44(2)	C(22)–C(23)	1.44(2)
C(23)–C(24)	1.38(2)	C(25)–C(26)	1.38(3)
C(25)–C(29)	1.43(3)	C(26)–C(27)	1.43(2)
C(27)–C(28)	1.42(3)	C(28)–C(29)	1.41(3)

monomeric triphenylphosphine derivative (+)-**3**, a typical reaction of chloride-bridged binuclear complexes of palladium[9] (Scheme 3). The CD spectrum of (+)-**3** is compared with that of (+)-**1** in Fig. 2. The results also showed that the absolute configuration of the ferrocene moiety in (+)-**3** was same as that in (+)-**1**, consistent with the addition of triphenylphosphine leading only to cleavage of the di-μ-chloro bridges without breaking of Pd–C and Pd–N bonds.

As has been previously described, the (*S*)-leucinato complexes of cyclopalladated ferrocenylimines can be successfully converted into dimers with the same configuration in the ferrocene moiety, but their single crystals are difficult to obtain. Therefore, the optically active dimer (+)-**1** was chosen to determine the absolute configuration by X-ray diffraction. The structure is shown in Fig. 3. Selected bond lengths and angles are listed in Tables 1 and 2, respectively. The structure shows clearly that (+)-**1** is a binuclear complex of palladium, and that both the palladium atoms are linked to *ortho* positions of the substituted ferrocenyl rings resulting in two five membered metallocycles. The two metallocycles, which are nearly planar, form a dihedral angle of 62.70° with each other. The plane

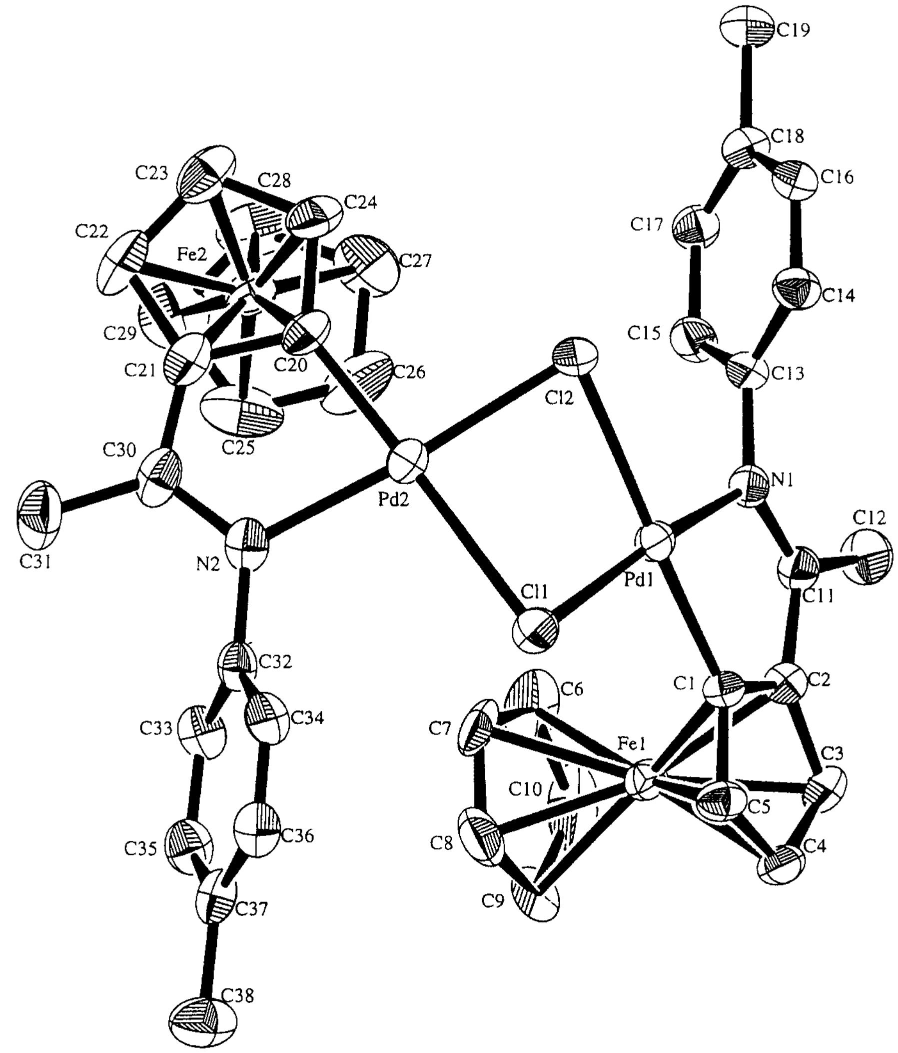


Fig. 3 Molecular structure of complex (R_p,R_p)-**1**.

Table 2 Selected bond angles (°) for complex (R_p,R_p)-**1**

Cl(1)–Pd(1)–Cl(2)	87.0(1)	Cl(1)–Pd(1)–N(1)	168.7(3)
Cl(1)–Pd(1)–C(1)	92.5(3)	Cl(2)–Pd(1)–N(1)	100.6(2)
Cl(2)–Pd(1)–C(1)	177.2(3)	N(1)–Pd(1)–C(1)	80.4(4)
Cl(1)–Pd(2)–Cl(2)	86.6(1)	Cl(1)–Pd(2)–N(2)	100.5(3)
Cl(1)–Pd(2)–C(20)	179.2(4)	Cl(2)–Pd(2)–N(2)	169.7(2)
Cl(2)–Pd(2)–C(20)	93.4(4)	N(2)–Pd(2)–C(20)	79.5(5)
Pd(1)–Cl(1)–Pd(2)	81.96(9)	Pd(1)–Cl(2)–Pd(2)	82.55(9)
Pd(1)–N(1)–C(11)	116.4(7)	Pd(1)–N(1)–C(13)	122.2(7)
C(11)–N(1)–C(13)	120.9(9)	Pd(2)–N(2)–C(30)	115.6(8)
Pd(2)–N(2)–C(32)	121.4(7)	C(30)–N(2)–C(32)	122(1)
Pd(1)–C(1)–Fe(1)	119.9(5)	Pd(1)–C(1)–C(2)	113.5(7)
Pd(1)–C(1)–C(5)	138.7(9)	C(3)–C(2)–C(11)	133(1)
C(1)–C(2)–C(11)	116.8(10)	N(1)–C(11)–C(12)	128(1)
N(1)–C(11)–C(2)	112.3(9)	N(1)–C(13)–C(14)	119.2(10)
C(2)–C(11)–C(12)	118.9(10)	Pd(2)–C(20)–Fe(2)	124.1(6)
N(1)–C(13)–C(15)	121.9(10)	Pd(2)–C(20)–C(24)	138(1)
Pd(2)–C(20)–C(21)	114.1(9)	C(20)–C(21)–C(30)	116.7(10)
C(22)–C(21)–C(30)	133(1)	N(2)–C(30)–C(21)	113(1)
N(2)–C(30)–C(31)	125(1)	C(21)–C(30)–C(31)	120(1)
N(2)–C(32)–C(33)	120(1)	N(2)–C(32)–C(34)	121(1)

Pd(1)Cl(2)Pd(2) forms a dihedral angle of 129.67° with plane Pd(2)Cl(1)Pd(1). Owing to the co-ordination between the palladium atoms and the nitrogen atoms, the angles Pd(1)–C(1)–C(2), C(1)–C(2)–C(11), Pd(2)–C(20)–C(21) and C(20)–C(21)–C(30) are decreased to 113.5, 116.8, 114.1 and 116.7°, respectively, compared with the normal value of 126°.[7a] The Pd(1)–N(1) and Pd(2)–N(2) distances are 2.071(8) and 2.091(9) Å, respectively, suggesting the formation of Pd–N bonds. The two halves of the molecule are in a *cis* arrangement and exhibit identical planar chirality (*R* configuration).[10] So the compound (+)-**2** had the same absolute *R* configuration in the ferrocene moiety, and (−)-**2** had the *S* configuration, and (+)-**2**, (−)-**2**, (+)-**1** and (+)-**3** were assigned as (R_p,S_c)-**2**, (S_p,S_c)-**2**, (R_p,R_p)-**1** and R_p-**3**, respectively.

Experimental

General

Melting points were measured on a WC-1 apparatus and are uncorrected. Elemental analyses were determined with a Carlo Erba 1160 elemental analyzer. Proton NMR spectra were recorded on a Bruker DPX 400 spectrometer using Me_2SO as the solvent and $SiMe_4$ as an internal standard, IR spectra on a Perkin-Elmer FTIR 1750 spectrophotometer. Preparative TLC was performed on dry silica gel plates developed with dichloromethane–acetone (1 : 1). Optical rotations at 5890 Å were determined by a Perkin-Elmer 341 polarimeter at 20 °C. The CD spectra were recorded on GJASCO J-20C automatic recording spectropolarimeter at 20 °C.

Syntheses

[Pd{$C_5H_5FeC_5H_3C(CH_3)$=N($C_6H_4CH_3$-4)}(*S*-LeuO)] 2. To a methanol suspension (10 ml) of complex **1** (1.0 g, 1.1 mmol) was added a slight excess of (*S*)-leucine (0.16 g, 1.2 mmol) and Na_2CO_3 (0.13 g, 1.2 mmol) and stirred for 6 h at room temperature until the solution became clear. After evaporation of the solvent *in vacuo* the crude residue was treated with CH_2Cl_2 in order to remove the unchanged amino acid. Further evaporation of the CH_2Cl_2 and treatment of the residue with CH_2Cl_2–light petroleum (bp 60–90 °C) (1:3) afforded a 1:1 mixture of diastereomers **2** in 84% yield. Their separation was easily achieved by TLC of the mixture on a silica gel plate developed with dichloromethane–acetone (1:1); the first band was (R_p,S_c)-**2**, the second (S_p,S_c)-**2**.

(R_p,S_c)-(+)-[Pd{$C_5H_5FeC_5H_3C(CH_3)$=N($C_6H_4CH_3$-4)}(*S*-LeuO)] (R_p,S_c)-**2**: red crystals, mp >250 °C (decomp.), $[\alpha]_D^{20}$ +2209.3 deg cm^3 g^{-1} dm^{-1} (*c* 0.0086 g per 100 ml in CH_3OH), R_f 0.68 (Found: C, 54.32; H, 5.48; N, 5.15. Calc. for $C_{25}H_{30}FeN_2O_2Pd$: C, 54.32; H, 5.47; N, 5.07%). IR(KBr): 3287, 3091, 2955, 2867, 1619, 1561, 1508, 1474, 1106, 1001, 817, 722 and 669 cm^{-1}. ^1H NMR: δ 4.66 (d, 1 H, J = 2.0, H-3), 4.60 (d, 1 H, J = 2.4, H-5), 4.37 (t, 1 H, J = 2.2, H-4), 4.32 (s, 5 H, H-1′), 7.17 (d, 2 H, J = 8.0, NC_6H_4), 7.00 (d, 2 H, J = 8.0, NC_6H_4), 2.05 (s, 3 H, CH_3); 2.31 (s, 3 H, CH_3), 1.53 [m, 1 H, $CH(CH_3)_2$], 1.66 (m), 1.85 (m, 2 H, CH_2), 3.20 (m, 1 H, NH_2CH), 0.88, 0.86 [d, 6 H, J = 6.6 Hz, $(CH_3)_2CH$].

(S_p,S_c)-(−)-[Pd{$C_5H_5FeC_5H_3C(CH_3)$=N($C_6H_4CH_3$-4)}(*S*-LeuO)] (S_p,S_c)-**2**: red crystals, mp >250 °C (decomp.), $[\alpha]_D^{20}$ −2344.8 deg cm^3 g^{-1} dm^{-1} (*c* 0.0116 g per 100 ml in CH_3OH), R_f 0.58 (Found: C, 54.32; H, 5.42; N, 5.12. Calc. for $C_{25}H_{30}FeN_2O_2Pd$: C, 54.32; H, 5.47; N, 5.07%). IR(KBr): 3290, 3092, 2954, 2868, 1618, 1561, 1508, 1471, 1106, 1001, 815, 720 and 669 cm^{-1}. ^1H NMR: δ 4.72 (d, 1 H, J = 2.0, H-3), 4.61 (d, 1 H, J = 2.4, H-5), 4.38 (t, 1 H, J = 2.2, H-4), 4.32 (s, 5 H, H-1′), 7.18 (d, 2 H, J = 8.0, NC_6H_4), 6.98 (d, 2 H, J = 8.0, NC_6H_4), 2.06 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 1.68 [m, 1 H, $CH(CH_3)_2$], 1.92, 1.78 (m, 2 H, CH_2), 3.17 (m, 1 H, NH_2CH), 0.95, 0.99 [2d, 6 H, J = 6.4 Hz, $(CH_3)_2CH$].

R_p,R_p-(+)-[{PdCl[$C_5H_5FeC_5H_3C(CH_3)$=N($C_6H_4CH_3$-4)]}$_2$] (R_p,R_p)-1. A methanol solution (1 ml) of 0.1 g of complex (R_p,S_c)-**2** and 2 mol of LiCl was mixed with acetic acid (6 ml). The mixture was stirred at room temperature for about 10 min, then filtered, and washed with light petroleum three times. The solid obtained was recrystallized from CH_2Cl_2–light petroleum (bp 60–90 °C) to produce compound (R_p,R_p)-**1**. Red crystals, yield 92.4%, mp >210 °C (decomp.), $[\alpha]_D^{20}$ +3212.5 deg cm^3 g^{-1} dm^{-1} (*c* 0.0080 g per 100 ml in $CHCl_3$) (Found: C, 49.92; H, 3.91; N, 2.93. Calc. for $C_{19}H_{18}ClFeNPd$: C, 49.82; H, 3.96; N, 3.06%). IR(KBr): 3090, 2920, 1551, 1508, 1474, 1105, 999, 817, 721 and 693 cm^{-1}. ^1H NMR: δ 5.14 (2 H, H-3), 4.73 (2 H, H-5), 4.48 (2 H, H-4), 4.38 (s, 10 H, H-1′), 2.01 (s, 6 H, CH_3), 2.31 (s, 6 H, CH_3), 7.14 (d, 4 H, J = 8.0, NC_6H_4) and 6.94 (d, 4 H, J = 6.8 Hz, NC_6H_4).

Compound (R_p)-3. This was prepared by the published method.[7a] Red crystals, yield 79.2%. mp >220 °C (decomp.). $[\alpha]_D^{20}$ +1704.5 deg cm^3 g^{-1} dm^{-1} (*c* 0.0088 g per 100 ml in $CHCl_3$) (Found: C, 61.48; H, 4.67; N, 1.93. Calc. for $C_{37}H_{33}ClFeNPPd$: C, 61.72; H, 4.62; N, 1.94%). IR(KBr): 3067, 3049, 2921, 1569, 1507, 1480, 1094, 998, 817, 758 and 700 cm^{-1}. ^1H NMR: δ 3.15 (1 H, H-3), 4.65 (1 H, H-5), 4.17 (1 H, H-4), 3.30 (s, 5 H, H-1′), 2.05 (s, 3 H, CH_3); 2.31 (s, 3 H, CH_3), 7.15 (d, 2 H, J = 7.6, NC_6H_4), 6.89 (d, 2 H, J = 7.6 Hz, NC_6H_4), 7.48 m, 7.70 m (15 H, PPh_3).

Crystal structure determination of complex (R_p,R_p)-1

Crystal data. $C_{38}H_{36}Cl_2N_2Fe_2Pd_2$, M = 916.12, red prismatic, crystal size 2.70 × 0.10 × 1.00 mm, monoclinic, space group $P2_1$ (no. 4), a = 11.64(1), b = 12.083(2), c = 13.004(2) Å, β = 94.445(3)°, Z = 2, V = 1824.1 Å^3, D_c = 1.668 g cm^{-3}, F(000) = 912, μ(Mo-Kα) = 19.25 cm^{-1}.

Data collection. All measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo-Kα radiation (λ = 0.71070 Å). The data were collected at 15 ± 1 °C to a maximum 2θ value of 55.0°. A total of 45 images of 4.00° oscillation were collected, each being exposed for 16.0 min. The crystal-to-detector distance was 110.00 mm with the detector at the zero swing position. The data were corrected for Lorentz-polarization effects. The structure was solved by direct methods[11] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3374 observed reflections [$I > 3.00\sigma(I)$] and 416 variable parameters. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The maximum and minimum peaks on the final Fourier-difference map corresponded to 1.89 and −1.45 e Å^{-3}, respectively. The absolute configuration of complex (R_p,R_p)-**1** was confirmed by the significance of the difference between the two sigma weighted R factors, as judged by the Hamilton test.[12] The final R factors were 0.042 (R' = 0.062) and 0.043 (0.063) for the R and S configuration in the ferrocene moiety, respectively. All calculations were performed using the TEXSAN crystallographic software package.[13]

CCDC reference number 186/1177.

See http://www.rsc.org/suppdata/dt/1998/3727/ for crystallographic files in .cif format.

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