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# Isolation and absolute configurations of diastereomers of a dimeric chloro-bridged planar chiral cyclopalladated derivative of ferrocene

Gang Zhao, Qi-Guang Wang and Thomas C. W. Mak *

*Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong*

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## Abstract

Two diastereomers of a dimeric chloro-bridged planar chiral cyclopalladated derivative of ferrocene were isolated in enantiomerically pure form and their absolute configurations have been determinated by single-crystal X-ray analysis. © 1998 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Chiral cyclopalladated compounds are of great interest as a consequence of their useful applications in many areas, such as (i) materials chemistry,[1] (ii) resolution,[2] (iii) the determination of enantiomeric excess[3] and absolute configuration of chiral compounds,[4] and (iv) the promotion of asymmetric Diels–Alder reactions.[5] Although many cyclopalladated derivatives of ferrocene are known,[1] most of them have been obtained as racemic mixtures. The isolation and X-ray crystal structure analysis of a related enantiomerically pure $C_2$-symmetric complex has been reported;[6] however, its stereoisomer has not been obtained and direct comparison of their structure characteristics is impossible so far. Moreover, there are six possible stereoisomers for a dimeric chloro-bridged planar chiral cyclopalladated derivative of ferrocene, and it is generally difficult to obtain these compounds in enantiomerically pure form.[7] Isolation and absolute configuration determination of this kind of compound are very important for understanding its stereochemistry. Here we present a simple and highly stereoselective synthesis of planar chiral cyclopalladated derivatives of ferrocene.

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* Corresponding author. E-mail: tcwmak@cuhk.edu.hk

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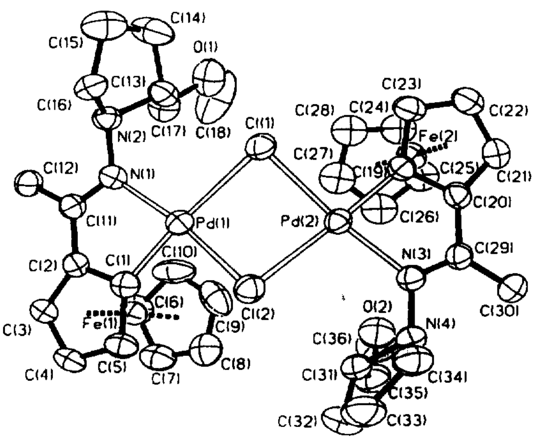
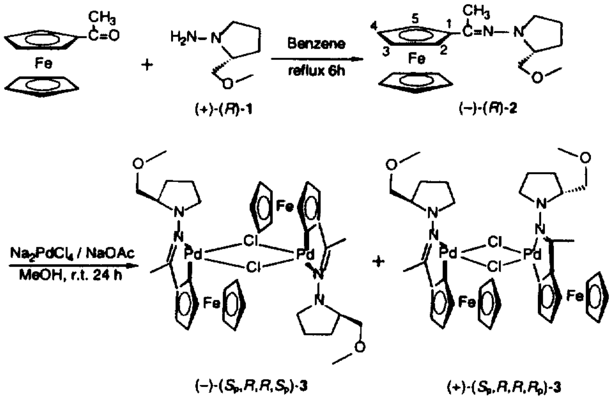


Fig. 1. Molecular structure (30% thermal ellipsoids) and absolute configuration of (−)-($S_p$,$R$,$R$,$S_p$)-**3** with atom-numbering scheme. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 1.957(6), Pd(1)–N(1) 2.081(5), Pd(1)–Cl(1) 2.485(2), Pd(1)–Cl(2) 2.339(2), N(1)–C(11) 1.308(8), C(2)–C(11) 1.435(8), C(1)–C(2) 1.444(8), Cl(1)–Pd(1)–Cl(2) 84.14(6), C(1)–Pd(1)–N(1) 80.1(2), C(2)–C(1)–Pd(1) 113.4(4), C(1)–C(2)–C(11) 116.5(5), C(2)–C(11)–N(1) 113.4(5), C(11)–N(1)–Pd(1) 116.4(4), C(1)–Pd(1)–Cl(2) 91.9(2), Cl(1)–Pd(1)–N(1) 103.9(1)

## 2. Results and discussion

Ferrocenylimine (−)-($R$)-**2** was readily prepared from acetylferrocene by condensation with (+)-($R$)-1-amino-2-(methoxymethyl)pyrrolidine (+)-($R$)-**1** in dry benzene. Asymmetric cyclopalladation of (−)-($R$)-**2** with sodium tetrachloropalladate(II) and sodium acetate trihydrate in methanol at room temperature gave an isomeric mixture of new compounds (−)-($S_p$,$R$,$R$,$S_p$)-**3** and (+)-($S_p$,$R$,$R$,$R_p$)-**3** in 75% yield with a high level of stereoselectivity [d.e.=92.5% ($^1$H NMR)], and enantiopure samples were obtained by separation through column chromatography. Their structural relationship was elucidated by $^1$H NMR, thin-layer chromatography and single-crystal X-ray analysis. As shown in Figs 1 and 2, two ferrocenyl units of $S_p$ configuration are bridged by two chlorides in (−)-($S_p$,$R$,$R$,$S_p$)-**3**, but one unit of $S_p$ configuration and another of $R_p$ configuration are so connected in (+)-($S_p$,$R$,$R$,$R_p$)-**3**. Accordingly these two compounds are diastereomers.



With reference to the mean plane of the Pd and Cl atoms, the pair of ferrocenyl groups take a *cis* arrangement in (−)-($S_p$,$R$,$R$,$S_p$)-**3**, but a *trans* arrangement in (+)-($S_p$,$R$,$R$,$R_p$)-**3**. The $Pd_2Cl_2$ ring is significantly folded in (−)-($S_p$,$R$,$R$,$S_p$)-**3** but nearly planar in (+)-($S_p$,$R$,$R$,$R_p$)-**3** [the angle between the two planes defined by the atoms Pd(1), Cl(1), Cl(2) and Pd(2), Cl(1), Cl(2) is 50.0° for (−)-($S_p$,$R$,$R$,$S_p$)-**3**

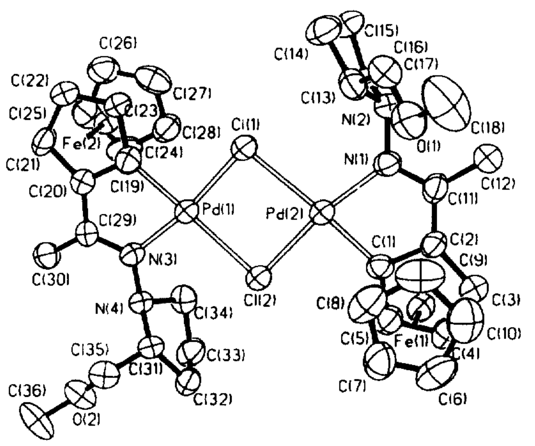
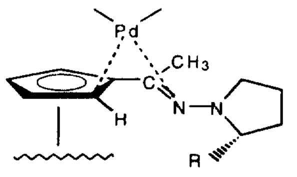


Fig. 2. Molecular structure (30% thermal ellipsoids) and absolute configuration of (+)-($S_p$,$R$,$R$,$R_p$)-**3** with atom-numbering scheme. Selected bond lengths (Å) and angles (°): Pd(1)–C(1) 1.951(4), Pd(1)–N(1) 1.999(4), Pd(1)–Cl(1) 2.480(1), Pd(1)–Cl(2) 2.275(1), N(1)–C(11) 1.288(5), C(2)–C(11) 1.401(6), C(1)–C(2) 1.417(6), Cl(1)–Pd(1)–Cl(2) 86.68(4), C(1)–Pd(1)–N(1) 81.2(2), C(2)–C(1)–Pd(1) 112.5(3), C(1)–C(2)–C(11) 114.8(4), C(2)–C(11)–N(1) 116.3(4), C(11)–N(1)–Pd(1) 115.2(3), C(1)–Pd(1)–Cl(2) 89.9(1), Cl(1)–Pd(1)–N(1) 102.3(1)

and 11.9° for (+)-($S_p$,$R$,$R$,$R_p$)-**3**]. Each palladium atom in the metallacycle is in a slightly distorted square-planar coordination environment. In both structures, the pair of cyclopentadienyl rings are each planar and nearly parallel to each other [tilt angle: 2.1° for (−)-($S_p$,$R$,$R$,$S_p$)-**3** and 4.5° for (+)-($S_p$,$R$,$R$,$R_p$)-**3**], and the two rings involved in the bicyclic system formed by fusion of the palladocycle with the ferrocenyl $C_5H_3$ moiety are approximately co-planar, the relevant dihedral angle being 0.8° for (−)-($S_p$,$R$,$R$,$S_p$)-**3** and 2.7° for (+)-($S_p$,$R$,$R$,$R_p$)-**3**]. The diastereoselectivity of the orthopalladation of ferrocenylimine (−)-($R$)-**2** can be rationalised by the following steric repulsion model.



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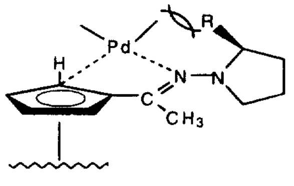

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## 3. Experimental

$^{1}$H NMR and $^{13}$C-{$^{1}$H} NMR were recorded on a Bruker DPX 300 instrument using $CDCl_3$ (99.8%) as the solvent. Optical rotations were measured in $CHCl_3$ in a 1 dm cell at 20°C with a Perkin–Elmer Model 341 polarimeter. Elemental analyses were performed by MEDAC Ltd of the Department of Chemistry at Brunel University. Acetylferrocene and (+)-($R$)-**1** were products of Aldrich and used as received.

### 3.1. Preparation of (−)-(R)-2

Acetylferrocene (1.76 g, 7.70 mmol) and (+)-($R$)-**1** (1.0 g, 7.7 mmol) were dissolved in dry benzene (100 mL) in which 5 Å molecular sieves (3.0 g) were introduced. The red solution was refluxed on an oil bath for about 6 h, and then carefully filtered. The filtrate was reduced to dryness and washed with $n$-hexane to produce (−)-($R$)-**2** as a brown powder (yield: 2.25 g, 86%). Characterization data: m.p.

67–69°C; $[\alpha]_D^{20}$=−431.8 (*c* 1.0, $CHCl_3$); selected $^1H$ NMR data: δ 2.29 (s, 3H, $CH_3C{=}N$), 3.28 (m, 5H, $OCH_2$, $OCH_3$), 4.10 [s, 5H, $C_5H_5$), 4.40 [s, 2H, $H^3$, $H^4$ ($C_5H_4$)], 4.67 [s, 2H, $H^2$, $H^5$ ($C_5H_4$)]; selected $^{13}C$-{$^1H$} NMR data: δ 17.4 (N=C*Me*), 70.4 ($C_5H_5$), 72.9 [$C^2$, $C^5$ ($C_5H_4$)], 76.2 [$C^3$, $C^4$ $C_5H_4$)]; anal. calcd for $C_{18}H_{24}N_2OFe$: C, 63.54; H, 7.11; N, 8.24. Found: C, 63.42; H, 7.21; N, 8.25.

### 3.2. Preparation of (−)-($S_p$,R,R,$S_p$)-3 and (+)-($S_p$,R,R,$R_p$)-3

The imine (+)-(*S*)-**3** (0.34 g, 1.0 mmol) was added to a methanolic (30 mL) solution containing $Na_2PdCl_4$ (0.30 g, 1.0 mmol) and NaOAc·$3H_2O$ (0.14 g, 1.0 mmol). The resulting mixture was stirred at room temperature for 24 h. The mixture was eluted through a silica 60 column with 10:1 chloroform:*n*-hexane. Concentration of the eluted solution of two successive red bands produced (−)-($S_p$,*R*,*R*,$S_p$)-**3** and (+)-($S_p$,*R*,*R*,$R_p$)-**3** in that order, which were recrystallized from dichloromethane:*n*-hexane (1:3) as red plates [product ratio 96:4, total yield 0.39 g (75%)].

Characterization data for (−)-($S_p$,*R*,*R*,$S_p$)-**3**: m.p.>210° (dec.); $[\alpha]_D^{20}$=−2720.2 (c 1.0 in $CHCl_3$); selected $^1H$ NMR data: δ 2.33 (s, 6H, $CH_3C{=}N$), 3.23 (m, 10H, $OCH_2$, $OCH_3$), 4.20 [d, *J*=2.4 Hz, 2H, $H^3$ ($C_5H_3$)], 4.26 [s, 10H, ($C_5H_5$)], 4.44 [d, *J*=1.5 Hz, 2H, $H^5$ ($C_5H_3$)], 4.72 [t, *J*=8.1, 2H, $H^4$ ($C_5H_3$)]; selected $^{13}C$-{$^1H$} NMR data: δ 15.7 (N=C*Me*), 70.5 [$C^5$ ($C_5H_3$)], 70.2 [$C^3$ ($C_5H_3$)], 68.3 [$C^4$ ($C_5H_3$)], 71.6 ($C_5H_5$), 102.8 [$C^1$ ($C_5H_3$)], 187.4 (C=N); anal. calcd for $C_{36}H_{46}Cl_2Fe_2N_4O_2Pd_2$: C, 44.94; H, 4.82; N, 5.82. Found: C, 44.80; H, 4.78; N, 5.92.

For (+)-($S_p$,*R*,*R*,$R_p$)-**3** m.p.>210° (dec.); $[\alpha]_D^{20}$=−2900.8 (c 1.0 in $CHCl_3$); selected $^1H$ NMR data: δ 2.21 (s, 6H, $CH_3C{=}N$), 3.36 (m, 10H, $OCH_2$, $OCH_3$), 4.18 [s, 2H, $H^3$ ($C_5H_3$)], 4.30 [s, 10H, ($C_5H_5$)], 4.24 [s, 2H, $H^5$ ($C_5H_3$)], 4.67 [t, *J*=19.8, 2H, $H^4$ ($C_5H_3$)]; selected $^{13}C$-{$^1H$} NMR data: δ 15.8 (N=C*Me*), 71.2 [$C^5$ ($C_5H_3$)], 68.0 [$C^3$ ($C_5H_3$)], 66.2 [$C^4$ ($C_5H_3$)], 74.3 ($C_5H_5$), 102.0 [$C^1$ ($C_5H_3$)], 187.6 (C=N); anal. calcd for $C_{36}H_{46}Cl_2Fe_2N_4O_2Pd_2$: C, 44.94; H, 4.82; N, 5.82. Found: C, 44.90; H, 4.89; N, 5.73.

### 3.3. Crystallography

(−)-($S_p$,*R*,*R*,$S_p$)-**3**: Monoclinic, space group $P2_1$ (No. 4), *a*=12.948(3) Å, *b*=11.090(2) Å, *c*=13.302(3) Å, β=95.65(3), *Z*=2, ρ=1.681 g $cm^{-3}$. Of the 6500 reflections collected, 6355 reflections ($F>4\sigma(F_o)$) were used for the refinement. The final residuals were *R*1=3.73%, *wR*2=10.64%, and GOF=0.998. For (+)-($S_p$,*R*,*R*,$R_p$)-**3**: monoclinic, space group $P2_1$ (No. 4), *a*=10.709(2) Å, *b*=8.386(2) Å, *c*=20.150(4) Å, β=94.08(3)°, *Z*=2, ρ=1.770 g $cm^{-3}$. All 5681 reflections collected ($F>4\sigma(F_o)$) were used for the refinement. The final residuals were *R*1=7.10%, *wR*2=19.12%, and GOF=1.044. Intensity data were collected on an MSC/Rigaku RAXIS IIC imaging-plate diffractometer at 294 K using graphite-monochromatized Mo-$K_\alpha$ radiation (λ=0.7107 Å) from a rotating-anode generator operating at 50 kV and 90 mA. A self-consistent semi-empirical absorption correction based on symmetry-equivalent data was applied. The crystal structures were determined by the direct method and refined using the SHELXL-PC package.[8]

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