



Pergamon

Tetrahedron: Asymmetry 9 (1998) 2253–2257

TETRAHEDRON:
ASYMMETRY

Synthesis of optically-active planar chiral derivatives of ferrocene. Crystal structures of alkyne insertion products

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Received 23 March 1998; accepted 18 May 1998

Abstract

Asymmetric cyclopalladation of new chiral ferrocenylimine (*S*)-(-)-[$\{\eta^5\text{-C}_5\text{H}_4\text{CH}=\text{NCH}(\text{CH}_3)(\text{c-C}_6\text{H}_{11})\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}$, (*S*)-(-)-**3**, gave di- μ -chloro-bridged cyclopalladated (*R*_p,*S*,*S*,*R*_p)-(+)-[Pd{($\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}(\text{CH}_3)(\text{c-C}_6\text{H}_{11})\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\mu\text{-Cl})_2$, (*R*_p,*S*,*S*,*R*_p)-(+)-**4**. Treatment of (*R*_p,*S*,*S*,*R*_p)-(+)-**4** or (*S*_p,*S*,*R*,*S*,*S*,*R*,*S*,*S*_p)-(+)-[Pd{($\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}(\text{CH}_3)(\text{c-C}_6\text{H}_{11})\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\mu\text{-Cl})_2$, (*S*_p,*S*,*R*,*S*,*S*,*R*,*S*,*S*_p)-(+)-**6**, with diphenylacetylene yielded the corresponding bis(alkyne) insertion products (*R*_p,*S*)-(+)-[Pd{($\eta^3\text{-(C}_6\text{H}_5\text{C}=\text{CC}_6\text{H}_5)_2$)PdCl}($\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}(\text{CH}_3)(\text{c-C}_6\text{H}_{11})\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\mu\text{-Cl})_2$, (*R*_p,*S*)-(+)-**5**, and (*S*_p,*S*,*R*,*S*)-(-)-[Pd{($\eta^3\text{-(C}_6\text{H}_5\text{C}=\text{CC}_6\text{H}_5)_2$)PdCl}($\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}(\text{CH}_3)(\text{c-C}_6\text{H}_{11})\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\mu\text{-Cl})_2$, (*S*_p,*S*,*R*,*S*)-(-)-**7**, respectively. The absolute configurations of (*R*_p,*S*)-(+)-**5** and (*S*_p,*S*,*R*,*S*)-(-)-**7** have been determined by single-crystal X-ray analysis. © 1998 Elsevier Science Ltd. All rights reserved.

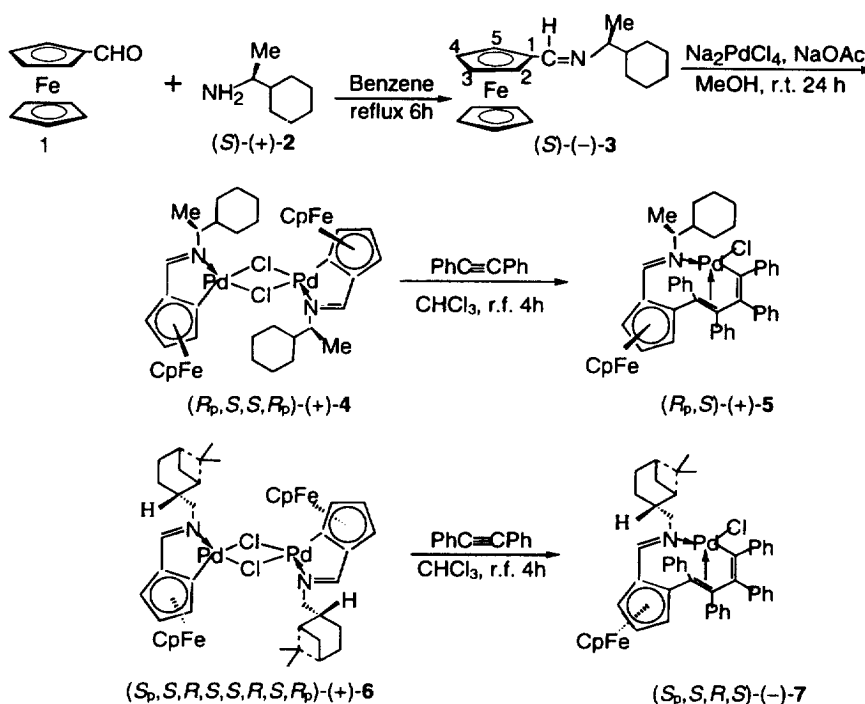
1. Introduction

Although the general utility of chiral cyclopalladated complexes in asymmetric synthesis¹ is well-known, few optically-active cyclopalladated compounds containing the ferrocenyl moiety have been synthesized.^{2,3} Pfeffer et al. have described the reaction of chloro-bridged cyclopalladated dimers with a variety of substituted alkynes under different conditions.⁴ However, to our knowledge, there is no known crystal structure determination of any planar chiral derivative of ferrocene containing an η^3 -butadienyl unit. Here we present the synthesis of optically-active di- μ -chloro-bridged cyclopalladated dimers which react readily with diphenylacetylene to afford monomeric complexes containing an η^3 -butadienyl ligand, whose absolute configurations have been established by single-crystal X-ray analysis.

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2. Results and discussion

The ferrocenyylimine (*S*)-(-)-**3** was obtained from the reaction between ferrocenecarboxaldehyde and (*S*)-(+)-1-cyclohexylethylamine in benzene. Asymmetric cyclopalladation of the ferrocenyylimine with Na_2PdCl_4 and $\text{NaOAc} \cdot 3\text{H}_2\text{O}$ in MeOH gave the corresponding di- μ -chloro-bridged dimer (R_p, S, S, R_p)-(+)-**4**. Treatment of (R_p, S, S, R_p)-(+)-**4** or ($S_p, S, R, S, S, R, S, S_p$)-(+)-**6**³ with diphenylacetylene yielded the corresponding bis(alkyne) insertion compounds (R_p, S)-(+)-**5** and (S_p, S, R, S)-(-)-**7**, respectively (Scheme 1).



^1H NMR in CDCl_3 showed that the two peaks due to the pairs H^2 , H^5 and H^3 , H^4 of the ferrocenylylmines split into three signals (H^3 , H^4 , H^5), and comparison of the ^{13}C - $\{^1\text{H}\}$ NMR spectra of free imines and their 1,2-disubstituted compounds showed splitting of the resonance due to the C^3 , C^4 pair of carbon atoms, since the formation of the metallacycle involves a decrease in the symmetry of the substituted cyclopentadienyl ring. The diastereoselectivity of cyclopalladation was very high, as no trace of other isomers was found (^1H NMR). Single crystal X-ray analysis was used to establish the absolute configuration of the planar chirality created: R_p for planar chirality of the ferrocenyl moiety, S_c at C(16) for (R_p, S)-(+)-**5** (Fig. 1); S_p for the ferrocenyl moiety, S_c at C(18) and C(20) and R_c at C(17) for (S_p, S, R, S)-(-)-**7** (Fig. 2). In each, the palladium atom is effectively four-coordinated, since it is bound to a chloro ligand, the nitrogen atom, the terminal carbon atom C(14) of the η^3 -butadienyl fragment, and the mid-point of the C(11)–C(12) bond (hereafter referred to as X).

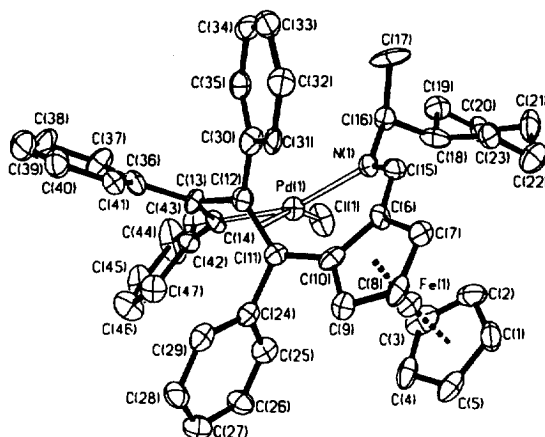


Fig. 1. Molecular structure (30% thermal ellipsoids) and absolute configuration of (R_p,S)-(+)-**5** with atom-numbering scheme. Selected bond lengths (Å) and angles (°): Pd(1)–N(1), 2.12(1); Pd(1)–Cl(1), 2.313(4); Pd(1)–C(14), 1.93(1); Pd(1)–C(11), 2.18(1); Pd(1)–C(12), 2.15(1); Pd(1)–X, 2.030; Cl(1)–Pd(1)–N(1), 92.4(4); Cl(1)–Pd(1)–C(14), 99.5(5); N(1)–Pd(1)–X, 99.9; C(14)–Pd(1)–X, 73.3; C(11)–C(12)–C(13)–C(14), –53.9

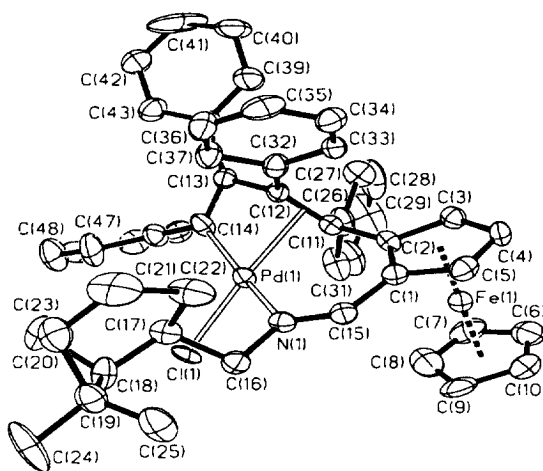


Fig. 2. Molecular structure (30% thermal ellipsoids) and absolute configuration of (S_p,S,R,S)-(-)-**7** with atom-numbering scheme. Selected bond lengths (Å) and angles (°): Pd(1)–N(1), 2.169(3); Pd(1)–Cl(1), 2.391(1); Pd(1)–C(14), 1.972(4); Pd(1)–C(11), 2.192(4); Pd(1)–C(12), 2.186(4); Pd(1)–X, 2.065; Cl(1)–Pd(1)–N(1), 93.2(1); Cl(1)–Pd(1)–C(14), 96.7(1); N(1)–Pd(1)–X, 100.3; C(14)–Pd(1)–X, 74.0; C(11)–C(12)–C(13)–C(14), 58.6

3. Experimental

^1H NMR and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra were recorded on a Bruker DPX 300 instrument using CDCl_3 (99.8%) and SiMe_4 as the solvent and internal standard, respectively. Optical rotations were measured in chloroform solution 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. Ferrocenecarboxaldehyde, (S)-(+)-1-cyclohexylethylamine, and 5 Å molecular sieves were products of Aldrich and used as received.

3.1. Preparation of (S)-(-)-[$\{\eta^5\text{-C}_5\text{H}_4\text{CH}=\text{NCH}(\text{CH}_3)(c\text{-C}_6\text{H}_{11})\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}$, (S)-(-)-3

Ferrocenecarboxaldehyde (2.14 g, 10 mmol) and (S)-(+)-2 (1.27 g, 10 mmol) were dissolved in dry benzene (100 ml) into 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 (S)-(-)-3 as a brown powder (yield: 2.65 g, 82%). Characterization data; m.p. 77–78°C; $[\alpha]_{\text{D}} -153.1$ (*c* 1.0 in CHCl_3); ^1H NMR: δ 0.81–1.37 (m, 10H, CH_2), 1.67 (m, 4H, CH_3+CHCy), 2.67 (m, 1H, MeCHCy), 4.11 [s, 5H, (C_5H_5)], 4.25 [s, 2H, H^3 , H^4 (C_5H_4)], 4.52 [d, $J=23.4$ Hz, 2H, H^2 , H^5 (C_5H_4)], 7.92 (s, 1H, $\text{CH}=\text{N}$); ^{13}C - $\{^1\text{H}\}$ NMR: δ 20.6, 26.8, 27.0, 30.4, 43.9, (Cy), 31.8 (CH_3), 68.4 (C–N), 69.3 (C_5H_5), 72.7 [C^2 , C^5 (C_5H_4)], 81.4 [C^3 , C^4 (C_5H_4)], 158.7 ($\text{CH}=\text{N}$); anal. calcd for $\text{C}_{19}\text{H}_{25}\text{NFe}$: C, 70.60; H, 7.79; N, 4.33. Found: C, 70.39; H, 7.81; N, 4.23.

3.2. Preparation of (R_p, S, S, R_p)-(+)-[$\overline{\text{Pd}\{\{\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}(\text{CH}_3)(c\text{-C}_6\text{H}_{11})\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}(\mu\text{-Cl})}_2$] (R_p, S, S, R_p)-(+)-4

Imine (S)-(-)-3 (0.32 g, 1.0 mmol) was added to a methanolic (30 ml) solution containing Na_2PdCl_4 (0.30 g, 1.0 mmol) and $\text{NaOAc}\cdot 3\text{H}_2\text{O}$ (0.14 g, 1.0 mmol). The resulting mixture was stirred at room temperature for 24 h and then vacuum dried. The product was extracted into chloroform and isolated as a red solid *via* column chromatography (silica 60, 10:1 chloroform:*n*-hexane as eluent). Yield: 0.35 g (76%). Characterization data for (R_p, S, S, R_p)-(+)-4: $[\alpha]_{\text{D}} +409.3$ (*c* 1.0, CHCl_3); ^1H NMR: δ 0.86–1.25 (m, 20H, CH_2), 1.67 (m, 8H, CH_3+CHCy), 4.25 [s, 2H, H^3 (C_5H_3)], 4.35 (s, 10H, C_5H_5), 4.78 [s, 4H, H^4 , H^5 (C_5H_3)], 7.76 (s, 2H, $\text{CH}=\text{N}$); ^{13}C - $\{^1\text{H}\}$ NMR: δ 18.3, 26.8, 27.0, 27.1, 29.3, 41.8, (Cy), 31.7 (CH_3), 66.9 (C–N), 68.4 [C^4 (C_5H_3)], 71.7 [C^5 (C_5H_3)], 74.8 [C^3 (C_5H_3)], 71.9 (C_5H_5), 171.2 ($\text{CH}=\text{N}$); anal. calcd for $\text{C}_{38}\text{H}_{48}\text{Cl}_2\text{Fe}_2\text{N}_2\text{Pd}_2$: C, 49.17; H, 5.21; N, 3.02. Found: C, 48.80; H, 4.87; N, 2.98.

3.3. Preparation of (R_p, S)-(+)-[$\{\{\eta^3\text{-(C}_6\text{H}_5\text{C}=\text{CC}_6\text{H}_5)_2\}\overline{\text{PdCl}(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}(\text{CH}_3)(c\text{-C}_6\text{H}_{11})\}}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}$] (R_p, S)-(+)-5, and (S_p, S, R, S)-(-)-[$\{\{\eta^3\text{-(C}_6\text{H}_5\text{C}=\text{CC}_6\text{H}_5)_2\}\overline{\text{PdCl}(\eta^5\text{-C}_5\text{H}_3\text{CH}=\text{NCH}_2\text{-CHCH}_2\text{CH}_2\text{CHC}(\text{CH}_3)_2\text{CHCH}_2)\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)\}$] (S_p, S, R, S)-(-)-7

A quantity (0.25 mmol) of (R_p, S, S, R_p)-(+)-4 or ($S_p, S, R, S, S, R, S, S_p$)-(+)-6,³ was dissolved in 30 ml of CHCl_3 and then $\text{PhC}\equiv\text{CPh}$ (0.178 g, 1 mmol) was added. The mixture was refluxed for 4 h, allowed to evaporate to *ca.* 5 ml, and isolated *via* column chromatography (silica 60, chloroform as eluent). The red solid was subsequently recrystallized as red needles from ethanol. Yield: 0.28 g (69%) and 0.26 g (62%), respectively. Characterization data for (R_p, S)-(+)-5: $[\alpha]_{\text{D}} +1237.3$ (*c* 1.0, CHCl_3); ^1H NMR: δ 0.79–1.58 (m, 10H, CH_2), 1.76 (m, 4H, CH_3+CHCy), 3.32 (m, 20H, aromatic), 4.14 (s, 5H, C_5H_5), 4.34 [s, 1H, H^3 (C_5H_3)], 4.62 [t, $J=3.0$ Hz, 2H, H^4 , H^5 (C_5H_3)], 6.55–7.56 (m, 20H, aromatic), 8.74 (s, 1H, $\text{CH}=\text{N}$); ^{13}C - $\{^1\text{H}\}$ NMR: δ 18.4, 27.0, 27.2, 27.3, 28.8, 43.9, (Cy), 31.3 (CH_3), 65.6 (C–N), 72.4 [C^4 (C_5H_3)], 73.1 [C^5 (C_5H_3)], 75.1 [C^3 (C_5H_3)], 71.9 (C_5H_5), 126.5, 127.4, 128.1, 128.2, 131.9, 132.2 (Ph and =C), 163.4 ($\text{CH}=\text{N}$); anal. calcd for $\text{C}_{47}\text{H}_{44}\text{ClFeNPd}$: C, 68.79; H, 5.40; N, 1.71. Found: C, 68.68; H, 5.65; N, 1.73. (S_p, S, R, S)-(-)-7: $[\alpha]_{\text{D}} -545.0$ (*c* 1.0, CHCl_3); ^1H NMR: δ 0.90–2.35 (m, 15H, myrtanyl), 2.97 (m, 1H, NCH_2), 4.17 (s, 5H, C_5H_5), 4.45 [s, 1H, H^3 (C_5H_3)], 4.67 [t, $J=2.7$ Hz, 1H, H^5 (C_5H_3)], 4.71 [s, 1H, H^4 (C_5H_3)], 6.57–7.63 (m, 20H, aromatic), 8.70 (s, 1H, $\text{CH}=\text{N}$); ^{13}C - $\{^1\text{H}\}$ NMR: δ 19.4, 21.7, 23.6, 27.0, 28.7, 34.6, 35.1, 38.9, 39.4, 41.7, 43.7, 46.0 (myrtanyl), 70.3 [C^4 (C_5H_3)], 73.6 [C^5 (C_5H_3)], 75.8

[C³(C₅H₃)], 72.3 (C₅H₅), 126.6, 127.5, 128.0, 128.2, 131.7 (Ph and =C), 173.3 (CH=N); anal. calcd for C₄₉H₄₆ClFeNPd: C, 69.50; H, 5.44; N, 1.65. Found: C, 69.38; H, 5.52; N, 1.60.

3.4. Crystallography

(R_p,S)-(+)-5·C₂H₅OH: orthorhombic, space group *P*2₁2₁2₁ (No. 19), *a*=22.850(2) Å, *b*=36.100(3) Å, *c*=10.500(2) Å, *Z*=8, ρ=1.329 g cm⁻³. Of the 16865 reflections collected, 10544 reflections (*F*>4σ(*F*_o)) were used for the refinement. The final residuals were *R*1=9.31%, *wR*2=16.39% and GOF=1.151. (S_p,S,*R*,S)-(-)-7·½H₂O: monoclinic, space group *P*2₁ (No. 4), *a*=17.408(3) Å, *b*=11.997(2) Å, *c*=20.665(4) Å, β=90.29(3), *Z*=4, ρ=1.309 g cm⁻³. Of the 12540 reflections collected, 12506 reflections (*F*>4σ(*F*_o)) were used for the refinement. The final residuals were *R*1=7.65%, *wR*2=21.92% and GOF=1.037. Intensity data were collected on a MSC/Rigaku RAXIS IIC imaging-plate diffractometer at 294 K using graphite-monochromatized Mo-*K*_α 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 reflections was applied. The crystal structures were determined by the direct method and refined using the SHELXL-PC package.⁵ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

This work is supported by Hong Kong Research Grants Council Earmarked Grant CUHK 4179/97P.

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