

Note

Syntheses and structural characterization of novel heteroannular cyclopalladated ferrocenylimine

Xue Mei Zhao, Xin Qi Hao, Bin Liu, Mao Lin Zhang, Mao Ping Song *, Yang Jie Wu *

Department of Chemistry, Zhengzhou University, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Zhengzhou 450052, PR China

Received 26 June 2005; received in revised form 23 August 2005; accepted 29 August 2005

Available online 4 October 2005

Abstract

A new heteroannular cyclopalladated ferrocene derivative $[\text{PdCl}\{\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CH}_2\text{N}=\text{CH}-\text{C}_4\text{H}_3\text{S}\}(\text{PPh}_3)]$ (**6**) was synthesized and characterized by IR, ^1H NMR, ^{13}C NMR, high resolution mass spectroscopy, and its molecular structure was further confirmed by X-ray crystal structure determination. According to the crystal structure, the palladium atom is bound to the unsubstituted Cp ring, showing the four-coordinate structure typical of palladium complexes. A preliminary application of these novel cyclopalladated complexes in Mizoroki–Heck reaction is also to be demonstrated in this paper.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Heteroannular; Ferrocenylimine; Crystal structure; Cyclopalladated

1. Introduction

Cyclopalladated compounds derived from N-donor ligands have attracted great interest in the last decade due to their wide variety of interesting and novel applications in the fields of organic synthesis, catalysis, and photochemistry [1–4]. However, among all cyclopalladated ferrocenylimine derivatives reported so far, the most widely studied systems are based on the formation of the chelated five- or six-membered metallocycles depending on some directing atom that becomes a ligand with the metal. López's and our laboratory have reported the cyclopalladation of some ferrocenylimines. It is found that the reaction occurs predominantly at the *ortho*-position of the substituted cyclopentadienyl ring to afford the corresponding cyclopalladated derivatives [5,6].

It is of interest to try to extend the scope of this reaction. Here, we will describe the synthesis of heteroannular cyclopalladated ferrocene derivative via the direct cyclopalla-

dated reaction of the Schiff base of ferrocenylmethylamine. We have found that in this novel cyclopalladation derivative, the palladium atom is directed into the unsubstituted Cp ring, forming a new chelated large-membered metallocycle. In addition, this cyclopalladated reaction is, to the best of our knowledge, the first example of heteroannular cyclopalladated ferrocene derivative.

2. Results and discussion

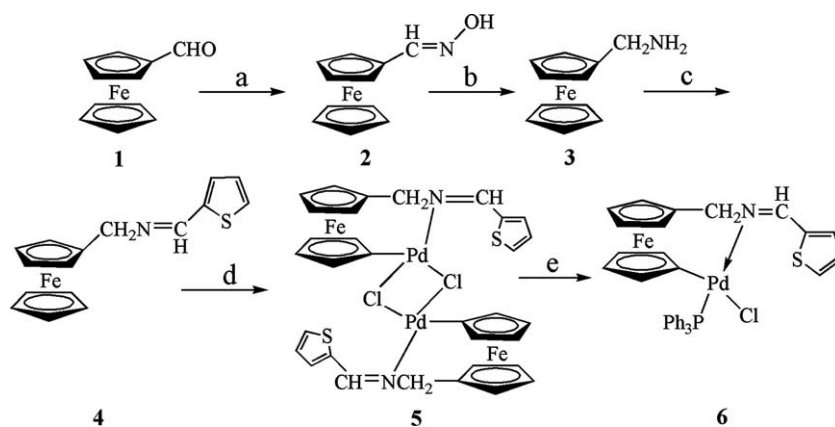
2.1. Synthesis

Cyclopalladated ferrocene derivative **6** is synthesized as follows (Scheme 1). We employ formylferrocene (**1**) as the starting material to prepare the desired cyclopalladated compound. Ferrocenecarbaldehyde oxime (**2**) has been obtained on treatment of the formylferrocene (**1**) with hydroxylamine hydrochloride in 80% yield. Ferrocenylmethylamine (**3**) was prepared by reduction of **2** in 79% yield. Ferrocenylimine (**4**) was obtained on treatment of **3** with thiophenecarboxaldehyde in 55% yield.

Ferrocenylimine (**4**) underwent palladation readily when treated with mole equivalents of lithium

* Corresponding authors. Fax: +86 371 67783012 (M.P. Song); +86 371 67766667 (Y.J. Wu).

E-mail addresses: mpsong9350@zzu.edu.cn (M.P. Song), wjy@zzu.edu.cn (Y.J. Wu).



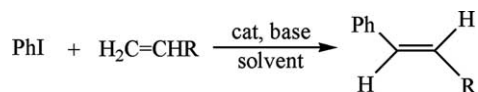
Scheme 1. (a) $\text{NH}_2\text{OH} \cdot \text{HCl}$, CH_3OH , NaHCO_3 , r.t., 3 h (b) LiAlH_4 , THF, reflux, 6 h. (c) RCHO , $\text{C}_2\text{H}_5\text{OH}$, r.t. (d) Li_2PdCl_4 , CH_3OH , r.t., 20 h. (e) PPh_3 , CH_2Cl_2 , r.t., 2 h.

tetrachloropalladate (II) in the presence of sodium acetate in dry methanol for about 20 h at room temperature, and the resulting precipitates were isolated as a brown-red powder, which is insoluble in all common organic solvents, and which can be assigned to a binuclear complex of palladium **5**. Since the solid readily underwent a bridge-splitting reaction with ligand triphenylphosphine to produce the monomeric triphenylphosphine derivative (**6** over yield 76%), which is a typical reaction of a chlorine-bridged binuclear complex of palladium [7–9]. So the compound **5** was characterised only by IR. The new compounds **4** and **6** were sufficiently characterized by physical and spectroscopic data. The solid-state structures were confirmed by X-ray crystallographic analysis (see Figs. 1 and 2).

2.2. Spectral properties of **4** and **6**

The IR spectra of **4** displays two absorption bands at around 1000 and 1100 cm^{-1} and this feature is in accordance with the structures of mono-substituted ferrocene derivatives [10]. But in compound **6**, the absorption bands at 1000 and 1100 cm^{-1} have not been observed, indicating no unsubstituted Cp ring in the molecule. In addition, the $\text{C}=\text{N}$ absorptions of **6** are shifted to lower wavenumbers by 8.73 cm^{-1} in comparison with **4**, indicating that nitrogen is coordinated to palladium through its lone pair [11]. The strong absorptions at 740 and 690 cm^{-1} observed in compound **6**, a feature of the mono-substituted benzene ring, are assigned to the δ (CH) of PPh_3 . These IR features are in good agreement with the proposed structures for the compounds **4** and **6**.

In the ^1H NMR spectra of compound **4**, a singlet that appears at δ 4.17 ppm corresponds to the unsubstituted Cp ring and a downfield singlet at 8.34 ppm is for the proton of the methine. But in compound **6**, these five protons do not exist, which further confirms that the compound **6** is



Scheme 2. $\text{R} = \text{COOEt}$, COOMe , Ph , CN , $\text{COOCH}_2\text{CH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_4\text{CH}_3$.

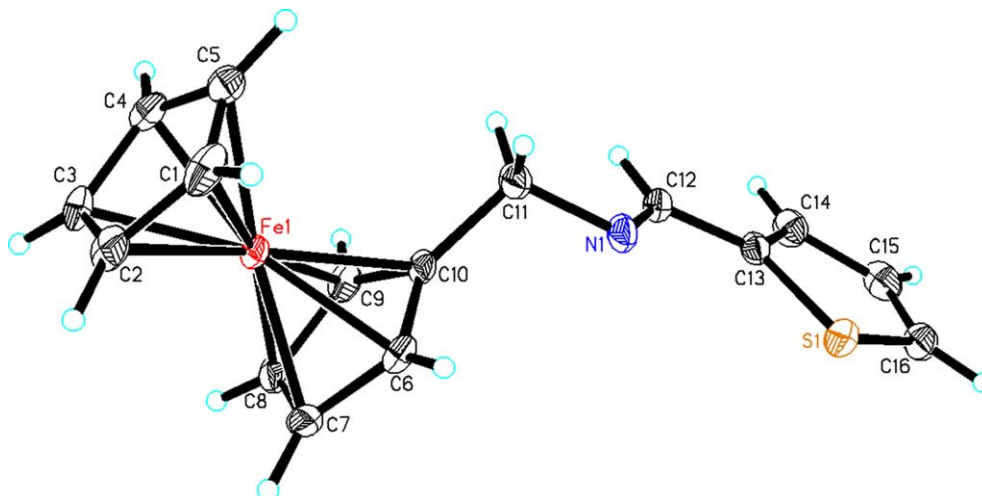


Fig. 1. Molecular structure of **4**.

completely consistent with a heteroannular structure. The proton signals of methine are shifted to high fields. It must be caused by the existence of intramolecular N → Pd coordination.

2.3. Crystal structures of **4** and **6**

The single crystal structures of $[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2\text{N}=\text{CH}-\text{C}_4\text{H}_3\text{S}]$ and $[\text{PdCl}\{\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CH}_2\text{N}=\text{CH}-\text{C}_4\text{H}_3\text{S}\}(\text{PPh}_3)]$ have been determined. The structures are shown in Figs. 1 and 2. Crystallographic and data collection parameters for **4** and **6** are summarized in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3.

In the solid-state (Fig. 1), **4** displays a *trans*-configuration with the *N*-ferrocenyl-methyl moiety and the thiophene ring lying on the opposite sides of C=N bond. The thiophene ring is almost coplanar with the C=N=C–C plane for **4**. The carbon atom at the 11-position is in the plane of the cyclopentadienyl ring (the C7–C6–C10–C11 and C8–C9–C10–C11 torsion angles are $-178.1(2)^\circ$ and $177.9(2)^\circ$, respectively), while the nitrogen atom is deviated from this plane (the C6–C10–C11–N1 and C9–C10–C11–N1 torsion angles are $77.3(3)^\circ$ and $-99.8(3)^\circ$, respectively) to avoid the ferrocene moiety. The C=N bond length is 1.2523 Å.

The solid-state structure of **6** (Fig. 2) is completely consistent with that proposed by the spectral data. The unsubstituted cyclopentadienyl ring is palladated, resulting in a new metallocycle. The palladium atom is coordinated to

P1, N1, C11 and C1, showing the four-coordinate structure typical of the palladium complexes. The angles between adjacent atoms in the coordination sphere lie in the region of 89.7° for N1 Pd1C1, and 88.9° for C1Pd1P1. The phosphine molecule and the imino nitrogen adopt a *trans* arrangement with P1Pd1N1 angle of 175.5° . The Pd–ligand distances are similar to those found in other palladated compounds. The Pd–N distance of 2.092 Å is comparable with the values found in compounds with a Pd–N bond (ca. 2.0 Å), suggesting the formation of a Pd–N bond in compound **6**. The ferrocene moiety has planar Cp rings which were not completely parallel, with interplanar angle 2.4° . The S–Pd distance is 3.086 Å, which is slightly shorter than the sum of the Van der Waals radii of palladium and sulfur atom (3.540 Å), indicating the faint intramolecular coordination of S → Pd. The C=N bond length is 1.262 Å.

3. Application in Mizoroki–Heck reaction

We use compounds **5** and **6** as a new kind of catalysts in Mizoroki–Heck reaction for the arylation of olefin derivatives with iodobenzene (see Scheme 2).

As a preliminary study, two solvents (dioxane, DMF) were used. We find that dioxane is a suitable solvent, giving the fastest reaction and a good yield, and Et_3N is a good base in the process (Table 4).

It was noteworthy that all of these reactions studied showed high regioselectivity for *trans*-coupling, and no

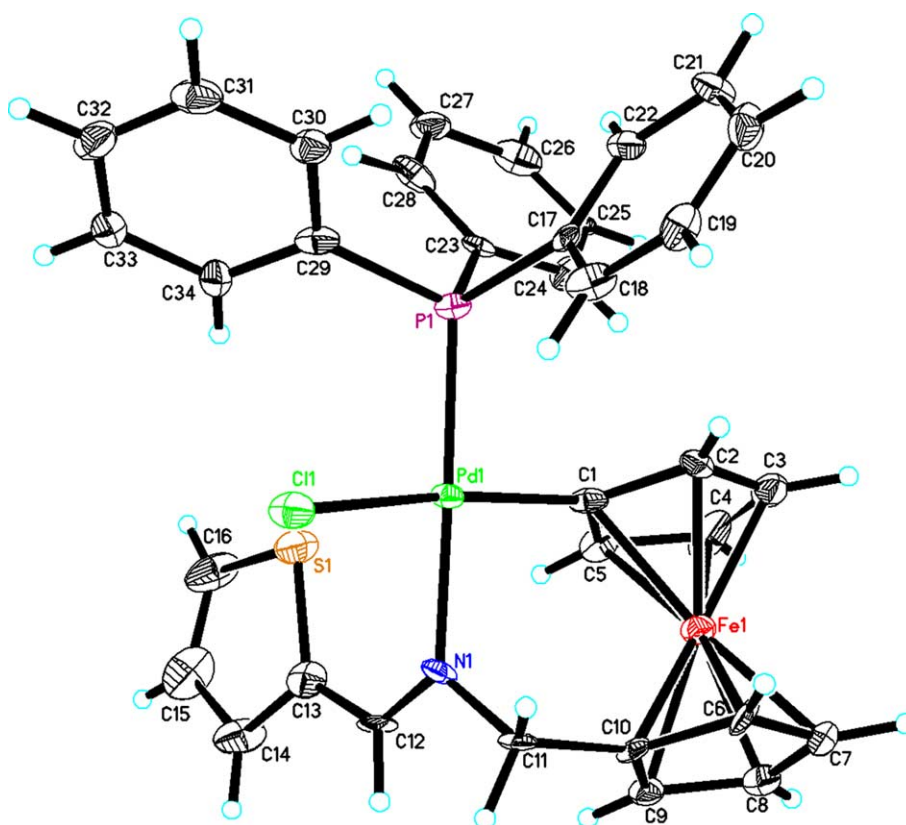


Fig. 2. Molecular structure of **6**.

Table 1
Crystallographic and data collection parameters for **4** and **6**

	4	6
Empirical formula	C ₁₆ H ₁₅ FeNS	C ₃₄ H ₂₉ ClFeNPPdS
Formula weight	309.20	712.31
Temperature (K)	291(2)	291(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>c</i>
Unit cell dimensions		
<i>a</i> (Å)	5.8781(12)	14.750(3)
<i>b</i> (Å)	12.149(2)	22.622(5)
<i>c</i> (Å)	19.752(4)	19.306(4)
β (°)	97.57(3)	110.32(3)
Volume (Å ³)	1398.2(5)	6041(2)
<i>Z</i>	4	4
Calculated density (Mg m ⁻³)	1.469	1.566
Absorption coefficient (mm ⁻¹)	1.212	1.311
<i>F</i> (000)	640	2880
Crystal size (mm)	0.20 × 0.18 × 0.18	0.20 × 0.18 × 0.18
θ Range for data collection (°)	1.97–27.49	1.44–23.50
Index ranges	0 ≤ <i>h</i> ≤ 7, −15 ≤ <i>k</i> ≤ 15, −25 ≤ <i>l</i> ≤ 25	0 ≤ <i>h</i> ≤ 16, −25 ≤ <i>k</i> ≤ 25, −20 ≤ <i>l</i> ≤ 19
Reflections collected	5119	12479
Independent reflections [<i>R</i> _{int}]	2974 [0.0256]	7323 [0.0890]
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2974/0/173	7323/0/706
Goodness-of-fit on <i>F</i> ²	1.082	1.090
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0370, <i>wR</i> ₂ = 0.0820	<i>R</i> ₁ = 0.0981, <i>wR</i> ₂ = 0.1991
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0507, <i>wR</i> ₂ = 0.0866	<i>R</i> ₁ = 0.1736, <i>wR</i> ₂ = 0.2274
Largest differences in peak and hole (e/Å ³)	0.346 and −0.372	2.971 and −0.879

Table 2
Selected bond distances (Å) and angles (°) for **4**

C10–C11	1.495(3)
N1–C12	1.2523(3)
C11–N1	1.473(3)
C12–C13	1.460(3)
C6–C10–C11	126.0(2)
Fe1–C10–C11	127.85(16)
C11–N1–C12	117.2(2)
C12–C13–C14	127.3(3)
C9–C10–C11	126.4(3)
C10–C11–N1	110.2(2)
N1–C12–C13	123.1(3)
C12–C13–S1	121.7(2)

cis-product was found. Further studies on the reaction conditions and reaction mechanism are in progress.

4. Experimental

4.1. General

All reagents and solvents were purchased from commercial sources and were further purified by standard methods, if necessary. Melting points were measured on a WC-1

Table 3
Selected bond distances (Å) and angles (°) for **6**

C10–C11	1.479(12)
N1–C12	1.262(11)
Pd1–N1	2.092(8)
Pd1–P1	2.263(3)
N1–C11	1.462(11)
C12–C13	1.447(13)
Pd1–C1	2.016(10)
C6–C10–C11	128.7(8)
C9–C10–C11	122.6(7)
N1–C11–C10	112.8(8)
Pd1–N1–C11	118.0(5)
N1–C12–C13	127.6(10)
N1–Pd1–P1	175.5(2)
Pd1–C1–C2	125.2(7)
Pd1–C1–Fe1	122.7(5)
Fe1–C10–C11	123.6(6)
C11–N1–C12	115.9(8)
Pd1–N1–C12	126.0(7)
N1–Pd1–C1	89.7(3)
C1–Pd1–P1	88.9(3)
Pd1–C1–C5	127.7(7)
C1–Fe1–C10	105.5(4)

Table 4
Results of Mizoroki–Heck reactions with catalysts **5** and **6**

Entry	R	Cat. (mol%)	<i>T</i> (°C)	Time (h)	%Yield ^a
1	Ph	5 (2.4 × 10 ⁻²)	140	22	71
2	Ph	6 (2.4 × 10 ⁻²)	140	22	75
3	COOMe	5 (2.4 × 10 ⁻²)	100	5	85
4	CN	5 (2.7 × 10 ⁻²)	140	12	46
5	COOEt	5 (3.2 × 10 ⁻²)	100	16	87
6	COOEt	6 (3.2 × 10 ⁻²)	100	16	92
7	COOCH ₂ CH(C ₂ H ₅)- (CH ₂) ₄ CH ₃	6 (3.2 × 10 ⁻²)	140	18	77
8	COOCH ₂ CH(C ₂ H ₅)- (CH ₂) ₄ CH ₃	5 (3.2 × 10 ⁻²)	140	18	71

Reaction conditions: PhI (1 mmol), olefin (1.5 mmol), Et₃N (1 mmol), solvents (3 mL).

^a Isolated yields, based on PhI, average of two runs.

instrument and are uncorrected. Infrared spectra were obtained with a Bruker VECTOR 22 spectrophotometer. ¹H NMR spectra were recorded on a Bruker DPX 400 instrument using CDCl₃ (99.8%) as the solvent and TMS as an internal standard. Elemental analyses were determined with a Carlo Erba 1106 Elemental Analyzer. HRMS were determined on a Waters Q-ToF Micro MS/MS System ESI spectrometer. Chromatographic work was carried out using silica gel under reduced pressure. The compounds **1–3** were synthesized according to [12,13]. Their melting points and IR data were consistent with those of literatures. A lithium tetrachloropalladate (II) solution in methanol (0.1 M) was prepared by stirring two equivalents of anhydrous lithium chloride and one equivalent of anhydrous palladium chloride in methanol until a homogeneous solution was formed.

4.2. Preparation of the compound 4

The compound **4** is prepared in three steps successfully, according to the published procedure. It is a new ferrocenylketimine and characterized as follows: Orange crystals, yield 55%, m.p. 99–101 °C; IR (KBr): ν_{\max} 3094, 2862, 1634, 1102, 1042, 1002 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.33 (s, 1H), 7.39 (d, $J = 5.2$ Hz, 1H), 7.29 (d, $J = 3.6$ Hz, 1H), 7.06 (t, $J = 3.6, 5.2$ Hz, 1H), 4.50 (s, 2H), 4.19 (d, $J = 1.6$ Hz, 2H), 4.16 (s, 5H), 4.14 (t, $J = 1.6, 3.6$ Hz, 2H) ppm; ^{13}C NMR (400 MHz, CDCl_3): δ 59.2 (CH_2), 67.9 (5CH), 68.5 (2CH), 68.6 (2CH), 85.8 (C), 127.3 (CH), 128.8 (CH), 130.3 (CH), 142.7 (C), 154.0 (CH) ppm; Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{FeNS}$: C, 62.15; H, 4.89; N, 4.53. Found: C, 62.14; H, 4.55; N, 4.80%; HRMS (ESI) m/z 309.0261 (calcd for $\text{C}_{16}\text{H}_{15}\text{FeNS}$, m/z 309.0275).

4.3. Preparation of the compound 6

A solution of 0.5 mmol lithium tetrachloropalladate (II) and 0.5 mmol of **4** in 18 mL of methanol was stirred for about 20 h and then filtered, and the brown-red solid **5** was obtained. The solid was washed many times with methanol and then was treated with PPh_3 (0.025 mmol) in CH_2Cl_2 at room temperature for 20 min and then filtered. The filtrate was concentrated in vacuo and the residue was recrystallized from CH_2Cl_2 –petroleum ether (60–90 °C) (1:1, v/v), to give the compound **6**, 76% overall yield. It is characterized as follows: Red crystal, m.p. 187–190 °C; IR (KBr): ν_{\max} 3081, 1625, 1097, 1024, 740, 688 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.30 (d, $J = 10.8$ Hz, 1H), 7.69 (d, $J = 3.3$ Hz, 1H), 7.57 (d, $J = 4.9$ Hz, 1H), 7.15 (t, $J = 4.2$ Hz, 1H), 7.38 (t, $J = 7.0$ Hz, 3H), 7.64 (2d, $J = 7.4$ Hz, 6H), 7.33–7.29 (m, 6H), 4.85 (d, $J = 12.4$ Hz, $\text{CH}_2\text{-H}$), 3.97 (d, $J = 12.4$ Hz, $\text{CH}_2\text{-H}$), 4.36–3.32 (m, 8H) ppm; ^{13}C NMR (400 MHz, CDCl_3): δ 60.1 (CH_2), 66.2 (CH), 66.6 (CH), 66.0 (CH), 67.4 (C), 69.1 (CH), 69.3 (CH), 72.0 (CH), 74.5 (CH), 73.0 (CH), 83.0 (C), 126.9 (CH), 127.1 (3CH), 127.8 (3CH), 130.2 (C, 3CH), 130.9 (C), 131.5 (C), 132.2 (CH), 134.8 (3CH), 134.9 (3CH), 136.5 (CH), 138.2 (C), 155.0 (CH) ppm; Anal. Calcd. for $\text{C}_{34}\text{H}_{29}\text{ClFeNPPdS}$: C, 57.33; H, 4.10; N, 1.97. Found: C, 57.42; H, 4.09; N, 1.90%; HRMS calcd for $\text{C}_{34}\text{H}_{29}\text{FeNPPdS}$ (ESI^+) 676.0143, Found: 676.0170; calcd for Cl (ESI^-) 34.9689, Found: 34.9690.

4.4. General procedure for Mizoroki–Heck reaction of iodobenzene

10 mmol of iodobenzene, 15 mmol of olefin, 10 mmol of Et_3N and catalyst were dissolved in 3 mL certain solvent and stirred at 100 or 140 °C in an oil bath. After cooling, the reaction mixture was diluted with water and extracted with CH_2Cl_2 for several times. The combined organic phase was dried with MgSO_4 . After the removal of the solvent in vacuo, the residue was analyzed by GC (dissolved in

1,4-dioxane, undecane as internal standard) or purified by TLC on silica gel (the purified products were identified by m.p. and by ^1H NMR, and consistent with those of relevant literatures).

4.5. Structure determination for 4 and 6

Crystals of **4** and **6** were obtained by recrystallization from CH_2Cl_2 –petroleum ether solution at r.t., respectively. A single crystal suitable for X-ray analysis was mounted on a glass fiber. All measurements were made on a Rigaku-IV imaging plate area detector with graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization factors. The structure was solved by direct methods [14] and expanded using Fourier techniques and refined by full-matrix least-squares methods. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. All calculations were performed using the TEXSAN [15] crystallographic software package of Molecular Structure corporation.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 274548. Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033, or e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We are grateful to the China National Science Foundation (20472074), the Natural Science Foundation of Henan Province (0411020200) and the Specialized Research Fund for the Doctoral Program of Higher Education (SRFDP) (20040459008) for their financial support for this work.

References

- [1] (a) R.G. Newkome, W.E. Puckett, V.K. Gupta, E. Kiefer, *Chem. Rev.* 86 (1986) 451; (b) I. Omae, *Coord. Chem. Rev.* 83 (1988) 137; (c) B.M. Trost, D.L. Van Vranken, *Chem. Rev.* 96 (1996) 395; (d) A.D. Ryabov, *Chem. Rev.* 90 (1990) 403.
- [2] (a) P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano, E. Sola, *Coord. Chem. Rev.* 117 (1992) 215; (b) A.S. Gruber, D. Zim, G. Ebeling, A.L. Monteiro, J. Dupont, *Org. Lett.* 2 (2000) 2187; (c) X.L. Cui, Y.J. Wu, C.X. Du, L.R. Yang, Y. Zhu, *Tetrahedron: Asymmetry* 10 (1999) 1255; (d) G.J. Gruter, G.P.M. Vanklink, O.S. Akkerman, F. Bickelhaupt, *Chem. Rev.* 95 (1995) 2405; (e) E. Negishi, C. Coperet, S. Ma, S.Y. Liou, F. Liu, *Chem. Rev.* 96 (1996) 365.
- [3] (a) R. Bosque, C. López, J. Sales, X. Solans, M. Font-Bardía, *J. Chem. Soc., Dalton Trans.* (1994) 735;

- (b) G. Zhao, Q. Wang, T.C.W. Mak, *Organometallics* 17 (1998) 3437.
- [4] (a) A.D. Ryabor, *Synthesis* (1985) 233;
(b) C. López, R. Bosque, X. Solans, M. Font-Bardia, *Tetrahedron: Asymmetry* 7 (1996) 2527;
(c) C. López, R. Bosque, *J. Organomet. Chem.* 524 (1996) 247;
(d) C. López, R. Bosque, X. Solans, M. Font-Bardia, *J. Organomet. Chem.* 535 (1997) 99;
(e) C. López, R. Bosque, X. Solans, M. Font-Bardia, *J. Organomet. Chem.* 539 (1997) 99;
(f) C. López, J. Granell, *J. Organomet. Chem.* 555 (1998) 211;
(g) M. Benito, C. López, X. Solans, M. Font-Bardia, *Tetrahedron: Asymmetry* 9 (1998) 4219;
(h) A. Caubet, C. López, R. Bosque, X. Solans, M. Font-Bardia, *J. Organomet. Chem.* 577 (1999) 292;
(i) R. Bosque, C. López, X. Solans, M. Font-Bardia, *Organometallics* 18 (1999) 1267;
(j) M. Benito, C. López, X. Morvan, *Polyhedron* 18 (1999) 2583;
(k) C. López, A. Caubet, X. Solans, M. Font-Bardia, *J. Organomet. Chem.* 598 (2000) 87.
- [5] (a) C. López, J. Sales, X. Solans, R. Zquiak, *J. Chem. Soc., Dalton Trans.* 15 (1992) 2321;
(b) R. Bosque, C. López, J. Sales, X. Solans, M. Font-Bardia, *J. Chem. Soc., Dalton Trans.* 5 (1994) 735;
(c) R. Bosque, C. López, J. Sales, X. Solans, *J. Organomet. Chem.* 483 (1994) 61.
- [6] (a) S.Q. Huo, Y.J. Wu, Y. Zhu, L. Yang, *J. Organomet. Chem.* 470 (1994) 17;
(b) Y.J. Wu, S.Q. Huo, Y. Zhu, L. Yang, *J. Organomet. Chem.* 481 (1994) 235;
(c) S.Q. Huo, Y.J. Wu, X.A. Mao, H.Z. Yuan, *Tetrahedron* 50 (1994) 10467;
(d) S.Q. Huo, Y.J. Wu, C.X. Du, Y. Zhu, H.Z. Yuan, X.A. Mao, *J. Organomet. Chem.* 483 (1994) 139;
(e) Y.J. Wu, Y.H. Liu, K.L. Ding, H.Z. Yuan, X.A. Mao, *J. Organomet. Chem.* 505 (1995) 37.
- [7] J.C. Gaunt, B.L. Shaw, *J. Organomet. Chem.* 102 (1975) 511.
- [8] A. Kasahara, T. Izumi, M. Maemura, *Bull. Chem. Soc. Jpn.* 50 (1977) 1878.
- [9] S.Q. Huo, Y.J. Wu, C.X. Du, Y. Zhu, H.Z. Yuan, X.A. Mao, *J. Organomet. Chem.* 483 (1994) 139.
- [10] M. Roseblum, R.B. Woodward, *J. Am. Chem. Soc.* 80 (1958) 5443.
- [11] (a) S.P. Molnar, M. Orchin, *J. Organomet. Chem.* 16 (1969) 169;
(b) M. Orchin, P.L. Schimdt, *Coord. Chem. Rev.* 2 (1968) 345;
(c) M. Onoue, K. Minami, K. Nakagawa, *Bull. Chem. Soc. Jpn.* 43 (1970) 3480.
- [12] P.J. Graham, R.V. Lindsey, G.W. Parshall, M.L. Peterson, G.M. Whitman, *J. Am. Chem. Soc.* 79 (1957) 3416.
- [13] F. Ossola, P. Tomasin, *Inorg. Chim. Acta* 353 (2003) 292.
- [14] A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, *J. Appl. Crystallogr.* 27 (1994) 435.
- [15] Crystal Structure Analysis Package, Molecular Structure Corporation (1985 and 1992).