This article was downloaded by: [Northeastern University] On: 26 November 2014, At: 12:43 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gcoo20

Synthesis of 2,5-diferrocenyl fivemembered heterocyclic compounds and their electrochemistry

Yu-Qiang Hu^a, Li-Min Han^a, Ning Zhu^a, Hai-Long Hong^a & Rui-Jun Xie^a

^a Chemical Engineering College, Inner Mongolia University of Technology, Hohhot, P.R. China

Accepted author version posted online: 09 Sep 2013. Published online: 18 Oct 2013.

To cite this article: Yu-Qiang Hu, Li-Min Han, Ning Zhu, Hai-Long Hong & Rui-Jun Xie (2013) Synthesis of 2,5-diferrocenyl five-membered heterocyclic compounds and their electrochemistry, Journal of Coordination Chemistry, 66:19, 3481-3497, DOI: <u>10.1080/00958972.2013.841902</u>

To link to this article: <u>http://dx.doi.org/10.1080/00958972.2013.841902</u>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <u>http://www.tandfonline.com/page/terms-and-conditions</u>

Synthesis of 2,5-diferrocenyl five-membered heterocyclic compounds and their electrochemistry

Taylor & Francis

Tavior & Francis Group

YU-QIANG HU, LI-MIN HAN*, NING ZHU, HAI-LONG HONG and RUI-JUN XIE

Chemical Engineering College, Inner Mongolia University of Technology, Hohhot, P.R. China

(Received 30 March 2013; accepted 21 August 2013)

A series of 2,5-diferrocenyl substituted five-membered heterocyclic compounds, 2,5-diferrocenyl-1phenylpyrrole (1), 2,5-diferrocenyl-1-(4-fluorophenyl)-pyrrole (2), 2,5-diferrocenyl-1-(4-ethoxyphenyl)-pyrrole (3), 2,5-diferrocenyl-1-(4-ethylphenyl)-pyrrole (4), 2,5-diferrocenylthiophene (5), and 2,5-diferrocenylfuran (6), were synthesized using one-pot cycloaddition of ferrocenyl alkyne and characterized by elemental analysis, FT-IR, MS, and NMR. The molecular structures of 1, 2, 5, and 6 were determined using single-crystal X-ray diffraction. Electronic communication between two ferrocenyl units of 1-6 was investigated using cyclic voltammetry. These compounds have two well-resolved electrochemically reversible one-electron-transfer processes using [NBu₄] [PF₆] as the supporting electrolyte. The electrochemical studies reveal that electronic communication between two ferrocenyl units depend on the heteroatoms.

Keywords: Diferrocenyl; Five-membered heterocyclic compounds; Electronic communication

1. Introduction

Multi-ferrocenyl (Fc) compounds have received attention because of their synthetic accessibility and redox properties [1, 2]. In particular, π -covalently linked multi-ferrocenyl derivatives have been extensively regarded as model molecules for studying intramolecular electronic communication, because they have very good stability in the neutral state as well as oxidized state during one-electron-transfer processes [3–16]. We have examined the factors that affect electron transfer processes of aliphatic carbon-bridged diferrocenyl derivatives and found that the charge density of the carbon bridge was the key factor for intramolecular electronic communication of two ferrocenyl units bridged by phenyl, which exhibited the strength of the charge transfer which depends on the electron-donating or electron-withdrawing character of the substituents on phenyl and the planar character of the central phenyl core [19]. Herein, we vary the heteroatom of the five-membered cyclic core to modify the electronic communication between the two ferrocenyls in heterocyclic

^{*}Corresponding author. Email: hanlimin@imut.edu.cn

^{© 2013} Taylor & Francis



Figure 1. The molecular structure of 1. Hydrogens have been omitted for clarity.

ring systematically. Hence, the electrochemical model molecules, diferrocenyl pyrrole, thiophene, and furan were synthesized.

2,5-Diferrocenyl five-membered heterocyclic compounds, such as 2,5-diferrocenyl pyrrole, thiophene or furan, have been prepared by Negishi cross-coupling reaction of 2,5-dibromo-substituted pyrrole, thiophene, or furan derivatives with FcZnCl in the presence of Pd as a catalyst [20]. To avoid low-temperature and multi-step procedures which are indispensable parts of the cross-coupling Negishi reaction, we explored a new one-pot synthetic method to prepare the 2,5-diferrocenyl pyrrole, thiophene, and furan derivatives. The electrochemical behaviors of all compounds were determined by cyclic voltammetry and the electronic communication between two ferrocenyl units bridged by pyrrole, thiophene, and furan cores are discussed.

2. Experimental

2.1. General procedures

All operations were carried out under an atmosphere of purified argon. All solvents were dried and distilled according to standard procedures. The reactions were monitored by thin-layer chromatography (TLC). 1,4-Diferrocenyl-1,3-diyne was prepared according to literature methods [21]. Aniline, 4-ethylaniline, 4-ethoxyaniline, and 4-fluoroaniline were commercially available. Infrared spectra were obtained with a Thermo Nicolet FT-IR spectrometer using KBr pellets for sample preparation. Elemental analyzes were carried out with an Elementar var III-type analyzer. ¹H- and ¹³C-NMR spectra were recorded on a Bruker Avance III 500 FT-MHz apparatus in deuterated CDCl₃ solution. Mass spectra were obtained on a Shimadzu LCMS-2020 mass spectrometer. Crystal (1) was determined on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Cu-K ($\lambda = 1.54184$ Å) radiation, and other crystals (2, 5, and 6) were determined with graphite-monochromated Mo-K_{α} ($\lambda = 0.71073$ Å) radiation. Data were collected using the φ and ω scan techniques. The structures were solved using direct methods and expanded using Fourier techniques. Absorption correction based on SADABS was applied. Structure solution and refinement were performed using the SHELXSL 97 software.



Figure 2. The molecular structure of 2. Hydrogens have been omitted for clarity.

Cyclic voltammetry was performed on a platinum disk electrode in a dichloromethane solution of **1–6** with tetra-n-butylammonium hexafluorophosphate [NBu₄][PF₆] (0.1 M) as the supporting electrolyte, at a scan rate of 100 mV s⁻¹. The reference electrode was an Ag/Ag⁺ electrode and the auxiliary electrode was a coiled platinum wire. Oxygen was purged from the one-compartment cell before each electrochemical run.

2.2. Synthesis of 1

1,4-Diferrocenyl-1,3-butadiyne (210.2 mg, 0.5 mM), aniline (2.5 mL, 27.4 mM), and CuCl (2.4 mg, 0.024 mM) were added to a sealed tube under argon and stirred for 24 h at 100 °C. The reaction solution was cooled to room temperature, the solvent removed in vacuo, and the residue was subjected to chromatographic separation on a silica gel column (2.0 × 15 cm) using a mixture of dichloromethane/petroleum ether (1/4, v/v) to elute the product at room temperature. The first orange band was 1,4-diferrocenyl-1,3-butadiyne. The second yellow band was 1 (165 mg). The single crystal of 1 was obtained by recrystallizing from hexane/dichloromethane (4/1, v/v) at room temperature. Yield: 64.7%, m.p. 192–195 °C. Anal. Calcd for C₃₀H₂₅NFe₂: C, 70.48; H, 4.93; N, 2.74. Found: C, 70.49; H, 5.44; N, 2.66%. IR (KBr disk): 3089 cm⁻¹ [Cp, v_{C-H}]; 3050 cm⁻¹ [Ph, v_{C-H}]; 1602 cm⁻¹ [Cp, v_{C-C}]; 1497 cm⁻¹ [C₄H₂N, v_{C-C}]; 1419 cm⁻¹ [Ph, v_{C-C}]; 1104, 1000 cm⁻¹ [Cp, δ_{C-H}]; 820 cm⁻¹ [Cp, γ_{C-H}]; 769, 695 cm⁻¹ [Ph, γ_{C-H}]. ¹H-NMR (CDCl₃, δ): 7.31–7.50 (m, 5H, C₆H₅), 6.38 (s, 2H, C₄H₂N), 3.84–4.01 (m, 18H, Cp). ¹³C-NMR (CDCl₃, δ): 140.03, 129.91, 128.74, 128.64 (C₆H₅), 107.96 (C₄H₂N), 79.08 (C*i*–C₄H₂N), 77.26, 77.01, 76.75, 69.39, 67.43, 66.64 (Cp). MS (ESI, relative abundance): 511.3 (M⁺, 100%).

2.3. Synthesis of 2

1,4-Diferrocenyl-1,3-butadiyne (210.9 mg, 0.5 mM), 4-fluoroaniline (2.5 mL, 26.1 mM), and CuCl (2.4 mg, 0.024 mM) were added to a sealed tube under argon and stirred for 24 h



Figure 3. The molecular structure of 5. Hydrogens have been omitted for clarity.

at 100 °C. The reaction solution was cooled to room temperature, the solvent removed in vacuo, and the residue was subjected to chromatographic separation on a silica gel column (2.0 × 15 cm) using a mixture of dichloromethane/petroleum ether (1/4, v/v) to elute the product at room temperature. The first orange band was 1,4-diferrocenyl-1,3-butadiyne. The second yellow band was **2** (180 mg). The single crystal of **2** was obtained by recrystallizing from hexane/dichloromethane (4/1, v/v) at room temperature. Yield: 68.0%, m.p. 240–242 °C. Anal. Calcd for C₃₀H₂₄FNFe₂: C, 68.09; H, 4.57; N, 2.65. Found: C, 67.78; H, 4.94; N, 2.53%. IR (KBr disk): 3093 cm⁻¹ [Cp, v_{C-H}]; 1602 cm⁻¹ [Cp, v_{C-C}]; 1513 cm⁻¹ [C₄H₂N, v_{C-C}]; 1415 cm⁻¹ [Ph, $v_{C=C}$]; 1104, 1003 cm⁻¹ [Cp, δ_{C-H}]; 835 cm⁻¹ [Cp, γ_{C-H}]; 816 cm⁻¹ [Ph, γ_{C-H}]. ¹H-NMR (CDCl₃, δ): 7.14–7.24 (m, 4H, C₆H₄), 6.39 (s, 2H, C₄H₂N), 3.87–4.03 (m, 18H, Cp). ¹³C-NMR (CDCl₃, δ): 163.35, 161.37, 135.97, 132.26, 131.37 (C₆H₄), 108.21 (C₄H₂N), 78.91 (C*i*–C₄H₂N), 77.27, 77.01, 76.76, 70.26, 70.14, 70.11, 69.85, 69.72, 69.42, 67.55, 66.91 (Cp). MS (ESI, relative abundance): 529.1 (M⁺, 100%).

2.4. Synthesis of 3

1,4-Diferrocenyl-1,3-butadiyne (210.5 mg, 0.5 mM), 4-ethoxyaniline (2.5 mL, 19.4 mM), and CuCl (2.4 mg, 0.024 mM) were added to a sealed tube under argon and stirred for 24 h at 100 °C. The reaction solution was cooled to room temperature, the solvent removed in vacuo, and the residue was subjected to chromatographic separation on a silica gel column (2.0 × 15 cm) using a mixture of dichloromethane/petroleum ether (1/4, v/v) to elute the product at room temperature. The first orange band was 1,4-diferrocenyl-1,3-butadiyne. The second yellow band was **3** (181 mg). Yield: 56.1%, m.p. 217–219 °C. Anal. Calcd for C₃₂H₂₉ONFe₂: C, 69.22; H, 5.26; N, 2.52. Found: C, 67.78; H, 4.94; N, 2.53%. IR (KBr disk): 3085 cm⁻¹ [Cp, v_{C-H}]; 2984, 2918 cm⁻¹ [OC₂H₅, v_{C-H}]; 1610 cm⁻¹ [Cp, $v_{C=C}$]; 1509 cm⁻¹ [C4H₂N, $v_{C=C}$]; 1104, 1049 cm⁻¹ [Cp, δ_{C-H}]; 812 cm⁻¹ [Cp, γ_{C-H}]; 754 cm⁻¹ [Ph, γ_{C-H}]. ¹H-NMR (CDCl₃, δ): 6.99–7.25 (m, 4H, C₆H₄), 6.34 (s, 2H, C₄H₂N), 3.89–4.03 (m, 18H, Cp), 1.49–1.54 (m, 5H, OC₂H₅). ¹³C-NMR (CDCl₃, δ): 159.09, 132.65, 130.82, 114.36 (C₆H₄), 107.63 (C₄H₂N), 79.19 (C*i*–C₄H₂N), 77.27, 77.01, 76.76, 69.37, 67.48, 66.40 (Cp), 63.80, 14.86 (OC₂H₅). MS (ESI, relative abundance): 555.2 (M⁺, 100%).



Figure 4. The molecular structure of 6. Hydrogens have been omitted for clarity.

2.5. Synthesis of 4

1,4-Diferrocenyl-1,3-butadiyne (210.4 mg, 0.5 mM), 4-ethylaniline (2.5 mL, 20.1 mM), and CuCl (2.4 mg, 0.024 mM) were added to a sealed tube under argon and stirred for 24 h at 100 °C. The reaction solution was cooled to room temperature, the solvent removed in vacuo, and the residue was subjected to chromatographic separation on a silica gel column



Scheme 1. The syntheses of 1-4.

 $(2.0 \times 15 \text{ cm})$ using a mixture of dichloromethane/petroleum ether (1/4, v/v) to elute the product at room temperature. The first orange band was 1,4-diferrocenyl-1,3-butadiyne. The second yellow band was 4 (165 mg). Yield: 61.2%, m.p. 236–240 °C. Anal. Calcd for $C_{32}H_{29}NFe_2$: C, 71.27; H, 5.42; N, 2.60. Found: C, 67.78; H, 4.94; N, 2.53%. IR (KBr disk): 3089 cm⁻¹ [Cp, v_{C-H}]; 2964, 2921 cm⁻¹ [C₂H₅, v_{C-H}]; 1513 cm⁻¹ [C₄H₂N, $v_{C=C}$]; 1419 cm⁻¹ [Ph, $v_{C=C}$]; 1104, 1003 cm⁻¹ [Cp, δ_{C-H}]; 843 cm⁻¹ [Cp, γ_{C-H}]; 761 cm⁻¹ [Ph, γ_{C-H}]. ¹H-NMR (CDCl₃, δ): 7.22–7.32 (m, 4H, C₆H₄), 6.36 (s, 2H, C₄H₂N), 3.87–4.01 (m, 18H, Cp), 2.77–2.82 (m, 2H, CH₂), 1.33–1.36 (m, 3H, CH₃). ¹³C-NMR (CDCl₃, δ): 144.91, 137.52, 132.28, 129.63, 128.09 (C₆H₄), 107.80 (C₄H₂N), 79.19 (C*i*–C₄H₂N), 77.27, 76.76, 69.39, 67.40, 66.52 (Cp), 28.59, 15.44 (C₂H₅). MS (ESI, relative abundance): 539.2 (M⁺, 100%).

2.6. Synthesis of 5

Method 1: 1,4-diferrocenyl-1,3-butadiyne (210.4 mg, 0.5 mM), sodium sulfide nonahydrate (600.3 mg, 2.74 mM), CuCl (5.1 mg, 0.05 mM), and dry DMF (5 mL) were added to a sealed tube under argon and stirred for 24 h at 150 °C, then cooled to room temperature. The residue was washed with water (3×5 mL), extracted with CH₂Cl₂ (3×15 mL), and dried over MgSO₄. The solvents were removed in vacuo, and the residue was subjected to chromatographic separation on a silica gel column (2.0×20 cm) using a mixture of dichloromethane/petroleum ether (1/5, v/v) to elute the product at room temperature. The first orange band was 1,4-diferrocenyl-1,3-butadiyne. The second orange band was 5 (27 mg). Single crystals of 5 were obtained by recrystallizing from hexane/dichloromethane (1/1, v/v) at room temperature. Yield: 20.2%.

Method 2: Ferroceneacetylene (210.6 mg, 1.0 mM), sulfur powder (80.1 mg, 1.0 mM), Mo (CO)₆ (53.2 mg, 0.2 mM), and dry benzene (30 mL) were added to a sealed tube under argon and stirred for 72 h at 80 °C, then cooled to room temperature. The solvents were removed in vacuo, and the residue was subjected to chromatographic separation on silica gel column (2.0×20 cm) using a mixture of dichloromethane/petroleum ether (1/5, v/v) to elute the product at room temperature. The first orange band was ferroceneacetylene. The second orange band was 5 (136 mg). Single crystals of 5 were obtained by recrystallizing from hexane/dichloromethane (1/1, v/v) at room temperature. Yield: 60.1%.

Compound 5 obtained by methods 1 and 2 show same characterization data, m.p. 215 °C. Anal. Calcd for $C_{24}H_{20}SFe_2$: C, 63.75; H, 4.46. Found: C, 63.95; H, 4.28.





Scheme 3. The synthesis of 6.

IR (KBr disk): 3077 cm⁻¹ [Cp, v_{C-H}]; 1653 cm⁻¹ [Cp, $v_{C=C}$]; 1404 cm⁻¹ [C₄H₂S, $v_{C=C}$]; 1100, 1026 cm⁻¹ [Cp, δ_{C-H}]; 808 cm⁻¹ [Cp, γ_{C-H}]. ¹H-NMR (CDCl₃, δ): 6.80 (s, 2H, C₄H₂S), 4.07–4.60 (m, 18H, Cp). ¹³C-NMR (CDCl₃, δ): 142.98, 140.64 (C*i*–C₄H₂S), 122.33, 121.72 (C₄H₂S), 80.47, 77.26, 76.75, 69.93, 69.43, 68.58, 66.56 (Cp). MS (ESI, relative abundance): 452.0 (M⁺, 100%).

2.7. Synthesis of 6

1,4-Diferrocenyl-1,3-butadiyne (210.3 mg, 0.5 mM), 2,5-norbornadiene (7.0 μ L 0.75 mM), Pd(PPh₃)₃Cl₂ (26.7 mg, 0.025 mM), KOH (42.1 mg, 0.75 mM), and dry dioxane (3 mL) were added to a sealed tube under argon and stirred for 24 h at 120 °C, then cooled to room temperature. The residue was washed with water (3 × 5 mL), extracted with CH₂Cl₂ (3 × 15 mL), and dried over MgSO₄. The solvents were removed in vacuo, and the residue was subjected to chromatographic separation on a silica gel column (2.0 × 15 cm) using a mixture of dichloromethane/petroleum ether (1/3, v/v) to elute the product at room temperature. The first orange band was 1,4-diferrocenyl-1,3-butadiyne. The second orange band was 6 (12.4 mg). The single crystal of 6 was obtained by recrystallization from hexane/ dichloromethane (1/1, v/v) at room temperature. Yield: 5.7%, m.p. 224–226 °C. Anal. Calcd for C₂₄H₂₀OFe₂: C, 66.10; H, 4.62. Found: C, 66.22; H, 4.59. IR (KBr disk): 3081 cm⁻¹ [Cp, v_{C-H}]; 1581 cm⁻¹ [Cp, v_{C-C}]; 1432 cm⁻¹ [C4H₂O, v_{C-C}]; 1105, 1013 cm⁻¹ [Cp, δ_{C-H}]; 807 cm⁻¹ [Cp, γ_{C-H}]. ¹H-NMR (CDCl₃, δ): 6.15 (s, 2H, C₄H₂O), 4.15–4.67 (m, 18H, Cp). ¹³C-NMR (CDCl₃, δ): 152.07 (*Ci*–C₄H₂O), 105.26 (C₄H₂O), 77.26, 77.00, 76.75, 69.38, 68.43, 65.17 (Cp). MS (ESI, relative abundance): 436.1 (M⁺, 100%).

3. Results and discussion

A series of 2,5-diferrocenyl heterocycles including pyrrole, thiophene, and furan (1–6) were synthesized using one-pot cycloaddition of 1,4-diferrocenyl-1,3-butadiyne with aromatic amine, $Na_2S \cdot 9H_2O$, or KOH, rather than by the traditional Nigishi cross-coupling reaction [21, 22]. The synthetic processes and characterizations are discussed in detail.

3.1. Synthesis of 1–4

Compounds 1–4 must be synthesized in an inert environment, otherwise the main product would be a self-coupled azo-benzene derivative if there is even a trace of oxygen in the reaction system (scheme 1). Compounds 3 and 4 were synthesized in yields of 23.4% (3) and 27.1% (4), lower than the that by Negishi reactions. The low yield could be ascribed to trace oxygen which was not removed completely from the reaction solution. We performed the experiments to synthesize 3 and 4 again, when oxygen was removed thoroughly from

the reaction system by argon bubbling, then the isolated yields of **3** and **4** increased to 56.1 and 61.2%, close to that of the Negishi reactions.

To further prove that trace oxygen is the key factor for reducing the yields of the desired product, we used 1,4-diferrocenyl-1,3-butadiyne reacting with 4-methoxyaniline in air, the main product was 4-methoxyazobenzene (the molecular structure and synthetic procedure of 4-methoxyazobenzene are described in the Supplementary material) and only a trace of 2,5-diferrocenyl-1-(4-methoxy-phenyl)-pyrrole was obtained.

These experimental results clearly show that oxygen promotes the self-coupled reaction to form the azo-benzene derivative and hinders the cycloaddition reaction to form a pyrrole ring. In summary, anaerobic condition is the key factor for one-pot cycloaddition.

3.2. Synthesis of 5

The synthesis of **5** can be obtained through cycloaddition of 1,4-diferrocenyl-1,3-butadiyne with $Na_2S\cdot9H_2O$ catalyzed by CuCl (scheme 2 method 1) in a very low yield of 20.2%, even if the mole ratio of $Na_2S\cdot9H_2O$ was five times more than that of 1,4-diferrocenyl-1,3-butadiyne. Fortunately, **5** could be prepared in a yield of 63.5% when ferrocenyl acetylene reacted with sulfur catalyzed by Mo (CO)₆ (scheme 2 method 2) [23], which was higher than the Nigeshi cross-coupling reactions of ferrocenylzinc chloride and dihalothiophene [24].

3.3. Synthesis of 6

Compound **6** was prepared by the reaction of 1,4-diferrocenyl-1,3-butadiyne with KOH in the presence of $Pd(PPh_3)_3Cl_2$ as catalyst (scheme 3) [25]. This one-pot cycloaddition synthesis could avoid low-temperature and multi-step procedures required by cross-coupling Negishi reactions. However, the yield of **6** is 5.7%, lower than Negishi reactions (62.1%) [26]. The possible reason of low yield could be ascribed to inefficient $Pd(PPh_3)_3Cl_2$ catalyst. Higher yield (65–92%) could be obtained in similar reactions adopting gold or copper as catalysts [27, 28]. Hence, the high yield synthetic method using 1,4-diferrocenyl-1,3-butadiyne as precursor to prepare furan derivatives would be studied through efficient catalysts in our future works.

3.4. Characterization of 1-6

The compounds were confirmed by FT-IR, ¹H-NMR, ¹³C-NMR, elemental analysis, and MS (corresponding data listed in the experimental section). The molecular structures of **1**, **2**, **5**, and **6** were determined by single-crystal X-ray diffraction and are shown in figures 1–4. Crystal data and relevant structural parameters are listed in table 1 and selected bond lengths, angles, and torsion angles are listed in tables 2-4.

3.5. Intermolecular interactions of 6

The crystal structure of **6** includes two independent molecules. Hydrogen carbon bond lengths of H(56A)–C(19), H(27A)–C(5), H(13A)–C(4), and H(47A)–C(14) are 2.827, 2.872, 2.884, and 2.816 Å (figure 5(A)), respectively, showing intermolecular interactions exist in the twin molecules. The T-shaped conformation is edge-to-face C–H··· π interactions formed by C–H of one molecule and π -bond of another molecule. Similar C–H··· π interactions also appears in other molecules [29].

Table 1. Crystal data and relevant st	iructural parameters of $1, 2, 5$ and 6 .			
Compounds	1	2	5	6
Empirical formula	$C_{30}H_{25}Fe_2N$	$\mathrm{C}_{30}\mathrm{H}_{24}\mathrm{FFe}_{2}\mathrm{N}$	$C_{24}H_{20}Fe_2S$	$C_{24}H_{20}Fe_{2}O$
Formula weight	511.21	529.20	452.16	436.10
Temperature (K)	293(2)	296(2)	293(2)	293(2)
Wavelength (Å)	1.54184	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	<i>P</i> -1	<i>P</i> -1	Pnma	Pnma
a (Å)	5.9217(4)	5.9056(9)	8.123(5)	8.246(13)
b (Å)	13.2228(10)	12.2523(19)	23.748(5)	9.926(17)
c (Å)	15.8550(14)	16.612(3)	9.779(4)	22.82(4)
α (°)	66.798(8)	75.101(2)	90.00	90.09(3)
β (°)	85.360(6)	80.710(2)	90.00	90.11(4)
7 ()	77.503(6)	80.508(2)	90.00	90.04(3)
Volume $(Å^3), Z$	1114.00(15), 2	1136.7(3), 2	1886.4(14), 4	1868(5), 4
Density $(Mg m^{-3})$	1.524	1.546	1.592	1.551
$\mu \ (\mathrm{mm}^{-1}), F \ (000)$	10.572, 528	1.304, 544	1.654, 928	1.564, 896
Crystal size (mm)	0.40 imes 0.30 imes 0.01	0.20 imes 0.05 imes 0.05	0.30 imes 0.15 imes 0.10	0.20 imes 0.15 imes 0.10
θ Range	3.03 - 67.24	1.90-28.34	2.5-27.5	3.0572 - 29.2543
Limiting indices	$-7 \le h \le 7, -14 \le k \le 15,$	$-7 \le h \le 7, -15 \le k \le 16,$	$-10 \le h \le 10, -12 \le k \le 11,$	$-10 \le h \le 10, -12 \le k \le 12,$
	$-16 \le 1 \le 18$	$0 \le 1 \le 22$	$-30 \le 1 \le 30$	$-29 \le 1 \le 16$
Reflections collected	3970	10,852	2140	6841
Independent reflections	3970	4424	1942	3483
Completeness to θ	99.8%	99.5%	96.7%	96.0%
Maximum and minimum	0.9016 and 0.1012	0.9377 and 0.7805	1.0000 and 0.9000	0.8593 and 0.7450
Data/restraints/parameters	3970/1014/229	10,852/0/308	2140/178/118	6841/0/469
Goodness-of-fit on F^2	1.087	0.948	1.081	1.080
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.1044, wR_2 = 0.2812$	$R_1 = 0.0733, wR_2 = 0.1470$	$R_1 = 0.0789, WR_2 = 0.2371$	$R_1 = 0.0817, wR_2 = 0.2254$
R indices (all data)	$R_1 = 0.1278, wR_2 = 0.3040$	$R_1 = 0.2032, wR_2 = 0.1982$	$R_1 = 0.0839, wR_2 = 0.2425$	$R_1 = 0.1312, wR_2 = 0.2522$
Largest diff. peak/hole (e. $Å^{-3}$)	1.327/-1.152	0.585/-0.760	2.393/-2.551	0.903/-0.957

ف
Ъ
Ц
ч,
2
÷
Ĕ
0
E.
š
Ĕ
5
a
-
a
Ξ
5
Ы
\mathbf{s}
nt
/a1
5
ē
-
ă
a
ta
da
÷
ŝta
Š
5
-
-
е
0

Table 2. Sele	cted bond length	ıs (Å) and angle	s (°) of 1 , 2 and	5.						
Compounds			Bond It	engths				Bond	angles	
1	C14-C15	1.471(12)	C13-C14	1.356(13)	C12-C13	1.413(14)	N1-C14-C15	123.0(7)	N1-C11-C1	122.7(8)
	C11-C12	1.373(13)	C11-C1	1.476(13)	NI-C11	1.387(12)	C14-N1-C11	109.5(7)	C12-C13-C12	108.7(9)
2	C22-C7	1.468(6)	C7-C8	1.360(6)	C8-C9	1.404(6)	N1-C10-C15	122.3(4)	N1-C7-C22	122.8(4)
	C9-C10	1.372(6)	C10-C15	1.469(6)	N1-C7	1.384(5)	C7–N1–C10	109.1(3)	C10-C9-C8	107.9(4)
5	C9-C11	1.477(6)	C11-C12	1.534(7)	C12-C12	1.548(9)	C9-C11-S1	115.3(4)	C12-C11-S1	118.7(3)
	C12-C11	1.534(7)	C11-C9	1.477(6)	S1–C11	1.732(6)	C11-S1-C11	89.1(4)	C11-C12-C12	106.7(2)

and
2
) of 1,
٩
angles
and
7
C
lengths
bond
Selected
able 2.

Compounds				Torsion	angles			
1	Fe1-C1-C11-N1	-138.34	Fe2-C15-C14-N1	-133.01	Fel-C1-C11-C12	41.22	Fe2-C15-C14-C13	51.13
	C14-N1-C25-C26	-66.54	N1-C14-C15-C19	-39.73	N1-C11-C1-C2	-47.25	C12-C11-N1-C14	0.73
2	Fe1-C15-C10-N1	-142.24	Fe2-C22-C7-N1	-138.94	Fe1-C15-C10-C9	40.17	Fe2-C22-C7-C8	43.38
	C3-C4-N1-C10	-74.02	N1-C10-C15-C14	-49.25	N1-C7-C22-C23	-47.09	C9-C10-N1-C7	-0.31
5	Fe1-C9-C11-S1	-83.38	Fe1-C9-C11-S1	83.38	Fe1-C9-C11-C12	95.53	Fe1-C9-C11-C12	-95.53
	S1-C11-C9-C10	5.31	S1-C11-C9-C10	5.31	C12-C11-S1-C11	-2.44	C12-C11-C9-C10	175.78
9	Fe1-C8-C4-O2	-80.64	Fe2-C24-C6-02	80.84	Fe1-C8-C4-C20	96.27	Fe2-C24-C6-C30	-99.12
	01-C3-C18-C13	-9.32	01-C11-C23-C17	7.96	C31-C3-O1-C11	0.75	C20-C4-C8-C7	-173.21
	Fe3-C18-C3-O1	80.81	Fe4-C23-C11-01	-81.63	Fe3-C18-C3-C31	-97.46	Fe4-C23-C11-C16	98.14
	02-C4-C8-C7	9.88	02-C6-C24-C26	-8.57	C20-C4-O2-C6	-0.66	C31-C3-C18-C13	172.41

و.
and
S
નં
of 1 ,
\odot
angles
torsion
Selected
Table 3.

S	elected bond l	lengths (Å) of	6	Se	elected bond	angles (°) of 6	
Mole	cule 1	Mole	cule 2	Molecul	e 1	Molecul	e 2
O1–C3 C3–C31 C16–C31 C11–C16 O1–C11 C3–C18 C11–C23	$\begin{array}{c} 1.388(10)\\ 1.333(11)\\ 1.418(11)\\ 1.337(11)\\ 1.390(8)\\ 1.457(10)\\ 1.457(11) \end{array}$	O2-C4 C4-C20 C20-C30 C6-C30 O2-C6 C4-C8 C6-C24	$\begin{array}{c} 1.388(9)\\ 1.359(10)\\ 1.438(11)\\ 1.359(11)\\ 1.395(8)\\ 1.442(10)\\ 1.415(11)\end{array}$	C3-O1-C11 C16-C11-O1 C11-C16-C31 C3-C31-C16 C31-C3-O1 O1-C3-C18 O1-C11-C23	105.7(7) 109.8(7) 107.1(7) 107.7(8) 109.7(7) 116.4(8) 115.4(7)	C4-O2-C6 C30-C6-O2 C6-C30-C20 C4-C20-C30 C20-C4-O2 O2-C4-C8 O2-C6-C24	107.1(6) 109.2(7) 107.2(7) 107.0(7) 109.5(6) 116.4(6) 117.4(7)

Table 4. Selected bond lengths and angles of 6.

Intermolecular interactions not only lead to repeating unit in a cell, but also influence the crystal data. The bond lengths of C3–C31, C16–C31, C11–C16, and O1–C11 are 1.333 (11), 1.418(11), 1.337(11), and 1.390(8) Å, respectively, shorter than C4–C20, C20–C30, C6–C30, and O2–C6. The C3–C18 and C11–C23 bond lengths are 1.457(10) and 1.457 (11) Å longer than C4–C8 and C6–C24 (table 4).

There is experimental evidence that torsion angles have been affected by C–H··· π interactions. Stacking of this type of intermolecular interaction does not have to be a perfect face-to-face alignment of the atoms, but can also be an offset or slipped packing [30]; hence, the packing gives torsion angles having different values in twin molecules. For example, the torsion angles O1–C3–C18–C13 (-9.32°), O2–C4–C8–C7 (9.88°), O1–C11–C23–C17 (7.96°), and O2–C6–C24–C26 (-8.57°) (table 3) exhibit different values which could be attributed to intermolecular interactions of C–H··· π system as reported [31]. The dihedral angle between the plane C4–O2–C6–C30–C20 and the plane O1–C3–C11–C16–C31 is 77.12°, which also can be attributed to C–H··· π interactions (figure 5(B)).

3.6. Electrochemistry

The redox potential of **1–6** was determined using cyclic voltammetry. All compounds display two well-resolved redox waves from 0 to 0.8 V (figures 6 and 7), which are assigned to the two Fe^{II}/Fe^{III} redox couples. The electrochemical data are listed in table 5. From the Ipa/Ipc (\approx 1) values of each couple, the redox processes were electrochemically reversible one-electron-transfer processes [32].



Figure 5. The figures of intermolecular interaction of 6.

The difference in the first oxidation potentials of ferrocenyl unit in 1–4 can be ascribed to the electronic effect of nitrogen. The charge density of nitrogen in pyrrole is affected by the substituents (scheme 1). The first oxidation potential increases when the substituent functionality changes from electron-donating **3** (4-OC₂H₅) 17 mV and **4** (4-C₂H₅) 55 mV to **1** (4-H) 58 mV to electron-withdrawing **2** (4-F) 89 mV. Therefore, the nature of the substituent affects the electron density of ferrocenyls via interaction of nitrogen.

The first oxidation potentials of 5 (217 mV) and 6 (184 mV) are higher than those of 1-4, illustrating that thiophene and furan rings have stronger electron-withdrawing effects than the pyrrole ring. However, according to the electronegativity principle of Pauling (electronegativity: O 3.5 > N 3.0 > S 2.5 [33], the first oxidation potential of 5 should be the smallest of the compounds. In order to explain the unexpected first oxidation potential of 5 and 6, we investigated the π -conjugation of 5 and 6. Both dihedral angles of the two cyclopentadiene planes to the thiophene plane of 5 are 8.93° . The dihedral angles of the four cyclopentadiene planes within twin molecules (6) to the furan plane are different; the dihedral angle formed by plane O2-C4-C6-C20-C30 to C12-C14-C24-C26-C41 is 11.20°, the plane O2-C4-C6-C20-30 to C5-C7-C8-C19-C43 is 10.40°, the plane O1-C3-C11-C16-C31 to C9-C10-C17-C23-C35 is 11.47°, and the plane O1-C3-C11-C16-C31 to C13-C15-C18-C25-C2 is 10.88°. Hence, the average dihedral angles are 10.64° and 11.33° . The two dihedral angles of **1** have a small difference with each other, the plane N1-C11-C12-C13-C14 to C15-C16-C17-C18-C19 is 40.11° and N1-C11-C12-C13-C14 to C1-C2-C3-C4-C5 is 47.35° (Supplementary material). In theory, the smaller value of dihedral angle indicates more coplanarity between the cyclopentadienyl planes and the heterocyclic plane, increasing π -conjugation effects. Therefore, the order of π -conjugation effect between two ferrocenyl units bridged by heterocycle is 5 $(\text{Ea}_1 = 217 \text{ mV}) > 6$ $(\text{Ea}_1 = 184 \text{ mV}) > 1$ $(\text{Ea}_1 = 58 \text{ mV})$, which indicates the electron-withdrawing inductive effect of sulfur can be transmitted to ferrocenyls more effectively than to oxygen.

The electronic communication effect of 1–6 was discussed through comparing the oxidation potential differences (ΔE) between two ferrocenyl units. For 1–4, the ΔE values are larger than 290 mV, showing strong electronic communication exist in 1–4 (table 5) [1]. The ΔE values increase, compared to 1 (314 mV), when an electron-donating group is introduced into the phenyl, hence, 3 (4-OC₂H₅) (328 mV) and 4 (4-C₂H₅) (324 mV) show



Figure 6. The cyclic voltammograms of 1 (green line), 2 (black line), 3 (blue line) and 4 (red line) (see http://dx.doi.org/10.1080/00958972.2013.841902 for color version).



Figure 7. The cyclic voltammograms of 1 (black line), 5 (red line) and 6 (blue line) (see http://dx.doi.org/10.1080/00958972.2013.841902 for color version).

larger separation of ferrocenyl-based redox processes, while the introduction of electron-withdrawing group in 2 (4-F) (292 mV) leads to a decrease in ΔE value. These experimental results are in agreement with the substituent effects and deeply influence ferrocenyl electronic communication via interaction of nitrogens.

The ΔE values are also affected by π -conjugation, as investigated by the torsion angles of **1** and **2** (table 3). The torsion angles Fe1–C1–C11–N1 (-138.34°) and Fe2–C15–C14–N1 (-133.01°) of **1** are smaller than Fe1–C15–C10–N1 (-142.24°) and Fe2–C22–C7–N1 (-138.94°) of **2**, showing ferrocenyl units had stronger conjugation with the pyrrole core in **1** than **2**. At the same time, the torsion angle C24–N1–C25–C26 (-66.75°) of **1** is also smaller than C3–C4–N1–C10 (-74.02°) of **2**, showing phenyl had stronger conjugation with pyrrole in **1** than **2**. Hence, the total conjugation of **1** is stronger than **2**, suggesting a stronger degree of electronic interaction between two ferrocenyl units in **1**; therefore, stronger electronic communication exists in **1** (ΔE = 314 mV) than **2** (ΔE = 292 mV).

The ΔE of **6** ($\Delta E = 161$ mV) is larger than **5** ($\Delta E = 139$ mV), in agreement with electronegativity principle of Pauling (electronegativity: O 3.5 > S 2.5). The torsion angles (table 3) of two cyclopentadiene planes to heterocycle plane of **1**, **5**, and **6** have been investigated to measure the conjugation effect. The torsion angles N1–C14–C15–C19 (-39.73°) and N1–C11–C1–C2 (-47.25°) of **1** are larger than the torsion angles O1–C3–C18–C13 (-9.32°), O1–C11–C23–C17 (7.96°), O2–C4–C8–C7 (9.88°), and O2–C6–C24–C26 (-8.57°) of **6**, and the torsion angles S1–C11–C9–C10 (-5.31°) and S1–C11–C9–C10

Compounds	Ea ₁ (mV)	Ea ₂ (mV)	$\Delta E \text{ (mV)}$	ΔE (mV) Ref.
1	58	372	314	315 ^a , 450 ^b [20, 33]
2	89	381	292	
3	17	345	328	_
4	55	379	324	_
5	217	356	139	260 ^a [20, 33]
6	184	345	161	290 ^b [20, 33]

Table 5. The electrochemical data of 1-6.

Notes: ^aSupporting electrolyte: [NBu₄] [PF₆].

^bSupporting electrolyte: [NBu₄] [B(C₆F₅)₄].



Figure 8. The charge transfer model of the 2,5-diferrocenyl five-membered heterocyclic compounds.

 (5.31°) of **5** are the smallest among these three compounds. If the ferrocenyl cyclopentadienyls and the heterocyclic core have more coplanarity, there is more intermetallic electron transfer interaction. Hence, the order of ΔE should be 5 > 6 > 1 deduced by torsion angles; however, the order is **1** (314 mV) > **6** (161 mV) > **5** (139 mV), indicating the heteroatom is the key factor for electronic communication rather than conjugation.

Similar electrochemical models of 2,5-diferrocenyl five-membered heterocyclic derivatives have been studied [20, 34, 35]. Compound 1 displayed the same ΔE using the same supporting electrolyte ([NBu₄][PF₆]) as in our work, and the ΔE increases to 450 mV (table 5) with [NBu₄][B(C₆F₅)₄] as supporting electrolyte [34]. Similar derivatives have also been determined using [NBu₄][B(C₆F₅)₄] as supporting electrolyte, exhibiting the same trend of ΔE to substituents as with our experiment results. For example, ΔE decreased when the substituent functionality changed from electron-donating 4-methoxyl (460 mV) and 4-methyl (455 mV) to 4-H (450 mV) to electron-withdrawing 3-fluorophenyl (425 mV) [35]. The ΔE of 2,5-diferrocenylfuran (290 mV) is larger than 2,5-diferrocenylthiophene (260 mV) [20], and the same results were observed in this article.

In general, the shorter distance of the bimetal center indicates stronger electrostatic interaction and expressed larger ΔE [7, 36]. However, the order of Fe1–Fe2 distances is 1 (8.518 Å) > 5 (7.084 Å) > 6 (6.611, 6.614 Å), which disagrees with the ΔE variation trend 1 (314 mV) > 6 (161 mV) > 5 (139 mV). Hence, the electronic communication of two ferrocenyl units is not affected by the Fe–Fe distance [37, 38].

NMR studies confirmed that electronic communication is not affected by aromaticity of the central five-membered heterocyclic rings. The chemical shifts of β -H of **1**, **5**, and **6** are 6.383, 6.806, and 6.152 ppm (Supplementary material), respectively. Hence, the aromaticity order of five-membered heterocycles is **5** > **1** > **6** [39]. The π -covalently linked bridge with more aromatic properties should have stronger intermetallic electron transfer interaction [40]. Hence, the order of ΔE should be **5** > **1** > **6** according to aromaticity. However, the order is **1** > **6** > **5** in our experimental results. The NMR studies confirmed no electron transfer within the C₄ unsaturated spacers between terminal ferrocenyl moieties (figure **8**(A)).

Electronic character of the heteroatom is for the electronic communication of the 2,5-diferrocenyl five-membered heterocycle compounds. There is a non-significant relationship between electrochemistry and the distance of bimetal or chemical shifts of β -H, indicating that electron transfer does not select the aromatic bridge spacer. Hence, electron transfer between two ferrocenyl units of **1–6** selects a relatively shorter heteroatom-linked bridge (figure 8(B)).

4. Conclusion

A series of 2,5-diferrocenyl substituted five-membered heterocyclic compounds, 2,5-diferrocenyl-1-phenylpyrrole (1), 2,5-diferrocenyl-1-(4-fluorophenyl)-pyrrole (2),

Y.-Q. Hu et al.

2,5-diferrocenyl-1-(4-ethoxyphenyl)-pyrrole (3), 2,5-diferrocenyl-1-(4-ethylphenyl)-pyrrole (4), 2,5-diferrocenylthiophene (5), and 2,5-diferrocenylfuran (6), were synthesized by onepot cycloaddition with ferrocenyl alkynes as precursors. Electronic communication between two ferrocenyl units was investigated by cyclic voltammetry. Charge transfers of 1-6 were from the shorter heteroatom bridge, rather than the electrostatic or aromatic rings.

Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 947276, 878311, 926209, and 930796 for **1**, **2**, **5**, and **6**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: t44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk). Supplemental data for this article can be accessed http://dx.doi.10.1080/00958972.2013.841902.

Acknowledgements

We are grateful to the Natural Science Foundation of China (NSFC-21062011), the Natural Science Foundation of Inner Mongolia (2012ZD01), and the Natural Science Foundation of Inner Mongolia University of Technology (X201207).

References

- [1] S. Barlow, D. O'Hare. Chem. Rev., 97, 637 (1997).
- [2] G.M. Brown, T.J. Meyer, D.O. Cowan, C. LeVanda, F. Kaufman, P.V. Roling, M.D. Rausch. *Inorg. Chem.*, 14, 506 (1975).
- [3] D.O. Cowan, J. Park, C.U. Pittman, Y. Sasaki, T.K. Mukherjee, N.A. Diamond. J. Am. Chem. Soc., 94, 5110 (1972).
- [4] T. Yamamoto, K. Seki, A. Yamamoto, I. Motoyama, H. Sano. Inorg. Chim. Acta, 73, 75 (1983).
- [5] T.Y. Dong, T.J. Ke, S.M. Peng, S.K. Yeh. Inorg. Chem., 28, 2103 (1989).
- [6] A.C. Ribou, J.P. Launay, M.L. Sachtleben, H. Li, C.W. Spangler. Inorg. Chem., 35, 3735 (1996).
- [7] W.H. Morrison Jr, S. Krogsrud, D.N. Hendrickson. Inorg. Chem., 12, 1998 (1973).
- [8] D.E. Richardson, H. Taube. Coord. Chem. Rev., 60, 107 (1984).
- [9] D. Astruc. Acc. Chem. Res., 30, 383 (1997).
- [10] C.B. Hollandsworth, W.G. Hollis Jr, C. Slebodnick, P.A. Deck. Organometallics, 18, 3610 (1999).
- [11] N. Camire, U.T.M. Westerhoff, W.E. Geiger. J. Organomet. Chem., 637, 823 (2001).
- [12] J. Alvarez, A.E. Kaifer. Organometallics, 18, 5733 (1999).
- [13] S.N. Qin, J.R. Hu, Z.L. Chen, F.P. Liang. J. Coord. Chem., 64, 3718 (2011).
- [14] F. Javed, A.A. Altaf, A. Badshah, M.N. Tahir, M. Siddiq, Z.U. Rehman, A. Shah, S. Ullah, B. Lal. J. Coord. Chem., 65, 969 (2012).
- [15] Z.S. Liu, N. Zhu, L.M. Han, R.J. Xie, H.L. Hong, Q.L. Suo. J. Coord. Chem., 65, 2804 (2012).
- [16] R.J. Xie, L.M. Han, Y.Y. Gao, N. Zhu, H.L. Hong, Q.L. Suo. J. Coord. Chem., 65, 4086 (2012).
- [17] R.J. Xie, L.M. Han, Q.L. Suo, H.L. Hong, M.H. Luo. J. Coord. Chem., 63, 1700 (2010).
- [18] R.J. Xie, L.M. Han, N. Zhu, H.L. Hong, Q.L. Suo. J. Coord. Chem., 64, 3180 (2011).
- [19] R.J. Xie, L.M. Han, N. Zhu, H.L. Hong, Q.L. Suo, P. Fu. Polyhedron, 38, 7 (2012).
- [20] A. Hildebrandt, D. Schaarschmidt, R. Claus, H. Lang. Inorg. Chem., 50, 10623 (2011).
- [21] S.R. Drake, R. Khattar. Organomet. Synth., 4, 234 (1988).
- [22] S. Hyuga, Y. Chiba, N. Yamashina, S. Hara, A. Suzuki. Chem. Lett., 1757, (1987).
- [23] P. Mathur, A.K. Singh, V.K. Singh, P. Singh, R. Rahul, S.M. Mobin, C. Thone. Organometallics, 24, 4793 (2005).
- [24] J.M. Speck, R. Claus, A. Hildebrandt, T. Ruffer, E. Erasmus, L.V. As, J.C. Swarts, H. Lang. Organometallics, 31, 6373 (2012).

- [25] Q.W. Zheng, R.M. Hua, T. Yin. Curr. Org. Synth., 10, 161 (2013).
- [26] M. Yuguchi, M. Tokuda, K. Orito. J. Org. Chem., 69, 908 (2004).
- [27] H. Jiang, W. Zeng, Y. Li, W. Wu, L. Huang, W. Fu. J. Org. Chem., 77, 5179 (2012).
- [28] P. Nun, S. Dupuy, S. Gaillard, A. Poater, L. Cavallod, S.P. Nolan. Catal. Sci. Technol., 1, 58 (2011).
- [29] M.H. Luo, L.M. Han, N. Zhu, H.L. Hong, R.J. Xie, Q.L. Suo, L.H. Weng. J. Coord. Chem., 63, 3805 (2010).
- [30] C. Janiak. J. Chem. Soc., Dalton Trans., 3885 (2000).
- [31] B.M. Matheus, J.C. Martinez, J. Rius, C. Miravitlles. Acta Crystallogr., 47, 1744 (1991).
- [32] L.M. Han, L.F. Zhang, G.B. Zhang, Z.G. Yin. Chin. J. Inorg. Chem., 24, 1807 (2008).
- [33] M.B. Smith, J. March. March's Advanced Organic Chemistry, 1, 17 (2007).
- [34] A. Hildebrandt, D. Schaarschmidt, H. Lang. Organometallics, 30, 556 (2011).
- [35] A. Hildebrandt, H. Lang. Dalton Trans., 11831 (2011).
- [36] W.Y. Liu, Y.F. Yuan, L.Y. Zhang. J. Chin. Univ., 19, 1251 (1998).
- [37] J.R. Wright, K.J. Shaffer, C.J. McAdam, J.D. Crowley. Polyhedron, 36, 73 (2012).
- [38] U. Pfaff, A. Hildebrandt, D. Schaarschmidt, T. Hahn, S. Liebing, J. Kortus, H. Lang. Organometallics, 31, 6761 (2012).
- [39] M.B. Smith, J. March. March's Advanced Organic Chemistry, 1, 54 (2007).
- [40] C. Patoux, C. Coudret, J.P. Launay, C. Joachim, A. Gourdon. Inorg. Chem., 36, 5037 (1997).