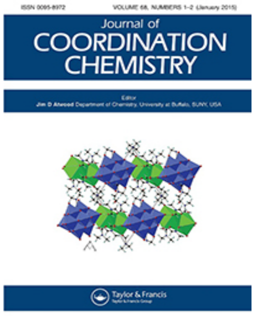

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Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

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To cite this article: Wei-Guo Jia, Dan-Dan Li, Hui Zhang, Yuan-Chen Dai & En-Hong Sheng (2015) Preparation and structure of zinc complexes containing pincer ligands and their application for Knoevenagel condensation in water, Journal of Coordination Chemistry, 68:2, 220-228, DOI: 10.1080/00958972.2014.978308

To link to this article: http://dx.doi.org/10.1080/00958972.2014.978308

Journal of Coordination Chemistry, 2015
Vol. 68, No. 2, 220–228, http://dx.doi.org/10.1080/00958972.2014.978308

Preparation and structure of zinc complexes containing pincer ligands and their application for Knoevenagel condensation in water

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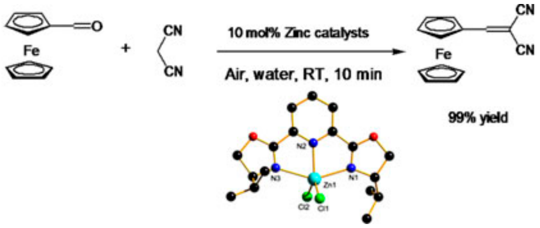
(*Received 24 July 2014; accepted 25 September 2014*)



Two zinc complexes with Pybox ligands, 2,6-bis[4′,4′-dimethyloxazolin-2′-yl]pyridine (Dm-pybox) (**1a**) and 2,6-bis[4′-isopropyloxazolin-2′-yl]pyridine (*i*-Pr-pybox) (**1b**), have been synthesized and characterized. Reactions of zinc chloride with the pyridine-based pincer ligands result in formation of (Dm-Pybox)$ZnCl_2$ (**2a**) and (*i*-Pr-Pybox)$ZnCl_2$ (**2b**), respectively. Both complexes have been characterized by elemental analysis, NMR and IR spectra. The molecular structures of **2a** and **2b** have been determined by X-ray crystallography. Complex **2b** is efficient in catalyzing Knoevenagel condensation of ferrocenecarboxaldehyde with activated methylene compounds in water.

Keywords: Pincer; Zinc; Ferrocenecarboxaldehyde; Knoevenagel; Structure

1. Introduction

Pincer ligands and their complexes play a crucial role in organometallic and coordination chemistry as well as in catalysis, and enhance the stability of complexes, allowing steric and electronic changes that control the reactivity of their complexes [1]. Various transition metal complexes with different pincer ligands, such as Fe [2], Co [3], Ni [4], Ir [5], Rh [6], Ru [7], Pd [8], etc., have been developed due to their application in modern chemistry.

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Among these transition metal pincer complexes, zinc complexes with pincer-type ligands are the least studied [9]. Zinc reagents are one of the most important synthetic tools in modern organic synthesis. A particularly attractive synthetic feature of zinc catalysis is its abundant, cheap, and non-toxic properties. Organic chemists have been interested in using zinc complexes as catalysts in organic synthesis [10]. All types of bonds formed in zinc-catalyzed or zinc-mediated organic reaction processes, particularly C–C, C–N, and C–O bond formation, have been reported [11]. Zinc complexes are also good catalysts in the polymerization of caprolactone and lactide [12]. Organozinc reagents R_2Zn or RZnX are widely used organometallic reagents in organic synthesis [13].

The Knoevenagel condensation of aldehydes with activated methylene compounds is a common and useful method for C–C bond formation [14]. A series of zinc compound catalyzed Knoevenagel condensation reactions have been reported, including inorganic zinc salts [15], metal–organic frameworks [16] and nano materials [17]. However, to the best of our knowledge, the Knoevenagel condensation catalyzed by Pybox Zn(II) complexes was not previously reported.

In order to understand the chemistry of zinc complexes containing Pybox ligands and their potential application in the Knoevenagel condensation reaction, herein, we report an easy synthesis of two zinc complexes with Pybox ligands, Dm-Pybox (**1a**) and *i*-Pr-Pybox (**1b**), and their application for Knoevenagel condensation of ferrocenecarboxaldehyde with activated methylene compounds in water.

2. Experimental

2.1. *Materials and measurements*

All manipulations were carried out under nitrogen using standard Schlenk and vacuum-line techniques. All solvents were purified and degassed by standard procedures. The starting materials, 2,6-bis[4′,4′-dimethyloxazolin-2′-yl]pyridine (Dm-pybox) (**1a**) and 2,6-bis[4′-isopropyloxazolin-2′-yl]pyridine (*i*-Pr-pybox) (**1b**), were synthesized according to procedures described in the literature [18]. Other chemicals were analytical grade and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz or 500 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to $CDCl_3$ (7.26 ppm for ^{1}H and 77 ppm for ^{13}C) or internal TMS. IR spectra were recorded on a Nicolet AVATAR-360IR spectrometer. Elemental analyses were performed on an Elementar III vario EI Analyzer. Mass spectra were performed on a Micromass GCT-MS spectrometer.

2.2. *Preparation of 2a and 2b*

2.2.1. Synthesis of dichloro[2,6-bis(4′,4′-dimethyloxazolin-2-yl)pyridine]zinc (Dm-Pybox) $ZnCl_2$ (2a). In a 100 mL round-bottomed flask, Dm-pybox (**1a**) (136 mg, 0.5 mM), $ZnCl_2$ (68 mg, 0.5 mM), 20 mL methanol, and 15 mL CH_2Cl_2 were placed. The mixture was stirred at room temperature overnight and then the solvent was removed with a rotary evaporator; the resulting solid was washed with methanol and then dried in vacuo. The product was recrystallized from CH_2Cl_2/hexane to give white crystals. Yield: (170 mg, 83%). Anal. Calcd for $C_{15}H_{19}Cl_2N_3O_2Zn$ (409.62): C, 43.98; H, 4.68; N, 10.26. Found: C, 43.70; H, 4.66; N, 10.35%. ^{1}H NMR (500 MHz $CDCl_3$): 1.65 (s, $4CH_3$, 12H), 4.23 (s, $2CH_2$, 4H), 8.04 (d, pyridine, 2H), 8.26 (t, pyridine, 1H) ppm. IR (KBr cm^{-1}): 2978 (m), 1662 (m), 1653 (m), 1589 (s), 1558 (m), 1458 (m), 1396 (m), 1377 (m), 1336 (m), 1288 (m), 1201 (s), 1139 (m), 1076 (m), 1020 (m), 975 (m), 935 (m), 839 (m), 758 (m), 678 (m).

2.2.2. Synthesis of dichloro[2,6-bis(4-isopropyloxazolin-2-yl)pyridine]zinc (i-Pr-Pybox) ZnCl$_2$ (2b). Complex **2b** was prepared by the same procedure as described above for **2a** using *i*-Pr-Pybox (**1b**) (151 mg, 0.5 mM) and ZnCl$_2$ (68 mg, 0.5 mM). Yield: (164 mg, 75%). Anal. Calcd for $C_{17}H_{23}Cl_2N_3O_2Zn$ (437.67): C, 46.65; H, 5.30; N, 9.60. Found: C, 46.55; H, 5.68; N, 9.71%. ^{1}H NMR (500 MHz CDCl$_3$): 1.01 (d, 2CH$_3$, 6H), 1.12 (d, 2CH$_3$, 6H), 2.34 (m, 2CH, 2H), 4.50 (s, 2CH$_2$, 4H), 8.06 (d, pyridine, 2H), 8.28 (t, pyridine, 1H) ppm. IR (KBr cm^{-1}): 2958 (w), 1662 (m), 1587 (s), 1481 (m), 1383 (m), 1321 (m), 1276 (m), 1196 (m), 1080 (m), 1020 (m), 966 (m), 926 (m), 829 (m), 748 (m), 669 (m).

2.3. *General procedure for Knoevenagel condensation of ferrocenecarboxaldehyde with activated methylene compounds*

(*i*-Pr-Pybox)ZnCl$_2$ (**2b**) (10.9 mg, 0.025 mM, 0.1 equiv) was added in H$_2$O (0.5 mL), then ferrocenecarboxaldehyde (53.4 mg, 0.25 mM, 1.0 equiv) and activated methylene compound (0.5 mM, 2.0 equiv) were added. The mixture was stirred at room temperature for few minutes, after which the crude reaction mixture was loaded directly onto a column of silica gel and purified by column chromatography to give the solid.

2.3.1. 2-Ferrocenylidenemalononitrile (3a) [19]. Violet solid (64 mg, 98% Yield). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.72 (s, 1H), 4.98 (s, 2H), 4.85 (s, 2H), 4.33 (s, 5H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 163.38, 115.27, 114.46, 75.44, 74.22, 71.92, 71.27.

2.3.2. 3 5-Ferrocenylidene-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (3b). Bluish violet solid (85 mg, 97% Yield). ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.45 (s, 1H), 5.32 (s, 2H), 4.91 (s, 2H), 4.28 (s, 5H), 3.39 (s, 3H), 3.36(s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 163.42, 161.23, 160.98, 151.74, 76.32, 73.52, 70.75, 69.22, 28.93, 27.97. HRMS (EI) *m*/*z* Calcd for $C_{17}H_{16}FeN_2O_3$ [M$^+$] 352.0510, found 352.0507.

2.3.3. 5-Ferrocenylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (3c) [20]. Violet solid (76 mg, 93% Yield). ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.38 (s, 1H), 5.24 (s, 2H), 4.91 (s, 2H), 4.28 (s, 5H), 1.75 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 164.02, 160.57, 160.33, 106.10, 103.50, 76.07, 75.77, 74.56, 70.62, 27.08.

2.3.4. Ethyl 2-cyano-3-ferrocenylacrylate (3d). Red solid (74 mg, 96% Yield). ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.16 (s, 1H), 5.00 (s, 2H), 4.70 (s, 2H), 4.29 (q, J = 7.08 Hz, 2H), 4.24 (s, 5H), 1.35 (t, J = 7.05 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 163.48, 158.90, 117.10, 97.37, 74.29, 73.38, 72.00, 70.78, 69.84, 62.29, 14.41. HRMS (EI) *m*/*z* Calcd for $C_{16}H_{15}FeNO_2$ [M$^+$] 309.0452, found 309.0448.

Table 1. Crystallographic data and structure refinement parameters for **2a** and **2b**.

	2a	**2b**
Empirical formula	$C_{15}H_{19}Cl_2N_3O_2Zn$	$C_{17}H_{23}Cl_2N_3O_2Zn$
Formula weight	409.60	437.65
Crystal system, Space group	Monoclinic, $P2_1/c$	Triclinic, $P1$
a (Å)	10.0465(5)	7.4773(7)
b (Å)	15.9664(8)	8.4534(8)
c (Å)	11.3488(6)	8.7905(8)
α (°)	90	112.835(2)
β (°)	98.8040(10)	96.955(2)
γ (°)	90	101.741(2)
Volume (Å^3), Z	1798.97(16), 4	488.90(8), 1
D_c (mg m^{-3})	1.512	1.486
μ (Mo-Kα) (mm^{-1})	1.673	1.544
F (0 0 0)	840	226
θ Range (°)	2.05–27.49	2.58–27.48
Limiting indices	−13, 12; −20, 14; −14, 14	−9, 6; −10, 10; −11, 11
Reflections/unique [R(int)]	4128/3655 [0.0332]	2678/2633 [0.0202]
Completeness to θ (°)	27.49 (99.9%)	27.48 (99.2%)
Data/restraints/parameters	4128/0/212	2678/3/232
Goodness-of-fit on F^2	1.142	1.096
Final R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0357$, $wR_2 = 0.0359$	$R_1 = 0.0267$, $wR_2 = 0.0269$
R indices (all data)	$R_1 = 0.0942$, $wR_2 = 0.0834$	$R_1 = 0.0691$, $wR_2 = 0.0690$
Largest diff. peak/hole (e Å^3)	0.347/−0.357	0.394/−0.389

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o{}^2| - |F_c{}^2|)^2/\Sigma w|F_o{}^2|^2]^{1/2}$.

2.4. *X-ray structure determination*

Diffraction data of **2a** and **2b** were collected on a Bruker AXS SMART APEX diffractometer, equipped with a CCD area detector using Mo Kα radiation ($\lambda = 0.71073$ Å). All data were collected at 223 K and the structures were solved by direct methods, and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL) [21]. SADABS [22] absorption corrections were applied to the data, all non-hydrogen atoms were refined anisotropically, and hydrogens were located at calculated positions. All calculations were performed using the Bruker Smart program. A summary of the crystallographic data and

Table 2. Selected bond lengths (Å) and angles (°) for **2a** and **2b**.

	2a	**2b**
Zn1–N1	2.2969(18)	2.276(3)
Zn1–N2	2.1446(16)	2.120(3)
Zn1–N3	2.2311(17)	2.381(3)
Zn1–Cl1	2.2658(5)	2.2239(8)
Zn1–Cl2	2.2299(6)	2.2313(8)
N1–Zn1–N2	72.73(6)	74.80(10)
N1–Zn1–N3	145.56(6)	147.52(9)
N2–Zn1–N3	73.71(6)	72.74(10)
N1–Zn1–Cl1	96.20(5)	98.56(7)
N1–Zn1–Cl2	98.94(5)	99.71(7)
N2–Zn1–Cl1	103.44(4)	124.74(7)
N2–Zn1–Cl2	134.46(5)	113.54(7)
N3–Zn1–Cl1	98.86(5)	98.75(7)
N3–Zn1–Cl2	98.94(5)	94.29(7)
Cl1–Zn1–Cl2	122.07(2)	121.59(3)

selected experimental information are given in table 1; selected bond angles and distances are given in table 2.

3. Results and discussion

3.1. *Structural description of 2a and 2b*

When zinc chloride was treated with Dm-Pybox (**1a**) and *i*-Pr-Pybox (**1b**) in CH_2Cl_2/MeOH at room temperature, white crystals of pincer zinc complexes [(**2a**) and (**2b**)] were isolated in moderate yields, respectively, after recrystallization [(**2a**, 83%); (**2b**, 75%)]. Complexes **2a** and **2b** were fully characterized by IR, NMR spectroscopy, and elemental analysis. The ^{1}H NMR spectra of **2a** in $CDCl_3$ show singlet resonances due to methyl fragment at δ 1.65 ppm; the pyridyl group has two resonances at δ 8.04 and 8.26 ppm and the signals of the methylene in the oxazoline rings are at δ 4.23 ppm. The ^{1}H NMR spectra of **2b** show signals at 1.01, 1.12, 2.34, 4.50, 8.06, and 8.28 ppm with ratio 6 : 6 : 2 : 4 : 2 : 1. Infrared spectra of the complexes in the solid state exhibit intense C=N stretching of oxazoline at 1662 cm^{-1}.

Crystals of **2a** and **2b** suitable for X-ray crystallographic diffraction were obtained by slow diffusion of diethyl ether into a concentrated solution of the complexes in dichloromethane. Crystallographic data and details of data collection and refinement for **2a** and **2b** are summarized in table 1; the important bond lengths and angles are given in table 2. The molecular structures of **2a** and **2b** are shown in figures 1 and 2.

As shown in figures 1 and 2, **2a** and **2b** are isostructural. As expected, pyridine-based pincer ligand is coordinated tridentate to zinc by the pyridyl nitrogen and two oxazoline nitrogens. The coordination sphere around Zn(II) is best described as midway between trigonal bipyramidal and square pyramidal (figure 1) [23]. Since **2a** is not an exact C_2 symmetry plane in the solid-state, the Zn is out of the plane formed by three nitrogens by 0.2127 Å. The Zn–N distances (2.2969(18), 2.1446(16), and 2.2311(17) Å) in **2a** are

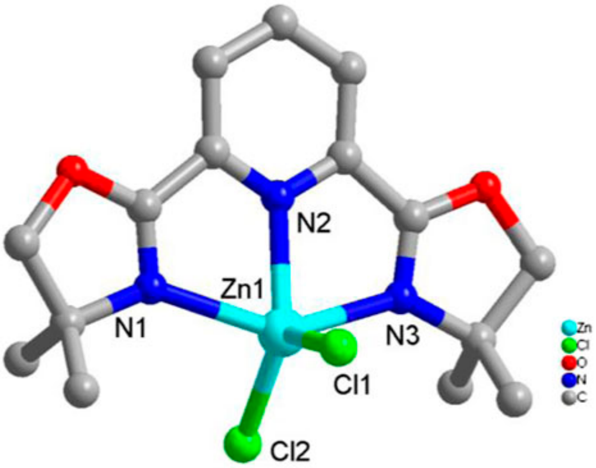


Figure 1. Molecular structure of **2a** with all hydrogens omitted for clarity.

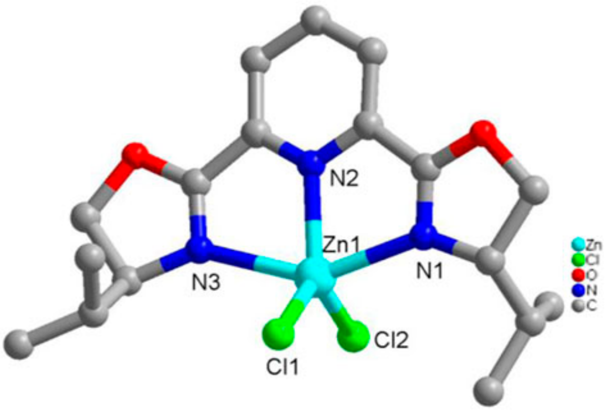
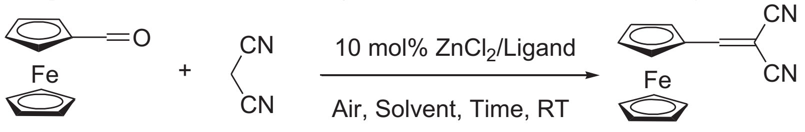


Figure 2. Molecular structure of **2b** with all hydrogens omitted for clarity.

compatible with a typical single bond length between zinc center and nitrogen reported previously [24], and can be compared with that of other Zn complexes containing the 3N-2X (X = halogen) ligand set [25].

The molecular structure of **2b** is shown in figure 2. The Zn–N distances for **2b** are 2.276 (3), 2.120(3), and 2.381(3) Å, respectively. The parameter τ is 0.39 for **2b**, while for **2a** is 0.43 [23]. Both complexes have distorted structures, indicating that the different alkyl groups in the oxazoline ring have little effect on molecular structures of zinc complexes with pincer ligands.

Table 3. The optimized conditions for Knoevenagel condensation of ferrocenecarboxaldehyde with malononitrile.



3a

Entry	[Zn] catalysts	Amt. of [Zn] (M%)	Ligand	Amt. of ligand (M%)	Solvent	Time (min)	Yield (%)[a]
1					THF	15	–
2	$ZnCl_2$	10			THF	15	30
3			**1a**	10	THF	15	10
4			**1b**	10	THF	15	9
5	**2a**	10			THF	15	31
6	**2b**	10			THF	15	46
7	**2b**	1			THF	15	11
8	**2b**	5			THF	15	35
9	**2b**	15			THF	15	89
10	**2b**	10			THF	10	18
11	**2b**	10			MeOH	10	97
12	**2b**	10			MeCN	10	14
13	**2b**	10			DMF	10	93
14	**2b**	10			DMSO	10	91
15	**2b**	10			NMP	10	95
16	**2b**	10			H_2O	10	99
17	**2a**	10			H_2O	10	90

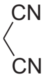
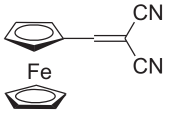
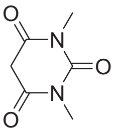
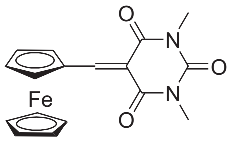
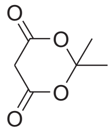
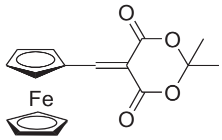
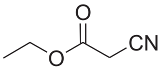
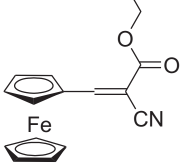
[a] Isolated yield.

3.2. *Pincer zinc complexes application for Knoevenagel condensation in water*

Zn compounds have been applied in many organic syntheses, and this prompted us to explore Pybox Zn(II) complexes as catalysts for Knoevenagel condensation of ferrocenecarboxaldehyde with active methylene compounds under ambient conditions, especially in a green medium.

Initially, the reaction was carried out with 0.5 mM of ferrocenecarboxaldehyde and malononitrile in 0.5 mL THF under ambient air. No reaction was observed in the absence of metal catalyst (table 3, entry 1). However, 30% yield was obtained in the presence of 10 M% $ZnCl_2$ catalysts (table 3, entry 2). Only 10 and 9% products of the Knoevenagel condensation were obtained in a control experiment with only ligands **1a** and **1b** (table 3, entries 3 and 4). However, 31 and 46% yields of desired product were observed using **2a** and **2b** as catalysts (table 3, entries 5 and 6). Lower yield was obtained with lower catalyst loading 1 and 5 M% catalysts (table 3, entries 7 and 8). The yield was improved to 89% with 15 M% of **2b** catalyst (table 3, entry 9). Next, we focused on appropriate solvents, evaluating a range

Table 4. Knoevenagel condensation of ferrocenecarboxaldehyde with various active methylene compounds.

Entry	Substrate	Product	Time (min)	Yield (%)[a,b]
1		 **3a**	5	99
2		 **3b**	5	97
3		 **3c**	25	93
4		 **3d**	50	96

[a] Isolated yield.
[b] Reaction condition: ferrocenecarboxaldehyde (0.25 mM), activated methylene compound (0.5 mM, 2.0 equiv), 10 M% **2b** catalyst, and 0.5 mL H_2O, under air.

of polar solvents using the model reaction between ferrocenecarboxaldehyde and malononitrile (table 3, entries 11–16). Using methanol as the solvent furnished 97% yield of the product 2-ferrocenylidenemalononitrile in 10 min (table 3, entry 4). However, only 14% yield was observed with acetonitrile as the solvent (table 3, entry 12). The model reactions also occurred with other polar solvents, for example, DMF (93%), DMSO (91%), and NMP (95%) (table 3, entries 13, 14 and 15). To our surprise, 99% yield was attained with water as the solvent in 10 min.

With the best reaction conditions on hand, we started to expand the scope and efficiency of this methodology. Ferrocenecarboxaldehyde with various active methylene compounds was also investigated to provide the desired products in high yields (table 4: **3b**, **3c**, and **3d**), for example, 5-ferrocenylidene-1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione (**3b**), 5-ferrocenylidene-2,2-dimethyl-1,3-dioxane-4,6-dione (**3c**), and ethyl 2-cyano-3-ferrocenylacrylate (**3d**), were obtained from the corresponding active methylene compounds in 97, 93, and 96% yields, respectively (table 4).

4. Conclusion

We have reported two zinc complexes with pyridine-based pincer-type ligands. A combination of spectroscopic studies and X-ray crystallography confirmed the structures of **2a** and **2b**. Complex **2b** is efficient in catalyzing Knoevenagel condensation of ferrocenecarboxaldehyde with activated methylene compounds in water.

Supplementary materials

The crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-926447 (**2a**) and CCDC-926448 (**2b**) (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Acknowledgements

We acknowledge financial support from the National Nature Science Foundation of China [grant number 21102004], and the Natural Science Foundation of the Anhui Higher Education Institutions of China [grant number KJ2011A146], the Project-sponsored by SRF for ROCS and Special and Excellent Research Fund of Anhui Normal University.

Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2014.978308].

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