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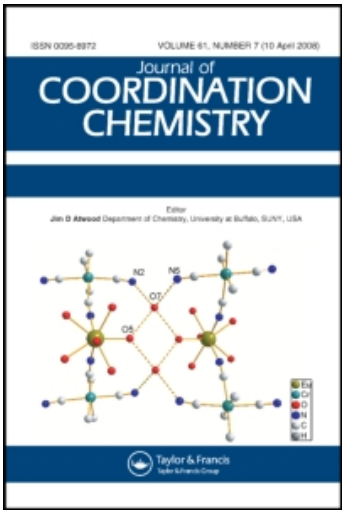

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Synthesis, structure, and fungicidal activity of thia- and aza-ferrocenophanes

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Synthesis, structure, and fungicidal activity of thia- and aza-ferrocenophanes

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Reaction of bridging dicyclopentadienyl disodium $E(CH_2COCpNa)_2$ (E = S or NPh, Cp = cyclopentadienyl) with $FeCl_2$ yields thia- and aza-[5]ferrocenophanes $E(CH_2COCp)_2Fe$ [E = S (**1**) and NPh (**2**)]. Treatment of $C_{14}H_8(CH_2SCH_2COCpNa)_2$ ($C_{14}H_8$ = 9,10-anthracenyl) with $FeCl_2$ affords dithia-[12]ferrocenophane $C_{14}H_8(CH_2SCH_2COCp)_2Fe$ (**3**), while similar reaction of $C_6H_4(CH_2SCH_2COCpNa)_2$ (C_6H_4 = 1,4-phenyl) with $FeCl_2$ provides a mixture of dithia-[12]ferrocenophane $C_6H_4(CH_2SCH_2COCp)_2Fe$ (**4**) and tetrathia-[12,12]ferrocenophane $[C_6H_4(CH_2SCH_2COCp)_2Fe]_2$ (**5**), which are separated easily by column chromatography. These five compounds were characterized by IR and NMR spectroscopic analyses and the structures of **2** and **3** were further confirmed by single crystal X-ray diffraction. The electrochemical behaviors of **1**–**4** were investigated by cyclic voltammetry. In addition, their fungicidal activities against *Alternaria solani*, *Cercospora arachidicola*, *Physalospora piricola*, and *Botrytis cinerea* were tested *in vitro*.

Keywords: Ferrocenophane; Electrochemical property; Fungicidal activity; Bioorganometallic chemistry

1. Introduction

Ferrocene and its derivatives have high stability in aqueous and aerobic media as well as characteristic redox behaviors [1]. For example, the applications of ferrocenyl derivatives in bioorganometallic chemistry have remarkable achievements in recent years [2, 3]. Many ferrocenyl derivatives display broad biological activities, such as antimalarial [2], antitumor [3], and antifungal [4, 5] activities. A large number of ferrocene-based ligands incorporated with potential O, S, and N donors have been exploited to generate multimetallic complexes with intriguing structures and unusual properties [6–8]. Ferrocenophanes, a class of functionalized ferrocenyl derivatives with one or more bridges between two cyclopentadienyl groups, have also been extensively investigated because of their fascinating structures and unique chemical

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properties [9–11]. Besides carbon-based bridged ferrocenophanes [9], heteroatoms (such as N- [12–15] and S- [12, 16–19] group elements) and metal-bridged [12, 20] ferrocenophanes are widely known. Due to the incorporation of heteroatoms, these functionalized ferrocenophanes exhibit good affinity to various anions and cations, and were used as selective electrochemical sensors for ion recognition [21, 22]. Recent investigations have shown that ferrocenophane derivatives have strong antitumor potential [23]. To continue to look for novel ferrocenyl derivatives with potential biological activities, and gain a further insight into their biological activities, we herein report the synthesis, electrochemical properties, and fungicidal activities of thia- and aza-ferrocenophanes.

2. Experimental

2.1. *Materials and measurements*

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Solvents were dried by standard methods prior to use. All reactions were carried out under argon using standard Schlenk and cannula techniques. NMR spectra were recorded on a Bruker AV300 spectrometer using $CDCl_3$ as solvent. IR spectroscopic data were obtained from a Bruker Equinox 55 spectrometer as KBr discs. Elemental analyses were carried out on a Yanaco CHN Corder MT-3 elemental analyzer. HR mass spectra were carried out on an IonSpec QFT–ESI spectrometer. Cyclic voltammetric experiments were performed on a LK 2005 electrochemical analyzer equipped with a three-electrode assembly with 0.1 mol L^{-1} $(n\text{-Bu})_4NPF_6$ as supporting electrolyte and CH_3CN as solvent. The working electrode was a Pt disk ($\phi = 2$ mm), and the reference was a SCE electrode. A Pt filament was used as an auxiliary electrode. The sweep rate was 100 mV s^{-1}. $E_{1/2}$ values were determined as $(E_{pa} + E_{pc})/2$. Electrochemical data reported here are related to that of the ferrocenium/ferrocene redox couple. $S(CH_2CO_2C_2H_5)_2$ [24], $C_{14}H_8(CH_2SCH_2CO_2C_2H_5)_2$ ($C_{14}H_8 = 9,10$-anthracenyl) [25], $C_6H_4(CH_2SCH_2CO_2C_2H_5)_2$ ($C_6H_4 = 1,4$-phenyl) [26], and $PhN(CH_2COCpNa)_2$ [27] were prepared by the methods from literature.

2.2. *Preparation of $S(CH_2COCpNa)_2$, $C_{14}H_8(CH_2SCH_2COCpNa)_2$, and $C_6H_4(CH_2SCH_2COCpNa)_2$*

To a solution of cyclopentadienyl sodium in 40 mL of THF at room temperature (prepared from the reaction of cyclopentadiene (60 mmol) with Na (50 mmol)), $S(CH_2CO_2C_2H_5)_2$ (25 mmol), $C_{14}H_8(CH_2SCH_2CO_2C_2H_5)_2$ (25 mmol), or $C_6H_4(CH_2SCH_2CO_2C_2H_5)_2$ (25 mmol) was added. The reaction mixture was stirred and heated at reflux for 24 h. During this period, a yellow-colored precipitate formed gradually. On cooling the mixture to room temperature, the precipitate was filtered off, washed with absolute ether, and dried in vacuum to yield air-sensitive yellow solids of $S(CH_2COCpNa)_2$ (80%), $C_{14}H_8(CH_2SCH_2COCpNa)_2$ (70%), and $C_6H_4(CH_2SCH_2COCpNa)_2$ (42%), respectively. These compounds were stable under oxygen- and water-free conditions and stored for several months at $-10^{\circ}C$ without notable decomposition.

2.3. *Preparation of $S(CH_2COCp)_2Fe$ (1)*

The mixture of iron powder (0.53 mmol, 30 mg) and anhydrous ferric chloride (1 mmol, 0.16 g) in 40 mL of THF was stirred and heated at reflux for 6 h. After cooling to room temperature, $S(CH_2COCpNa)_2$ (1.5 mmol, 0.44 g) was added to the above-mentioned solution. The reaction mixture was continuously stirred and heated at reflux for 6 h. The solvent was removed under reduced pressure, the residual solid was purified through a column of silica gel using $CH_2Cl_2/CH_3CO_2C_2H_5$ (V : V = 20 : 1) as eluent. After removing the solvent, the crude product was recrystallized from CH_2Cl_2/hexane to yield red crystals of **1**. Yield: 0.14 g (31%). ^{1}H-NMR: δ 3.40 (s, 4H, CH_2), 4.51, 4.87 (t, $J = 1.8$ Hz, t, $J = 1.8$ Hz, 4H, 4H, C_5H_4) ppm. ^{13}C-NMR: δ 39.6 (CH_2), 71.4, 74.0, 77.9 (C_5H_4), 199.2 (CO) ppm. Anal. Calcd for $C_{14}H_{12}FeO_2S$(%): C, 56.02; H, 4.03. Found (%): C, 55.83; H, 3.84. IR (KBr, cm^{-1}): ν(CO) 1671.8 vs.

2.4. *Preparation of $PhN(CH_2COCp)_2Fe$ (2)*

This compound was obtained by similar method using $PhN(CH_2COCpNa)_2$ instead of $S(CH_2COCpNa)_2$ as described above for **1**. After removing the solvent, the residual solid was purified through a column of silica gel using $CH_2Cl_2 : CH_3CO_2C_2H_5$ (V : V = 6 : 1) as eluent. Yield: 30%. ^{1}H-NMR: δ 4.14 (s, 4H, CH_2), 4.53, 4.83 (t, $J = 2.1$ Hz, t, $J = 2.1$ Hz, 4H, 4H, C_5H_4), 6.96, 7.06, 7.36–7.41 (t, $J = 7.3$ Hz, d, $J = 8.1$ Hz, m, 1H, 2H, 2H, C_6H_5) ppm. ^{13}C-NMR: δ 62.2 (CH_2), 71.1, 74.1, 78.4 (C_5H_4), 114.4, 120.0, 129.9, 149.5 (C_6H_5), 201.9 (CO) ppm. Anal. Calcd for $C_{20}H_{17}FeNO_2$(%): C, 66.87; H, 4.77; N, 3.90. Found (%): C, 66.39; H, 4.41; N, 4.06. IR (KBr, cm^{-1}): ν(CO) 1671.6 vs.

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2.5. *Preparation of $C_{14}H_8(CH_2SCH_2COCp)_2Fe$ (3)*

This compound was obtained by similar method using $C_{14}H_8(CH_2SCH_2COCpNa)_2$ instead of $S(CH_2COCpNa)_2$ as described above for **1**. Yield: 40%. ^{1}H-NMR: δ 3.28 (s, 4H, $C_{14}H_8CH_2$), 3.61 (s, 4H, $COCH_2$), 4.01, 4.97 (t, $J = 1.8$ Hz, s, 4H, 4H, C_5H_4), 7.65–7.68, 8.42–8.45 (m, m, 4H, 4H, $C_{14}H_8$) ppm. ^{13}C-NMR: δ 27.6 (CH_2), 37.8 ($COCH_2$), 69.8, 74.0, 78.4 (C_5H_4), 125.1, 126.5, 129.4, 130.3 ($C_{14}H_8$), 197.4 (CO) ppm. Anal. Calcd for $C_{30}H_{24}FeO_2S_2 \cdot 0.5CH_2Cl_2$ (%): C, 63.27; H, 4.35. Found (%): C, 63.66; H, 3.92. IR (KBr, cm^{-1}): ν(CO) 1667.5 vs.

2.6. *Preparation of $C_6H_4(CH_2SCH_2COCp)_2Fe$ (4) and $[C_6H_4(CH_2SCH_2COCp)_2Fe]_2$ (5)*

These two compounds were obtained by similar method using $C_6H_4(CH_2SCH_2COCpNa)_2$ instead of $S(CH_2COCpNa)_2$ as described above for **1**. After removing the solvent, the residual solid was separated by a column of silica gel using CH_2Cl_2:$CH_3CO_2C_2H_5$ (V : V = 20 : 1) as eluent to give **4** first, which was recrystallized from benzene to yield red crystals of **4**. Yield: 6.4%. ^{1}H-NMR: δ 3.47 (s, 4H, $C_6H_4CH_2$), 3.82 (s, 4H, $COCH_2$), 4.35, 4.41 (t, $J = 1.8$ Hz, t, $J = 1.8$ Hz, 2H, 2H,

C_5H_4), 7.46 (s, 4H, C_6H_4) ppm. ^{13}C-NMR: δ 36.5 (CH_2), 37.6 ($COCH_2$), 70.4, 75.2, 79.0 (C_5H_4), 130.2, 137.3 (C_6H_4), 197.9 (CO) ppm. Anal. Calcd for $C_{22}H_{20}FeO_2S_2.C_6H_6$ (%): C, 65.37; H, 5.09. Found (%): C, 64.95; H, 5.54. HRMS (ESI, m/z): 459.0148 (Calcd for $C_{22}H_{20}FeNaO_2S_2$: 459.0152, $[M+Na]^+$, 100%). IR (KBr, cm^{-1}): ν(CO) 1653.2 vs. After isolation of **4**, compound **5** was obtained subsequently. Yield: 2.1%. ^{1}H-NMR: δ 3.36 (s, 8H, $C_6H_4CH_2$), 3.79 (s, 8H, $COCH_2$), 4.49, 4.70 (t, $J = 1.8$ Hz, t, $J = 1.8$ Hz, 8H, 8H, C_5H_4), 7.37 (s, 8H, C_6H_4) ppm. Anal. Calcd for $C_{44}H_{40}Fe_2O_4S_4$ (%): C, 60.55; H, 4.62. Found (%): C, 60.16; H, 5.10. HRMS (ESI, m/z): 873.0583 (Calcd for $C_{44}H_{41}Fe_2O_4S_4$: 873.0587, $[M+H]^+$, 100%). IR (KBr, cm^{-1}): ν(CO) 1655.1 vs.

2.7. *Crystal structure determinations*

Red crystals of **2** and **3** suitable for X-ray analyses were obtained by slow diffusion of hexane into their CH_2Cl_2 solution at room temperature. Intensity data were collected on a Bruker SMART CCD diffractometer for **2** and Rigaku Saturn CCD diffractometer for **3**. Semi-empirical absorption corrections were applied. The structures were resolved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 software package [28, 29]. All non-hydrogen atoms were refined anisotropically. A summary of their fundamental crystal data is listed in table 1.

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Table 1. Crystallographic data for **2** and **3**.

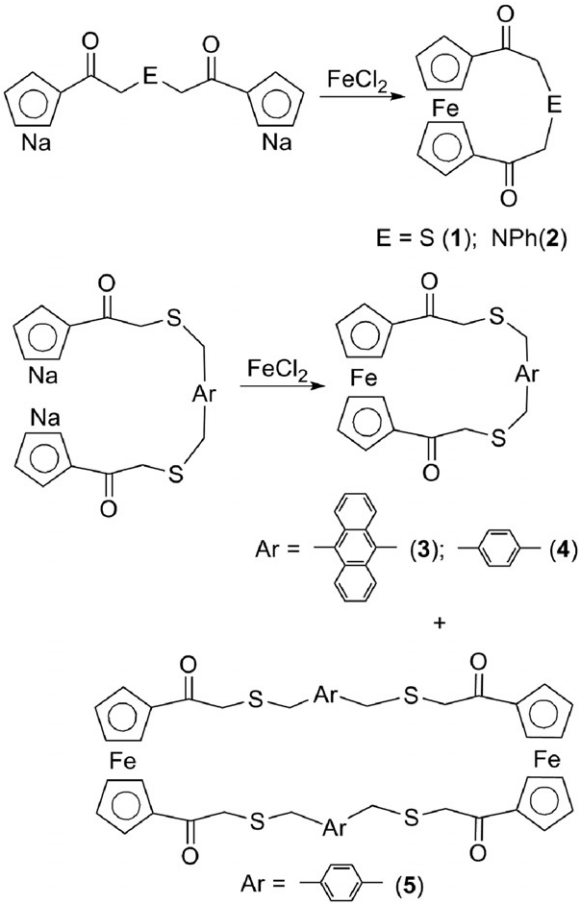
Compound	**2**	**3**·0.5CH_2Cl_2
Empirical formula	$C_{20}H_{17}FeNO_2$	$C_{30.5}H_{25}ClFeO_2S_2$
Formula weight	359.20	578.92
Temperature (K)	294(2)	113(2)
Wavelength (Å)	0.71073	0.71070
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	7.656(2)	9.856(2)
b	16.661(3)	12.746(3)
c	12.122(2)	20.428(4)
α	90	90
β	96.987(3)	98.691(3)
γ	90	90
Volume (Å^3), Z	1534.9(5), 4	2536.7(9), 4
Calculated density (g cm^{-3})	1.554	1.516
Absorption coefficient (mm^{-1})	0.994	0.893
F(000)	744	1196
Crystal size (mm^3)	0.22 × 0.20 × 0.16	0.24 × 0.20 × 0.16
2θ range for data collection (°)	4.18–52.72	3.78–55.78
Reflections collected	8514	23599
Independent reflections	3116 [R(int) = 0.0406]	6026 [R(int) = 0.0658]
Observed reflections ($I > 2\sigma(I)$)	2215	4944
Parameters	217	345
Goodness-of-fit on F^2	0.999	1.123
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0384$, $wR_2 = 0.0832$	$R_1 = 0.0653$, $wR_2 = 0.1384$

3. Results and discussion

3.1. *Synthesis and characterization of thia- and aza-ferrocenophanes*

Thia-[5]ferrocenophane $S(CH_2COCp)_2Fe$ (**1**) has been prepared previously by the reaction of 1,1′-bis(α-bromoacetyl)ferrocene [30] or 1,1′-bis(chloroacetyl)ferrocene [31] with Na_2S. Here, we found that it can also be obtained by the reaction of bridging dicyclopentadienyl disodium $S(CH_2COCpNa)_2$ with $FeCl_2$ (scheme 1). At the same time, the treatment of $PhN(CH_2COCpNa)_2$ or $Ar(CH_2SCH_2COCpNa)_2$ (Ar = 9,10-anthracenyl or 1,4-phenyl) with $FeCl_2$ yields aza-[5]ferrocenophane $PhN(CH_2COCp)_2Fe$ (**2**), dithia-[12]ferrocenophanes $Ar(CH_2SCH_2COCp)_2Fe$ [Ar = 9,10-anthracenyl (**3**), and 1,4-phenyl (**4**)], respectively. During the reaction of $C_6H_4(CH_2SCH_2COCpNa)_2$ (C_6H_4 = 1,4-phenyl) with $FeCl_2$, macrocyclic tetrathia-[12, 12]ferrocenophane $[C_6H_4(CH_2SCH_2COCp)_2Fe]_2$ (**5**) has been obtained along with **4**.

Compounds **1**–**4** are soluble in chlorinated solvents, whereas **5** has low solubility in these solvents and even in strongly polar DMF or DMSO. Compounds **1**–**5** were



Scheme 1. Synthesis of thia- and aza-ferrocenophanes.

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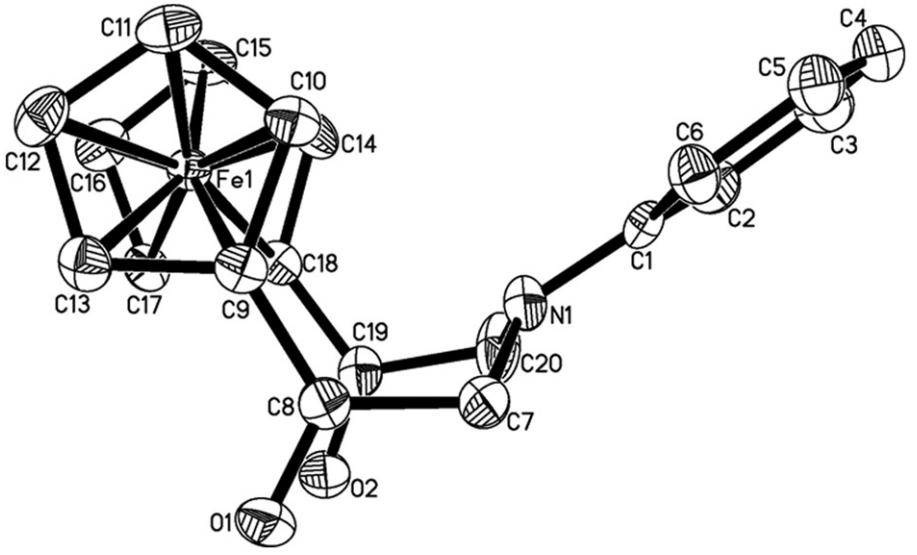

Figure 1. Molecular structure of **2** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (°): C8–O1, 1.218(3); C19–O2, 1.207(3); C1–N1, 1.411(3); C7–N1, 1.443(4); C20–N1, 1.466(4); C7–C8, 1.531(4) Å; and C7–C8–O1, 117.5(3); C9–C8–O1, 120.6(3); C18–C19–O2, 122.0(3); C20–C19–O2, 120.7(3); C1–N1–C7, 119.2(2); C7–N1–C20, 113.3(3); N1–C7–C8, 117.5(2).

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characterized by IR and NMR spectroscopies and exhibit simple spectroscopic characteristics due to their high symmetry. Their IR spectra show a strong absorption band at 1653–1672 cm^{-1} attributed to the carbonyl. The NMR spectra also support the proposed structures. The ^{1}H-NMR spectra display the expected integration values and peak multiplicities. For example, two pseudo-triplet peaks are observed between 4 and 5 ppm, corresponding to the proton signals of mono-substituted ferrocene. Three corresponding carbon signals of mono-substituted ferrocene appear at 69–70 ppm in their ^{13}C-NMR spectra. In addition, the carbonyl carbon signals in **1**–**4** are observed at 197–201 ppm.

The structure of **2** has been confirmed by X-ray diffraction analyses, which is shown in figure 1. Two cyclopentadienyl groups are eclipsed and almost parallel. The dihedral angle between them is 2.4°. The five bridged atoms as well as two carbonyl oxygens adopt a chair-like conformation. The phenyl ring is pseudo-equatorially oriented and nearly perpendicular to two cyclopentadienyl planes. The dihedral angle of the phenyl plane with the C9–C13 and C14–C18 cyclopentadienyl planes is 97.6° and 96.1°, respectively. The C_{alkyl}–N bond distances (1.443(4) and 1.466(4) Å) are slightly longer than the C_{aryl}–N bond distance (1.411(3) Å), but comparable to those in *N*-aryl-aza-[3]ferrocenophanes, such as *N*-4-*tert*-butylphenyl-2-aza-[3]ferrocenophane (**A**) (1.44(1) and 1.46(1) Å) [32]. The C_{alkyl}–N–C bond angle (113.3(3)°) in **2** is also similar to the corresponding angle of **A** (113.6(8)°).

The molecular structure of dithia-[12]ferrocenophane **3** is illustrated in figure 2. Two cyclopentadienyl rings adopt an eclipsed conformation, similar to that in **2**. The dihedral angle of two cyclopentadienyl planes is only 1.2°, smaller than that in **2** and other thia-ferrocenophanes, such as FcS_2CH_2 (Fc = ferrocenyl) [16]. The anthracenyl ring is almost perpendicular to two cyclopentadienyl planes with the dihedral angles of

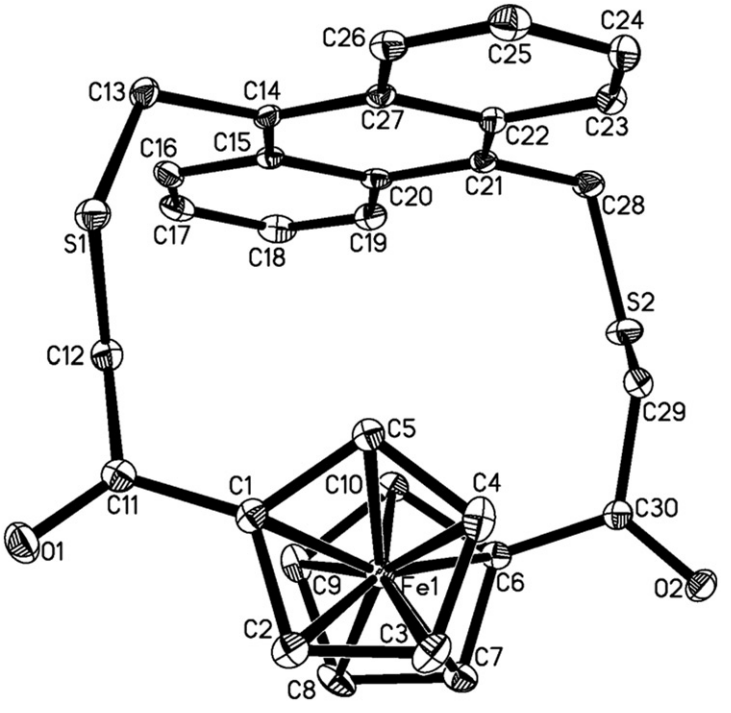

Figure 2. Molecular structure of **3** with thermal ellipsoids at the 30% probability level. The uncoordinated solvent is omitted for clarity. Selected bond distances (Å) and angles (°): C11–O1, 1.219(4); C30–O2, 1.224(4); C12–S1, 1.818(4); C13–S1, 1.827(3); C28–S2, 1.831(4); C29–S2, 1.823(4); C11–C12, 1.512(5) Å; and C12–C11–O1, 121.2(3); C11–C12–S1, 107.7(2); C14–C13–S1, 115.4(2); C12–S1–C13, 101.4(2); C29–C30–O2, 120.8(3); C21–C28–S2, 114.3(2); C30–C29–S2, 109.9(2); C28–S2–C29, 100.8(2).

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91.4° for the C1–C5 plane and 91.9° for the C6–C10 plane. The geometric parameters related to the carbonyl groups show no marked differences between **1**, **2**, and **3**. For instance, similar carbonyl bond distances (1.219(2) Å and 1.225(2) Å in **1** [31], 1.218(3) and 1.207(3) Å in **2** as well as 1.219(4) and 1.224(4) Å in **3**, respectively) are observed. The average C–S bond distance is 1.825 Å, compared to those in the previously reported thia-ferrocenophanes, such as FcS_2CH_2 (average 1.815 Å of C_{alkyl}–S bond distance) [16], tetrathia-[7.7]ferrocenophane (average 1.813 Å) [33], and **1** (1.811(2) and 1.812(2) Å) [31], whereas, the C–S–C angles (C12–S1–C13 101.4(2)° and C28–S2–C29 100.8(2)°) are similar to those in tetrathia-[7.7]ferrocenophane (101.4(3)° and 100.9(3)°) [33], and slightly smaller than the corresponding C–S–C angle (102.25(9)°) in **1** [31].

3.2. *Electrochemical properties*

The electrochemical properties of **1**–**4** were examined by cyclic voltammetry at room temperature in CH_3CN. These four compounds exhibit a reversible one-electron redox process for the ferrocenyl group with $E_{1/2}$ of 80 mV for **1**, 31 mV for **2**, 138 mV for **3** and 137 mV for **4**. Compound **2** shows an additional quasi-reversible wave with $E_{1/2}$ of 368 mV, possibly associated with the species formed by electron transfer from amine to

Table 2. The fungicidal activities of **1–4**.

	Inhibition ratio (%) (50 μg mL^{-1})				
Compound	**1**	**2**	**3**	**4**	Propiconazole
A. solani	40.0	64.0	56.0	60.0	100.0
C. arachidicola	40.9	50.0	36.4	31.8	100.0
P. piricola	68.9	88.5	49.2	47.5	100.0
B. cinerea	85.7	100.0	78.6	71.4	100.0

the Fe(III) center produced by the initial oxidation of the ferrocenyl group [34]. The redox potential of the ferrocenyl group in **3** is similar to that of **4** owing to their similar structures. In addition, an irreversible oxidative peak is observed at 864 mV in **3**, possibly corresponding to the anthracenyl group [35].

3.3. *Fungicidal activities*

Preliminary *in vitro* tests for fungicidal activities of **1–4** were carried out by the fungi growth inhibition method [36]. These four compounds were dissolved in DMF at a concentration of 50 μ mL^{-1}. The data are summarized in table 2, which indicate that these compounds show medium fungicidal activities against *Alternaria solani*, *Cercospora arachidicola*, *Physalospora piricola*, and *Botrytis cinerea*, but higher than other acylferrocenyl derivatives [5, 37]. These four compounds, especially the aza-[5]ferrocenophane **2**, show high antifungal activities against *B. cinerea*. The inhibition percentage of **2** for *B. cinerea* is up to 100% *in vitro*. Moreover, this compound also displays high inhibition percentage for *P. piricola* (88.5%).

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Supplementary material

CCDC-751268 for **2** and 751269 for **3** contain the supplementary crystallographic data for this article. These data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk).

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