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Synthesis, electrochemical properties and fungicidal activity of 1,1′-bis(aroyl)ferrocenes and their derivatives

Yan-Ye Dou, Yun-Fu Xie and Liang-Fu Tang*

Reaction of functionalized cyclopentadienyl sodium $CH_3O_2CArC(O)CpNa$ (Ar = aryl and Cp = cyclopentadienyl) with $FeCl_2$ in a 2 : 1 ratio gives 1,1′-bis(aroyl)ferrocenes $[CH_3O_2CArC(O)Cp]_2Fe$ in reasonable yields. Upon treatment of these aroyl compounds with $NaBH_4$, the ketone carbonyl is reduced to yield compounds $[CH_3O_2CArCH(OH)Cp]_2Fe$, while with the stronger reductive reagent $LiAlH_4$, diols $[HOCH_2ArCH(OH)Cp]_2Fe$ are obtained. All new compounds were characterized by IR and NMR spectroscopic analyses. Their electrochemical behavior was investigated by cyclic voltammetry. The structure of $[CH_3O_2CC_{10}H_6C(O)Cp]_2Fe$ was further confirmed by single crystal X-ray diffraction analysis. In addition, the fungicidal activities of these new compounds were also determined *in vitro*. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: ferrocene; bioorganometallic chemistry; electrochemical property; fungicidal activity

Introduction

Ferrocence has been extensively used as a starting material for the synthesis of versatile ferrocenyl derivatives owing to its high stability in aqueous and aerobic media.[1] Ferrocenyl derivatives have also been expected to play a key role as electron chemical probes for the electron-transfer process in biological molecules owing to their reversible redox characteristics.[2] It is known that the incorporation of the ferrocenyl fragment into organic molecules can improve their biological activity.[3,4] All these attractive properties have spurred rapid development of the applications of ferrocenyl derivatives in bioorganometallic chemistry in recent years.[3–6] Many ferrocenyl derivatives have shown a broad range of biological activity, such as antimalarial,[4,5] antitumor[5–9] and antifungal[10–15] activity. Recent investigations have shown that ferrocenoyl[16–19] and ferrocenyl alcohol[20,21] derivatives have also exhibited good biological activity. In order to continue to seek novel ferrocenyl derivatives with potential biological activity, we herein report the synthesis, electrochemical property and fungicidal activity of 1,1′-bis(aroyl)ferrocenes and their reductive products.

Experimental

Materials and measurements

All reactions were carried out under an argon atmosphere using standard Schlenk and Cannula techniques. Hexane, ether and THF were distilled from sodium and benzophenone ketyl prior to use. NMR spectra were obtained on a Bruker AV300 spectrometer using $CDCl_3$ as solvent unless otherwise noted, and the chemical shifts were reported in parts per million with respect to the reference. IR spectral data were obtained using a Bruker Equinox 55 spectrometer with KBr disks or Nujol mulls. Elemental analyses were carried out on an Elementar Vairo EL analyzer. Melting points were measured using an X-4 digital melting-point apparatus and were uncorrected. Cyclic voltammetric experiments were performed at room temperature on an LK 2005 electrochemical analyzer equipped with a three-electrode assembly with 0.1 M Bu_4NPF_6 as supporting electrolyte and CH_3CN as solvent. The working electrode was a Pt disk (diameter = 2 mm), and the reference was an SCE electrode. A Pt filament was used as an auxiliary electrode. $E_{1/2}$ values were determined as $(E_{pa} + E_{pc})/2$. Electrochemical data reported here are related to those of the ferrocenium/ferrocene redox couple.

Synthesis

Preparation of functionalized cyclopentadienyl sodium

(*p*-Methoxycarbonylbenzoyl)cyclopentadienyl sodium [*p*-$CH_3O_2CC_6H_4C(O)CpNa$] and (*m*-methoxycarbonylbenzoyl) cyclopentadienyl sodium [*m*-$CH_3O_2CC_6H_4C(O)CpNa$] were prepared in a similar method used to obtain (4-methoxycarbonyl-1-naphthoyl)cyclopentadienyl sodium [$CH_3O_2CC_{10}H_6C(O)CpNa$].[22] The solution of cyclopentadienyl sodium in 40 ml of THF, prepared from the reaction of cyclopentadiene (157.6 mmol) with Na (104 mmol), was added dropwise to the refluxing solution of dimethyl dicarboxylate (100 mmol) in 100 ml of THF. After addition, the reaction mixture was stirred and refluxed for 25 h. Cooling to room temperature, the precipitation was filtered off, washed with absolute ether, and dried in vacuum to yield air-sensitive yellow solids of *p*-$CH_3O_2CC_6H_4C(O)CpNa$ (78%) and *m*-$CH_3O_2CC_6H_4C(O)CpNa$ (75%), respectively.

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* *Correspondence to: Liang-Fu Tang, Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China. E-mail: lftang@nankai.edu.cn*

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

*Preparation of [$CH_3O_2CC_{10}H_6C(O)Cp]_2Fe$ (**1**)*

The mixture of iron powder (0.14 g, 2.5 mmol) and anhydrous ferric chloride (0.65 g, 4 mmol) in 40 ml THF was stirred and refluxed for 6 h until the solution became off-white. After cooling to room temperature, $CH_3O_2CC_{10}H_6C(O)CpNa$ (3.6 g, 12 mmol) was added to the above-mentioned solution. Then, the reaction mixture was stirred and refluxed continuously for 6 h. Again cooling to room temperature, the reaction mixture was filtered off. The filtrate was concentrated to dryness under reduced pressure, and 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** (1.8 g, 48%); m.p. 209–211 °C. ^1H NMR: $\delta = 4.08$ (s, 6H, CH_3), 4.67, 4.85 (s, s, 4H, 4H, C_5H_4), 7.49, 7.62, 8.06, 8.88 (m, m, m, d, 2H, 4H, 4H, 2H, $C_{10}H_6$) ppm. ^{13}C NMR: $\delta = 52.99$ (CH_3), 72.67, 74.51, 80.81 (C_5H_4), 124.18, 125.56, 126.14, 127.17, 127.96, 128.18, 129.62, 130.41, 131.45, 140.98 ($C_{10}H_6$), 167.45 (CO_2CH_3), 199.38 ($C{=}O$) ppm. IR (KBr, cm^{-1}): $\nu(CO_2CH_3)$ 1725.0 vs, ν ($C{=}O$) 1645.9 vs. Anal. found: C, 70.34; H, 4.12; calcd for $C_{36}H_{26}FeO_6$ C, 70.83; H, 4.29%.

*Preparation of (p-$CH_3O_2CC_6H_4C(O)Cp)_2Fe$ (**2**)*

This compound was obtained similarly using p-$CH_3O_2CC_6H_4C(O)CpNa$ instead of $CH_3O_2CC_{10}H_6C(O)CpNa$ as described above for **1**. After recrystallization from CH_2Cl_2–hexane, red crystals of **2** were obtained. Yield: 43%; m.p. 200 °C (dec.). ^1H NMR: $\delta = 4.00$ (s, 6H, CH_3), 4.62, 4.91 (s, s, 4H, 4H, C_5H_4), 7.82, 8.07 (d, d, 4H, 4H, C_6H_4) ppm. ^{13}C NMR: $\delta = 52.42$ (CH_3), 73.17, 74.74, 79.26 (C_5H_4), 127.87, 129.57, 132.95, 142.55 (C_6H_4), 166.23 (CO_2CH_3), 197.10 ($C{=}O$) ppm. IR (KBr, cm^{-1}): $\nu(CO_2CH_3)$ 1723.4 vs, ν ($C{=}O$) 1626.1 vs. Anal. found: C, 66.09; H, 4.58; calcd for $C_{28}H_{22}FeO_6$ C, 65.90; H, 4.35%.

*Preparation of [m-$CH_3O_2CC_6H_4C(O)Cp]_2Fe$ (**3**)*

This compound was obtained similarly using m-$CH_3O_2CC_6H_4C(O)CpNa$ instead of $CH_3O_2CC_{10}H_6C(O)CpNa$ as described above for **1**. After recrystallization from CH_2Cl_2–hexane, red crystals of **3** were obtained. Yield: 46%; m.p. 150–152 °C. ^1H NMR: $\delta = 3.96$ (s, 6H, CH_3), 4.68, 4.96 (s, s, 4H, 4H, C_5H_4), 7.51, 7.94, 8.18, 8.58 (t, d, d, s, 2H, 2H, 2H, 2H, C_6H_4) ppm. ^{13}C NMR: $\delta = 52.37$ (CH_3), 73.23, 74.79, 79.25 (C_5H_4), 128.73, 129.38, 130.16, 132.38, 132.78, 139.03 (C_6H_4), 166.20 (CO_2CH_3), 196.70 ($C{=}O$) ppm. IR (KBr, cm^{-1}): $\nu(CO_2CH_3)$ 1722.5 vs, ν ($C{=}O$) 1645.9 vs. Anal. found: C, 66.17; H, 4.44; calcd for $C_{28}H_{22}FeO_6$ C, 65.90; H, 4.35%.

*Preparation of [$CH_3O_2CC_{10}H_6CH(OH)Cp]_2Fe$ (**4**)*

The mixture solvent of absolute methanol and THF (10 ml, v/v, 1 : 1) was added to the mixture of **1** (0.26 g, 0.43 mmol) and $NaBH_4$ (40 mg, 1.06 mmol). The reaction mixture was stirred for 2 h at room temperature to yield a yellow solution. After completion of the reaction, dilute hydrochloric acid was added to adjust the pH value of the solution to 7. The solvent was removed under reduced pressure, and the residual was purified through a column of silica gel using CH_2Cl_2–$CH_3CO_2C_2H_5$ (v/v, 10 : 1) as eluent. After removing the solvent, the residual was recrystallized from CH_2Cl_2–hexane to yield yellow solids of **4** (0.18 g, 67%); m.p. 179–181 °C. ^1H NMR: $\delta = 3.97$ (s, 6H, CH_3), 4.07, 4.16, 4.22, 4.32, (s, s, s, s, 2H, 2H, 2H, 2H, C_5H_4), 5.69 (s, 2H, OH, this peak disappeared when D_2O was added), 6.04 (s, 2H, $CHOH$), 7.44, 7.87, 8.74 (m, m, d, 6H, 4H, 2H, $C_{10}H_6$) ppm. ^{13}C NMR: $\delta = 52.28$ (CH_3), 67.91, 68.05, 68.22, 68.33, 68.64 (C_5H_4), 92.87 ($CHOH$), 122.55, 124.06, 126.26, 126.46, 126.71, 127.26, 129.75, 131.03, 131.45, 144.25 ($C_{10}H_6$), 167.97 (CO_2CH_3) ppm. IR (KBr, cm^{-1}): ν (OH) 3277.6 s, $\nu(CO_2CH_3)$ 1718.2 vs; (Nujol, cm^{-1}): ν (OH) 3264.4 s, $\nu(CO_2CH_3)$ 1718.8 vs. Anal. found: C, 70.03; H, 4.98; calcd for $C_{36}H_{30}FeO_6$ C, 70.37; H, 4.92%.

*Preparation of [p-$CH_3O_2CC_6H_4CH(OH)Cp]_2Fe$ (**5**)*

This compound was obtained similarly using **2** instead of **1** as described above for **4**. After recrystallization from CH_2Cl_2–hexane, yellow solids of **5** were obtained. Yield: 63%; m.p. 186–188 °C. ^1H NMR: $\delta = 3.90$ (s, 6H, CH_3), 4.09, 4.24 (s, s, 4H, 4H, C_5H_4), 4.21 (s, 2H, OH, this peak disappeared when D_2O was added), 5.57 (s, 2H, $CHOH$), 7.44, 7.95 (d, d, 4H, 4H, C_6H_4) ppm. IR (KBr, cm^{-1}): ν (OH) 3248.6 s, $\nu(CO_2CH_3)$ 1718.4 vs; (Nujol, cm^{-1}): ν (OH) 3226.6 s, $\nu(CO_2CH_3)$ 1717.0 vs. Anal. found: C, 65.36; H, 5.24; calcd for $C_{28}H_{26}FeO_6$ C, 65.38; H, 5.10%.

*Preparation of [m-$CH_3O_2CC_6H_4CH(OH)Cp]_2Fe$ (**6**)*

This compound was obtained similarly using **3** instead of **1** as described above for **4**. After recrystallization from CH_2Cl_2–hexane, yellow solids of **6** were obtained. Yield: 72%; m.p. 142–145 °C. ^1H NMR: $\delta = 3.89$ (s, 6H, CH_3), 4.08, 4.19, 4.25 (s, s, m, 2H, 2H, 4H, C_5H_4), 5.29 (s, 2H, OH, this peak disappeared when D_2O was added), 5.47 (s, 2H, $CHOH$), 7.27, 7.45, 7.83, 7.99 (t, d, d, s, 2H, 2H, 2H, 2H, C_6H_4) ppm. ^{13}C NMR: $\delta = 52.34$ (CH_3), 66.66, 67.42, 68.15, 68.79, 71.71 (C_5H_4), 93.97 ($CHOH$), 127.50, 128.57, 128.90, 130.24, 130.84, 144.28 (C_6H_4), 167.15 (CO_2CH_3) ppm. IR (KBr, cm^{-1}): ν (OH) 3259.5 s, ν (CO_2CH_3) 1721.4 vs. Anal. found: C, 65.03; H, 4.89; calcd for $C_{28}H_{26}FeO_6$ C, 65.38; H, 5.10%.

*Preparation of [$HOCH_2C_{10}H_6CH(OH)Cp]_2Fe$ (**7**)*

The solution of **1** (0.2 g, 0.33 mmol) in THF (10 ml) was added dropwise to the stirred solution of $LiAlH_4$ (50 mg, 1.32 mmol) in 20 ml of absolute ether. After completion of addition, the reaction mixture was stirred and refluxed for 2 h. Cooled with an ice-bath, 0.5 ml water, 0.5 ml NaOH solution (15%) and 0.5 ml of water in succession were added dropwise to the reaction mixture. The reaction mixture was stirred for 30 min and filtered off, the solid was washed with ether (3 × 10 ml). The organic layer was separated and dried with anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, the residual was purified through a column of silica gel using CH_2Cl_2–CH_3OH (v/v, 20 : 1) as eluent. After removing the solvent, the residual was recrystallized from CH_2Cl_2–hexane to yield yellow solids of **7** (94 mg, 51%); m.p. 210 °C (dec.). ^1H NMR: $\delta = 3.99$ (s, 4H, CH_2), 4.06, 4.15, 4.46 (s, m, s, 2H, 4H, 2H, C_5H_4), 5.27 (s, 4H, OH, this peak disappeared when D_2O was added), 6.10 (s, 2H, $CHOH$), 7.74, 7.89, 7.95, 8.77 (s, t, d, d, 6H, 2H, 2H, 2H, $C_{10}H_6$) ppm. IR (KBr, cm^{-1}): ν (OH) 3396.0 br and vs; (Nujol, cm^{-1}): ν (OH) 3256.7 br. Anal. found: C, 72.71; H, 5.84; calcd for $C_{34}H_{30}FeO_4$ C, 73.13; H, 5.41%.

*Preparation of [p-$HOCH_2C_6H_4CH(OH)Cp]_2Fe$ (**8**)*

This compound was obtained similarly using **2** instead of **1** as described above for **7**. After recrystallization from CH_2Cl_2–hexane, yellow solids of **8** were obtained. Yield: 48%; m.p. 163–165 °C. ^1H NMR: $\delta = 4.03$ (s, 4H, CH_2), 4.16, 4.33, 4.59 (s, s, m, 2H, 2H, 4H,

C_5H_4), 3.12, 5.18 (s, s, 2H, 2H, O*H*, these two peaks disappeared when D_2O was added), 5.47 (s, 2H, C*H*OH), 7.39, 7.94 (d, d, 4H, 4H, C_6H_4) ppm. ^{13}C NMR: $\delta = 52.30$ (CH_2), 66.47, 67.45, 68.28, 68.79, 71.77 (C_5H_4), 98.87 (CHOH), 126.29, 129.96, 148.76 (C_6H_4) ppm. IR (KBr, cm^{-1}): ν (OH) 3396.0 vs. Anal. found: C, 67.85; H, 5.32; calcd for $C_{26}H_{26}FeO_4$ C, 68.13; H, 5.72%.

*Preparation of [m-$HOCH_2C_6H_4CH(OH)Cp]_2Fe$ (**9**)*

This compound was obtained similarly using **3** instead of **1** as described above for **7**. After recrystallization from CH_2Cl_2/hexane, yellow solids of **9** were obtained. Yield: 46%; m.p. 136–138 °C. ^1H NMR: $\delta = 4.07$ (s, 4H, CH_2), 4.17, 4.25, 4.50 (s, s, m, 2H, 2H, 4H, C_5H_4), 3.03, 5.19 (s, s, br, br, 2H, 2H, CHO*H* and CH_2OH, these two peaks disappeared when D_2O was added), 5.37 (s, 2H, C*H*OH), 7.13, 7.18 7.24, 7.34 (d, d, t, s, 2H, 2H, 2H, 2H, C_6H_4) ppm. ^{13}C NMR: $\delta = 65.14$ (CH_2), 66.84, 67.53, 68.17, 68.66, 72.01 (C_5H_4), 94.17 (CHOH), 124.97, 125.75, 126.33, 128.53, 141.30, 144.22 (C_6H_4) ppm. IR (KBr, cm^{-1}): ν (OH) 3392.1 br and vs. Anal. found: C, 68.21; H, 5.46; calcd for $C_{26}H_{26}FeO_4$ C, 68.13; H, 5.72%.

X-ray crystallography

Red crystals of **1** suitable for X-ray analyses were obtained by slow evaporation of its CH_2Cl_2–hexane solutions at −10 °C. Intensity data were collected at 293 K on a Bruker Apex II CCD diffractometer equipped with graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) using the ω scan mode. All data were corrected by a semi-empirical method using SADADS[23] program. The program SAINT[24] was used for integration of the diffraction profiles. The structures were solved by direct methods using the SHELXS program of the SHELXTL-97 package and refined with SHELXL.[25] All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data are listed in Table 1.

Table 1. Crystal data and refinement parameters for **1**

Formula	$C_{36}H_{26}FeO_6$
Formula weight	610.42
Crystal size (mm)	0.27 × 0.16 × 0.06
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	18.239(4)
b (Å)	9.904(2)
c (Å)	7.610(1)
β (deg)	96.870(3)
V (Å)^3	1364.7(6)
Z	2
D_c (g cm^{-3})	1.485
F(000)	632
μ(mm^{-1})	0.603
No. of unique reflections	2409
No. of observed reflections [$I > 2\sigma(I)$]	1694
No. of parameters	197
Goodness-of-fit	1.008
Residuals R, R_w	0.0422, 0.0958

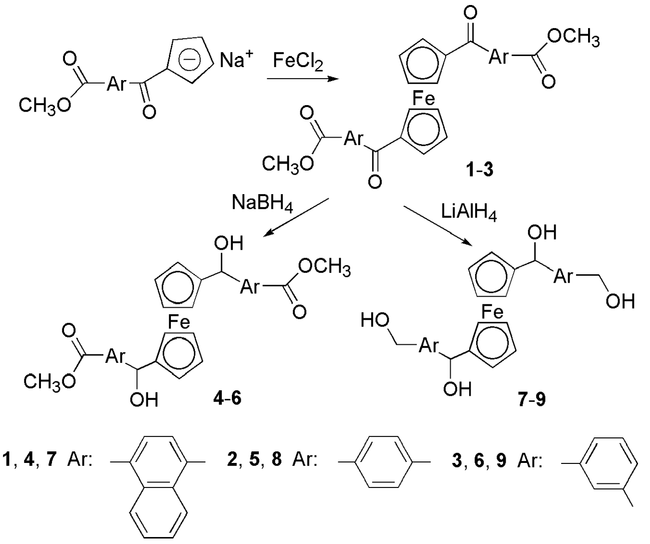
Results and Discussion

Synthesis and reactivity of 1,1′-bis(aroyl)ferrocenes

The reaction of functionalized cyclopentadienyl sodium $CH_3O_2CArC(O)CpNa$ with $FeCl_2$ in a 2 : 1 ratio in THF gave 1,1′-bis(aroyl)ferrocenes (**1–3**) in reasonable yields (Scheme 1). Upon treatment of these three compounds with $NaBH_4$, the ketone carbonyl was reduced to yield compounds **4–6**. When the stronger reductive reagent $LiAlH_4$ was employed, diols **7–9** were obtained.

All the above-described compounds were characterized by elemental and spectroscopic analyses. The IR spectra of compounds **1–3** show two kinds of typical carbonyl stretching bands. The characteristic absorption of the ester carbonyl was observed between 1722 and 1725 cm^{-1}, while the corresponding characteristic absorption of the ketone carbonyl appeared in the range 1626–1646 cm^{-1}. In the reductive products **4–6**, the ketone carbonyl disappeared, and a new absorption attributed to the hydroxyl group was observed between 3226 and 3278 cm^{-1} as a strong broad peak. Furthermore, no carbonyl absorption peaks were observed in compounds **7–9**, which only showed a strong broad peak between 3256 and 3396 cm^{-1} attributed to the hydroxyl group, consistent with the expectation that the ketone and ester carbonyls had been reduced by $LiAlH_4$ to the hydroxyl groups. The ^{13}C NMR spectra also supported the proposed structures of compounds **1–9**. For example, the ^{13}C NMR spectra of compounds **1–3** clearly showed two sets of carbonyl (C=O) signals. Their ketone carbonyl and ester carbonyl signals were observed at *ca* 197 and 167 ppm. In compounds **4–6**, only the signal of the ester carbonyl carbon atom was observed, while the signal of the ketone carbonyl carbon atom disappeared. In addition, no signal attributed to the ketone and ester carbonyl carbon atoms was observed in fully reduced products **7–9**. It is noteworthy that the NMR spectra of reductive products **4–9** exhibited unequivalent cyclopentadienyl ring resonances of both protons and carbons, possibly owing to the influence of the adjacent chiral carbon.

The molecular structure of compound **1** was further confirmed by crystal X-ray diffraction analysis, as shown in Fig. 1. The geometric parameters were extremely similar to those reported in the 1,1′-bis(aroyl)ferrocenes of other $Fc(COAr)_2$ type compounds (Fc = ferrocenyl). For instance, the ketone carbonyl bond length of



Scheme 1.

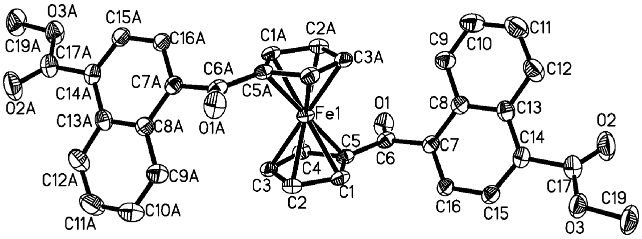


Figure 1. The molecular structure of compound **1**. The thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Symmetry operations of 'A' are $-x + 1$, $-y + 1$, $-z$. Key geometric parameters: C6–O1, 1.211(5); C17–O2, 1.199(6); C17–O3, 1.316(6); C19–O3, 1.446(6) Å; C1–C5–C6, 128.0(3); C5–C6–C7, 118.3(3); C15–C14–C17, 118.9(5); C14–C17–O3, 111.8(4); O2–C17–O3, 123.2(5); C17–O3–C19, 116.0(4)°.

C6–O1 [1.211(5) Å] was similar to the corresponding bond [1.21(1) Å] in $Fc(COC_6H_4OH)_2$.[26] It is interesting that two cyclopentadienyl planes as well as two naphthyl planes were parallel to each other. The dihedral angle between the cyclopentadienyl plane and the naphthyl plane was 120.2°. The ketone carbonyl group had a good conjugated relationship with the cyclopentadienyl ring instead of the naphthyl plane, with the O1 and C6 atoms slightly deviating from the cyclopentadienyl plane (only −0.0047 Å for O1 and 0.0290 Å for C6, respectively), but markedly deviating from the naphthyl plane (0.5811 Å for O1 and −0.2787 Å for C6, respectively). Furthermore, the torsion angles of C1–C5–C6–O1 [179.5(4)°] and O1–C6–C7–C16 [−122.4(5)°] also indicated that this carbonyl group π-system is coplanar with the adjacent cyclopentadienyl ring system, instead of the naphthyl phane. On the other hand, the ester carbonyl group had poor coplanarity with the naphthyl plane. The O2 and C17 atoms significantly deviated from the naphthyl plane (0.4225 Å for O2 and −0.1473 Å for C17, respectively). These results are also in agreement with the fact that the IR spectra showed a relatively low-frequency absorption band for the conjugated ketone carbonyl in compounds **1–3** and a common absorption band for the nonconjugated ester carbonyl in compounds **1–6**.

Electrochemical properties

The electrochemical properties of compounds **1–9** were investigated with cyclic voltammetry at room temperature in the CH_3CN solution. The voltammetric data are listed in Table 2. All compounds exhibited a reversible one-electron redox process of the ferrocenyl group. The peak potentials ($E_{1/2}$) of the aroyl derivtives **1–3** were remarkably positively shifted compared with those in their reductive products **4–9**, consistent with the inductive effects being due to the electron-withdrawing aroyl group at the ferrocenyl group in compounds **1–3** decreasing the electron density around the iron atom.

Table 2. Electrochemical data of compounds **1–9**. The sweep rate was 100 mV s^{-1}

Compound	1	2	3	4	5	6	7	8	9
$E_{1/2}$(mV)	559	518	505	59	63	86	27	62	68

Table 3. The fungicidal activities of compounds **1–9**

Compound	Inhibition ratio (%) (50 ppm) 1	2	3	4	5	6	7	8	9
Gibbereila zeae	0.0	33.3	0.0	27.1	0.0	33.3	4.2	10.4	6.3
Alternaria solani	0.0	0.0	0.0	0.0	16.7	0.0	0.0	0.0	0.0
Cercospora arachidicola	9.1	3.9	5.2	9.1	45.0	9.1	3.9	5.2	14.3
Physolospora piricola	9.7	41.9	3.2	12.9	32.3	19.4	9.7	9.7	16.1
Fusarium oxysporum	13.2	21.1	0.0	0.0	5.9	0.0	5.3	0.0	0.0

Fungicidal activities

Preliminary *in vitro* tests for fungicidal activity of compounds **1–9** were carried out using the reported fungi growth inhibition method.[27] All compounds were dissolved in DMF at a concentration of 50 ppm. The data are summarized in Table 3, which shows that these compounds show relatively low fungicidal activity, similar to other acylferrocenyl derivatives.[28] The aroyl compound **2** displayed some degree of antifungal activity to *Gibbereila zeae* (33.3%) and *Physolospora piricola* (41.9%), while compound **5** was active against *Cercospora arachidicola* (45.0%) and *Physolospora piricola* (32.3%). Compound **6** also displayed activity against *Gibbereila zeae* (33.3%). In addition, the diols **7–9** showed low inhibition percentage for all tested fungi *in vitro*.

Supplementary materials

CCDC number 655537 for **1** contains the supplementary crystallographic data for this paper. Copies of this information may be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or web site: www.ccdc.cam.ac.uk).

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