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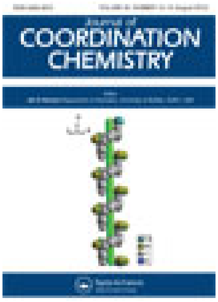

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Detecting the electron density of benzene using ferrocene as an indicator

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Detecting the electron density of benzene using ferrocene as an indicator

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Ferrocenylbenzene (**1**) and ferrocenylbenzene tricarbonylchromium (**2**) were synthesized and characterized. NMR chemical shifts of benzene in **2** are shifted upfield compared to those of **1**. We attribute the NMR spectrum of **2** to the reduced magnetic anisotropy effect of the benzene ring. Herein, we associate the electron density of the benzene ring in **1**, **2**, and p-ferrocenylaniline with the oxidation potential of the ferrocenyl group. The increased oxidation potential of ferrocene showed that the electron density of the benzene ring in **2** is reduced compared to that of **1**, and the reduced oxidation potential of ferrocene indicates that the electron density of the benzene ring in p-ferrocenylaniline increased compared to that of **1**. Therefore, ferrocene could be used as an electrochemical probe to predict the electron density of the benzene ring in **1**, **2**, and p-ferrocenylaniline.

Keywords: Electron density; NMR Spectra; Magnetic anisotropy effect; Electrochemical property

1. Introduction

Electron density of benzene has been investigated using the intensity of the colors of complexes between benzene derivatives and tetracyanoethylene by Kolb [1] and fluorine-19 NMR data in arene metal complexes by Ogorodnikova in 1990 [2]. The unusual NMR spectrum of benzene tricarbonylchromium received attention [3, 4] with a variety of interpretations, such as partial re-hybridization of the ring carbon atoms [5], reducing total electron density of the ring by the $Cr(CO)_3$ unit [6], changes in effective excitation energy [7], and decrease in magnetic anisotropy of the benzene ring [8]. These explanations are not independent or precise. We want to find a convenient method to determine the factors that influence the upfield shift of the NMR signals. Synthesis and applications of ferrocenyl-substituted benzene have been pursued for several years [9, 10]; we found that some phenomena can be elucidated through electrochemical properties of ferrocene [11–13]. Therefore, ferrocene could be used as an electrochemically sensitive probe to detect the electron density of the benzene ring [14, 15]. Though we had studied the NMR spectrum of a new ferrocenylbenzene

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tricarbonylchromium complex before, the influence of the tricarbonylchromium unit on the electrochemical properties of ferrocene was not studied [8].

In this article, two model compounds, ferrocenylbenzene (**1**) and ferrocenylbenzene tricarbonylchromium (**2**), were synthesized and used to show the relationship between the electron density of the benzene ring and the oxidation potential of ferrocene. Through carefully analyzing the NMR spectra and comparing the oxidation potential of the ferrocenyl unit of **1** and **2**, association between NMR spectra of the benzene ring and the oxidation potential of ferrocene in **1** and **2** was established. After $Cr(CO)_3$ coordination to benzene, the oxidation potential in **2** increased and the electron density of the benzene ring was also reduced, which made the NMR chemical shifts move upfield. We also found that the oxidation potential of ferrocene in p-ferrocenylaniline decreased compared to that of **1**, which showed that the electron density of the benzene ring increased compared to that of **1**.

2. Experimental

2.1. *General procedure*

All reactions and manipulations were carried out under Ar with standard inert atmosphere and Schlenk techniques. All solvents were dried and distilled according to standard procedures prior to use. Reactions were monitored by thin layer chromatography. Column chromatography was performed with the use of 200–300 mesh silica gel. $Cr(CO)_6$ was purchased from Alfa Aesar company.

IR spectra were measured on a Nicolet FT-IR spectrometer using KBr pellets. Elemental analyses were carried out on an Elementar var III-type analyzer. NMR spectra were recorded at room temperature on an Inova 500 MHz NMR spectrometer. Mass spectra were determined using a Micromass LCT instrument. Cyclic voltammetry experiments were performed with a CHI-760 C electrochemical analyzer. All measurements were carried out at 0°C with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a non-aqueous Ag/AgCl reference electrode. The mixture of acetonitrile and CH_2Cl_2 (1 : 1, v/v) was used as solvent, and $0.1\,mol\,L^{-1}$ tetrabutylammonium perchlorate was used as the supporting electrolyte.

2.2. *Synthesis of phenylferrocene (1)*

Phenylferrocene (**1**) was synthesized by reaction of ferrocene and aniline diazonium salt described by Broadhead and Pauson [16]. m.p.: 107–109°C (dec); Anal. Calcd for $C_{16}H_{14}Fe$ (%): C, 73.31; H, 5.38. Found: C, 73.34; H, 6.04. IR (KBr disk, cm^{-1}): $\gamma_{C\text{–}H}$: 816 (vs, ferrocene), $\nu_{C\text{–}H}$: 3089 (vs, ferrocene) $\nu_{C=C}$: 1505, 1598 (benzene). ^1H NMR (500 MHz, $CDCl_3$): δ 4.03–4.64 (9H, unsubstituted Cp and substituted Cp of ferrocenyl group), δ 7.17–7.20 (m, 1H, 4-H of benzene ring), 7.25–7.30 (m, 2H, 3,5-2H of benzene ring), 7.47–7.49 (m, 2H, 2,6-2H of benzene ring); ^{13}C NMR (125 MHz, $CDCl_3$): δ 66.6, 69.0, 69.7, 71.1, 85.6 (ferrocenyl carbon atoms), 126.1, 126.3, 128.4, 139.3 (benzene carbon atoms); MS (ESI, *m*/*z*): 262.3 (M^+). The crystallographic data and parameters of **1** could be found in work reported by Fan [17].

2.3. *Synthesis of ferrocenylbenzene tricarbonylchromium (2)*

A modified procedure affords **2** according to the literature [18]. A mixture of **1** (65 mg, 0.25 mmol) and $Cr(CO)_6$ (130 mg, 0.65 mmol) in 1,4-dioxane (6 mL) and diethylene glycol dimethyl ether (3 mL) was refluxed for 12 h at 110°C under argon. After cooling to room temperature, the solvent was removed under vacuum and the residue was subjected to chromatography on silica gel, and elution with hexane/CH_2Cl_2 (4 : 1, v/v), giving an orange red solid (62 mg). Orange red plate crystal was obtained by recrystallizing from hexane–CH_2Cl_2. Yield 58.9%; m.p.: 175–177°C (dec); Anal. Calcd for $C_{19}H_{14}CrFeO_3$ (%): C, 57.32; H, 3.54. Found: C, 57.55; H, 3.13. IR (KBr disk, cm^{-1}): $\nu_{C=O}$: 1859(vs), 1945(vs), $\gamma_{C\text{–}H}$: 804 (vs, ferrocene), $\nu_{C\text{–}H}$: 2957 (vs, ferrocene), $\nu_{C=C}$: 1478, 1536 (benzene). ^1H NMR (500 MHz, $CDCl_3$): δ 4.12–4.52 (9H, ferrocenyl-H), δ 5.22 (t, $J = 6.5$, 1H, benzene C-H), δ 5.43–5.52 (m, 4H, benzene C–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 67.0, 69.7, 69.9, 69.9, 81.5 (ferrocenyl carbon atoms), 90.1, 90.4, 93.4, 111.4 (benzene carbon atoms), 233.5 (CO).

Benzenechromium tricarbonyl (**3**) was prepared in a similar synthetic method of **2**. NMR data for **3** are: ^1H NMR (500 MHz, $CDCl_3$): δ 5.33 (benzene C–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 232.8 (CO), 92.7 (benzene carbon). Other analytical data could be found in work reported by our research group [8].

3. Results and discussion

3.1. *The unusual NMR spectra of 2 and 3*

It can be concluded through NMR data that the chemical shifts of **2** and **3** are shifted upfield compared to that of **1** and benzene. Benzene produces magnetic anisotropy [8] with protons of benzene deshielded, appearing at low field. Therefore, NMR chemical shifts of the protons and carbon atoms in the benzene of **1** and benzene are observed between 7.17 ppm and 7.49 ppm or between 126.05 ppm and 139.30 ppm [19].

However, protons of benzene in **2** and **3** resonate at higher fields (*ca* 2 ppm) than that of **1** and benzene. The difference in molecular suggests that the electron withdrawing $Cr(CO)_3$ causes the upfield chemical shifts. The $Cr(CO)_3$ accepts electron density from the arene π-orbitals in **2** and **3** [4, 20], which could be found by measuring the electrochemical properties of the ferrocenyl groups (increased oxidation potential of ferrocenyl).

3.2. *Crystal structures of 1 and 2*

The molecular structure of **2** has been established by single-crystal X-ray diffraction. The crystallographic data and parameters for structure refinements are given in table 1. Selected bond lengths for **1** and **2** are listed in table 2. The molecular structure of **2** is shown in figure 1.

The six C–C bond lengths of the benzene ring in **2** range from 1.415 to 1.378 Å, longer than in **1**, showing significant expansion of the aromatic ring upon $Cr(CO)_3$ coordination. Therefore, the conjugative effect of the benzene ring in **2** decreased, and then the ring current density of the benzene ring was reduced. The dihedral angles

Table 1. Crystal data and structure refinement for **2**.

Empirical formula	$C_{19}H_{14}CrFeO_3$
Formula weight	398.15
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions (Å)	
a	6.475(18)
b	13.404(4)
c	9.949(3)
Volume (Å^3)	825.6(4)
Absorption coefficient (nm^{-1})	1.549
θ range for data collection (°)	2.6–26.8
Calculated density (mg mm^{-3})	1.602
F(000)	404
Goodness-of-fit on F^2	1.018
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0274$, $wR_2 = 0.0640$
Largest difference peak and hole (e Å^{-3})	0.18, −0.37

Table 2. Selected bond lengths (Å) for **1** and **2**.

Bond lengths (Å) for **1**[a]				Bond lengths (Å) for **2**			
C11–C12	1.387(5)	C14–C15	1.361(7)	C11–C12	1.415(4)	C15–C14	1.378(5)
C12–C13	1.397(6)	C15–C16	1.361(6)	C12–C13	1.401(4)	C15–C16	1.406(4)
C13–C14	1.367(7)	C11–C16	1.387(5)	C14–C13	1.408(5)	C11–C16	1.408(4)

[a] Data from reference [17].

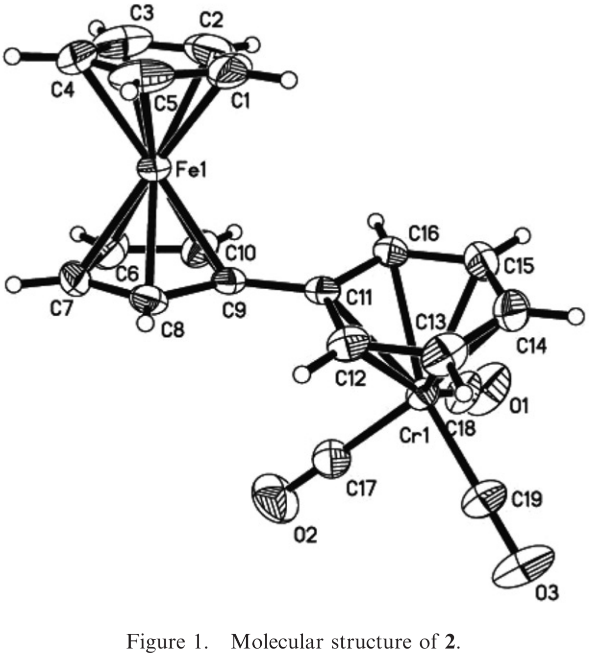

Figure 1. Molecular structure of **2**.

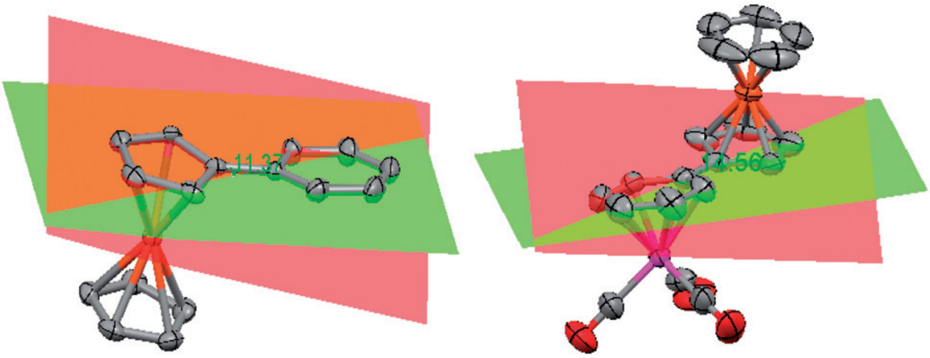

Figure 2. The dihedral angles between Cp and benzene rings of **1** and **2**.

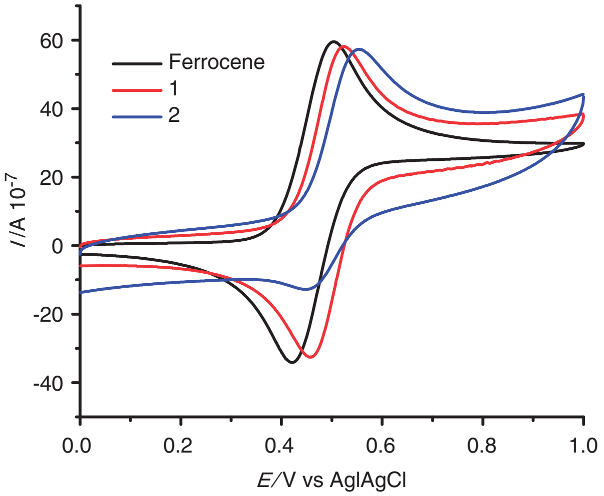

Figure 3. The cyclic voltammetry of ferrocene, **1** and **2**.

between Cp ring and benzene ring change only slightly from 11.37° (**1**) to 14.56° (**2**) (figure 2), indicating that the dihedral angles have little influence on the NMR spectra of the benzene ring. From the molecular structures of **1** and **2**, we conclude that $Cr(CO)_3$ would produce a large influence on the electron density of benzene, which can also be identified by electrochemistry. Thus, the upfield shift of the NMR spectra of **2** is also reflected in the changes of molecular structures.

3.3. *Electrochemical properties of 1, 2, and p-ferrocenylaniline*

Changes of the electron density of the benzene ring in **1**, **2**, and p-ferrocenylaniline can be detected by the oxidation potentials of the ferrocenyl unit. The redox processes of ferrocene, **1** and **2** determined by cyclic voltammetry are depicted in figure 3. The oxidation potentials of the ferrocenyl unit of ferrocene, **1** and **2** were 0.508, 0.525, and 0.553 V (table 3), respectively. The oxidation potential difference between **1** and

Table 3. The redox potentials of ferrocene, **1**, and **2**.

Compound	Ferrocene	**1**	**2**
Oxidation potential (V)	0.508	0.525	0.553
Reduction potential (V)	0.421	0.456	0.448

ferrocene was 0.017 V, indicating electronic interactions between Ph unit and the ferrocenyl unit. Ph acted as an electron-withdrawing group to increase the oxidation potential of the ferrocenyl unit in **1** [14]. Comparing oxidation potentials of the ferrocenyl units of **1** and **2** shows $Cr(CO)_3(\eta^6\text{-Ph})$ increased the oxidation potential. The electron-withdrawing effect of $Cr(CO)_3(\eta^6\text{-Ph})$ was stronger than that of Ph, proving that $Cr(CO)_3$ coordinated to ferrocenylbenzene could reduce the electron density of the benzene ring and then decrease the magnetic anisotropy shifting the benzene ring in **2** upfield compared to **1**. Electron-donating groups (amino group) on benzene could increase the electron density of the benzene ring [21]. It is clear from our results that the oxidation of the ferrocenyl unit would shift to lower potential compared with **1**. From the literature [22] p-ferrocenylaniline has an oxidation wave at 0.409 V, lower than the oxidation potential of ferrocene (0.473 V). Thus increase or decrease in oxidation potential of ferrocene connected to benzene would be an indicator for the reduction or addition of electron density of the benzene ring.

4. Conclusions

Phenylferrocene (**1**) and ferrocenylbenzene tricarbonylchromium (**2**) have been synthesized and characterized. Ferrocene was used as a probe to detect the electron density of the benzene rings in **1**, **2**, and p-ferrocenylaniline by electrochemistry. The molecular structures and electrochemical properties of **1** and **2** indicate that the magnetic anisotropy effect of the benzene ring decreases by reducing the electron density of the benzene ring after $Cr(CO)_3$ coordination with **1**, making the NMR chemical shifts of **2** upfield compared to that of **1**. Larger electron density of the benzene ring in p-ferrocenylaniline than in **1** was indicated by the oxidation potential. Thus, ferrocene could be used as an electrochemical probe to predict the electron density of a benzene ring.

Supplementary material

Crystallographic data for the structural analysis has been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 852819 for **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 21 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk). ^1H, ^{13}C-NMR spectra of **1** and **2** are provided in supplementary online material.

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