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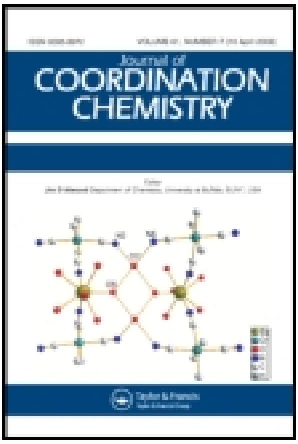

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Synthesis, structure, and NMR spectra of a new ferrocenylbenzene tricarbonylchromium complex

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Synthesis, structure, and NMR spectra of a new ferrocenylbenzene tricarbonylchromium complex

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Complex **1** (1,2,4-triferrocenylbenzene tricarbonylchromium), possessing four heterometals, has been synthesized efficiently by a new method in one pot. Through detailed study on the NMR chemical shifts of **1** and the ligand **2**, the NMR chemical shifts of **1** shift upfield from those of **2**. The NMR spectra of **1** have reduced magnetic anisotropy of benzene after $Cr(CO)_3$ coordination with **2**. The ferrocenyl groups have electron donating effect on the central benzene ring of **1**.

Keywords: Synthesis; NMR spectra; Ferrocenylbenzene tricarbonylchromium complex; Ring current

1. Introduction

Multi-ferrocenyl compounds have received considerable attention due to their redox reactions, detectable intervalence charge transfer (IVCT), electron transfer processes [1–4] and their potential applications in the molecular electronic devices [5–7]. Synthesis and electrochemistry of multi-ferrocenyl substituted benzenes have received attention. For example, Patoux [8] reported synthesis and intermolecular electron transfer of diferrocenylbenzenes; Yu [9] reported the synthesis and electrochemical properties of 1,3,5-triferrocenylbenzene. Studies on the influence of the structure on NMR spectra of metal complexes provide additional impetus for pursuit of new benzene-metal complexes. Simion [10] studied NMR spectral changes of benzenes coordinated to transition metals. Therefore, a new organometallic complex (1,2,4-triferrocenylbenzene tricarbonylchromium), with four metals, was synthesized by a new method based on our previous study [11]. The relationship between the molecular structure and NMR chemical shifts has been studied in detail. Electron donation of the ferrocenyl to the benzene occurs in this complex.

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2. Experimental

2.1. *General procedure*

All reactions and manipulations were carried out under argon using standard Schlenk line techniques. All solvents were dried and deoxygenated prior to use according to standard procedures. Reactions were monitored by thin layer chromatography (TLC). Chromatographic separations and purification were performed on 200–300 mesh silica gel. $Co_2(CO)_8$ and $Cr(CO)_6$ were purchased from Aldrich and used as received. Ferrocenyl acetylene and 1,2,4-triferrocenylbenzene were prepared according to the reported methods [11, 12].

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. ^1H and ^{13}C NMR spectra in $CDCl_3$ were recorded on Inova or Bruker 500 MHz NMR spectrometers and referenced to residual protonic solvent or TMS. Mass spectra were determined using a Micromass LCT instrument. The crystal structure of **1** was measured on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo-Kα (0.71073 Å) radiation. Data were collected at 20°C using the f and w scan techniques. The structure was solved by direct methods and expanded using Fourier technique. An absorption correction based on SADABS was applied. The structure solution and refinement were performed by SHELXSL 97.

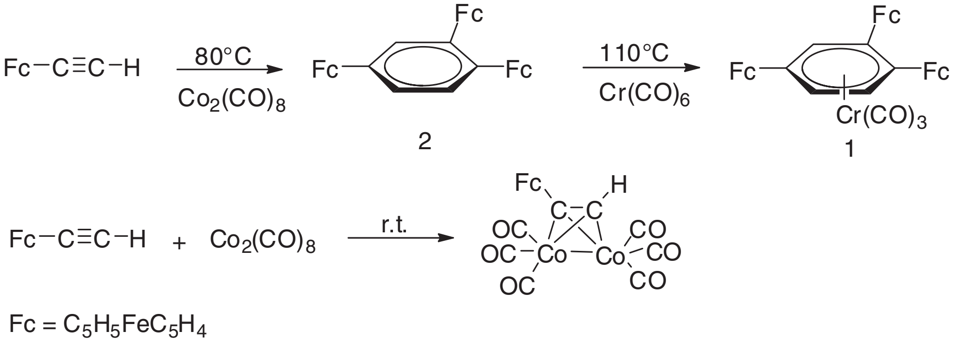
2.2. *Synthesis of 1,2,4-triferrocenylbenzene tricarbonylchromium*

A mixture of ferrocenyl acetylene (170 mg, 0.81 mmol) and $Co_2(CO)_8$ (90 mg, 0.26 mmol) in 1,4-dioxane (20 mL) and diethylene glycol dimethyl ether (5 mL) was stirred at 80°C under argon. After the ferrocenyl acetylene was completely consumed as determined by TLC, $Cr(CO)_6$ (80 mg, 0.36 mmol) was added and the reaction solution was refluxed for 24 h at 110°C. After removal of solvent under vacuum, the residue was subjected to chromatography on silica gel, and elution with hexane/CH_2Cl_2 (3 : 1, v/v) gave an orange red solid (63 mg). Orange red plate crystals were obtained by recrystallizing from hexane-CH_2Cl_2. Yield 30%; m.p.: 226–227°C (dec); Anal. Calcd for $C_{39}H_{30}CrFe_3O_3$ (%): C, 61.14; H, 3.95. Found: C, 61.48; H, 3.72%. IR (KBr disc, cm^{-1}): $\nu_{C=O}$: 1857(vs), 1945(vs), $\nu_{C=C}$: 1490, 1550. ^1H NMR (500 MHz, $CDCl_3$): δ 3.88–4.64 (27H, ferrocenyl-H), 5.62, 6.12, 6.20 (3H, benzene C–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 66.8–72.3, 81.6, 84.6, 85.2 (ferrocenyl carbons), 89.0, 94.0, 96.6, 108.1, 109.4, 111.4 (aromatic carbons), 234.2 (CO); HRMS (ESI) Calcd for $C_{39}H_{30}CrFe_3O_3$ $[M]^+$: 765.9648; Found: 765.9643.

NMR data for 1,2,4-triferrocenylbenzene (ligand **2**) are: ^1H NMR (500 MHz, $CDCl_3$): δ 4.03–4.75 (27H, ferrocenyl-H), 7.36 (dd, $J = 8.0$, 1.0, 1H, benzene C–H), 7.66 (d, $J = 8.0$, 1H, benzene C–H), 7.89 (d, $J = 1.0$, 1H, benzene C–H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 66.3–70.8, 85.4, 87.5, 88.1 (ferrocenyl carbons), 123.6, 128.9, 131.2, 135.0, 136.1, 136.9 (aromatic carbons); other analysis data can be found in reference reported by our research group [11].

2.3. *Synthesis of benzenechromium tricarbonyl*

A mixture of $Cr(CO)_6$ (93 mg, 0.42 mmol) in benzene (2 mL), 1,4-dioxane (3 mL) and diethylene glycol dimethyl ether (2 mL) was refluxed for 10 h at 110°C under argon.



Scheme 1. The synthetic processes of **1**.

After removal of the solvent under vacuum, the residue was subjected to chromatography on silica gel, and elution with hexane/CH_2Cl_2 (10 : 1, v/v) gave an orange solid (32.8 mg). Yield 37.5%; m.p.: 152–154°C (dec); Anal. Calcd for $C_9H_6CrO_3$ (%): C, 50.48; H, 2.82. Found: C, 50.17; H, 2.96. IR (KBr disc, cm^{-1}): $\nu_{C=O}$: 1964(vs), 1855(vs). ^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).

3. Results and discussion

Complex **1** was efficiently synthesized in one pot by the reaction of ferrocenyl acetylene with $Co_2(CO)_8$ and then with $Cr(CO)_6$ (scheme 1). However, different reaction conditions could produce different products. The target intermediate **2** could be obtained only at 80°C or higher [11], otherwise only [$Co_2(CO)_6(\mu_2,\eta_2$-ferrocenylacetylene)] could be produced at room temperature by the reaction of ferrocenyl acetylene with $Co_2(CO)_8$ (scheme 1) [12, 13]. This suggests that $Co_2(CO)_6(\mu_2,\eta_2$-ferrocenylacetylene) reacts with acetylene at higher temperature to produce the cyclic compound. The $Co_2(CO)_8$ could also directly make ferrocenyl acetylene cyclize to form the ferrocenylbenzene; the mechanism was proposed in the literature [11, 14]. The desired complex **1** could be achieved in one pot after addition of $Cr(CO)_6$ without purification of the intermediate ferrocenylbenzene **2**. The successful synthesis of **1** was confirmed by elemental analysis, IR, ^1H, ^{13}C NMR, and MS. The molecular structure of **1** was further determined using X-ray single crystal diffraction. To assess the effect of the ferrocenyls on **1**, (benzene)$Cr(CO)_3$ was synthesized by reaction of benzene and $Cr(CO)_6$ and determined by elemental analysis, IR, ^1H, and ^{13}C NMR.

3.1. *Crystal molecular structure of 1,2,4-triferrocenylbenzene tricarbonylchromium (1)*

The molecular structure of **1** has been established by single-crystal X-ray diffraction. The crystallographic data and parameters for structure refinements are given in table 1;

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

Molecular formula	$C_{39}H_{30}CrFe_3O_3$	Absorption coefficient (nm^{-1})	1.720
Molecular weight	766.18	θ range for data collection (°)	1.83–26.00
Crystal system	Monoclinic	Calculated density ($Mg\,m^{-3}$)	1.607
Space group	*P21/c*	*F* (000)	1560
Unit cell dimensions (Å)			
a	11.152(4)	Goodness-of-fit on F^2	0.700
b	12.884(4)	Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0374$, $wR_2 = 0.0576$
c	22.557(7)	Largest difference peak and hole (e $Å^{-3}$)	0.495 and −0.297
Volume ($Å^3$)	3166.3(18)		

Table 2. Selected corresponding bond lengths (Å) of benzene ring for **1** and **2**.

1				**2**[a]			
C4–C5	1.404(4)	C7–C8	1.403(4)	C1–C2	1.385(3)	C4–C5	1.386(4)
C5–C6	1.426(3)	C8–C9	1.385(4)	C2–C3	1.398(3)	C5–C6	1.368(4)
C6–C7	1.404(4)	C4–C9	1.417(4)	C3–C4	1.383(3)	C1–C6	1.407(3)

[a] Data from ref. [11].

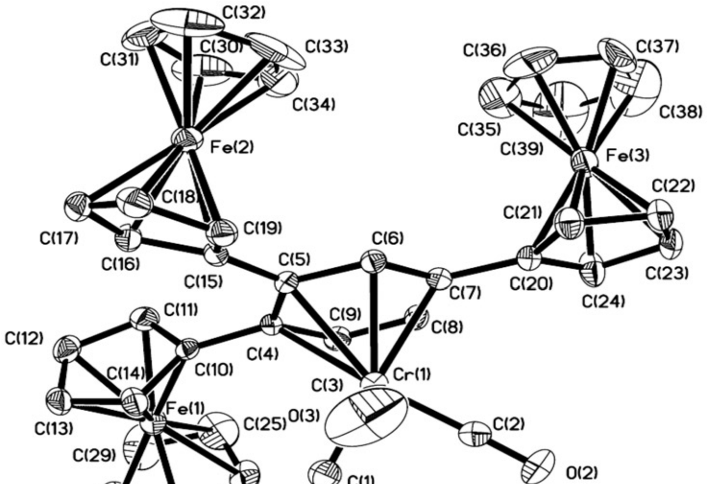


Figure 1. Molecular structure of **1**.

selected bond lengths are listed in table 2. The molecular structure of **1** is shown in figure 1.

The bond lengths of benzene ring in **1** are longer than those in **2**, showing significant expansion of the benzene ring coordinated to $Cr(CO)_3$. Therefore, the π–π resonance or π electron delocalization of the benzene ring in **1** decreases and the ring current

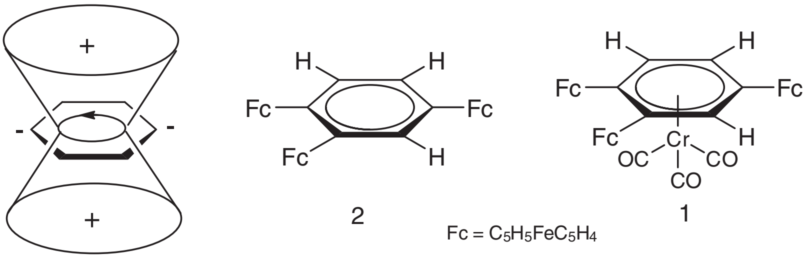


Figure 2. Shielding (+) and deshielding (−) zones of benzene ring.

of benzene was reduced. Thus the NMR chemical shifts of benzene in **1** shift upfield compared to **2**.

3.2. *The NMR spectra of 1*

Before the unusual NMR spectra of **1** are discussed, the magnetic anisotropy of benzene should be well-known. The ring current of benzene produces large deshielding zones (−) and shielding zones (+) (figure 2). When the protons or carbons lie within the deshielding zone, the NMR chemical shifts are downfield and within the shielding region the NMR chemical shifts are observed upfield [15, 16]. Therefore, NMR chemical shifts of the protons and carbons in the benzene ring of **2** are observed between 7.36 and 7.89 ppm or between 123.631 and 136.85 ppm.

However, the characteristic feature of the ^{1}H-NMR chemical shifts of **1** is that the protons of benzene resonate at significantly higher (*ca.* 2 ppm) fields than those of **2**, which indicates that $Cr(CO)_3$ makes this upfield shift. In ^{1}H-NMR, coordination to $Cr(CO)_3$ produces a large upfield shift in the ^{13}C-NMR spectra of **1**, showing the electron withdrawing effect after $Cr(CO)_3$ coordinates to ferrocenylbenzene. The transfer of electron density from the arene π-orbitals to 3-D-orbitals of chromium in **1** quench or decrease the ring current of benzene ring, reducing the magnetic anisotropy effect of benzene ring [10, 17]. Thus the NMR chemical shifts of benzene in **1** shift upfield (figure 2). This is also observed in benzenechromium tricarbonyl.

The carbons of the ferrocenyl groups connected to benzene resonate at 81.62, 84.56, 85.21 in the ^{13}C-NMR spectra of **1** and the corresponding carbons of **2** resonate at 85.42, 87.52, 88.09, but no substituted ferrocene resonate at 67.88 [18], indicating that the carbons in the ferrocenyl groups connected to benzene ring also shift upfield from **2**. The upfield shift of carbons in the ferrocenyl groups connected to benzene indicate that $Cr(CO)_3$ coordinated to ferrocenylbenzene could reduce the ring current of benzene and decrease the magnetic anisotropy.

The hydrogens of benzenechromium tricarbonyl resonate at 5.33 and the corresponding hydrogens of **1** resonate at 5.62, 6.12, 6.20, showing the ferrocenyl groups have electron-donating effect on the benzene of **1**. The larger electron density of benzene ring on **1** produced by ferrocenyl groups could increase the ring current of the central benzene and enhance the magnetic anisotropy effect, making the chemical shifts of the benzene ring on **1** downfield slightly from those of benzenechromium tricarbonyl.

4. Conclusion

An organometallic complex (1,2,4-triferrocenylbenzene tricarbonylchromium) has been synthesized efficiently in one pot. The NMR chemical shifts of **1** are shifted upfield from those of **2**, produced by reducing the magnetic anisotropy effect of benzene caused by reducing the ring current after $Cr(CO)_3$ coordination with **2**. The ferrocenyl groups have electron-donating effect on the central benzene of **1**, making the benzene ring shift downfield slightly from benzenechromium tricarbonyl.

Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 813066. 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). ^{1}H, ^{13}C-NMR spectra of **1**, **2** and benzenechromium tricarbonyl are provided in supplementary online material.

Acknowledgments

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