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Synthesis of the first 1,3-disubstituted 1,3-butadienyl heteroannular bridged [4]ferrocenophane

Kai-Qiang Wu^a, Li-Li Xie^a, Yong-Fan Zhang^a, Feng-Bo Xu^b, Yao-Feng Yuan^{a,b,c,*}

^a Department of Chemistry, Fuzhou University, Qi Shan Campus, 2 Xue Yuan Road, Fuzhou, Fujian 350108, China

^b State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

^c State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

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ABSTRACT

An unusual heteroannular cyclization of methyl 4-(((1'-(trimethylsilyl)ethynyl)ferrocenyl)ethynyl)benzoate (**11**) under the basic desilylation condition yielded 1,1'-(1-methoxy-3-(4'-(methoxycarbonyl) phenyl)-1,3-butadienylene)ferrocene (**7**), the first reported <math>1,3-disubstituted 1,3-butadienyl heteroannular bridged [4]ferrocenophane. Compound **7** has been characterized by elemental analysis, IR spectra, ¹H NMR spectroscopy and X-ray diffraction analysis. The electrochemical behavior has been investigated by cyclic voltammetry. The DFT calculation results of **7** are also reported.

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1. Introduction

Ferrocenophanes have attracted great attention due to their unique structures and properties, as well as their potential applications in the preparation of organometallic polymers [1–10]. Strained ferrocenophanes are one of the most important classes of such compounds which have been used in the preparation of high molecular weight polymers via ring-opening polymerization (ROP) [11–16] or ring-opening metathesis polymerization (ROMP) [17–21] with different monomers.

The ROMP products containing π -conjugated organic spacers are of particular interest because of their promising electronic, optical, and magnetic properties afforded by potential interactions of the iron centers through the π -network.

A pioneering study performed by Grubbs and co-workers showed that the ROMP of 1,3-butadiene heteroannular bridged [4]ferrocenophanes 1,4-(1,1'-ferrocenediyl)-1,3-butadiene (1) and 1,4-(1,1'-ferrocenediyl)-1-methoxy-1,3-butadiene (2) (Chart 1) produced polymers with poor solubility and low molecular weight [21].

In recent years, great efforts have been made to enhance the solubility of the conjugated polymers. Lee et al. conducted several structural modifications [22–24] on the 1,3-butadienyl bridging unit of the parent compound **2**, first synthesized by Pudelski and Callstrom

* Corresponding author. Department of Chemistry, Fuzhou University, Qi Shan Campus, 2 Xue Yuan Road, Fuzhou, Fujian 350108, China. Tel./fax: +86 591 2286 6161. *E-mail address:* yaofeng_yuan@fzu.edu.cn (Y.-F. Yuan). through a heteroannular cyclization reaction under basic condition (aqueous KOH in methanol) [25,26]. All of the resulting [4]ferrocenophanes were "1-monosubstituted", bearing an alkyl (*t*-butyl) [22,23] or aryl (phenyl or mesityl) [24] group at the 1-position of the 1,3-butadienyl bridging unit (see **3**, **4** and **5** in Chart 1). ROMP of these monomers afforded soluble polymeric materials with high molecular weight. Unfortunately, the conductivities upon doping remained relatively low, merely on the order of 10^{-5} S cm⁻¹.

More recently, Butenschön et al. reported the transannular addition of phenols to 1,1'-dialkynylferrocenes under acidic alkyne metathesis condition, leading to the isolation of a series of "1,2,3-trisubstituted" phenoxy[4]ferrocenophanedienes (**6**) (Chart 1) [27]. The ROMP of these [4]ferrocenophanes were not examined.

To the best of our knowledge, "disubstituted" 1,3-butadienyl heteroannular bridged [4]ferrocenophane has not previously been reported. We are interested in developing an easily adaptable synthetic route to "disubstituted" 1,3-butadienyl heteroannular bridged [4]ferrocenophanes with donor or acceptor group attached to the butadienyl bridging unit, which upon ROMP may provide π -conjugated organometallic polymers with novel optoelectronic properties.

In this contribution, we present the synthesis, electrochemistry and theoretical calculation results of the first "1,3-disubstituted" 1,3-butadienyl heteroannular bridged [4]ferrocenophane 1,1'-(1methoxy-3-(4'-(methoxycarbonyl)phenyl)-1,3-butadienylene)ferrocene (7) (Scheme 1), an unexpected species obtained during our preparation of alkynyl-bridged multiferrocenyl molecular wires. Compound 7 was formed through an intramolecular heteroannular

⁰⁰²²⁻³²⁸X/\$ – see front matter @ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.jorganchem.2010.12.032



Chart 1.

cyclization reaction when the desilylation reaction of the (trimethylsilyl)ethynyl substituted ferrocene derivative was conducted under a basic condition. X-ray crystallographic analysis provided further confirmation of the structure of **7**.

2. Results and discussion

As shown in Scheme 1, the Sonogashira coupling reaction [28,29] between 1-ethynyl-1'-iodoferrocene (**8**) and methyl 4-iodobenzoate (**9**) catalyzed by 1 mol% of Pd(Ph₃P)₂Cl₂ and 2 mol% Cul in THF/diisopropylamine gives **10** in 78% yield after column chromatographic purification over silica gel. **8** is used in excess to ensure the complete consumption of **9**, and consequently simplifies the purification process. In a similar fashion, the coupling reaction of **10** and excess trimethylsilylacetylene gives **11** in 56% yield after column chromatography.

Treatment of a deoxygenated solution of **11** in methanol/diethyl ether with potassium carbonate at room temperature [30,31] was expected to vield a terminal ferrocenvl alkyne for further framework extension. However, in contrast to our expectation, the reaction affords air and moisture stable compound 7 as the only detectable product in 66% isolated yield. We note a recent publication of Sita et al. describing the frustrating desilylation outcome of (trimethylsilyl)ethynyl ferrocene derivative 12, the reaction mixture had not been separated and characterized because of its complexity [32]. Therefore, terminal alkyne with a skeleton like 13 depicted in Chart 2 is difficult to synthesize via conventional desilylation of its trimethylsilyl-protected precursor [25,26,32]. In addition, it is worthwhile to mention that steric hindrance may stabilize the terminal alkyne as it cumbered the approach of the two 1,1'-alkynyl portions and subsequent cyclization to afford ferrocenophanes. Two examples formerly reported are shown in Chart 2 (14 and 15, both bearing bulky groups) [33,34].

A possible reaction pathway for the formation of **7** is illustrated in Scheme 2 [25,26]. Desilylation of **11** generates ferrocenyl alkyne **16** as intermediate, which subsequently suffers methoxide attack at an ethynyl carbon α to the Cp ring followed by intramolecular cyclization onto the β -carbon of the ethynyl group on the opposing Cp ring. Proton abstraction from methanol gives **7** and regenerates methoxide ion.







Adopting the synthetic route illustrated in Scheme 1, many structural analogs of **7** can be prepared by changing the haloarene coupling partner of **8** in the first step. Moreover, taking advantage of the vinyl ether group, further transformation of those [4]ferrocenophanes would be convenient as previously reported in detail by others [22-24].

Single crystals of **7** suitable for X-ray diffraction studies were obtained by slow diffusion of hexane into its CH₂Cl₂ solution. Fig. 1 shows the molecular structure of **7** [35].

The cyclopentadienyl (Cp) rings are planar to ± 0.009 Å. C–C bond lengths for the two Cp rings fall in a range from 1.398 Å to 1.435 Å. The Cp rings are staggered as indicated by a mean twist angle of 30.37° found for torsion angle of type C(n)-RC(1)-RC(2)-C(11-n) (for the definition of RC(1) and RC(2), see the caption of Fig. 1). The Fe1-RC(1) and Fe1-RC(2) distances are 1.6337(4) and 1.6370(4) Å, respectively, both slightly shorter than the distance found in ferrocene [36-38]. The lengths of C-C single bond connecting unsaturated groups (C6-C11, C1-C14, C12-C13, C12-C16, C19-C22) are all very close to the standard value of a simple sp^2-sp^2 C–C single bond (1.48 Å). The dihedral angle between the benzene ring and the ethylenic plane defined by the phenylsubstituted C=C double bond is about 39.97°. The benzene ring is nearly perpendicular to the Cp rings, as shown by the dihedral angles between the benzene ring and the two Cp rings, 84.82(18)° for Cp(1) ring and $80.7(2)^{\circ}$ for Cp(2) ring.

The 1,3-butadienyl heteroannular bridge imposes ring tilt in **7**, as manifested by the dihedral angle between the Cp rings of 10.8 $(2)^{\circ}$. Comparison of Fe1–ring-carbon distances shows that the Cp rings separation is smallest at the heteroannular bridge. Bond angle distortion of the 1,3-butadienyl bridging unit is listed in the caption of Fig. 1 (four C–C–C bond angles consist of C1, C6, C11, C12, C13, C14). An average bond angle of about 129° indicates a considerable expansion from the ideal sp²-hybridized angle of 120°. Twist in the heteroannular bridge is revealed by analysis of the torsional angle data. While torsional angles of C1–C14–C13–C12 and C13–C12–C11–C6 are nearly negligible, **7** exhibits a considerable C14–C13–C12–C11 torsional angle $(-44.2(5)^{\circ})$, hence the carbon chain connecting the Cp rings is helically distorted [27].

The Cp ring tilt angle and bond angle distortion in the heteroannular bridge have been suggested to be indications of strain in ferrocenophanes [39]. These two structure features of **7** as described above are similar to **2**, **4** and **5** [24,26], thus the strain is reserved after the introduction of 4'-(methoxycarbonyl)phenyl, making **7** a promising candidate for ROMP.



Scheme 2. Proposed mechanism of the heteroannular cyclization reaction.



Fig. 1. ORTEP view of 7 (50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å), bond angles (deg) and torsional angles (deg): Fe1-C1 = 2.000(3), Fe1-C6 = 2.013(3), C6-C11 = 1.466(5), C11-C12 = 1.338(4), C12-C13 = 1.477(4), C13-C14 = 1.339(4), C1-C14 = 1.478(4), C12-C16 = 1.491(4), C19-C22 = 1.480(5), O1-C14 = 1.372(4); RC(1)-Fe1-RC(2) = 172.85(9), C6-C11-C12 = 128.4(3), C11-C12-C13 = 128.1(3), C11-C12-C16 = 119.4(3), C12-C13-C14 = 131.4(3), C13-C14-C1 = 128.4(3); C6-C11-C12-C13 = -0.8 (5),C11-C12-C13-C14 = -44.2(5),C12-C13-C14-C1 = 2.8(5); RC(1) and RC(2) denote the centroids of Cp(1) rings (atoms C1 to C5) and Cp(2) rings (atoms C6 to C10), respectively.

The electrochemistry of 1 mM solutions of **7** and ferrocene in acetonitrile was studied. Tetrabutylammonium hexafluorophosphate was used as the electrolyte in these experiments in which the data were collected at various scan rates.

The electrochemistry of **7** was substantially irreversible between 0.00 and +0.80 V, unlike most of the 1-monosubstituted 1,3-butadienyl heteroannular bridged [4]ferrocenophanes. Cyclic voltammogram of **7** obtained at a scan rate of 10 mV s⁻¹ shows a similar feature to the unsubstituted [4]ferrocenophanes **1** [21]. The cathodic peak current diminished relative to the anodic peak current (Fig. 2). As the scan rate increased, the reduction peak became more significant. The lower amount of reduction current is likely due to the instability of the oxidized form of **7** in acetonitrile solvent.

The $E_{1/2}$ value of **7** was determined to be 0.57 V vs Ag/AgCl electrode from data collected at a scan rate of 200 mV s⁻¹ with peak-to-peak separation of 95 mV, although a ratio of cathodic peak current to anodic peak current of only 0.5 was measured at this scan rate (Fig. 2). Compared with ferrocene ($E_{1/2} = 0.44$ V), a $\Delta E_{1/2}$ value of 130 mV for **7** was obtained, significantly larger than that of **2** (90 mV) [26].



Fig. 2. Cyclic voltammograms of 1 mM solutions of **7** in 0.10 M tetrabutylammonium hexafluorophosphate in acetonitrile recorded at different scan rates using a glassy carbon working electrode.



Fig. 3. Diagrams of the surfaces and energies of HOMO and LUMO for 2 and 7.

Density functional theory (DFT) calculations of **2** and **7** have been carried out to gain a deeper insight into their electronic properties. **2** was chosen for comparison because of its similarity in structure with **7**. The geometric parameters employed in the calculations were based on their crystal structural data. The surfaces of HOMO and LUMO along with the orbital energy for each level are depicted in Fig. 3.

The HOMOs of both **2** and **7** involve π orbitals localized on the 1,3-butadienyl bridging unit with significant contribution from iron. The LUMO is dominated by the π^* orbitals of, for **2**, the 1,3butadienyl bridging unit with little contribution from iron, while for **7**, the 4'-(methoxycarbonyl)phenyl group and the C=C double bond it attached to. Compared with 2, the incorporation of 4'-(methoxycarbonyl)phenyl group in 7 lowers the energy levels of the frontier molecular orbitals (FMOs), especially the LUMO. Therefore, the band gap between FMOs (4.22 eV for 2 and 3.65 eV for **7**) is reduced, probably due to the extension of conjugation. The difference of Mulliken atomic charges of iron in 2 and 7 (0.958 and 0.954, respectively) is negligible, however, cyclic voltammetric experiments revealed a modest potential difference of 40 mV (vide supra). The discrepancy between experimental deductions and calculation results is believed to be a reflection of the environmental variation of practical electrochemical measurement.

3. Conclusions

We have discovered a heteroannular cyclization reaction of methyl 4-(((1'-(trimethylsilyl)ethynyl)ferrocenyl)ethynyl)benzoate (**11**) that leads to the formation of novel 1,3-disubstituted 1,3-butadienyl heteroannular bridged [4]ferrocenophane **7**. X-ray crystal structure study revealed modest strain in **7**. Further studies of the cyclization reaction, including the extension of the reaction to prepare analogous [4]ferrocenophanes, as well as the synthetic transformation and ROMP of the resulting [4]ferrocenophanes, are currently in progress.

4. Experimental

4.1. General

All manipulations involving air-sensitive materials were carried out by using standard Schlenk techniques under an atmosphere of nitrogen. Chromatography was performed on silica gel (100–200 mesh). $Pd(Ph_3P)_2Cl_2$ was purchased from Acros and used as received. Solvents were dried by standard methods and distilled under nitrogen before use. **8** [40] and **9** [41] were prepared according to literature procedures.

¹H NMR spectra were recorded in CDCl₃ solutions using a Bruker AVANCE 400 spectrometer. Chemical shifts are given in ppm relative to internal tetramethylsilane. IR spectra were recorded in KBr pellets with a Perkin–Elmer Spectrum 2000 spectrophotometer (4000–400 cm⁻¹). Melting points were determined on a Shenguang WRS-1B apparatus and are uncorrected. Mass spectra (ESI) were obtained from a ThermoFinnigan DECAX-30000 LCQ Deca XP spectrometer. Elemental analysis was performed on an Elementar Vario MICRO instrument. Cyclic voltammetry was performed on a CHI 620C electrochemical analyzer (CH Instruments, Inc.) in a standard three-electrode system. A glassy carbon working electrode was employed in conjunction with an Ag/AgCl (3.0 M KCl) reference electrode and a platinum wire counter electrode. Geometry optimizations were performed at the B3LYP/6-311G(d) DFT level using the Gaussian 03 program [42].

4.2. Methyl 4-((1'-iodoferrocenyl)ethynyl)benzoate (10)

To a deoxygenated solution of 957 mg (2.85 mmol) of **8** and 731 mg (2.79 mmol) of **9** in 25 mL of THF/diisopropylamine (4:1, v/v) solvent mixture was added 20 mg (0.028 mmol) of Pd(Ph₃P)₂Cl₂ and 11 mg (0.058 mmol) of Cul. The resulting mixture was heated at 60 °C for 60 h and then cooled to room temperature. The solvent was removed in vacuo, and the residue was redissolved in CH₂Cl₂ and filtered through a short silica gel column. The crude product was purified by column chromatography. An orange band eluting with 4:1 petroleum ether/CH₂Cl₂ afforded 1023 mg (78%) of **10** as an orange–red oil. IR (KBr) 3441, 2948, 2206, 1720, 1708, 1603, 1435, 1405, 1307, 1275, 1171, 1107, 1016, 811, 767, 694 cm^{-1. 1}H NMR (400 MHz) δ 8.00 (d, *J* = 8.4 Hz, 2H, PhH), 7.56 (d, *J* = 8.4 Hz, 2H, PhH), 4.59–4.25 (m, 8H, CpH), 3.93 (s, 3H, OCH₃). Mass (*m*/z): 472.2 [(*M* + 2)⁺].

4.3. Methyl 4-(((1'-(trimethylsilyl)ethynyl)ferrocenyl)ethynyl) benzoate (11)

To a stirred solution of 198 mg (0.422 mmol) of 10 in 12 mL of THF/ diisopropylamine (1:1, v/v) solvent mixture at 4 °C was added 6 mg (0.008 mmol) of Pd(Ph₃P)₂Cl₂, 3 mg (0.016 mmol) of CuI and 88 mg (0.899 mmol) of trimethylsilylacetylene. The reaction mixture was stirred for a further 30 min at 4 °C and then heated at 50 °C for 36 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was redissolved in CH₂Cl₂ and filtered through a short silica gel column. The crude product was purified by column chromatography using a 5:1 petroleum ether/CH₂Cl₂ solvent system. An orange band eluted which, after removal of solvent in vacuo, afforded 104 mg (56%) of **11** as an orange crystalline solid. mp 138.6-140.0 °C. IR (KBr) 3442, 2953, 2208, 2151, 1717, 1605, 1436, 1406, 1276, 1251, 1176, 1163, 1109, 928, 855, 768, 697 cm⁻¹. ¹H NMR $(400 \text{ MHz}) \delta 7.99 (d, J = 6.8 \text{ Hz}, 2H, PhH), 7.54 (d, J = 6.8 \text{ Hz}, 2H, PhH),$ 4.49 (m, 4H, CpH), 4.29 (m, 4H, CpH), 3.92 (s, 3H, OCH₃), 0.20 (s, 9H, Si (CH₃)₃). Anal. Calcd for C₂₅H₂₄FeO₂Si: C, 68.18; H, 5.49. Found: C, 68.28; H, 5.50. Mass (*m*/*z*): 440.9 [*M*⁺].

4.4. 1,1'-(1-Methoxy-3-(4'-(methoxycarbonyl)phenyl)-1,3-butadienylene)ferrocene (7)

18 mg of **11** (0.04 mmol) was dissolved in 5 mL of methanol/ diethyl ether (3:2, v/v). To this deoxygenated solution was added 17 mg of K_2CO_3 (0.123 mmol), and the mixture was stirred for 24 h at room temperature. The solvents were removed in vacuo, and the mixture was redissolved in CH_2Cl_2 and washed with H_2O . The organic layer was dried over Na₂SO₄. After evaporation of the solvent, the crude product was purified by column chromatography using a 5:1 petroleum ether/CH₂Cl₂ solvent system. The second band was collected and evaporated to give 10 mg (66%) of **7** as an orange—red powder. mp 137.3—139.2 °C. IR (KBr) 3094, 3008, 2950, 2928, 2849, 1713, 1630, 1600, 1462, 1437, 1406, 1310, 1282, 1224, 1202, 1177, 1143, 1106, 1016, 983, 830, 804, 774 cm⁻¹. ¹H NMR (400 MHz) δ 8.04 (d, *J* = 8.4 Hz, 2H, PhH), 7.70 (d, *J* = 8.4 Hz, 2H, PhH), 6.19 (s, 1H, CpCH = CPh), 4.69 (s, 2H, CpH), 4.61 (s, 2H, CpH), 4.31 (s, 2H, CpH), 4.28 (s, 2H, CpH), 3.93 (s, 3H, PhCOOCH₃), 3.81 (s, 1H, CpC (OMe) = CH), 3.49 (s, 3H, CpC(OCH₃)). Anal. Calcd for C₂₃H₂₀FeO₃: C, 69.02; H, 5.04. Found: C, 69.34; H, 5.08. Mass (*m*/*z*): 400.6 [*M*⁺].

4.5. X-ray structure determination

Suitable single crystal of **7** was mounted on glass fiber for X-ray measurement. Data were collected at 293(2) K on a Rigaku Saturn 724 CCD diffractometer with graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) following standard procedures. The structure was solved and refined using the SHELX suite of programs [43].

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Appendix A. Supplementary material

CCDC-770371 contains the supplementary crystallographic data for compound **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

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- [35] Crystal data for **7**: C₂₃H₂₀FeO₃, $\dot{M}_w = 400.24 \text{ g mol}^{-1}$, T = 293(2) K, monoclinic, space group C2/c, a = 37.625(8), $\dot{A}, b = 7.3748(15)$, $\dot{A}, c = 14.197(3)$, $\dot{A}, \beta = 110.86$ (3)°, V = 3681.1(13), \dot{A}^3 , Z = 8, $\rho_{calcd} = 1.444 \text{ g cm}^{-3}$, $\mu = 0.840 \text{ mm}^{-1}$, F (000) = 1664; θ range 3.1–27.5°; reflections, 14784 measured, 4227 independent ($R_{int} = 0.0360$), final R indices [$I > 2\sigma(I)$] $R_1 = 0.0564$, $wR_2 = 0.1500$, R indices (all data) $R_1 = 0.0630$, $wR_2 = 0.1593$. The goodness of fit on F^2 was 1.290.

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