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Synthesis and characterization of ferrocenyl and bis(ferrocenyl) alkynes and polyynes: crystal structure of 1,4-bis(ferrocenyl)butadiyne and third order nonlinear optical properties of 1,8-bis(ferrocenyl)octatetrayne

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Abstract

A simple method, utilizing a coupling reaction between ethynylferrocene and *cis*-1,2-dichloroethylene catalyzed by $Pd(PPh_3)_4/CuI$ or $Pd(PPh_3)_2Cl_2/CuI$, for the stepwise preparation of ferrocenylbutadiyne is described. Complete ^1H and ^{13}C NMR characterization of $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)(C{\equiv}C)_nH$ ($n = 1, 2$), $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)(C{\equiv}C)_n(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$ ($n = 2, 4$) and $Z\text{-}(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)C{\equiv}C\text{–}CH{=}CHCl$, an X-ray crystal structure study of 1,4-bis(ferrocenyl)butadiyne, and the third order nonlinear optical behavior (second molecular hyperpolarizability, γ) of 1,8-bis(ferrocenyl) octatetrayne are reported.

1. Introduction

Bis(ferrocenyl)acetylene and 1,4-bis(ferrocenyl)butadiyne have been recognized as good model systems for studies of intervalence charge-transfer transitions through π-conjugation [1]. It has been reported recently [2a] that 1,4-bis(ferrocenyl)butadiyne exhibited a large third order nonlinear optical response $\chi^{(3)}$, and that other ferrocenyl compounds have interesting nonlinear optical properties [2b–2j]. We therefore began [2j] a systematic study of the synthesis, structure and reactivity of ferrocenyl alkynes and polyynes.

The synthetic method for preparing symmetric and unsymmetric ferrocenyl polyynes was originally developed by Schlögl in the mid 1960s [3]. Their method for preparing terminal polyynes $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)(C{\equiv}C)_nH$ required fundamentally different starting materials for different values of n. The ferrocenyl and bis(ferrocenyl) alkynes were characterized only by IR and UV/VIS spectroscopy, and elemental analysis. The compounds, $(\eta^5\text{-}C_5Me_5)M[(\eta^5\text{-}C_5H_2Me_2)C{\equiv}C(\eta^5\text{-}C_5H_2Me_2)]\text{–}M(\eta^5\text{-}C_5Me_5)$ ($M = Fe$, Ni), have been prepared recently using an entirely different methodology [1d]. In this report, we describe a simple stepwise route to ferrocenylbutadiyne, which could, in principle, be extended to the preparation of higher terminal ferrocenyl polyyne homologues. ^1H and ^{13}C NMR characterization of a series of ferrocenyl and bis(ferrocenyl) alkynes (Scheme 1), are presented along with the crystal and molecular structure of 1,4-bis(ferrocenyl)butadiyne, and the third order optical polarizability, γ, of 1,8-bis(ferrocenyl)octatetrayne.

2. Results and discussion

2.1. Synthesis

Ethynylferrocene (**1**) was prepared in good yield according to a literature procedure [4] from reaction of acetylferrocene with Vilsmeier's complex, via α-chloro-β-formyl-vinyl-ferrocene. 1,4-Bis(ferrocenyl)butadiyne (**2**) and 1,8-bis(ferrocenyl) octatetrayne (**5**) were prepared by the copper-catalyzed oxidative homo-coupling of the corresponding terminal ferrocenyl alkynes, **1** and ferrocenylbutadiyne (**4**) respectively, based on the procedure of Schlögl and Steyrer [3a] (Scheme 2). However, reaction yields of **2** and **5** in our hands were

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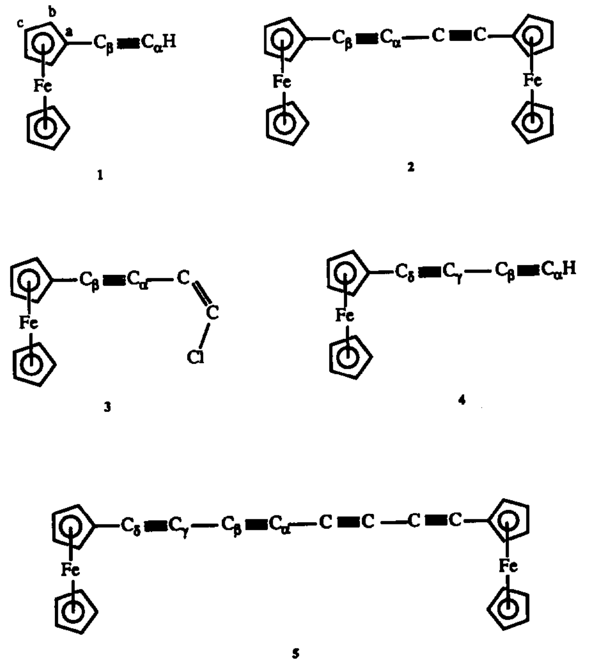
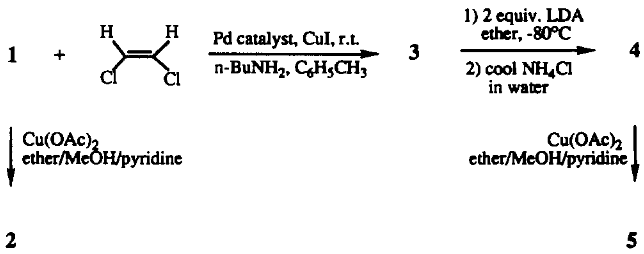


Scheme 1.



Scheme 2.

unexpectedly low. In an attempt to modify the reaction procedure, it was found that either reflux under nitrogen or oxygen flush at room temperature, in ether/MeOH/pyridine in the presence of Cu(OAc)$_2$, gave similar yields (38% and 41%). During purification by column chromatography, a black immobile band was observed in both cases. As terminal butadiynes can be polymerized catalytically [5], the formation of ferrocenyl-polyyne polymers might affect the yield of the homo-coupling reaction. Further investigation is in progress.

Compound **4** was synthesized by a two step sequence starting with ethynylferrocene, as illustrated in Scheme 2. Ethynylferrocene was coupled with *cis*-1,2-dichloroethylene in toluene in the presence of a Pd catalyst, CuI and ^{n}BuNH$_2$ to form 1-chloro-4-ferrocenylbut-1-ene-3-yne (**3**). This general method for preparing terminal diynes was reported recently by Kende and Smith [6]. In their work, Pd(PPh$_3$)$_4$ was used as catalyst. For comparison, we employed both Pd(PPh$_3$)$_4$ and Pd(PPh$_3$)$_2$Cl$_2$ for the cross coupling reaction under the identical conditions and found that reaction yields were comparable (72% and 77%). This result is consistent with other studies in which a bis(triphenylphosphine) complex "Pd(PPh$_3$)$_2$" is the active catalytic species [7]. We recommend using Pd(PPh$_3$)$_2$Cl$_2$ instead of Pd(PPh$_3$)$_4$ as the former is more stable and easier to prepare, and the reaction yield was indeed slightly higher. A chloroethylene/alkyne ratio

TABLE 1. ^{1}H and ^{13}C NMR parameters for compounds **1–5**

	Compound				
	1	2	3	4	5
^{1}H chem. shift [a]					
η-C$_5$H$_5$	4.20	4.25	4.22	4.23	4.25
η-C$_5$H$_4$	4.18, 4.44	4.23, 4.45	4.23, 4.47	4.23, 4.50	4.23, 4.50
C≡CH	2.70			2.37	
HC=CH			5.96, 6.36 (d, 7.3) [b]		
^{13}C chem. shift [a]					
η-C$_5$H$_5$	70.0	70.1	70.1	70.3 (m, 176.8) [c]	70.4
η-C$_5$H$_4$					
C_a	63.9	63.7	64.4	62.2 (broad)	61.6
C_b	68.7	69.2	69.1	69.4 (m, 171.9) [c]	70.0
C_c	71.7	72.1	71.5	72.4 (m, 180.6) [c]	72.8
C≡C					
C_α	73.5	71.0	97.0	68.7 (d, 257.4) [c]	63.7
C_β	82.6	79.1	79.6	68.9 (d, 51.2) [c]	70.1
C_γ				69.9 (d, 5.6) [c]	70.1
C_δ				75.9 (s)	78.9
C=C			112.6, 126.6		

[a] In ppm; coupling constants in Hz, given in parentheses. [b] $J_{^1H-^1H}$. [c] $J_{^{13}C-^1H}$.

of 2.5 : 1 was used to minimize the formation of the sideproduct, *cis*-1,2-bis(ferrocenylethynyl)ethylene. The higher ratio gives improved yields compared with the 2 : 1 ratio suggested previously [6]. *Trans* elimination of HCl from **3** using tetrabutylammonium fluoride as base, as per methodology of Kende and Smith [6], gave a low conversion (23%) for the ferrocenyl compound. We find that the use of two equivalents of lithium diisopropylamide gives yields as high as 80%. This method offers a simple way to prepare ferrocenylbutadiyne under mild conditions. The orange-brown compound **4** was not noticeably photosensitive. Unlike other terminal butadiynes [8], **4** can be stored as a solid in a refrigerator under air for several months without decomposition. However, it does decompose slowly in solutions exposed to air at room temperature.

2.2. NMR characterization

The infrared and UV/VIS spectra of **1**, **2**, **4** and **5** were identical to those described in previous reports [3,4]. The C≡C stretch of **3** occurs at 2208 cm^{-1}. The UV/VIS absorption bands of **3** were observed at λ_{max} = 280 nm and 348 nm, as well as a tail at 448 nm.

Compounds **1–5** were fully characterized by ^1H and ^{13}C NMR spectroscopy, and the data are listed in Table 1. Proton resonances for η-C_5H_5 and η-C_5H_4 groups in **1–5** are quite similar; however, ^1H chemical shifts for the C≡CH protons in **1** (δ 2.70) and **4** (δ 2.37) are significantly different. The methyne proton in **4** is thus deshielded with respect to that in **1**. This could be a result of either increased anisotropy or a stronger paramagnetic effect of the butadiyne moiety in **4** compared with a monoyne group in **1**. The *cis*-ethylene configuration of **3** is indicated by the proton coupling pattern (doublet) and coupling constant, $^3J(^1H-^1H)$ = 7.3 Hz.

The ^{13}C NMR spectra were assigned on the basis of chemical shifts, signal intensities, and coupling constants, as well as literature references [9]. Similarly to ^1H resonances, ^{13}C chemical shifts of η-C_5H_5 and η-C_5H_4 do not show significant differences among **1–5**. Chemical shifts of the C≡C groups are more informative. It has been reported that the chemical environment of polyyne carbons can be identified by the ^{13}C chemical shifts, even for a symmetric pentayne compound [10]. Unambiguous assignment of Fc–C_δ≡C_γ–C_β≡C_αH was achieved by comparing the proton coupled and decoupled ^{13}C NMR spectra. Measured coupling constants for **4** decrease rapidly in the order, $^1J(^{13}C-^1H)$ = 257.4 Hz, $^2J(^{13}C-^1H)$ = 51.2 Hz, $^3J(^{13}C-^1H)$ = 5.6 Hz and $^4J(^{13}C-^1H) \sim 0$ Hz, and are comparable to those in other terminal diyne systems [9,10]. In general, with increasing length of the polyyne chain, the corresponding ^{13}C resonances shift upfield, due to the ring current anisotropy of triple bonds. The further the alkyne carbon is away from the ferrocenyl group, the more the resonance moves upfield, due to smaller effects of the aromatic cyclopentadienyl moiety on the ^{13}C chemical shift.

TABLE 2. Selected bond distances (Å) and angles (°) for **2**

Fe(1)–C(1)	2.035(2)	Fe(1)–C(2)	2.043(2)
Fe(1)–C(3)	2.057(2)	Fe(1)–C(4)	2.054(2)
Fe(1)–C(5)	2.036(2)	Fe(1)–C(1′)	2.038(2)
Fe(1)–C(2′)	2.045(2)	Fe(1)–C(3′)	2.052(2)
Fe(1)–C(4′)	2.046(2)	Fe(1)–C(5′)	2.031(2)
C(1)–C(2)	1.434(2)	C(1)–C(5)	1.438(3)
C(1)–C(6)	1.421(3)	C(2)–C(3)	1.414(3)
C(3)–C(4)	1.416(3)	C(4)–C(5)	1.420(3)
C(1′)–C(2′)	1.425(3)	C(1′)–C(5′)	1.420(3)
C(2′)–C(3′)	1.408(3)	C(3′)–C(4′)	1.416(3)
C(4′)–C(5′)	1.415(3)	C(6)–C(7)	1.203(3)
C(7)–C(7A)	1.373(4)	($A = 1 - x, -y, 1 - z$)	
C(2)–C(1)–C(5)	107.5(2)	C(2)–C(1)–C(6)	126.2(2)
C(5)–C(1)–C(6)	126.3(2)	C(1)–C(2)–C(3)	107.8(2)
C(2)–C(3)–C(4)	108.7(2)	C(3)–C(4)–C(5)	108.3(2)
C(1)–C(5)–C(4)	107.7(2)	C(2′)–C(1′)–C(5′)	107.4(2)
C(1′)–C(2′)–C(3′)	108.3(2)	C(2′)–C(3′)–C(4′)	108.2(2)
C(3′)–C(4′)–C(5′)	108.0(2)	C(1′)–C(5′)–C(4′)	108.2(2)
C(1)–C(6)–C(7)	178.4(2)	C(6)–C(7)–C(7A)	179.3(3)

2.3. X-ray structure determination on 1,4-bis(ferrocenyl)butadiyne

The solid-state topological polymerization of end-capped symmetric and unsymmetric butadiynes is one of the most effective methods to prepare ordered crystalline polybutadiyne materials [11]. The crystal and molecular structure of **2** was therefore of interest and a study was carried out by single crystal X-ray diffraction. To our knowledge, this is the first X-ray structure of a metallocenyl polyyne. Selected bond lengths and angles for **2** are listed in Table 2, atomic coordinates and equivalent isotropic displacement coefficients are given in Table 3. A crystal packing diagram (Fig. 1) shows that **2** is not favored for solid-state topological polymerization, as the molecules do not pack in a parallel fashion at a reasonable distance. This is presumably a function of the bulk and rigidity of the ferrocenyl end groups.

The molecular structure (Fig. 2) of **2** shows some interesting features. The molecule sits on a crystallographic center of inversion. The two Cp rings on the ends are co-planar with the linear –C≡C–C≡C– acetylenic linkage. The angles C(1)–C(6)–C(7) and C(6)–C(7)–C(7a) are 178.4(2)° and 179.3(3)°, respectively. The two rings in each ferrocenyl group are eclipsed, probably due to a small ring rotation barrier, and the dihedral angle between the two Cp rings on each ferrocenyl group is 3.3° with Cp′ bent slightly

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **2**

	x	y	z	U_{eq} [a]
Fe(1)	2024.3(3)	1857.0(2)	1526.7(2)	30.81(8)
C(1)	3932(2)	587(2)	2243(2)	42.1(5)
C(2)	2608(3)	−92(2)	1475(2)	43.2(5)
C(3)	2591(3)	460(2)	380(2)	46.3(5)
C(4)	3873(3)	1479(2)	449(2)	47.4(6)
C(5)	4708(2)	1572(2)	1596(2)	46.3(6)
C(1′)	878(3)	2601(2)	2848(2)	47.1(6)
C(2′)	−457(3)	2048(2)	2016(2)	50.0(6)
C(3′)	−406(3)	2706(3)	978(2)	53.8(6)
C(4′)	952(3)	3669(2)	1150(2)	51.7(6)
C(5′)	1750(3)	3603(2)	2302(2)	47.6(6)
C(6)	4369(3)	349(2)	3431(2)	50.7(6)
C(7)	4775(3)	131(2)	4430(2)	54.7(6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

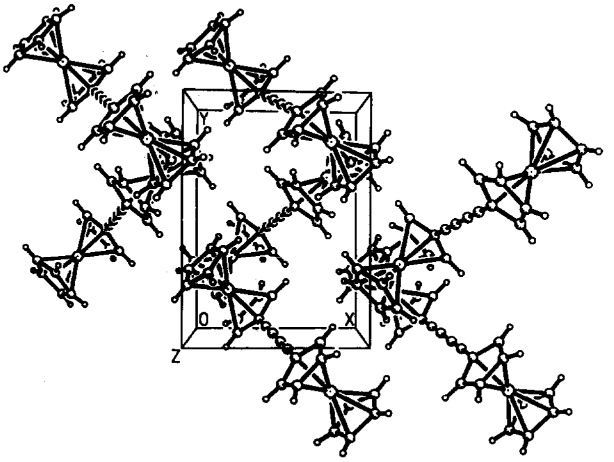


Fig. 1. Packing diagram for **2**, viewed down the z axis.

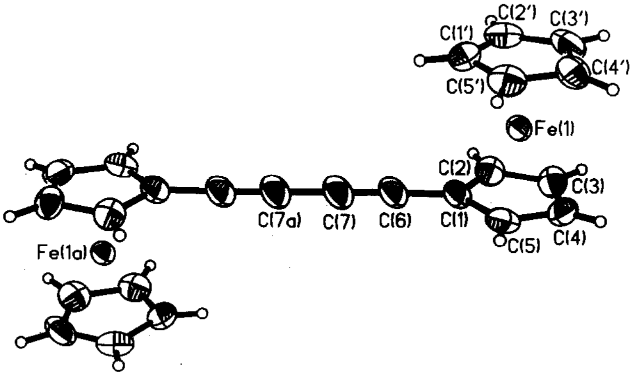


Fig. 2. ORTEP view of the molecular structure of **2**.

towards the alkyne group. The bond lengths, C(6)–C(7) = 1.203(3) Å and C(7)–C(7a) = 1.373(4) Å, are in the range normally observed for sp-hybridized carbon–carbon distances for C≡C and ≡C–C≡. π-Electron delocalization in the C_4 acetylenic linkage is probably not strong enough to be observed in the structure of **2**.

Many attempts to grow suitable single crystals of **5** for X-ray study failed. Only two octatetraynes, 1,8-bis(phenyl)octatetrayne [12] and 1,8-bis(trimethylsilyl)octatetrayne [13], have been studied by X-ray diffraction. Although standard deviations are large in both structures, the central C–C single bond lengths, 1.32 Å and 1.33 Å respectively, are believed to be shorter than the normal sp-hybridized carbon–carbon single bond. Enhanced electronic delocalization for C_8 polyynes is expected.

2.4. *Third order nonlinear optical properties of 1,8-bis(ferrocenyl)octatetrayne*

The third order optical polarizability of compound **5** was measured using the DC electric field induced second harmonic (EFISH) generation technique with a fundamental laser wavelength of 1.91 μm. As **5** is symmetrically substituted, and therefore has no permanent dipole moment along the conjugation direction, only the scalar part of the electronic third order polarizability contributes to the EFISH signal. The experimental apparatus and data reduction methodology have been reported in detail previously [14]. In $CHCl_3$ solution, an off-resonance $\gamma(-2\omega, \omega, \omega, 0)$ value of 110×10^{-36} esu was measured. This value is in the same range as other linearly conjugated molecules with similar conjugation lengths [15]. For example, 1,8-bis(4-(2-ethylhexyloxy)phenyl)octatetraene was found to have an off-resonance $\gamma(-3\omega, \omega, \omega, \omega)$ value of 251×10^{-36} esu by third harmonic generation (THG) measurements. Previous studies [2f] have concluded that, as far as their influence on hyperpolarizabilities are concerned, ferrocenyl moieties have similar donor properties to methoxyphenyl groups. Thus, if the cyclopentadienyl rings are considered as part of the conjugation of **5**, the present result suggests that the conjugated triple bond linkage is inferior to a conjugated double bond linkage of comparable length. It is difficult to compare our results for **5** with those reported for **2** in ref. 2(a) as no molecular hyperpolarizability values were given. In addition, the potential exists for resonance enhancement when making THG measurements on colored compounds. It is for this reason that the EFISH technique was employed for our measurement. However, the extended conjugation in **5**, relative to that in **2**, which leads to a lower transition energy, should also lead to a significantly higher optical nonlinearity. We believe that this is the first reported nonresonant second hyperpolarizability for a conjugated tetrayne compound.

3. Conclusion

A simple method for preparing ferrocenylbutadiyne from ethynylferrocene, via a palladium/copper catalyzed coupling reaction, is reported. This represents a new approach for the stepwise synthesis of metallocenyl polyynes. Thus, coupling of the terminal diyne product with additional *cis*-ClHC=CHCl followed by dehydrohalogenation would be expected to yield the terminal triyne, etc. Improvements in the two step general methodology [6] for the preparation of terminal butadiynes from terminal alkynes are also reported. The ferrocenyl and bis(ferrocenyl) alkynes were characterized by complete assignments of their ^{13}C NMR spectra. The single crystal X-ray study indicates that 1,4-bis(ferrocenyl)butadiyne does not pack favorably for solid-state topological polymerization. The value of γ for 1,8-bis(ferrocenyl)octatetrayne is consistent with extended conjugation through the tetrayne chain.

4. Experimental details

All reactions were carried out under a dry nitrogen atmosphere using Schlenk and glove-box techniques, unless otherwise stated. Solvents were distilled under nitrogen from appropriate drying agents. Water used for preparation purposes was degassed. *Cis*-1,2-dichloroethylene (Aldrich) was distilled under nitrogen. Ethynylferrocene was prepared as previously described with a slight modification [4].

Infrared spectra were measured as Nujol mulls on a Perkin Elmer 983 spectrometer using KBr plates. UV/VIS spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer using standard, dual window, quartz cells. Spectroscopic grade solvents were used for all measurements. NMR experiments were performed on Bruker AC200 or AM250 instruments at the operating frequencies of ^{1}H-200, 250 MHz and ^{13}C-50, 63 MHz. ^{1}H chemical shifts were referenced to residual protons in $CDCl_3$ (7.24 ppm) and ^{13}C chemical shifts to $CDCl_3$ (77.0 ppm), and are reported relative to tetramethylsilane.

4.1. Preparation of 1-chloro-4-ferrocenylbut-1-ene-3-yne (3)

Ethynylferrocene (1.8 g, 8.6 mmol) was treated with *n*-butylamine (3.2 g, 43 mmol), *cis*-1,2-dichloroethylene (2.1 g, 21.4 mmol), CuI (0.25 g, 1.3 mmol) and Pd $(PPh_3)_2Cl_2$ (0.30 g, 0.43 mmol) dissolved in 60 ml of toluene. The mixture was stirred at room temperature for 16 h, and the solvent was removed under vacuum. The residue was taken up in hexane and the organic salts were filtered off. The crude product was purified by column chromatography on neutral alumina using benzene/hexane (1:1) as the eluting solvent. The product **3** (1.8 g, 6.6 mmol) was the major brown-orange band and was isolated as red-orange crystals from hexane in 77% yield. Mp. 54–56°C. Anal. calc'd. for $C_{14}H_{11}FeCl$: C, 62.16; H, 4.10. Found: C, 61.97; H, 4.02. UV/VIS ($CHCl_3$) 448 nm (ϵ 370), 332 nm (ϵ 1100), 300 nm (ϵ 10000), 252 nm (ϵ 13000).

4.2. Preparation of ferrocenylbutadiyne (4)

To a solution of diisopropylamine (1.6 ml, 11 mmol) in 50 ml of diethyl ether at −40°C, 1.6 M n-butyllithium (7.1 ml, 11 mmol) in hexane was added. The mixture was stirred for 0.5 h and then cooled to −80°C in an acetone/dry ice bath. The chloroenyne **3** (1.4 g, 5.2 mmol) in 10 ml of diethyl ether was added and the solution was allowed to warm to room temperature after 4.5 h. The reaction was quenched with a cool and saturated aqueous NH_4Cl solution. The ether phase was washed with additional NH_4Cl solution, dried over sodium sulfate, and the solvent was removed *in vacuo*. The crude product was chromatographed on an alumina column using hexane/diethyl ether (4:1) as the eluting solvent. The bright orange-brown product (0.94 g, 4.2 mmol) was collected and isolated from hexane in 81% yield.

4.3. Crystal structure determination for 2

Dark red prisms, $C_{24}H_{18}Fe_2$; $M = 418.1$; monoclinic, space group $P2_1/c$ (No. 14); $a = 7.547(1)$, $b = 10.222(2)$, $c = 11.852(2)$ Å; $\beta = 97.96(1)°$; $V = 905.6(3)$ Å^3; $Z = 2$; $D_{calcd} = 1.533$ g cm^{-1}; $F(000) = 428$; $T = 295 \pm 1$ K; $\lambda = 0.71073$ Å; $\mu(\text{Mo K}\alpha) = 16.05$ cm^{-1}.

A crystal of dimensions 0.40 × 0.39 × 0.37 mm was mounted on glass fiber on a Siemens *R3m/V* diffractometer. Accurate unit cell dimensions were calculated from linear least-squares refinement of 25 reflections well distributed in reciprocal space with $22 < 2\theta < 32°$. Data were collected by the 2θ–θ scan method ($3.5 \leqslant 2\theta \leqslant 60.0°$) using variable scan rates (3.26–29.30° min^{-1}) and a scan width of 2.4° plus Kα separation. The intensities of two standard reflections were monitored every 100 measurements, and they exhibited only statistical fluctuations. From a total of 2657 unique reflections measured, 2162 with $F > 6.0\sigma(F)$ were considered observed and used in the structure solution and refinement [16]. Data were corrected for Lorentz and polarization effects, and for absorption (face indexed numerical method, transmission factors = 0.5382–0.6180). The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares. Hydrogen atoms were located in difference maps and refined with isotropic thermal parameters. Refinement of 155 parameters (data-to-parameter ratio = 13.9) led to convergence at $R = 0.028$ with $R_w = 0.043$. An empirical weighting scheme of the form $w^{-1} = \sigma^2(F) + 0.0012\ F^2$ was included in the final cycles of refinement. The largest peak in the final difference Fourier was 0.29 e Å^{-3}, and the largest hole was -0.26 e Å^{-3}. Scattering factors and anomalous dispersion coefficients were taken from ref. 17. The atomic coordinates, bond lengths, angles, and thermal parameters are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Any request should be accompanied by the full literature citation for this communication.

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