

Mono- and diferrocenyl complexes with electron-accepting moieties formed by the reaction of ferrocenylalkynes with tetracyanoethylene

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Reaction of tetracyanoethylene with ethynylferrocene, diferrocenylacetylene, and diferrocenyldiacetylene in dichloromethane solution at room temperature produced 1 : 1 adducts of 2,5-dicyano-3-ferrocenylhexa-2,4-dienedinitrile (**1**), 2,5-dicyano-3,4-diferrocenylhexa-2,4-dienedinitrile (**2**), and 2,5-dicyano-3-ferrocenyl-4-ferrocenylethynylhexa-2,4-dienedinitrile (**3**), respectively, under mild conditions. X-ray structure determination of **1–3** showed that they exhibit *s-cis*-butadiene conformations in the solid state. Cyclic voltammograms showed that there are negligible electronic communications between the ferrocenyl moieties in **2** and **3**, probably because of the highly twisted structures.

Introduction

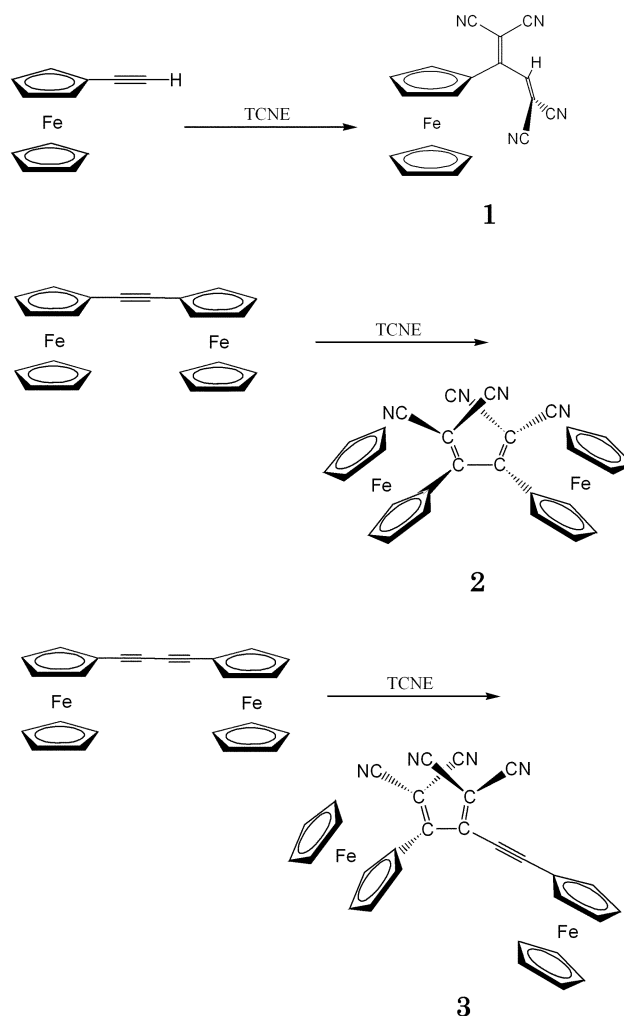
The synthesis and characterization of new ferrocene-based compounds have become an intriguing area of research in the field of materials science.¹ Among them, the charge-transfer (CT) complexes formed by the reaction of ferrocene derivatives with tetracyanoethylene (TCNE) are of considerable interest from the viewpoint of solid-state physical properties such as magnetism and conductivity.² TCNE is known to show varying reactivity towards electron-rich compounds,³ and its addition reactions to metal acetylides are well documented; they give cyclobutenyls, or buta-1,3-dien-2-yl complexes by subsequent ring-opening, as reported in cyclopentadienyl and arene complexes of W,⁴ Ru,⁵ Fe,⁶ and Ni,⁷ as well as in square planar platinum complexes.⁸ During our investigations on the synthesis of ferrocene-based CT complexes, we have found that acetylene-substituted ferrocenes results in addition products rather than CT complexes. Thus, ferrocenylalkynes were shown to exhibit a reactivity analogous to metal acetylides towards TCNE, producing 1,1,4,4-cyanobutadiene-type products. Such highly polarizable ferrocene derivatives may be of interest because the synthesis and characterization of new ferrocenyl compounds with electron-accepting moieties have attracted considerable interest in recent years, from the viewpoint of functional dyes or nonlinear optical (NLO) materials.⁹ Also interesting in conjugated ferrocene system are the electronic communications between terminal ferrocene subunits,¹⁰ and thus we have investigated adducts with one and two ferrocene units. In this paper, we describe the synthesis, structures and electrochemical properties of the 1 : 1 addition products of TCNE with ethynylferrocene, diferrocenylacetylene, and diferrocenyldiacetylene.

Results and discussion

Reaction of ferrocenyl acetylenes with TCNE

Reaction of TCNE with ethynylferrocene, diferrocenylacetylene, and diferrocenyldiacetylene, in dichloromethane solutions at room temperature resulted in 1 : 1 adducts of 2,5-dicyano-3-ferrocenylhexa-2,4-dienedinitrile (**1**), 2,5-dicyano-3,4-diferrocenylhexa-2,4-dienedinitrile (**2**), and 2,5-dicyano-3-ferrocenyl-4-ferrocenylethynylhexa-2,4-dienedinitrile

(**3**), respectively (Scheme 1). The reactions proceeded smoothly for **1** and **3** at room temperature, with a relatively quick completion of half a day, although it was much slower for **2**, which



Scheme 1

Table 1 ^{13}C and ^1H NMR data for **1–3**

	Compound		
	1	2	3
^{13}C chem. shift ^a			
$\delta(\text{Cp})$	72.34	72.44	71.53, 72.72
$\delta(\text{C}_5\text{H}_4)$	71.23, 73.70, 76.30	71.41, 72.06, 74.18, 75.43, 75.55	70.57, 72.90, 73.39, 73.43, 73.47, 73.72, 74.27, 76.06
$\delta(\text{CC})$	154.01, 164.99	171.53	147.54, 168.84
$\delta(\text{C}(\text{CN})_2)$	95.11	— ^b	85.31
$\delta(\text{CN})$	109.54, 110.72, 113.14, 113.75	113.55, 113.92	111.38, 112.11, 112.92, 113.91
$\delta(\text{C}\equiv\text{C})$			107.83, 124.16 59.25 ^c
^1H chem. shift ^a			
$\delta(\text{C}_5\text{H}_5)$	4.44	4.44	4.39, 4.43
$\delta(\text{C}_5\text{H}_4)$	5.05	4.10, 4.71, 4.96, 5.55	4.68–4.70, 4.72, 4.78, 4.93, 5.00, 5.05, 5.38
$\delta(\text{C}\equiv\text{CH})$	7.68		

^a In ppm. ^b Not observed. ^c Could not be assigned.

could be accounted for by the severe steric hindrance (*vide infra*). The reaction kinetics of **1** could be analyzed in terms of second-order reaction kinetics by monitoring the UV absorption of the product at 635 nm, and the rate constant was determined to be *ca.* $0.8 \text{ mol dm}^{-3} \text{ s}^{-1}$ at 24 °C, for a $0.5 \times 10^{-3} \text{ mol dm}^{-3}$ solution. Interestingly, the reaction also occurred in the solid state by grinding ethynylferrocene and TCNE for 30 min in a mortar with a pestle. The solid-state reaction proceeded *via* a greenish intermediate state, and the reaction may be initiated by the transient formation of charge-transfer complexes. These compounds are considered to be produced by the cycloaddition of TCNE to the triple bond, followed by the cleavage of the C–C bond. This kind of reaction is reported in electron-rich metal acetylides, and thus the reactivity of the ferrocenyl-alkynes may be attributed to the strongly electron-releasing nature of the ferrocene system. It is noted that no further addition of TCNE occurred to **3**, even in the presence of excess of the electrophile.

In the UV-vis region, compounds **1–3** exhibited strong absorptions at around 350 nm, and broad ones at around 630 nm, in dichloromethane solution. The former absorptions are assignable to $\pi\text{-}\pi^*$ transitions in the tetracyanobutadiene moiety, and the latter ones are assignable to intramolecular CT transitions. The reaction products are stable in dichloromethane, but they gradually decompose in polar media such as DMSO and acetonitrile. The structures of **1–3** were confirmed by X-ray crystallography (*vide infra*). These complexes have *s-cis* conformations in the solid state, which seem to be sterically favorable over *s-trans* conformations, as reported for other 1,3-diyne complexes.^{4–8}

The ^1H and ^{13}C NMR data of **1–3** are shown in Table 1. The ^1H NMR spectrum of complex **1** showed only a single peak for the substituted Cp ring protons at room temperature, which is probably because of coincidental overlap, while a slight splitting of the lines could be observed at -50 °C. On the other hand, the ^1H NMR spectra of **2** and **3** at room temperature exhibited four separate peaks for the substituted ring protons. In analogy to the case of buta-1,3-dien-2-yl complexes of platinum,⁸ it may be highly probable that the internal rotation about the C–C(Cp) bond may be prevented because of severe steric hindrance, especially in **2** and **3**, although no detailed information is available from the present NMR spectra.

Molecular structures of **1–3**

The molecular structures of **1–3** were also determined by means of X-ray crystallography. Selected bond lengths and angles for **1**, **2**, and **3** are listed in Tables 2, 3, and 4, respectively. Crystallographic parameters are listed in Table 6.

The ORTEP diagram of **1** is shown in Fig. 1. The butadiene-2,3-diyne moiety shows a twisted structure, with the *s-cis* con-

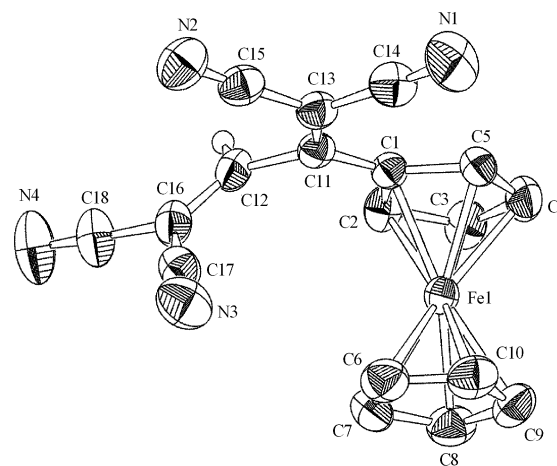
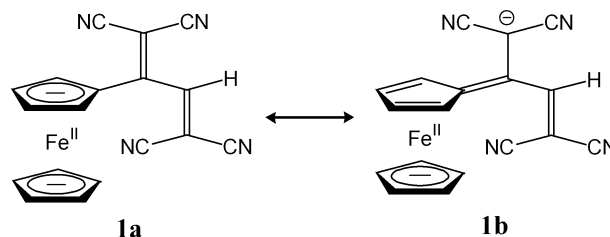


Fig. 1 An ORTEP drawing of **1** with the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

formation. The torsion angle of C(13)–C(11)–C(12)–C(16) is $60.4(3)^\circ$. The distance between the dicyanomethylene carbons, C(13) and C(16), is 3.14 Å, and thus there is no chemical bond between them. The ferrocenyl rings have the eclipsed conformation, with a staggering angle of 2.9° . The average Fe–C(Cp) distance is 2.047 Å, which is a typical value for neutral ferrocenes. It is noted that the substituted Cp ring and the adjacent dicyanoethylene moiety are almost coplanar, with a torsion angle of $5.1(1)^\circ$, and thus an interaction is expected through conjugation between these moieties. Indeed, detailed examination of the geometry suggests that there may exist a slight contribution of the fulvene-type resonance structure (**1b**), as shown in Scheme 2; the bond lengths of C(2)–C(3) and C(4)–



Scheme 2

C(5) are 1.409(3) and 1.409(4) Å, respectively, which are significantly shorter than C(1)–C(2) and C(1)–C(5), at 1.457(3) and 1.445(3) Å, respectively (Table 2). Moreover, the C(11)–C(13) bond length of 1.365(3) Å is significantly longer than that of C(12)–C(16), namely 1.337(3) Å, and the C(1)–C(11) bond

Table 2 Selected bond lengths (Å) and torsion angles (°) for **1**

Bond lengths			
Fe(1)–C(Cp1 ^a)	2.033(2)–2.060(2)	C(1)–C(11)	1.446(3)
Avg.	2.047	C(11)–C(12)	1.485(3)
Fe(1)–C(Cp2 ^b)	2.032(3)–2.061(2)	C(11)–C(13)	1.365(3)
Avg.	2.047	C(12)–C(16)	1.337(3)
C(1)–C(2)	1.457(3)	C(14)–N(1)	1.146(3)
C(1)–C(5)	1.445(3)	C(15)–N(2)	1.138(4)
C(2)–C(3)	1.409(3)	C(17)–N(3)	1.134(4)
C(3)–C(4)	1.423(4)	C(18)–N(4)	1.130(3)
C(4)–C(5)	1.409(4)	Fe(1)–Cp1 ^a	1.647(1)
C(Cp2 ^b)–C(Cp2 ^b)	1.403(4)–1.419(4)	Fe(1)–Cp2 ^b	1.658(1)
Avg.	1.412		
Torsion angles			
Cp1 ^a –Cp2 ^b	3.8(1)	C(2)–C(1)–C(11)–C(13)	3.6(2)
Cp1 ^a –plane 1 ^c	5.1(1)	C(5)–C(1)–C(11)–C(13)	9.4(4)
plane 1 ^c –plane 2 ^d	60.1(1)	C(13)–C(11)–C(12)–C(16)	60.4(3)

^a Cp1: C(1)–C(2)–C(3)–C(4)–C(5). ^b Cp2: C(6)–C(7)–C(8)–C(9)–C(10). ^c Plane 1: C(11)–C(13)–C(14)–C(15). ^d Plane 2: C(12)–C(16)–C(17)–C(18).

Table 3 Selected bond lengths (Å) and torsion angles (°) for **2**

Bond lengths			
Fe(1)–C(Cp1 ^a)	2.020(5)–2.051(5)	C(Cp1 ^a)–C(Cp1 ^a)	1.415(7)–1.438(6)
Avg.	2.038	Avg.	1.425
Fe(1)–C(Cp2 ^b)	2.033(6)–2.052(6)	C(Cp2 ^b)–C(Cp2 ^b)	1.39(1)–1.43(1)
Avg.	2.041	Avg.	1.414
Fe(2)–C(Cp3 ^c)	2.026(4)–2.047(4)	C(Cp3 ^c)–C(Cp3 ^c)	1.400(6)–1.450(5)
Avg.	2.036	Avg.	1.424
Fe(2)–C(Cp4 ^d)	2.034(4)–2.047(5)	C(Cp4 ^d)–C(Cp4 ^d)	1.401(7)–1.420(7)
Avg.	2.039	Avg.	1.412
Fe(1)–Cp1 ^a	1.638(2)	C(21)–C(23)	1.352(6)
Fe(1)–Cp2 ^b	1.650(4)	C(22)–C(26)	1.366(6)
Fe(2)–Cp3 ^c	1.637(2)	C(24)–N(1)	1.134(6)
Fe(2)–Cp4 ^d	1.648(3)	C(25)–N(2)	1.132(6)
C(1)–C(21)	1.457(6)	C(27)–N(3)	1.134(6)
C(11)–C(22)	1.445(5)	C(28)–N(4)	1.141(6)
C(21)–C(22)	1.505(5)		
Torsion angles			
Cp1 ^a –Cp2 ^b	1.9(3)	C(1)–C(21)–C(22)–C(11)	70.2(5)
Cp3 ^c –Cp4 ^d	3.6(2)	C(2)–C(1)–C(21)–C(23)	23.1(4)
Cp1 ^a –plane 1 ^e	27.2(2)	C(5)–C(1)–C(21)–C(23)	22.3(7)
Cp3 ^c –plane 2 ^f	23.4(2)	C(12)–C(11)–C(22)–C(26)	21.9(4)
Plane 1 ^e –plane 2 ^f	75.2(2)	C(15)–C(11)–C(22)–C(26)	20.2(7)
		C(23)–C(21)–C(22)–C(26)	74.7(5)

^a Cp1: C(1)–C(2)–C(3)–C(4)–C(5). ^b Cp2: C(6)–C(7)–C(8)–C(9)–C(10). ^c Cp3: C(11)–C(12)–C(13)–C(14)–C(15). ^d Cp4: C(16)–C(17)–C(18)–C(19)–C(20). ^e Plane 1: C(21)–C(23)–C(24)–C(25). ^f Plane 2: C(22)–C(26)–C(27)–C(28).

length of 1.446(3) is shorter than that of C(11)–C(12), at 1.485(3) (Table 3). The conjugation may account for the slight red-shift of the UV-vis absorption band in **1** relative to **2** and **3**, although the difference is small.

The ORTEP diagram of **2** is shown in Fig. 2 (selected bond lengths and angles in Table 3). The molecular structure has quasi-C₂ symmetry in the crystal. This compound assumes a highly twisted structure, with the *s-cis* conformation of the

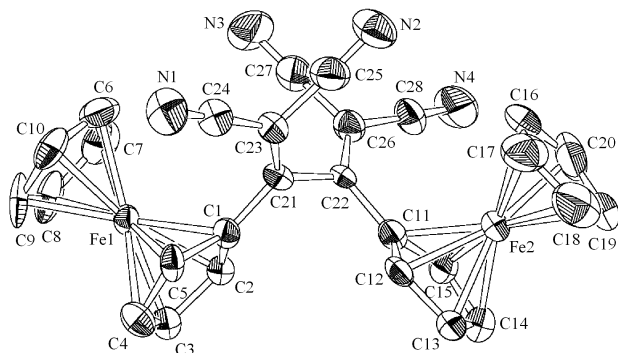


Fig. 2 An ORTEP drawing of **2** with the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

butadiene-2,3-diyl moiety. The torsion angles of C(1)–C(21)–C(22)–C(11) and C(23)–C(21)–C(22)–C(26) are 70.2(5) and 74.7(5)°, respectively. The torsion angles between the dicyanoethylene moieties and the adjacent Cp rings are 27.2(2) and 23.4(2)°, for Fe(1) and Fe(2), respectively. In contrast to the case of **1**, no bond alternations were observed in substituted Cp rings in **2**. This is consistent with the larger torsion angle of the Cp rings with respect to the dicyanoethylene moiety, as mentioned above, which prevent conjugation between them. Another factor should be the weaker electron-withdrawing nature of the tetracyanobutadiene moiety in **2** relative to **1** due to the presence of the additional ferrocene unit. The distance between the dicyanomethylene carbons, C(23) and C(26), is 3.15 Å, and there is no bonding between them. The ferrocenyl rings have an eclipsed conformation, with staggering angles of 3.4 and 6.8°, for Fe(1) and Fe(2), respectively. The average Fe–C(Cp) distances are 2.039 and 2.038 Å, for Fe(1) and Fe(2), respectively, which are typical values for neutral ferrocenes. The intramolecular Fe–Fe distance is 6.93 Å.

The ORTEP diagram of **3** is shown in Fig. 3. The crystals of **3** formed by vapor-diffusion involved one molecule of neutral TCNE in the unit cell, which shows normal bond lengths. The compound **3** was a 1 : 1 adduct, similar to that observed with other diacetylene–TCNE adducts,^{4–7} leaving one triple bond

Table 4 Selected bond lengths (Å) and torsion angles (°) for **3**

Bond lengths			
Fe(1)–C(Cp1 ^a)	2.031(5)–2.078(5)	C(Cp1 ^a)–C(Cp1 ^a)	1.420(8)–1.450(7)
Avg.	2.052	Avg.	1.432
Fe(1)–C(Cp2 ^b)	2.025(6)–2.081(5)	C(Cp2 ^b)–C(Cp2 ^b)	1.412(7)–1.438(8)
Avg.	2.057	Avg.	1.425
Fe(2)–C(Cp3 ^c)	2.027(6)–2.055(6)	C(Cp3 ^c)–C(Cp3 ^c)	1.401(1)–1.440(8)
Avg.	2.043	Avg.	1.422
Fe(2)–C(Cp4 ^d)	2.027(7)–2.090(7)	C(Cp4 ^d)–C(Cp4 ^d)	1.361(1)–1.51(1)
Avg.	2.051	Avg.	1.408
Fe(1)–Cp1 ^a	1.650(3)	C(1)–C(21)	1.464(7)
Fe(1)–Cp2 ^b	1.662(3)	C(11)–C(24)	1.427(8)
Fe(2)–Cp3 ^c	1.644(3)	C(21)–C(22)	1.495(7)
Fe(2)–Cp4 ^d	1.664(4)	C(21)–C(25)	1.358(7)
C(26)–N(1)	1.155(7)	C(22)–C(23)	1.398(8)
C(27)–N(2)	1.140(7)	C(22)–C(28)	1.371(8)
C(29)–N(3)	1.143(8)	C(23)–C(24)	1.213(8)
C(30)–N(4)	1.166(7)	C(31)–C(32) ^g	1.445(8)
C(32)–N(5) ^g	1.147(7)	C(31)–C(33) ^g	1.436(8)
C(33)–N(6) ^g	1.150(8)	C(31)–C(31*) ^g	1.336(9)
Torsion angles			
Cp1 ^a –Cp2 ^b	3.5(2)	plane 1 ^e –plane 2 ^f	68.8(2)
Cp1 ^a –Cp3 ^c	76.5(3)	C(1)–C(21)–C(22)–C(23)	60.5(9)
Cp3 ^c –Cp4 ^d	1.8(3)	C(2)–C(1)–C(21)–C(25)	6.9(13)
Cp1 ^a –plane 1 ^e	13.5(2)	C(5)–C(1)–C(21)–C(25)	11.1(7)
Cp3 ^c –plane 2 ^f	12.7(2)	C(25)–C(21)–C(22)–C(28)	66.6(10)

^a Cp1 : C(1)–C(2)–C(3)–C(4)–C(5). ^b Cp2 : C(6)–C(7)–C(8)–C(9)–C(10). ^c Cp3 : C(11)–C(12)–C(13)–C(14)–C(15). ^d Cp4 : C(16)–C(17)–C(18)–C(19)–C(20). ^e Plane 1 : C(21)–C(25)–C(26)–C(27). ^f Plane 2 : C(22)–C(28)–C(29)–C(30). ^g Bond lengths in TCNE.

Table 5 Redox potentials of **1–3** and ferrocenylalkynes^a

	$E_{1/2}^{ox}(1)/V$	$E_{1/2}^{ox}(2)/V$	$E_{1/2}^{red}/V$
1	0.42		–0.78
2	0.43		–0.78 (irr.)
3	0.33	0.41	–1.05 (irr.)
Ethynylferrocene	0.15		
Diferrocenylacetylene	–0.11	0.08	
1,4-Diferrocenylbutadiyne	0.14	0.23	

^a Potentials vs. $\text{FcCp}_2/\text{FcCp}_2^+$, in CH_2Cl_2 solutions containing 0.1 mol L^{-1} $n\text{Bu}_4\text{NClO}_4$, scan rate 100 mV s^{-1} .

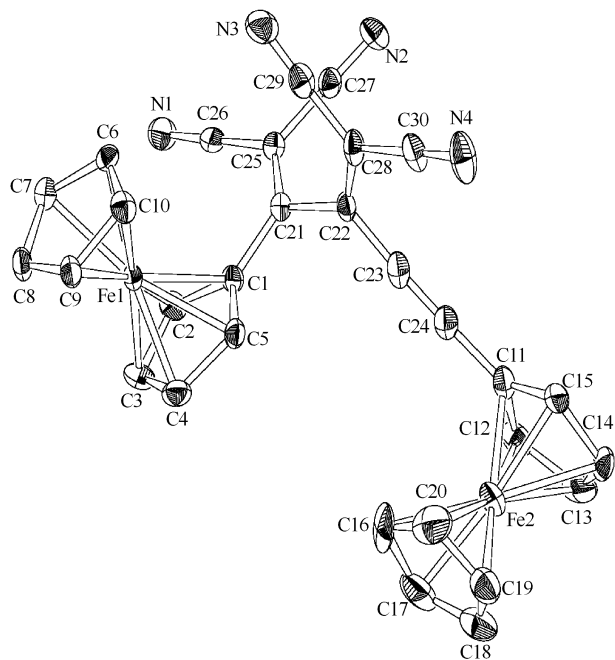


Fig. 3 An ORTEP drawing of **3** with the atom numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

unreacted. This compound assumes a highly twisted structure, with an *s-cis* conformation of the butadiene-2,3-diyl moiety. The torsion angles of C(1)–C(21)–C(22)–C(23) and C(25)–

C(21)–C(22)–C(28) are 60.5(9) and 66.6(10)°, respectively. The distance between the dicyanomethylene carbons, C(25) and C(28), is 3.15 Å, and there is no bonding between them. The ferrocenyl rings have the eclipsed conformation, with staggering angles of 9.1 and 17.4°, for Fc(1) and Fc(2), respectively. The average Fe–C(Cp) distances are 2.055 and 2.047 Å for Fe(1) and Fe(2), respectively, which are typical values for neutral ferrocenes. The intramolecular Fe–Fe distance is 7.35 Å. The bond lengths in the acetylene carbon chains are 1.427(8), 1.213(8), and 1.398(8) Å, for C(11)–C(24), C(24)–C(23), and C(23)–C(22), respectively, (see Table 4) which are normal values for C–C and C≡C bonds. The C(21)–C(22) bond length is 1.495(7) Å. The torsion angles of the substituted Cp rings with respect to the nearer dicyanoethylene moiety are 13.5(2) and 12.7(2) for Fc(1) and Fc(2), respectively, and no bond alternations were observed in Cp rings in **3**, similar to the case of complex **2**.

Redox properties

The redox potentials of **1–3** (vs. $\text{FcCp}_2/\text{FcCp}_2^+$) are listed in Table 5, together with those for the corresponding ferrocenylalkynes. The cyclic voltammograms of **1** and its precursor ethynylferrocene¹⁰ are shown in Fig. 4. The redox waves of the ferrocenyl moieties for **1–3** were observed at around 0.4 V, and the donating abilities of the products are much weaker than the

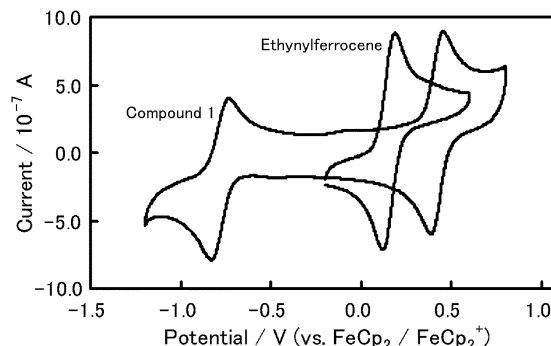


Fig. 4 Cyclic voltammograms of **1** and ethynylferrocene (vs. $\text{FcCp}_2/\text{FcCp}_2^+$) in CH_2Cl_2 solutions containing 0.1 mol L^{-1} $n\text{Bu}_4\text{NClO}_4$.

Table 6 Crystallographic parameters for 1–3

	1	2	3·(TCNE) _{0.5}
Formula	C ₁₈ H ₁₀ N ₄ Fe	C ₂₈ H ₁₈ N ₄ Fe ₂	C ₃₃ H ₁₈ N ₆ Fe ₂
<i>T</i> /K	296	296	100
Formula weight	338.15	581.86	610.24
Color, habit	Black, block	Black, block	Black, prism
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> /Å	9.691(3)	11.755(3)	7.570(4)
<i>b</i> /Å	10.043(5)	12.482(3)	13.463(7)
<i>c</i> /Å	8.646(4)	16.933(2)	13.906(8)
<i>a</i> ^o	90.21(5)		106.06(1)
<i>β</i> ^o	105.49(3)	98.47(1)	99.24(1)
<i>γ</i> ^o	71.15(3)		91.08(1)
<i>V</i> /Å ³	764.3(6)	2457.5(9)	1341.2(12)
<i>Z</i>	2	4	2
<i>d</i> _{calcd} /g cm ⁻³	1.469	1.573	1.511
<i>μ</i> (Mo Kα)/cm ⁻¹	9.89	13.68	11.16
Dimensions/mm	0.6 × 0.5 × 0.1	0.5 × 0.2 × 0.1	0.3 × 0.1 × 0.07
Radiation	Mo Kα	Mo Kα	Mo Kα
Diffractometer	Rigaku AFC5S	Rigaku AFC5S	Rigaku Mercury
No. of reflections	3717	6197	5993
No. of observations	3208	3486	4445
Refl./param. ratio	15.42	11.32	11.43
<i>R</i> ₁ , <i>R</i> _w ^a	0.037; 0.114	0.043; 0.126	0.080; 0.244

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|; R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

ferrocenylalkynes due to the addition of the strongly electron-withdrawing moieties. In biferrocene analogues, the splitting of the redox waves is a measure of the communication between the two ferrocene units.¹⁰ In complex **2**, only a single redox wave was observed, indicating the absence of communication between the ferrocene units. This is consistent with the highly twisted structure of **2**, in which π – π through-bond interactions are prevented. In complex **3**, two redox waves for the ferrocene moieties were observed at 0.33 and 0.41 V, which we assign to the redox processes of Fe(2) and Fe(1), respectively. Because this compound is highly twisted as in the case of **2**, the potential difference may arise merely from the substituent effect. The redox processes originating from the tetracyanobutadiene moiety were observed as quasi-reversible redox waves at –0.78 V for **1**, and as irreversible reduction waves at –0.78 and –1.05 V for **2** and **3**, respectively.

Conclusion

We have investigated the reaction of acetylene-substituted ferrocenes with TCNE and fully characterized the 1,1,4,4-cyanobutadiene-type addition products. The ferrocenylalkynes were thus found to exhibit an analogous reactivity to metal acetylides towards TCNE, which may be ascribable to the electron-releasing nature of the ferrocene system. A related example is the addition reaction of vinylferrocene with TCNE,¹¹ but the reaction affords a non-conjugated compound. The present type of reaction may be useful as a new method to synthesize highly polarizable ferrocene derivatives, which would be interesting from the viewpoint of functional dyes or NLO materials.

Experimental

General methods

Diferrocenyldiacetylene,¹² diferrocenyldiacetylene,¹³ and diferrocenyldiacetylene¹⁴ were synthesized according to literature methods. ¹H and ¹³C NMR spectra were measured on a JEOL ECP-400 Fourier transform spectrometer (¹H at 400 MHz, ¹³C at 100 MHz) in chloroform-*d* or tetrachloroethane-*d*₂ solutions in the temperature range –60 – 120 °C. UV-vis spectra were recorded on a Shimadzu MultiSpec-1500, and reaction rates were monitored for 0.5 × 10⁻³ mol L⁻¹ solutions at 24 °C.

Infrared spectra were recorded on a JASCO FT-IR 230 spectrometer using KBr pellets in the 4000–400 cm⁻¹ range. Cyclic voltammograms were recorded with an ALS/chi electrochemical-analyzer model 600A. Measurements were performed in dichloromethane solutions containing 0.1 mol L⁻¹ *n*Bu₄N-ClO₄ as the supporting electrolyte, at a scan rate of 100 mV s⁻¹, with Cp₂Fe/Cp₂Fe⁺ as a reference. A working electrode of a platinum wire was used.

Preparation

2,5-Dicyano-3-ferrocenyl-hexa-2,4-dienedinitrile (1). Diferrocenyldiacetylene (10 mg, 4.9 × 10⁻² mmol) and TCNE (6.7 mg, 5.2 × 10⁻² mmol) was dissolved in chloroform (2 ml), mixed, and left at room temperature for overnight. A vapor diffusion of pentane into the solution over four days afforded blue–black prismatic crystals of **1**. Yield: 10 mg, 60%. The reaction also occurred in the solid state by grounding ethynylferrocene and TCNE for 30 min in a mortar with a pestle. As the reaction proceeds, the color turned green and finally gave blue–black powder of **1**. ¹H and ¹³C NMR data are summarized in Table 1. *v*_{max}/cm⁻¹ 2229, 2222 and 2213 (C≡N) (KBr). Found: C 64.19, H 3.10, N 16.85; C₁₈H₁₀N₄Fe requires: C 63.93, H 2.98, N 16.57%. *λ*_{max}/nm (CH₂Cl₂) 350 (*ε*/M⁻¹ cm⁻¹ = 9650) and 632 (2080).

2,5-Dicyano-3,4-diferrocenyl-hexa-2,4-dienedinitrile (2). This compound was obtained by the same procedure for **1**, except that the starting material was diferrocenyldiacetylene. Due to the slow reaction rate, the starting materials were recovered mainly and the yield of the blue–black prismatic crystals of **2** was 8%, under the same condition to **1**. *v*_{max}/cm⁻¹ 2219 (C≡N) (KBr). Found: C 64.27, H 3.52, N 10.70; C₂₈H₁₈N₄Fe₂ requires: C 64.40, H, 3.47, N 10.73%. *λ*_{max}/nm (CH₂Cl₂) 345 (*ε*/M⁻¹ cm⁻¹ = 24450) and 626 (5310).

2,5-Dicyano-3-ferrocenyl-4-ferrocenylethynyl-hexa-2,4-dienedinitrile (3). This compound was obtained by the same procedure for **1**, except that the starting material was diferrocenyldiacetylene. Blue–black prismatic crystals, Yield 91%. Structural analysis revealed that the crystals formed by the vapor-diffusion method contain one molecule of TCNE in the unit cell. *v*_{max}/cm⁻¹ 2226 (C≡N) and 2169 (C=C) (KBr). Found: C 65.27, H 3.22, N 12.05; C_{31.5}H₁₈N₅Fe₂ {= 3·(TCNE)_{0.25}}

requires: C 65.43, H 3.14, N 12.11%. λ_{\max}/nm (CH_2Cl_2) 386 ($\epsilon/\text{M}^{-1}\text{cm}^{-1} = 16090$) and 627 (6850).

X-Ray crystal structure determination

All the X-ray data were collected using Mo K α radiation on a Rigaku AFC-5S four circle diffractometer. Pertinent crystallographic parameters and refinement data are listed in Table 6. The structures were solved by direct methods and refinement converged using full-matrix least squares method. Atomic scattering factors and anomalous dispersion ($\Delta f'$ and $\Delta f''$) were taken from the literature.¹⁵ All the calculations were carried out using the teXsan crystallographic software package.¹⁶ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at ideal positions using a rigid model. Structure analyses of **2** revealed that there seems to be some solvent molecules of chloroform incorporated in the crystals but they seem to easily escape from the crystals and were not located. The crystal of **3** formed by vapor-diffusion was found to involve one molecule of neutral TCNE in the unit cell.

CCDC reference numbers 184798–184800.

See <http://www.rsc.org/suppdata/dt/b2/b204168e/> for crystallographic data in CIF or other electronic format.

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