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Tetraferrocenyl-[3]-cumulene [1]

Benno Bildstein *, Manuela Schweiger, Holger Kopacka, Klaus Wurst

Institut für Allgemeine, Anorganische, und Theoretische Chemie, Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

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Abstract

Tetraferrocenyl-[3]-cumulene (tetraferrocenylbutatriene) is synthesized from tetraferrocenyl-methoxy-hydroxy-butyne by reduction with stannous chloride. Other reducing agents, including iron carbonyls, samarium(II) iodide, low-valent titanium, and trimethylchlorosilane/zinc, failed or gave inferior results. With the McMurry reagent the reduction goes further and tetraferrocenylbutadiene is obtained. The title compound is an electron-rich cumulene, as shown by cyclic voltammetry. Due to steric shielding of the central cumulene functionality, no established butatriene reactivity (complex formation or dimerization) is observed, but simple ferrocene-based redox or charge-transfer chemistry is possible. © 1998 Elsevier Science B.V.

Keywords: Iron; Ferrocene; Cumulene; Butatriene; Butadiene; X-ray structure; Electrochemistry

1. Introduction

Quasi-one-dimensional molecules with conjugated redox-active termini are under active investigation in the field of molecular electronics due to their anticipated application as ‘‘molecular wires’’ [1–11]. Ferrocene compounds, which find increasing use in the broader context of materials science [12], are useful in this respect because of their fully reversible ferrocene/ferrocenium couple [13]. We are currently engaged in a project on perferrocenylated cumulenes [14–16] which can be envisaged as model compounds for such molecular wires. Related chemistry on *metalla*-cumulenes is currently investigated by the groups of Gladysz, Lapinte, Werner, Dixneuf, and Fischer [2] [17]. Besides the electrochemical properties of such systems we are also investigating the reactivity of these cumulenic metallocenes (nucleophilic reactivity of the cumulenic subunit, cycloadditions, cyclooligomerizations, charge-transfer complex formation), which is anticipated to be strongly influenced by the powerful electron-donating effect of the ferrocenyl substituents [18,19]. However, steric hindrance prevents in the case of tetraferrocenylethylene [14] and tetraferrocenylallene [16] the observation of the desired reactivity at the cumulenic carbons. Here we report on the synthesis, properties, and reactivity of tetraferrocenyl-[3]-cumulene as the next higher homologue in this series of perferrocenylated cumulenes.

2. Results and discussion

2.1. Synthesis

Tetrasubstituted butatrienes ([3]-cumulenes) are classically synthesized by nucleophilic addition of a dimetalated propynol to a ketone [20,21] with successive reductive dehydration by stannous chloride in glacial acetic acid [22]. Following this procedure we observed no reaction of dilithiated 1,1-diferrocenylprop-2-yn-1-ol [15] with diferrocenylketone [23]. Therefore a protecting group for the hydroxy functionality of diferrocenylpropynol was sought to avoid possible side reactions and to enhance the nucleophilicity of the metal propynide. Earlier we found that a trimethylsilyl group is unsuitable for this purpose [15] due to spontaneous elimination of trimethylsilyloxide with subsequent propargylium ↔ allenium isomerization. Nevertheless, the methylation of mono-lithiated diferrocenylpropynol with methyl iodide in analogy to published procedures

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* Corresponding author. E-mail: benno.bildstein@uibk.ac.at

[1] Dedicated to Professor Gottfried Huttner on the occasion of his 60th birthday.

[2] Compare references 8, 10, 11, 12, and 13 cited in Ref. [16].

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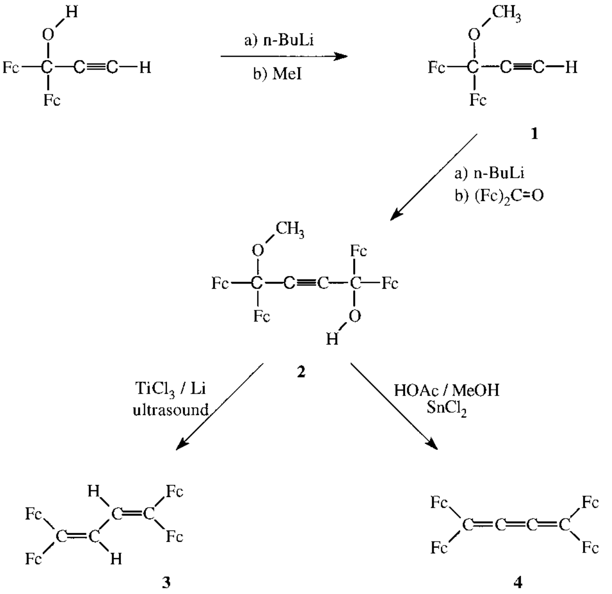

Scheme 1. Synthesis of compounds (**1**)–(**4**).

[24] provides 1,1-diferrocenyl-1-methoxy-prop-2-yne (**1**) in 96% yield (Scheme 1) as an extremely valuable synthon, not only for the preparation of the target compound tetraferrocenyl-[3]-cumulene (**3**), but also for higher cumulenes with up to five cumulated carbon bonds [25,26].

Lithiated methoxypropyne (**1**) does react in the desired manner with diferrocenylketone to produce 1,1,4,4-tetraferrocenyl-4-hydroxy-1-methoxy-but-2-yne (**2**), although in a disappointing low yield of approximately 28%. Despite many attempts to optimize this reaction (metal–lithium exchange, temperature, solvent, stoichiometric or catalytic amounts of various Lewis acids, etc.) no improved reaction conditions could be found which allow the isolation of (**2**) in higher yield. The reason is the unavoidable formation of the dark blue tetraferrocenyl-[5]-cumulene as the main product, which is generated by a formal dimerization [27–30] of an intermediate diferrocenyl-alkenylidenecarbene. This interesting cumulene, its formation, structure, physical and chemical properties will be the subject of a forthcoming publication [25].

The reduction of (**2**) with stannous chloride under standard reaction conditions [22] did at first not provide the desired cumulene (**4**) at all. Hence other reducing agents were tried, including low-valent titanium according to McMurry [31–34], zinc/trimethylchlorosilane as a modified Clemmensen reducing system [35,36], samarium(II) iodide [37,38], and iron carbonyls [39].

The McMurry reduction does not give access to the cumulene (**4**), instead the ‘‘over-reduced’’ butadiene (**3**) is obtained in 69% yield. In retrospective, this result is not so unexpected, because for tetraphenylbutadiene it has long been known that reduction to a dianion by strongly reducing alkali metals is possible [40–45] and in our case the McMurry reagent is present in the reaction mixture in a large excess, thereby forming the dianion which is protonated upon aqueous work-up to afford butadiene (**3**).

With the Zn/Me_3SiCl Clemmensen reducing system as a milder reducing agent in comparison to low-valent titanium, (**2**) is consumed quantitatively but cumulene (**4**) can unfortunately only be isolated in a very low yield of 5%. This is due to the formation of a mixture of (**3**), (**4**) and other unidentified products which results in heavy losses of (**4**) upon purification by column chromatography. Similar problems were encountered upon reacting (**2**) with SmI_2. As reported in the literature [39], the usual outcome of the reaction of a 2-butyne-1,4-diol with iron carbonyls ($Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$) is a (butatriene)hexacarbonyldiiron complex, formed from the precursor by a concerted reduction/complexation mechanism. In our case complex formation is obviously prevented by the steric bulk of the four ferrocenyl substituents (compare X-ray structures below) but reduction might be feasible. The experimental result corroborates this anticipation: with an excess of the reducing agent $Fe_2(CO)_9$ cumulene (**4**) is formed, albeit the reaction does not go to completion under a variety of conditions with a mixture of the starting material (**2**) and the product (**4**) as the final outcome.

Because no satisfactory synthesis with these alternative methods was possible, the classic procedure using Sn^{2+} as the reductant was modified to afford the desired cumulene (**4**) finally in preparative acceptable amount: with a solvent mixture of glacial acetic acid and methanol and with a ferrocene stoichiometric ratio of $Sn^{2+}/(\mathbf{2}) = 6/1$ the tetraferroenyl-[3]-cumulene (**4**) is obtained after work-up in 74% yield.

2.2. Spectroscopy and structure

In addition to the characterization of diferrocenylmethoxypropyne (**1**) by the usual spectroscopic methods (see Section 4) an X-ray crystal structure analysis was performed (Table 1Fig. 1). Interestingly, two crystallographically independent molecules (two conformers) are observed which differ slightly in their bond lengths and angles. Of these two molecules only one (molecule A) is shown in Fig. 1. Overall, the molecular structure of (**1**) is in accord with the expectations and presents no unusual features with regard to structural parameters, but it serves as an unequivocal proof of the connectivity of the molecule.

The molecular structure of tetraferrocenyl-hydroxymethoxy-butyne (**2**) in the solid state (Fig. 2, Table 1) is in agreement with the results obtained from NMR measurements in solution. The observed bond lengths and angles are in the normal range with the exception of the

Table 1
Crystal data and structure refinement for **1**, **2**, **3**

	1	**2**	**3**
Molecular formula	$C_{24}H_{22}Fe_2O$	$C_{45}H_{39}Fe_4O_2 \cdot 3/4CH_2Cl_2$	$C_{44}H_{38}Fe_4$
Formula weight	438.12	899.86	790.14
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$Pca2_1$ (No. 29)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (pm)	1326.9(2)	1131.0(2)	1229.5(4)
b (pm)	1239.6(2)	1725.1(3)	1087.2(3)
c (pm)	2316.1(4)	1952.8(2)	1345.6(2)
α (°)	90	90	90
β (°)	90	98.01(1)	112.82(2)
γ (°)	90	90	90
Volume (nm^3)	3.8096(11)	3.7729(10)	1.6579(7)
Z	8	4	2
Temperature (K)	213	213	218
Density, calc. (mg m^{-3})	1.528	1.584	1.583
Absorption coefficient (mm^{-1})	1.533	1.653	1.748
F(000)	1808	1846	812
Color, habit	yellow block	orange platelet	red platelet
Crystal size (mm)	0.60 × 0.25 × 0.25	0.55 × 0.55 × 0.4	0.5 × 0.4 × 0.2
θ-range for data collection (°)	4.03–23.00	3.08–21.41	3.29–24.00
Index ranges	$-1 \leq h \leq 14$, $-1 \leq k \leq 13$, $-25 \leq l \leq 1$	$-1 \leq h \leq 11$, $-1 \leq k \leq 17$, $-19 \leq l \leq 20$	$-1 \leq h \leq 11$, $-1 \leq k \leq 12$, $-15 \leq l \leq 14$
Reflections collected	3434	5200	3174
Independent reflections	2848 ($R_{int} = 0.0273$)	4039 ($R_{int} = 0.0387$)	2465 ($R_{int} = 0.0348$)
Reflections with $I > 2\sigma(I)$	2516	2789	2050
Absorption correction	none	ψ-scan	ψ-scan
Max. and min. transmission	–	0.987 and 0.769	0.970 and 0.684
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2848/1/487	3664/0/491	2465/0/217
Goodness-of-fit on F^2	1.047	1.063	1.026
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0318$, $wR_2 = 0.0679$	$R_1 = 0.0462$, $wR_2 = 0.0917$	$R_1 = 0.0389$, $wR_2 = 0.1012$
R indices (all data)	$R_1 = 0.0419$, $wR_2 = 0.0725$	$R_1 = 0.0854$, $wR_2 = 0.1085$	$R_1 = 0.0506$, $wR_2 = 0.1083$
Absolute structure parameter	0.16(3)	–	–
Largest diff. peak and hole (e nm^{-3})	295 and -343	609 and -409	533 and -746

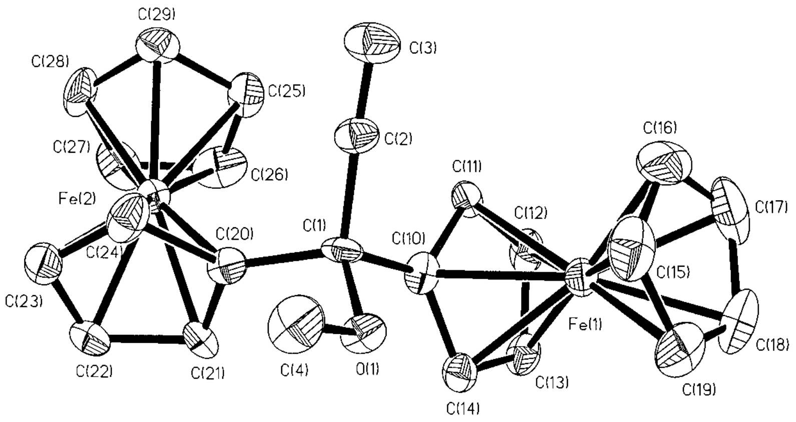

Fig. 1. Molecular structure of molecule (A) of 1,1-diferrocenyl-1-methoxy-prop-2-yne (**1**), showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Distances: C(1)–C(10) = 150.3(9), C(1)–C(2) = 148.5(9), C(2)–C(3) = 115.7(10), C(1)–C(20) = 153.3(9), C(1)–O(1) = 145.7(8) pm. Angles: O(1)–C(1)–C(10) = 105.7(5)°, O(1)–C(1)–C(2) = 109.6(5)°, O(1)–C(1)–C(20) = 108.2(5)°, C(10)–C(1)–C(20) = 112.4(5)°, C(2)–C(1)–C(10) = 110.6(5)°, C(2)–C(1)–C(20) = 110.2(5)°, C(1)–C(2)–C(3) = 177.6(8)°.

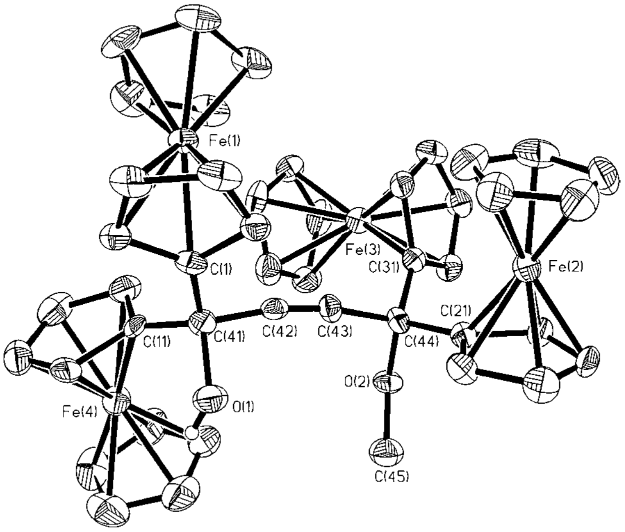

Fig. 2. Molecular structure of 1,1,4,4-tetraferrocenyl-4-hydroxy-1-methoxy-but-2-yne (**2**), showing the atom-numbering scheme. Cyclopentadienyl carbons of ferrocene 1 are C(1)–C(10), for ferrocene 2 are C(21)–C(30), for ferrocene 3 are C(31)–C(40), and for ferrocene 4 are C(11)–C(20), respectively. Hydrogen atoms, except of hydroxyl-H, and one molecule dichloromethane are omitted for clarity. Distances: C(41)–C(42) = 151.8(10), C(42)–C(43) = 116.8(8), C(43)–C(44) = 148.2(9), C(41)–O(1) = 145.3(8), C(44)–O(2) = 145.3(7), O(2)–C(45) = 143.0(8) pm. Angles: C(41)–C(42)–C(43) = 171.3(8)°, C(42)–C843)–C(44) = 170.9(8)°.

propyne moiety, which deviates from linearity [C(41)–C(42)–C(43) = 171.3(8)°, C(42)–C(43)–C(44) = 170.9(8)°] due to steric repulsion of two ferrocenyl groups. The hydroxy and methoxy groups are in a formally staggered conformation [torsion angle O(1)–C(41)–C(44)–O(2) = 62.63(58)°] so that the four ferrocenyl substituents can minimize steric congestion. Overall, Fig. 2 gives an impression of the spatial requirements of the four terminal ferrocenyl substituents attached to a C$_4$-bridging prop-2-yne ligand.

As discussed above, tetraferrocenylbutadiene (**3**) is —in the context of this project on perferrocenylated cumulenes— an undesired ''over-reduced'' product. Because of the limited amount of material available (in total 13 mg), no complete spectroscopic characterization was attempted. Luckily, single crystals were obtained, allowing unambiguous structural characterization by X-ray analysis (Table 1, Fig. 3). Butadiene (**3**) crystallizes in the monoclinic space group P2$_1$/n with two molecules per unit cell and half a molecule in the asymmetric unit. Each molecule will be produced from the half molecule by a center of symmetry. The ferrocenyl substituents are arranged in the anticipated alternating up/down fashion to minimize steric congestion, analogous to tetraferrocenylethylene [14], with twist angles of similar value [C(22)–C(21)–C(20)–C(16) = 22.17(50)°, C(22)–C(21)–C(10)–C(6) = 30.47(58)°] in reference to the adjacent two C=C planes. The butadiene backbone is planar [C(21)–C(22)–C(22a)–C(21a) = 180°] and shows normal alternating bond lengths [C(21)–C(22) = 137.3(5), C(22)–C(22a) = 142.9(7) pm] similar in value to those of the recently published tetra-t-butyl-butadiene [46–48].

Tetraferrocenyl-[3]-cumulene (**4**), the target compound of this work, is a burgundy red stable solid (m.p.

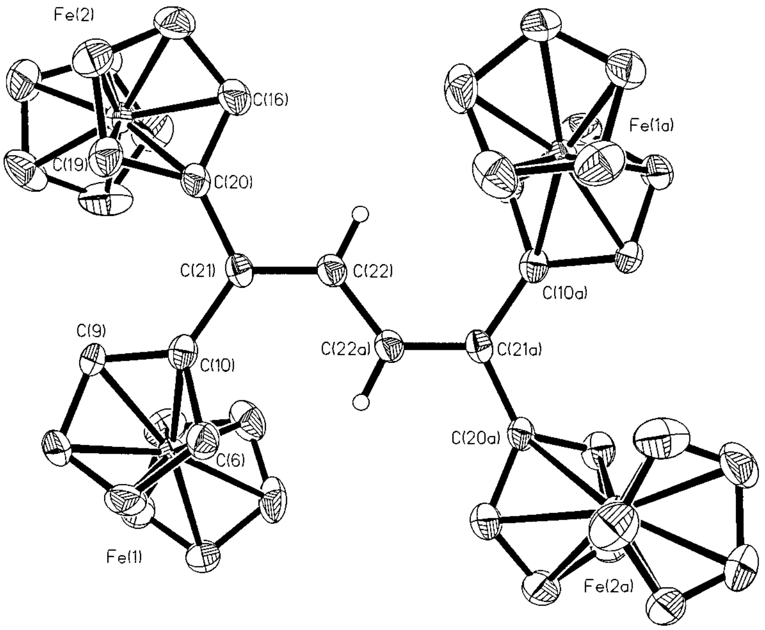

Fig. 3. Molecular structure of 1,1,4,4-tetraferrocenyl-buta-1,3-diene (**3**), showing the atom-numbering scheme; numbering of the ferrocenyl carbons is analogous to Fig. 1 and Fig. 2; hydrogen atoms are omitted for clarity. Distances: C(21)–C(22) = 137.3(5), C(21)–C(20) = 147.8(5), C(21)–C(10) = 148.2(5), C(22)–C(22a) = 142.9(7) pm. Angles: C(22)–C(21)–C(20)–C(16) = 22.17(50)°, C(22)–C(21)–C(10)–C(6) = 30.47(58)°, C(21)–C(22)–C(22a)–C(21a) = 180°.

190°C, dec.) which is only slightly soluble in common organic solvents, similar to other tetra(aryl)substituted butatrienes [43–45]. The high stability allows detection of the molecular ion ($m/z = 788$) as the base peak in the mass spectrum. The intense cumulenic stretching vibration $\nu_{C=C=C=C}$ is observed in the Raman spectrum at 1905 cm^{-1}, in accord with symmetry rules [43] and comparable in value to Raman absorptions of metallacumulenes [17]. UV–Vis spectra of tetraferrocenylethylene [14], -allene [16], -butadiene (**3**), and -butatriene (**4**) are shown in Fig. 4. In concurrence with data on tetraphenylcumulenes [43], the λ_{max} absorption of (**4**) is red-shifted in direct comparison to the corresponding allene, butadiene, or olefin.

Due to the low solubility of (**4**) and the unfavorable relaxation of the quaternary cumulenic carbons only the signals of the cyclopentadienyls ($\delta = 69.07, 69.54, 70.18$ [$Cp_{unsubst}$ and C(2,2′) and C(3,3′) of Cp_{subst}; 85.70 [C(1) of Cp_{subst}]) are detectable by ^{13}C NMR spectroscopy. The corresponding proton NMR shows the typical pattern of a normal monosubstituted ferrocene ($\delta = 4.29$ [5H, $Cp_{unsubst}$]; 4.49, 4.90 [2 × 2H, Cp_{subst}]), indicative of non-restricted rotation of these magnetically equivalent ferrocenyl substituents. Therefore in solution (i) no racemic mixture of helically chiral rotamers exist, in analogy to tetraferrocenylallene [16] but in contrast to tetraferrocenylethylene [14], and (ii) no stereoisomerism (cis/trans or syn/anti with respect to the ferrocenyl substituents) is observed. Unfortunately, no solid state structure of (**4**) is available, because only poorly diffracting single crystals could be obtained up to now. The main interest in such a crystal structure analysis would focus on the cumulenic subunit: relative bond lengths of interior versus terminal C=C bonds, and linearity of the cumulenic bridge [49–53]. In comparison to other conjugated ferrocene systems, (**4**) shows a ^{57}Fe Mössbauer absorption which is only marginally affected by the bridging ligand between the terminal ferrocene moieties [54].

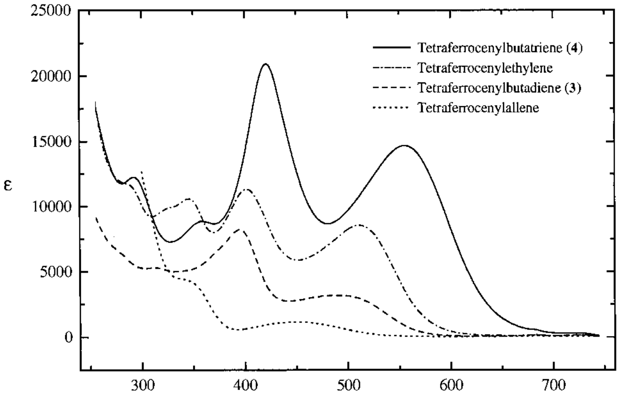

Fig. 4. Comparison of UV–vis absorptions of tetraferrocenylbutatriene (**4**), -ethylene, -butadiene (**3**), and -allene.

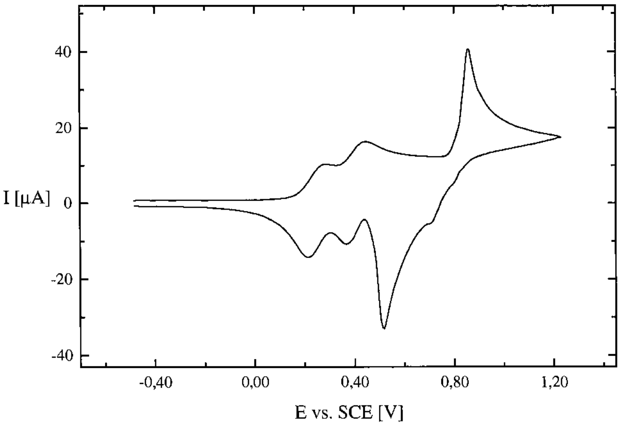

Fig. 5. Voltammogram of tetraferrocenyl-[3]-cumulene (**4**).

2.3. Redox chemistry and reactivity

Electrochemical measurements were performed to evaluate the possible reactivity of (**4**) in redox reactions. Cyclic voltammetry reveals two reversible one-electron waves (+0.25 and +0.41 V versus SCE) corresponding to ($\mathbf{4}^{+}$) and ($\mathbf{4}^{(2+)}$); for the higher oxidized species the potentials are obscured by electrode absorptions (Fig. 5). The first half-wave oxidation potential is therefore 0.23 V lower in comparison to ferrocene itself (0.48), indicating substantial electronic communication between the ferrocenyl substituents through the [3]-cumulenic bridging ligand. This is in contrast to tetraferrocenylallene where no such interaction exists [16]. On the cathodic side, the reduction to the mono- or di-anion cannot be observed in dichloromethane due to solvent decomposition below −1.5 V. The first reduction potential of (**4**) can be estimated to be out of the measurable range (in CH_2Cl_2) by comparison with the known reduction of tetraphenylbutatriene by alkali metals or biphenyl-alkali metal adducts [55].

According to these electrochemical results the preparative oxidation of (**4**) by one equivalent $AgBF_4$ [56] was attempted but the isolated polar product (presumably ($\mathbf{4}^{+}$) · $\mathbf{BF_4}$) escaped further characterization (X-ray, EPR, Mössbauer) because of its limited stability.

Metallocenes are known to form charge transfer (CT) complexes not only with traditional acceptors like tetracyanoethylene and tetracyano-*p*-quinodimethane [3], but also with [60]fullerene [57–60]. In analogy to ferrocene itself, tetraferrocenyl-[3]-cumulene (**4**) should obviously be capable of such intermolecular interactions with C_{60}, and from the cyclovoltammetric results one would expect a weak CT complex with basically neutral components. Co-crystallization of (**4**) and C_{60} from carbon

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[3] Compare Ref. [12], Ch. 8, p. 433.

disulfide solution yields nicely shaped black crystals, which contain both components according to MS, IR, TLC, but attempted X-ray crystallography of the ''best'' available crystal (0.2 × 0.2 × 0.09 mm) gave a disappointing result: only very few weak reflexes were detectable, precluding any structure analysis. Unfortunately, this is a common situation with CT complexes of weak electron donors with C_{60} and has been noted by others before [61–64]; in our experience similar problems are usually encountered with CT adducts of other ferrocene derivatives [4]. The difficulties in obtaining X-ray quality crystals are most likely due to either disordering or to non-stoichiometric CT complex formation.

Besides this essentially ferrocene-based redox or CT chemistry of (**4**), we also probed the potential reactivity of the cumulene functionality. Although the crystal structure of the precursor tetraferrocenyl-hydroxy-methoxy-butyne (**2**) (see above) serves as an indication of the steric shielding of the [3]-cumulene subunit, the following reactions were investigated, but without success: thermal or photochemical activation with or without added metal carbonyls [$Ni(CO)_2(P(C_6H_5)_3)_2$, $W(CO)_6$] did not result in any either rearranged, dimerized, or metal-carbonyl containing product, as might have been anticipated from such reactivity of other butatrienes [65–72]. Only protonation by HBF_4 is possible; this reaction —which yields a green α-ferrocenyl-stabilized cation in analogy to similar systems [15]— can be conveniently used for easy detection of (**4**) by TLC.

3. Conclusions

Tetraferrocenyl-[3]-cumulene is prepared from the corresponding 1-methoxy-4-hydroxy-prop-2-yne by reduction with stannous chloride in a solvent mixture of acetic acid and methanol. Other reducing systems, including Zn/Me_3SiCl, SmI_2, $Fe_2(CO)_9$ and $TiCl_3/Li/$ultrasound failed or gave inferior yields. In the case of the McMurry reduction tetraferrocenylbutadiene is the final product, formed most likely from an intermediate tetraferrocenyl-[3]-cumulene dianion. Tetraferrocenyl-[3]-cumulene is a very stable compound with a quite unreactive cumulenic moiety, due to steric hindrance by the four bulky ferrocenyl substituents. The first half-wave oxidation potential is shifted cathodically by 0.23 V in comparison to ferrocene, demonstrating increased donor capacity mediated by the cumulenic moiety.

4. Experimental

Standard techniques and instrumentation for spectroscopic and physical measurements have been described elsewhere [14–16,35].

Cyclic voltammetric measurements were performed at room temperature with a POS 88 Potentiostat (Bank Elektronik), using a standard three electrode apparatus, an atmosphere of purified argon, CH_2Cl_2 as solvent, and 0.1M tetrabutylammonium hexafluorophosphate ($[TBA]PF_6$) as the conducting salt. The signals were referenced to the saturated calomel electrode (SCE) by calculating the corresponding half-wave potentials from cobaltocenium/cobaltocene as an internal standard versus SCE (SCE; $E_{1/2} = -0.87$ V).

X-ray structure determinations of (**1**), (**2**), (**3**) (Tables 1–4, Figs. 1–3). General procedures of data collection, structure solution, and refinement were as recently published [14–16]. The authors have deposited atomic coordinates for all structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge, CB2 1EW, UK.

*4.1. 1,1-Diferrocenyl-1-methoxy-prop-2-yne (**1**)*

A Schlenk vessel was charged with 1.239 g (2.92 mmol) 1,1-diferrocenylpropynol [15] dissolved in 70 ml THF. The solution was cooled to −70°C under protection from air and lithiated with 1.46 ml of a 2.0 molar (2.92 mmol) n-butyl lithium/pentane solution. The stirred mixture was allowed to reach −20°C and 1.00 ml (16 mmol, 5.50 mole equivalents) methyl iodide was added. Standard aqueous work-up yielded 1.223 g (2.79 mmol, 95.6%) (**1**) as a yellow, microcrystalline solid: m.p. 109–130°C. Anal. Found: C, 65.76; H, 5.09. $C_{24}H_{22}Fe_2O$. Calc.: C, 65.79; H, 5.06%. IR (KBr): cm^{-1} 3245m, 3099w, 3081w, 2950w, 2823w, 2111w, 1652w, 1468m, 1412m, 1393m, 1258s, 1231s, 1108s, 1081s, 1065s, 820s, 670s, 509s, 498s, 492s, 457s. MS (FAB): m/z(%) 439.5(31) ($M^+ + H$), 438.5(100) (M^+), 407.5(39) ($M^+–OCH_3$), 287.2(26) ($M^+–OCH_3$, –FeCp), 286.2(94) ($M^+–OCH_3$, –FeCp, +H). ^1H NMR ($CDCl_3$): δ 2.80 (s, 1H, ≡C–H), 3.26 (s, 3H, OCH_3), 4.11 (br s, 14H, Cp_{subst} and $Cp_{unsubst}$), 4.23 (m, 2H, Cp_{subst}), 4.37 (m, 2H, Cp_{subst}). ^{13}C NMR ($CDCl_3$): δ 51.6 (CH_3); 67.2, 67.4, 67.7 (Cp_{subst}); 69.2 ($Cp_{unsubst}$); 73.9, 83.0, 92.2 (propyne). X-ray structure (Tables 1 and 2, Fig. 1): single crystals were obtained from dichloromethane/n-hexane.

*4.2. 1,1,4,4-Tetraferrocenyl-4-hydroxy-1-methoxy-but-2-yne (**2**)*

A solution of 400 mg (0.91 mmol) (**1**) in 70 ml THF was cooled to −70°C and lithiated with 0.46 ml of a

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[4] For example, tetraferrocenyl-ethylene, -allene, and pentamethylferrocene derivatives behave similarly [B. Bildstein, K. Wurst et al., unpublished].

Table 2
Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **1**

	×	y	z	U_{eq}
molecule A				
Fe(1)	1975(1)	7973(1)	9740(1)	24(1)
Fe(2)	2303(1)	12599(1)	9805(1)	23(1)
O(1)	1417(3)	9740(3)	10825(2)	24(1)
C(1)	2062(5)	10220(5)	10386(3)	21(2)
C(2)	3134(5)	10103(5)	10558(3)	24(2)
C(3)	3972(6)	9981(6)	10679(3)	34(2)
C(4)	1547(6)	10114(6)	11408(3)	39(2)
C(10)	1854(5)	9602(5)	9841(3)	21(2)
C(11)	2572(5)	9351(5)	9400(3)	24(2)
C(12)	2066(5)	8779(5)	8959(3)	31(2)
C(13)	1043(5)	8660(5)	9123(3)	27(2)
C(14)	908(5)	9163(5)	9666(3)	25(2)
C(15)	2380(7)	7353(6)	10513(4)	42(2)
C(16)	3147(6)	7194(7)	10095(4)	50(2)
C(17)	2745(7)	6555(6)	9643(4)	55(2)
C(18)	1731(6)	6350(5)	9774(4)	46(2)
C(19)	1510(6)	6830(6)	10314(3)	37(2)
C(20)	1786(5)	11417(5)	10332(3)	23(2)
C(21)	983(5)			
C(29)	3801(5)	12826(5)	9610(3)	30(2)
molecule B				
Fe(3)	184(1)	2152(1)	7648(1)	24(1)
Fe(4)	430(1)	6776(1)	7586(1)	27(1)
O(2)	1072(4)	4933(3)	6541(2)	27(1)
C(5)	416(5)	4458(5)	6971(3)	22(2)
C(6)	−645(5)	4500(5)	6786(3)	26(2)
C(7)	−1494(6)	4517(6)	6638(3)	37(2)
C(8)	926(6)	4590(6)	5961(3)	34(2)
C(30)	738(5)	3281(5)	7078(3)	23(2)
C(31)	1514(5)	2935(5)	7462(3)	27(2)
C(32)	1627(5)	1797(5)	7389(3)	31(2)
C(33)	945(6)	1433(5)	6970(3)	32(2)
C(34)	389(5)	2358(5)	6766(3)	27(2)
C(35)	−980(6)	2809(6)	8108(4)	46(2)
C(36)	−231(7)	2406(7)	8472(3)	48(2)
C(37)	−125(7)	1309(7)	8378(4)	56(3)
C(38)	−792(7)	1022(6)	7933(4)	51(2)
C(39)	−1308(6)	1941(7)	7770(3)	41(2)
C(40)	561(5)	5133(5)	7509(3)	24(2)
C(41)	−196(5)	5428(5)	7919(3)	29(2)
C(42)	265(6)	6046(5)	8360(3)	32(2)
C(43)	1307(6)	6167(5)	8225(3)	32(2)
C(44)	1483(5)	5595(5)	7701(3)	24(2)
C(45)	105(7)	7362(6)	6766(4)	42(2)
C(46)	−710(6)	7514(6)	7132(4)	45(2)
C(47)	−384(7)	8173(6)	7603(4)	53(2)
C(48)	653(7)	8413(6)	7515(4)	49(2)
C(49)	946(7)	7916(6)	7000(4)	47(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.0 molar (0.92 mmol) n-butyl lithium solution in n-pentane. After stirring for 40 min 363 mg (0.91 mmol) diferrocenylketone [23] was added and the mixture was allowed to react further at room temperature overnight, resulting in a dark blue solution due to unavoidable formation of tetraferrocenyl-[5]-cumulene [25,26]. Chromatography (basic alumina, n-hexane/dichloromethane as eluent with 0.1 ml triethylamine as base to avoid cation formation) yielded (besides unreacted diferrocenylketone and tetraferrocenyl-[5]-cumulene) 212 mg (0.254 mmol, 27.8%) (**2**) as red crystals: m.p. 104°C, dec. Anal. Found: C, 64.61; H, 4.83. $C_{45}H_{40}Fe_4O_2$. Calc.: C, 64.64; H, 4.82%. IR (KBr): cm^{-1} 3508m, 3103w, 2954w, 2854w, 2825w, 1634w, 1468w, 1455w, 1412w, 1393w, 1246w, 1204w, 1108s, 1003s, 986m, 820s, 506s, 484s. MS (FAB): m/z(%) 836.1(52) (M^+), 819.1(37) (M^+–OH), 805(100) (M^+–OCH_3), 788.1(67)

Table 3
Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **2**

	×	y	z	U_{eq}
Fe(1)	695(1)	6262(1)	3665(1)	21(1)
Fe(2)	4561(1)	8384(1)	5364(1)	27(1)
Fe(3)	5293(1)	8112(1)	2540(1)	25(1)
Fe(4)	4869(1)	4579(1)	2990(1)	31(1)
O(1)	3953(4)	5103(3)	4589(2)	33(1)
O(2)	6746(4)	7095(2)	4013(2)	25(1)
C(1)	2105(5)	5653(4)	4157(3)	23(2)
C(2)	1752(6)	6239(4)	4602(3)	26(2)
C(3)	536(6)	6103(4)	4690(3)	33(2)
C(4)	149(6)	5438(4)	4303(4)	31(2)
C(5)	1117(6)	5153(4)	3978(3)	24(2)
C(6)	1249(6)	6894(4)	2889(4)	35(2)
C(7)	591(7)	7365(4)	3284(4)	37(2)
C(8)	−573(7)	7043(4)	3257(4)	37(2)
C(9)	−622(7)	6378(5)	2840(4)	40(2)
C(10)	498(7)	6283(4)	2619(4)	42(2)
C(11)	3395(5)	5050(4)	3360(3)	21(2)
C(12)	3334(6)	4214(4)	3345(4)	30(2)
C(13)	3360(6)	3960(4)	2658(4)	40(2)
C(14)	3431(6)	4621(5)	2239(4)	42(2)
C(15)	3446(6)	5300(4)	2660(4)	34(2)
C(16)	6417(6)	4568(5)	3698(4)	48(2)
C(17)	6261(7)	3864(5)	3326(6)	57(3)
C(18)	6245(6)	4038(5)	2623(5)	52(2)
C(19)	6346(6)	4848(5)	2548(4)	48(2)
C(20)	6451(6)	5168(5)	3217(5)	43(2)
C(21)	5678(5)	7732(4)	4855(3)	22(2)
C(22)	6260(6)	8432(4)	5118(3)	29(2)
C(23)	6288(6)	8435(4)	5842(3)	34(2)
C(24)	5738(7)	7757(4)	6035(4)	37(2)
C(25)	5364(6)	7314(4)	5440(3)	29(2)
C(26)	2902(6)	8478(5)	4780(4)	42(2)
C(27)	3494(7)	9191(5)	4820(4)	44(2)
C(28)	3750(7)	9413(4)	5520(5)	48(2)
C(36)	5405(7)	7002(4)	2216(3)	36(2)
C(37)	4319(6)	7330(4)	1906(3)	33(2)
C(38)	4605(6)	7991(4)	1517(3)	31(2)
C(39)	5856(7)	8060(4)	1593(4)	38(2)
C(40)	6356(6)	7443(5)	2022(4)	39(2)
C(41)	3366(6)	5533(4)	3997(3)	25(2)
C(42)	4042(6)	6287(4)	3957(3)	22(2)
C(43)	4673(6)	6827(4)	3996(3)	23(2)
C(44)	5607(6)	7433(4)	4116(3)	23(2)
C(45)	7242(6)	6562(4)	4537(4)	39(2)
C(46)	−81(10)	8873(7)	5431(6)	64(4)
Cl(1)	−991(4)	9573(2)	5590(3)	119(2)
Cl(2)	−536(4)	8301(3)	4745(2)	121(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **3**

	x	y	z	U_{eq}
Fe(1)	6263(1)	1808(1)	3279(1)	24(1)
Fe(2)	3618(1)	−1963(1)	1525(1)	24(1)
C(1)	5668(4)	3212(4)	3966(3)	40(1)
C(2)	6451(4)	3683(4)	3505(3)	38(1)
C(3)	5968(4)	3401(4)	2395(3)	37(1)
C(4)	4890(4)	2756(4)	2153(3)	41(1)
C(5)	4710(4)	2635(4)	3133(4)	39(1)
C(6)	7189(3)	544(4)	4440(3)	28(1)
C(7)	7910(3)	1034(4)	3936(3)	34(1)
C(8)	7373(3)	767(3)	2814(3)	30(1)
C(9)	6312(3)	117(3)	2634(3)	25(1)
C(10)	6175(3)	−31(3)	3642(3)	23(1)
C(11)	2255(4)	−746(4)	826(3)	43(1)
C(12)	2041(4)	−1843(4)	221(3)	40(1)
C(13)	2965(4)	−2040(4)	−123(3)	46(1)
C(14)	3770(4)	−1051(5)	266(3)	47(1)
C(15)	3329(4)	−259(4)	847(3)	47(1)
C(16)	3634(4)	−2419(4)	2994(3)	32(1)
C(17)	3520(4)	−3497(4)	2369(3)	37(1)
C(18)	4517(4)	−3565(4)	2088(3)	36(1)
C(19)	5252(4)	−2534(3)	2549(3)	30(1)
C(20)	4725(3)	−1815(3)	3132(3)	23(1)
C(21)	5222(3)	−723(3)	3810(3)	21(1)
C(22)	4840(3)	−500(3)	4627(3)	24(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Symmetry transformations to generate equivalent atoms: $-x+1$; $-y$; $-z+1$.

(M^+–OCH_3, –OH), 667(80) (M^+–OCH_3, –FeCp, –OH). ^{1}H NMR (THF-D_8): δ 3.32 (s, 3H, OCH_3), 3.58 (s, 10H, $Cp_{unsubst}$), 4.20 (m, 6H, Cp_{subst}), 4.26 (s, 10H, $Cp_{unsubst}$), 4.44 (m, 6H, Cp_{subst}), 4.53 (m, 2H, Cp_{subst}), 4.58 (m, 2H, Cp_{subst}), 5.51 (s, 1H, OH). ^{13}C NMR (THF-D_8): δ 52.2 (CH_3); 66.7–70.18 (Cp_{subst} and $Cp_{unsubst}$). X-ray structure (Tables 1–3, Fig. 2): single crystals were obtained from dichloromethane/n-hexane.

*4.3. 1,1,4,4-Tetraferrocenyl-buta-1,3-diene (**3**)*

A Schlenk vessel, containing a mixture of 20 ml dimethoxyethane (DME), 44 mg $TiCl_3 \cdot 3THF$ (0.12 mmol) and 3 mg (0.43 mmol) Li powder, was immersed in an ultrasound cleaning bath and sonicated for 30 min, resulting in a dark suspension of low-valent titanium. After adding 20 mg (0.024 mmol) (**2**) under protection from air the suspension was stirred at room temperature overnight. Work-up: insoluble materials were filtered off through a short plug of alumina, the solution was evaporated to dryness, and the crude product mixture chromatographed, yielding 13 mg (0.016 mmol, 69%) (**3**) as red crystals: m.p. 150°C, dec. IR (KBr): cm^{-1} 3591w, 3093w, 2927w, 2858w, 1727w, 1630w, 1461w, 1391w, 1264w, 1125w, 1108s, 1061m, 1036m, 1000m, 951w, 859w, 808s, 704w, 652w, 575w, 473s. MS (EI, 70 eV): m/z(%) 790(100) (M^+), 788(25) (M^+–2H), 605(9) (M^+–Fc), 418(12) (M^+–2H, –2Fc), 395(19) (M^+–2Fc–CH=CH). UV–Vis (CH_2Cl_2) (Fig. 4): λ_{max}/log ϵ 313/3.72, 396/3.91, 487/3.50 nm/log ϵ. ^{1}H NMR, ^{13}C NMR, and elemental analysis were not attempted because of only 13 mg material available. X-ray structure (Tables 1 and 4, Fig. 3): single crystals were obtained from dichloromethane/ether.

*4.4. Tetraferrocenyl-[3]-cumulene (tetraferrocenylbutatriene) (**4**)*

A solution of 327 mg (1.73 mmol, 6.0 mole equivalents) $SnCl_2$ in 10 ml 50% acetic acid was combined with a suspension of 241 mg (0.289 mmol, 1.0 mole equivalents) (**2**) in 25 ml methanol. The color of the mixture changed from yellow to brown upon addition of the reductant, and upon refluxing, to dark purple. The mixture was heated to reflux for two hours. Aqueous work-up yielded 169 mg (0.214 mmol, 74%) (**4**) as a burgundy red microcrystalline solid: m.p. 104°C, dec. Anal. Found: C, 67.02; H,4.62. $C_{44}H_{36}Fe_4$. Calc.: C, 67.05; H, 4.60%. IR (KBr): cm^{-1} 3095w, 2962w, 2927w, 1634w, 1569w, 1412w, 1389w, 1288w, 1262w, 1198w, 1106m, 1057m, 1027m, 1001s, 903m, 816m, 805m, 793m, 488m, 471s. Raman: $\nu_{C=C=C=C}$ 1905 cm^{-1}. MS (EI, 70 eV): m/z(%) 788(100) (M^+), 602(10) (M^+–Fc, +H), 394(16) (M^+–2Fc–C=C). UV–Vis (CH_2Cl_2) (Fig. 4): λ_{max}/log ϵ 292/4.09, 359/3.95, 421/4.32, 555.5/4.17 nm/log ϵ. ^{1}H NMR (CD_2Cl_2): δ 4.29 (s, 20H, $Cp_{unsubst}$), 4.49 (br s, 8H, Cp_{subst}), 4.90 (br s, 8H, Cp_{subst}). ^{13}C NMR (CD_2Cl_2): δ 69.07, 69.54, 70.18 ($Cp_{unsubst}$ and C(2,2′) and C(3,3′) of Cp_{subst}); 85.70 (C(1) of Cp_{subst}); not observed: cumulenic carbon signals. CV (CH_2Cl_2; 20°C, Fig. 5) [V]: 0.25, 0.41.

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