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In situ synthesis of the first C_7 cumulene $(Fc)_2C{=}C{=}C{=}C{=}C{=}C{=}C(Fc)_2$ via deprotonation of its conjugate acid $[(Fc)_2C_7H(Fc)_2]^+BF_4^-$ (Fc = ferrocenyl)

Benno Bildstein *, Wolfgang Skibar, 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

Copper-mediated cross-coupling of diferrocenyl propargylic and homopropargylic C_3 and C_4 building blocks yields an α,ω-dimethoxy-tetraferrocenyl C_7 cumulene precursor together with a C_8 homo-coupled byproduct. Subsequent acid-promoted twofold elimination of methanol gives access to tetraferrocenylheptapentaenylium tetrafluoroborate which can be deprotonated by non-nucleophilic strong bases to cumulene $(Fc)_2C_7(Fc)_2$. Although this compound can be handled in solution only, UV–vis spectroscopic evidence and trapping experiments (hydrolysis and transition metal complex formation) support the existence of this first compound containing seven cumulated carbons. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene; Iron; Cumulene; Heptahexaene; X-ray structures

1. Introduction

The chemistry of carbon-rich organometallic compounds containing linear, conjugated sp carbon chains has attracted much interest in recent years due to their potential use in molecular electronics and/or materials science [1]. Within this area, compounds with acetylenic and/or cumulenic rigid rods [2] connecting metal carbene endgroups ('metall**a**cumulenes' $L_n[M]{=}(C{=}C)_n{=}[M]L_n$) have received a great deal of attention [3,4]. In contrast, 'metall**o**cumulenes' $[M]_2C{=}C_n{=}C[M]_2$ with σ-bonded organometallic termini on the cumulene moiety are comparatively unexplored although such systems are closely related to simple organic cumulenes $R_2C{=}C_n{=}CR_2$ which are known to be stable and isolable up to a chain length of six cumulated carbons [5]. Interestingly, no organic C_7 cumulene with seven cumulated carbons has ever been reported [6] and longer even-numbered cumulenes C_8 [7] and C_{10} [8] seem to be stable in solution only. On the other hand, we have shown earlier that ferrocenyl metall**o**cumulenes $(Fc)_2C_n(Fc)_2$ with a chain length of up to six carbons can be prepared by synthetic methods which take into account the special electronic and steric properties of the metallocenyl groups [9]. Electrochemical and UV–vis measurements showed that for even-numbered cumulenes $(Fc)_2C_n(Fc)_2$ with $n = 2, 4, 6$ the electronic communication through the sp carbon chain decreases with increasing length of the cumulene moiety, whereas odd-numbered cumulenes $(Fc)_2C_n(Fc)_2$ with $n = 3, 5$ are electronically decoupled due to the orthogonal and therefore non-interacting pairs of ferrocenyl termini [9]. Accordingly, one would expect that elongated odd-numbered cumulenes [C_7, C_9, C_{11}, etc] are in general more stable than the increasingly electron-rich and reactive even-numbered cumulenes. Hence there is a good chance of synthesizing a tetraferrocenyl-C_7-cumulene on electronic arguments [5c], in addition, the four bulky ferrocenyl substituents will kinetically stabilize the sp carbon chain.

In this report we summarize our synthetic approaches toward tetraferrocenylheptapentaene $(Fc)_2C_7(Fc)_2$ and its chemical and physical properties.

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* Corresponding author. Tel.: +43-512-5075141; fax: +43-512-5072934.

E-mail address: benno.bildstein@uibk.ac.at (B. Bildstein).

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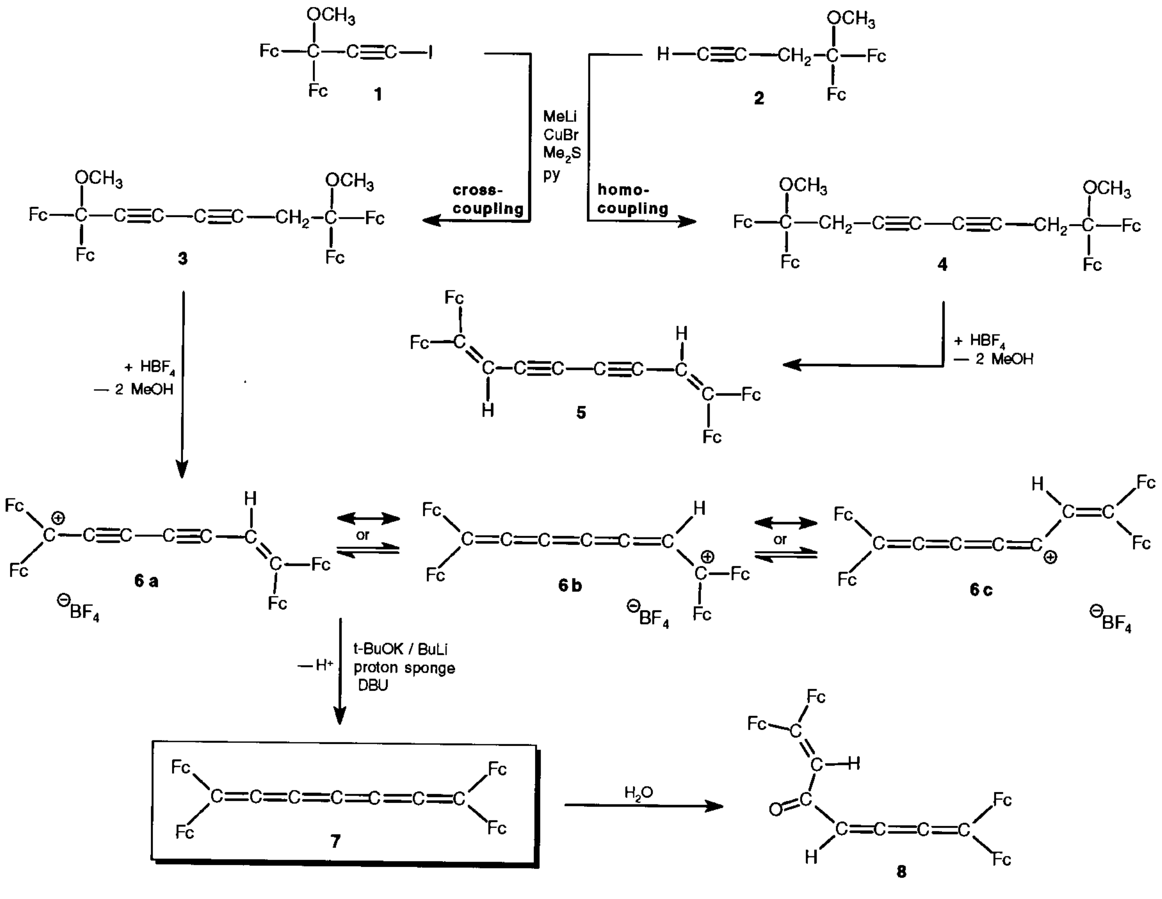
2. Results and discussion

The general synthetic strategy to form the C_7 sp carbon chain is based on the preparation of the shorter homologue $(Fc)_2C_5(Fc)_2$ [10], only one additional acetylene unit has to be introduced in the precursors (Scheme 1). Accordingly, diferrocenyl(iodo)-methoxypropyne (**1**) [10] was cross-coupled with diferrocenylmethoxybutyne (**2**) [10] to afford the desired heptadiyne **3** (25% yield) and the homo-coupled octadiyne **4** (45% yield) as byproduct. We undertook a few attempts to optimize this reaction in terms of selectivity (cross vs homocoupling) using Pd catalyzed Sonogashira protocols [11], however, no substantial improvements were possible. Precursors **3** and **4** have been characterized by the usual spectroscopic methods (compare Section 4) and the data are in agreement with the structural formulas in Scheme 1. In addition, an X-ray structure (Table 1) of heptadiyne **3** clearly showed the seven carbon subunit with four ferrocenyl endgroups, relevant bond distances and angles are given in the figure caption of Fig. 1.

Both compounds **3** and **4** contain two terminal methoxy groups adjacent to ferrocenyl substituents which strongly stabilize α-carbenium centers [12]. Hence addition of one equivalent of tetrafluoroboric acid caused elimination of two equivalents of methanol in accord with the two pairs of terminal ferrocenyl groups, yielding highly unsaturated red ($\lambda_{max} = 508.5$ nm, $\log \varepsilon = 4.13$) octadiendiyne **5** and purple ($\lambda_{max} = 856$ nm, $\log \varepsilon = 4.26$) cumulated carbenium salt **6a**,**b**,**c**, respectively. Compound **5** is fully characterized by spectroscopic techniques (compare experimental part) and an X-ray single structure analysis (Table 1) gave further proof of the identity of **5** (Fig. 2).

Cumulenium salt **6a**,**b**,**c** is a very unusual air-stable carbenium salt. The stability of the electron-deficient carbenium center of **6a**,**b**,**c** is due to the presence of four terminal ferrocene donors in combination with the unsaturation of the conjugating C_7 sp carbon chain. FAB mass spectroscopy gave the molecular ion of the cation (*m*/*z* 825) and IR spectroscopy showed a very intense cumulene stretching vibration at 2099 cm^{-1}, very similar in value as in the shorter homologue $[(Fc)_2C_5H(Fc)_2]^+BF_4^-$ [10]. ^1H-NMR spectroscopy gave one signal ($\delta = 5.97$ ppm) for the C_7H subunit together with resonances of at least three magnetically nonequivalent ferrocenyl groups. In the ^{13}C-NMR spectrum, seven sp/sp^2 carbon signals ($\delta = 92.9$, 100.7, 101.7, 150.3, 162.80, 162.88, 162.91 ppm) were detected for



Scheme 1. Synthesis of compounds **1**–**8** (Fc = ferrocenyl)

Table 1
Crystal data and structure refinement for **3** and **5**

	3	**5**
Molecular formula	$C_{49}H_{44}Fe_4O_2$	$C_{48}H_{38}Fe_4$
Formula weight	888.24	838.18
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	1782.4(2)	1601.48(7)
b (Å)	1198.0(1)	1274.25(3)
c (Å)	1791.3(5)	1758.86(8)
α (°)	90	90
β (°)	97.85(1)	99.239(2)
γ (°)	90	90
V (Å^3)	3.7891(12)	3.5427(2)
Z	4	4
Temperature (K)	213(2)	213(2)
D_{calc} (Mg m^{-3})	1.557	1.571
Absorption coefficient (mm^{-1})	1.543	1.641
F(000)	1832	1720
Color, habit	Orange, plate	Red, prism
Crystal size (mm)	0.6 × 0.38 × 0.24	0.25 × 0.14 × 0.07
θ range for data collection (°)	3.02–22.50	1.60–21.00
Index ranges	$0 \leq h \leq 17$ $0 \leq k \leq 12$ $-19 \leq l \leq 19$	$0 \leq h \leq 18$ $0 \leq k \leq 14$ $-20 \leq l \leq 20$
Reflections collected	4987	7315
Independent reflections	4805 [$R_{int} = 0.0211$]	3803 [$R_{int} = 0.0266$]
Reflections observed $I > 2s(I)$	3865	2686
Absorption correction	ψ-scan	None
Max/min transmission	1.000/0.792	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4524/0/497	3494/0/470
Goodness-of-fit on F^2	1.032	1.005
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0307$ $wR_2 = 0.0636$	$R_1 = 0.0385$ $wR_2 = 0.0929$
R indices (all data)	$R_1 = 0.0473$ $wR_2 = 0.0714$	$R_1 = 0.0632$ $wR_2 = 0.1070$
Extinction coefficient	0.00053(5)	0.00026(11)
Max diff peak/hole (e × nm^{-3})	279 and −259	1021 and −276

the C_7H moiety besides the acceptor-shifted ferrocene carbon resonances. Unfortunately, no suitable single crystals could be obtained until now and therefore the precise structure of this cumulated carbenium salt cannot be derived from the available spectroscopic data. However, the known cation-stabilizing mechanism of ferrocenyl groups interacting with a neighbouring electron-deficient carbenium center involves important resonance contribution by a (η^6-fulvene)(η^5-cyclopentadienyl)iron(II) [12], hence on electronic arguments one would consider formulas **6a** and **6b** as the predominant structural forms. In addition, the very similar spectroscopic IR and UV–vis data of **6a**,**b**,**c** in comparison with its shorter homologue $[(Fc)_2C_5H(Fc)_2]^+$ BF_4^- [10] indicates that the additional two sp carbons do not interact significantly with the carbenium center, therefore structure **6a** with only slightly conjugating acetylenic subunits is the most probable structural form (as opposed to the more conjugated cumulene structure **6b**). On the side and from an application oriented perspective we note that carbenium salt **6a**,**b**,**c** (λ_{max} = 856 nm, log ε = 4.26) may be viewed as a new organometallic [13] near-infrared absorbing dye [14] and a new ferrocene-based [15] NLO chromophore [16].

From a chemical viewpoint **6a**,**b**,**c** is the conjugate acid of tetraferrocenylheptahexaene $(Fc)_2C{=}C{=}C{=}C{=}C{=}C{=}C(Fc)_2$, the target compound of this work. Hence deprotonation of **6a**,**b**,**c** by suitable non-nucleophilic and suffiently strong bases should in

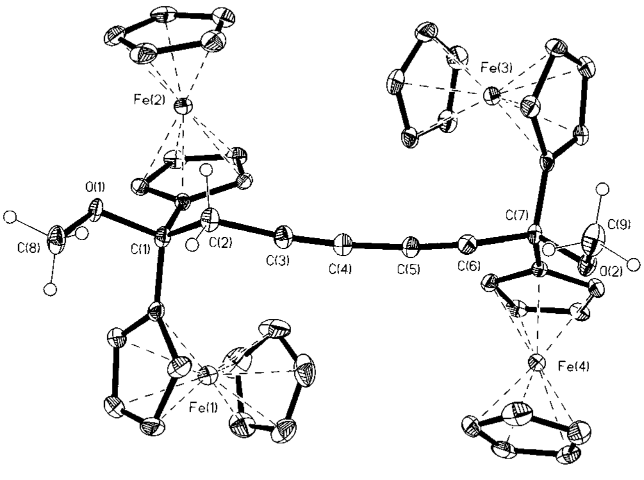


Fig. 1. Molecular structure of **3**, showing the atom numbering scheme. Ferrocenyl hydrogen atoms are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(10)–C(19), for ferrocene 2 C(20)–C(29), for ferrocene 3 C(30)–C(39), and for ferrocene 4 C(40)–C(49), respectively. Selected bond distances (pm): C(1)–C(2) = 154.6(5), C(2)–C(3) = 146.7(5), C(3)–C(4) = 118.5(4), C(4)–C(5) = 137.7(5), C(5)–C(6) = 119.5(4), C(6)–C(7) = 148.6(5).

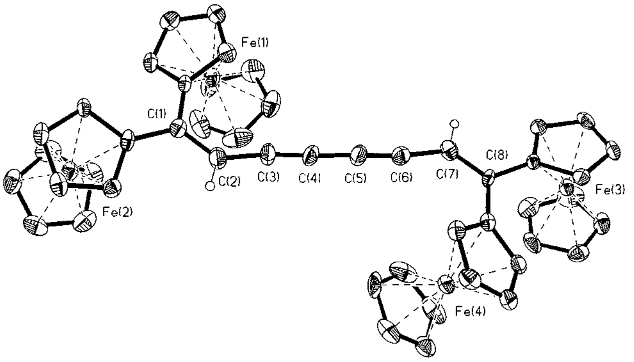


Fig. 2. Molecular structure of **5**, showing the atom numbering scheme. Ferrocenyl hydrogen atoms are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1–4 are numbered analogously as in Fig. 1. Selected bond distances (pm): C(1)–C(2) = 136.8(6), C(2)–C(3) = 141.0(7), C(3)–C(4) = 120.4(7), C(4)–C(5) = 136.7(8), C(5)–C(6) = 121.5(7), C(6)–C(7) = 141.8(7), C(7)–C(8) = 134.8(6).

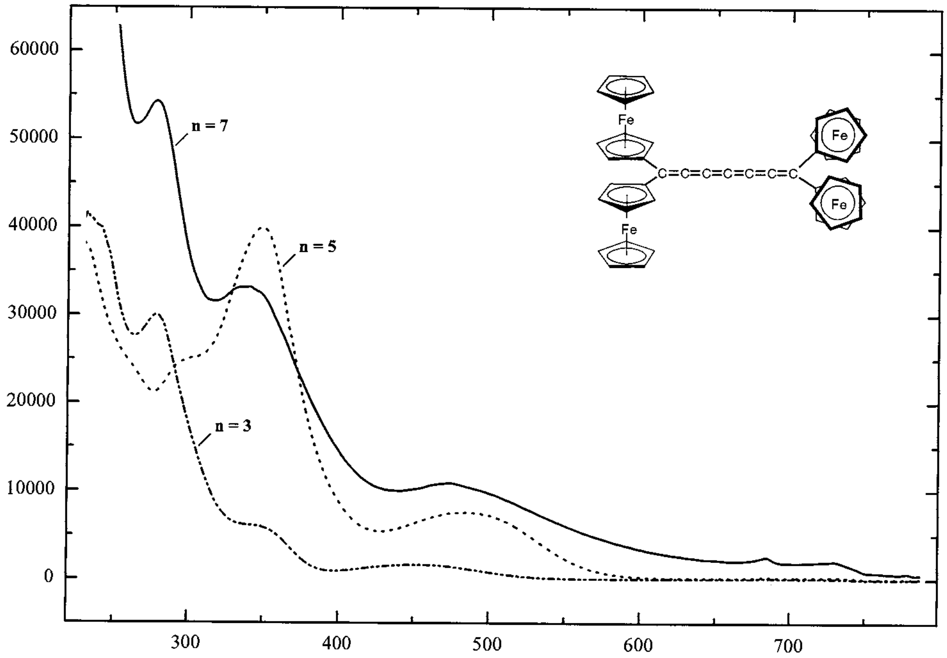


Fig. 3. UV–vis spectra of odd-numbered cumulenes $(Fc)_2C_n(Fc)_2$ with $n = 3, 5, 7$.

principle afford the desired C_7 cumulene. Based on our experience [10] with the shorter homologue $[(Fc)_2C_5H(Fc)_2]^+BF_4^-$ where attempted deprotonation with common basic reagents such as *t*-butyl lithium, lithium diisopropylamide, and potassium *t*-butoxide only afforded nucleophilic addition products, these common reagents were not tried in the present case. We screened on a small scale a number of strong hindered bases for this reaction, and indeed, direct deprotonation of **6a**,**b**,**c** proved possible with either (a) the 'superbasic' mixture of *n*-butyl lithium with potassium *t*-butoxide (*t*-BuOK/*n*-BuLi) [17], or (b) 'proton sponge' 1,8-bis(-dimethylamino)naphthalene [18], or (c) 'DBU' 1,8-diazabicyclo[5.4.0]undec-7-ene [19], yielding burgundy red solutions of **7** (vide infra). Experimentally, the course of the deprotonation could be followed by a rather slow fading in color (from dark purple to red within 5–12 h) of mixtures of THF solutions of **6a**,**b**,**c** with the basic reagents (b) and (c), whereas an almost immediate reaction was observed with super base (a), indicating decreasing kinetic basicity in the order (a) ≫ (b) > (c). Qualitatively, common TLC analysis of the red solutions (without protection from air) showed a red apolar product which was converted within a few min into a more polar red follow-up compound, suggesting formation of the same air-sensitive product with all three basic reagents. In addition, exposure of these TLC plates to HCL vapor gave a dark purple spot corresponding in its properties to the starting material **6a**,**b**,**c**, suggesting that deprotonation has occurred to cumulene **7** which may be protonated to **6a**,**b**,**c** if a strong acid is present before hydrolysis occurs. These observations strongly supported the existence of **7** as a red and air-sensitive but nevertheless surprisingly stable compound and consequently we set out to isolate and characterize this first C_7 cumulene.

For over two years we have been modifying the experimental conditions (choice and concentration of base, solvent, reaction period, workup procedure, etc) to get access to pure cumulene **7**, but without success—very much to our frustration. Our 'best' conditions are deprotonation of **6a**,**b**,**c** in THF with super base *t*-BuOK/*n*-BuLi and subsequent filtration over Celite® under an atmosphere of argon, yielding an air-sensitive red THF solution of **7**. Fig. 3 shows a UV–vis spectrum of this solution ($\lambda_{max} = 278$, 341, 474 mn) in comparison with the absorptions of the shorter odd-numbered cumulenes $(Fc)_2C_3(Fc)_2$ ($\lambda_{max} = 279$, 345, 447 nm) [20] and $(Fc)_2C_5(Fc)_2$ ($\lambda_{max} = 286$, 349, 483 nm) [10]. As anticipated, on increasing the length of the cumulene chain the position of the bands are almost unshifted, in accordance with the orthogonal and electronically decoupled π orbitals of odd-numbered cumulenes ruling out interaction between the two end-capping pairs of ferrocenyl termini. However, the longest wavelength bands become slightly more intense, suggesting a small increase of the MLCT band as a consequence of a lowering of the energy of the π* orbitals of the cumulene due to the presence of one, two, and three conjugated cumulene π bonds in the series $(Fc)_2C{=}C{=}C(Fc)_2$, $(Fc)_2C{=}C{=}C{=}C{=}C(Fc)_2$, and $(Fc)_2C{=}C{=}C{=}C{=}C{=}C{=}C(Fc)_2$.

Repeated attempts to crystallize **7** from these THF solutions under a variety of conditions met with failure, and when all volatiles were removed in vacuo at temperatures as low as possible only brown amorphous and quite insoluble material was obtained. FAB mass spectrometry of this material did not show any reasonable molecular ion, indicating decomposition and/or oligomerization of **7** in the solid state. Therefore measurement of further spectroscopic properties of **7** are precluded by its bulk instability. It has been observed earlier for organic C_8 [7] and C_{10} [8] cumulenes that such compounds are detectable in solution only and our results on $(Fc)_2C_7(Fc)_2$ **7** suggest that also C_7 cumulenes in general behave in an analogous manner. This indicates also that four ferrocenyl termini give insufficient steric protection to prevent intermolecular decomposition pathways of the C_7 cumulene chain.

The older literature on organic aromatic C_8 [7] and C_{10} [8] cumulenes–in combination with modern concepts in supramolecular chemistry–gives a possible clue how such reactive species might be stabilized: It has been observed in the case of tetraphenyloctaheptaene $(C_6H_5)_2C_8(C_6H_5)_2$ [7a] that host–guest chemistry allowed isolation of crystalline adducts in which intermolecular decomposition of the cumulene guest is precluded by spacing due to the host lattice. Various aromatic compounds have been employed as hosts, a guiding principle was the use of structurally related compounds and/or precursors of the cumulene. Specifically, benzophenone and 1,1,8,8-tetraphenyl-octa-2,4,6-triyne-1,8-diol (and other aromatics) were employed and in the case of the ketone a stable compound which retained its typical purple cumulene color was obtained [7a]. We adapted this strategy and cocrystallized ferrocenyl cumulene **7** with 1,1,6,6-tetraphenyl-hexa-2,4-diyne-1,6-diol which is (i) of comparable length as C_7 cumulene **7**, (ii) capable of forming hydrogen bonds between a nucleophilic guest like **7**, and (iii) known for its extensive supramolecular chemistry with a range of organic compounds [21]. However, when concentrated THF solutions of **7** and 1,1,6,6-tetraphenyl-hexa-2,4-diyne-1,6-diol were combined under various conditions, only amorphous brown material was obtained and none of the desired crystalline 1:1 or 1:2 host–guest complex. The negative outcome of these experiments might be rationalized by either the wrong choice of host or a principal difficulty of host–guest-complex formation of odd-numbered cumulenes with their orthogonal pairs of substituents.

To further prove the existence of cumulene **7** and/or to screen its reactivity, the following trapping experiments were performed: (i) Hydrolysis (Scheme 1). Deliberate exposure of cumulene **7** to moisture resulted in addition of H_2O with partial destruction of the cumulene sp moiety, the only tractable product was heptatetraenone **8** which was formed obviously via the corresponding cumulene enol. Compound **8** was characterized by MS, NMR, and IR spectroscopy; the most prominent features are observation of the molecular ion in the positive mode FAB mass spectrum, detection of four nonequivalent ferrocenyl groups and two vinyl/cumulenyl hydrogen signals in the ^{1}H-NMR spectrum, and an intense carbonyl band plus a weak cumulene absorption in the IR spectrum (compare Section 4). We also note that the same ketone could not be obtained by reaction of cumulenium salt **6a**,**b**,**c** with aqueous base, indicating that cumulene **7** is a necessary progenitor of ketone **8**. (ii) Coordination chemistry. Cumulenes in general [22] and also tetraferrocenylcumulenes [9,23] are capable of forming olefin-like metal complexes with electron-rich late transition metal fragments. Reactions of solutions of **7** with $Fe_2(CO)_9$, $RhCl(PR_3)_3$, $IrCl(CO)(PR_3)_2$, $Ni(CO)_2(PR_3)_2$, and $Pt(PR_3)_4$, respectively, yielded very dark reaction mixtures which were free of the starting material **7** according to TLC analysis, indicative of complex formation in each case. However, only in the reaction with Pt(0) it was possible to isolate a red compound (after the usual workup and column chromatography) in minimal amounts (ca 3 mg). FAB mass spectroscopy of this material gave two intense high-mass peaks corresponding to $Pt(PR_3)_2$ and $(Fc)_2C_7(Fc)_2$ **7**, but no signal of the expected molecular ion of $[(Fc)_2C_7(Fc)_2][Pt(PR_3)_2]$. Unfortunately, repeated attempts to scale up this reaction did not allow isolation of more material, therefore we have no additional informative spectroscopic properties for this complex. (iii) Cycloadditions. Tetraferrocenyl-C_6-cumulene has been shown to yield novel [2 + 2] cycloadducts with acceptor-substituted dienophiles like tetracyanoethylene (TCNE), dimethyl acetylenedicarboxylate (DMAD), and fullerene C_{60} [23]. Therefore we were interested if C_7 cumulene **7** will react in an analogous manner. On interaction of **7** with fullerene C_{60} or DMAD no stable cycloadducts could be observed, indicating insufficient electrophilicity of DMAD and C_{60} or insufficient nucleophilicity of **7**, respectively. We had shown earlier that only the very electron-rich tetraferrocenyl-C_6-cumulene affords isolable fullerene [2 + 2] cycloadducts, in contrast to less electron-rich organic C_6 arylcumulenes [23]. However, on reaction of **7** with the highly electrophilic TCNE [24] an immediate reaction at room temperature was observed, but we were unable to isolate a pure product from the obtained reaction mixture, due to the complex product distribution and due to the lability of the obtained compounds on attempted chromatographic separation.

3. Summary

Synthetically, a protonated C_7 cumulene sp carbon chain with four ferrocenyl termini can be prepared by cross-coupling of diferrocenyl-methoxy-propargylic/homopropargylic C_3 and C_4 precursors followed by acidinduced elimination of methanol, yielding an air-stable cumulenium salt $[(Fc)_2C_7H(Fc)_2]^+BF_4^-$. Deprotonation using strong and sterically hindered bases affords air-sensitive solutions of tetraferrocenyl-C_7-cumulene $(Fc)_2C{=}C{=}C{=}C{=}C{=}C{=}C(Fc)_2$ (tetraferrocenylheptahexaene, tetraferrocenyl[6]cumulene) as indicated by its UV–vis spectrum, TLC analysis, and conversion to the starting material on treatment with mineral acid.

Chemically, this first C_7 cumulene is stable in solution only and decomposes to insoluble oligomerized/polymerized untractable material on attempted isolation. Trapping experiments aiming at metal complex formation and cycloaddition with transition metal electrophiles or acceptor-substituted olefins, respectively, gave support for the existence of the cumulene in some cases, although due to the lability of the complexes/cycloadducts none of these derivatives could be synthesized in preparative amounts. On the other hand, hydrolysis affords a highly unsaturated ketone formed by addition of one equivalent of water via the corresponding cumulene enol. Taken together, these results indicate that tetraferrocenyl-C_7-cumulene is a rather weak π-donor with a cumulene moiety of low nucleophilicity and of comparable low reactivity as in its shorter homologue tetraferrocenyl-C_5-cumulene. The limited steric protection of the C_7 sp carbon chain by the four ferrocenyl endgroups is insufficient for a kinetic stabilization of most C_7-cumulene derivatives.

4. Experimental

4.1. General

Reactions of air-sensitive materials were carried out using standard Schlenk techniques. Solvents were carefully deoxygenated, purified, and dried prior to use. Spectroscopic measurements (IR, MS, NMR, UV–vis, X-ray analysis) were performed with instruments and techniques as described previously [25].

*4.2. Synthesis of 1,1,7,7-tetraferrocenyl-1,7-dimethoxy-hepta-2,4-diyne (**3**) and 1,1,8,8-tetraferrocenyl-1,8-dimethoxy-octa-3,5-diyne (**4**)*

A Schlenk vessel was charged with 273 mg (0.60 mmol) 1,1-diferrocenyl-1-methoxy-but-3-yne [10] and 100 ml of dry THF. The solution was cooled to −60°C, 0.38 ml of a 1.6 molar solution (0.61 mmol) of methyllithium in ether was added, the cooling bath was removed and the stirred mixture was allowed to warm to room temperature (r.t.). After lithiation was complete, the solution was cooled to −60°C and 700 mg (3.4 mmol) of $Cu[(CH_3)_2S]Br$ was added. The cooling bath was removed and the mixture was allowed to warm to r.t. A color change from yellow to red indicated that transmetalation had occured. Solvents and volatile materials were evaporated on a vacuum line until approximately a 5 ml residual mixture was obtained. The vessel was back-filled with argon and 50 ml of dry, freshly distilled argon-saturated pyridine and 341 mg (0.60 mmol) of 3,3-diferrocenyl-1-iodo-3-methoxy-propyne [10] was added. This mixture was refluxed for half an hour, then all volatiles were removed in vacuo, leaving an oily pyridine-containing residue. Workup: To aid in removal of pyridine, dichloromethane and hexane was added, the Schlenk vessel was immersed in an ultrasonic bath and sonicated for 15 min, and the mixture of solvents was removed in vacuo, yielding a brown solid residue. The crude product mixture was dissolved in dichloromethane, the organic layer was washed with three portions of water, and dried over Na_2SO_4. Chromatography (basic alumina, *n*-hexane:ether 4:1) yielded 137 mg (0.154 mmol, 25.5%) **3** and 125 mg (0.138 mmol, 20.8%) **4**.

Data for **3**: yellow crystals, m.p. 182°C. ^{1}H-NMR ($CDCl_3$): 3.29 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 3.40 (s, 2H, CH_2), 4.10 (m, 4H, Cp_{subst}), 4.16 (s, 20H, $Cp_{unsubst}$), 4.20 (m, 6H, Cp_{subst}), 4.33–4.38 (m, 6H, Cp_{subst}). ^{13}C-NMR ($CDCl_3$): 32.0 (CH_2); 51.6 (OCH_3); 52.0 (OCH_3); 67.2, 67.3, 67.4, 67.7 (Cp_{subst}); 69.2, 69.3 ($Cp_{unsubst}$); 76.4, 78.9 ($C\equiv C$); 92.1, 93.3 (C(1) of Cp_{subst}). MS (EI 70 eV): 888 (M^+, 58%), 857 (M^+ $-OCH_3$, 91%), 856 (M^+-OCH_3-H, 100%), 826 (M^+-2 OCH_3, 22%), 736 (M^+-OCH_3-FeCp, 62%), 705 (M^+-2 OCH_3-FeCp, 28%). IR (KBr): 3093w, 2935w, 2823w, 2250w ($\nu_{C\equiv C}$), 1638m, 1414w, 1391w, 1283w, 1264w, 1241w, 1108s, 1081s, 1046m, 1032m, 1003m, 938w, 820s, 683w, 511m, 494s, 480m. Anal. Calc. (found): C, 66.26 (66.46), H 4.99 (4.97)%. X-ray analysis (Table 1, Fig. 1): single crystals were obtained from dichloromethane–*n*-hexane.

Data for **4**: yellow microcrystalline solid, m.p. 178–179°C. ^{1}H-NMR ($CDCl_3$): 3.29 (s, 10H, $OCH_3 + CH_2$), 4.11 (s, 20H, $Cp_{unsubst}$), 4.15 (m, 8H, Cp_{subst}), 4.30 (m, 8H, Cp_{subst}). ^{13}C-NMR ($CDCl_3$): 31.4 (CH_2); 51.6 (OCH_3); 67.1, 67.2, 67.4 (Cp_{subst}); 69.2 ($Cp_{unsubst}$); 75.3 ($C\equiv C$); 93.7 (C(1) of Cp_{subst}). (+)-FAB-MS: 903 (M^+ + H, 60%), 902 (M^+, 100%), 871 (M^+-OCH_3, 30%), 719 (M^+-2 OCH_3-FeCp, 14%). IR (KBr): 3079w, 2925w, 2819w, 1636w, 1412m, 1273w, 1216w, 1108s, 1084s, 1055m, 1040w, 1025m, 1000m, 847w, 820s, 708w, 523m, 500s, 488s, 457w, 423w. Anal. Calc. (found): C, 66.56 (66.62), H 5.14 (5.12)%.

*4.3. Synthesis of 1,1,8,8-tetraferrocenyl-octa-1,7-dien-3,5-diyne (**5**)*

A Schlenk vessel was charged with 56 mg (0.062 mmol) **4** and 30 ml of dichloromethane. To this yellow solution was added 21 μl of a 54% etheral tetrafluoroboric acid solution (0.15 mmol), and an immediate color change from yellow to burgundy red indicated elimination of methanol. Workup: The solution was filtered through a short plug of basic alumina and washed with three portions of hexane. Removal of solvents on a rotary evaporator yielded 26 mg (0.031 mmol, 50%) **5**: red microcrystalline solid, m.p. 189°C. ^{1}H-NMR ($CDCl_3$): 4.19 (s, 10H, $Cp_{unsubst}$), 4.24 (s, 10H, $Cp_{unsubst}$), 4.33 (m, 4H, Cp_{subst}), 4.38 (m, 4H, Cp_{subst}), 4.62 (m, 4H, Cp_{subst}), 5.11 (m, 4H, Cp_{subst}), 6.22 (s, 2H, C=CH). ^{13}C-NMR ($CDCl_3$): 68.9, 69.0, 69.9 (Cp_{subst}); 70.0 ($Cp_{unsubst}$); 70.1 (Cp_{subst}); 86.1 (C(1) of Cp_{subst}); 101.8 (C=CH). MS (EI, 70 eV): 840.5 (M^+ + 2H, 52%), 838.5 (M^+, 100%). IR (KBr): 3097w, 2923w, 2854w, 2105w ($\nu_{C\equiv C}$), 1634w, 1553m, 1468w, 1412w, 1385w, 1265w, 1192w, 1108s, 1071m, 1040m, 1001m, 897w, 859w, 810s, 492s, 471s, 452w. UV–vis (nm/ε): 288/25700, 416/24550, 508.5/13500. Anal. Calc. (found): C, 68.78 (68.83), H 4.57 (4.56)%. X-ray analysis (Table 1, Fig. 2): single crystals were obtained from dichloromethane/*n*–hexane.

*4.4. Synthesis of 1,1,7,7-tetraferrocenyl-heptapentaen-1-ylium tetrafluoroborate (**6a**,**b**,**c**)*

A Schlenk vessel was charged with 63 mg (0.071 mmol) **3** and 5 ml of dichloromethane. To this yellow solution was added 11 μl of a 54% etheral tetrafluoroboric acid solution (0.08 mmol), and an immediate color change from yellow–purple indicated elimination of methanol. Workup: The product was precipitated by addition of 60 ml of *n*-hexane, filtered off and washed with three portions of ether and dried in vacuo, yielding 62 mg (0.068 mmol, 96%) **6a**,**b**,**c**: purple microcrystalline solid, m.p. 150°C (dec). ^{1}H-NMR (CD_2Cl_2): 4.32 (s, 5H, $Cp_{unsubst}$), 4.46 (s, 5H, $Cp_{unsubst}$), 4.58 (s, 12H, $Cp_{subst} + Cp_{unsubst}$), 4.80 (s, 4H, Cp_{subst}), 5.30 (s, 6H, Cp_{subst}), 5.86 (s, 4H, Cp_{subst}), 5.97 (s, 1H, C_7H^+). ^{13}C-NMR (CD_2Cl_2): 70.4, 71.1, 71.4, 71.7, 74.9 (Cp_{subst}); 78.1 ($Cp_{unsubst}$); 78.8, 78.9 (C(1) of Cp_{subst}); 84.9 ($Cp_{unsubst}$); 92.9, 100.7, 101.7, 150.3, 162.80, 162.88, 162.91 (C_7H^+). (+)-FAB-MS: 826 ($M^+ + H$, 57%), 825 (M^+, 100%). IR (KBr): 3110w, 2923w, 2858w, 2099s ($\nu_{C=C=C=C=C=CH-C}$), 1526s, 1470s, 1438s, 1414s, 1385m, 1353m, 1328m, 1306w, 1268s, 1108s, 1084s, 1065s, 1034s, 1003m, 834s, 702m, 479m. UV–vis (nm/ε): 388.0/25000, 542.5/12000, 855.5/18000. Anal. Calc. (found): C, 61.90 (61.83), H 4.09 (4.11)%.

*4.5. Preparation of a solution of 1,1,7,7-tetraferrocenylheptahexaene (**7**) by deprotonation of **6a**,**b**,**c** and hydrolysis of **7** under formation of 1,1,7,7-tetraferrocenyl-hepta-1,4,5,6-tetraen-3-one (**8**)*

A Schlenk vessel was charged with 100 ml of THF and cooled to −86°C. 20 mg (0.18 mmol) potassium *t*-butoxide was added, followed by 0.06 ml of a 2.0 molar pentane solution of butyllithium (0.12 mmol). The stirred mixture was allowed to warm to −30°C and 70 mg (0.077 mmol) of **6a**,**b**,**c** was added in one portion, resulting in an almost immediate color change from purple to red. Note: if proton sponge or DBU was used as the base, the deprotonation was much slower (5–12 h), therefore these reagents were not used in preparative reactions (vide supra). The solution was filtered under argon through a short column of basic alumina, resulting in a brownish red solution. TLC analysis (in air) gave a burgundy red apolar main product which was stable up to 10 min on the TLC plate, exposure to HCL vapor resulted in a purple coloring of this product, indicating reformation or protonation, respectively, to the starting material **6a**,**b**,**c**. All attempts to isolate **7** from this solution under strictly anhydrous conditions were unsuccessful (vide supra), but measurement of a UV–vis spectrum was possible (Fig. 3): $\lambda_{max}/\varepsilon = 278.0/54200$, 340.0/33200, 474.0/10900. Evaporation of the THF solution of **7** on a rotary evaporator (without protection from air) resulted in a brown material which was dissolved in dichloromethane and chromatographed (basic alumina, *n*-hexane:ether 2:1) yielding 13 mg (0.0154 mmol, 20%) **8**: dark red powder, m.p. 93–95°C. ^{1}H-NMR ($CDCl_3$): 4.13, 4.16, 4.19, 4.21 (each signal: s, 5H, $Cp_{unsubst}$); 4.34, 4.39, 4.46, 4.63, 4.88, 4.97, 5.03 (16H in total, each signal: m, Cp_{subst}); 6.08, 6.87 (each signal: s, 1H, C=CH). (+)-FAB-MS: 842 (M^+, 100%), 776 (M^+ –CpH), 656 (M^+–FcH), 591 (M^+–FcH–Cp). IR (KBr): 3091w, 2922w, 2854w, 2148s ($\nu_{C=C=C=C}$), 1688w, 1619m ($\nu_{C=O}$), 1543m, 1461m, 1411m, 1264m, 1209w, 1161m, 1106s, 1026s, 1002s, 819s, 731m, 695w, 592w, 557w, 487s. UV–vis (nm/ε): 375.0/8000, 537.0/4600.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 157273 for compound **3** andCCDC 157274 for compound **5**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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