Cationic and Neutral [4]-Cumulenes C═C═C═C═C with Five Cumulated Carbons and Three to Four Ferrocenyl Termini

Benno Bildstein,*[†,‡] Manuela Schweiger,[†] Holger Kopacka,[†]
Karl-Hans Ongania,[§] and Klaus Wurst[†]

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

Received January 20, 1998

Starting from 1,1-diferrocenyl-1-methoxypropyne, the first air-stable C_5-cumulenium salt $(Fc)_2C{=}C{=}C{=}C{=}C(Fc)^+BF_4^-$ (Fc = ferrocenyl) can be synthesized by a metalation, iodination, cross-coupling, and dehydration sequence. Attempted nucleophilic attack of ferrocenyl carbanion affords only radical decomposition products and none of the desired tetraferrocenyl-C_5-cumulene $(Fc)_2C{=}C{=}C{=}C{=}C(Fc)_2$. In contrast, reaction with phenyllithium yields the nucleophilic addition product $(Fc)_2C{=}C{=}C(R)C{\equiv}CFc$ ($R = C_6H_5$) with 100% regioselectivity. Starting from diferrocenyl ketone, the first air-stable protonated C_5-cumulenium salt $(Fc)_2CCH{=}C{=}C{=}C(Fc)_2{}^+BF_4^-$ is prepared by stepwise substitution of propyne with diferrocenyl(methoxy)methyl groups and subsequent 2-fold dehydration. Addition of methoxide affords $(Fc)_2C{=}C{=}C(R)CH{=}C(Fc)_2$ ($R = OCH_3$); attempted conversion to tetraferrocenyl-C_5-cumulene $(Fc)_2C{=}C{=}C{=}C{=}C(Fc)_2$ by thermal elimination of methanol in vacuo fails but yields an unusual cyclobutene dimer with eight ferrocenyl substituents. Finally, deprotonation of $(Fc)_2CCH{=}C{=}C{=}C(Fc)_2{}^+BF_4^-$ with "super base" *n*-BuLi/*t*-BuOK gives access to tetraferrocenyl-C_5-cumulene $(Fc)_2C{=}C{=}C{=}C{=}C(Fc)_2$, one of the very few C_5-cumulenes known. IR, Raman, UV−vis, MS, NMR, Mössbauer spectroscopy, cyclic voltammetry, and X-ray crystallography are used for a detailed characterization of these metallocenylcumulene compounds.

Introduction

Bimetallic compounds with linear conjugated carbon ligands connecting electroactive termini are of current interest due to their anticipated useful properties in molecular electronics[1] and nonlinear optics.[2] For such applications the electronic communication between the electroactive moieties should be as efficient as possible, depending on the degree of conjugation through the unsaturated bridging carbon ligand. The best available building blocks in this respect are acetylenic/cumulenic sp carbon chains whose chemistry has been extensively developed in recent years.[3] This progress is partially due to the ease of synthesis of even carbon chain compounds by modern ethynyl C−C coupling reactions.[4] With regard to the redox-active end groups most of the work in this area has focused on metallacumulenes with late transition metal complex fragments as termini.[3]

In this context, the advantageous properties of ferrocene in terms of chemical stability and reversibility of the ferrocene/ferrocenium couple[5] might prove useful. So far our efforts in synthesizing such ferrocenyl cumulenes have afforded stable systems with up to six cumulated carbons.[6] 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-releasing ability of the ferrocenyl substituents.[7] However, in the case of the shorter

---

[†] Institut für Allgemeine, Anorganische und Theoretische Chemie.

[‡] E-mail: benno.bildstein@uibk.ac.at. Telefax: Int. code + 512-507-2934.

[§] Institut für Organische Chemie.

(1) Reviews: (a) Ward, M. D. *Chem. Ind.* **1996**, 568. (b) Astruc. D. *Electron Transfer and Radical Processes in Transition Metal Chemistry;* VCH: New York, 1995, chapters 1−4. (c) Astruc, D. *Acc. Chem. Res.* **1997**, *30*, 383. (d) Bunz, U. H. F. *Angew. Chem.* **1996**, *108*, 1047; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 969.

(2) Long, N. J. *Angew. Chem.* **1995**, *107*, 37; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 4, 21.

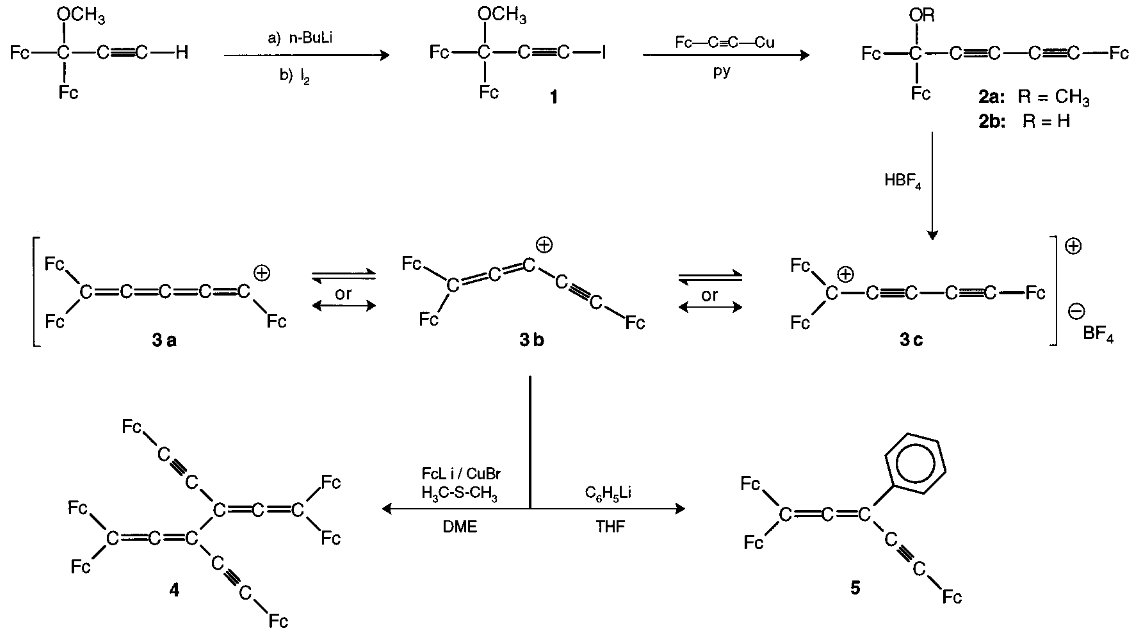
(3) Leading references: (a) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775. (b) Bartik, T.; Bartik, B.; Brady, M.; Dembinski, R.; Gladysz, J. A. *Angew. Chem.* **1996**, *108*, 467; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 414. (c) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7127. (d) Lass, R. W.; Steinert, P.; Wolf, J.; Werner, H. *Chem. Eur. J.* **1996**, *2*, 19. (e) Werner, H.; Wiedemann, R.; Mahr, N.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1996**, *2*, 561. (f) Roth, G.; Fischer, H. *Organometallics* **1996**, *15*, 1139. (g) Roth, G.; Fischer, H. *Organometallics* **1996**, *15*, 5766. (h) Touchard, D.; Pirio, N.; Toupet, L.; Fettouhi, M.; Ouahab, L.; Dixneuf, P. H.*Organometallics* **1995**, *14*, 5263. (i) Lavastre, O.; Plass, J.; Bachmann, P.; Guesmi, S.; Moinet, C.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 184. (j) Woodworth, B. E.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 828.

(4) (a) Stang, P. J.; Diederich, F. *Modern Acetylene Chemistry*; VCH: Weinheim, Germany, 1995. (b) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1988. (c) Brandsma, L.; Verkruijsse, H. D. *Syntheses of Acetylenes, Allenes, and Cumulenes*; Elsevier: Amsterdam, 1981.

(5) Geiger, W. E. Organometallic Radical Processes. In *Journal of Organometallic Chemistry Library*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; Vol. 22, Chapter 5, p 142.

S0276-7333(98)00023-5 CCC: $15.00
Publication on Web 05/13/1998

Scheme 1. Synthesis of Compounds 1−5



members in this series (tetraferrocenylethylene,[6a] -allene,[6c] and -butatriene[6d]) steric hindrance prevents the observation of the desired reactivity at the cumulenic carbons. Here we report on the synthesis and properties of tetraferrocenyl-C_5-cumulene and two unusual cationic precursors, which are rare examples of stable odd carbon cumulenes with a [4]-cumulene C=C=C=C=C moiety.

In comparison to the numerous complexes[3] with an even number of carbon atoms linking two transition metal fragments—a consequence of the synthetic methodology based on cross-coupling of acetylenic building blocks—there exist only very few organometallic species[3d,3f,8] with a C_5 sp carbon chain, and these compounds are not directly comparable to our systems because electronically they represent [5]- or [6]-metallacumulenes with five ([M]=C=C=C=C=C) or six ([M]=C=C=C=C=C=[M]) cumulated double bonds, respectively. In essence, these metallacumulenes[3] are typical Fischer carbene complexes[9] with extended unsaturated carbene ligands,[10] in contrast to ferrocenylcumulenes which are organic cumulenes with organometallic (metallocenyl) endgroups. Purely organic cumulenes with mainly aromatic substituents are relatively easily accessible for systems with an even number of carbons,[11] contrary to odd-numbered cumulenes in general, for which only three examples with a C_5-cumulenic backbone have been reported.[12]

Results and Discussion

Synthesis and Properties of Triferrocenyl-[4]-cumulenium Tetrafluoroborate (3) and Its Attempted Conversion to Tetraferrocenyl-[4]-cumulene (11). Our recent success in synthesizing tetraferrocenylallene[6c] from a triferrocenyl-C_3-cumulenic cation[6b] by formal nucleophilic addition of a ferrocenyl carbanion prompted us to try an analogous synthetic sequence for the preparation of the homologous tetraferrocenyl-[4]-cumulene (**11**) (Scheme 1).

As published recently, diferrocenylmethoxypropyne[6d] is a valuable propargylic synthon with a protected hydroxyl group. Metalation and subsequent halogenation under standard reaction conditions[4b] afforded iodomethoxypropyne (**1**) in 62% yield. In addition to its characterization by the usual spectroscopic methods (see Experimental Section) an X-ray crystal structure analysis proves unambiguously the connectivity of the molecule (Figure 1, Table 1). Selected bond lengths and angles are listed in the caption of Figure 1 and are in line with expectations.

Cross coupling of **1** with ferrocenylethynylcopper[13] in pyridine as solvent yielded triferrocenyl-C_5-methoxypentadiyne (**2a**), together with triferrocenyl-C_5-hydroxy-

---

(6) (a) Bildstein, B.; Denifl, P.; Wurst, K.; André, M.; Baumgarten, M.; Friedrich, J.; Ellmerer-Müller, E. *Organometallics* **1995**, *14*, 4334. (b) Lukasser, J.; Angleitner, H.; Schottenberger, H.; Kopacka, H.; Schweiger, M.; Bildstein, B.; Ongania, K.-H.; Wurst, K. *Organometallics* **1995**, *14*, 5566. (c) Bildstein, B.; Kopacka, H.; Schweiger, M.; Ellmerer-Müller, E.; Ongania, K.-H.; Wurst, K. *Organometallics* **1996**, *15*, 4398. (d) Bildstein, B.; Schweiger, M.; Kopacka, H.; Wurst, K. *J. Organomet. Chem.* **1998**, in press. (e) Herber, R.; Bildstein, B.; Denifl, P.; Schottenberger, H. *Inorg. Chem.* **1997**, *36*, 3586. (f) Bildstein, B.; Kopacka, H.; Schweiger, M.; Wurst, K. In part reported at the 211th National Meeting of the American Chemical Society, New Orleans, LA, American Chemical Society, Washington, DC, 1996; INOR 0218.

(7) (a) Watts, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 8, Chapter 59, p 1051. (b) Watts, W. E. *J. Organomet. Chem. Libr.* **1979**, *7*, 399.

(8) (a) Weng, W.; Bartik, T.; Gladysz, J. A. *Angew. Chem.* **1994**, *106*, 2269; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2199. (b) Xia, H. P.; Wu, W. F.; Ng, W. S.; Williams, I. D.; Jia, G. *Organometallics* **1997**, *16*, 2940. (c) Péron, D.; Romero, A.; Dixneuf, P. H. *Gazz. Chim. Ital.* **1994**, *124*, 497. (d) Touchard, D.; Haquette, P.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *J. Am. Chem. Soc.* **1994**, *116*, 11157.

(9) (a) Fischer, E. O. *Angew. Chem.* **1974**, *86*, 651. (b) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. (c) *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic: Dordrecht/Boston/London, 1989.

(10) Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348.

(11) Fischer, H. In *The Chemistry of Alkenes* Patai, S., Ed.; Interscience Publishers: London, 1964; Chapter 13, pp 1025−1159.

(12) (a) Kuhn, R.; Fischer, H.; Fischer, H. *Chem. Ber.* **1964**, *97*, 1760. (b) Irngartinger, H.; Götzmann, W. *Angew. Chem.* **1986**, *98*, 359; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 340. (c) Kuhn, R.; Schulz, B. *Chem. Ber.* **1963**, *96*, 3200.

(13) (a) Rausch, M. D.; Siegel, A.; Klemann, L. P. *J. Org. Chem.* **1966**, *31*, 2703. (b) Polin, J.; Schottenberger, H.; Schwarzhans, K. E. *Z. Naturforsch.* **1996**, *51b*, 1683.

Table 1. Crystal Data and Structure Refinement for 1, 2b, 5, 6a, 10, 11

	1	**2b**	**5**
mol formula	$C_{24}H_{21}Fe_2IO$	$C_{35}H_{28}Fe_3O$	$C_{41}H_{32}Fe_3$
fw	564.01	632.12	692.22
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (pm)	737.6(2)	1042(3)	980.1(1)
b (pm)	1415.8(4)	1229.5(2)	993.8(1)
c (pm)	1037.1(3)	1285.0(3)	1636.2(3)
α (deg)	90	64.29(1)	75.19(1)
β (deg)	96.11(2)	68.86(1)	87.65(1)
γ (deg)	90	66.50(1)	89.77(1)
V (nm^3)	1.0769(5)	1.3247(5)	1.5394(4)
Z	2	2	2
temp (K)	293(2)	223(2)	213(2)
d(calcd) (Mg/m^3)	1.739	1.585	1.493
abs coeff (mm^{-1})	2.792	1.649	1.424
F(000)	556	648	712
color, habit	yellow platelet	orange prism	red prism
cryst size (mm)	0.4 × 0.35 × 0.1	0.25 × 0.15 × 0.09	0.5 × 0.3 × 0.25
θ range for data collcn (deg)	3.13−5.00	3.05−21.99	3.04−22.49
index ranges	$-3 \le h \le 7$ $-1 \le k \le 16$ $-12 \le l \le 12$	$-1 \le h \le 10$ $-11 \le k \le 12$ $-13 \le l \le 13$	$0 \le h \le 9$ $-10 \le k \le 10$ $-17 \le l \le 17$
no. of rflns collcd	3255	3833	4193
no. of indep rflns	2467 ($R_{int} = 0.0172$)	3182 ($R_{int} = 0.0221$)	3863 ($R_{int} = 0.0358$)
no. of rflns with $I > 2\sigma(I)$	2285	2430	3172
abs cor	ψ-scan	none	none
max and min transm	1.000 and 0.627		
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/params	2467/1/253	3180/0/356	3636/0/397
goodness-of-fit on F^2	1.060	1.038	1.036
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0265$ w$R_2 = 0.0599$	$R_1 = 0.0357$ w$R_2 = 0.0675$	$R_1 = 0.0525$ w$R_2 = 0.1332$
R indices (all data)	$R_1 = 0.0309$ w$R_2 = 0.0623$	$R_1 = 0.0597$ w$R_2 = 0.0775$	$R_1 = 0.0696$ w$R_2 = 0.1571$
largest diff peak and hole (e·nm^{-3})	279 and −381	352 and −317	577 and −581

	6a	**10**	**11**
mol formula	$C_{24}H_{22}Fe_2O$	$C_{90}H_{74}Fe_8 \cdot 1.5CH_2Cl_2 \cdot 0.5C_7H_8$	$C_{45}H_{36}Fe_4$
fw	438.12	1775.75	800.14
cryst syst	monoclinic	triclinic	tetragonal
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$I4_1/a$ (No. 88)
a (pm)	1139.3(3)	1440.4(2)	1541.2(2)
b (pm)	980.9(3)	1537.9(2)	1541.2(2)
c (pm)	1730.6(4)	2069.5(5)	1434.1(3)
α (deg)	90	73.17(2)	90
β (deg)	103.35(2)	74.35(2)	90
γ (deg)	90	69.71(2)	90
V (nm^3)	1.8818(9)	4.0418(12)	3.4064(9)
Z	4	2	4
temp (K)	213(2)	213(2)	218(2)
d(calcd) (Mg/m^3)	1.546	1.459	1.560
abs coeff (mm^{-1})	1.552	1.539	1.703
F(000)	904	1820	1640
color, habit	red platelet	red prism	red rectangular prism
cryst size (mm)	0.45 × 0.27 × 0.13	0.39 × 0.21 × 0.14	0.28 × 0.14 × 0.14
θ range for data collcn (deg)	2.77−22.00	2.01−19.00	2.64−19.43
index ranges	$0 \le h \le 11$ $-1 \le k \le 10$ $-18 \le l \le 17$	$0 \le h \le 12$ $-12 \le k \le 13$ $-18 \le l \le 18$	$-14 \le h \le 1$ $0 \le k \le 14$ $0 \le l \le 13$
no. of rflns collcd	2667	6319	836
no. of indep rflns	2296 ($R_{int} = 0.0338$)	5959 ($R_{int} = 0.0371$)	736 ($R_{int} = 0.0236$)
no. of rflns with $I > 2\sigma(I)$	1858	4246	554
abs cor	ψ-scan	none	none
max and min transm	0.960 and 0.859		
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/params	2169/0/252	5435/17/555	694/0/112
goodness-of-fit on F^2	1.063	1.055	1.066
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0325$ w$R_2 = 0.0669$	$R_1 = 0.0673$ w$R_2 = 0.01646$	$R_1 = 0.0362$ w$R_2 = 0.0701$
R indices (all data)	$R_1 = 0.0496$ w$R_2 = 0.0735$	$R_1 = 0.1019$ w$R_2 = 0.1926$	$R_1 = 0.0601$ w$R_2 = 0.0779$
largest diff peak and hole (e·nm^{-3})	233 and −279	895 and −556	315 and −140

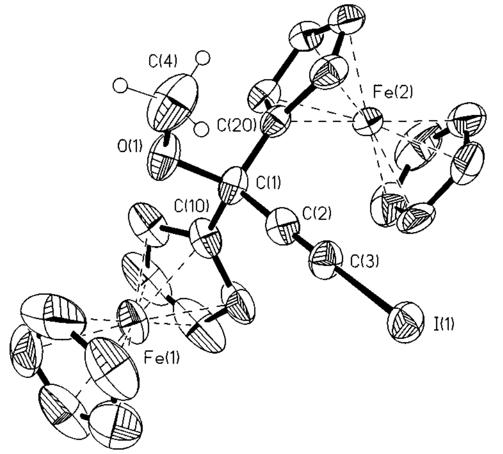


Figure 1. Molecular structure of **1**, showing the atom-numbering scheme. Ferrocenyl hydrogen atoms are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(10)−C(19) and for ferrocene 2 C(20)−C(29), respectively. Selected bond distances: C(1)−C(2) = 149.0(8), C(1)−O(1) = 144.8(6), C(2)−C(3) = 117.6(8), C(3)−I(1) = 200.2(6) pm.

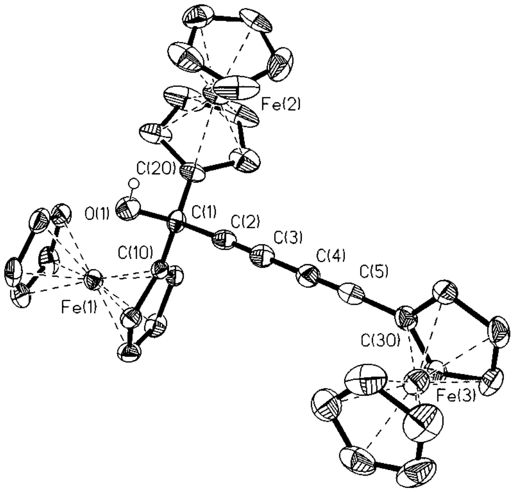


Figure 2. Molecular structure of **2b**, showing the atom-numbering scheme. Ferrocenyl hydrogen atoms are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(10)−C(19), for ferrocene 2 C(20)−C(29), and for ferrocene 3 C(30)−C(39), respectively. Selected bond distances: C(1)−O(1) = 143.4(5), C(1)−C(2) = 148.2(6), C(2)−C(3) = 118.6(6), C(3)−C(4) = 139.0(7), C(4)−C(5) = 121.1(6) pm.

pentadiyne (**2b**), formed in part by unavoidable hydrolysis of preparative amounts of crude **2a** during chromatographic workup on basic alumina. The use of basic alumina was necessary to avoid dehydration of **2a** to cation **3**, which cannot be eluted from the stationary phase due to immobilization. An X-ray structure of **2b** (Figure 2, Table 1) shows the linear C(1)−C(5) backbone with alternating single and triple bonds, as anticipated and in consonance with spectroscopic data.

Compounds **2b** (an α-metallocenyl alcohol) and **2a** (an α-metallocenyl ether) readily eliminated H_2O or CH_3OH, respectively, upon treatment with fluoroboric acid, analogously to the homologous triferrocenylpropargylic alcohol $(Fc)_2C(OH)C{\equiv}CFc$.[6b] The resulting green air-stable carbenium salt **3** is the first representative of an isolable C_5-cumulenic cation (compare structure **3a**) with unprecedented stability, induced by the powerful electron-releasing property[7,6b] of the three ferrocenyl substituents.

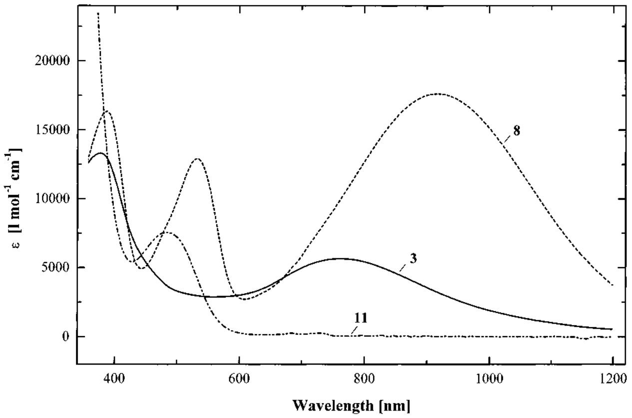
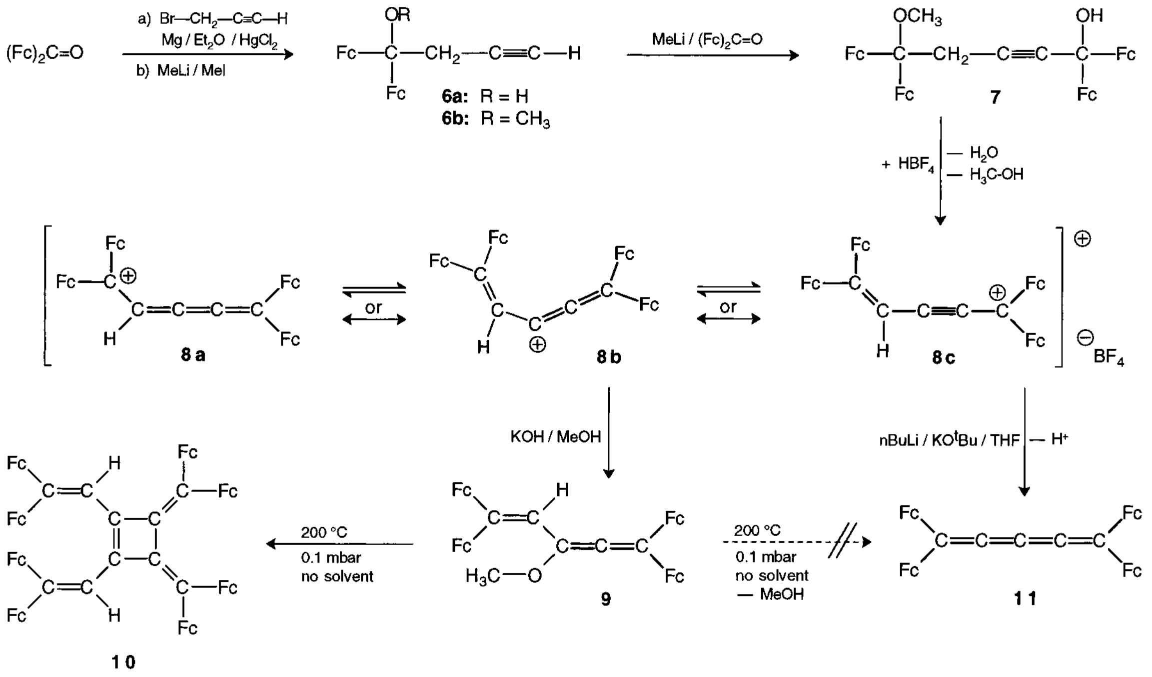


Figure 3. Comparison of the UV−vis spectra of **3**, **8**, and **11**.

Although the identity of **3** is clearly established by high-resolution positive FAB mass spectroscopy, which gives the molecular ion of the cation (*m/z* 615.014 46) in excellent agreement with the calculated exact mass (calcd for $C_{35}H_{27}Fe_3$: 615.016 09), the precise structure of **3** is difficult to assess on the basis of the spectroscopic information available. Possible structures include [4]-cumulene **3a**, ethynyl-[2]-cumulene **3b**, and the butadiynyl carbenium salt **3c**, respectively, as depicted in Scheme 1. In each case, the five nonequivalent carbons of the C_5 bridging subunit would be expected to give rise to five ^{13}C resonances, but the five observed quaternary ^{13}C signals (δ = 83.6, 93.1, 94.1, 99.7, 149.1 ppm) allow no clear distinction between alkyne or cumulene carbons. Also, UV−vis data (λ_{max} = 761 nm; Figure 3) and IR spectroscopic data (intense cumulenic stretching vibration at 2163 cm^{-1}) are of not much help in assigning an exact structure to compound **3**, because these values are very similar and almost unshifted to those of the two carbons shorter homologue $(Fc)_2C{=}C{=}C$-$(Fc)^+$.[6b] On electronic reasons one would consider structures **3a**,**c** only and neglect structure **3b** completely, because the mechanism of stabilization of electron-deficient carbenium ions by α-metallocenyl substituents involves significant resonance contribution from an (η^6-fulvene)(η^5-cyclopentadienyl)iron(II) form,[6b,7] which is only possible for cations with their positive charge located in α-position to the metallocenyl groups. Mössbauer spectroscopy of **3** indicates a temperature-dependent population of the contributing forms **3a**−**c** with the butadiynyl structure **3c** being the predominant form at low temperature and the cumulenic forms **3a** and/or **3b** becoming more prevalent with increasing temperature.[6e] Whatever the precise structure of **3** is, from a preparative point of view it serves as a potential C_5-cumulenic precursor of the desired tetraferrocenyl-[4]-cumulene (**11**), in analogy to our experience with triferrocenyl-[2]-cumulenium tetrafluoroborate as the key synthon in the synthesis of tetraferrocenyl-[2]-cumulene (tetraferrocenylallene).[6c]

Upon attempted (formal) nucleophilic addition of ferrocenyl carbanion under optimized reaction conditions[6c] a number of products were formed, indicating the involvement of radical species in the course of this reaction, which proceeds most likely by a SET mechanism, entirely in analogy to the situation in the preparation of tetraferrocenylallene.[6c] From this mixture of products only one compound could be isolated in pure

Scheme 2. Synthesis of Compounds 6a−11



form and in a very low yield of 17% (total amount of material: 9 mg). Therefore most spectroscopic analyses were precluded, but high-resolution positive FAB mass spectroscopy clearly showed this product **4** to be a dimer of triferrocenyl-[4]-cumulene radical with a molecular ion (*m*/*z* 1230.051 02) in very good agreement with the calculated exact mass (calcd for $C_{70}H_{54}Fe_6$: 1230.032 19). Unfortunately, the weak absorption at 2182 cm^{-1} in the IR spectrum does not allow one to distinguish between possible C_5- and C_3-cumulenic and C_2-ethynyl subunits. On the basis of steric arguments, color of **4**, reaction of **4** with hydrochloric acid [no formation of a purple protonated cumulenic cation (compare the properties of **8** discussed below), but formation of a dark-brown unstable product which resembles tetraferrocenylpropylium chloride[6c]] and in light of the structure of **5** (see below) we favor for this dimer **4** the bis(1,1,5-triferrocenylpenta-1,2-dien-4-yn-3-yl) structure shown in Scheme 1 over the equally possible bis(1,1,5-triferrocenylpenta-1,2,3,4-tetraen-5-yl) structure. We cannot rule out that the desired teraferrocenyl-[4]-cumulene (**11**) was formed in low yield in this reaction, but for preparative purposes this method of synthesis is certainly unsatisfactory.

Cumulene salt **3** was reacted with phenyllithium (a less reducing nucleophile in comparison to ferrocenyllithium) instead of ferrocenyl carbanion in an attempt to adjust the experimental conditions under which nucleophilic addition at the terminal carbon of the cumulenic C_5 unit is possible. However, the isolated product **5** was shown by spectroscopic analyses and by X-ray structure analysis (Figure 4, Table 1) to be a regioisomer of the anticipated product. This results suggests that only tetraferrocenylallene,[6c] but no higher cumulenes with an odd number of cumulated carbons, can be synthesized by reaction of a ferrocenyl carbanion substrate with the respective triferrocenylcumulenium salts.

Synthesis, Properties, and Reactivity of Tetraferrocenyl-C_5H Salt (8) and Its Deprotonation to

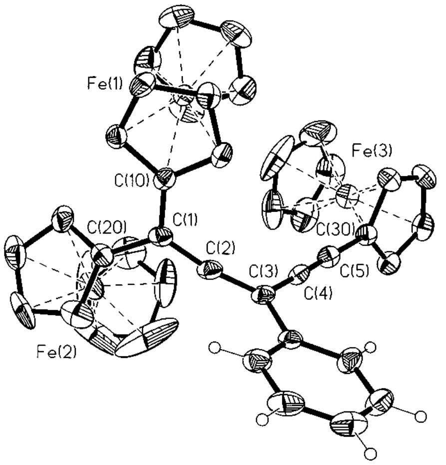


Figure 4. Molecular structure of **5**, showing the atom-numbering scheme. Ferrocenyl hydrogen atoms are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(10)−C(19), for ferrocene 2 C(20)−C(29), and for ferrocene 3 C(30)−C(39), respectively. Selected bond distances: C(1)−C(2) = 132.5(8), C(2)−C(3) = 131.6(8), C(3)−C(4) = 144.6(8), C(4)−C(5) = 119.2(8) pm.

Tetraferrocenyl-[4]-cumulene (11). As an alternative method for the synthesis of cumulene **11** a new strategy involving propargylic starting materials was developed. The general idea was to effect first the formation of a more or less saturated system incorporating already all four terminal ferrocenyl substituents connected by a C_5 bridging ligand and then try to find methods to convert this bridging ligand to an unsaturated C_5-cumulene (Scheme 2).

Starting from propargyl bromide the corresponding allenylmagnesium bromide was prepared under the proper experimental conditions,[4b] including performing the reaction in ether, activating the magnesium with mercury(II) chloride, and keeping the reaction temperature below 10 °C. This reagent allows in general the synthesis of butynylic alcohols from aldehydes,[4b] and

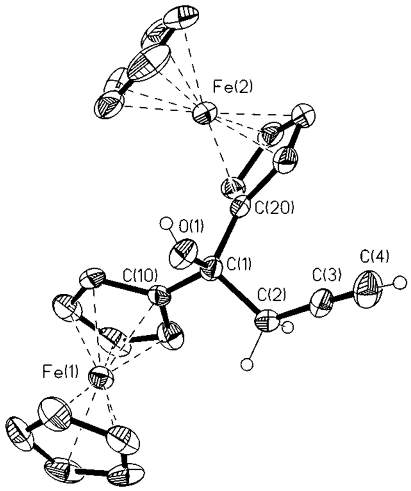


Figure 5. Molecular structure of **6a**, showing the atom-numbering scheme. Ferrocenyl hydrogen atoms are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(10)−C(19) and for ferrocene 2 C(20)−C(29), respectively. Selected bond distances: C(1)−O(1) = 143.4(4), C(1)−C(2) = 153.9(5), C(2)−C(3) = 145.2(5), C(3)−C(4) = 116.4(6) pm.

we adapted this reaction to prepare the corresponding 1,1-diferrocenyl-but-3-yn-1-ol (**6a**) from diferrocenyl ketone[14] accordingly. To our pleasant surprise, this reaction worked very well, resulting in up to 96% yield, although in our experience nucleophilic additions to diferrocenyl ketone are sometimes difficult to perform.

The hydroxy functionality of **6a** was protected by conversion to the respective methyl ether **6b** by methods devoloped earlier for diferrocenylpropynol.[6d] Diferrocenylmethoxybutyne **6b** was metalated with methyllithium and the second equivalent of diferrocenyl ketone was linked by a similar nucleophilic addition reaction, affording tetraferrocenyl(methoxy)hydroxybutyne **7** in quantitative yield. All three compounds **6a**,**b** and **7** are fully characterized by the usual spectroscopic methods; the obtained data are in line with the expectations. Suitable single crystals for an X-ray structure analysis could be obtained for 1,1-diferrocenyl-but-3-yn-1-ol (**6a**) (Figure 5, Table 1).

Chemically, these three compounds have as a common structural motif α-ferrocenyl hydroxy or methoxy functionalities, which can be readily eliminated upon reaction with acid as H_2O or CH_3OH, respectively, due to the cation-stabilizing effect of the adjacent metallocenyl groups.[6b,7] Hence any proton source should be avoided during workup and handling of these compounds. On the other hand, we wanted to take advantage of this reactivity with regard to increasing the unsaturation of the C_5 bridging ligand connecting the two pairs of ferrocenyl termini in **7**. Adding tetrafluoroboric acid to a solution of **7** in dichloromethane immediately yielded an air-stable purple precipitate **8** whose precise structure was not clear at first. After some initial confusion it soon became evident that with *1* equiv of H^+ elimination of *H_2O and CH_3OH* has occurred. This remarkable acid promoted bis-elimination may be compared with the related dehydration of propargylic progenitors induced by acidic alumina in the synthesis of metallacumulenes,[3] but to our knowledge such a simultaneous elimination of H_2O and CH_3OH—effecting formation of two double bonds in one step—is without precedent in cumulene chemistry. Most likely, addition of H^+ generates first a diferrocenyl stabilized carbenium ion (either by abstraction of H_2O or CH_3OH), as anticipated,[7] with accompanying increased acidity of the methylene moiety,[15] and the second elimination of either H_2O or CH_3OH takes place readily, facilitated by the conjugation in the final product.

The identity of **8** is clearly established by high-resolution positive FAB mass spectroscopy, which gives the molecular ion of the cation (*m*/*z* 801.026 91) in excellent agreement with the calculated exact mass (calcd for $C_{45}H_{37}Fe_4$: 801.029 771). The bond geometry and electronic structure of **8** can be described by three possible structures **8a**−**c** depicted in Scheme 2. Similarly as in the case of compound **3**, the precise structure of **8** is difficult to assess on the basis of the spectroscopic data. The most prominent features are a very intense donor-shifted (in comparison to **3**) cumulenic stretching vibration at 2090 cm^{-1} in the IR spectrum of **8** and a bathochromic shift of the λ_{max} of 917 nm for **8** in comparison to 761 nm for **3** (Figure 3), suggesting extensive conjugation or delocalization, respectively. On electronic arguments, as discussed above, only structures **8a**,**c** with the electron-deficient carbenium center located in α-position to the stabilizing ferrocenyl substituents[6b,7] would be expected to contribute to the charge dispersal. ^1H and ^{13}C NMR spectra are very complex, allowing no clear distinction between different contributing structures **8a**−**c**. Specifically, the detection of more than five ^{13}C resonances (106.0, 110.4, 126.8, 135.2, 154.8, 160.4, 167.8 ppm) for the five nonequivalent carbons of the C_5H linkage between the two pairs of terminal ferrocenyl substituents and the quite complex ^1H NMR spectrum with only one assignable cumulene chain signal at 5.95 ppm (but other C_5H resonances might be obscured by overlapping ferrocenyl signals) indicate an equilibrium among structural isomers **8a**−**c**. In the ^{57}Fe Mössbauer spectrum of **8** (see Experimental Section) only one well-resolved doublet is observed, with isomer shift (IS) and quadrupole splitting (QS) values very similar to those of ferrocene and with no evidence of two or more distinguishable sites, in contrast to the Mössbauer absorption of **3**.[6e] This obviously shows that regardless of the true nature of the nonsymmetric C_5-bridging subunit in **8** (with concomitant inequivalency of the ferrocenyl groups) this asymmetry cannot be resolved by Mössbauer spectroscopy. It should be noted, however, that the line width of the Mössbauer resonances in **8** are 15% larger than those observed under similar conditions for **11**, while the temperature dependence of the recoil-free fraction is 35% larger for **8** than **11**.

From a synthetic point of view, cumulene salt **8** is the conjugate acid of tetraferrocenyl-[4]-cumulene **11**—the target compound of this project. Hence interaction with an appropriate base should in principle give access to **11**. At this point it is interesting to note that in a recently published study of a related metallacumulene salt with a symmetric C_5H linkage between the metal complex termini no such deprotonation proved possible.[8b] Therefore we attempted at first to effect this removal

---

[14] O'Connor Salazar, D. C.; Cowan, D. O. *J. Organomet. Chem.* **1991**, *408*, 219 and references therein.

[15] Bunton, C. A.; Watts, W. E. *Tetrahedron Lett.* **1977**, 2049.

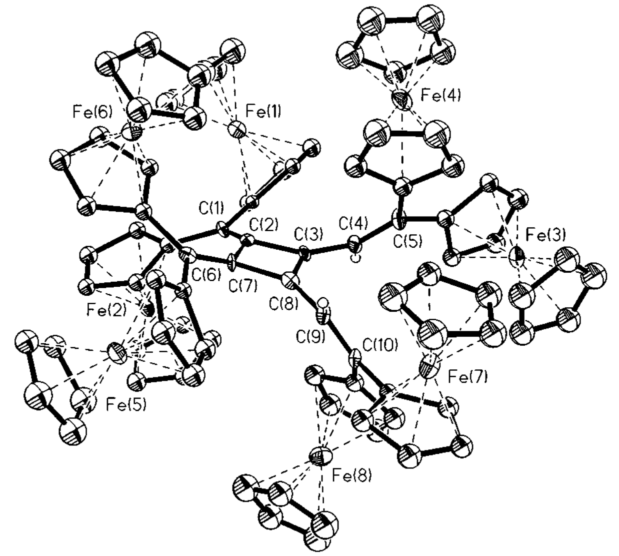


Figure 6. Molecular structure of **10**, showing the atom-numbering scheme. Ferrocenyl hydrogen atoms and solvent molecules (dichloromethane and toluene) are omitted for clarity. Only carbon atoms C(1)−C(10) and iron atoms Fe(1)−Fe (4) could be refined anisotropically, due to an insufficient data-to-parameter ratio. Cyclopentadienyl carbons of ferrocene 1 are C(11)−C(20), for ferrocene 2 C(21)−C(30), for ferrocene 3 C(31)−C(40), for ferrocene 4 C(41)−C(50), for ferrocene 5 C(51)−C(60), for ferrocene 6 C(61)−C(70), for ferrocene 7 C(71)−C(80), and for ferrocene 8 C(81)−C(90), respectively. Selected bond distances: C(1)−C(2) = 136(2), C(2)−C(3) = 150(2), C(3)−C(4) = 145(2), C(4)−C(5) = 133(2), C(2)−C(7) = 150(2), C(3)−C(8) = 135(2), C(6)−C(7) = 135(2), C(7)−C(8) = 149(2), C(8)−C(9) = 144(2), C(9)−C(10) = 133(2) pm.

of H^+ by an indirect sequence in analogy to the preparation of nucleophilic Wanzlick/Arduengo carbenes from the corresponding methanol adducts.[16] Methoxypentatriene **9** could be readily prepared from cumulenium salt **8** by nucleophilic attack of methoxide (Scheme 2). The regioselectivity of this substitution (3-methoxy-penta-1,2,4-triene in contrast to 5-methoxy-1,2,3-triene and 5-methoxy-1-en-3-yne) is clearly established from NMR spectroscopic data and is most likely a consequence of steric hindrance in the 1- and 5-positions of cumulenium tetrafluoroborate **8**. Upon attempted thermal elimination of methanol in vacuo under conditions which have been successfully applied in the case of Wanzlick/Arduengo carbenes[16] none of the desired cumulene **11** was formed. The isolated product **10** is an unusual cyclobutene which can be envisioned as a head-to-head dimer ([2 + 2]-cyloadduct) of reduced **8** with the two hydrogens of the 2 equiv of protonated cumulene precursors still attached to the unsaturated linkage (Figure 6, Table 1). The reducing agent in this process is unknown, but clearly this method of synthesis is of no value for the preparation of **11**.

To finally get access to tetraferrocenyl-[4]-cumulene (**11**) we tested a number of bases to effect deprotonation of **8**. The formation of **9** by reacting **8** with methoxide showes that a nonnucleophilic base is needed for this conversion. Common basic reagents such as *n*-butyllithium, *tert*-butyllithium, lithium diisopropylamide, potassium *tert*-butoxide, etc., only afforded nucleophilic addition products analogous to **9**. Last, the "superbasic" mixture[17] of *n*-butyllithium with potassium *tert*-butoxide cleanly deprotonated **8** under formation of cumulene **11** in 46% isolated yield. In retrospect, the difficulties in deprotonating **8** are mainly a consequence of its high reactivity as an electrophile with possible bases (which are inherently also nucleophiles) and not a consequence of its high basicity. For example, cumulene **11** is not protonated by water, suggesting a pK_a value of less than 14.

Tetraferrocenyl-[4]-cumulene (**11**) is an air stable solid (mp 150 °C, dec) of red color (Figure 3). Interestingly, in the positive mode FAB mass spectrum using nitrobenzyl alcohol (NOBA) as matrix the molecular ion M + 1H and the adduct M + NOBA (analogous to **9**) can be detected. The four ferrocenyl substituents are magnetically equivalent and show ^1H and ^{13}C NMR spectral patterns typical of monosubstituted ferrocene compounds. The five carbons of the symmetric cumulene subunit are observed at 116.0, 158.2, and 178.2 ppm, respectively. The intense Raman absorption of the C=C=C=C=C moiety is detected at 2035 cm^{-1}. A direct comparison with other C_5-cumulenes cannot be made because there have been reported in the literature only three organic C_5-cumulenes,[12] but without Raman data; nevertheless, this value compares well with those of even-numbered metallacumulenes [Re]=C=C=C=C=[Re] reported recently by Gladysz et al.[3a] Despite the presence of four ferrocenyl substituents in this cumulene only two reversible oxidations ($E^1_{1/2} = +0.45$, $E^2_{1/2} = +0.54$ V vs SCE) at a potential very similar to the oxidation of ferrocene (Fc/Fc$^+$: $E_{1/2} = +0.48$ V vs SCE) could be detected by cyclic voltammetry. It has been noted before[12b] that odd (C=C=C, C=C=C=C=C) and even (C=C=C=C, C=C=C=C=C=C) cumulenes differ significantly in their degree of conjugation along the cumulene linkage; in the former with an even number of cumulated double bonds no resonance interaction with participation of canonical forms with triple bonds is possible. In consonance with this limited conjugation in odd cumulenes the half-wave potentials of **11** are unshifted in comparison to ferrocene (similar as in tetraferrocenylallene[6c]), and the UV−vis absorption (Figure 3) of **11** is less intense with a λ_{max} at lower wavelength in comparison to tetraferrocenylethylene[6a] and -butatriene.[6d] In the ^{75}Fe Mössbauer spectrum of **11** one doublet with IS and QS parameters similar to those of ferrocene are observed, as anticipated, but as noted above, the detailed temperature dependence of these parameters is currently being examined in greater detail and will be reported.

The solid-state structure of **11** (Figures 7 and 8, Table 1) reveals a linear cumulene with orthogonal π-planes, as expected for an odd-numbered cumulene with an even number of cumulated double bonds. The four ferrocenyl substituents are symmetry-related by a 4-fold rotoinversion axis; therefore the observed perfect linearity of the cumulene linkage is a consequence of crystal-

---

[16] (a) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J.-P.; Ebel, K.; Brode, S. *Angew. Chem.* **1995**, *107*, 119; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1021. (b) Enders, D.; Breuer, K.; Teles, J. H. *Liebigs Ann. Chem.* **1996**, 2019. (c) Enders, D.; Breuer, K.; Teles, J. H.; Ebel, K. *J. Prakt. Chem.* **1997**, *339*, 397.

[17] (a) Schlosser, M. *Mod. Synth. Methods* **1992**, *6*, 227. (b) Schlosser, M. *Pure Appl. Chem.* **1988**, *60*, 1627. (c) Caubere, P. *Chem. Rev.* **1993**, *93*, 2317.

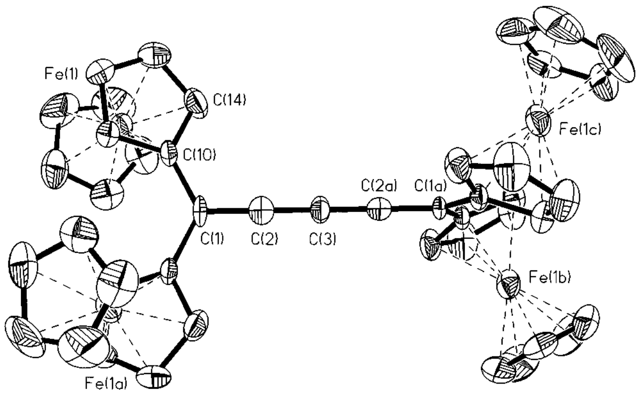


Figure 7. Molecular structure of **11**, showing the atom-numbering scheme. Ferrocenyl hydrogen atoms are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(10)−C(19). Selected bond lengths and angles: C(1)−C(2) = 133.2(12), C(2)−C(3) = 128.7(10) pm; C(2)−C(1)-C(10) = 117.4(3), C(2)−C(1)-C(10a) = 117.4(3), C(10)−C(1)-C(10a) = 125.1(7), C(2)−C(1)-C(10)−C(14) = 21.8(6)°.

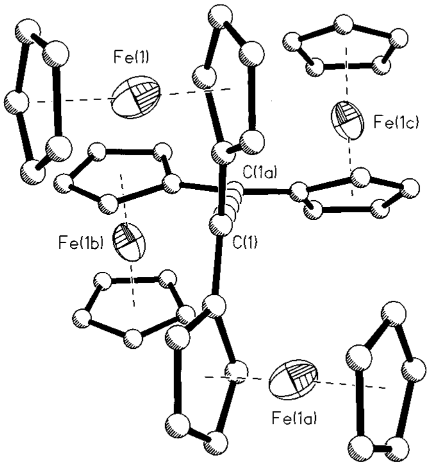


Figure 8. Molecular structure of **11**, viewed down the cumulene axis C(1)−C(2)-C(3)−C(2a)−C(1a), showing the orthogonality of the cumulenic π-planes.

lographic symmetry. The terminal cumulene bond [C(1)−C(2) = 133.2(12) pm] is longer in comparison to the central bond [C(2)−C(3) = 128.7(10) pm] due to the sp^2 hybridization of the terminal carbons C(1), C(1′) versus the sp hybridization of the central carbons C(2), C(3), C(2′). These values concur with published data of two other pentatetraenes which have been characterized by single-crystal structure analysis.[12b] Steric repulsion of the geminal ferrocenyl substituents leads to (i) deviations from the theoretical bond angle of 120° at the terminal carbon C(1) [C(2)−C(1)−C(10) = 117.4(3)°, C(2)−C(1)−C(10a) = 117.4(3)°, C(10)−C(1)−C(10a) = 125.1(7)°] and (ii) twisted metallocenyl groups [torsion angle C(2)−C(1)−C(10)−C(14) = 21.8(6)°], as has been observed similarly in other tetraferrocenylcumulenes.[6]

The chemical reactivity of **11** is currently under investigation and will be reported in due course. In comparison to the shorter homologues tetraferrocenylethylene,[6a] -allene,[6c] and -butatriene,[6d] where steric hindrance by the four bulky ferrocenyl substituents prevents any electrophilic attack, this is not the case any more for **11**, where the cumulene subunit is of sufficient length to allow interaction with other reagents.

Summary

The efficient stabilization of adjacent electron-deficient carbenium centers by ferrocenyl substituents allows the preparation of triferrocenyl-C_5-cumulenium tetrafluoroborate $(Fc)_2C{=}C{=}C{=}C{=}C(Fc)^+BF_4^-$, the first stable cumulene cation of this type. Attempted conversion to the corresponding neutral tetraferrocenyl-C_5-cumulene $(Fc)_2C{=}C{=}C{=}C{=}C(Fc)_2$ by nucleophilic attack with a ferrocenyl carbanion synthon under conditions which have been successfully applied in the synthesis of the shorter homologue tetraferroceny-C_3-cumulene $(Fc)_2C{=}C{=}C(Fc)_2$ met with failure. An alternative route with tetraferrocenyl-C_5H-cumulenium tetrafluoroborate as key progenitor yields tetraferrocenyl-C_5-cumulene $(Fc)_2C{=}C{=}C{=}C{=}C(Fc)_2$ by deprotonation with super base. A thorough characterization of this first metallocene C_5-cumulene has been carried out, including IR, Raman, UV−vis, MS, NMR, CV, Mössbauer spectroscopy, and X-ray crystal structure analysis.

Experimental Section

General Comments. Standard techniques and instrumentation for spectroscopic and physical measurements,[6b] cyclic voltammetric[18,6d] and ^{57}Fe Mössbauer[6e] spectroscopic measurements, and X-ray structure determinations[19] have been described previously.

3,3-Diferrocenyl-1-iodo-3-methoxyprop-1-yne (1). A Schlenk vessel was charged with 100 mg (0.23 mmol) of 1,1-diferrocenyl-1-methoxyprop-2-yne[6d] dissolved in 30 mL of THF. The solution was cooled to −70 °C under protection from air, lithiated with 0.12 mL of a 2.0 M (0.23 mmol) *n*-butyllithium/pentane solution, and stirred for 1 h. A 60 mg (0.23 mmol) amount of I_2 was added in one portion, the cooling bath was removed, and stirring was continued for 3 h. Workup: The mixture was hydrolyzed by addition of 1 mL of H_2O, solvents and other volatile materials were removed in vacuo on a rotary evaporator, the residue was dissolved in Et_2O, and the ethereal solution was washed with two portions of a 5% aqueous $Na_2S_2O_3$ solution and two portions of H_2O. The red solution was dried with Na_2SO_4 and evaporated to dryness, yielding the crude product together with unreacted 1,1-diferrocenyl-1-methoxyprop-1-yne. Chromatography (basic Al_2O_3, *n*-hexane/Et_2O, 9:1) afforded 80 mg (62% yield) of pure 3,3-diferrocenyl-1-iodo-3-methoxyprop-1-yne (**1**).

Data for 1. Yellow, air-stable powder, mp 160 °C, dec. Anal. Calcd for $C_{24}H_{21}Fe_2IO$: C, 51.11; H, 3.75. Found: C, 50.98; H, 3.76. MS (EI, 70 eV): *m*/*z* 564 (M^+, 54%); 533 ($M^+ - OCH_3$, 5%), 412 ($M^+ - C{\equiv}CI$, 100%). IR (KBr): 3085 w, 2987 w, 2943 w, 2929 w, 2817 w, 2184 w, 1644 w, 1465 m, 1409 w, 1393 m, 1258 m, 1231 m, 1104 s, 1084 s, 1071 s, 1046 s, 1021 s, 940 m, 876 m, 503 s, 490 s cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 3.28 (3H, s, OCH_3); 4.12 (14H, br s, subst and unsubst Cp); 4.17 (2H, br s, subst Cp); 4.33 (2H, br s, subst Cp). ^{13}C NMR ($CDCl_3$, δ): 52.1 (OCH_3); 67.3, 67.4, 67.7, 69.3 (Cp); 92.4 ($C{\equiv}CI$). Single crystals were obtained from CH_2Cl_2/Et_2O (Table 1, Figure 1, Supporting Information).

1,1,5-Triferrocenyl-1-methoxypenta-2,4-diyne (2a) and 1,1,5-Triferrocenyl-1-hydroxypenta-2,4-diyne (2b). A suspension of 209 mg (0.77 mmol) of ferrocenylethynylcopper[13] in 50 mL of dry, deoxygenated pyridine was heated to 60 °C, and 433 mg (0.77 mmol) of **1** was added under an atmosphere

---

[18] Bildstein, B.; Hradsky, A.; Kopacka, H.; Malleier, R.; Ongania, K.-H. *J. Organomet. Chem.* **1997**, *540*, 127.

[19] Hradsky, A.; Bildstein, B.; Schuler, N.; Schottenberger, H.; Jaitner, P.; Ongania,. K.-H.; Wurst, K.; Launay, J.-P. *Organometallics* **1997**, *16*, 392.

of argon. The mixture was stirred, and soon a red solution was obtained, indicating dissolution of the organocopper reagent with subsequent C−C-coupling. Workup: Solvents were removed in vacuo and the crude residue was dissolved in dichloromethane, filtered through a short plug of basic Al_2O_3 to remove inorganic salts, and chromatographed (basic Al_2O_3, *n*-hexane/Et_2O, 40:1). The first fraction is a mixture of diferrocenylbutadiyne and 1,1,5-triferrocenyl-1-methoxypenta-2,4-diyne (**2a**), the second fraction is pure 1,1,5-triferrocenyl-1-methoxypenta-2,4-diyne (**2a**), and the third fraction is 1,1,5-triferrocenyl-1-hydroxypenta-2,4-diyne (**2b**), respectively. The more polar **2b** is formed by unavoidable hydrolysis of **2a** on the column and was eluted with *n*-hexane/Et_2O, 1:1. In total 186 mg (0.29 mmol, 37.7% yield) of **2a** and 197 mg (0.31 mmol, 40.3% yield) of **2b** were obtained.

Data for 2a. Orange powder, mp 159 °C, dec. Anal. Calcd for $C_{36}H_{30}Fe_3O$: C, 66.92; H, 4.68. Found: C, 66.85; H, 4.66. MS (EI, 70 eV): *m/z* 646 (M^+, 97%), 615 ($M^+ - OCH_3$, 20%), 494 ($M^+ - OCH_3 - CpFe$, 100%), 373 ($M^+ - OCH_3 - 2CpFe$, 74%). IR (KBr): 3101 w, 2935 w, 2835 w, 2225 m, 2144 w, 1640 w, 1408 w, 1227 m, 1135 m, 1107 m, 1088 s, 999 m, 941 m, 839 m, 818 s, 530 m, 513 s, 492 s, 466 s cm^{-1}. ^1H NMR (CD_2Cl_2, δ): 3.34 (3H, s, OCH_3); 4.15 (4H, m, subst Cp); 4.18 (10H, s, unsubst Cp); 4.23 (4H, m, subst Cp); 4.31 (5H, br s, unsubst Cp); 4.37 (2H, m, subst Cp); 4.59 (2H, m, subst Cp). ^{13}C NMR (CD_2Cl_2, δ): 52.0 (OCH_3); 67.3, 67.4, 67.5, 67.7, 69.4, 69.6, 70.3, 72.4 (Cp); 92.5 ($C{\equiv}C$).

Data for 2b. Orange powder, mp 180 °C, dec. Anal. Calcd for $C_{35}H_{28}Fe_3O$: C, 66.50; H, 4.46. Found: C, 66.23; H, 4.45. MS (FAB): *m/z* 632 (M^+, 100%), 615 ($M^+ - OH$, 38%), 494 ($M^+ - OH - CpFe$, 82%). IR (KBr): 3541 m, 3105 w, 2223 m, 2146 m, 1636 w, 1410 w, 1389 w, 1314 m, 1135 w, 1106 s, 1028 m, 1001 s, 831 m, 820 s, 799 m, 531 m, 511 s, 488 s, 463 s cm^{-1}. Single crystals were obtained from CH_2Cl_2 (Table 1, Figure 2, Supporting Information).

1,1,5-Triferrocenylpenta-1,2,3,4-tetraen-5-ylium Tetrafluoroborate (3). A 154 mg (0.24 mmol) amount of **2a** was dissolved in 30 mL of Et_2O in a round-bottom flask without protection from air (alternatively, a mixture of **2a**,**b** can be used with similar results, but due to the inferior solubility of **2b** the necessary amount of solvent increases considerably). The solution was stirred and 0.0335 mL (0.25 mmol) of a 54% solution of fluoroboric acid in Et_2O was added by syringe, resulting in precipitation of a green solid. The suspension was stirred further for 10 min to complete dehydration. Workup: The solid product was filtered off, washed with three portions of Et_2O, and dried in vacuo, yielding 134 mg (0.19 mmol, 80.1%) of 1,1,5-triferrocenylpenta-1,2,3,4-tetraene-5-ylium tetrafluoroborate (**3**).

Data for 3. Green, air-stable powder, mp not observed, >290 °C. Anal. Calcd for $C_{35}H_{27}BF_4Fe_3$: C, 59.89; H, 3.88. Found: C, 60.02; H, 3.89. HRMS (FAB): *m/z* 615.014 46 (M^+ of cation; exact mass calcd for $C_{35}H_{27}Fe_3$, 615.016 09). UV−vis (CH_2Cl_2; λ_{max}/log ϵ; Figure 3): 377/4.12, 761/3.75 nm. IR (KBr): 3112 w, 2163 s, 1710 w, 1414 m, 1385 m, 1329 m, 1108 s, 1082 s, 1046 s, 1034 s, 1005 m, 835 m, 702 m, 461 m cm^{-1}. ^1H NMR (CD_2Cl_2, δ): 4.38 (5H, s, unsubst Cp); 4.58 (10H, s, unsubst Cp); 4.74 (2H, br s, subst Cp); 5.30 (6H, br s, subst Cp); 5.87 (4H, br s, subst Cp). ^{13}C NMR (CD_2Cl_2, δ): 61.8, 71.3, 72.1, 73.4, 75.0, 78.2, 85.3 (Cp); 83.6, 93.1, 94.1, 99.7, 149.1 ($C{-}C{\equiv}C{-}C{\equiv}C \leftrightarrow C{=}C{=}C{-}C{\equiv}C \leftrightarrow C{=}C{=}C{=}C{=}C$).

Bis(1,1,5-triferrocenylpenta-1,2-dien-4-yn-3-yl) (4). A Schlenk vessel was charged with 30 mL of dry, deoxygenated dimethoxyethane (precooled to −55 °C), 44 mg (0.23 mmol) of monolithioferrocene[20] (*caution: pyrophoric powder!*), 140 mg (0.67 mmol) of CuBr·Me_2S complex, and 62 mg (0.09 mmol) of **3** under an atmosphere of argon. The resulting dark green suspension was stirred at −55 °C for 4 h and then the mixture was allowed to warm to room temperature overnight, resulting in a brown suspension. For workup, all volatile material was removed in vacuo and the residue was dissolved in a mixture of dichloromethane and *n*-hexane and purified by chromatography (basic alumina; eluents *n*-hexane, *n*-hexane/ether (9/1), and *n*-hexane/ether (1/1). The first fractions in the less polar eluents contain ferrocene, biferrocene, and other noncharacterized yellow products. With *n*-hexane/ether (1/1) a mixture of two red products was obtained. Further chromatographic separation of this mixture was not possible, but crystallization afforded 9 mg (0.007 mmol, 17% yield) of **4**.

Data for 4. Red, air-stable powder, mp not observed, >290 °C. HRMS (FAB): *m/z* 1230.051 02 (M^+; exact mass calcd for $C_{70}H_{54}Fe_6$, 1230.032 19). IR (KBr): 3091 m, 2958 m, 2925 m, 2856 m, 2182 w, 1725 w, 1629 m, 1459 m, 1412 m, 1381 m, 1293 m, 1262 s, 1105 s, 1055 s, 1026 s, 1001 s, 887 m, 818 s, 744 m, 486 s cm^{-1}. NMR and elemental analyses were not attempted due to the limited amount of material available.

1,1,5-Triferrocenyl-3-phenylpentadi-1,2-en-4-yne (5). A Schlenk tube charged with 60 mL of THF was cooled to −90 °C, and 233 mg (0.33 mmol) of **3** was added in one portion with protection from air, resulting in a green solution/suspension. A 0.20 mL volume of a 1.8 M solution of phenyllithium in cyclohexane/ether (70/30) (0.36 mmol) was added, and an immediate color change from green to red-brown occurred. Stirring was continued for 5 h. Workup: Solvents were removed in vacuo, and the residue was dissolved in ether. Chromatography (basic alumina, *n*-hexane/ether, 3:1) yielded 31 mg (0.045 mmol, 13.5%) of **5**.

Data for 5. Yellow, air-stable powder, mp 140 °C. Anal. Calcd for $C_{41}H_{32}Fe_3$: C, 71.14; H, 4.66. Found: C, 71.06; H, 4.68. MS (FAB): *m/z* 691.5 (M^+, 100%). IR (KBr): 3089 w, 2964 w, 2925 w, 2856 w, 2202 w, 1638 w, 1596 w, 1492 w, 1447 w, 1410 w, 1262 m, 1106 s, 1057 m, 1027 m, 1003 s, 816 s, 789 m, 768 m, 697 m, 627 w, 502 s cm^{-1}. ^1H NMR (CD_2Cl_2, δ): 4.24−4.32 (21H, m, subst and unsubst Cp); 4.55−4.61 (6H, m, subst Cp); 7.27−7.76 (5H, m, phenyl). ^{13}C NMR (CD_2Cl_2, δ): 68.6, 70.3, 71.7, 78.8, 81.4, 92.2, 95.9 (Cp and $C{=}C{=}C$ and $C{\equiv}C$); 126.6, 127.9, 128.9, 134.7 (phenyl). Single crystals were obtained from CH_2Cl_2/Et_2O (Table 1, Figure 4, Supporting Information).

1,1-Diferrocenyl-but-3-yn-1-ol (6a). A solution of allenylmagnesium bromide (7.60 mmol) in 150 mL of ether was prepared according to the published procedure.[4b] To this stirred solution was added at −40 °C a suspension of 2.0 g (5.02 mmol) of diferrocenyl ketone[14] in 60 mL of ether. The mixture was stirred overnight in a cooling bath which kept the reaction temperature below 10 °C, resulting in a yellow suspension. Aqueous workup and chromatography (basic alumina, *n*-hexane/ether, 10:1) yielded 2.107 g (4.81 mmol, 96%) of **6a**.

Data for 6a. Yellow, air-stable powder, mp 89 °C. Anal. Calcd for $C_{24}H_{22}Fe_2O$: C, 65.79; H, 5.06. Found: C, 65.62; H, 5.04. MS (EI, 70 eV): *m/z* 438 (M^+, 89%); 436 ($M^+ - 2H$, 18%), 397.5 ($M^+ - CH_2C{\equiv}CH - H$, 100%), 300 ($M^+ - FeCp - OH$, 73%). IR (KBr): 3552 m, 3537 m, 3444 m, 3319 m, 3298 m, 3259 m, 3095 w, 2946 w, 2121 w, 1638 w, 1412 m, 1106 s, 1063 m, 1046 m, 1025 m, 1003 m, 845 m, 814 s, 629 m, 486 s, 463 m cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.14 (1H, t, $C{\equiv}CH$); 2.81 (1H, s, OH); 3.13 (2H, d, CH_2); 4.10−4.17 (6H, m, subst Cp); 4.18 (10H, s, unsubst Cp); 4.28−4.31 (2H, m, subst Cp). ^{13}C NMR ($CDCl_3$, δ): 34.4 (CH_2); 66.3, 67.1, 67.5, 68.6, 70.6, 71.8 (Cp); 81.4 ($C{\equiv}CH$). Single crystals were obtained from CH_2Cl_2/Et_2O (Table 1, Figure 5, Supporting Information).

1,1-Diferrocenyl-1-methoxy-but-3-yne (6b). A Schlenk round-bottom flask was charged with 1.362 g (3.11 mmol) of **6a** dissolved in 125 mL of THF. The solution was cooled to −80 °C under protection from air and lithiated with 2.08 mL of a 1.5 M (3.12 mmol) methyllithium/ether solution. The stirred mixture was allowed to warm to −50 °C, and 1.00 mL

---

[20] (a) Guillaneux, D.; Kagan, H. B. *J. Org. Chem.* **1995**, *60*, 2502. (b) Rebiere, F.; Samuel, O.; Kagan, H. B. *Tetrahedron Lett.* **1990**, *31*, 3121. (c) Buchmeiser, M.; Schottenberger, H. *J. Organomet. Chem.* **1992**, *436*, 223.

(16 mmol, 5.14 mequiv) of methyl iodide was added. After stirring of the solution overnight and standard aqueous workup and chromatography (basic alumina, *n*-hexane/ether, 2:1) 1.30 g (2.88 mmol, 93%) of **6b** was obtained.

Data for 6b. Yellow, microcrystalline solid, mp 87−90 °C. Anal. Calcd for $C_{25}H_{24}Fe_2O$: C, 66.41; H, 5.35. Found: C, 66.20; H, 5.34. MS (EI, 70 eV): *m*/*z* 452 (M^+, 100%), 420 ($M^+ - OCH_3 - H$, 57%), 413 ($M^+ - CH_2C{\equiv}CH$, 99%), 398 ($M^+ - CH_2C{\equiv}CH - OCH_3$, 74%). IR (KBr): 3298 w, 3278 m, 3087 w, 2934 w, 2113 w, 1634 w, 1418 w, 1264 m, 1098 s, 1061 w, 1025 m, 1003 m, 826 s, 814 s, 783 m, 673 m, 652 m, 625 w, 523 m, 479 s, 457 m cm^{-1}. ^1H NMR ($CDCl_3$, δ): 2.14 (1H, t, $C{\equiv}CH$); 3.25 (2H, d, CH_2); 3.39 (3H, s, OCH_3); 4.09 (10H, s, unsubst Cp); 4.14−4.21 (4H, m, subst Cp); 4.28−4.31 (4H, m, subst Cp). ^{13}C NMR ($CDCl_3$, δ): 31.6 (CH_2); 51.8 (OCH_3); 66.9, 67.2, 67.4, 69.1, 71.3 (Cp).

1,1,5,5-Tetraferrocenyl-1-methoxy-pent-3-yn-5-ol (7). A solution of 1.30 g of (2.88 mmol, 2 mequiv) of **6b** in 100 mL of THF was cooled to −60 °C and lithiated with 1.92 mL of a 1.5 M (2.88 mmol, 2.0 mequiv) methyllithium/ether solution. The cooling bath was removed, and 572 mg (1.44 mmol, 1.0 mequiv) of diferrocenyl ketone[14] was added in one portion. Stirring was continued overnight at room temperature, and the resulting solution was filtered through a short plug of basic alumina. Solvents and other volatile materials were removed in vacuo, the residue was dissolved in ether, and the product was crystallized at −30 °C during 1 week. The crystals were collected on a filter funnel, washed with two portions of *n*-hexane, and dried in vacuo, yielding 1.220 g (1.43 mmol, 99.6%) of **7**.

Data for 7. Yellow, microcrystalline solid, mp 170 °C. Anal. Calcd for $C_{46}H_{42}Fe_4O_2$: C, 64.98; H, 4.98. Found: C, 64.69; H, 5.00. MS (EI, 70 eV): *m*/*z* 850.5 (M^+, 100%), 833.4 ($M^+ - OH$, 15%), 681.3 ($M^+ - OH - OCH_3 - FeCp$, 11%). IR (KBr): 3531 m, 3095 w, 2944 w, 2829 w, 2234 w, 1634 w, 1412 w, 1391 w, 1380 w, 1318 w, 1260 w, 1106 s, 1098 m, 1055 m, 1038 m, 1019 m, 1003 m, 863 w, 818 s, 486 s, 463 m cm^{-1}. ^1H NMR ($CDCl_3$, δ): 3.00 (1H, s, OH); 3.46 (2H, s, CH_2); 3.72 (3H, s, OCH_3); 4.09−4.13 (1H, m, unsubst and subst Cp); 4.19−4.24 (14H, m, unsubst and subst Cp); 4.30−4.32 (4H, m, subst Cp); 4.36−4.39 (4H, m, subst Cp). ^{13}C NMR ($CDCl_3$, δ): 33.1 (CH_2); 52.2 (OCH_3); 65.6, 67.0, 67.2, 67.3, 67.6, 67.7, 67.9, 68.9, 69.0, 76.5 (Cp); 94.7 ($C{\equiv}C$).

1,1,5,5-Tetraferrocenylpenta-2,3,4-trien-1-ylium Tetrafluoroborate (8). To a solution of 302 mg (0.36 mmol) of **7** in 10 mL of dichloromethane was added 1.1 mequiv of tetrafluoroboric acid (53 μL of a 54% ethereal solution). The color of the mixture changed from yellow to purple, and the product was precipitated by addition of 80 mL of *n*-hexane. The purple solid was filtered off, washed with three portions of ether, and dried in vacuo, yielding 306 mg (0.345 mmol, 95.7%) of 1,1,5,5-tetraferrocenylpenta-2,3,4-trien-1-ylium tetrafluoroborate (**8**).

Data for 8. Air-stable purple solid; mp not observed,>290 °C, dec. Anal. Calcd for $C_{45}H_{37}Fe_4BF_4$: C, 60.87; H, 4.20. Found: C, 61.01; H, 4.19. MS (EI, 70 eV): *m*/*z* 802.5 (M^+ of cation + H, 12%), 801 (M^+ of cation, 21%), 800 (M^+ of cation − H, 11%), 680.5 (M^+ of cation − FeCp, 10%). HRMS (FAB): *m*/*z* 801.026 91 (M^+ of cation; exact mass calcd for $C_{45}H_{37}Fe_4$, 801.029 771). UV−vis (CH_2Cl_2; $\lambda_{max}/\log \epsilon$; Figure 3): 387/4.21, 534/4.11, 917/4.25 nm. IR (KBr): 3097 w, 2964 w, 2925 w, 2856 w, 2090 s, 1636 w, 1525 w, 1466 s, 1436 s, 1414 m, 1382 m, 1353 m, 1302 m, 1264 w, 1125 m, 1108 s, 1084 s, 1003 m, 824 s, 704 m, 477 m cm^{-1}. ^1H NMR (CD_2Cl_2, δ): 4.39 (10H, s, unsubst Cp), 4.47−4.70 (16H, m, unsubst and subst Cp), 5.24 (6H, m, subst Cp), 5.61 (4H, subst Cp), 5.95 (1H, m, C_5H). ^{13}C NMR (CD_2Cl_2, δ): 73.7, 74.1, 74.7, 75.4, 76.3, 76.4, 76.7, 77.0, 77.6, 78.0, 78.7, 80.3, 81.8, 82.4, 82.6, 84.9, 89.2, 90.3, 90.6, 90.7 (Cp); 106.0, 110.4, 126.8, 135.2, 154.8, 160.4, 167.8 (C_5H). ^{57}Fe Mössbauer data (90 K): $IS = 0.521 \pm 0.001$ mm s^{-1}; $QS = 2.120 \pm 0.003$ mm s^{-1}.

1,1,5,5-Tetraferrocenyl-3-methoxypenta-1,2,4-triene (9). A 64 mg (0.072 mmol) amount of **8** was dissolved in 15 mL of methanol in a round-bottom flask. One pellet of KOH was added, and the mixture was sonicated in a laboratory ultrasonic cleaning bath for 1 min. The color of the solution immediately changed from purple to yellow. Solvents were removed in vacuo, the orange residue was dissolved in ether, and the organic solution was washed with three portions of H_2O and dried with Na_2SO_4. After removal of solvent and drying in vacuo 54 mg (0.065 mmol, 90%) of 1,1,5,5-tetraferrocenyl-3-methoxypenta-1,2,4-triene (**9**) was obtained.

Data for 9. Yellow, microcrystalline solid, mp 136 °C. Anal. Calcd for $C_{46}H_{40}Fe_4O$: C, 66.39; H, 4.84. Found: C, 66.22; H, 4.86. MS (FAB): *m*/*z* 832.2 (M^+, 92%), 801 ($M^+ - OCH_3$, 46%), 680 ($M^+ - OCH_3 - FeCp$, 100%), 615 ($M^+ - OCH_3 - H$, 31%). IR (KBr): 3095 w, 2962 w, 2927 w, 2856 w, 2819 w, 2194 w, 1634 w, 1463 w, 1410 w, 1262 m, 1246 w, 1106 s, 1075 s, 1052 m, 1038 m, 1025 m, 1001 s, 926 w, 818 s, 687 w, 486 s cm^{-1}. ^1H NMR ($CDCl_3$, δ): 3.34 (3H, s, OCH_3); 4.07−4.45 (32H, m, unsubst and subst Cp); 4.79 (2H, m, subst Cp); 5.31 (2H, m, subst Cp); 6.40 (1H, s, $C{=}CH{-}C{=}C{=}C$). ^{13}C NMR ($CDCl_3$, δ): 52.2 (OCH_3); 67.1, 67.3, 67.7, 67.8, 68.4, 68.9, 69.1, 69.3, 69.8 (Cp); 93.4, 102.7, 160.2 ($C{=}CH{-}C{=}C{=}C$).

1,2-Bis(diferrocenylmethylidene)-3,4-bis(1,1′-diferrocenylvinyl)cyclobut-3-ene (10). A Schlenk tube was charged with a solution of 54 mg (0.064 mmol) of **9** in 10 mL of ether. By removal of the ether in vacuo a thin film of **9** was obtained. Heating under vacuum to 200 °C for 30 min by means of an IR lamp (375 W/220 V) connected to a variable resistor[21] yielded a brown crude product which was dissolved in dichloromethane. Insoluble materials were removed by filtration through a short plug of basic alumina, the solution was evaporated, the residue was chromatographed (basic alumina, *n*-hexane/ether, 2 of 1) to remove unreacted starting material, and the product **10** was obtained from crystallization at −30 °C from a *n*-hexane solution, affording 16 mg (0.001 mmol, 30.8%) of **10**.

Data for 10. Red crystals, mp 170 °C, dec. MS (FAB): *m*/*z* 1604.9 ($M^+ + 3H$, 21%), 1603.9 ($M^+ + 2H$, 57%), 1602.9 ($M^+ + H$, 94%), 1602.0 (M^+, 100%), 801 ($M^+/2$, 25%), 680 ($M^+/2 - FcH$, 19%). IR (KBr): 3091 w, 2962 s, 2927 s, 2858 m, 2364 w, 1729 s, 1638 m, 1461 m, 1412 m, 1382 m, 1291 s, 1264 s, 1119 s, 1106 s, 1073 s, 1034 s, 1001 s, 816 s, 747 m, 484 s, 471 s cm^{-1}. UV−vis (dichloromethane; $\lambda_{max}/\log \epsilon$): 393/4.46, 474/4.17 nm. NMR and elemental analysis were not attempted due to the limited amount of material available.

Single crystals were obtained from dichloromethane/ether/toluene (Table 1, Figure 6, Supporting Information).

1,1,5,5-Tetraferrocenylpenta-1,2,3,4-tetraene (11). A Schlenk vessel was charged with 60 mL of dry, deoxygenated THF and cooled to −76 °C. A 38 mg (0.34 mmol, 1.5 mequiv) amount of potassium *tert*-butoxide, 0.17 mL (0.34 mmol, 1.5 mequiv) of a 2.0 M *n*-butyllithium solution in *n*-pentane, and 200 mg (0.29 mmol, 1.0 mequiv) of **8** were added under protection from air. Upon addition of **8**, a dark green solution/suspension was obtained which changed its color to purple within 1 min. The reaction was allowed to continue for 1 h, during which time the temperature rose to −48 °C. Workup: Solvents were removed in vacuo, and the residue was dissolved in a mixture of dichloromethane/ether and filtered through a short plug of basic alumina. The filtrate was evaporated, the crude product was washed with small portions of *n*-hexane to remove apolar side products until the *n*-hexane fractions were colorless, and the product was dried in vacuo, affording 83 mg (0.104 mmol, 46%) of 1,1,5,5-tetraferrocenylpenta-1,2,3,4-tetraene (**11**).

---

(21) Pool, G. C.; Teuben, J. H. IR Radiation as a Heat Source in Vacuum Sublimation. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 3, p 31.

Data for 11. Red microcrystalline solid, mp 150 °C, dec. Anal. Calcd for $C_{45}H_{36}Fe_4$: C, 67.55; H, 4.53. Found: C, 67.51; H, 4.52. MS (FAB; matrix: nitrobenzyl alcohol): *m*/*z* 953 (M^+ + nitrobenzyl alcohol, 45%), 802 ($M^+ + 2H$, 48%); 801 ($M^+ + H$, 100%), 800 (M^+, 37%), 680 ($M^+ - FeCp + H$, 51%), 615 ($M^+ - Fc$, 30%). IR (KBr): 3098 w, 2960 w, 2929 m, 2858 w, 2030 w, 1729 m, 1686 w, 1466 m, 1412 m, 1380 m, 1285 s, 1108 s, 1061 m, 1048 m, 1025 m, 1001 s, 901 m, 822 s, 488 s, 479 s, 465 s cm^{-1}. Raman: 2035 s cm^{-1} (C=C=C=C=C). UV−vis (CH_2Cl_2; λ_{max}/log ϵ; Figure 3): 349/4.60, 483/3.88 nm. ^1H NMR (CD_2Cl_2, δ): 4.27 (20H, s, unsubst Cp); 4.38 (8H, m, subst Cp); 4.71 (8H, m, subst Cp). ^{13}C NMR (CD_2Cl_2, δ): 69.2, 69.4, 70.3, 82.1 (Cp); 116.0 (C(1) of C=C=C=C=C); 158.2 (C(2) of C=C=C=C=C); 178.2 (C(3) of C=C=C=C=C). ^{57}Fe Mössbauer data (90 K): IS = 0.533 ± 0.003 mm s^{-1}; QS = 2.347 ± 0.001 mm s^{-1}. CV (CH_2Cl_2, 295 K, V vs SCE): $E_{1/2}{}^1 = +0.45$, $E_{1/2}{}^2 = +0.54$. Single crystals were obtained from CH_2Cl_2/Et_2O (Table 1; Figures 7 and 8; Supporting Information).

Acknowledgment. We thank Prof. Rolfe Herber, Racah Institute of Physics, The Hebrew University, Jerusalem, Israel, for Mössbauer spectroscopic measurements and Dipl.Phys. Karl-Joachim Schuchter, Renishaw GmbH, Pliezhausen, Germany, and Dr. Anette Zimmermann, Renishaw plc, Gloucestershire, U.K., for measurement of Raman spectra. This work was supported in part by the European HCM-Project "Electron and Energy Transfer in Model Systems and their Implications for Molecular Electronics" (Grant No. CHRX-CT94-0538) and by a research scholarship by the Austrian Federal Ministry of Science and Traffic (granted to M.S.).

Supporting Information Available: Tables of crystal data and structure refinement details, anisotropic thermal parameters, fractional atomic coordinates, isotropic thermal parameters for the non-hydrogen atoms, all bond lengths and angles, and fractional atomic coordinates for the hydrogen atoms for **1**, **2b**, **5**, **6a**, **10**, and **11** (51 pages). Ordering information is given on any current masthead page.

OM980023A