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Cationic and neutral cumulene sp-carbon chains with ferrocenyl termini

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Contents

Abstract

The synthesis, physical and chemical properties of cationic $(Fc)_2C{=}C_n{=}C(Fc)^+$ and neutral $(Fc)_2C{=}C_n{=}C(Fc)_2$ cumulenes with ferrocenyl substituents and with up to ten cumulated carbons is summarized. In comparison to metallacumulenes and to purely organic cumulenes, the combination of a cumulenic backbone with directly attached ferrocenyl substituents significantly alters the usually observed reactivity and/or stability. The terminal metallocenyl groups serve as redox-active centers, inductive donors, and sterically encumbered groups, effecting (i) electronic coupling through the bridging cumulene ligand, (ii) stabilization of

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adjacent electron-deficient carbenium centers, (iii) increased nucleophilic reactivity of the cumulene moiety, and (iv) steric hindrance with accompanying reduced reactivity for shorter cumulenes and enhanced stability for longer cumulenes. The chemical reactivity of sterically unhindered neutral cumulenes $(Fc)_2C{=}C_n{=}C(Fc)_2$ includes complex formation with late transition metals, ferrocenophane formation with zero-valent Ni, and cycloadditions with olefins, alkynes, and fullerenes. $(Fc)_2C{=}C_n{=}C(Fc)^+$ salts are novel organometallic non-linear optical materials which show significant second-order non-linear optical properties.

Keywords: Cumulene; Ferrocene

1. Introduction

Rigid-rod conjugated molecules [1] with electroactive end groups are of intense interest due to their anticipated applications as nanoelectronic devices [2–5] or as non-linear optical materials [6]. Within this wide area of research [1] compounds containing a bridging sp-carbon chain (oligoynes or cumulenes) between organometallic moieties are especially attractive due to the unsaturated and therefore conjugating bridging all-carbon ligand and due to the many possible modifications of the terminal organometallic group with regard to type of metal, oxidation state, and choice of peripheral co-ligands [7–10]. Depending on the oxidation state of the organometallic substituents such 'metallacumulenes' can exist either in their cumulene form $[M]{=}(C{=}C)_n{=}[M]$ or in their oligoyne form $[M]{-}(C{\equiv}C)_n{-}[M]$, respectively.

An alternative to these *metalla*cumulenes are *organic* cumulenes $R_2C{=}(C)_n{=}CR_2$ with electroactive substituents. Purely organic cumulenes with alkyl or aryl substituents are isolable with up to six cumulated carbons and have been claimed to be detectable in solution with up to ten cumulated carbons [11,12]. Here we summarize our results on cationic $(Fc)_2C{=}(C)_n{=}C(Fc)^+$ and neutral $(Fc)_2C{=}(C)_n{=}C(Fc)_2$ ferrocenyl cumulenes. There are a number of good reasons for the choice of ferrocenyl substituents as termini: (i) Fc/Fc^+ is probably the most stable redox pair in organometallic chemistry [13], allowing the electrochemical investigation of electronic communication through the bridging cumulene ligand; (ii) Fc groups are known to effectively stabilize adjacent electron-deficient carbenium ions [14,15], giving access to novel conjugated (cumulenic) carbenium salts of unprecedented stability; (iii) the cylindrical Fc moiety is a quite bulky group, offering the possibility to synthesize long kinetically stabilized cumulenes; and (iv) Fc is an electron donor comparable in strength to *p*-methoxyphenyl [16], thereby increasing the nucleophilicity of the carbons of the cumulenic bridging ligand. These effects (i)–(iv) will increase with the number of ferrocenyl groups bonded to the cumulene moiety, therefore our interest is focused on the chemistry of perferrocenylated cationic and neutral cumulenes with three or four Fc groups, respectively. A pictorial representation of some of the chemical properties discussed below is given in Scheme 1 for the case of tetraferrocenylhexapentaene (tetraferrocenyl[5]-cumulene).

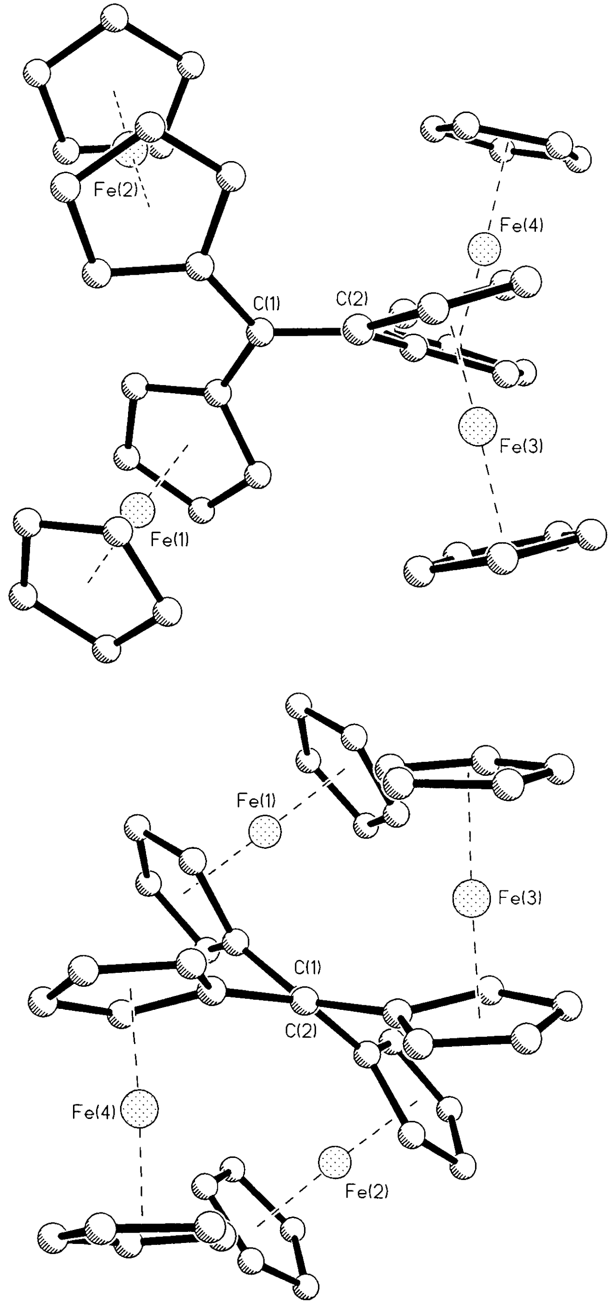
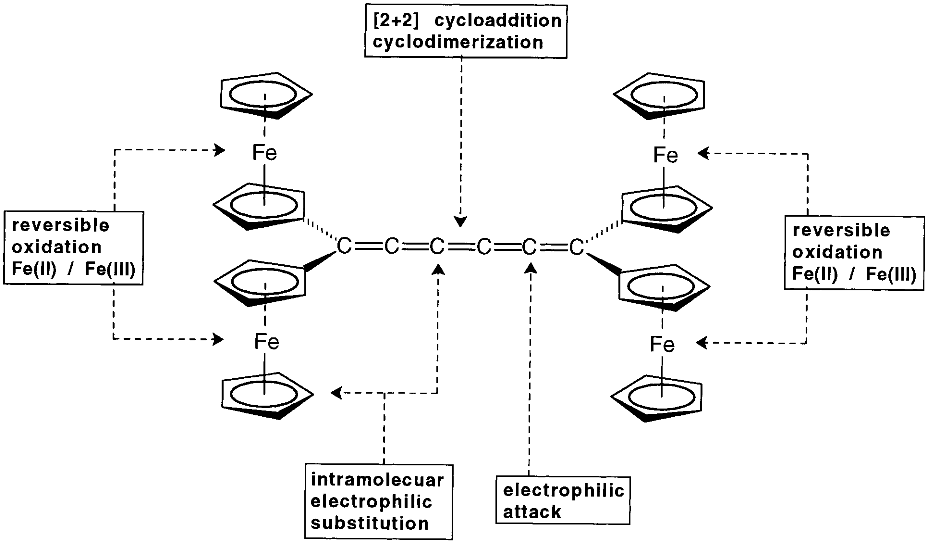


Fig. 1. Two views (a) and (b) of the single crystal structure [17] of tetraferrocenylethylene (**3**).

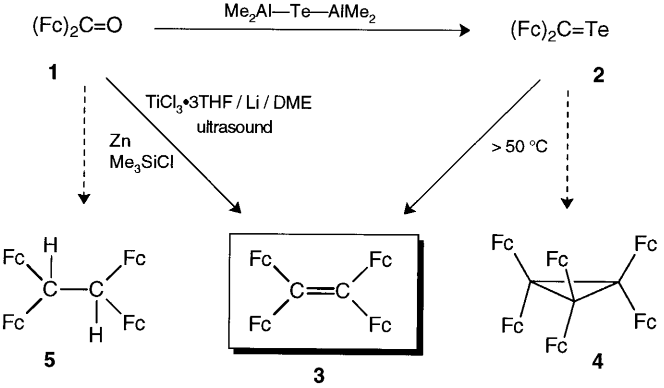


Scheme 1. Summary of some chemical properties of tetraferrocenyl[5]cumulene.

2. Tetraferrocenylethylene

Although tetraferrocenylethylene $(Fc)_2C{=}C(Fc)_2$ (**3**) is by definition not a cumulene, this compound is the logical starting member in the series of perferrocenylated cumulenes $(Fc)_2(C)_n(Fc)_2$ ($n = 2, 3, 4$ ...). According to Scheme 2 olefin **3** can be prepared by three synthetic routes [17].

First, diferrocenylketone (**1**) [18], which is the key starting material for all ferrocenyl cumulene compounds, can be converted to the corresponding telluroketone (**2**) [19] by reaction with bis(dimethylaluminum) telluride which is the most efficient oxygen–tellurium exchange reagent [20]. Thermal extrusion of elemental



Scheme 2. Synthesis of tetraferrocenylethylene (**3**).

tellurium affords **3** in admixture with traces of hexaferrocenylcyclopropane (**4**). One might at first assume that this reaction pathway involves diferrocenylcarbene intermediates, but more likely is a mechanism with formation of a [2 + 2] cycloadduct of diferrocenyltelluroketone followed by twofold elimination of tellurium [17]. At this point we note that the generation of diferrocenylcarbene is not possible starting from either diferrocenyldiazomethane [21] prepared by oxidation of diferrocenylhydrazone [22], or by attempted deprotonation of diferrocenylmethylium salts with various bases [23] in analogy to the successful synthesis of Wanzlick/Arduengo-carbenes from the corresponding imidazolium salts [24]. Hence the earlier claimed stabilization of carbenes by α-ferrocenyl substituents [25,26] seems to be unjustified.

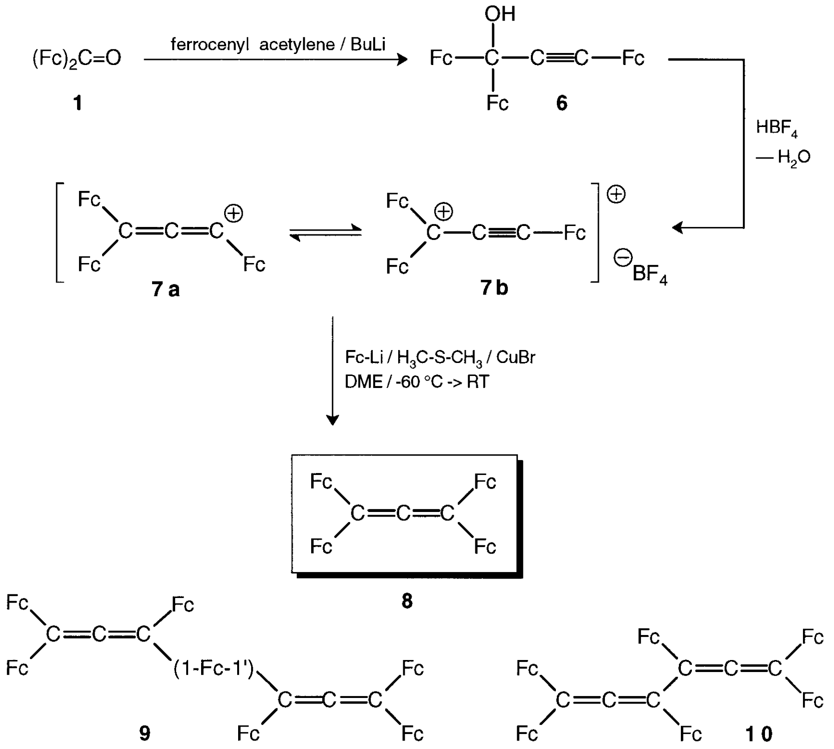
Second, ultrasound promoted McMurry reaction of ketone **1** with low-valent titanium yields a mixture of olefin **3** and tetraferrocenylethane (**5**) [17]. Third, trimethylchlorosilane modified Clemmensen reduction [27] of **1** affords the same products **3** and **5** [17], similarly as the reduction of diferrocenylketone (**1**) with elemental Mg in the presence of catalytic amounts of MgI_2 [28].

Tetraferrocenylethylene (**3**) is one of the most distorted olefins known (Fig. 1). Due to the presence of four close ferrocenyl groups a propeller-like structure with an elongated ($d_{C=C} = 138.1$ pm) and twisted (35°) double bond is observed in the solid state, resulting in a molecule of D_2 symmetry with helical chirality [17], similar as in other (purely organic) sterically crowded olefins [29]. ^{1}H NMR spectroscopy shows an ABCD spin system for the four hydrogens of the substituted Cp rings of the magnetically equivalent four ferrocenyl groups, indicative of non-rotating ferrocenyl moieties, hence also in solution a racemic mixture is present. Resolution of the enantiomers can be achieved by HPLC on a chiral stationary phase, although no complete baseline separation proved possible up to now [30]. In concurrence with the elongated and weakened double bond observed in the single crystal structure analysis, a very low corresponding stretching vibration $\nu_{C=C} = 1474$ cm^{-1} is detected in the Raman spectrum. Cyclic voltammetry shows four distinct oxidations ($E_{1/2} = 0.09$, 0.26, 0.41, 0.62 V versus SCE) in accord with the number of ferrocenyl substituents. Compared to the oxidation potential of ferrocene (0.31–0.32 V), the first half-wave oxidation potential (0.09 V) of tetraferrocenylethylene (**3**) is significantly lower, close to the value of pentamethylferrocene (0.14 V) [31], illustrating strong electronic communication between the four electron-donating ferrocenyl substituents. ^{57}Fe Mössbauer spectroscopy of **3** gives hyperfine parameters very similar in value to those of other ferrocene derivatives [32], showing that γ ray resonances of ferrocenes are mainly determined by the Cp ring–iron interaction and insensitive to the structural details of σ-bonded moieties.

Chemical reactivities of olefin **3** are limited to some typical ferrocene properties, i.e. Friedel–Crafts acylation [17] and clathrate formation with fullerene C_{60} [33], on the other hand the central double bond is completely unreactive owing to its steric shielding by the four metallocenyl substituents.

3. Tetraferrocenylallene (tetraferrocenyl[2]cumulene)

Tetraferrocenylallene is the shortest cumulene in this series of perferrocenylated cumulenes. Although a few allenes with one or two ferrocenyl substituents have been synthesized by straightforward organic transformations [34], the synthesis of tetraferrocenylallene cannot be achieved by reactions which proved successful in the case of arylated allenes [35], due to severe steric hindrance by the four bulky ferrocenyl termini. On the other hand, the electronic stabilization of adjacent electron-deficient carbenium centers [14,15] allows the synthesis of (triferrocenyl)allenylium/propargylium tetrafluoroborate **7a**/**7b** [36], which can be envisaged as the first air-stable cumulenic carbenium salt (Scheme 3).



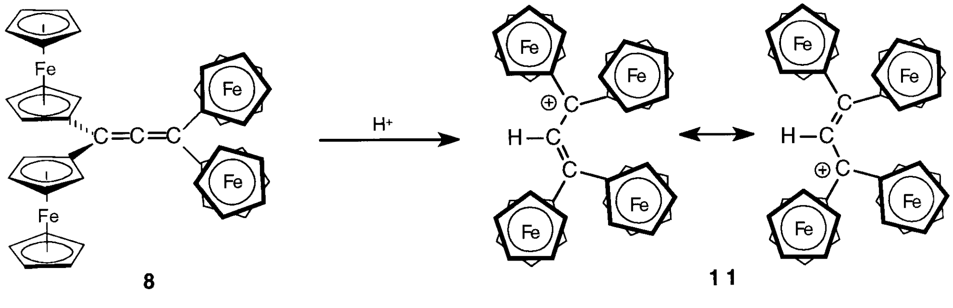
Scheme 3. Synthesis of tetraferrocenyl[2]cumulene (**8**).

The dark green color ($\lambda_{max} = 760$ nm) of **7a**/**7b** and the observation of a very intense IR cumulene stretching vibration ($\nu_{C=C=C} = 2151$ cm^{-1}) is indicative of predominance of formula **7a** [36] and the two strucures **7a** and **7b** are in thermal equilibrium, as can be shown by variable temperature ^{57}Fe Mössbauer spectroscopy [32]. In comparison to recently reported (arene)Cr(CO)$_3$-stabilized propargyl-allenyl cations [37], compound **7a**/**7b** gets its unprecedented stability from the combined electronic and steric effects of three ferrocenyl substituents.

Cumulenic carbenium salt **7a**/**7b** was used as the progenitor of tetraferrocenylallene (**8**) (Scheme 3). However, the formally simple nucleophilic addition of a ferrocenyl carbanion proved in fact more complex than expected and radical coupling byproducts **9** and **10** were always formed in addition to the desired allene (**8**) as the main product [35].

Tetraferrocenyl[2]cumulene (**8**) is a regular orange allene with a linear C_3 carbon chain and with perpendicular π-planes (Fig. 2). The ^1H and ^{13}C NMR spectral data show unexceptional chemical shifts and an AA′BB′ spin system for the hydrogens of the substituted cyclopentadienyl rings, ruling out the existence of helically chiral enantiomers. Cyclic voltammetric measurements give three reversible waves ($E^1_{1/2} = 0.32$, $E^2_{1/2} = 0.42$, $E^{3,4}_{1/2} = 0.52$ V versus SCE), with the first two oxidations corresponding to one-electron transfers and the third oxidation to a non-separated two-electron transfer. The first oxidation occurs at a potential identical to that of ferrocene, showing negligible electron-donation through the C_3 carbon chain due to the orthogonality of the two π-systems of the [2]cumulene. The observation of only four oxidation processes corresponds with the number of ferrocenyl substituents, but on the other hand it indicates that a hypothetical radical cation $(Fc)_2C{=}C{=}C(Fc)_2^{+}$ analogous to Berndt's tetra-*tert*-butylallene radical cation [38] is non-existent.

Organic electron-rich allenes $R_2C{=}C{=}CR_2$ (R = dialkylamino and/or alkoxy) have been reported to be strong nucleophiles [39] forming donor-stabilized allylic cationic or ylidic products with cationic (i.e. H^+) or neutral (i.e. S_n, CO_2, CS_2, SO_2) electrophiles. As noted in the introduction, the ferrocenyl moiety is an electron-donor comparable in strength to *p*-methoxy-phenyl and also an effective stabilizing group for α-carbenium ions. Therefore we expected tetraferrocenylallene (**8**) to form similar cationic or ylidic products when reacted with such electrophiles. However, only protonation yielding a brown allylium salt (**11**) of limited stability and no reaction with the other reagents proved possible (Scheme 4), due to steric hindrance in the planar allylium system. In direct comparison, an allylium salt with only three ferrocenyl substituents is much more stable [36]. Therefore, ferrocenyl-analogs of Ziegler's tetraphenylallyl [40,41] and Koelsch's pentaphenylallyl [42,43] radical cannot be synthesized.



Scheme 4. Protonation of allene (**8**).

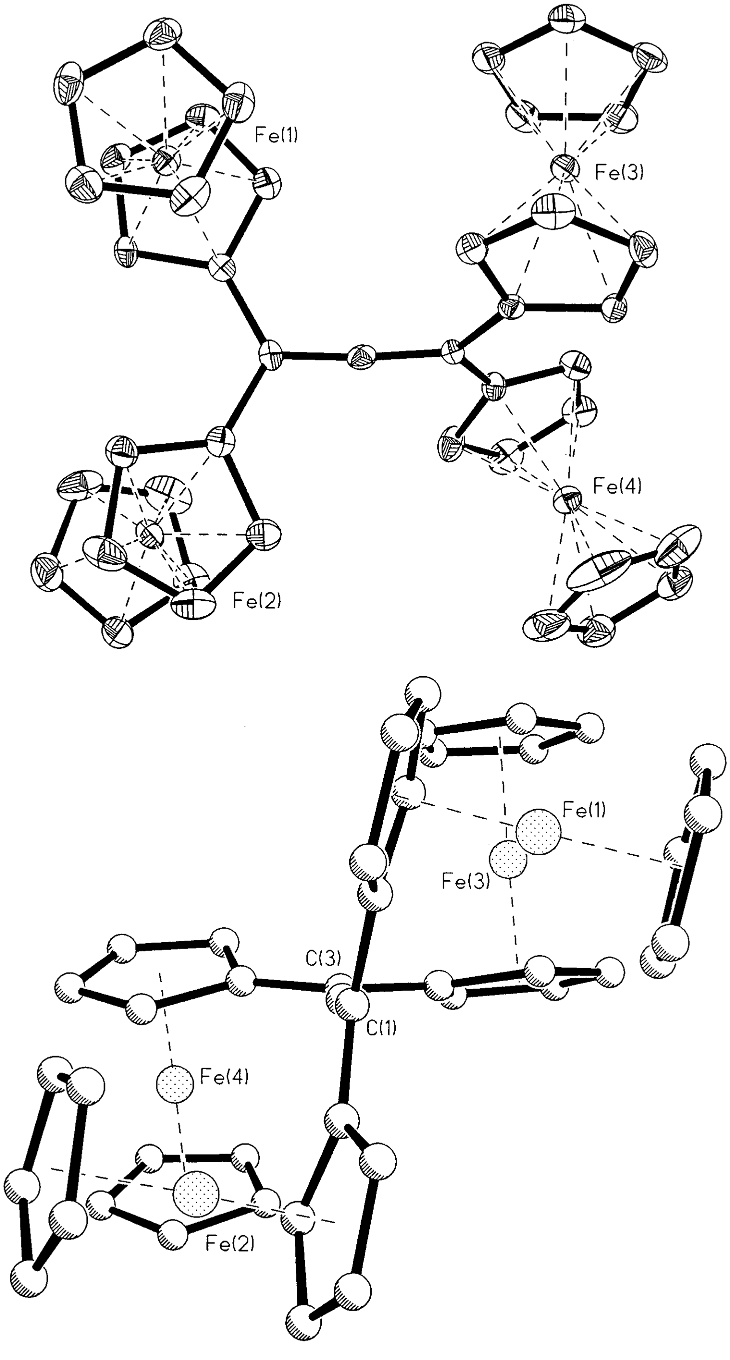
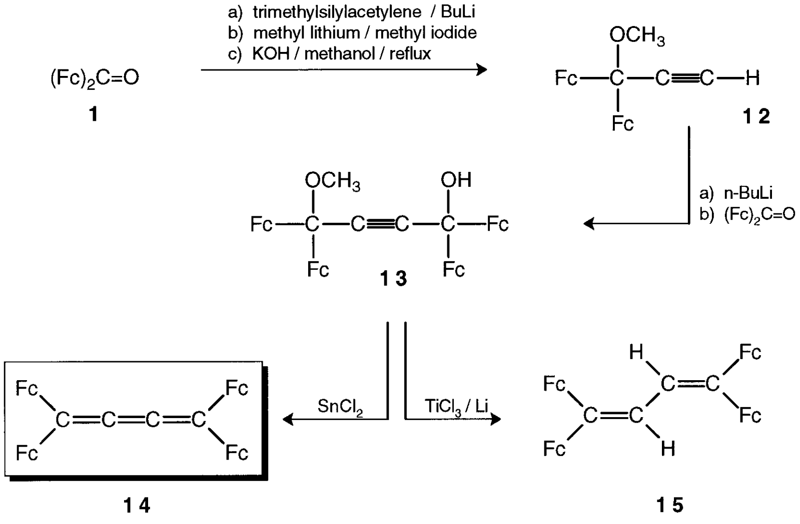


Fig. 2. Two views (a) and (b) of the single crystal structure [35] of tetraferrocenyl[2]cumulene (**8**).

4. Tetraferrocenylbutatriene (tetraferrocenyl[3]cumulene)

Organic tetrasubstituted butatrienes are easily synthesized by interaction of ketones with dimetalated propynols, followed by reduction. With diferrocenylmethoxypropyne (**12**) as an O-protected propynol an analogous reaction sequence is possible (Scheme 5) [33]: nucleophilic addition of metalated **12** to diferrocenylketone yields 1,1,4,4-tetraferrocenyl-1-hydroxy-4-methoxy-butyne (**13**), and reduction with stannous chloride finally affords the desired tetraferrocenyl[3]cumulene (**14**). The choice of reducing agent in this reaction is crucial, with other reductants (e.g. Zn/trimethylchlorosilane, SmI_2, $Fe(CO)_5$, $Fe_2(CO)_9$, low-valent titanium) only traces of **14** were obtained or over-reduced products like tetraferrocenylbutadiene (**15**) were observed, respectively.

Cumulene **14** is a red ($\lambda_{max} = 556$ nm) compound which is only slightly soluble in common organic solvents, similar to other organic tetra(aryl)substituted C_4-cumulenes [11,12]. Proton NMR showed once again regular undistorted ferrocenyl substituents, indicative of non-restricted rotation of the four magnetically equivalent ferrocenyl groups; therefore as found for allene (**8**) no racemic mixture of helically chiral rotamers are present and no stereoisomers (*cis*/*trans* or *syn*/*anti*) with respect to the C_4 carbon chain exist. Due to the low solubility, no signals were observed for these quaternary carbons in the ^{13}C NMR spectrum of **14**. The symmetrically substituted C_4 chain gives rise to an intense stretching vibration ($\nu_{C=C=C=C} = 1905$ cm^{-1}) in the Raman spectrum, comparable to the value of metallacumulene $L_nRe{=}C{=}C{=}C{=}C{=}ReL_n$ ($\nu_{Re=C=C=C=C=Re} = 1883$ cm^{-1}) [44]. ^{57}Fe Mössbauer spectroscopy of cumulene **14** gave hyperfine parameters close to those of ferrocene and other ferrocenyl cumulenes [32], showing that the isomer shift and quadrupole splitting are insensitive to the nature of the ligand bridging the ferrocenyl termini.



Scheme 5. Synthesis of tetraferrocenyl[3]cumulene (**14**).

All attempts to grow suitable single crystals for a structure analysis failed owing to the low solubility of **14**. However, synchrotron X-ray powder diffraction data were measured and Rietveld refinement was possible [45], giving proof of the connectivity of the molecule, although only an apparent polymeric structure was obtained owing to disordering problems (Fig. 3). Most interesting, in this case the ferrocenyl substituents adopt a *syn* conformation with regard to the C_4 chain, although an *anti* arrangement with less steric interaction of the two pairs of ferrocenyl termini was expected.

Electrochemical measurements of **14** gave only two reversible one-electron oxidations ($E^1_{1/2} = 0.25$, $E^2_{1/2} = 0.41$ V versus SCE); in comparison to tetraferrocenylallene (**8**) there is substantial electronic communication owing to the planarity of the two π-systems of the terminal carbons of the C_4 carbon chain.

In terms of chemical reactivity, cumulene **14** is still quite unreactive because of steric shielding of the cumulene carbon chain: only protonation yielding dark green 1,1,4,4-tetraferrocenyl-buta-2,3-dien-1-ylium salts proved possible. However, attempted late transition metal complex formation failed. Clathrate formation with fullerene C_{60} is possible, although the crystals obtained diffracted only very poorly, most likely owing to the often encountered statistical disordering in charge transfer complexes of fullerenes with weak donors like metallocenes [33].

5. Tetraferrocenylpentatetraene (tetraferrocenyl[4]cumulene)

In general, cumulenes with five carbons are quite difficult to synthesize and only very few examples of organic $R_2C{=}C{=}C{=}C{=}CR_2$ compounds are known [11,12]. In analogy to the successful synthesis of tetraferrocenylallene (**8**) by nucleophilic addition of a ferrocenyl carbanion equivalent to triferrocenyl[2]cumulene salt **7a**/**7b**, we anticipated that an analogous preparation of $(Fc)_2C{=}C{=}C{=}C{=}C(Fc)_2$ might be feasible. Accordingly, diferrocenylmethoxypropyne (**12**) was elongated by cross-coupling of the corresponding iodide (**13**) with copper ferrocenylacetylide to yield triferrocenylpentadiyne (**14**) (Scheme 6) [46].

Elimination of methanol was effected by addition of fluoroboric acid, affording triferrocenyl[4]cumulenium tetrafluoroborate **15a**/**15b**/**15c** as a green air-stable powder. No clear distinction between the possible structures **15a**, **15b**, **15c** is possible according to the available spectroscopic data, however it is quite evident from UV–vis data ($\lambda_{max} = 761$ nm), IR spectroscopy (very intense cumulene vibration at 2163 cm^{-1}), ^{57}Fe Mössbauer spectroscopy [32] (two resolvable doublets with a temperature-dependent population), and ^{13}C NMR shifts (five signals in the range 83.6–149.1 ppm) that a conjugated C_5 carbon chain with major cumulene character is present. Using this novel cumulenium salt as the progenitor of the desired tetraferrocenyl[4]cumulene, however, met with failure. No nucleophilic addition of a ferrocenyl carbanion was possible owing to redox reactions resulting (inter alia) in the formation of hexaferrocenyl-C_{10} compound (**16**). On the other hand, the reaction of the ambident electrophile **15a**/**15b**/**15c** with phenyl lithium showed that nucleophilic addition is possible, but the observed 100% regioselectivity (C(3) versus

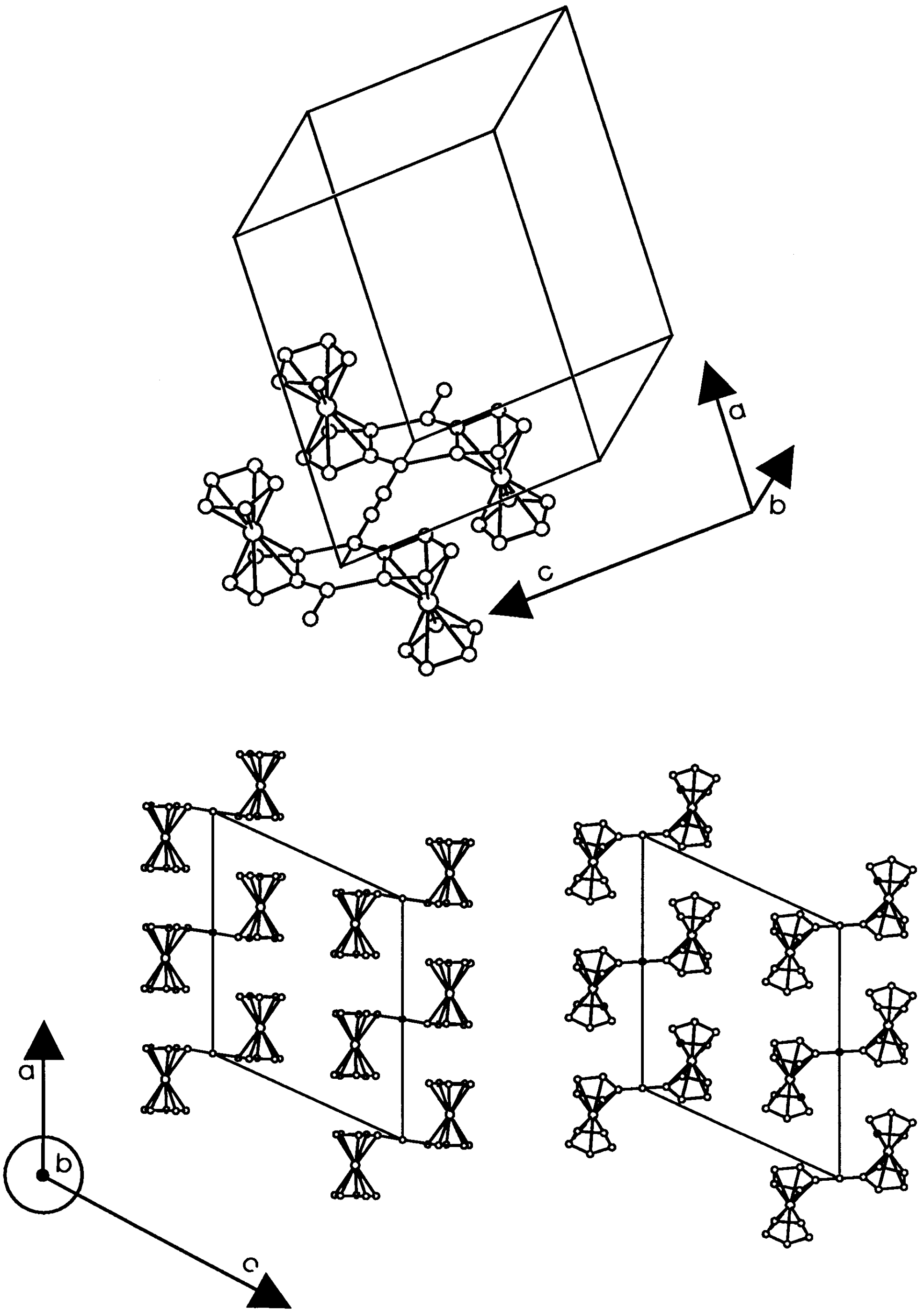
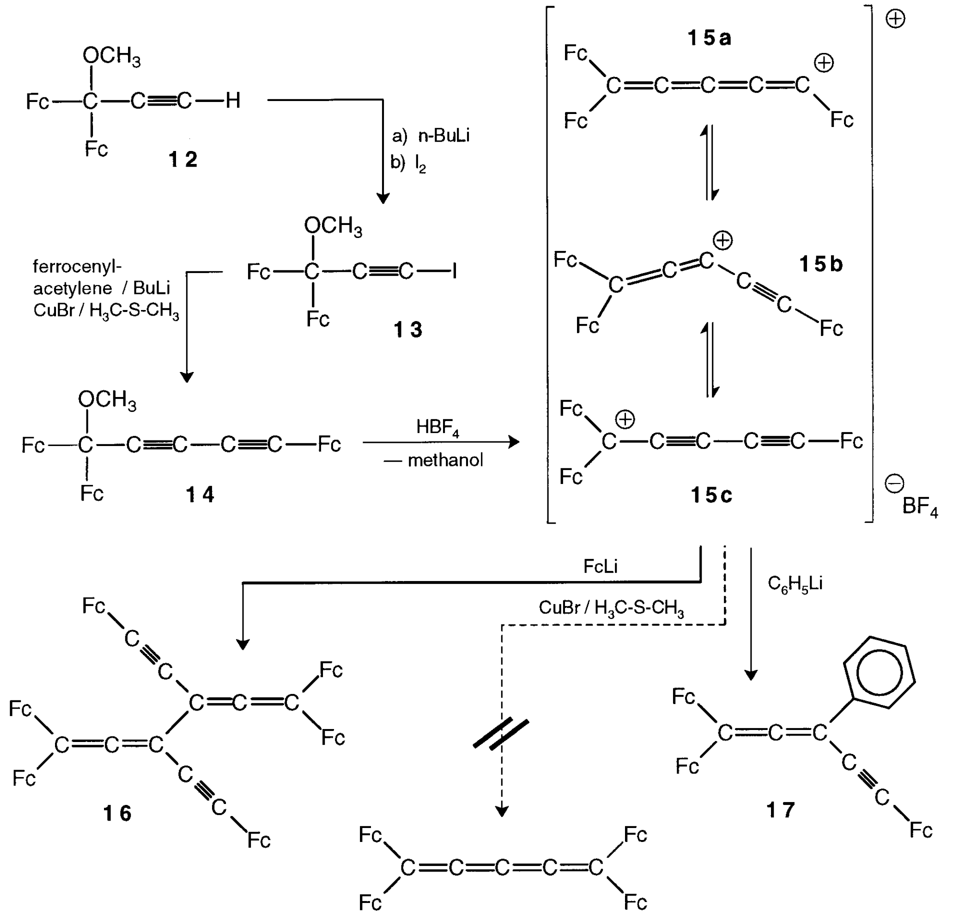


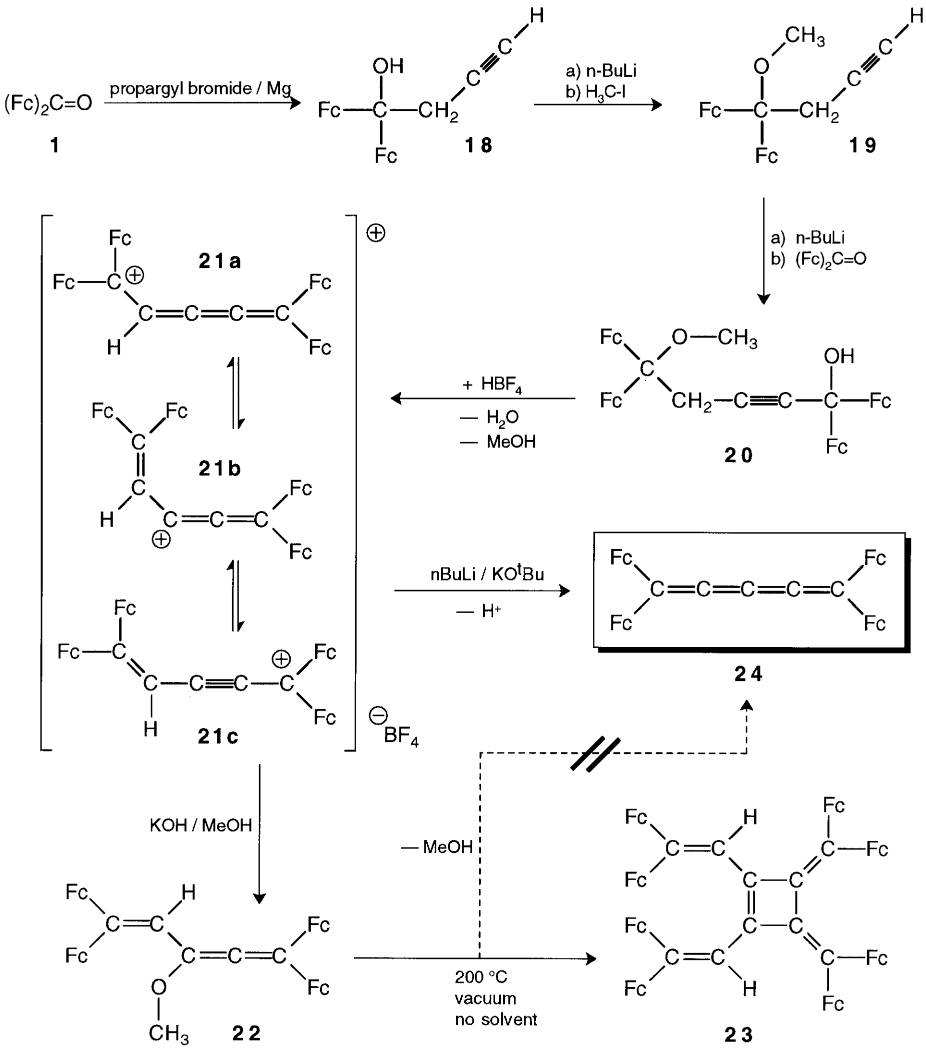
Fig. 3. Synchrotron X-ray powder structure [45] of tetraferrocenyl[3]cumulene (**14**).



Scheme 6. Synthesis of triferrocenyl[4]cumulenium tetrafluoroborate (**15a**/**15b**/**15c**) and attempted conversion to tetraferrocenyl[4]cumulene.

C(5) attack) of the product **17** suggested that [4]cumulenes cannot be synthesized by this methodology.

Nevertheless, the desired tetraferrocenyl[4]cumulene can be prepared by an alternative strategy (Scheme 7) [46]: starting from diferrocenylketone (**1**), hydroxybutyne (**18**) is readily synthesized. After protecting the hydroxyl group as the corresponding *O*-methyl ether (**19**), metalated **19** reacts with diferrocenylketone to form 1,1,5,5-tetraferrocenyl-1-hydroxy-5-methoxy-pent-2-yne (**20**) as the key progenitor of [4]cumulenes. Most unusual, elimination of H_2O and methanol can be effected by addition of only one equivalent of proton, forming an air-stable purple cumulene salt **21a**/**21b**/**21c** (IR: $\nu_{\mathrm{cumulene}} = 2090\ \mathrm{cm}^{-1}$; UV–vis: $\lambda_{\max} = 917$ nm; ^{13}C NMR: seven signals for the C_5-bridge in the range 106.0–167.8 ppm), which is the conjugate acid of the desired tetraferrocenyl[4]cumulene. Deprotonation was first



Scheme 7. Synthesis of tetraferrocenyl[4]cumulene (**24**).

attempted by elimination of methanol in vacuo from the methoxide-adduct (**22**), in analogy to similar chemistry in the synthesis of free Wanzlick/Arduengo-carbenes from the corresponding methanol adducts [47]. However, only an unusual [2 + 2] cycloadduct (**23**) could be isolated. Direct deprotonation of **21a**/**21b**/**21c** is possible with the superbasic mixture [48] of *n*-butyl lithium with potassium *tert*-butoxide, forming tetraferrocenyl[4]cumulene **24** in 46% isolated yield.

Tetraferrocenyl[4]cumulene **24** is an air-stable red ($\lambda_{max} = 483$ nm) compound. NMR spectroscopy shows four magnetically equivalent ferrocenyl substituents and the chemical shifts of the symmetric cumulene moiety are detected at 116.0, 158.2, and 178.2 ppm, respectively. The intense $\nu_{C=C=C=C=C}$ is observed at 2035 cm^{-1} in the Raman spectrum, comparable to values of metallacumulenes [44]. The ^{57}Fe Mössbauer spectroscopic properties of **24** are similar to those of other ferrocenyl

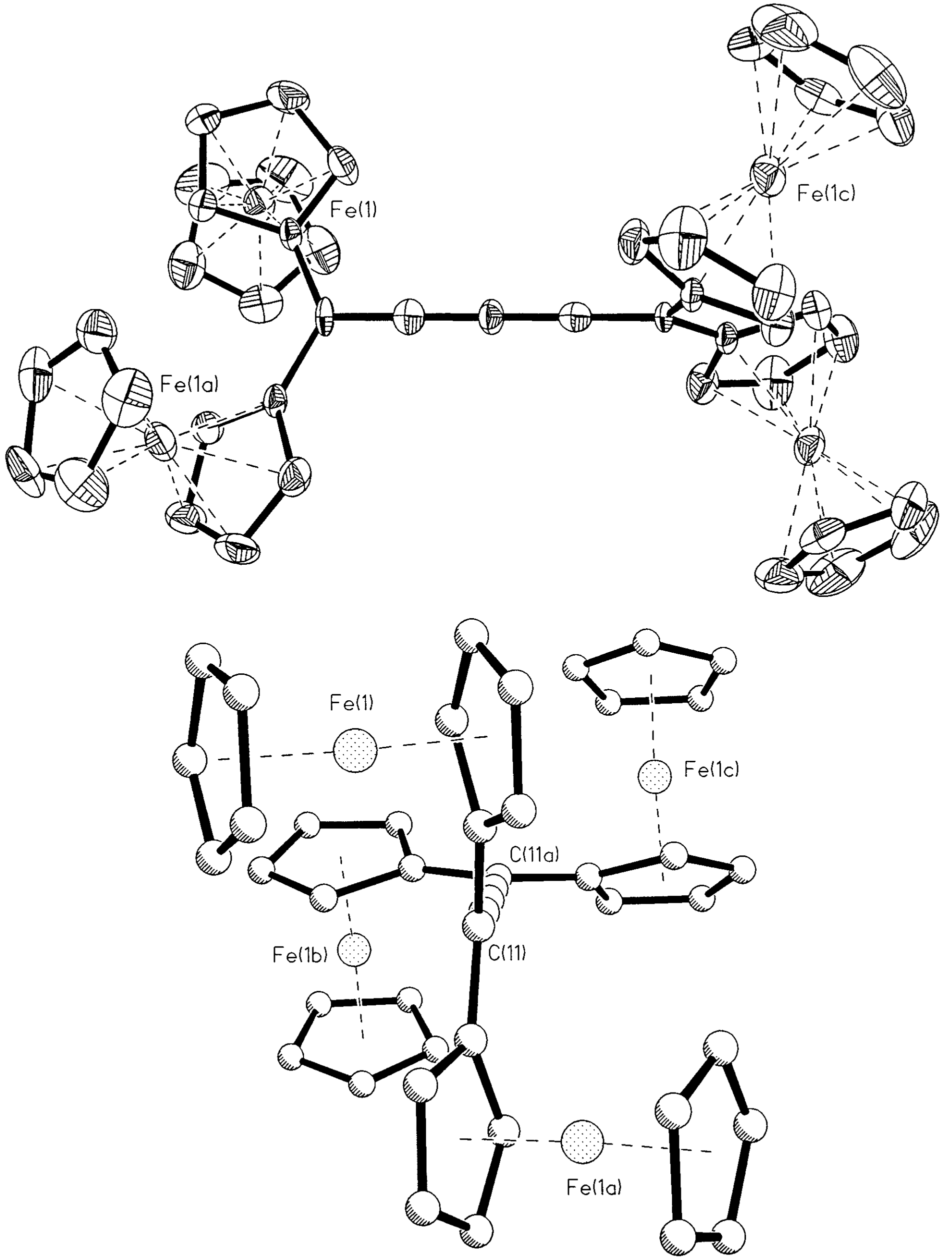


Fig. 4. Two views (a) and (b) of the single crystal structure [46] of tetraferrocenyl[4]cumulene (**24**).

cumulene compounds [32]. The single crystal structure analysis (Fig. 4) shows a linear cumulene with orthogonal π-planes, as anticipated for an odd-numbered cumulene with an even number of double bonds. The cumulene moiety has longer terminal bond distances [C(1)–C(2) = 133.2 pm] and shorter central bonds [C(2)–C(3) = 128.7 pm], in consonance with reported data [49] for two other organic [4]cumulenes, owing to the sp^2 hybridization of the terminal carbons versus the sp hybridization of the central carbons.

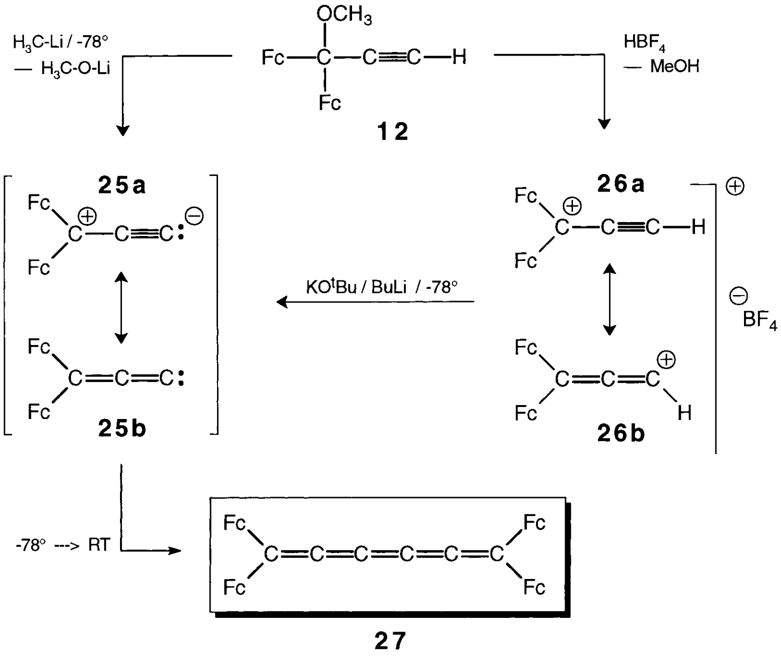
Cyclic voltammetry gives only two reversible oxidations ($E^1_{1/2} = 0.45$, $E^2_{1/2} = 0.54$ V versus SCE) at potentials quite similar to the oxidation of ferrocene, indicating only minor electronic communication between the ferrocenyl substituents through the bridging cumulene ligand. Odd-numbered cumulenes (C_3, C_5, C_7, ...) are in general electronically decoupled [50] owing to the orthogonality of the π-planes of the terminal carbons, thereby preventing conjugation between substituents bonded to these carbons.

In contrast to the sterically shielded shorter [2]- and [3]-cumulenes (**8** and **14**), tetraferrocenyl[4]cumulene (**24**) has a cumulenic carbon chain of sufficient length to interact with transition metal electrophiles. For example, reaction with tetrakis(triphenylphosphine)Pt(0) yields a stable complex $[(Fc)_2C_5(Fc)_2][(H_5C_6)_3P]_2Pt(0)$, the first metal complex of a C_5 cumulene [51].

6. Tetraferrocenylhexapentaene (tetraferrocenyl[5]cumulene)

The preparation of [5]cumulenes is most easily accomplished by formal dimerization of ethenylidenecarbenes [11,12,52,53]. Deprotonation of diferrocenylmethoxypropyne (**12**) followed by elimination of methoxide yields zwitterion (**25a**) or diferrocenylethenylidenecarbene (**25b**), respectively, which formally dimerizes to afford tetraferrocenyl[5]cumulene (**27**) (Scheme 8) [54]. The same intermediate **25a**/**25b** can also be synthesized from the isolable diferrocenyl carbenium salt (**26a**/**26b**) by deprotonation with a non-nucleophilic base.

Tetraferrocenyl[5]cumulene (**27**) is an air-stable blue ($\lambda_{max} = 624$ nm) compound [54]. Fig. 5 shows a comparison of all tetraferrocenylcumulenes $(Fc)_2C_n(Fc)_2$ described so far. Clearly evident is the increasing bathochromic shift with increasing chain length and the differences between even-numbered (C_2, C_4, C_6) and odd-numbered (C_3, C_5) cumulenes. This is due to conjugation through the bridging cumulene ligand in the case of even-numbered cumulenes and electronic decoupling in the case of odd-numbered cumulenes because of the orthogonality of the terminal π-systems. The symmetric cumulene moiety of **27** gives rise to an intense Raman band at 1973 cm^{-1}. The ^{13}C NMR spectral shifts of these cumulene carbons (119.8, 119.9, 140.8 ppm) and ^1H NMR data (regular, undistorted magnetically equivalent ferrocenyl groups) are similar as in the other ferrocenyl cumulenes, therefore no *cis*/*trans* or *syn*/*anti* isomers are present in solution. Also, ^{57}Fe Mössbauer parameters of **27** do not differ from those of cumulenes **3**, **8**, **14**, **24**. Electrochemical measurements [54] showed that C_6 cumulene **27** can be reduced and oxidized by a two-electron cumulene-centered reduction at −1.39 V, a four-electron ferrocene-



Scheme 8. Synthesis of tetraferrocenyl[5]cumulene (**27**).

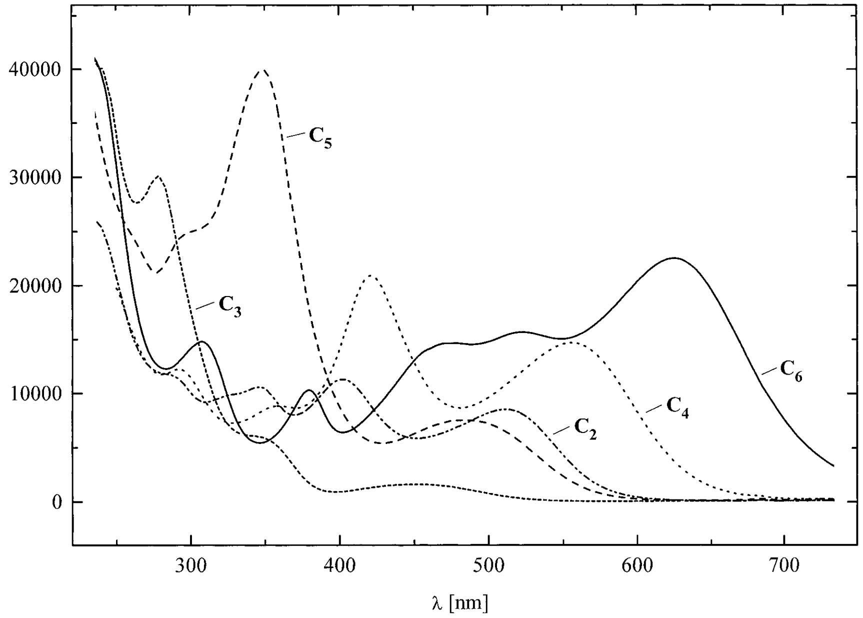
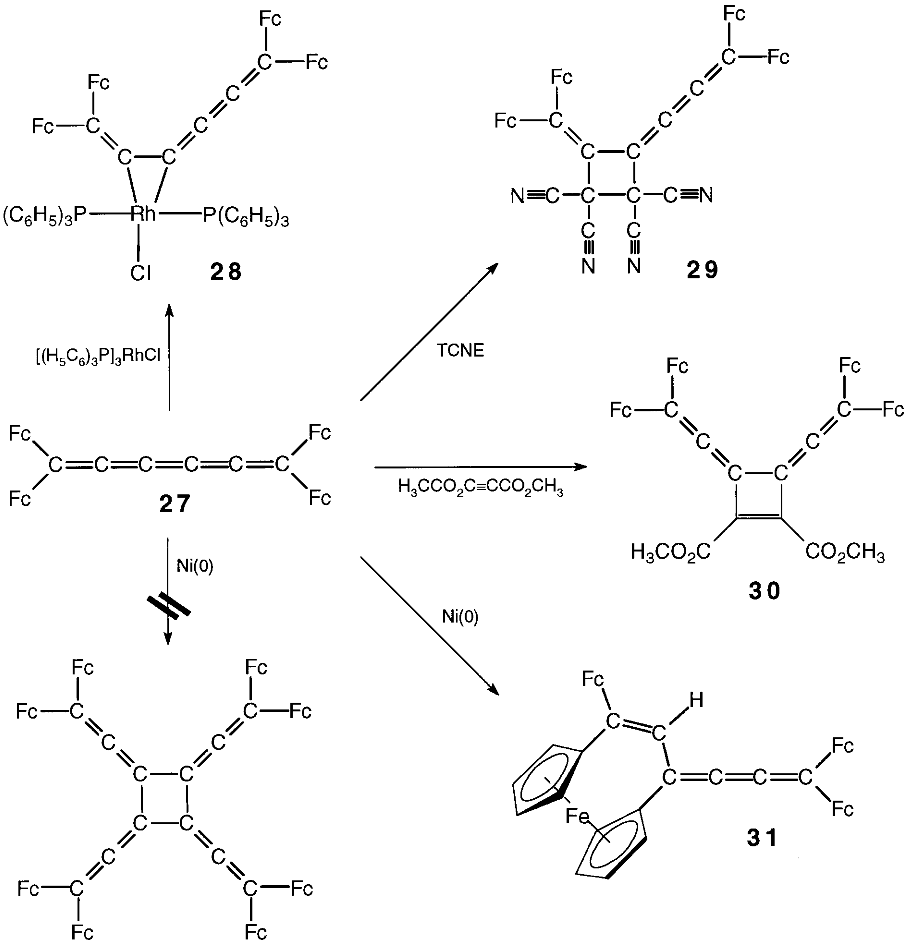


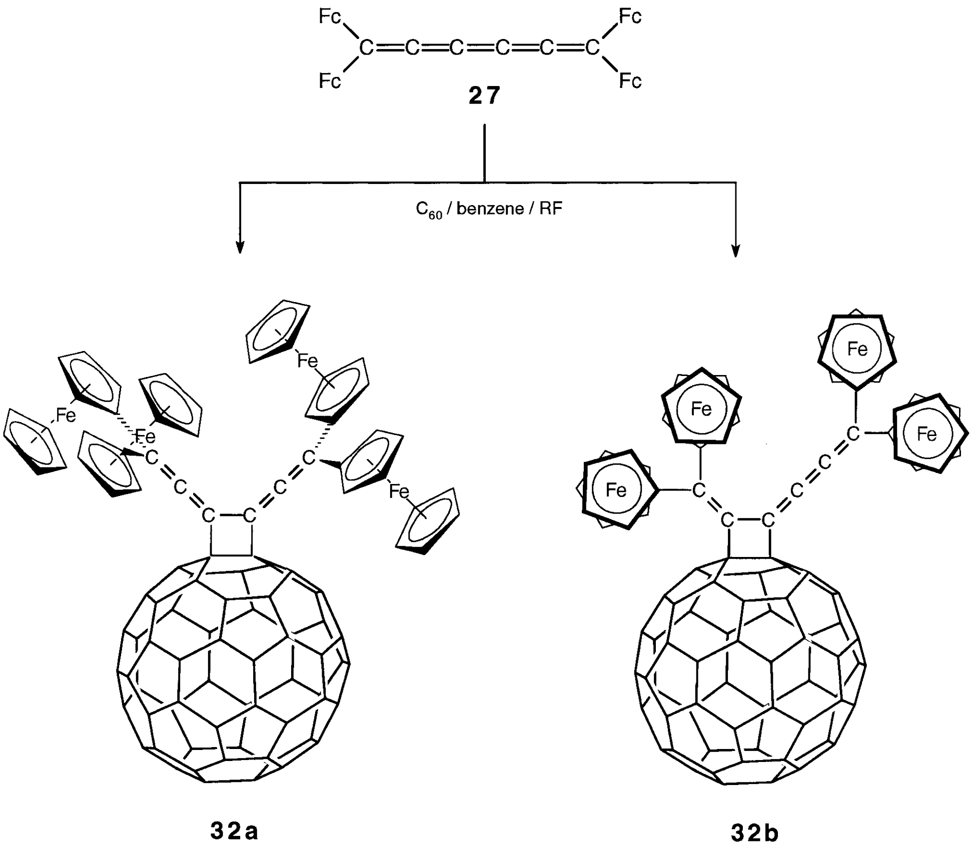
Fig. 5. Comparison of the UV–vis spectra of $(Fc)_2C_n(Fc)_2$ ($n = 2, 3, 4, 5, 6$) [54].

centered oxidation at + 0.23 V, and a two-electron cumulene-centered oxidation at + 0.83 V, respectively. In comparison with the electrochemical data of cumulenes **3**, **8**, **14**, **24** it is obvious that with increasing chain length the degree of electronic communication between the four ferrocenyl termini decreases, as might be anticipated.

Tetraferrocenyl[5]cumulene (**27**) shows a rich chemistry, including transition metal complex formation, [2 + 2] cycloadditions with olefins, alkynes, and fullerenes, and on attempted radialene formation an intramolecular aromatic substitution is observed, yielding an unusual [3]ferrocenophane (Schemes 9 and 10) [54]: Rh-complex (**28**) is formed on interaction of cumulene **27** with Wilkinson's catalyst. NMR spectroscopy shows six ^{13}C signals with couplings to ^{103}Rh and ^{31}P, indicative of an unsymmetric coordination of the metal fragment. Fig. 6 shows the single



Scheme 9. Reactivities of tetraferrocenyl[5]cumulene (**27**).



Scheme 10. [2 + 2] Cycloaddition of tetraferrocenyl[5]cumulene (**27**) with C_{60}.

crystal structure; the cumulene ligand is significantly bent with alternating C–C distances, as has been observed before in three other structures of organic [5]cumulenes with Rh(I) [55–57]. Tetracyanoethylene reacts with cumulene **27** to give an unsymmetric [2 + 2] cycloadduct (**29**), whereas dimethyl acetylendicarboxylate yields a symmetric cyclobutene (**30**), probably for steric reasons. It is well known that the easiest access to [4]radialenes is by transition metal promoted cyclodimerization of cumulenes [58], however, cumulene **27** reacts with zero-valent Ni to afford [3]ferrocenophane (**31**) by an intramolecular electrophilic aromatic substitution, induced by an unstable Ni(O)–cumulene complex [54].

The shorter cumulenes **3**, **8**, **14**, **24** react with fullerene C_{60} only by charge-transfer complex formation, forming clathrates similar to the reaction between simple metallocenes and C_{60} [33]. In marked contrast, tetraferrocenyl[5]cumulene (**27**) yields green [2 + 2] cycloadducts (**32a** and **32b**), which are the first cumulene derivatives of fullerenes (Scheme 10) [54]. Of these two regioisomers only the unsymmetric adduct (**32b**) could be purified and isolated by column chromatogra-

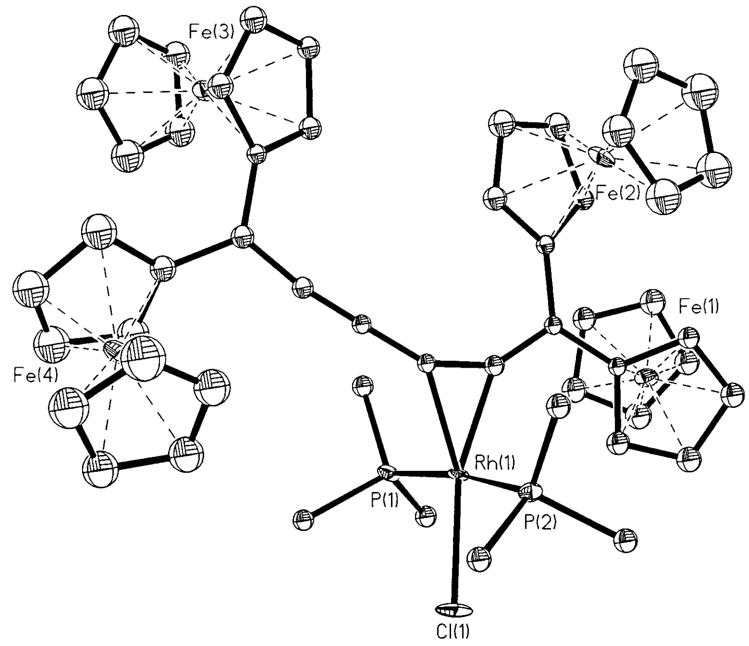


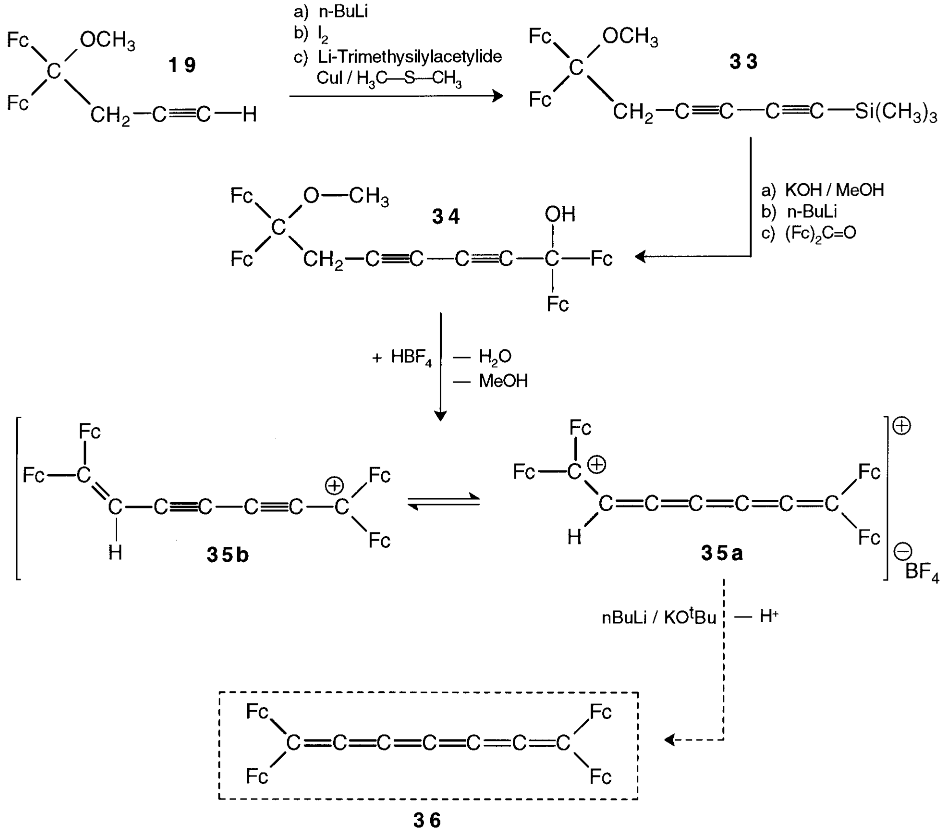
Fig. 6. Single crystal structure [54] of Rh(I) complex **28** (phenyl carbons C(2)–C(6) of the triphenylphosphine groups are omitted for clarity).

phy, owing to unavoidable permanent immobilization of **32a** on the column. Electrochemistry of **32b** showed cumulene-centered reductions and oxidations, fullerene-centered reductions, and ferrocene-centered oxidations, respectively.

7. Tetraferrocenylheptahexaene (tetraferrocenyl[6]cumulene) and higher cumulenes

No [6]cumulenes have been reported in the literature, most likely owing to the synthetic difficulties in the preparation of odd-numbered carbon chains, as opposed to the straightforward elongation of even-numbered sp-carbon chains by established methods in acetylene chemistry [11,12]. However, as has been described above for the case of C_5-cumulene **24**, diferrocenylmethoxybutyne (**19**) is a valuable synthon which serves also as the key starting compound for higher odd-numbered cumulene homologs (Scheme 11) [59].

Elongation of **19** by cross-coupling with acetylide and subsequent nucleophilic addition of deprotected hexadiyne **33** with diferrocenylketone yields 1,1,7,7-tetraferrocenyl-1-hydroxy-7-methoxy-hepta-2,4-diyne (**34**). The C_7 carbon subunit is clearly seen in the crystal structure analysis of **34** (Fig. 7). Addition of fluoroboric acid causes elimination of H_2O and of methanol (analogous as in the case of the C_5 homolog **20**), yielding a purple air-stable cumulenium tetrafluoroborate (**35a**/**35b**) with spectroscopic data (IR: $\nu_{\text{cumulene}} = 2099$ cm^{-1}; UV–vis: $\lambda_{\text{max}} = 856$ nm; ^{13}C



Scheme 11. Synthesis of tetraferrocenyl[6]cumulene (**36**).

NMR: seven signals for the C_7-bridge in the range 93–163 ppm) indicative of significant conjugation and cumulene character. Preliminary attempts to deprotonate tetraferrocenylcumulenium salt **35a**/**35b** (the conjugate acid of the desired tetraferrocenyl[6]cumulene) show that a burgundy–red product is formed in solution, but until now our efforts to isolate tetraferrocenyl[6]cumulene (**36**) have not been successful. However, trapping experiments with tetrakis(triphenylphosphine)Pt(0) indicated that a complex of formula $[(Fc)_2C_7(Fc)_2][(H_5C_6)_3P]_2Pt$ can be synthesized, giving strong support of the existence of tetraferrocenyl[6]cumulene (**36**) as the first C_7 cumulene [59].

With those building blocks thus far available, we were interested in how long such ferrocenyl substituted sp-carbon chains can be made (Scheme 12) [59]. Diferrocenylmethoxypropyne (**12**) can be elongated by standard acetylene chemistry to the corresponding diferrocenylmethoxypentadiyne. Cross-coupling of the two derivatives **37** and **38** yields 1,1,10,10-tetraferrocenyl-1,10-dimethoxy-2,4,6,8-tetrayne (**39**) as a stable yellow solid. A single crystal structure shows an almost linear tetrayne sp-carbon chain (Fig. 8), similar as in comparable [M]–(C≡C)$_4$–[M]

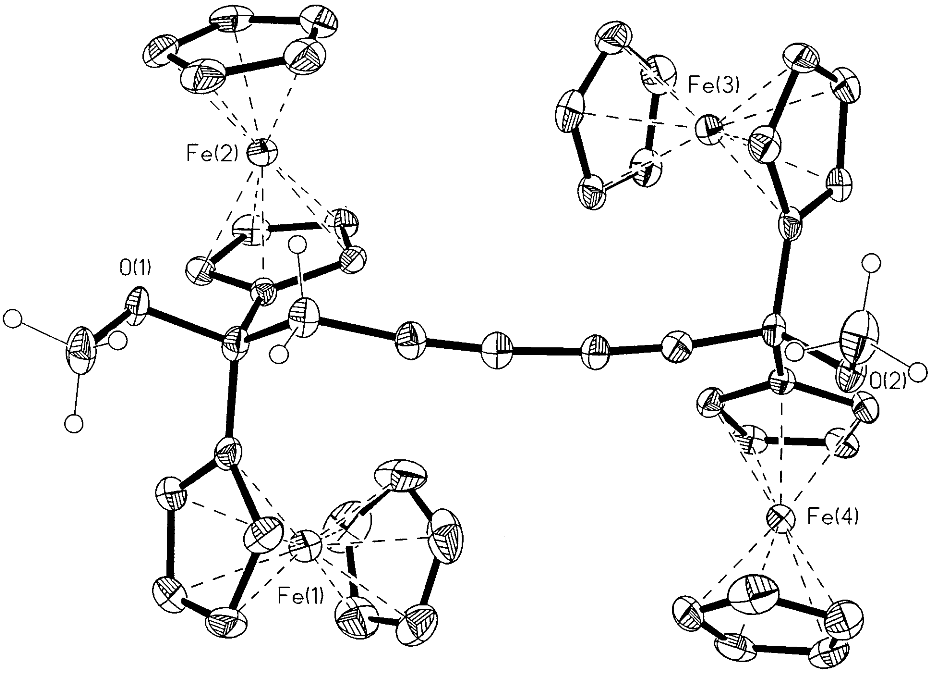
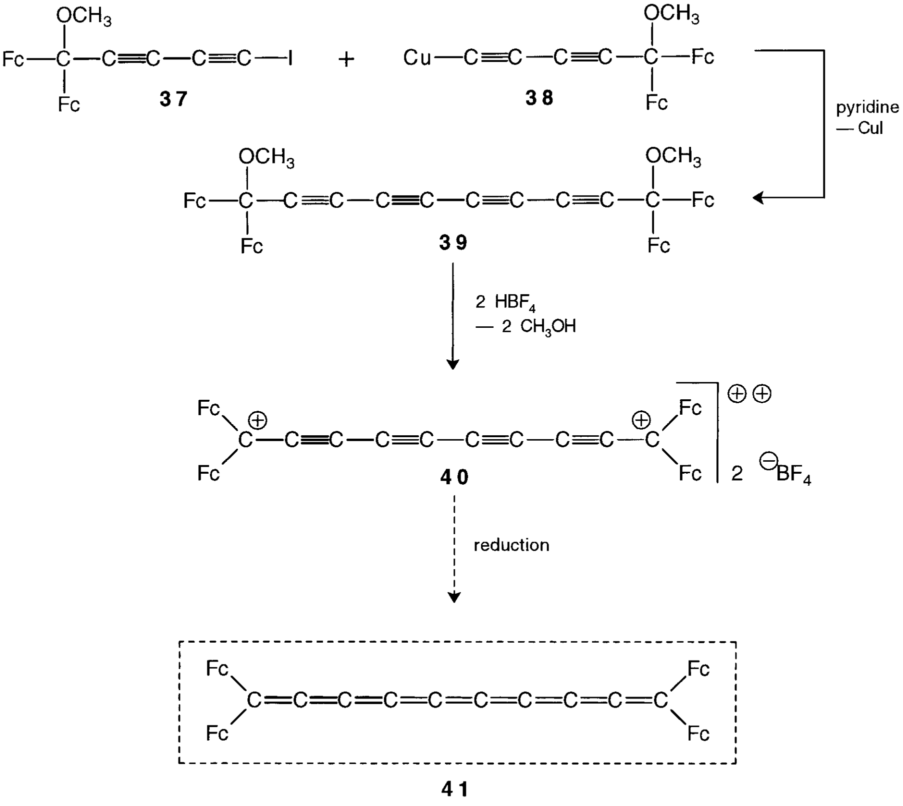


Fig. 7. Single crystal structure [59] of **34**.

metalla-tetraynes [60]. Addition of tetrafluoroboric acid effects elimination of two equivalents of methanol, yielding the novel green dication **40**. This air-stable isolable salt is probably one of the most stable carbodications known [61], and ongoing efforts are directed toward its clean reduction to afford finally tetraferrocenyl[9]cumulene (**41**) [59].

8. Triferrocenyl[*n*]cumulenium salts (*n* = 2, 4, 6, 8)

During the course of our synthetic approaches to odd-numbered tetraferrocenylcumulenes (C_3, C_5) we have used triferrocenylcumulenium salts **7a**/**b** and **15a**/**15b**/**15c** as precursors of the corresponding tetraferrocenylcumulenes. These ferrocenyl-stabilized cations are of interest not only from a synthetic or structural point of view, respectively, but also as members of a series of potential novel non-linear optical (NLO) materials. Obviously, the cations of these cumulenium salts contain the necessary structural elements of molecular NLO materials: ferrocenyl moieties as powerful σ/π-electron donor groups, the carbenium center as a σ/π-electron acceptor group, and a π-conjugated polarizable cumulenic bridge connecting donor and acceptor (Scheme 13). In collaboration with J. Heck and T. Meyer-Friedrichsen from the University of Hamburg (Germany) [62], the second-order NLO properties of tetrafluoroborates of **7a**/**7b**, **15a**/**15b**/**15c**, and **42a**/**42b**



Scheme 12. Synthesis of tetraferrocenyl[9]cumulene (**41**).

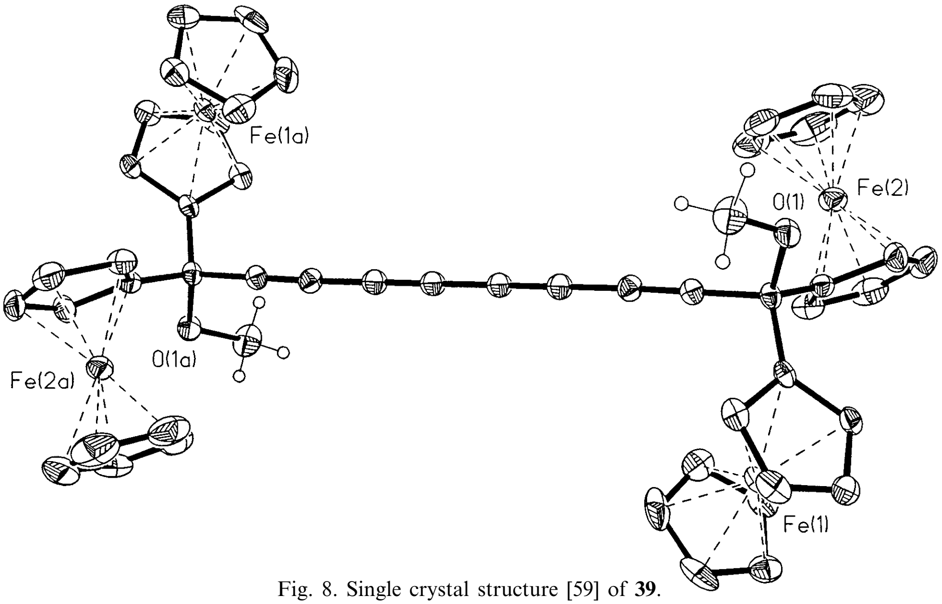
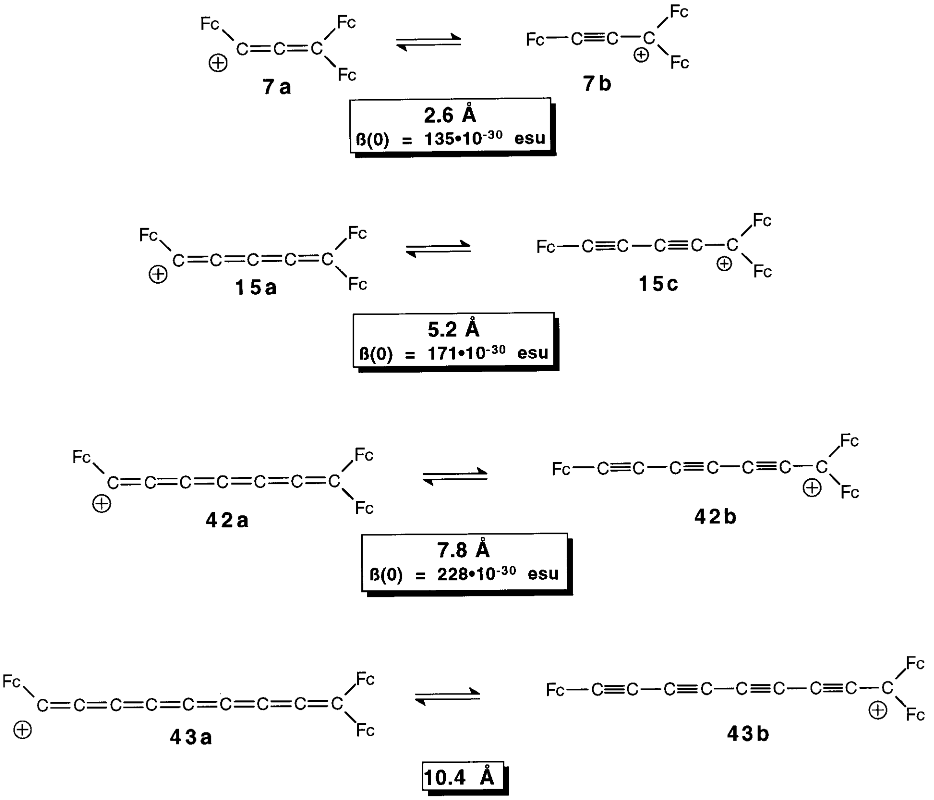


Fig. 8. Single crystal structure [59] of **39**.



Scheme 13. NLO properties of triferrocenyl[*n*]cumulenium tetrafluoroborates (*n* = 2, 4, 6, 8).

(synthesized by methods analogous as described above) have been measured by the hyper-Rayleigh scattering technique [63], showing significant zero-frequency β_0 values in comparison to those of other organometallic complexes [64]. As indicated in Scheme 13, the β_0 values increase steadily with increasing length of the cumulenic bridge between donor and acceptor group, therefore even higher values might be anticipated for elongated homologs like triferrocenyl[8]cumulenium salt **43a**/**43b**.

9. Conclusions

The synthesis of ferrocenyl cumulenes is a challenging task. However, taking advantage of the cation-stabilizing capacity of ferrocenyl groups, synthetic methods have been developed giving access to cationic and neutral cumulenes with up to ten carbons. These compounds containing an sp-carbon chain and directly attached ferrocenyl termini show unique physical, structural, and chemical properties:

The electronic communication between the ferrocenyl termini through the bridging sp-carbon ligand depends on the number of cumulated carbons and on the length of the cumulene chain, as shown by cyclic voltammetry and by UV–vis spectroscopy. In general, odd-numbered cumulenes $(Fc)_2C_n(Fc)_2$ ($n = 3, 5, \ldots$) are electronically decoupled, whereas even-numbered cumulenes $(Fc)_2C_n(Fc)_2$ ($n = 2, 4, 6, \ldots$) show decreasing electronic communication with increasing chain length. ^{57}Fe Mössbauer spectroscopy allows the differentiation of distinct iron sites in the case of triferrocenyl[n]cumulenium salts $(Fc)_2C_n(Fc)^+BF_4^-$, but is insensitive to the length of the cumulene chain in the case of neutral tetraferrocenyl[n]cumulenes $(Fc)_2C_n(Fc)_2$.

Structurally, the bulky ferrocenyl endgroups effectively shield the sp-carbon chain of the shorter cumulenes $(Fc)_2C_n(Fc)_2$ ($n = 2, 3, 4$), preventing thereby any electrophilic attack at these carbons. In contrast, the longer neutral cumulenes $(Fc)_2C_n(Fc)_2$ ($n = 5, 6, \ldots$) show a rich chemistry of the sp-carbon chain, including transition metal complex formation, ferrocenophane formation, and [2 + 2] cycloadditions with olefins, alkynes, and (most interesting) also with fullerenes.

Cumulenium salts $(Fc)_2C_n(Fc)^+BF_4^-$ ($n = 3, 5, 7$) are the first isolable species of this kind, owing to the combined stabilizing effects of the three ferrocenyl termini. They show significant second-order non-linear properties which increase in value with increasing sp-carbon chain length.

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