Mono- and Bis(allenes) with Three to Seven Ferrocenyl Substituents

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Tetraferrocenylallene is synthesized in 49% yield from triferrocenylallenylium tetrafluoroborate by nucleophilic addition of 1-cuprioferrocene. Other, more conventional approaches failed, due to steric hindrance or the known reluctance of a diferrocenyl-substituted sp^2 carbon to undergo condensation reactions. Side products include triferrocenyl(2-tetrahydrofuranyl)allene, 1,1,3,4,6,6-hexaferrocenylhexane-1,2,4,5-tetraene, and 1,1′-bis(triferrocenylallenyl)ferrocene, indicating the involvement of allenyl radicals in the course of this reaction. X-ray crystal structure analyses show these allenes to be sterically congested cumulenes with interesting helical propeller conformations. Tetraferrocenylallene can be reversibly oxidized in three consecutive steps to the tetracation, as shown by low-temperature cyclic voltammetry. The expected nucleophilic reactivity of the central carbon of the allenic unit is hampered by the steric bulk of the metallocenyl substituents and only observed for the smallest electrophile possible, H^+, which yields a rather labile tetraferrocenylallylium cation.

Introduction

Conjugated carbon frameworks with a maximal number of ferrocenyl substituents are attractive target compounds with regard to their structure, stereochemistry, electrochemistry, and reactivity. The ferrocenyl substituents, linked directly with the conjugated carbon chain, are unique in terms of their extreme donor capacity[1] for neighboring electron-deficient carbenium centers and in terms of their molecular ("sandwich") geometry, which leads to steric protection of adjacent functional groups and to atropisomerism and metallocene chirality, if appropriately substituted or sterically congested.[2] Polyferrocenylated conjugated multistage redox systems are popular model compounds for molecular electronics[3] due to the fully reversible ferrocene/ferrocenium couple.[4] Recently we reported on tetraferrocenylethylene,[5] which can be envisaged as the first member ([1]cumulene) of a series of perferrocenylated cumulenes. We now extend this chemistry to the corresponding [2]cumulene, using the stable cumulenic triferrocenylallenylium tetrafluoroborate[6] as the key synthon for the preparation of ferrocenylated allenes. Our preliminary results on the higher members in this series, perferrocenylated [3]-, [4]-, and [5]cumulenes, have been briefly presented recently[7] and will be published in full detail in the near future. Our efforts within this project are focused on (i) the preparation of as long as possible cumulenic carbon chains with diferrocenyl-substituted termini (compare the related work on metallacumulenes by the groups of Gladysz,[8,9] Lapinte,[9,10] Werner,[9,11] Dixneuf,[9,12] and Fischer[9,13]), (ii) the electronic influence[1] of the ferrocenyl substituents on the reactivity of the cumulenic carbons (nucleophilic

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reactivity, cycloadditions, cyclooligomerizations[14]), (iii) the electrochemical behavior of these "molecular wires"[9] as model compounds for molecular electronics, and (iv) charge-transfer complex formation[15] with acceptors. In this context, tetraferrocenylallene—the prototypical perferrocenylated [2]cumulene—is the main target compound of this research, but it is of course a very "short" cumulene, which might not fulfill all expectations due to steric hindrance by the four ferrocenyl substituents. On the other hand, this steric *hindrance* might be useful as steric *protection*; therefore, tetraferrocenylallene is of further interest with respect to its reactivity as an electron-rich allene in direct comparison to the highly nucleophilic tetrakis(dimethylamino)allene[16] and with respect to its potential use as a progenitor of stable sterically protected radicals, analogous to Ziegler's[17] tetraphenylallyl radical, Koelsch's[18] pentaphenylallyl radical, and Berndt's[19] tetra-*tert*-butylallene radical cation.

Here we report the synthesis, characterization (NMR, IR, UV−vis, MS), structure (X-ray), electrochemistry (CV), and reactivity of allenes with three to seven ferrocenyl substituents.

Experimental Section

General Comments. Standard techniques and instrumentation for spectroscopic and physical measurements have been described elsewhere.[5,6] Triferrocenylallenylium tetrafluoroborate,[6] lithioferrocene,[20] ferrocenylcopper−dimethyl sulfide complex,[21] and 1,1′-dicuprioferrocene−dimethyl sulfide complex[21] were prepared according to published procedures.

Triferrocenyl(2-tetrahydrofuranyl)allene (1). A Schlenk vessel was charged with 125 mg (0.651 mmol) of lithioferrocene (*Caution!* pyrophoric powder!) and 40 mL of precooled (−70 °C) dry, deoxygenated THF under an atmosphere of argon. The resulting orange suspension was magnetically stirred at −70 °C, and 200 mg (0.295 mmol) of triferrocenylallenylium tetrafluoroborate was added in one portion with protection from air. The mixture was slowly warmed to room temperature within 4 h in the cooling bath with efficient stirring, during which time the brown suspension was gradually converted to a clear, red solution. A 1 mL amount of H_2O was added to hydrolyze excess lithioferrocene, and all volatile material was stripped off on a rotary evaporator. The residue was dissolved in dichloromethane, the organic phase was washed with three portions of H_2O, and the organic layer was dried with Na_2SO_4 and evaporated to dryness, affording 270 mg of a crude product mixture, consisting of ferrocene, biferrocene, triferrocenyl(2-tetrahydrofuranyl)allene (**1**), and traces of tetraferrocenylallene (**2**) and 1,1,3,4,6,6-hexaferrocenylhexane-1,2,4,5-tetraene (**3**). Column chromatography on neutral Al_2O_3 with *n*-hexane/Et_2O (3/1) as the mobile phase afforded 46 mg (0.069 mmol, 23.5% yield) of **1**: red-brown crystals; mp 182 °C dec. Anal. Calcd for $C_{37}H_{34}Fe_3O$: C, 76.11; H, 5.18; O, 2.42. Found: because of only 46 mg of material available and because **1** decomposes within days at room temperature according to NMR, no elemental analysis was attempted. HRMS (FAB): *m/z* 662.066 40 (M^+; exact mass calcd for $C_{37}H_{34}OFe_3$ 662.065 78). MS (EI, 40 eV): *m/z* 662 (100%) (M^+), 605 (24%) ($M^+ - CH_2CH_2CH_2O$), 591 (100%) (M^+ − tetrahydrofuranyl), 405 (20%) (M^+ − ferrocenyl, tetrahydrofuranyl). UV−vis data (hexane; λ_{max} (nm)/log ϵ): 447/2.9. IR data (KBr): 3094 m, 2957 w, 2924 w, 2857 w, 1636 m, 1458 w, 1412 m, 1281 w, 1107 s, 1051 m, 1003 s, 918 w, 819 s, 478 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.91 (1H, m, subst cp), 4.65−4.49 (5H, m, subst cp), 4.38−4.07 (22H, m (7H) and three s (15H), subst and unsubst cp and −CH− of C(2) of tetrahydrofuranyl), 3.90 (2H, t, J = 7.0 Hz, $-CH_2-$ of C(5) of tetrahydrofuranyl), 2.12 and 1.96 (each signal 2H, m, tetrahydrofuranyl). ^{13}C NMR ($CDCl_3$): δ 201.3, 107.9, 107.0 (C═C═C); 81.9, 73.7, 69.1, 68.5, 68.3, 68.1, 67.8, 67.5, 67.3, 67.0, 66.5 (ferrocenyl); 30.6, 29.3, 25.7, 19.6 (tetrahydrofuranyl).

Tetraferrocenylallene (2), 1,1,3,4,6,6-Hexaferrocenylhexane-1,2,4,5-tetraene (3), and 1,1′-Bis(triferrocenylallenyl)ferrocene (4). A Schlenk vessel was charged with 80 mL of dry, deoxygenated dimethoxyethane (precooled to −60 °C), 180 mg (0.938 mmol) of lithioferrocene (*Caution!* pyrophoric powder), and 225 mg (1.09 mmol) of $CuBr{\cdot}Me_2S$ complex under an atmosphere of argon. After the mixture was stirred at −60 °C for $^1/_2$ h, 475 mg (0.701 mmol) of triferrocenylallenylium tetrafluoroborate was added with protection from air in one portion and the resulting dark green suspension was warmed to room temperature within 4 h, resulting in a brown suspension. For workup, all volatile material was removed in vacuo, the residue was dissolved in dichloromethane, the organic solution was washed with two portions of a 5% $NaHCO_3$ solution and with one portion of H_2O, and the organic layer was dried with Na_2SO_4 and evaporated to dryness, yielding 524 mg of a product mixture. Separation of this mixture by column chromatography on neutral Al_2O_3 with *n*-hexane/Et_2O (2/1) as the mobile phase afforded ferrocene, biferrocene, 266 mg (0.343 mmol, 49% yield) of tetraferrocenylallene (**2**), 50 mg (0.0423 mmol, 12.1% yield) of 1,1,3,4,6,6-hexaferrocenylhexane-1,2,4,5-tetraene (**3**), and 18 mg (0.0132 mmol, 3.8% yield) of 1,1′-bis(triferrocenylallenyl)ferrocene (**4**) (yields are based on 0.701 mmol of triferrocenylallenylium tetrafluoroborate as the limiting reagent).

2: orange crystals, mp not observed, >200 °C dec. Anal. Calcd for $C_{43}H_{36}Fe_4$: C, 66.54; H, 4.68. Found: C, 65.84; H, 4.66. HRMS (FAB): *m/z* 776.022 03 (M^+; exact mass calcd for $C_{43}H_{36}Fe_4$ 776.021 46). MS (EI, 70 eV): *m/z* 776 (100%) (M^+), 656 (4%) (M^+ − Fe−cp), 591 (6%) (M^+ − ferrocenyl). UV−vis data (THF; λ_{max} (nm)/log ϵ): 449/3.4. IR data (KBr): 3093 m, 1636 w, 1412 m, 1279 m, 1106 s, 1054 m, 1001 s, 911 w, 818 s, 787 s, 515 s, 482 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.68 (8H, pseudo t, $^3J(^1H-^1H) = 1.8$ Hz, subst cp), 4.30 (8H, pseudo t, $^3J(^1H-^1H) = 1.8$ Hz, subst cp), 4.23 (20H, s, unsubst cp). ^{13}C NMR ($CDCl_3$): δ 204.7, 105.0 (C═C═C); 82.2, 69.3, 68.0, 67.7 (ferrocenyl). CV (CH_2Cl_2, 240 K; V): $E^1_{1/2} = +0.32$, $E^2_{1/2} = +0.42$, $E^{3/4}_{1/2} = +0.52$.

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3: orange crystals, mp not observed, >270 °C slow dec. Anal. Calcd for $C_{66}H_{54}Fe_6$: C, 67.05; H, 4.60. Found: C, 66.82; H, 4.63. HRMS (FAB): *m/z* 1182.0334 (M^+; exact mass calcd for $C_{66}H_{54}Fe_6$ 1182.0322). MS (FAB): *m/z* 1183.1 (3.3%) ($M^+ + H$), 1182.1 (2.1%) (M^+), 997.6 (2.2%) ($M^+ -$ ferrocenyl), 811.9 (1%) ($M^+ -$ two ferrocenyl), 745.7 (2.1%) ($M^+ -$ two ferrocenyl and one cp), 591.6 (100%) ($M^+/2$). UV−vis data (THF; λ_{max} (nm)/log ϵ): 450/3.4. IR data (KBr): 3093 m, 2960 w, 2925 w, 1634 m, 1412 m, 1264 m, 1107 s, 1053 s, 1024 s, 1001 s, 818 s, 737 m, 477 s cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.83, 4.79, 4.52, 4.43, 4.40, 4.36, 4.35, 4.26, 4.24, 4.18, 4.16, 4.06 (each signal 2H, m, subst cp); 4.33, 4.20, 3.86 (each signal 10H, s, unsubst cp). ^{13}C NMR ($CDCl_3$): δ 205.6, 112.4, 105.8 (C=C=C); 96.0, 91.3, 83.5, 72.2, 70.7, 70.5, 69.3, 69.1, 68.7, 68.50, 68.48, 68.40, 67.50, 67.47, 66.8 (subst cp); 70.2, 70.0, 69.8 (unsubst cp).

4: orange crystals, mp not observed, >270 °C slow dec. Anal. Calcd for $C_{76}H_{62}Fe_7$: C, 66.81; H, 4.57. Found: because of only 18 mg of material available, no elemental analysis was attempted. MS (FAB): *m/z* 1367.6 (100%) ($M^+ + H$), 1366.6 (100%) (M^+), 1246.6 (4.5%) ($M^+ -$ Fe−cp), 1182.1 (7.2%) ($M^+ -$ ferrocenyl), 591.6 (71.5%) ($C_3(Fc)_3$). IR data (KBr): 3091 w, 2962 m, 2925 m, 2856 w, 1636 w, 1464 w, 1412 m, 1262 s, 1106 s, 1025 s, 808 s, 687 m, 482 s cm^{-1}. Conclusive NMR and UV−vis data could not be obtained due to the limited amount of material (total yield 18 mg) and because of poor solubility in the common solvents.

Synthesis of 1,1,3,4,6,6-Hexaferrocenylhexane-1,2,4,5-tetraene (3) by Reaction of Triferrocenylallenylium Tetrafluoroborate with 1,1′-Dicuprioferrocene−Dimethyl Sulfide Complex. In a similar manner as above, 15 mg (0.0478 mmol) of 1,1′-dilithioferrocene−tmeda complex was converted to 1,1′-dicuprioferrocene−bis(dimethyl sulfide) complex and allowed to react with 100 mg (0.147 mmol) triferrocenylallenylium tetrafluoroborate in dimethoxyethane at low temperature. In contrast to the reaction with the monocuprated ferrocene above, this reaction yielded besides ferrocene and unreacted or hydrolyzed triferrocenylallenylium tetrafluoroborate (triferrocenylallenol or 1,3,3-triferrocenylprop-2-en-1-one, respectively) only **3** as product and, surprisingly, none of the expected 1,1′-bis(triferrocenylallenyl)ferrocene (**4**). After workup similar to that above, 41 mg (0.0347 mmol, 72.6% yield, based on the limiting reagent 1,1′-dilithioferrocene−tmeda complex) was obtained with analytical and spectral data as above.

1,1,3,3-Tetraferrocenylpropenylium Tetrafluoroborate (5). A 40 mg (0.052 mmol) amount of tetraferrocenylallene (**2**) was dissolved in a small Schlenk tube in 25 mL of dry, deoxygenated Et_2O under an atmosphere of argon. A 15 μL (0.11 mmol) amount of a 54% solution of fluoroboric acid in ether was added to the stirred orange solution. After further stirring at ambient temperature for 1 h, a brown, fluffy precipitate was formed, which was filtered off under argon, washed with three portions of dry ether, and dried in vacuo, yielding 24 mg (0.027 mmol, 52.5% yield) of 1,1,3,3-tetraferrocenylpropenylium tetrafluoroborate (**5**): brown powder, mp not available, slow decomposition without melting. Anal. Calcd for $C_{43}H_{37}BF_4Fe_4$: C, 59.78; H, 4.32. Found: because of only 24 mg material available, no elemental analysis was attempted. MS (EI, 70 eV): *m/z* 776 (80%) (M^+ of cation), 656 (100%) (M^+ of cation − Fe−cp), 591 (13%) (M^+ of cation − ferrocenyl). IR data (KBr): 2963 w, 2908 w, 1482 s, 1445 s, 1428 s, 1339 s, 1260 s, 1013 s, 793 s, 700 s, 664 s, 560 s, 479 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.04 (1H, s, allyl H), 5.10 (8H, broad m, subst cp), 4.98 (8H, m, subst cp), 4.37 (20H, s, unsubst cp). ^{13}C NMR ($CDCl_3$): δ 176.0 (C(1) and C(3) of allyl); 128.7 (C(2) of allyl); 86.7, 76.6, 73.0 (ferrocenyl).

X-ray Structure Determinations of 1, 2, and 4. Single crystals, suitable for X-ray analyses, were obtained by recrystallization from dichloromethane/*n*-hexane. A Siemens P4 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 71.073$ pm) was used for data collection. Crystal data, data collection, and refinement parameters of **1**, **2**, and **4** are summarized in Table 1. The unit cells were determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Data were measured via ω scans and corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from ref 22, and an empirical absorption correction[23] was made. The structures were solved by direct methods (SHELXS-86)[24] and refined by a full-matrix least-squares procedure using SHELXL-93.[25] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions. For complete crystallographic data, tables of bond lengths, bond angles, anisotropic thermal parameters, calculated hydrogen atomic coordinates, and final atomic coordinates, see the Supporting Information.

Results and Discussion

Synthesis. Only a limited number of ferrocenyl-substituted allenes have been reported in the literature to date,[26] and all of these compounds contain only one or two ferrocenyl groups. The synthesis of allenes with three or four ferrocenyl substituents is difficult for two reasons: the steric requirements and the electronic (donor) properties of the ferrocenyl moiety prevent preparation of bis-ferrocenylated sp^2 carbon compounds by conventional condensation reactions.[27] As has been noted before,[26c] possible synthetic routes to ferrocenylated allenes, in analogy to phenylated systems, are unfeasible because the necessary starting materials are unknown.

We attempted the condensation of diferrocenyl ketone with 1,1′-diferrocenylethylene by activating the ketone with mineral acid or with trimethylsilyl triflate,[28] following Wizinger's[29] and Ziegler's[17] tetraarylallene synthesis, which consists of first forming the tetrasubstituted allylium salt and second removing the allylic hydrogen with base, similarly to the preparation of tetrakis(dimethylamino)allene.[16] Protonation[30] or trimethylsilylation afforded the corresponding diferrocenyl(hydroxy or (trimethylsilyl)oxy)methylium salt, easily recognizable by its typical blue color,[1,31] but no further reaction occurred with 1,1′-diferrocenylethylene.

A second possible approach to this tetraferocenylallylium salt (**5**) would be a hydride abstraction from

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Table 1. Crystal Data and Structure Refinement Details for 1, 2, and 4

	1	**2**	**4**
mol formula	$C_{37}H_{34}Fe_3O$	$C_{43}H_{36}Fe_4$	$C_{76}H_{62}Fe_7 \cdot 2CH_2Cl_2$
fw	662.19	776.12	[1367.6]·[169.86]
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a (pm)	995.4(2)	1296.2(1)	2330.1(5)
b (pm)	1088.1(2)	1136.3(2)	1144.2(2)
c (pm)	1339.9(3)	2207.6(2)	2631.1(5)
α (deg)	88.15(3)	90	90
β (deg)	89.10(3)	95.16(1)	113.96(2)
γ (deg)	80.95(3)	90	90
V (nm^3)	1.4323(5)	3.2383(7)	6.410(2)
Z	2	4	4
temp (K)	188(2)	193(2)	213(2)
density (calcd) (Mg/m^3)	1.535	1.592	1.592
abs coeff (mm^{-1})	1.529	1.788	1.752
F(000)	684	1592	3136
color, habit	orange prism	orange prism	brown block
cryst size (mm)	0.55 × 0.25 × 0.20	0.6 × 0.2 × 0.08	0.35 × 0.3 × 0.18
θ range for data collection (deg)	4.03−26.00	3.11−21.99	3.03−21.00
index ranges	$-1 \le h \le 12$	$0 \le h \le 12$	$-1 \le h \le 23$
	$-13 \le k \le 13$	$-1 \le k \le 11$	$-1 \le k \le 11$
	$-15 \le l \le 16$	$-23 \le l \le 23$	$-26 \le l \le 24$
no. of rflns collected	6619	3897	4229
no. of indep rflns	5614 ($R_{int} = 0.0191$)	3470 ($R_{int} = 0.0311$)	3433 ($R_{int} = 0.0500$)
no. of rflns with $I > 2\sigma(I)$	4358	2692	2124
abs cor	*ψ*-scan	DIFABS	*ψ*-scan
max and min transmissn	0.936 and 0.856		0.895 and 0.664
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	5608/0/397	3466/0/424	3433/0/402
goodness of fit on F^2	1.045	1.040	1.030
final *R* indices ($I > 2\sigma(I)$)			
R1	0.0374	0.0356	0.0644
wR2	0.0769	0.0771	0.1368
R indices (all data)			
R1	0.0593	0.0574	0.1216
wR2	0.0882	0.0883	0.1672
largest diff peak and hole (e nm^{-3})	+554 and −280	+271 and −295	+644 and −709

1,1,3,3-tetraferrocenylprop-1-ene with trityl cation.[32] We tried to synthesize the tetraferrocenylpropene by nucleophilic addition of lithioferrocene to 1,1,3-triferrocenylallylium tetrafluoroborate,[6] thereby constructing the allene progenitor from a precursor which already incorporates the three-carbon linkage, but without success. The reason for the inaccessability of a tetraferrocenylallylium salt (**5**) by these two routes is most likely steric hindrance, understandable in the light of the results obtained from protonation of tetraferrocenylallene (**2**) (see below).

Propynes with a good leaving group at the propargylic position are classic starting materials for the synthesis of allenes by a nucleophilic substitution with an organometallic reagent.[33] Therefore, we adapted this methodology for the synthesis of perferrocenylated allenes, using the stable cumulene triferrocenylallenylium tetrafluoroborate[6] as the electrophile. In this case the steric and electronic properties of the ferrocenyl substituents, which prevent the synthesis of allenes by conventional methods, are of advantage in terms of sterically directing the incoming nucleophile to the terminal monosubstituted carbon of the ambident allenylium ↔ propargylium electrophile and in terms of electronically stabilizing the allenylium system by their inductive donor capacity,[6] thereby allowing a formally "true" S_N1 reaction without the need of displacing a nucleofuge (Scheme 1). Although this approach is successful and allows finally the synthesis of the target compound **2**, the reaction is more complicated than expected, because despite many attempts we were unable to find reaction conditions which allow the preparation of allene **2** exclusively. In addition to the desired product, other allenic ferrocenes were always obtained, depending on the solvent and on the type of nucleophilic ferrocenyl reagent used: reaction of triferrocenylallenylium tetrafluoroborate with lithioferrocene in THF fails to give allene **2** in preparative amounts; instead, triferrocenyl(2-tetrahydrofuranyl)allene (**1**), ferrocene, and biferrocene are the main products, in addition to only traces of tetraferrocenylallene (**2**) and the hexaferrocenyl bis(allene) **3**. Clearly, the solvent interacts preferentially with some type of intermediate formed from the allenylic cation and the ferrocenyl anion. This intermediate could be a triferrocenylallene radical or a radical carbenoid,[34] formed by reduction of the cation by lithioferrocene. The products ferrocene and (tetrahydrofuranyl)triferrocenylallene (**1**) are the outcome of a radical substitution reaction with THF,

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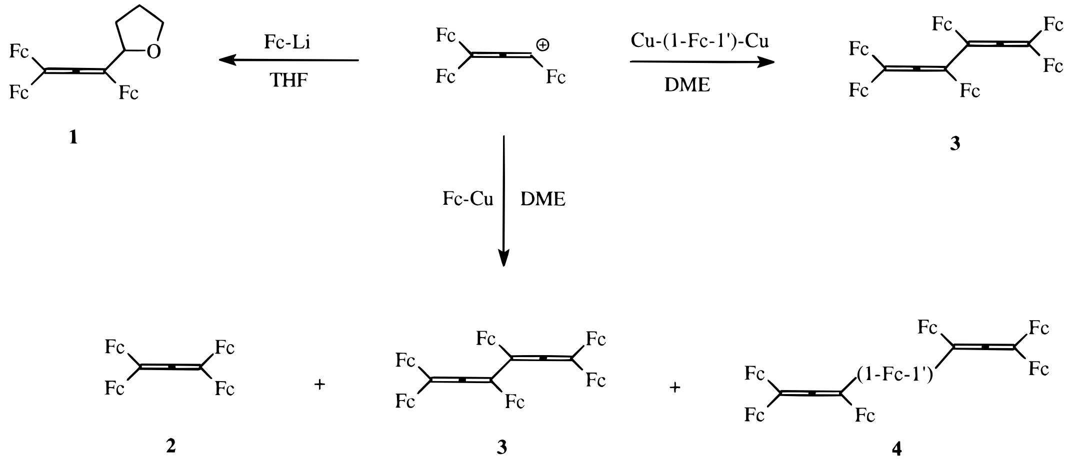
(34) This type of intermediate was pointed out to us by one of the reviewers. The only carbenoid intermediate we can envision, formed from triferrocenylallenylium cation and lithioferrocene, would be 1,1,3-triferrocenylprop-1-en-2,3-diyl, which is a valence bond isomer of 1,1,3-triferrocenylallen-3-yl; both of these intermediates are radicals.

Scheme 1. Preparation of Compounds 1−4[a]



[a] Legend: Fc = ferrocen-1-yl, (1-Fc-1′) = ferrocene-1,1′-diyl, THF = tetrafydrofuran, DME = dimethoxyethane.

whereas biferrocene and the traces of tetraferrocenylallene (**2**) and the hexaferrocenyl bis(allene) **3** are derived from symmetrical and asymmetrical radical coupling reactions, respectively. Although not all of the expected radical-derived products (triferrocenylallene and (tetrahydrofuranyl)ferrocene) have been observed, possibly due to solvent cage effects,[35] we believe that of the competing pathways of nucleophilic addition vs electron transfer,[36] the latter has to be responsible for the observed product distribution. The proposed intermediate triferrocenylallenylium radical has only fleeting existence; cyclic voltammetry of triferrocenylallenylium tetrafluoroborate showed only a nonreversible reduction at −0.32 V (vs SCE with ferrocene as internal standard), and attempted chemical one-electron reduction of triferrocenylallenylium tetrafluoroborate with lithium 4,4′-di-*tert*-butylbiphenylidene (Freeman reagent)[37] yielded none of the allenic products, which might be interpreted as further evidence of the operation of a *concerted* SET mechanism[36] with an unstable triferrocenylallenylium radical intermediate.

To avoid the formation of tetrahydrofuranyltriferrocenylallene (**1**) and to take into account the radical pathway of the interaction of triferrocenylallenylium tetrafluoroborate with the ferrocenyl carbanion, the reaction conditions were altered in the following manner. (i) Instead of THF as solvent, the less reactive DME (which is less prone to react as a hydrogen donor due to the larger dihedral angle with respect to the p-type orbitals on the oxygen)[38] was employed. (ii) Instead of lithioferrocene, ferrocenylcopper, complexed with dimethyl sulfide as coligand to improve the solubility and reactivity,[21,39] was used. These modifications resulted in an improved product distribution (Scheme 1): in addition to the desired main product, tetraferrocenylallene (**2**) (49% yield), also bis(allenes) **3** and **4** are formed in 12% and 4% yield, respectively, together with ferrocene and biferrocene. The formation of bis(allene) **3** and biferrocene indicates again the occurrence of (intermediate) triferrocenylallenylium and ferrocenyl radical species, which dimerize in DME, in contrast to their trapping by the more reactive solvent THF (see above).

The formation of bis(allene) **4** is more difficult to explain. One possibility would be the reaction of a dimetalated ferrocene, formed by self-metalation of the cuprioferrocene, with 2 equiv of triferrocenylallenylium tetrafluoroborate. The partial equilibration (scrambling) of monometalated ferrocene to ferrocene and dimetalated ferrocene (or the higher stability of di- vs monometalated ferrocene) has been repeatedly reported in the literature,[21,40] but this self-metalation of lithioferrocene could not be verified in a careful recent study by Kagan and Guillaneux.[20a] On the other hand, in a similar recent analysis of the lithiation of ferrocene by Mueller-Westerhoff and Sanders,[41] attempts to establish the presence or absence of such an equilibrium gave inconclusive results. Hence, the possibility of the formation of a dimetalated ferrocene in low yield (compare the 3.8% yield of **4**) by such a scrambling reaction cannot be ruled out, especially when one takes into consideration the complex nature of the Fc−Li/CuBr/$(CH_3)_2S$/THF system. In an attempt to synthesize bis(allene) **4** selectively, triferrocenylallenylium tetrafluoroborate was reacted with 1,1′-dicuprioferrocene complexed with tmeda and/or dimethyl sulfide under otherwise identical conditions. Surprisingly—and in contrast to the expectations—*none* of the desired **4** could be obtained; instead, the radical coupling product **3** was the sole allenic product. We have no real explanation for this finding, but it is a further illustration of the very sensitive nature of these reactions regarding solvent, counterion of the ferrocenyl nucleophiles, coligand(s) of the 1-cuprio and 1,1′-dicuprioferrocenes, and

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(41) Sanders, R.; Mueller-Westerhoff, U. T. *J. Organomet. Chem.* **1996**, *512*, 219.

Table 2. Pertinent Structural and Spectroscopic Parameters of Ferrocenylallenes 1−4

	1	2	3	4
bond length (pm) C(1)−C(2)	131.0(4)	131.6(7)	a	132.1(14)
bond length (pm) C(2)−C(3)	131.2(4)	132.1(7)	a	133.8(14)
bond angle (deg) C(1)−C(2)−C(3)	177.8(3)	175.0(5)	a	178.7(10)
angle (deg) of allenic π-planes	87.30(13)	82.70(18)	a	82.64(40)
torsion angle[b] (deg) C(1)−Cp of Fe(1)	−21.95(43)	−13.54(71)	a	19.35(146)
torsion angle (deg) C(1)−Cp of Fe(2)	−18.86(42)	−14.04(72)	a	19.53(140)
torsion angle (deg) C(3)−Cp of Fe(3)	10.21(44)	−12.91(73)	a	24.52(142)
torsion angle (deg) C(3)−Cp of Fe(4)		−17.23(75)	a	13.45(152)
$\delta(^{13}C)$ (ppm) C(1)	107.9	105.0	112.4	a
$\delta(^{13}C)$ (ppm) C(2)	201.3	204.7	205.6	a
$\delta(^{13}C)$ (ppm) C(3)	107.0	105.0	105.8	a
λ_{max}(nm)/log ϵ	447/2.9	449/3.4	450/3.4	a

[a] Not available. [b] Torsion angle C(1)−Cp of Fe(1) is defined as C(2)−C(1)−C(20)−C(21); the other torsion angles are defined analogously.

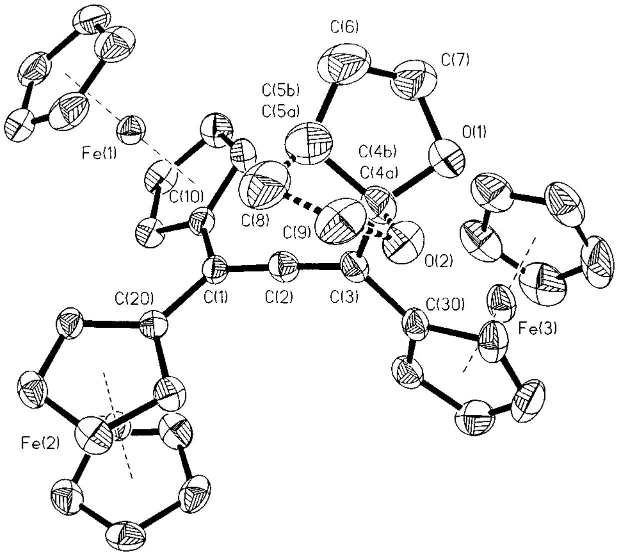

Figure 1. Molecular structure of **1**, showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(10)−C(19), for ferrocene 2 are C(20)−C(29), and for ferrocene 3 are C(30)−C(39), respectively.

redox potential of the mono- and diferrocenyl nucleophiles.

Nevertheless—from a preparative point of view—the target compound tetraferrocenylallene (**2**) can be prepared by combining triferrocenylallenylium tetrafluoroborate and cuprioferrocene in a *formal* nucleophilic addition reaction with reasonable yield; however, the other observed allenic byproducts and the different product distributions of these reactions, when the conditions are slightly changed, indicate a more complex (most likely radical in nature) reaction pathway.

Spectroscopy and Structure. Triferrocenyl(2-tetrahydrofuranyl)allene (**1**) shows NMR spectral properties in solution which are in accord with its existence as a racemic mixture with regard to the stereochemistry of the substituted tetrahydrofuranyl group. The ^{13}C signals of the allenic unit (δ 107.9, 201.3, 107.0 ppm) are unexceptional and are similar in value to those for other allenes.[26d] Single crystals suitable for an X-ray analysis (Tables 1 and 2) could be obtained, and the results are shown in Figures 1 and 2. The gross features of the structure of **1** are typical for a regular allene: the allenic carbons with normal bond lengths (C(1)−C(2) = 131.0(4) pm, C(2)−C(3) = 131.2(4) pm) are in an almost perfect linear arrangement (C(1)−C(2)−C(3) = 177.8(3)°) with orthogonal (87.30(13)°, Figure 2) planes of the π-bonds attached to the central allenic carbon. The three ferrocenyl substituents are slightly twisted (10.21(44) to 21.95(43)°) with reference to the C=C planes, a consequence of steric hindrance of the inner ortho hydrogens of the substituted cyclopentadienyl rings. Similar twisting has been observed in tetraferrocenylethylene.[5] In solution, there is no hindered rotation around the bonds C(1)−C(30) and C(1)−C(20) and the two ferrocenyl substituents of Fe(2) and Fe(3) become magnetically equivalent, whereas in the X-ray structure only one of the possible rotamers with regard to the pair of the two terminal ferrocenyl substituents is observed, obviously the result of crystal forces. Corresponding to the NMR spectral data in solution, the solid-state structure shows the 2-tetrahydrofuranyl substituent (disordered in a 1:1 ratio, Figures 1 and 2) in the two possible *R* and *S* configurations.

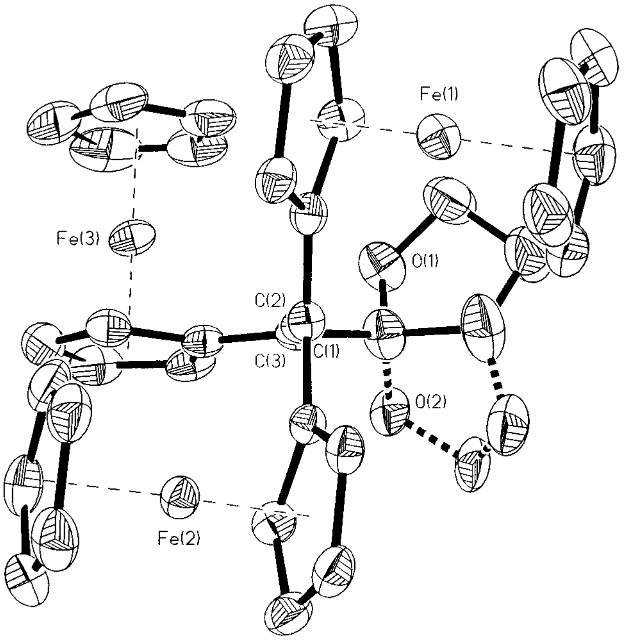

Figure 2. Molecular structure of triferrocenyl(2-tetrahydrofuranyl)allene (**1**), viewed down the allenic C(1)−C(2)−C(3) bond, showing the orthogonality of the allenic π-planes and the twisting of the ferrocenyl substituents.

Tetraferrocenylallene (**2**), the main target compound of this research, is a stable orange compound (mp >200 °C, dec), whose λ_{max} value (449 nm) is very close to the λ_{max} value (440 nm) of ferrocene,[42] indicating only weak

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(42) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603.

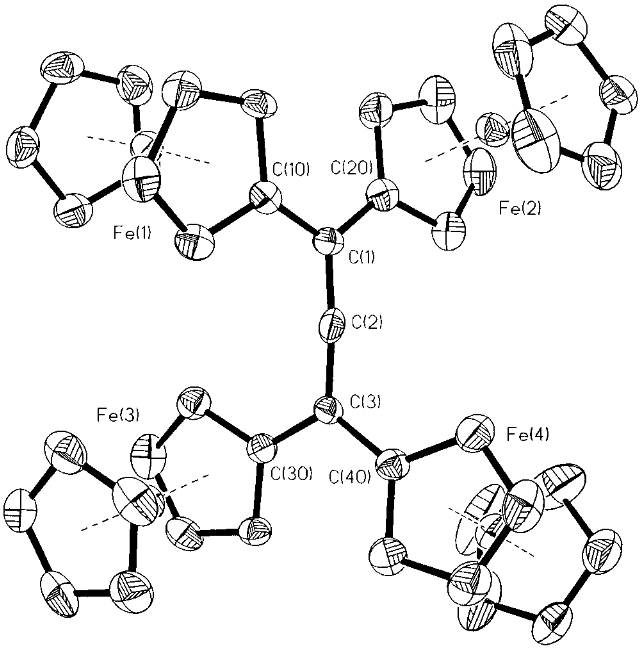

Figure 3. Molecular structure of tetraferrocenylallene (**2**), showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(10)–C(19), for ferrocene 2 are C(20)–C(29), for ferrocene 3 are C(30)–C(39), and for ferrocene 4 are C(40)–C(49), respectively.

interaction of the perpendicular π-planes of the allenic chromophore with the four ferrocenyl substituents, similar to other tetrasubstituted allenes.[43] The ^{13}C NMR spectral parameters (Table 2) of the exterior carbon atoms of the allenic unit are also unexceptional in comparison to other allenes,[33d] ruling out any special ferrocenyl-induced high-field shift. The ^{1}H NMR signals of the four hydrogens of the magnetically equivalent substituted cyclopentadienyl rings are two pseudotriplets, which are typical for monosubstituted ferrocenes; accordingly, the ferrocenyl substituents can (pairwise) freely rotate in solution, in contrast to tetraferrocenylethylene,[5] where helical chirality is observed due to hindered rotation. Cooling from ambient temperature to −60 °C does not change the appearance of these two pseudotriplets, showing that the rotation of the ferrocenyl substituents is still possible at this temperature; hence, no racemic mixture of helically chiral rotamers exists in solution. The solid-state structure (Tables 1 and 2, Figures 3–5) of **2** reveals a regular allenic unit, which deviates slightly from linearity (C(1)–C(2)–C(3) = 175.0(5)°, Figure 3) with perpendicular π-planes (82.70(18)°, Figure 4) close to the expected 90° angle. The ferrocenyl substituents are twisted (13.54(71)–17.23(75)°, Figure 5) in relation to the adjacent allenic π-planes, due to steric hindrance by the inner ortho hydrogens of the substituted cyclopentadienyl rings, resulting in a chiral conformation of the molecule in the asymmetric unit with two pairs of enantiomers in the unit cell, comparable to the helical propeller of tetraferrocenylethylene.[5] As noted above, in solution no chiral rotamer can be observed.

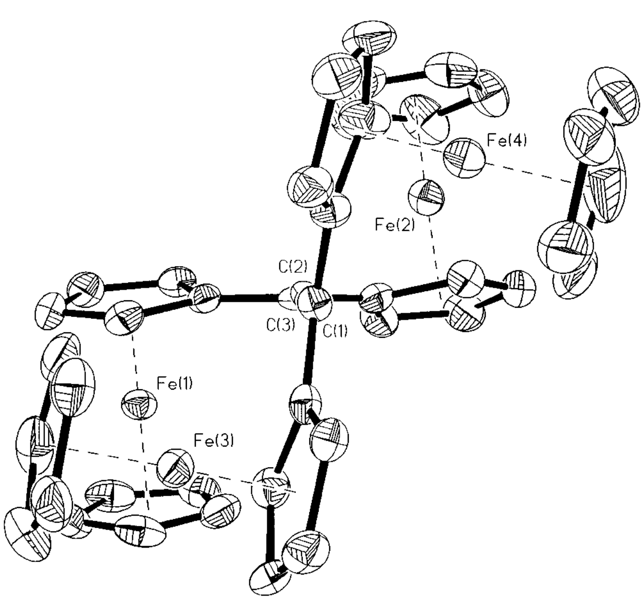

Figure 4. Molecular structure of tetraferrocenylallene (**2**), viewed down the allenic C(1)–C(2)–C(3) bond, showing the orthogonality of the allenic π-planes.

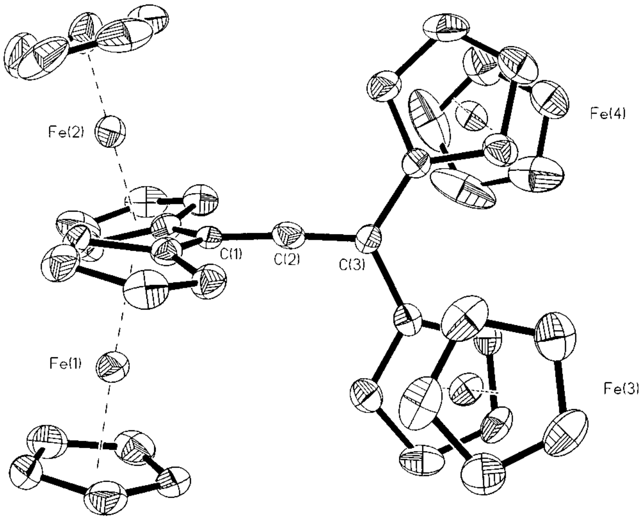

Figure 5. Molecular structure of tetraferrocenylallene (**2**), showing the twisting of the ferrocenyl substituents in reference to the allenic π-system.

1,1,3,4,6,6-Hexaferrocenylhexane-1,2,4,5-tetraene (**3**), a molecule of C_i (or, less likely, C_2) symmetry, has spectral properties for the allenic subunit (Table 2) which are very similar to those of allenes **1** and **2**. In addition to the signals for the isochronous hydrogens and carbons of the three formally different unsubstituted cyclopentadienyl rings, which are accidentally observed as only two signals, two-dimensional NMR reveals one separated signal for each hydrogen and each non-quaternary carbon of the three different substituted cyclopentadienyl rings, resulting in a set of 12 ^{1}H multiplets and 12 ^{13}C singlets (Figure 6). Consequently, in **3** restricted rotation of the ferrocenyl substituents leads to a vinyl (allenic) propeller conformation[44] with regard to the three ferrocenyl groups attached to the allenic backbone; two of these chiral triferrocenylallenyl units are linked together, with the center of symmetry inverting both halves of the molecule. Therefore, **3**

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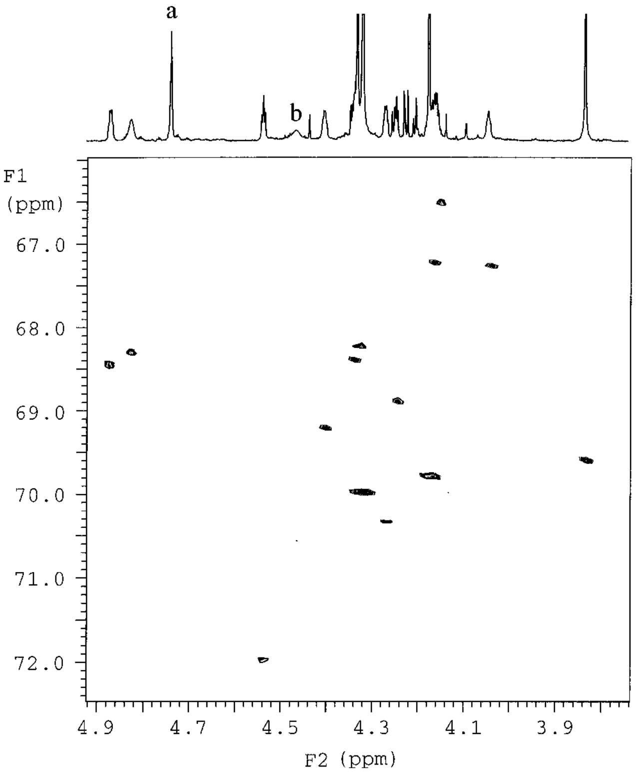


Figure 6. Pulsed field gradient enhanced HSQC of 1,1,3,4,6,6-hexaferrocenylhexane-1,2,4,5-tetraene (**3**) in THF-d_8: (a) H_2O; (b) impurity.

should be described more completely as *meso*-1,1,3,4,6,6-hexaferrocenylhexane-1,2,4,5-tetraene and constitutes the unusual case of a meso form of an orthogonal vinyl propeller. We are not aware of any other example in the literature, and clearly an X-ray crystal structure would be desirable, but we have not been able to obtain suitable crystals. Why restricted rotation of the ferrocenyl substituents (and helical chirality derived thereof) in solution is only observed for tetraferrocenylethylene[5] and **3**, but not for tetraferrocenylallene (**2**), is not clear.

The fourth allenic product, 1,1′-bis(triferrocenylallenyl)ferrocene (**4**), which has been obtained as a side product in small amounts, could not be characterized in solution by NMR due to the low solubility in all available solvents. Fortunately, in this case suitable single crystals could be obtained and the result is shown in Figures 7 and 8. The molecule belongs to the point group C_2 with the rotation axis passsing through Fe(1) of the 1,1′-disubstituted ferrocene which links the two triferrocenylallenyl subunits (Figure 7). These two subunits constitute helically chiral allenic vinyl propellers (Figure 8), analogously as in **3**. Overall, **4** is chiral and in the solid state the racemic mixture with four molecules (two pairs of enantiomers) in the unit cell is observed. The twisting of the ferrocenyl substituents ranges from 13.45(152) to 24.52(142)° (Figure 8, Table 2), similar in value to those in **1**, **2**, and tetraferrocenylethylene[5] and the bond lengths of the almost linear allenic unit are also similar to those of the other allenes.

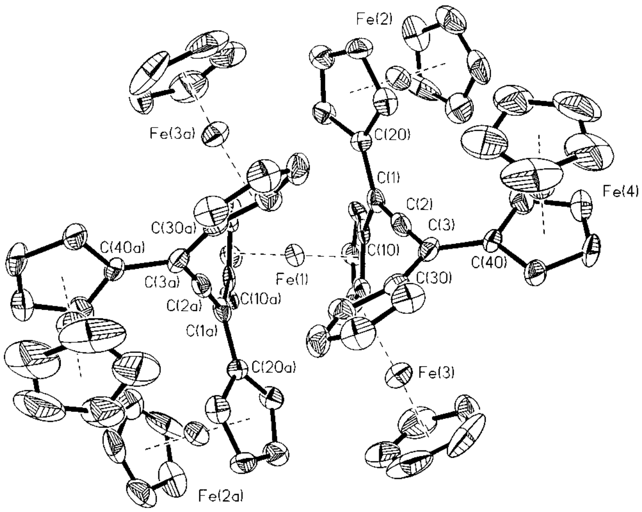


Figure 7. Molecular structure of 1,1′-bis(triferrocenylallenyl)ferrocene (**4**), showing the atom-numbering scheme. Hydrogen atoms and one molecule of CH_2Cl_2 are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(10)−C(14) and C(10a)−C(14a), for ferrocene 2 are C(20)−C(29), for ferrocene 3 are C(30)−C(39), and for ferrocene 4 are C(40)−C(49), respectively.

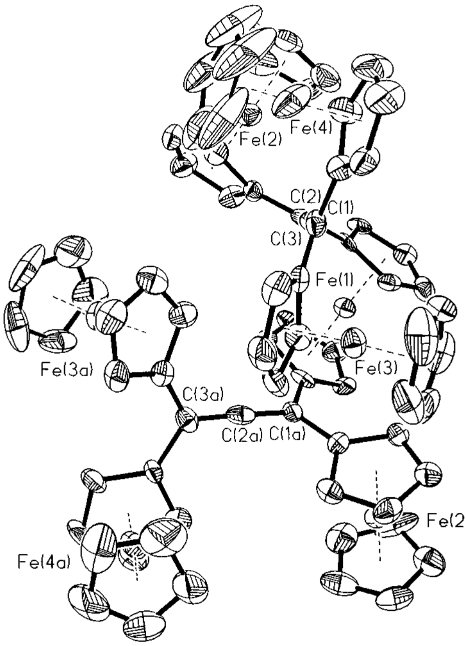


Figure 8. Molecular structure of **4**, viewed down the allenic C(1)−C(2)−C(3) bond, showing the orthogonality of the allenic π-planes and the twisting of the ferrocenyl substituents.

Reactivity. According to the objectives of this project on perferrocenylated cumulenes (see Introduction), three types of potential reactive behavior (electrochemistry, nucleophilic reactivity, and charge-transfer complex formation) of ferrocenylated allenes have been addressed, using tetraferrocenylallene (**2**) as the prototypical permetallocenylated allene. The results obtained from cocrystallization of **2** and fullerene C_{60} are not included in this paper and will be reported elsewhere, because until now only fragmentary structural characterization was possible.

Redox Chemistry. Low-temperature cyclic voltammetry reveals three reversible oxidation waves ($E^1{}_{1/2} = +0.32$, $E^2{}_{1/2} = +0.42$, $E^{3/4}{}_{1/2} = +0.52$ V), with the first two oxidations corresponding to one-electron transfers and the third oxidation to a simultaneous two-electron transfer (which is also nonseparated in the rectangular voltammogram), according to peak to peak separations and relative current increase of the signals (Figure 9).

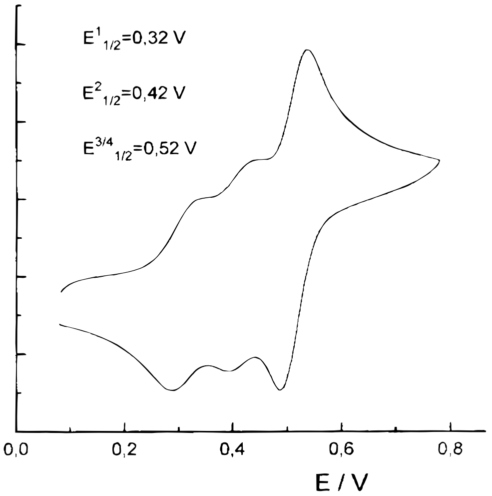
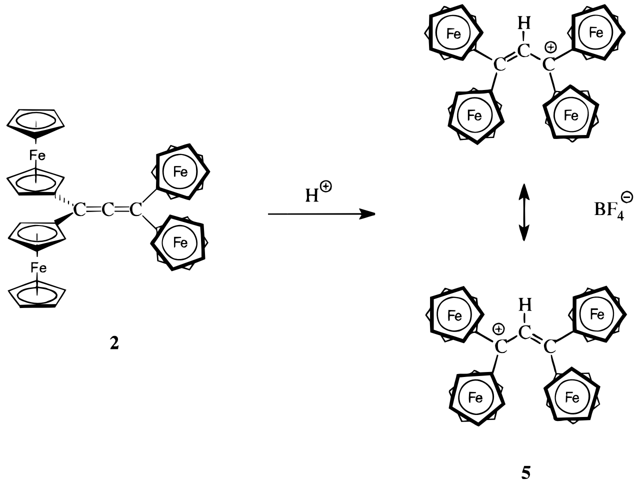


Figure 9. Voltammogram of tetraferrocenylallene (**2**).

Scheme 2. Protonation of Allene 2



These four oxidation steps are assigned to four metal-centered ferrocene/ferrocenium couples. The first oxidation potential is similar in value to that of ferrocene (0.31−0.32 V), indicating **2** to be a much weaker donor in comparison to tetraferrocenylethylene ($E^1_{1/2} = +0.09$ V),[5] and the complete oxidation process occurs in a much smaller potential range ($\Delta[E^1 - E^4] = 200$ mV, vs 530 mV for tetraferrocenylethylene), indicating reduced interaction of the ferrocenyl substituents due to the longer conjugation pathway and the orthogonality of the allenic π system. Overall, only four ferrocene/ferrocenium oxidation steps are observed; hence, no *allenic* radical cation in analogy to Berndt's[19] tetra-*tert*-butylallene radical cation seems to exist.

Nucleophilicity of the Central Allenic Carbon. Due to the electronic influence of the four ferrocenyl substituents as potent inductive donors,[1,6] nucleophilic interaction of the central carbon of allene **2** with electrophilic substrates might seem achievable. In analogy to such chemistry of tetrakis(dimethylamino)allene,[16] which reacts with electrophiles (H^+, CO_2, CS_2, SO_2, S) to yield highly stabilized cationic or ylidic allylium compounds, similar reactions were attempted with allene **2**. However, tetraferrocenylallene (**2**) fails to react with elemental sulfur, trimethylaluminum, or carbon disulfide. Only protonation (Scheme 2) with HCl or HBF_4 gives a dark brown tetraferrocenylpropenylium salt (**5**), whose properties are not in accord with the expected behavior: the lowered stability of this salt in comparison to other, less substituted but more stable allylium compounds[6] and the brown color in comparison to the usually observed dark green to blue color of such ferrocenylallylium systems[6] suggest **5** to be a distorted, nonplanar propenylium salt, which is therefore less stable and is not conjugated to the same extent. Scheme 2 illustrates how upon protonation the orthogonal allenic π-system is converted to a bent and planar allylium system; the corresponding 90° rotation of one of the terminal diferrocenyl methylidene ↔ methylium units together with the 60° bending in relation to the linear allene is not fully possible due to steric repulsion of the ferrocenyl substituents. As noted above, this steric situation prevents tetraferrocenylpropene, a possible precursor of **5**, to be synthesized by nucleophilic addition of lithioferrocene to 1,1,3-triferrocenylprop-1-ene.[6] The reason for the observed nonreactivity of allene **2** with other electrophiles (see above) is similarly steric in nature: these more voluminous reagents cannot attack the central allenic carbon, as has been deduced from inspection of van der Waals plots of allene **2**. An allylic system with four ferrocenyl substituents in the terminal positions is so crowded that chemistry analogous to Viehe's[16] tetrakis(dimethylamino) allene, Ziegler's[17] tetraphenylallyl radical, and Koelsch's[18] pentaphenylallyl radical is precluded by the steric bulk of the metallocenyl groups.

Summary. Synthetically, tetraferrocenylallene can be prepared by (formal) nucleophilic addition of cuprioferrocene to triferrocenylallenylium tetrafluoroborate. Side products include hexaferrocenyl bis(allene), heptaferrocenyl bis(allene), and (if the reaction is performed in THF) (tetrahydrofuranyl)triferrocenylallene. Structurally, these highly substituted allenes show interesting helical propeller conformations in the solid state and/or in solution. The reactivity of tetraferrocenylallene is limited to its protonation; with other (bulkier) electrophiles, no reaction is observed due to steric hindrance. Cyclic voltammetry shows tetraferrocenylallene to be a weak donor with a first oxidation potential identical in value with that of ferrocene.

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Supporting Information Available: Tables of crystal data and structure refinement details, anisotropic thermal parameters, fractional atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms, all bond lengths and angles, and fractional atomic coordinates for the hydrogen atoms for **1**, **2**, and **4** (26 pages). Ordering information is given on any current masthead page. The authors have deposited atomic coordinates for structures **1**, **2**, and **4** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW, U.K.

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