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Stable and Crystalline Allylium and Allenylium Salts with Ferrocenyl Substituents

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Allylic and allenylic carbenium ions, which have been reported in the literature to be labile or not isolable at all, have no inherent instability. Progressive substitution with ferrocenyl groups affords allylic cations, whose stability toward photochemical decay and nucleophilic collapse increases with increasing number of ferrocenyl substituents, if the allylic moiety is at least 2-fold-substituted with ferrocenes in the 1,3-positions. The unmatched cation-stabilizing capacity of metallocenes is illustrated in cyclopentadienyl(1,3-diferrocenyl-1-yliumpentalenyl)iron tetrafluoroborate, a compound which survives exposure to sunlight in aqueous solution for days. In addition to full characterization for these allylium salts by the usual analytical and spectroscopic methods, X-ray analysis of cyclopentadienyl(1,3-diferrocenyl-1-yliumpentalenyl)iron tetrafluoroborate showed (a) deviations of the regular conformation of the ferrocenyl substituents in the 1,3-positions that are similar to those observed in other simple metallocenyl-stabilized carbenium ions, indicative of electronic stabilization by intramolecular charge delocalization, (b) these two ferrocenyl substituents are structurally distorted in an unequal manner and seem to contribute unequally in this charge delocalization, but the observed dissymmetric structure is most likely the result of crystal forces, and (c) the annelated ferrocene of this formal pentalene system is undistorted, ruling out (together with results from solution NMR measurements) any significant conjugation; therefore, this cation should be envisaged as an allylium system and not as an antiaromatic cyclopentadienyl cation. In the case of allenylium ↔ propargylium ions, attachment of two ferrocenes results in labile or intermediate propargylium ions, which can be trapped with triethylamine to afford ammonium allenes, formally Lewis base complexed allenylium salts, with an interesting bent allene unit as is evidenced by single-crystal structure analysis. Introduction of a third ferrocene into the allenylium ↔ propargylium system affords 1,3,3-triferrocenylallen-1-ylium tetrafluoroborate, the first stable and fully characterized allenylium compound, with only minor resonance contributions from the propargylium structure, proven most clearly by the observation of an extremely intense and acceptor-shifted cumulenic stretching vibration of 2151 cm^{-1} in the IR spectrum.

Introduction

Stabilization of an α-carbenium moiety by π-ligand complexes of transition metals[1] has been achieved with a wide range of organometallic fragments, including (arene)tricarbonyl chromium,[2] (cyclopentadiene)tricarbonylmanganese,[3] (cyclopentadiene)dicarbonylnitrosylchromium,[4] (cyclobutadiene)tricarbonyliron,[5] nonacarbonyltricobalt alkylidyne,[6] hexacarbonyldicobalt alkyne,[7] bis(methylcyclopentadienyl)tetracarbonyldimolybdenum,[8] and metallocenes.[1,9] Of these carbenium-stabilizing groups, metallocenes are probably the most efficient donors for satisfying the electron-deficiency of the carbenium moiety, which was recognized soon after the discovery of ferrocene.[10] This chemistry has been developed over the last decades with numerous studies concerning structural and spectroscopic properties and applications in organic synthesis.[1,9,11] Within this area

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of research, ferrocenyl-stabilized carbenium ions are the most frequently studied systems, but the even higher donor-capacity of ruthenocene, osmocene, and permethylated metallocenes[12] is illustrated by the recent isolation of metallocene-stabilized dications.[13] In addition, contrary to the above mentioned carbonyl-containing donors, metallocenes allow the synthesis of the carbenium-isoelectronic heterocations phosphenium[14] and silicenium.[15] For carbocations, mainly simple carbenium ions have been studied and no stable allyl or allenyl cations have been isolated so far. Here we describe the synthesis, properties, and structure of such cations, which are substituted and hence stabilized by two or three ferrocene moieties. These cations are of interest as electron and energy transfer model systems for molecular electronics.

Experimental Section

General Comments. All of the reactions were carried out in the absence of air using standard Schlenk techniques and vacuum-line manipulations. Solvents were deoxygenated, purified, and dried prior to use. Instrumentation: Bruker AC 200 (^{1}H and ^{13}C NMR); Nicolet 510 FT-IR (IR); Bruins Instruments Omega 20 (UV–vis); Varian CH-7, Finnigan MAT 95 (MS); Siemens P4 (X-ray). Melting points were determined on a Kofler hot-plate apparatus. Microanalyses were obtained from the Department for Microanalysis, University of Vienna, Austria; and from the Analytical Department of Lenzing AG, Lenzing, Austria.

Monolithioferrocene,[16] ferrocenylcopper–dimethylsulfide complex,[17] *trans*-1,3-diferrocenylpropenone,[18] diferrocenyl ketone,[19] ethinylferrocene,[20] (trimethylsilyl)ethinylferrocene,[17,21] and cyclopentadienyl(3-ferrocenyl-1-oxy-pentalenyl)iron[22] were prepared according to published procedures.

***rac*-1,3-Diferrocenylprop-2-en-1-ol (CAS Registry No. 72971-83-6).** Since no analytical and spectral data were given in ref 18b, the experimental procedure is reported in detail: 0.487 g (1.15 mmol) of 1,3-diferrocenylprop-2-en-1-one was dissolved in 40 mL of THF in a Schlenk vessel under an atmosphere of argon and cooled to −60 °C. A 1.27 mL amount of a 1.0 M solution of lithium triethylborohydride (1.27 mmol) was syringed slowly to the stirred solution. The reaction mixture was warmed to room temperature, reduced in volume to approximately 10 mL, hydrolyzed by addition of 30 mL of H_2O, and extracted with three portions of Et_2O. The combined organic layers were dried with Na_2SO_4, the solvents were removed in vacuo, and the residue was purified by chromatography on neutral Al_2O_3 with Et_2O (a few drops of *tert*-butylamine were added to ensure basic conditions) as eluent: 0.350 g (0.82 mmol, 71.4%) of *rac*-1,3-diferrocenylprop-2-en-1-ol, orange crystals, mp not observable because of ready reoxidation by air of the solid alcohol to an oily mixture of alcohol and ketone. For the same reason, no elemental analysis was attempted. MS (EI, 70 eV): m/z 426 (M^+). Selected IR data (KBr): 3436 (ν_{OH}), 1656 ($\nu_{C=C}$) cm^{-1}. ^{1}H NMR (DMSO-d_6; *cp* refers to cyclopentadienyl): δ 4.43 (1H, s, −O−*H*), 3.46 (10H, s, *unsubst. cp*), 4.14 (4H, m, *subst. cp*), 4.21 (4H, m, *subst. cp*), 4.92 (1H, m, C*H*−OH), 6.00−6.36 (2H, m, −C*H*=C*H*−). ^{13}C NMR (DMSO-d_6): δ 66.2, 66.5, 66.7, 67.2, 67.3, 67.4, 68.5, 67.0, 69.3 (*ferrocenyl*), 91.8 (*C*−OH), 125.8 [−*C*H=CH−CH(OH)], 130.3 [−CH=*C*H−CH(OH)].

1,3-Diferrocenylallylium Triiodide (1a), 1,3-Diferrocenylallylium Hexafluorophosphate (1b), and 1,3-Diferrocenylallylium Tetrafluoroborate (1c) (CAS Registry No. 68093-14-1). A 0.220 g (0.516 mmol) amount of *rac*-diferrocenylprop-2-en-1-ol was dissolved in 50 mL of Et_2O. After addition of 60 mL of 2 N H_2SO_4, the mixture was shaken in a separatory funnel, the resulting green aqueous layer was quickly added to a solution of 0.830 g (5.00 mmol) of KI and 1.27 g (5.00 mmol) of I_2 in 50 mL of H_2O, and the precipitated green solid was filtered off, washed with three portions of H_2O, and dried in vacuo, yielding 0.190 g (0.24 mmol, 46.6%) of 1,3-diferrocenylallylium triiodide **(1a)**. Analogously, combining the 1,3-diferrocenylallylium hydrogensulfate solution with an aqueous solution of $NaPF_6$ yielded 0.420 g (0.758 mmol, 71.4%) of 1,3-diferrocenylallylium hexafluorophosphate **(1b)**. Addition of 1.5 mol equiv (based on starting alcohol) of a 54% solution of fluoroboric acid in ether to the solution of *rac*-diferrocenylprop-2-en-1-ol in Et_2O yielded 0.179 g (0.361 mmol, 72.8%) of 1,3-diferrocenylallylium tetrafluoroborate **(1c)**. Compounds **1a,c** are stable for a limited time only, after storage under argon at −30 °C for half a year, decomposition of the triiodide **1a** and the tetrafluoroborate **1c** were complete. The hexafluorophosphate **1b** showed NMR spectral parameters corresponding to less than 5% decomposition after storage at ambient temperature for 18 months.

Data for **1a**: Green microcrystalline solid. Mp not observable due to continuous decomposition on heating. Anal. Calcd

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for $C_{23}H_{21}Fe_2I_3$: C, 34.98; H, 2.68. Found: C, 35.12; H, 2.52. MS (FAB): *m/z* 409.03375 (M^+ of cation; exact mass calcd for $C_{23}H_{21}Fe_2$, 409.03420). UV–vis data: unstable in solution, not determined. IR data (KBr): 3081 w, 1696 m, 1652 m, 1561 vs, 1451 vs, 1412 s, 1380 s, 1287 s, 1231 vs, 1167 m, 1108 s, 1054 s, 1036 s, 1003 s, 976 s, 922 s, 893 m, 847 vs, 826 vs, 641 s, 502 vs, 473 s, 459 vs, 419 s cm^{-1}. ^1H and ^{13}C NMR: unstable in solution due to Watts-type[40] oligomerization, not determined.

Data for **1b**: Green microcrystalline solid. Mp not observable due to continuous decomposition on heating. Anal. Calcd for $C_{23}H_{21}Fe_2PF_6$: C, 49.86; H, 3.82. Found: C, 49.20; H, 4.14. MS (FAB): *m/z* 409.03305 (M^+ of cation; exact mass calcd for $C_{23}H_{21}Fe_2$, 409.03420). UV–vis data (acetonitrile; λ_{max}/log ϵ): 419/4.2, 767/3.9 nm/log ϵ. IR data (KBr): 3108 w, 1706 w, 1642 w, 1569 vs, 1451 s, 1412 m, 1380 m, 1287 s, 1235 vs, 1167 m, 1108 m, 1052 m, 1042 s, 978 m, 924 s, 849 vs, 644 s, 558 vs, 509 s, 498 s, 475 s, 461 vs, 423 s cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.43 (10H, s, *unsubst. cp*), 4.97 (4H, br s, *subst. cp*), 5.54 (4H, br s, *subst. cp*), 6.48 [1H, br s, *allyl H(2)*], 8.30 [2H, br s, *allyl H(1) and H(3)*]. ^{13}C NMR (CD_2Cl_2): δ 74.6, 76.6, 83.5, 87.4 (*ferrocenyl*), 126.0 (*allyl*), 157.7 (*allyl*).

Data for **1c**: Green microcrystalline solid. Mp not observable due to continuous decomposition on heating. Anal. Calcd for $C_{23}H_{21}Fe_2BF_4$: C, 55.71; H, 4.27. Found: C, 55.47; H, 4.19. MS (FAB): *m/z* 409.03445 (M^+ of cation; exact mass calcd for $C_{23}H_{21}Fe_2$, 409.03420). UV–vis data (acetonitrile; λ_{max}/log ϵ): 420/4.1, 751/3.8 nm/log ϵ. ^1H NMR (CD_2Cl_2): δ 4.45 (10H, s, *unsubst. cp*), 5.00 (4H, br s, *subst. cp*), 5.52 (4H, br s, *subst. cp*), 6.50 [1H, br s, *allyl H(2)*], 8.35 [2H, br s, *allyl H(1) and H(3)*]. ^{13}C NMR (CD_2Cl_2): δ 74.3, 76.4, 83.2, 87.4 (*ferrocenyl*), 125.7 (*allyl*), 157.7 (*allyl*).

1,1,3-Triferrocenylprop-2-en-1-ol (2). A Schlenk vessel was charged with 1.30 g (6.77 mmol) of monolithioferrocene and 100 mL of THF at −80 °C. To the resulting suspension was added 2.73 g (6.45 mmol) of 1,3-diferrocenylprop-2-en-1-one, and the mixture was stirred magnetically at −80 °C for 5 min. The cooling bath was removed, and the stirred mixture was warmed to room temperature. The solvent THF was removed in vacuo, the resulting crude alcoholate was hydrolyzed with ice/water, the product mixture (containing alcohol **2** and traces of unreacted propenone and ferrocene) was extracted with three portions of ether, and all volatile materials were removed in vacuo, yielding 3.66 g (6.00 mmol, 93%) of crude **2**. For analytical purposes a small portion was purified by chromatography on neutral Al_2O_3 with petroleum ether/diethyl ether: orange crystals, mp 165–168 °C (decomp). Anal. Calcd for $C_{33}H_{30}Fe_3O$: C, 64.96; H, 4.96; O, 2.62. Found: C, 65.13; H, 4.82; O, 2.70. MS (EI, 70 eV): *m/z* 610 (M^+). Selected IR data (KBr): 3527 (ν_{OH}), 1652 ($\nu_{C=C}$) cm^{-1}. ^1H NMR (C_6D_6): δ 2.57 (1H, s, $-O-$*H*), 3.96 (4H, m, *subst. cp*), 4.07–4.14 (19H, m, *unsubst. and subst cp*), 4.23 (2H, m, *subst. cp*), 4.32 (2H, m, *subst. cp*), 6.49–6.60 (2H, dd, *J* = 15.4 Hz, $-CH{=}CH-$). ^{13}C NMR ($CDCl_3$): δ 66.7, 66.9, 67.4, 67.9, 68.6, 68.9, 69.6, 89.6, 91.7 (*ferrocenyl*), 96.8 (*C*$-$OH), 124.0 ($-CH{=}CH-$), 132.6 ($-CH{=}CH-$).

1,1,3-Triferrocenylallylium Tetrafluoroborate (3a) and 1,1,3-Triferrocenylallylium Tetraphenylborate (3b). The crude 1,1,3-triferrocenylprop-2-en-1-ol (**2**) was dissolved in dry ether, and 1.5 mol equiv of a 54% solution of fluoroboric acid in ether was added dropwise to the stirred solution. The precipitated dark green cation tetrafluoroborate was filtered off, washed with 5 portions of ether, and dried in vacuo, yielding 2.63 g (3.87 mmol, 64.5%) of 1,1,3-triferrocenylallylium tetrafluoroborate (**3a**).

Conversion of 3a into the Corresponding Tetraphenylborate 3b. Combining a solution of 900 mg (1.32 mmol) of **3a** in 200 mL of dry methanol with a solution of 500 mg (1.46 mmol) of sodium tetraphenylborate in 3 mL of methanol produces a dark green precipitate, which was filtered off, washed with three portions of H_2O and three portions of Et_2O, and dried in vacuo, yielding 600 mg (0.66 mmol, 50%) of 1,1,3-triferrocenylallylium tetraphenylborate (**3b**). These allylium salts are air-stable in the solid state but have to be protected from light to avoid photochemical decomposition.

Data for **3a**: Mp not observed, >300 °C. Anal. Calcd for $C_{33}H_{29}BF_4Fe_3$: C, 58.29; H, 4.30. Found: C, 58.51; H, 4.33. MS (FAB): *m/z* 593.03149 (M^+ of cation; exact mass calcd for $C_{33}H_{29}Fe_3$, 593.03174). UV–vis data (acetonitrile; λ_{max}/log ϵ): 388/4.0, 451/4.2, 840/4.0 nm/log ϵ. IR data (KBr): 471 m, 807 m, 822 m, 1036 vs, 1090 vs, 1108 vs, 1264 s, 1281 s, 1436 s, 1457 s, 1557 vs cm^{-1}. ^1H NMR (CD_3CN): δ 4.39 (10H, s, *unsubst. cp*), 4.46 (5H, s, *unsubst. cp*), 5.10 (2H, m, *subst. cp*), 5.27 (4H, m, *subst. cp*), 5.31 (2H, m, *subst. cp*), 5.45 (4H, m, *subst. cp*), 6.67 [1H, d, *J* = 14.6 Hz, *allyl H(3)*], 8.66 [1H, d, *J* = 14.6 Hz, *allyl H(2)*]. ^{13}C NMR ($CDCl_3$): δ 72.2, 73.6, 74.4, 74.8, 75.0, 79.2, 79.4, 84.8, 86.2 (*ferrocenyl*); 128.5, 154.1, 180.5 (*allyl*).

Data for **3b**: Mp not observed, >300 °C. Anal. Calcd for $C_{57}H_{49}BFe_3$: C, 75.04; H, 5.41. Found: C, 75.11; H, 5.18. MS (EI, 70 eV): *m/z* 593.03295 (M^+ of cation; exact mass calcd for $C_{33}H_{29}Fe_3$, 593.03174). UV–vis data (acetonitrile; λ_{max}/log ϵ): 389/4.0, 451/4.2, 841/4.0 nm/log ϵ. IR data (KBr): 3096 w, 3055 m, 2984 w, 1553 vs, 1456 s, 1435 s, 1271 s, 1107 m, 829 m, 733 m, 704 s, 470 m cm^{-1}. ^1H NMR (CD_3CN): δ 4.37 (10H, s, *unsubst. cp*), 4.44 (5H, s, *unsubst. cp*), 5.07 (2H, m, *subst. cp*), 5.25 (4H, m, *subst. cp*), 5.29 (2H, m, *subst. cp*), 5.42 (4H, m, *subst. cp*), 6.65 [1H, d, *J* = 14.6 Hz, *allyl H(3)*], 6.86–6.79 (8H, m, *phenyl*), 6.98 (12H, m, *phenyl*), 8.64 [1H, d, *J* = 14.6 Hz, *allyl H(2)*]. ^{13}C NMR ($CDCl_3$): δ 68.8, 69.2, 69.9, 72.1, 73.4, 74.5, 75.1, 79.3, 79.9, 84.2, 85.8 (*ferrocenyl*); 121.7, 125.5, 136.3 (*phenyl*); 164.2 [q, $J(^{13}C-^{11}B)$ = 195 Hz, *C(1) of phenyl*)]; 127.9, 154.1, 180.6 (*allyl*).

Cyclopentadienyl(3-ferrocenyl-1-hydroxypentalenyl)iron (4) and Cyclopentadienyl(3-ferrocenyl-1-yliumpentalenyl)iron Tetrafluoroborate (5). In an analogous manner as described for *rac*-1,3-diferrocenylprop-2-en-ol (see above), reduction of cyclopentadienyl-(3-ferrocenyl-1-oxypentalenyl)iron with lithium triethylborohydride yielded cyclopentadienyl(3-ferrocenyl-1-hydroxypentalenyl)iron (**4**) as a red solid of limited stability; therefore only NMR spectroscopy was used for the characterization of this intermediate. ^1H NMR (C_6D_6): δ 2.02 (1H, d, *J* = 9.5 Hz, $-O-$*H*), 3.90–4.48 (17H, m and two s, *subst. and unsubst. cp*), 4.94–5.00 (1H, dd, *J* = 9.5 Hz, *J* = 2 Hz, $-C$*H*$-$OH), 6.05 (1H, d, *J* = 2 Hz, $-C$*H*$=$). ^{13}C NMR (C_6D_6): δ 61.9, 63.3, 66.4, 69.1, 69.2, 69.8, 70.0, 70.2, 72.2, 80.2, 94.0 (*ferrocenyl*), 96.5 (*C*$-$OH), 122.8 (*C*$-$OH), 132.3 ($-CH{=}C$), 142.6 ($-CH{=}C$). Addition of 1.5 mol equiv (based on starting alcohol) of a 54% solution of fluoroboric acid in ether to the solution of **4** in Et_2O yielded 0.147 g (0.30 mmol, 60%) of cyclopentadienyl(3-ferrocenyl-1-yliumpentalenyl)iron tetrafluoroborate (**5**) as a green, microcrystalline solid. Mp: not observable due to continuous decomposition on heating. MS (FAB): *m/z* 407.02230 (M^+ of cation; exact mass calcd for $C_{23}H_{19}Fe_2$, 407.01855). UV–vis data (acetonitrile; λ_{max}): unstable in solution; 356, 476, 637 nm were observed for freshly prepared solutions, and during measurement of the spectrum these absorptions shifted to lower values with decreasing ϵ, indicative of destruction of the chromophore. IR data (KBr): 3100 m, 1669 m, 1530 s, 1410 s, 1387 s, 1339 m, 1300 m, 1233 w, 1107 s, 1084 s, 834 m, 469 m, 436 m cm^{-1}. ^1H and ^{13}C NMR: unstable in solution; attempted NMR analysis yielded too many signals with broad appearance, indicating decomposition during FID accumulation.

Cyclopentadienyl(1,3-diferrocenyl-1-hydroxypentalenyl)iron (6) and Cyclopentadienyl(1,3-diferrocenyl-1-yliumpentalenyl)iron Tetrafluoroborate (7). A Schlenk vessel was charged with 1.21 g (6.3 mmol) of monolithioferrocene and 100 mL of THF at −80 °C. To the resulting suspension was added 2.52 g (6.0 mmol) of cyclopentadienyl-(3-ferrocenyl-1-oxypentalenyl)iron, and the mixture was stirred magnetically at −80 °C for 5 min. The cooling bath was removed, and the stirred mixture was warmed to room

Table 1. Crystal Data and Structure Refinement for 7, 10a,b, and 11

	7	**10a**	**10b**	**11**
mol formula	$C_{33}H_{27}BF_4Fe_3$	$C_{30}H_{34}F_3Fe_2NO_3S$	$C_{53}H_{54}BFe_2N$	$C_{33}H_{28}Fe_3O$
fw	677.9	657.34	827.48	608.10
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P1$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$Pca2_1$ (No. 29)
a (pm)	1311.1(4)	2011.4(3)	1548.6(4)	3983.0(5)
b (pm)	1320.2(4)	729.8(1)	1561.6(3)	584.1(2)
c (pm)	1621.0(6)	2055.5(7)	1833.7(5)	1064.6(4)
α (deg)	91.61(2)	90	90	90
β (deg)	95.40(2)	102.81(2)	108.71(2)	90
γ (deg)	100.30(2)	90	90	90
vol (nm^3)	2.746(2)	2.9422(12)	4.200(2)	2.4768(13)
Z	4	4	4	4
temp (K)	223(2)	213(2)	213(2)	193(2)
density (calcd) (Mg/m^3)	1.640	1.484	1.309	1.631
abs coeff (mm^{-1})	1.614	1.108	0.729	1.760
$F(000)$	1376	1360	1744	1248
color, habit	black block	orange platelet	red prism	orange block
cryst size (mm^3)	0.3 × 0.2 × 0.15	0.34 × 0.19 × 0.09	0.60 × 0.25 × 0.20	0.35 × 0.2 × 0.15
θ range for data collecn (deg)	2.02–19.99	2.56–18.00	3.01–21.00	3.07–22.49
index ranges	$-1 \le h \le 11; -13 \le k \le 12; -15 \le l \le 15$	$-13 \le h \le 20; -5 \le k \le 7; -19 \le l \le 20$	$-6 \le h \le 16; -11 \le k \le 17; -20 \le l \le 15$	$-36 \le h \le 42; -6 \le k \le 6; -8 \le l \le 11$
no. of rflns collecd	5302	2774	5594	2442
no. of indep rflns	4981 ($R_{int} = 0.0580$)	2008 ($R_{int} = 0.0369$)	4500 ($R_{int} = 0.0350$)	1882 ($R_{int} = 0.0410$)
no. of rflns with $I > 2\sigma(I)$	2977	1511	2960	1534
abs corr	DIFABS	ψ-scan	none	ψ-scan
max and min transm		0.926 and 0.838		0.953 and 0.765
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	4798/0/734	1872/0/285	4384/0/514	1810/0/333
goodness-of-fit on F^2	1.030	1.087	1.013	1.095
final R indices [$I > 2\sigma(I)$]	R1 = 0.0578; wR2 = 0.1042	R1 = 0.0792; wR2 = 0.1687	R1 = 0.0386; wR2 = 0.0701	R1 = 0.0578; wR2 = 0.1042
R indices (all data)	R1 = 0.1260; wR2 = 0.1394	R1 = 0.1118; wR2 = 0.2369	R1 = 0.0977; wR2 = 0.1153	R1 = 0.0685; wR2 = 0.1098
largest diff peak and hole (e nm^{-3})	383 and −393	510 and −354	377 and −386	430 and −391

temperature. The solvent THF was removed in vacuo, the resulting crude alcoholate was hydrolyzed with ice/water, the product mixture [containing alcohol **6** and traces of unreacted cyclopentadienyl(3-ferrocenyl-1-oxypentalenyl)iron and ferrocene] was extracted with three portions of ether, and all volatile materials were removed in vacuo, yielding crude **6**, which was used without further purification because of ready reoxidation and immobilization on basic alumina as the solid phase on attempted chromatography. Compound **6** was dissolved in dry ether, and 1.5 mol equiv of a 54% solution of fluoroboric acid in ether was added dropwise to the stirred solution. The precipitated dark blue cation tetrafluoroborate was filtered off, washed with five portions of ether, and dried in vacuo, yielding 2.09 g (3.1 mmol, 51.4%) of cyclopentadienyl-(1,3-diferrocenyl-1-yliumpentalenyl)iron tetrafluoroborate (**7**), which is air-stable in the solid state; for prolonged storage it should be protected from light to avoid photochemical decomposition. Mp not observed, >300 °C. Anal. Calcd for $C_{33}H_{27}Fe_3BF_4$: C, 58.47; H, 4.01. Found: C, 58.41; H, 4.28. MS (FAB): m/z 591.01611 (M^+ of cation; exact mass calcd for $C_{33}H_{27}Fe_3$, 591.01609). UV–vis data (acetonitrile; $\lambda_{max}/\log \epsilon$): 391/4.2, 558/3.5, 873/4.1 nm/log ϵ. IR data (KBr): 1040 s, 1063 s, 1084 s, 1106 s, 1127 s, 1412 s, 1445 s, 1509 vs, 1540 s cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.25 (10H, s, *unsubst. cp*), 4.39 (5H, s, *unsubst. cp*), 4.61 (2H, m, *subst. cp*), 4.74 (2H, m, *subst. cp*), 5.61–5.23 (5H, m, *subst. cp*), 5.58 (2H, d, J = 2.7 Hz, *subst. cp*), 6.19 (1H, t, J = 2.7 Hz, *allyl-H*). ^{13}C NMR (CD_2Cl_2): δ 70.2, 73.0, 75.0, 76.4, 79.4, 79.9, 82.2, 84.5, 88.8 (*ferrocenyl*); 127.7 (*allyl*), 162.6 (*allyl*).

X-ray Structure Determination of 7. (Figures 2–4) Single crystals, suitable for X-ray analysis, were obtained by recrystallization from dichloromethane. A Siemens P4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 71.073 pm) was used for data collection. Crystal data, data collection, and refinement parameters of **7** are summarized in Table 1. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Data were measured via ψ-scan and corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography*,[23] and an empirical absorption correction[24] was made. The structure was solved by direct methods, SHELXS-86,[25] and refined by a full-matrix least-squares procedure using SHELXL-93.[26] 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 supporting information.

1,1-Diferrocenyl-3-(trimethylsilyl)prop-2-yn-1-ol (8). A 0.80 mL (5.6 mmol) amount of ethynyl trimethylsilane [(trimethylsilyl)acetylene] was dissolved in 125 mL of THF and cooled to −60 °C in a Schlenk vessel under an atmosphere of argon. Addition of 3.6 mL (5.7 mmol) of a 1.6 M n-butyllithium solution in n-hexane and allowing the stirred mixture to warm to ambient temperature resulted in formation of lithium (trimethylsilyl)acetylide.[27] To this colorless solution was added 1.60 g (4.0 mmol) of diferrocenyl ketone in one portion, and the resulting red solution was stirred at room temperature for

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[23] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4, pp 72–98.

[24] (a) North, A. C. T.; Phillips, D.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351. (b) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

[25] Sheldrick, G. M. *SHELXS-86: Program for Crystal Structure Solutions*; University of Göttingen: Göttingen, Germany, 1986.

[26] Sheldrick, G. M. *SHELXL-93: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.

[27] Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam 1988.

20 h during which time the color of the solution gradually changed from red to orange. The mixture was hydrolyzed with 1 mL of water, all volatile materials were removed in vacuo, and the resulting brown residue was dissolved in dichloromethane, washed with two portions of a 5% $NaHCO_3$ solution, dried with Na_2SO_4, and evaporated to dryness. The crude product was purified by chromatography on neutral Al_2O_3 with *n*-hexane/ether (3/1) as eluent, yielding 1.53 g (76% based on starting diferrocenyl ketone) of yellow, crystalline **8**. Mp: 149−151 °C (decomp). Anal. Calcd for $C_{26}H_{28}Fe_2OSi$: C, 62.92; H, 5.69; O, 3.22. Found: C, 63.34; H, 5.74; O, 3.20. MS (EI, 70 eV): *m/z* 496 (M^+). Selected IR data (KBr): 3568 (ν_{OH}), 2182 ($\nu_{C\equiv C}$), 1250 (ν_{Si-C}) cm^{-1}. ^1H NMR (C_6D_6): δ 0.32 (9H, s, Si−C*H*$_3$), 2.92 (1H, s, −O−*H*), 3.97 (4H, m, *subst. cp*), 4.25 (10H, s, *unsubst. cp*), 4.49−4.40 (4H, m, *subst. cp*). ^{13}C NMR (C_6D_6): δ 0.2 (Si−*C*H$_3$); 66.0, 68.0, 69.5 (*ferrocenyl*); 86.9, 95.7, 109.8 (*propargyl*).

1,1-Diferrocenylprop-2-yn-1-ol (9). A 250 mL round bottom flask was charged with 1.68 g (30 mmol) of powdered KOH, 100 mL of methanol, and 1.49 g (3.0 mmol) of 1,1-diferrocenyl-3-(trimethylsilyl)prop-2-yn-1-ol (**8**). This orange solution was refluxed for 18 h to remove the trimethylsilyl protecting group,[28] during which time a yellow precipitate of potassium 1,1-diferrocenylprop-2-yn-1-oxide was formed. Methanol and all volatiles were removed in vacuo, the residue was hydrolyzed with 50 mL of H_2O, the product was extracted with three portions of Et_2O, washed with H_2O, dried with Na_2SO_4, and evaporated to dryness, yielding 1.25 g (98%) of yellow, crystalline 1,1-diferrocenylprop-2-yn-1-ol (**9**). Mp: 158 °C (decomp). Anal. Calcd for $C_{23}H_{20}Fe_2O$: C, 65.14; H, 4.75; O, 3.77. Found: C, 64.94; H, 4.70; O, 4.34. MS (EI, 70 eV): *m/z* 424 (M^+). Selected IR data (KBr): 3583 (ν_{OH}), 3271 ($\nu_{C\equiv C-H}$), 2109 ($\nu_{C\equiv C}$) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.77 (1H, s, C≡C−*H*), 3.09 (1H, s, −O−*H*), 4.12 (4H, m, *subst. cp*), 4.22 (10H, s, *unsubst. cp*), 4.27−4.32 (4H, m, *subst. cp*). ^{13}C NMR ($CDCl_3$): δ 65.5, 67.6, 67.8, 68.0, 69.0 (*ferrocenyl*); 71.5, 86.4, 94.8 (*propargyl*).

(3,3-Diferrocenylallenyl)triethylammonium Trifluoromethanesulfonate (10a) and (3,3-Diferrocenylallenyl)triethylammonium Tetraphenylborate (10b). To a solution of 424 mg (1.0 mmol) of 1,1-diferrocenylprop-2-yn-1-ol (**9**), dissolved in 30 mL of dry, deoxygenated dichloromethane in a small Schlenk tube was added 0.15 mL (1.1 mmol) of freshly distilled dry triethylamine. The brown solution was cooled in an ice/water bath, and after addition of 0.20 mL (1.1 mol) of trimethylsilyl trifluoromethanesulfonate[29] the mixture was stirred at 0 °C for 90 min and after warming to room temperature for additional 90 min at ambient temperature. The mixture was filtered through a bed of neutral Al_2O_3, prepared by pouring a slurry of Al_2O_3 in Et_2O into a small filter funnel, to absorb the polar product and to remove unreacted material and less polar side-products by washing with three portions of Et_2O. The product was eluted with ethanol, and after evaporation to dryness 354 mg (54%) of orange, crystalline (3,3-diferrocenylallenyl)triethylammonium trifluoromethanesulfonate (**10a**) was obtained. Performing the same reaction at −70 °C with inversed addition mode (first trimethylsilyl trifluoromethanesulfonate and second triethylamine) yields the product **10a** in 74% yield.

Conversion of 10a into the Corresponding Tetraphenylborate 10b. Combining a solution of 200 mg (0.304 mmol) of **10a** in 2 mL of dry methanol with a solution of 217 mg (0.634 mmol) of sodium tetraphenylborate in 0.5 mL of methanol produces a dark yellow precipitate, which was filtered off, washed with three portions of methanol and three portions of Et_2O, and dried in vacuo, yielding 174 mg (0.21 mmol, 69%) of (3,3-diferrocenylallenyl)triethylammonium tetraphenylborate (**10b**).

Data for **10a**: Mp 114 °C (decomp). Anal. Calcd for $C_{29}H_{34}BF_4Fe_2N$: C, 58.53; H, 5.76; N, 2.35. Found: C, 58.27; H, 5.62; N, 2.31. MS (FAB): *m/z* 508.13726 (M^+ of cation; exact mass calcd for $C_{29}H_{34}Fe_2N$, 508.13900); 407.01519 (M^+ of cation minus triethylamine; exact mass calcd for $C_{23}H_{19}Fe_2$, 407.01855). UV−vis data (acetonitrile; $\lambda_{max}/\log \epsilon$): 363/3.3, 455/3.0 nm/log ϵ. IR data (KBr): 3097 w, 2987 w, 2950 w, 1937 m ($\nu_{C=C=C}$), 1636 w, 1478 m, 1447 m, 1389 m, 1277 vs, 1264 vs, 1223 m, 1156 s, 1108 m, 1030 s, 830 s, 639 s, 519 m, 477 s cm^{-1}. ^1H NMR (CD_3CN): δ 1.31 (9H, t, J = 7.0 Hz, CH$_2$−C*H*$_3$), 3.38 (6H, q, J = 7.0 Hz, CH$_2$−CH$_3$), 4.22 (10H, s, *unsubst. cp*), 4.47 (4H, m, *subst. cp*), 4.69 (4H, m, *subst. cp*), 6.12 (1H, s, *allenyl-H*). ^{13}C NMR ($CDCl_3$): δ 8.5 (*C*H$_3$), 54.2 (*C*H$_2$); 68.5, 69.9, 77.6 (*ferrocenyl*); 106.6, 123.5, 195.2 (*allenyl*); (the ^{13}C signal of trifluoromethanesulfonate was not observed, probably due to unfavorable relaxation).

Data for **10b**: Mp 225 °C (decomp). Anal. Calcd for $C_{53}H_{54}BFe_2N$: C, 76.93; H, 6.58; N, 1.69. Found: C, 76.79; H, 6.47; N, 1.56. MS (FAB): *m/z* 508.13690 (M^+ of cation; exact mass calcd for $C_{29}H_{34}Fe_2N$, 508.13900); 407.01556 (M^+ of cation minus triethylamine; exact mass calcd for $C_{23}H_{19}Fe_2$, 407.01855). UV−vis data (acetonitrile; $\lambda_{max}/\log \epsilon$): 363/3.3, 455/3.0 nm/log ϵ. IR data (KBr): 3095 w, 3053 m, 3029 m, 2997 m, 2985 m, 1939 m ($\nu_{C=C=C}$), 1646 w, 1580 m, 1478 m, 1457 m, 1428 m, 1412 m, 1397 m, 1287 m, 1256 m, 1185 w, 1146 m, 1107 m, 1063 m, 1049 m, 1031 m, 1001 m, 823 s, 791 s, 742 s, 735 s, 708 s, 614 s, 512 m, 479 s cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.21 (9H, t, J = 7.0 Hz, CH$_2$−C*H*$_3$), 2.71 (6H, q, J = 7.0 Hz, CH$_2$−CH$_3$), 4.43 (10H, s, *unsubst. cp*), 4.71 (4H, m, *subst. cp*), 4.77 (2H, m, *subst. cp*), 4.80 (2H, m, *subst. cp*), 5.52 (1H, s, *allenyl-H*), 7.10−7.64 (20H, m, *phenyl*). ^{13}C NMR (CD_2Cl_2): δ 8.5 (*C*H$_3$), 54.5 (*C*H$_2$); 69.1, 69.2, 70.4, 70.6, 70.8, 77.8 (*ferrocenyl*); 105.5, 195.5 (*allenyl*, the third signal cannot be assigned unambiguously due to signal-overlap with the phenyl signals but is probably located at 122.4 according to the line shape of this signal); 122.4, 126.3, 136.4, (*phenyl*); 164.5 (q, J ($^{13}C-^{11}B$) = 195 Hz, *C1 of phenyl*).

X-ray Structure Determination of 10a. (Figures 5 and 6). Single crystals, suitable for X-ray analysis, were obtained by recrystallization from ethanol. Crystal data, data collection, and refinement parameters of **10a** are summarized in Table 1, and the general procedure was as described for **7**, except for isotropic refinement of the cyclopentadienyl carbons. The anion trifluoromethanesulfonate is disordered and was refined with two fixed positions for the sulfur atom (see Figure 6). For complete crystallographic data, tables of bond lengths, bond angles, anisotropic and isotropic thermal parameters, calculated hydrogen atomic coordinates, final atomic coordinates, see supporting information.

X-ray Structure Determination of 10b. (Figure 7.) Single crystals, suitable for X-ray analysis, were obtained by slow diffusion of methanol into a dichloromethane solution of **10b**. Crystal data, data collection, and refinement parameters of **10b** are summarized in Table 1, and the general procedure was as described for **7**. For complete crystallographic data, tables of bond lengths, bond angles, anisotropic thermal parameters, calculated hydrogen atomic coordinates, final atomic coordinates, see supporting information.

1,1,3-Triferrocenylprop-2-yn-1-ol (11). A 1.00 g (4.76 mmol) amount of ethinylferrocene (ferrocenylacetylene) was dissolved in 80 mL THF and cooled to −60 °C in a Schlenk vessel under an atmosphere of argon. Addition of 3.0 mL (4.8 mmol) of a 1.6 M *n*-butyllithium solution in *n*-hexane and allowing the stirred mixture to warm to ambient temperature resulted in formation of lithium ferrocenylacetylide. To this orange solution was added 1.33 g (3.34 mmol) of diferrocenyl ketone in one portion, and the resulting red solution was stirred at room temperature for 12 h, during which time the color of the solution gradually changed from red to brown with precipitation of yellow lithium 1,1,3-triferrocenylprop-2-yn-1-

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[29] Emde, H.; Domsch, D.; Feger, H.; Frick, U.; Götz, A.; Hergott, H. H.; Hofmann, K.; Kober, W.; Krägeloh, K.; Oesterle, T.; Steppan, W.; West, W.; Simchen, G. *Synthesis* **1982**, 1.

oxide. The mixture was hydrolyzed with 1 mL of dilute acetic acid, all volatile materials were removed in vacuo, and the resulting brown residue was dissolved in dichloromethane, washed with two portions of a 5% $NaHCO_3$ solution and with one portion of H_2O, dried with Na_2SO_4, and evaporated to dryness. The crude product was purified by chromatography on neutral Al_2O_3 with *n*-hexane/ether (1/1) as eluent, yielding 1.45 g (71% based on starting diferrocenyl ketone) of yellow, crystalline **11**. Mp: 155–156 °C (decomp). Anal. Calcd for $C_{33}H_{28}Fe_3O$: C, 65.18; H, 4.64; O, 2.63. Found: C, 64.80; H, 4.45; O, 2.84. MS (EI, 70 eV): *m*/*z* 608 (M^+). Selected IR data (KBr): 3551 (ν_{OH}), 2228 ($\nu_{C\equiv C}$) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.04 (1H, s, –O–*H*), 4.13 (4H, m, *subst. cp*), 4.22 (2H, m, *subst. cp*), 4.27 (10H, s, *unsubst. cp*), 4.32 (5H, s, *unsubst. cp*), 4.37 (4H, m, *subst. cp*), 4.54 (2H, m, *subst. cp*). ^{13}C NMR ($CDCl_3$): δ 67.7, 67.8, 68.6, 68.9, 69.7, 71.3 (*ferrocenyl*); 81.7, 88.5, 95.4 (*propargyl*).

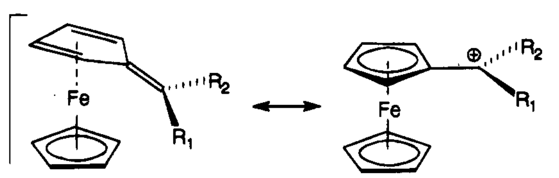
X-ray Structure Determination of 11. (Figure 8.) Single crystals, suitable for X-ray analysis, were obtained by recrystallization from dichloromethane/*n*-hexane. Crystal data, data collection, and refinement parameters of **11** are summarized in Table 1, and the general procedure was as described for **7**. For complete crystallographic data, tables of bond lengths, bond angles, anisotropic thermal parameters, calculated hydrogen atomic coordinates, final atomic coordinates, see supporting information.

Triferrocenylallenylium tetrafluoroborate (12). A round bottom flask was charged with 350 mg (0.576 mmol) of 1,1,3-triferrocenylprop-2-yn-1-ol (**11**) dissolved in 700 of mL dry Et_2O. Addition of 0.090 mL (0.66 mmol) of a 54% solution of fluoroboric acid in Et_2O precipitated the dark green product, which was filtered off, washed with two portions of Et_2O, and dried in vacuo, yielding 307 mg (0.453 mmol, 79%) of triferrocenylallenylium tetrafluoroborate (**12**). Similarly, using trifluoromethanesulfonic acid or a mixture of a solution of sodium tetraphenylborate, dissolved in glacial acid and trifluoromethanesulfonic acid, yielded triferrocenylallenylium trifluoromethanesulfonate and triferrocenylallenylium tetraphenylborate, respectively. Of these three products, only the tetrafluoroborate (**12**) is air-stable in the solid state and sufficiently stable in solution for a full characterization. Mp not observed, >300 °C. Anal. Calcd for $C_{33}H_{27}BF_4Fe_3$: C, 58.47; H, 4.01. Found: C, 57.00; H, 4.03. MS (FAB): *m*/*z* 591.01733 (M^+ of cation; exact mass calcd for $C_{33}H_{27}Fe_3$, 591.01609). UV–vis data (methanol; λ_{max}/log ϵ): 376/3.9, 445/4.1, 760/3.9 nm. IR data (KBr): 3104 w, 2151 s ($\nu_{C=C=C}$), 1630 w, 1468 s, 1438 m, 1412 m, 1385 m, 1250 w, 1084 vs, 1036 m, 834 m, 706 m, 477 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.35 (5H, s, *unsubst. cp*), 4.46 (10H, s, *unsubst. cp*), 4.76 (2H, m, *subst. cp*), 4.84 (2H, m, *subst. cp*), 5.28 (4H, m, *subst. cp*), 5.77 (4H, m, *subst. cp*). ^{13}C NMR ($CDCl_3$): δ 62.9, 72.4, 74.1, 74.3, 75.2, 77.5, 84.5, 90.2, (*ferrocenyl*); 96.0, 118.2, 155.6 (*allenyl*).

Results and Discussion

Stabilization of Carbenium Ions by Ferrocenyl Substituents. The phenomenon of the extraordinary stabilization of the carbenium ion center in α-metallocenyl cations has been adressed with a wide range of physical methods, mainly in solution by NMR spectroscopy[1,9,30] and for a limited number of cases in the crystalline state by X-ray spectroscopy.[8e,12a,b,30b,f,31] Together with the results obtained from ^{57}Fe Mössbauer studies[9,32] and ^{57}Fe NMR spectroscopy[33] the minimum-energy structure of Hückel calculations[34] with a bent exocyclic fulvenoid structure has been confirmed, although the amount of bending toward the metal (the dihedral angle of the exocyclic fulvene double bond) is dependent on sterical and electronic factors of the other substituents (Scheme 1). Therefore, it is generally agreed that these cations have important resonance contributions from the η^6-fulvene-η^5-cyclopentadienyl iron(II) form, similar to the well-known benzylic resonance in organic arene chemistry but with additional π-bonding of the metal with the exocyclic (formal) double bond. The direct participation of the iron atom in charge delocalization causes the two cyclopentadienyl rings to deviate from being parallel (tilt angle 4–5°) and forces the exocyclic substituent, bearing the positive charge, out of the plane of the cyclopentadienyl ring in a bent position in the direction of the iron atom (dihedral angle 10–20°). The partial double-bond character of the bond between the exocyclic cationic center and the ring carbon leads to hindered rotation around this bond with the consequence of optical activity for unsymmetrically substituted cations.[11a–c]

Scheme 1. Mesomeric Forms of Ferrocenylcarbenium Ions



Synthesis. In general, the synthesis of α-metallocenyl carbocations starts from the corresponding carbinols (other but less useful methods have been reported).[1,9] Treatment of the α-metallocenyl alcohol with a strong acid affords the oxonium ion, which forms the carbenium ion by exoelimination of H_2O under anchimeric assistence by the metal. All the allylium and allenylium salts in this work were prepared according to this general synthetic route, starting from the respective alcohols as precursors, which were prepared as outlined in Schemes 2 and 3.

The synthesis of allylium salts (Scheme 2) is readily accomplished by nucleophilic addition of either hydride (in the form of triethylborohydride) or monolithioferrocene with ferrocenylated enone systems, best available by the chalcone reaction[18b] or, for polynuclear derivatives, by the Benary reaction.[18d] Reaction with *trans*-1,3-diferrocenylpropenone or cyclopentadienyl(3-ferrocenyl-1-oxy-pentalenyl)iron, respectively, yields the corresponding allylic alcohols (some of these are rather unstable toward oxidation by air; see Experimental Section); subsequent protonation affords the target allylium salts **1**, **3**, **5**, and **7**.

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(30) (a) Braun, S.; Abram, T. S.; Watts, W. E. *J. Organomet. Chem.* **1975**, *97*, 429. (b) Lupan, S.; Kapon, M.; Cais, M.; Herbstein, F. H. *Angew. Chem.* **1972**, *84*, 1104; *Angew. Chem., Int. Ed. Engl.* **1972**, 1025. (c) Abram, T. S.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1522. (d) Abram, T. S.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1532. (e) Surya Prakash, G. K.; Buchholz, H.; Prakash Reddy, V.; de Meijere, A.; Olah, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 1097. (f) Turpeinen, U.; Kreindlin, A. Z.; Petrovskii, P. V.; Rubinskaya, M. I. *J. Organomet. Chem.* **1992**, *441*, 109.

(31) (a) Sime, R. L.; Sime, R. J. *J. Am. Chem. Soc.* **1974**, *96*, 892. (b) Behrens, U. *J. Organomet. Chem.* **1979**, *182*, 89.

(32) (a) Neshvad, G.; Roberts, R. M. G.; Silver, J. *J. Organomet. Chem.* **1982**, *236*, 237. (b) Watanabe, M.; Iwamoto, T.; Nakashima, S.; Sakai, H.; Motoyama, I.; Sano, H. *J. Organomet. Chem.* **1993**, *448*, 167.

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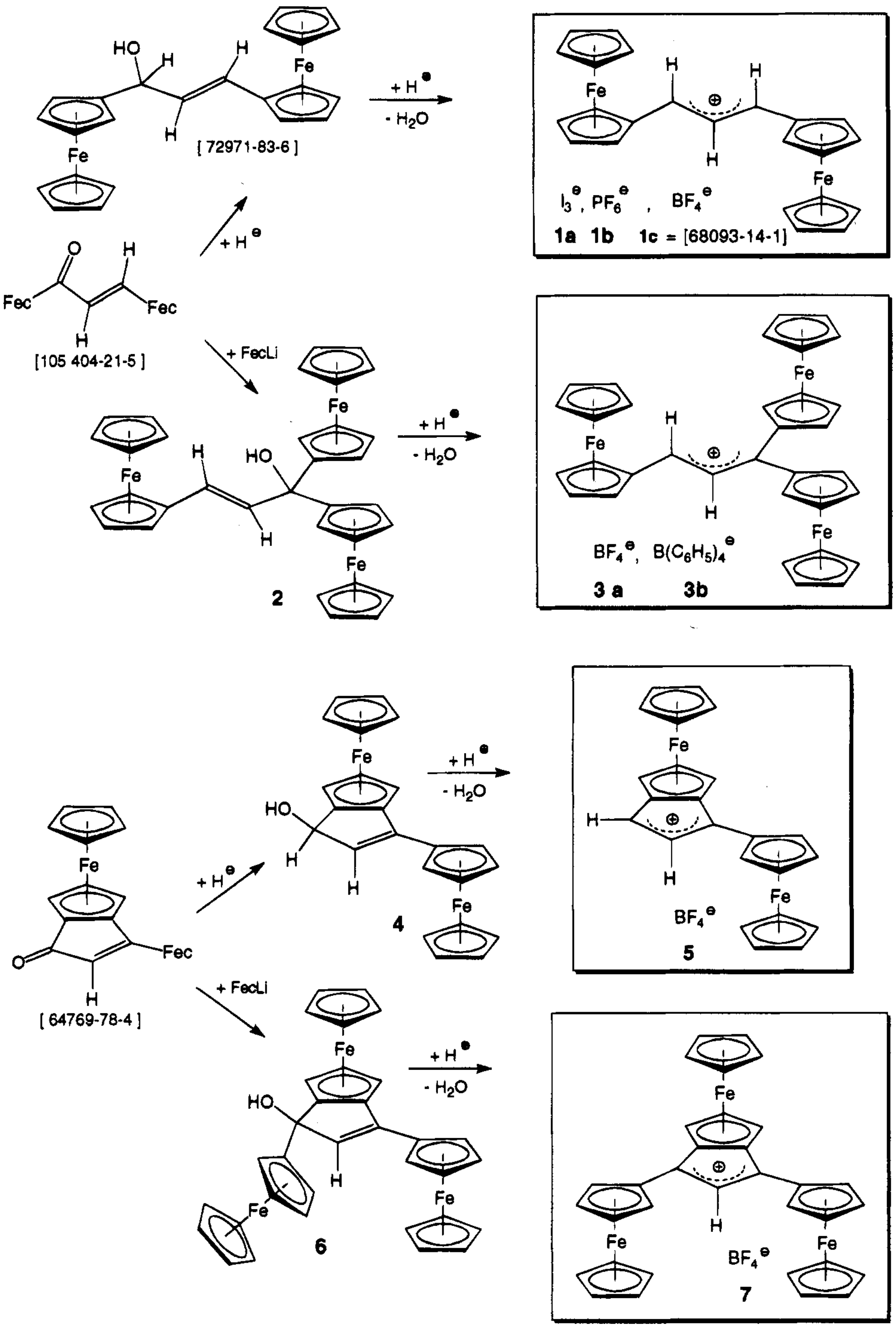
Scheme 2. Preparation of Compounds 1−7



For allenylium salts, the necessary progenitors are the corresponding propargyl alcohols, which are generally prepared by nucleophilic addition of metalated acetylenes to the carbonyl functionality of an aldehyde or a ketone.[27] First we attempted the preparation of a 1,1-diferrocenylallenylium salt, although in light of the limited stability of **5** (see below) it is unlikely that such an allenylium ion, with only hydrogen as a substituent on one end of the allene moiety, is stable and can be isolated in pure form. To synthesize the precursor alcohol **9**, it proved necessary to react diferrocenyl ketone with a trimethylsilyl-protected acetylene, because simply using lithium acetylide or the corresponding TMEDA complex met with failure, obviously because (trimethylsilyl)acetylide is the better nucleophile due to the donor effect of the trimethylsilyl group. Protonation of **9** with fluoroboric acid produces a blue precipitate, probably ethinyldiferrocenylmethylium tetrafluoroborate, which decomposed rapidly, therefore no further characterization was possible. This is in accord with the reported solvolytic collapse of analogous ferrocenyl propargylic compounds.[30d,35] Unexpectedly, this propargyl cation is also formed by combining (**9**) with trimethylsilyl trifluoromethanesulfonate with subsequent spontaneous elimination of (trimethylsilyl)oxide, a reaction we attempted to protect the hydroxy group of **9**. The intermediate ethinyldiferrocenylmethylium reacts with triethylamine to give **10a** and, after anion-

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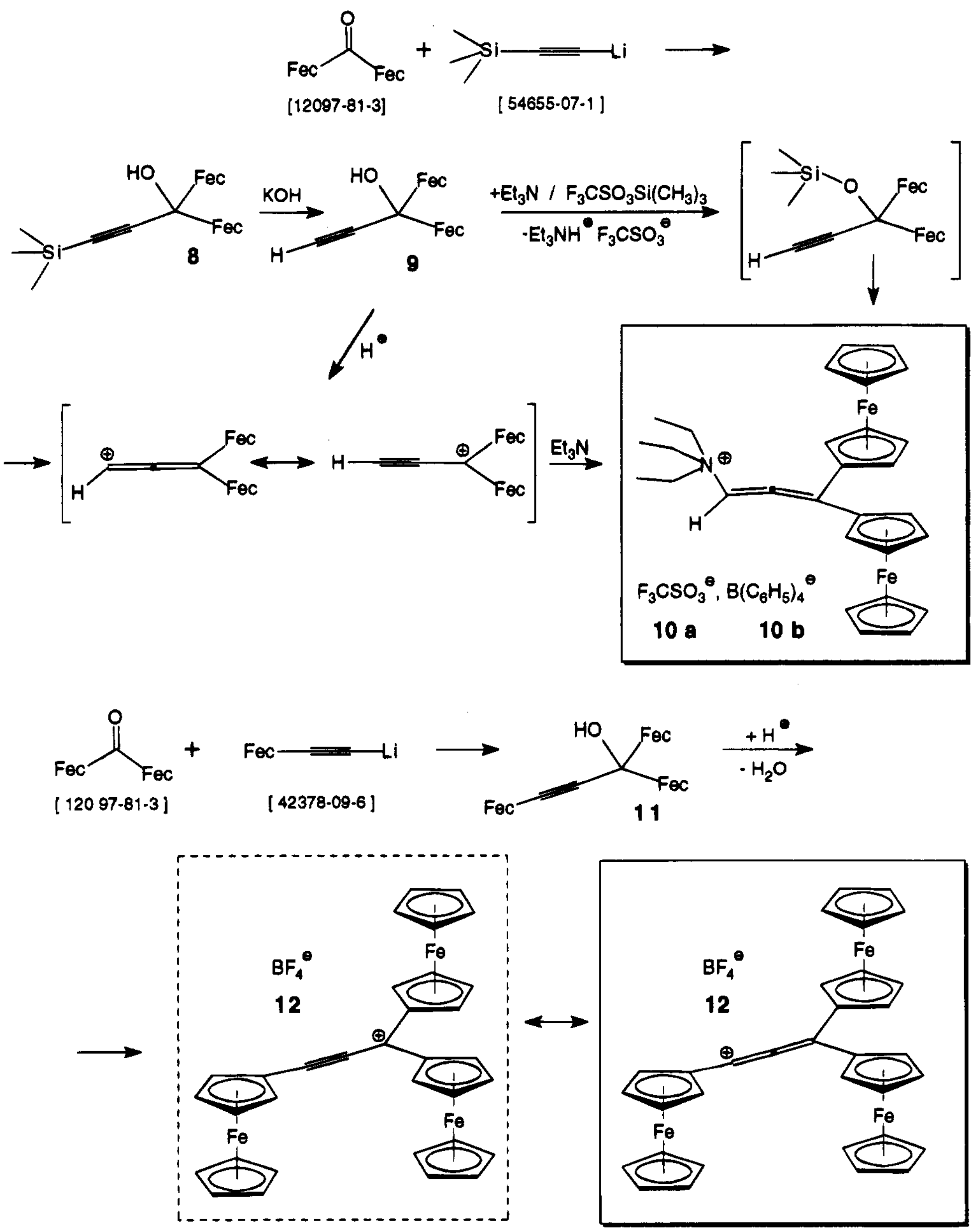
(35) Abram, T. S.; Watts, W. E. *J. Organomet. Chem.* **1975**, *87*, C39.

Scheme 3. Preparation of Compounds 8−12



exchange with sodium tetraphenylborate, **10b**, formally Lewis base stabilized allenylium salts with unusual bent allene moietes in the solid state.

Introduction of three ferrocenyl substituents by the reaction sequence shown in Scheme 3 affords the maximally substituted compounds **11** and **12**; in this case, the combined stabilization by three ferrocenyl units allows the isolation of **12** as a true allenylium salt with only a minor resonance contribution from the ethinylmethylium form.

Stability. As expected, increasing the number of ferrocenyl substituents increases the stability of the allylium salts as is evidenced by comparing the physical properties of **1a**−**c** versus **3a,b** and **5** versus **7**. A prerequisite to stable allylium systems is further the 1,3-disubstitution of the allylium moiety with two ferrocenes, thereby affording charge delocalization by the metallocenes in α-position to the formally two possible locations of the positive charge. Cation **5**, which does not fulfill this criterion, although it incorporates an annelated ferrocene, is therefore the least stable allylium salt and decomposes gradually in solution within minutes, preventing complete spectral characterization. On the other hand, the comparison of **3a,b** with the more stable **7** (both of these cations have three ferrocenes) indicates that the annelated central ferrocene participates in cation stabilization of the 1- and 3-positions, whereas in **3a,b** one of these two positions can interact with only one ferrocene. Interestingly, the cyclic allylium compounds **5** and **7** can formally be envisaged as the first stable cyclopentadienyl cations, but the known instability and antiaromaticiy of the parent cyclopentadienyl cation[36] makes this formulation extremely unlikely.

Allenylium salts with fewer than three ferrocenes are unstable or have only fleeting existence as the mesomeric propargylic cations, which either decompose by solvolytic collapse[30d,35] or can be trapped with triethylamine under formation of ammonium allenes **10a,b**.

The effect of the counteranions on the stability of the

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[36] (a) Breslow, R.; Hoffmann, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 2110. (b) Breslow, R.; Mazur, S. *J. Am. Chem. Soc.* **1973**, *95*, 584. (c) Lossing, F. P.; Traeger, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 1579. (d) Breslow, R.; Canary, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 3950.

allylium and allenylium salts is less clear, the existence and relative stability of these salts depends obviously on specific cation–anion interactions which are, in relation to the counter-anion, different for each type of cation. For example, hexafluorophosphate **1b** has a shelf-life of at least 1 year at ambient temperature and does not decompose in solution (allowing, for example, UV–vis measurements), whereas the tetrafluoroborate **1c** survives only for a few hours in solution. In contrast, for allenylium salt **12** only the tetrafluoroborate is sufficiently stable (see Experimental Section).

The nature of the decomposition pathways of α-metallocenyl carbenium ions is still under investigation.[12a] Spin-trapping experiments[37] and the isolation of radical coupling decomposition products has been taken as evidence for the existence of a singlet–triplet equilibrium by an intramolecular redox tautomerism. Direct observation of the paramagnetic triplet species by NMR[38] or by Mössbauer[12a] spectroscopy showed for ferrocenyl carbenium ions a population of the triplet state of less than 1%, which allows characterization of these essentially diamagnetic ions by standard NMR spectroscopy.

The relative reactivity of ferrocenyl stabilized carbeniumions, including **(1c)**, with H_2O and other nucleophiles ("solvolytic collapse" and/or nucleophilic addition) has been studied in detail,[11c,18b,35,39,40] but, contrary to the findings of Watts and co-workers,[39] we observe a much slower decomposition in this regard in solution. One reason for this discrepancy could be the reported light sensitivity[41] of metallocenyl cations; the photometric concentration determinations in these kinetic experiments could be responsible for an accelerated decomposition by photochemical activation. The primary degradation pathways for the less congested allylium salts are dimerizations and electrophilic cyclizations;[9,22a,40,42] these processes are extremely accelerated by irradiation. In this respect, allylium salt **(7)** is of extraordinary stability; it survives for days in aqueous solution at pH 7 under irradiation by sunlight.

Spectroscopy and Structure of Allylium Salts. The high stability of these allylium and allenylium salts permits accurate mass detection of the cations by high-resolution positive FAB-MS (see Experimental Section) for all synthesized ionic compounds, including **1a** and **5**, which decompose in solution, thereby preventing further characterization by NMR or UV–vis spectroscopy. The increase in stability of allylium compounds **1**–**7** with progressive incorporation of ferrocenyl substituents is paralleled by a bathochromic shift of the λ_{max} absorption (Figure 1) in the UV–vis spectra, reflecting the increasing conjugation with increasing number of ferrocenyl substituents. Table 2 summarizes pertinent ^1H and ^{13}C NMR data for the allylium salts. The chemical shifts of the central allylic hydrogen (H_β) and carbon (C_β) are very similar and show almost no influence by the substitution pattern. The relative distribution of positive charge to the 1- and 3-positions in **3a,b** as an unsymmetrically substituted allylium system is reflected by two different ^{13}C chemical shifts of the C_α and C_γ carbons; the more deshielded signal (δ 180 ppm) is assigned to the carbon atom adjacent to two ferrocenyl groups, which direct the positive charge to their α-position. The least stable allylium salts **1b,c** in this series (with the exception of **5**, see above), with only one ferrocene on each terminal carbon, show chemical shifts for these carbons (δ 157.7 ppm) differing by only 5 ppm in comparison to the most stable ferrocene-annelated allylium salt **7** (δ 162.6 ppm). The observed higher stability of **7** versus **1a**–**c** might therefore be attributed to mainly sterical protection of the allylium moiety by the annelated ferrocene, ruling out any significant electronic contribution in terms of an antiaromatic cyclopentadienyl cationic sytem.[36]

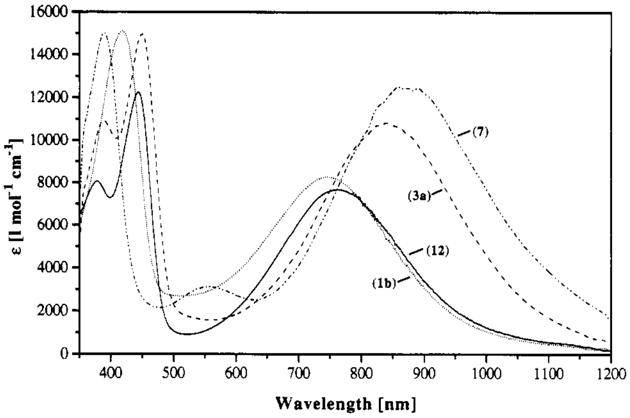

Figure 1. UV–vis–near-infrared spectra of allylium salts **1b**, **3a**, and **7** and of allenylium salt **12**.

Table 2. Allylium[a] ^1H and ^{13}C NMR Shifts (ppm)

	H_α	H_β	H_γ	C_α	C_β	C_γ
1b	8.30	6.48	8.30	157.7	126.0	157.7
1c	8.35	6.50	8.35	157.7	125.7	157.7
3a	8.66	6.67		154.1	128.5	180.5
3b	8.64	6.65		154.1	127.9	180.6
7		6.19		162.6	127.7	162.6

[a] Due to decomposition in solution no values for allylium salts **1a** and **5** were obtained. The labels α, β, and γ refer to the 1-, 2-, and 3-positions of the allylium moiety, respectively.

Single-crystal X-ray analysis was performed in order to obtain further information on the structure and factors governing the stability of **7**. The structure of allylium salt **7** consists of two crystallographically independent molecules, **A** and **B**, with tetrafluoroborate as counteranions (Figure 2). These two molecules differ slightly in their conformation; selected bond lengths and angles are given in Table 3. The occurrence of these two conformationally similar but distinctly different molecules indicates that the structure is governed not only by intramolecular (electronic) factors, which are of prime interest for a deeper understanding of the mechanism of carbenium-ion stabilization by ferrocenes, but also and of equal rank by crystal forces. Both molecules have a planar pentalenyl subunit (Figure 3); the two

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(40) (a) Perevalova, E. G.; Pushin, A. N.; Klimova, E. I.; Slovokhotov, Yu. L.; Struchkov, Yu. T. *Metalloorg. Khim.* **1989**, *2*, 1405. (b) Nesmeyanov, A. N.; Postnov, V. N.; Sazonova, V. A.; Galakhova, T. N.; Kuznetsov, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, *9*, 2172. (c) Boev, V. I.; Dombrovskii, A. V. *Zh. Obshch. Khim.* **1987**, *57*, 938.

(41) (a) Kerber, R. C.; Ehntholdt, D. J. *Synthesis* **1970**, 449 and references cited therein. (b) Miyazaki, H. *Chem. Abstr.* **1987**, *106*, JP Patent 61151544 A2, 41609f; July 10, 1986.

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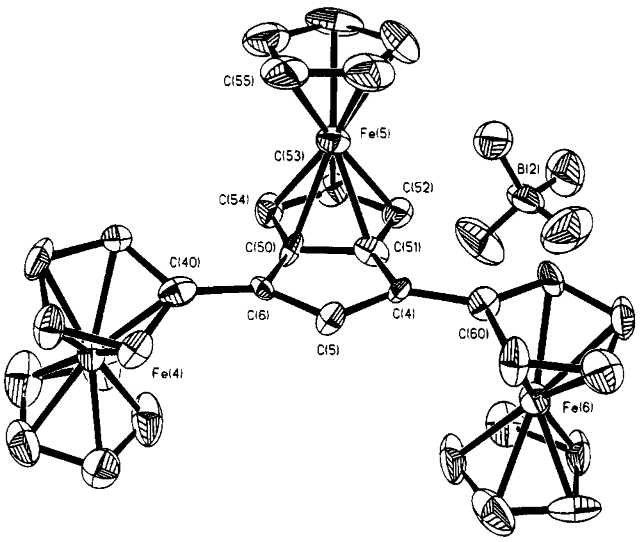

Figure 2. Molecular structure of **7**, molecule **B**, showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (pm) and Angles (deg) for 7

	molecule **A**	molecule **B**
Bond Lengths		
C(1)–C(2)/C(4)–C(5)	138.9(13)	140.7(13)
C(2)–C(3)/C(5)–C(6)	142.8(13)	140.4(13)
C(1)–C(10)/C(4)–C(60)	141.2(13)	145.7(14)
C(3)–C(30)/C(6)–C(40)	145.6(14)	145.6(14)
C(1)–C(20)/C(4)–C(51)	146.4(13)	144.9(14)
C(3)–C(21)/C(6)–C(50)	145.8(13)	145.3(14)
C(20)–C(21)/C(50)–C(51)	144.1(13)	138.9(14)
Fe(1)–C(1)/Fe(6)–C(4)	303.8(10)	295.3(10)
Fe(3)–C(3)/Fe(4)–C(6)	283.1(11)	311.4(10)
Bond Angles		
C(1)–C(2)–C(3)/C(4)–C(5)–C(6)	110.1(0.9)	108.5(0.9)
C(10)–C(1)–C(2)/C(60)–C(4)–C(5)	127.3(0.10)	125.0(0.11)
C(30)–C(3)–C(2)/C(40)–C(6)–C(5)	124.9(0.10)	126.1(0.10)
twist angle C(1)–C(10)/C(4)–C(60)[a]	13.43(0.53)	9.68(0.58)
twist angle C(3)–C(30)/C(6)–C(40)[a]	18.19(0.51)	21.89(0.51)
dihedral angle C(1)–C(10)/ C(4)–C(60)[b]	4.8(0.8)	9.8(0.8)
dihedral angle C(3)–C(30)/ C(6)–C(40)[b]	15.7(0.9)	0.08(0.7)
tilt angle ferrocene[Fe(1)]/ ferrocene[Fe(6)][c]	3.9	2.85
tilt angle ferrocene[Fe(3)]/ ferrocene[Fe(4)][c]	4.88	3.45

[a] Twist angle, the angle between cyclopentadienyl and pentalenyl planes. [b] Dihedral angle, the bending of the exocyclic ferrocenyl toward allylium. [c] Tilt angle, the deviation of cyclopentadienyl planes from parallelism [angle (centroid of $\mathrm{Cp}_{subst.}$) – (Fe)–(centroid of $\mathrm{Cp}_{unsubst.}$)].

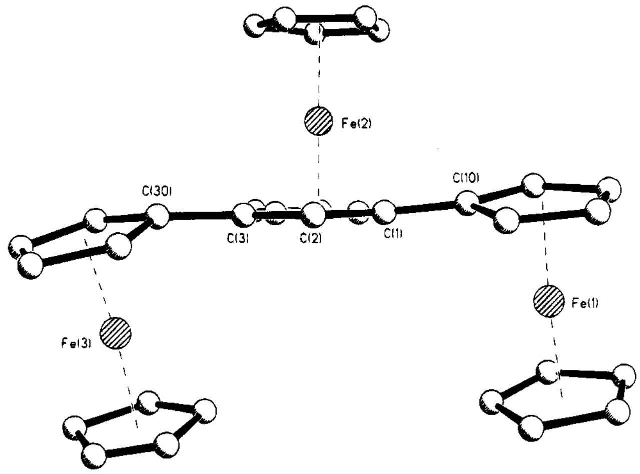

Figure 3. Molecular structure of **7**, molecule **A**, projecting into the pentalene plane.

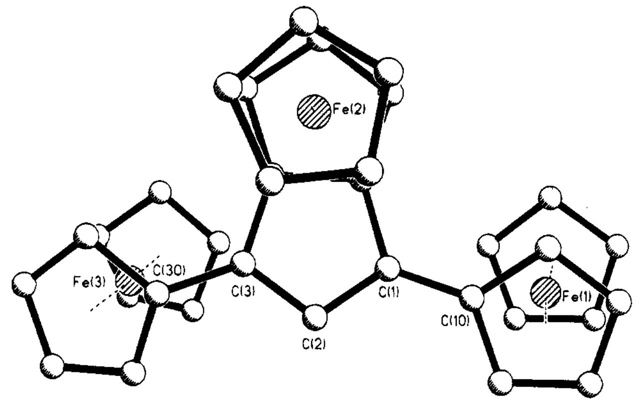

Figure 4. Molecular structure of **7**, molecule **A**, projecting perpendicular to the pentalene plane.

ferrocenyl substituents in 1- and 3-positions of the allylium moiety are twisted with values ranging from 9.7 to 21.9° (Table 3). The cyclopentadienyl rings of these ferrocenes are planar (max deviation 2.27 ± 1.23°), but not parallel, the corresponding ferrocene tilt angles (2.8–4.9°) are similar to reported values for other α-carbenium ferrocenes.[8c,30b,31] The bending of the ferrocenyl substituents toward the cationic allyl system, indicating a (weak) interaction of the iron atom with the α-C^+ is seen in the distances (Fe)–(α-C^+) and in the dihedral angles of the (α-C^+)–(ferrocene) bonds (Table 3; Figures 3 and 4). For symmetrically substituted allylic cations, the two terminal allylic positions are equal in terms of charge density and carry statistically only 50% of one positive charge, therefore one might expect an equal, but in comparison to simple carbenium ions (for example: diphenylferrocenylmethylium tetrafluoroborate[31b]), reduced bending of the two ferrocenyl substituents. In contrast to this expectation the two ferrocenyl substituents in both molecules **A** and **B** show unequal bending with values ranging from 0.08 to 15.7° and with corresponding (Fe)–(α-C^+) distances from 283.1 to 311.4 pm. Similar unequal bending has been observed in the crystal structure of diferrocenylmethylium tetrafluoroborate.[30b] The annelated ferrocene of the pentalene subunit is for both molecules a "normal" ferrocene, no significant deviations are observed, which is in accord with only steric, but not electronic, stabilization of the allylium moiety by this ferrocene. In summary, the expected distortions from the idealized ferrocene conformation are in both molecules observed for the ferrocenyl substituents in 1- and 3-positions of the allylic cation, albeit in varying degree, which is an indication of substantial contributions to the conformation by solid state packing effects.

Spectroscopy and Structure of Allenylium Salts. As described above, 1,1-diferrocenylallen-3-ylium tetrafluoroborate or the mesomeric ethinyldiferrocenylmethylium tetrafluoroborate (1,1-diferrocenylpropargylium tetrafluoroborate) is unstable or cannot be isolated in pure form, respectively (Scheme 3). However, the

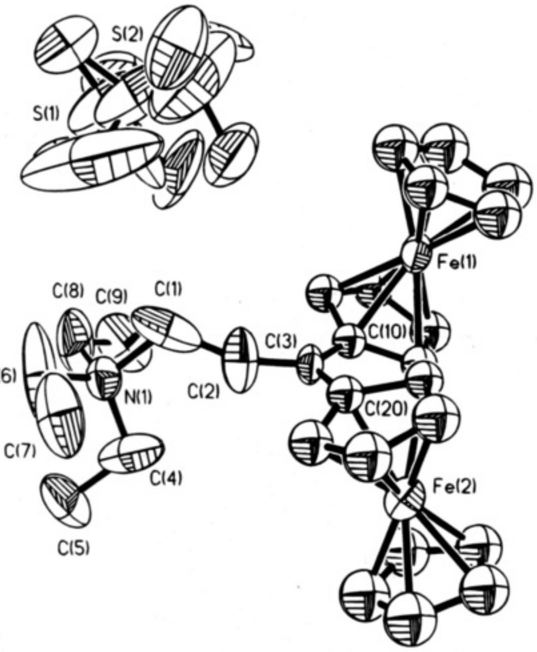

Figure 5. Molecular structure of **10a**, showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. The atom-numbering of the disordered trifluoromethanesulfonate is shown in Figure 6. Cyclopentadienyl carbons of ferrocene 1 are C(10)−C(19) and for ferrocene 2 C(20)−C(29), respectively.

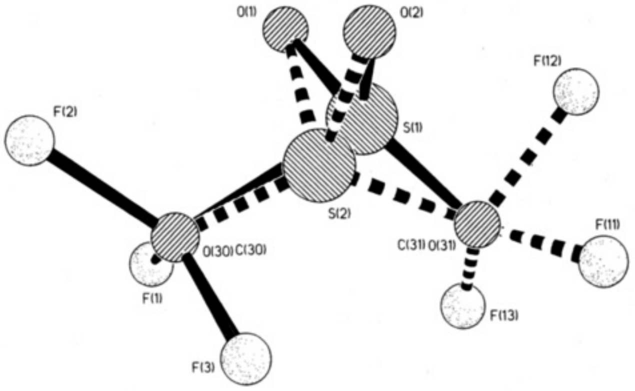

Figure 6. Atom-labeling for the disordered trifluoromethanesulfonate of **10a**.

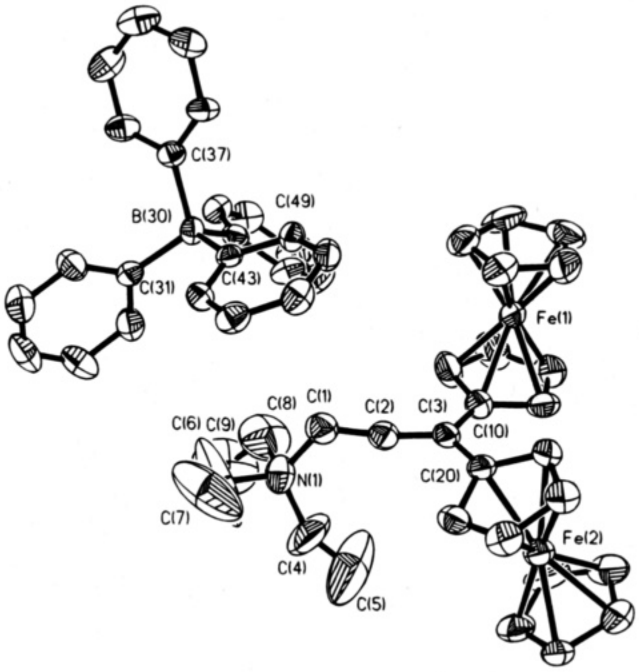

Figure 7. Molecular structure of **10b**, showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity. Cyclopentadienyl carbons of ferrocene 1 are C(10)−C(19), and for ferrocene 2 C(20)−C(29), respectively. Phenyl carbons of tetraphenylborate are C(31)−C(36), C(37)−C(42), C(43)−C(48), and C(49)−C(54), respectively.

Lewis acid−base complexes **10a,b** with triethylamine as the Lewis base can be envisaged as donor-stabilized allenylium salts. The high-resolution positive FAB mass spectra show the molecular ion of the triethylammonium allene cation in low intensity (approximately 5%) and, in accord with the formulation of **10a,b** as adducts of triethylamine with 1,1-diferrocenylallen-3-ylium, the corresponding peak of 1,1-diferrocenylallen-3-ylium as the most intense signals. The UV−vis spectra of the orange-colored **10a,b**, on the other hand, are typical for regular allenic chromophores (see Experimental Section), and are therefore not included in Figure 1. Also, the value and intensity of the $\nu_{C=C=C}$ vibrations (1937 cm^{-1} for **10a** and 1939 cm^{-1} for **10b** with medium intensity; expected range for $\nu_{C=C=C}$: 1950−1930 cm^{-1}) are indicative of a normal allene functionality. The ^{13}C NMR data (δ_{allene} 106.6, 123.5, 195.2 ppm for **10a** and 105.5, 122.4, 195.5 ppm for **10b**) are also in agreement with the formulation of these compounds as unexceptional allenes, whereas the ^{1}H NMR chemical shifts of the allenic hydrogen ($\delta_{C=C=C-H}$ 6.12 ppm for **10a** and 5.52 ppm for **10b**) are quite different for these two analogous salts with supposedly identical cations.

To clarify this discrepancy, single-crystal analyses were performed for **10a** and **10b** (Table 1). Figure 5 shows the molecular structure of **10a**, and Figure 6 shows the positional disorder of the trifluoromethanesulfonate. Although the residuals for this structure analysis are relatively high due to a non-optimal data to parameter ratio, the structure of the cationic part, which is of main interest in this context, is sufficiently defined because the inaccurancy is chiefly restricted to the trifluoromethanesulfonate, as can be seen by the large thermal ellipsoids of the anion in Figure 5. The bond lengths of the allene moiety [C(1)−C(2) = 143(3) pm, C(2)−C(3) = 127(2) pm] show a deceptively large value for the C(1)−C(2) bond (expected value for C=C=C: 131 pm), which might indicate a (not resolved) disorder of the C(1) atom, in agreement with the relatively high value of 150(2) pm (expected value for C(sp^2−Nsp^3): 142 pm) for the C(1)−N(1) bond. Despite these limitations, the most interesting structural feature is the unexpected angle C(1)−C(2)−C(3) of 161(2)° for the allenic unit. Even taking into consideration the aforementioned likely positional disorder of the C(1) atom, this surprising result is significant in terms of a qualitatively real nonlinearity. An analogous structure is shown by compound **10b** (Figure 7). In this case, no disordering was observed and the low residuals and the good data set (Table 1) allow a much more accurate description of the structure of the cationic part. In comparison to **10a**, the ethyl groups of the ammonium subunit are arranged in a less folded fashion, which is simply a consequence of the different space-filling requirements due to the larger anion with corresponding increased anion−cation distances in **10b**. The relevant bond lengths [C(1)−C(2) = 130.4(8) pm, C(2)−C(3) = 131.9(8) pm] and C(1)−N(1) = 149.6(7) are in good agreement with the expected values for allenic bonds, and the C(1)−N(1) bond length is very similar to the corresponding value in the structure of trifluoromethanesulfonate **10a**. The C(1)−C(2)−C(3) angle of the allenic linkage is 173.1(6)°, which confirms the nonlinear allenic unit, albeit to a lesser degree in comparison to **10a** (the possible reason for the value being too high in the structure of **10a** has been discussed above). In summary, these two structures show an unexpected bent allene moiety in the solid state for both ammonium allene compounds which is probably not attributable to packing effects. In solution, the difference of the ^{1}H NMR chemical shift of the allenic hydrogen with a deshielded signal in **10a** in comparison to **10b** arises most likely by an increase in the Coulomb attraction between anion and cation in **10a** due to the smaller anion−cation distance. The only electronic explanation for the bending of the allene unit we can offer at this point is a nonclassical distortion of the cumulenic system by (formal) interaction of a singlet 1,1-diferrocenylcarbene (the singlet carbene should be stabilized by the combined donor ability of the two ferrocenes) with a triethylammonium vinylidene; experimental and theoretical results for related systems have been published.[43]

So far all published attempts to isolate an allenylium compound met with failure,[44] but strong evidence for relatively important contributions of the allenylic resonance form to the total ion structure (compare the two mesomeric forms of **12** in Scheme 3) has been obtained from ^{13}C NMR measurements of triply substituted propargylic alcohols in acidic solution at low temperatures[44a−f] and from theoretical calculations.[44h] The reported instability of 1,3-diferrocenylallenylium trifluoroacetate,[30d] a cation with two ferrocenyl substituents at the terminal allenic carbons, shows for allenylium salts the need for additional stabilizing metallocenyl substituents (contrary to the allylic systems, where this 2-fold substitution effects sufficient stabilization). Consequently, the triply substituted propargylic alcohol (**11**) was prepared. In addition to the usual characterization by spectroscopic methods a single-crystal structure analysis was performed (Table 1; Figure 8). The bond lengths and angles of the propargylic unit [C(31)−C(32) = 146.9(13) pm, C(32)−C(33) = 118.0(13) pm; C(31)−C(32)−C(33) = 174.8(10)°, C(32)−C(33)−C(21) = 178.2(10)°] show the expected linear conformation with small deviations from linearity due to packing effects. From this progenitor, the green stable salt **12** precipitates upon treatment with HBF_4. The high-resolution positive FAB mass spectrum gives the molecular ion of the cation (*m*/*z* 591.01733), in excellent agreement with the calculated exact mass (calcd for $C_{33}H_{27}Fe_3$: 591.01609). The UV−vis spectrum of **12** (Figure 1) is very similar to the spectrum of **1b**, indicating charge delocalization not only by the ferrocene chromophors but also, and more importantly by conjugation of the ethinyl group with the electron deficient carbocation. IR spectroscopy shows a very intense cumulenic absorption (Figure 9) at 2151 cm^{-1}, and the high intensity points to an acceptor-substituted unsymmetric allene, which strongly supports the allenium form as the predominant resonance structure (Scheme 3). This is further corroborated by the marked ^{13}C NMR deshieldings of the terminal carbons of the allenium ↔ propargylium moiety in **12** [$\delta(C_\alpha)$ 155.6 ppm, $\delta(C_\beta)$ 96,0 ppm, $\delta(C_\gamma)$ 118.2 ppm] in comparison to the corresponding signals of the precursor alcohol **11** [$\delta(C_\alpha)$ 81.7 ppm, $\delta(C_\beta)$ 95.4 ppm, $\delta(C_\gamma)$ 88.5 ppm]; similar arguments have been reported for the analogous triphenylallenium ion, obtained from the corresponding alcohol upon dissolution in superacidic medium at −60 °C.[44c] Although so far no suitable single crystals for X-ray structure analysis could be obtained, from the combined spectroscopic results we conclude that **12** comes as close as possible to a true allenylium salt with unprecedented stability.

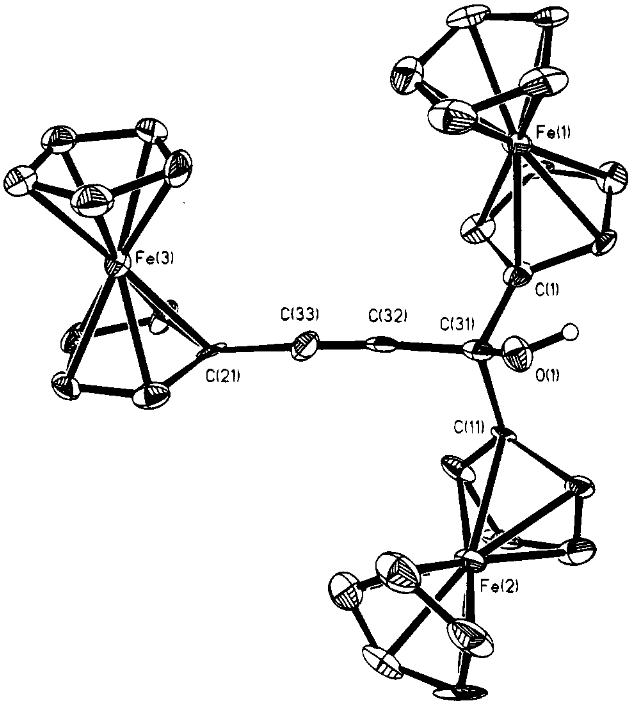

Figure 8. Molecular structure of **11**, showing the atom-numbering scheme. Hydrogen atoms are omitted for clarity, except for the hydroxyl hydrogen. Cyclopentadienyl carbons of ferrocene 1 are C(1)−C(10), for ferrocene 2 C(11)−C(20), and for ferrocene 3 C(21)−C(30), respectively.

Summary. The stability of allylium and allenylium cations can be increased by multiple incorporation of ferrocenyl substituents, allowing for the first time the isolation in pure form solid and air-stable representatives of these elusive species. Their structures in solution and in the solid state, investigated by NMR, IR, UV−vis, and single-crystal X-ray analysis, indicate ferrocene to be one of the most efficient stabilizing donors for electron deficient conjugated carbocations.

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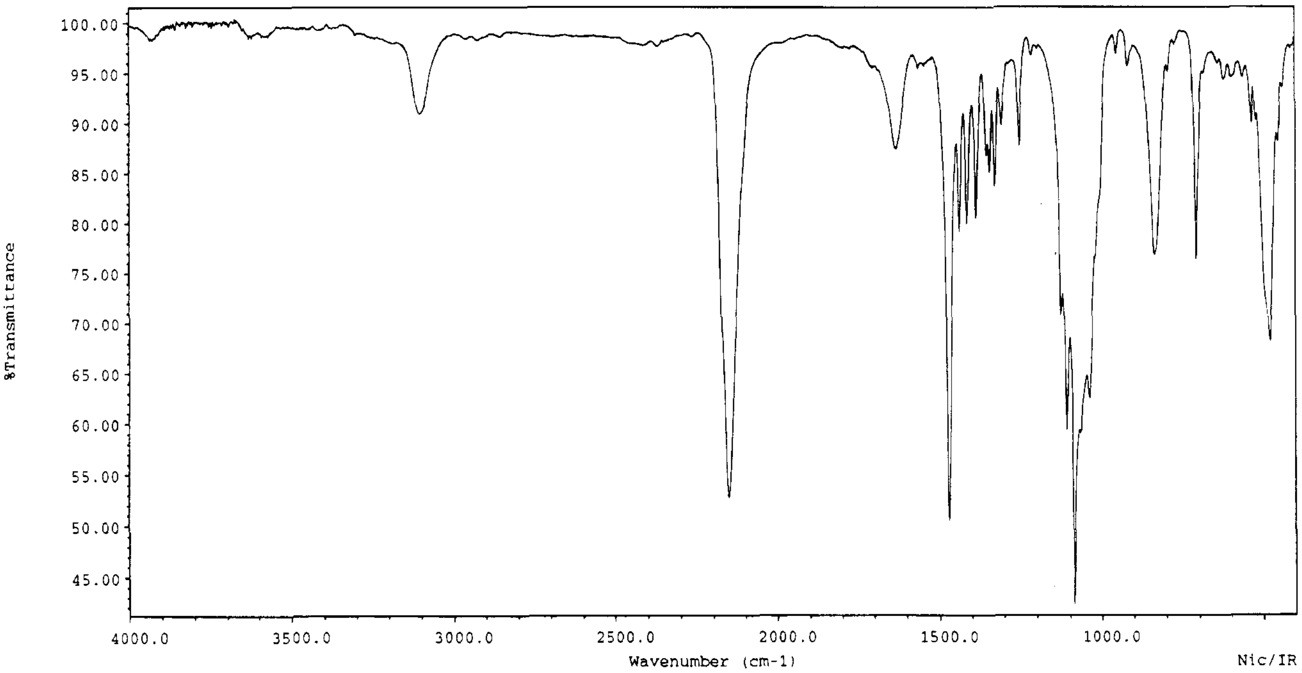

Figure 9. IR spectrum of allenylium tetrafluoroborate **12**.

Future work will focus on the electrochemistry and intervalence transfer of these model compounds for molecular electronics and on preparative chemistry, including the synthetic use of these electrophilic synthons and the chemical generation of neutral allylic radical or carbenoid species from the corresponding allylium salts. Results from Mössbauer measurements, which should give further insight into the role of the metallocenyl substituents as cation-stabilizing moieties and into the intramolecular electronic interaction among the conjugatively bridged ferrocenyl groups, will be reported in due course.

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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 **7**, **10a**,**b** and **11** (39 pages). Ordering information is given on any current masthead page. The authors have deposited atomic coordinates for structures **7**, **10a**,**b**, and **11** 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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