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Generation of ferrocenylvinyl cation $CpFeC_5H_4–C^+=CH_2$ by protonation of ferrocenylacetylene with Nafion and its reactions with SMe_2 and PPh_3 in $scCO_2$ giving onium salts

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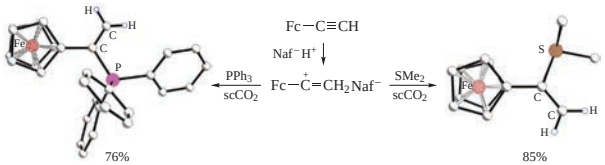
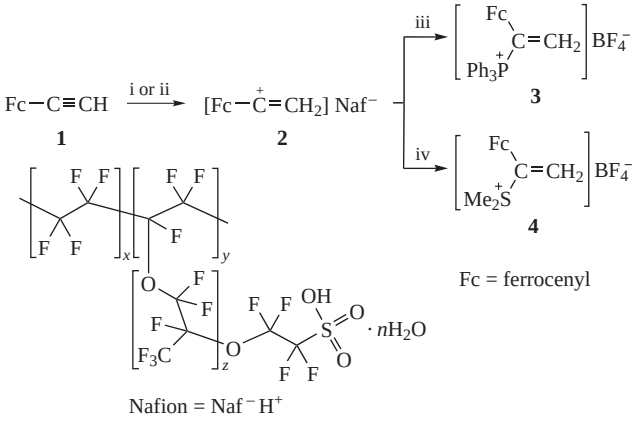
Cation $CpFeC_5H_4–C^+=CH_2$ was obtained by protonation of FcC≡CH with Nafion superacid in DMF or $scCO_2$ and characterized by NMR spectroscopy. The protonation in the presence of SMe_2 or PPh_3 affords new onium derivatives, which were isolated as the tetrafluoroborate salts.



The study of formation and transformations of reactive intermediates including carbocations is an important problem in organic chemistry. A high reactivity of vinylic cations makes quite difficult their studies in solution, in particular, by spectral methods.[1]

A series of the α-ferrocenylvinyl cations stabilized by the presence of alkyl substituents[2] was generated in trifluoroacetic acid and documented by ^{1}H NMR spectroscopy.[2(a),(b)] Nevertheless, the lifetime of original signals of the cations was very short due to the rapid addition of the acid converting the vinyl cations into the ferrocenylalkyl ones.[2(a)]

Herein, we report a method for generation and stabilization of the labile carbocations and their reactions with mononucleophiles exemplified by the unsubstituted ferrocenylvinyl cation, $CpFeC_5H_4–C^+=CH_2$. A protonation of ethynylferrocene **1** with Nafion,[3] a supersulfoacid specially prepared in DMF,[†] afforded compound $[CpFeC_5H_4–C^+=CH_2]^+[Naf]^–$ **2** (Scheme 1). The use of Nafion as the protonating agent increases a stability of labile cations, specifically vinyl ones, in solution, due to a poor nucleophilicity and considerable size of the acid anion sterically shielding the cationic center and thus hindering the addition of the acid to the double bond of the cation.



Scheme 1 *Reagents and conditions:* i, $Naf^–H^+$, $scCO_2$; ii, $Naf^–H^+$, DMF; iii, PPh_3, $scCO_2$, then $HBF_4·Et_2O$, CH_2Cl_2; iv, SMe_2, $scCO_2$, then $HBF_4·Et_2O$, CH_2Cl_2.

Dissolution of alkyne **1** at room temperature in Nafion/DMF affords a mixture of compounds **1** (a signal of the acetylene proton at δ 3.67 ppm), **2** and acetylferrocene (methyl group at δ 2.40 ppm has the cross peak with the carbon atom of the carbonyl group at δ 200.91 ppm in 2D-HMBC spectra, see Figure S1 in Online Supplementary Materials) in a ratio of 8.6:1:1.2. The signals of compound **2** can be observed for 12–14 h. The excess of acetylene **1** is necessary to maintain the concentration of the cation sufficient to register its ^{13}C NMR spectrum, because the concentration of the cation was decreasing during the NMR experiment as a result of a slow reaction of the cation with the residual water (after drying the Nafion samples) which was tightly bound to the sulfonic groups.

The assignments of the signals in the NMR spectra were made based on the cumulative data of one and two dimensional NMR

[†] *General procedure*. Nafion® 20 wt% solution of lower aliphatic alcohols–H_2O mix 527122 and Nafion®112 film (thickness 0.002 inches) were purchased from Aldrich. The 5% water content was not taken into account on calculation of equivalent proton content in Nafion film. Ethynylferrocene **1** was prepared by known method.[4] DMF-d_7 (99.5%) was distilled from P_2O_5 at reduced pressure (2 Torr). CD_2Cl_2 (D, 99.8%) was purchased from Cambridge Isotope Laboratories, Inc. Tetrafluoroboric acid (54% in diethyl ether) was purchased from Merck. CH_2Cl_2 was distilled from P_2O_5. High purity CO_2 (>99.997%, 0.001% H_2O) was used as received. High pressure pump (Thar Technologies, Inc.) was used and the pressure in the cell was maintained with an accuracy of at least ±0.1 MPa. NMR spectra were recorded on a Bruker Avance-600 spectrometer at 600.22 MHz for ^{1}H and 150.92 MHz for ^{13}C in DMF-d_7, Bruker Avance-400 spectrometer at 400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C (relative to Me_4Si), 128.38 MHz for ^{11}B (relative to H_3BO_3), 161.98 MHz for ^{31}P (relative to H_3PO_4) in CD_2Cl_2.

Preparation of **2** *in solution (Nafion–DMF-*d_7*)*. A solution of Nafion (d = 1.049, equiv. wt. 1.100; 0.05 equiv. H^+) (0.1 ml, 0.15 mmol) was transferred into a flask and the solvent was removed *in vacuo*. All further operations were performed under argon. The residue was dried *in vacuo* (2 Torr) over P_2O_5 excluding its darkening at 56 °C for 18 h. Then, dry (no water signals in the ^{1}H NMR spectrum) DMF-d_7 (1 ml, distilled *in vacuo* over P_2O_5 and kept over molecular sieves 3 Å for 30 days) was added. The solid residue dissolved completely within 20–24 h and the resulting solution was transferred into a NMR tube containing **1** (0.07 g, 0.3 mmol). At the final step, the mixture was shaken vigorously.

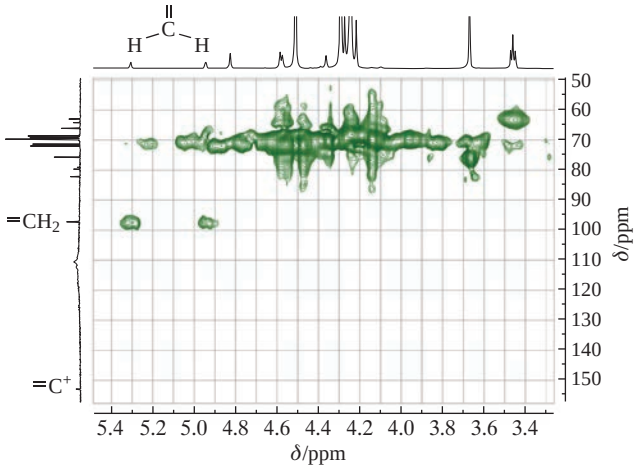


Figure 1 A fragment of the 2D-HMQC spectrum (600 MHz, DMF-d_7) of compounds **1**, **2**, and acetylferrocene.

experiments (Figure 1). The signals of the vinyl group in compound **2** in the region characteristic of vinyl hydrogens[2(*a*)] are observed (δ 4.94 and 5.30 ppm) as the doublets (^2J 2.0 Hz) and have cross peaks with the carbon atoms of the vinyl group at δ 153.5 (–C^+=) and 97.3 ppm (=CH_2). For the 2D-HMBC and 2D-HMQC NMR spectra of salt **2**, see Figure S1, S2, Online Supplementary Materials.

A considerable stability of salt **2** in the Nafion solution allowed us to speculate on the possible generation of cation **2** using the Nafion film[5] (sulfopolymer) as the protonating agent in supercritical carbon dioxide ($scCO_2$)[3(*e*)] followed by subsequent transformations. $scCO_2$ was chosen for having some advantages,[6] *i.e.* the absence of gas–liquid mass transfer limitations, relatively high rates of molecular diffusion and heat transfer, and the possibility of molecular interactions with the dissolved reacting species.[7]

Indeed, the reaction between compound **1** and the Nafion film in $scCO_2$ in the presence of PPh_3 or SMe_2 as the nucleophiles resulted in new onium ferrocene derivatives, complexes **3** and **4** (see Scheme 1), isolated as the tetrafluoroborates in 76 and 85% yields, respectively. The molecular formulas of complexes **3** and **4** were elucidated by NMR spectroscopy‡ (^{1}H, ^{13}C, ^{31}P, ^{11}B, 2D-HSQC for **3** and ^{1}H, ^{13}C, ^{11}B, 2D-HSQC for **4**; see Online Supplementary Materials) along with the single crystal X-ray diffraction analysis§ (Figure 2). The C(11) carbon atom is in the plane of the Cp ligand (the deviation is 0.02 Å in **3** and 0.01 Å in **4**) and has a planar surrounding [the sum of the angles at the C(11) atom in both compounds is 360.0°]. The C(1)–C(11) and C(11)–C(12) bond lengths in both compounds virtually coincide with the standard values of ordinary C_{sp^2}–C_{sp^2} and double C_{sp^2}=C_{sp^2} bond lengths (1.478 and 1.321 Å),[8] respectively. Thus, one may state that there is neither contribution of the fulvene-type structure in the cations nor additional coordination of the exocyclic unsaturated fragment to the ferrocene iron atom.

Both compounds crystallize in the chiral space groups ($P2_12_12_1$ for **3** and $P2_1$ for **4**) and their absolute configurations were determined based on anomalous scattering. The compounds differ in the orientation of the substituents at the C(11) atom relative to the Cp ring of ferrocene [the C(2)–C(1)–C(11)–C(12) torsion angle is 155.4° in **3** and 21.7° in **4**].

‡ For **3**: ^{1}H NMR (CD_2Cl_2) δ: 4.11 (m, 2H, C_5H_4), 4.21 (s, 5H, C_5H_5), 6.16 (d, 1H, =CH_2, $^3J_{HP}$ 16.0 Hz), 7.25 (d, 1H, =CH_2, $^3J_{HP}^{trans}$ 36.0 Hz), 7.6–7.7 (m, 6H, *o*-H_{Ph}), 7.7–7.8 (m, 6H, *m*-H_{Ph}), 7.93 (t, 1H, 3H, *p*-H_{Ph}, $^3J_{HH}$ 6.4 Hz). ^{13}C NMR (CD_2Cl_2) δ: 70.1 (2C, C_5H_4), 70.3 (2C, C_5H_4, $^3J_{CP}$ 3.2 Hz), 70.49 (5C, C_5H_5), 81.5 (C_i, C_5H_4, $^2J_{CP}$ 13.1 Hz), 117.2 (–CP^+=, $^1J_{CP}$ 30.4 Hz), 130.4 (6C, *m*-C_{Ph}, $^3J_{CP}$ 10.1 Hz), 131 (3C, *i*-C_{Ph}, $^1J_{CP}$ 59.4 Hz) 134.4 (6C, *o*-C_{Ph}, $^2J_{CP}$ 8.0 Hz), 135.6 (3C, *p*-C_{Ph}, $^4J_{CP}$ 2.3 Hz), 139.9 (=CH_2, $^2J_{CP}$ 8.0 Hz). ^{31}P NMR (CD_2Cl_2) δ: 22.19. ^{11}B NMR (CD_2Cl_2) δ: –1.12, see Figures S3–S7, Online Supplementary Materials.

For **4**: ^{1}H NMR (CD_2Cl_2) δ: 3.13 (6H, Me), 4.33 (5H, C_5H_5), 4.58 (4H, C_5H_4), 6.24 (H, =CH_2, $^2J_{HH}$ 2.4 Hz), 6.48 (H, =CH_2, $^2J_{HH}$ 2.4 Hz). ^{13}C NMR (CD_2Cl_2) δ: 27.7 (2C, Me), 68.4 (2C, C_5H_4), 70.5 (5C, C_5H_5), 71.2 (2C, C_5H_4), 78.09 (C_i, C_5H_4), 123.3 (=CH_2), 136.1 (–CS^+=). ^{11}B NMR (CD_2Cl_2) δ: –1.1, see Figures S8–S11, Online Supplementary Materials.

§ *Crystal data for* **3**·BF_4^-: $C_{30}H_{26}F_4BPFe$, M = 560.14, dark red crystals, orthorhombic, space group $P2_12_12_1$, a = 9.5948(6), b = 16.1709(10) and c = 16.2431(10) Å, V = 2520.2(3) Å^3, d_{calc} = 1.476 g cm^{-3}, Z = 4, μ(MoKα) = 7.10 cm^{-1}, T = 120(2) K, $2\theta_{max}$ = 56°, R_1 = 0.0611 for 5169 reflections with $I > 2\sigma(I)$, and wR_2 = 0.1213 for all 6038 unique reflections (R_{int} = 0.0763). Flack parameter 0.05(3).

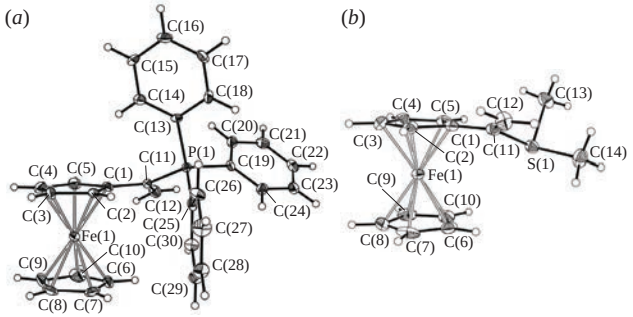


Figure 2 (*a*) Molecular structure of salt **3** (thermal ellipsoids drawn at the 50% probability level). Selected bond lengths (Å): Fe–C 2.035(5)–2.053(6) ⟨2.044⟩, C(1)–C(2) 1.443(7), C(1)–C(5) 1.436(7), C(2)–C(3) 1.421(7), C(3)–C(4) 1.404(9), C(4)–C(5) 1.420(8), C(1)–C(11) 1.474(7), C(11)–C(12) 1.321(8), P(1)–C(11) 1.807(5); selected angles (°): C(12)–C(11)–C(1) 122.9(5), C(12)–C(11)–P(1) 119.2(4), C(1)–C(11)–P(1) 117.9(4). (*b*) Molecular structure of salt **4** (thermal ellipsoids drawn at the 50% probability level). Selected bond lengths (Å): Fe–C 2.030(2)–2.056(2) ⟨2.039⟩, C(1)–C(2) 1.435(3), C(1)–C(5) 1.432(3), C(2)–C(3) 1.417(3), C(3)–C(4) 1.414(3), C(4)–C(5) 1.424(3), C(1)–C(11) 1.465(3), C(11)–C(12) 1.320(3), S(1)–C(11) 1.800(2); selected angles (°): C(12)–C(11)–C(1) 126.3(2), C(12)–C(11)–S(1) 120.8(2), C(1)–C(11)–S(1) 112.9(2).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.07.016.

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Crystal data for **4**·BF_4^-: $C_{14}H_{17}F_4SBFe$, M = 359.99, dark red crystals, monoclinic, space group $P2_1$, a = 7.3644(4), b = 10.3950(6) and c = = 9.9962(6) Å, β = 92.161(1)°, V = 764.69(8) Å^3, d_{calc} = 1.563 g cm^3, Z = 2, μ(MoKα) = 11.52 cm^{-1}, T = 120(2) K, $2\theta_{max}$ = 60°, R_1 = 0.0332 for 3768 reflections with $I > 2\sigma(I)$, and wR_2 = 0.0572 for all 4446 unique reflections (R_{int} = 0.0356). Flack parameter 0.023(17).

Crystal data were collected with a Bruker SMART APEX II diffractometer [λ(MoKα) = 0.71073 Å]. All calculations were performed using SHELXTL program package.[9]

CCDC 1523012 and 1523013 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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