Supporting Information for

Autocatalytic Formation of Fluorinated Ferrocenophanes from 1,1'-Bis(trifluorovinyl)ferrocene

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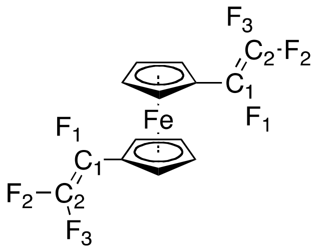
Experiments were carried out under argon, using standard Schlenk and vacuum line techniques. THF was dried over sodium/benzophenone. Iodoferrocenes were prepared according to the literature.[1] Other substances were obtained commercially and used as received. NMR spectra were recorded on a Jeol Lamda 400 and JEOL ECS400 spectrometer, respectively, using $CDCl_3$ as solvent. IR spectra were recorded on a Nicolet iS10 spectrometer with ATR Smart Dura Sampl/IR device. Mass spectra were recorded in EI mode on a MAT 711 device. Cyclic voltammetry experiments were performed on a CH-Instruments Electrochemical Workstation. The measurement cell consisted of a platinum working-, platinum counter- and an Ag/Ag^+ reference electrode. Measurements were carried out in 0.1 M solutions of Bu_4NPF_6 in dichloromethane with a scan rate of 100 mV and were referenced to the ferrocene/ferrocenium couple. The middle between anodic and cathodic peak was used as estimation for the redox potentials.

2: A Schlenk flask, equipped with a reflux condenser and $CaCl_2$ dry tube, was charged with 6.00 g (13.7 mmol) 1,1’-diiodoferrocene, 1.08 g (4.1 mmol) triphenylphosphine and 0.18 g (0.8 mmol) palladium(II)acetate and 120 ml $CF_2CFZnCl$-solution in THF (prepared according Burton et al.[2] and used as prepared). The mixture was refluxed for 5 h under rapid stirring. After the reaction was completed, the crude mixture was concentrated to about half of its volume and the same volume of pentane was added. The suspension was filtered through celite, which removed most of the grayish-black phosphine-palladium side products. In the next step, the mixture was extracted with brine and water for several times. The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under vacuum.

Drying under high vacuum afforded 4.6 g (97 %) of orange-brown crystals with a purity of > 95 %. Recrystallization from pentane at -80° C afforded the product analytically pure.



δ_H = 4.47 (AA', 4 H), 4.33 (BB', 4 H) (chemical shift values represent the centres of the multiplets). $\delta_C\{^1H\}$ = 66.80 (s, cp), 70.40 (s, cp), 73.87 (ddd, $^3J(^{13}C\text{-}^{19}F)$ = 1 Hz, $^3J(^{13}C\text{-}^{19}F)$ = 6 Hz, $^2J(^{13}C\text{-}^{19}F)$ = 25 Hz, ipso-*C*), 127.41 (ddd, $^2J(^{13}C\text{-}^{19}F)$ = 21 Hz, $^2J(^{13}C\text{-}^{19}F)$ = 51 Hz, $^1J(^{13}C\text{-}^{19}F)$ = 226 Hz), C_1), 152.16 (ddd, $^2J(^{13}C\text{-}^{19}F)$ = 49 Hz, $^1J(^{13}C\text{-}^{19}F)$ = 279 Hz, $^1J(^{13}C\text{-}^{19}F)$ = 289 Hz), C_2). δ_F = -99.95 (dd, $^3J(^{19}F\text{-}^{19}F)$ = 30 Hz, $^2J(^{19}F\text{-}^{19}F)$ = 80 Hz, F_2), -118.05 (dd, $^2J(^{19}F\text{-}^{19}F)$ = 80 Hz, $^3J(^{19}F\text{-}^{19}F)$ = 111 Hz, F_3), -172.24 (dd, $^3J(^{19}F\text{-}^{19}F)$ = 30 Hz, $^3J(^{19}F\text{-}^{19}F)$ = 111 Hz, F_1). *m/z* 346 (M^+, 75 %), 126 ($C_7H_4F_2$, 100). HRMS (EI): calcd: 345.98796, found: 345.98570. IR(neat): 551(m), 563(m), 647(w), 658(w), 819(s), 839(w), 867(s), 994(s), 1032(s), 1066(s), 1106(w), 1150(s), 1122(m), 1279(m), 1311(w), 1324(w), 1350(w), 1393(w), 1483(m), 1447(w), 1672(w), 1697(w), 1739(w), 1769(s), 2919(w), 2959(w), 3121(w). mp: 43-44° C.

The ^{19}F NMR spectrum of the trifluorovinyl groups exhibits an AMX pattern typical for this functional group. The resonances of the ^{19}F nuclei are observed as doublets of doublets within a large chemical shift range[S1] and with coupling constants[S1] typical for ^{19}F NMR spectra.

3 and **Oligomers**: A Schlenk tube was charged with 600 mg (1.72 mmol) of **2**. 2 ml of toluene were added and the soution was heated to 110° C for 2 h. The crude reaction mixture was subject to flash chromatography on silica with hexane as eluent. **3** appeared in the deep red first fraction. Recrystallization from pentane at 4° C afforded 30 mg (0.09 mmol, 5 %) of red crystals. Three fractions with lower R_f-values were eluted with mixtures of hexane and dichloromethane. The polarity was incresed slowly stepwise by increasing the concentration of dichloromethane in the eluent, starting with a ratio of 2:1 and ending with a ratio 1:2. These orange fractions contained oligomeric mixtures of the formula $[(C_2F_3)_2C_{10}H_8Fe]_n$. Average *n* values were calculated by integration of the resonances for the perfluorocylobutane ring (PFCB) versus the signals of the trifluorovinyl end groups (fraction 2: $n = 4$, fraction 3: $n = 5$, fraction 3: $n = 8$). Due to random formation of *cis*- and *trans*-isomers and a mixture of different molecular weights, all NMR-signals appear overlapped and/or broad. Except the integrations, spectra of all fractions were alike. Combined yield: 252 mg (42 %).

3: δ_H = 5.32 (m, 2H, Cp), 5.26 (m, 2H, Cp), 4.28 (m, 2H, Cp), 4.10 (m, 2H, Cp). $\delta_C\{^1H\}$ = 114.38 (trm, $^1J(^{13}C-^{19}F) \cong 298$ Hz, *C*F_2), 100.92 (dm, $^1J(^{13}C-^{19}F) \cong 250$ Hz, *C*F), 74.07 (m, ipso-*C*, Cp), 72.68 (Cp), 71.30 (m, Cp), 70.79 (m, Cp), 70.47 (m, Cp). δ_F = -121.19 (dm, 2F, $^2J(^{19}F-^{19}F) = 231$ Hz, CF_2), -129.36 (dm, 2F, $^2J(^{19}F-^{19}F) = 231$ Hz, CF_2), -152.79 (br, 2F, CF). In the ^{19}F NMR spectrum of **3** there exist three resonances for the six fluorine atoms which are pairwise chemically equivalent forming an AA'BB'CC' spin system. As all but the geminal coupling constants seems to be small the CF_2 groups are observed as an AB type spectrum which exhibits some additional splitting into multiplets. The CF group gives raise to only a broad resonance showing no further splitting. *m/z* 346 (M^+, 100 %), 220 ($C_7H_4F_4$ Fe, 39), 126 ($C_7H_4F_2$, 92). HRMS (EI): calcd: 345.9880, found: 345.9892. IR(neat): 602(m), 619(w), 660(w), 806(s), 830(w), 847(w), 877(w), 906(s), 957(w), 1012(s), 1040(w), 1070(s), 1100(w), 1164(s), 1184(s), 1228(w), 1259 (m), 1330(m), 1362(m), 1434(w), 1459(w), 1641(w), 1721(w), 1771(w), 2853(w), 2923(w), 2953(w), 3102(w), 3120(w). mp: 103-105° C

Oligomers: δ_H = 4.51-3.95 (Cp-*H*). δ_F = 100.15 (C_2F_3), 118.91 (C_2F_3), 124.53 (PFCB-CF_2), 125.16 (PFCB-CF_2), 128.61 (PFCB-CF_2), 129.20 (PFCB-CF_2), 163.30-164.31 (PFCB-CF), 166.57-167.24 (PFCB-CF), 172.25 (C_2F_3).

4, **5** *Method A:* 40 mg (0.12 mmol) of **2** were dissolved in dichloromethane and applied on a preparative silica TLC plate. Elution with dichloromethane/pentane (1:1) yielded 24 mg (0.07 mmol, 61 %) of **4** in the deep red first fraction. Small amounts of **5** appeared in the second fraction (< 5 %).

Method B: 104 mg (0.30 mmol) of **2** were dissolved in 10 ml of *tert.*-butanol and 10 ml of water were added. 594 mg (1.8 mmol) of potassium hexacyanoferrat(III) were added under rapid stirring to the orange solution. The colour changed fast to green-blue and stirring was continued over two hours at room temperature. The mixture was extracted with 2 x 20 ml dichloromethane and the dichloromethane layer was filtered through celite. ^{19}F NMR spectroscopy revealed a total consumption of **1** with **4** as main product. The solvent was then evaporated and the resulting brown crystalline material was subject to coloumn chromatography with dichloromethane/pentane (1:1) as eluent. The deep red main fraction contained 52 mg (0.15 mmol, 50 %) of **4**, followed by a small red-violet fraction, which contained 2 mg (0.006 mmol, 2%) of **5**.

Method C: 65 mg (0.19 mmol) of **2** were dissolved in 4 ml of *tert.*-butanol. 4 ml of water were added. A catalytic amount of 1 mg (0.003 mmol, 1.6 mol %) potassium hexacyanoferrate(III) was added under rapid stirring to the orange solution. Within one minute, the solution turned greenish-blue. Stirring was continued for 15 minutes. A total conversion to **4** was proved by ^{19}F NMR spectroscopy. 20 ml water were added, followed by an extraction with 2 x 20 ml of dichloromethane. The dichloromethane layer was then filtered through celite and the solvent was evaporated, yielding 55 mg of the crude product. Column chromatographic purification on silica with pentane/dichloromethane in a ratio of 1:1 as eluent was carried out in the next step. The deep red main fraction contained the product. 43 mg (0.13 mmol) of **4** were obatained in form of ruby red crystals (67 %) after evaporation of the solvent. Experiments in the same water/*tert.*-butanol system with catalytic amounts of either iodine or 2,3-dichloro-5,6-dicyanobenzoquinone as oxidants yielded within minutes as well a total conversion with **4** as product.

4: δ_H = 5.55 (ddm, 1H, $^3J(^1H-^{19}F)$ = 21 Hz, $^2J(^1H-^{19}F)$ = 46 Hz, CF*H*), 4.96 (m, 2H, Cp) 4.81 (m, 1H, Cp), 4.73 (m, 1H, Cp), 4.47 (m, 1H, Cp) 4.40 (m, 2H, Cp), 4.35 (m, 1H, Cp). δ_C {^{1}H, ^{19}F} = 70.87, 71.72, 71.81, 71.52, 73.07, 73.96, 74,58, 74,86, 76.07, 76.33 (Cp), 87.30 (*C*FH), 112.28 (CF_2), 116.48 (CF_2), 184.25 (*C*O). δ_F = -113.6 (d, 1F, $^2J(^{19}F-^{19}F)$ = 266 Hz), -116.9 (d, 1F, $^2J(^{19}F-^{19}F)$ = 268 Hz), -120.5 (d, 1F, $^2J(^{19}F-^{19}F)$ = 268 Hz), -124.9 (d 1F, $^2J(^{19}F-^{19}F)$ = 266 Hz), -178.1(m, 1F). *m/z* 344 (M^+, 100 %), 158 (M - $FeC_6F_2H_4O$, 58). HRMS (EI): calcd: 343.99231, found: 343.99042. IR (neat): 427 (w), 452 (w), 474 (m), 502 (s), 511 (m), 551 (m), 571 (m), 584 (w), 594 (w), 601 (w), 611 (w), 640 (w), 671 (w), 744 (w), 778 (w), 799 (s), 828 (s), 832 (s), 843 (m), 851 (m), 882 (w), 894 (w), 919 (s), 939 (w), 976 (m), 1013 (w), 1040 (m), 1053 (m), 1065 (s), 1091 (s), 1152 (s), 1170 (m), 1199 (m), 1216 (s), 1244 (s), 1285 (w), 1306 (w), 1332 (w), 1353 (w), 1374 (w), 1384 (w), 1413 (w), 1420 (w), 1448 (m), 1469 (w), 1684 (s), 1773 (w), 1793 (w), 1828 (w), 2855 (w), 2931 (w), 2955 (w), 3102 (w), 3115 (w), 3150 (w), 3441 (w). mp: 146° C.

5: δ_H = 4.92 (AA', 4H, Cp), 4.76 (BB', 4 H, Cp) (chemical shift values represent the centres of the multiplets). δ_F = 119.90 (s, CF_2). *m/z* 344 (M^+, 100 %). HRMS (EI): calcd: 339.98098, found: 339.98090. IR(neat): 554(m), 593(w), 608(w), 626(w), 645(w), 700(w), 748(s), 798(s), 829(s), 847(m), 917(m), 949(m), 1007(s), 1034(s), 1056(s), 1071(s), 1097(s), 1135(s), 1164(m), 1193(s), 1211(s), 1259(m), 1291(w), 1377(m), 1407(w), 1445(m), 1678(s), 2852(w), 2921(w), 2953(w), 3116(w). mp: subliming at 195 °C.

6: 150 mg (0.43 mmol) of **1** were dissolved in a mixture of 8 ml water and 8 ml *tert.*-butanol. 201 mg (3.5 mmol) of potassium fluoride and 856 mg (2.6 mmol) of potassium hexacyanoferrate(III) were added and the resulting greenish-dark mixture was stirred for 1 h. According to the ^{19}F NMR spectrum of the reaction mixture, **4** and **6** formed in a ratio of 2:1. The crude mixture was diluted with 40 ml of water and extracted two times with 40 ml of dichloromethane and was then subject to column chromatography on silica with pentane/dichloromethane (1:1) as eluent. 34 mg (0.09 mmol) of **6** were isolated in form of a yellow solid from the first fraction (22 %).

δ_H = 5.52 (dd, 1H, $^3J(^1H-^{19}F)$ = 23 Hz, $^2J(^1H-^{19}F)$ = 45 Hz, CF*H*), 4.32-4.57 (5 overlapping resonances at 4.57, 4.44, 4.42, 4.40, 4.32, 8H, Cp). δ_F = -87.21 (d, 1F, $^2J(^{19}F-^{19}F)$ = 285 Hz), -103.27 (d, 1F, $^2J(^{19}F-^{19}F)$ = 282 Hz), -108.80 (d, 1F, $^2J(^{19}F-^{19}F)$ = 272 Hz), -120.72 (d, 1F, $^2J(^{19}F-^{19}F)$ = 282 Hz), -122.09 (d, 1F, $^2J(^{19}F-^{19}F)$ = 285 Hz), -127.70 (d, 1F, $^2J(^{19}F-^{19}F)$ = 272 Hz), 171.29 (m, 1F). *m/z* 366 (M^+, 100).

HRMS (EI): calcd: 365.9942, found: 365.9959. IR(neat): 587(w), 650(w), 672(w), 686(w), 783(w), 767(m), 804(s), 834(s), 848(m), 858(m), 884(w), 913(s), 942(m), 989(m), 1035(s), 1052(s), 1105(s), 1117(s), 1145(s), 1213(m), 1243(m), 1268(m), 1294(w), 1347(w), 1384(w), 1395(w), 1471(w), 2850(w), 2919(w), 2955(w), 3116(w). mp: 71-73° C.

References:

S1 J. W. Emsley, J. Feeney, L. H. Sutcliff, High Resolution Nuclear Magnetic Resonance Spectroscopy, Pergamon Press, Oxford, 1966.