



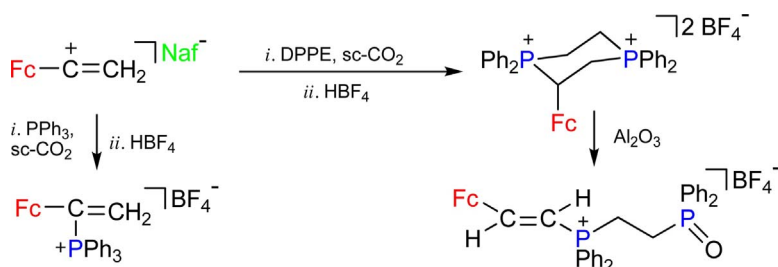
Phosphonium salts derived from α -ferrocenylvinyl cation *in situ* generated in sc -CO₂ from ethynylferrocene by Nafion film



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GRAPHICAL ABSTRACT



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ABSTRACT

A protonation of ethynylferrocene by nafion in sc -CO₂ in the presence of triphenylphosphine (PPh₃) or 1,2-bis(diphenylphosphino)ethane (DPPE) leads to a formation of novel (1-ferrocenylvinyl)phosphonium or ferrocenyl substituted bisphosphonium salt isolated as tetrafluoroborates 3 and 4, respectively. Ferrocenyl substituted bisphosphonium tetrafluoroborate 4 undergoes the hydrolytic cleavage of the P⁺-C(Fc) bond in the presence of Al₂O₃ at 25 °C to form ferrocenyl substituted phosphinyl phosphonium tetrafluoroborate 5. Complexes 3–5 were completely characterized by NMR spectra and their molecular structures elucidated by X-ray studies.

1. Introduction

Recently, we reported on the effective method of alkynes hydration with Nafion film in supercritical carbon dioxide (sc -CO₂) [1]. The non-toxic polymer superacid [2,3] Nafion is used as the heterogeneous acidic catalyst or reagent that effectively acts under mild conditions. It does not resinify the reaction products and can be easily separated from them. sc -CO₂ is the solvent of choice due to a number of advantages [4–11]. 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 are among them. It is these properties that have led sc -CO₂ to widespread use in chemistry and chemical technology [12–27]. We have chosen sc -CO₂ as

the solvent to ensure a uniform distribution of the reactants throughout the whole polymer matrix and high reaction rates at low temperatures that are of crucial importance for this study. It is known that the acid-catalyzed hydration of alkynes proceeds through the formation of vinyl-cations [28]. However, it was found that despite the presence of water in Nafion it is possible to avoid a formation of the ketone, the convenient product of hydration of a vinyl cation, if the protonation of alkyne proceeds in the presence of a nucleophile. In this case, the reaction gives rise an onium compound as the product [29].

Herein, we report on a mild conditions protonation of ethynylferrocene (1) by Nafion in sc -CO₂ in the presence of phosphines. The reaction leads to an intermediate formation of labile α -ferrocenyl vinyl cation (2) [29] that was found to react with PPh₃ or DPPE furnishing

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mono or diphosphonium salts isolated as the tetrafluoroborate salts **3** and **4**, respectively. In the presence of aluminum oxide, salt **4** undergoes the hydrolytic cleavage [30,31] of the P⁺-C(Fc) bond to form phosphine oxide (ferrocenylvinyl)phosphonium tetrafluoroborate **5**. It should be noted that structural relatives of phosphonium derivatives **3**–**5** are widely used in organic [32–35] and asymmetric synthesis [31,36], as the precursors of ylides [30,37–44] and frustrated Lewis pairs [45–47], and as radiolabels in SPECT and PET tomography [48]. Diphosphonium polymers exhibit enhanced thermostability and can be used to generate energy [49].

2. Experimental

2.1. General

Nafion® 20 wt.% solv. of lower aliphatic alcohols/H₂O mix 527122 and Nafion®112 film (thickness 0.002 in.) purchased from Aldrich was used for the protonation of **1**. The 5% water content was not taken into account on calculation of equivalent proton content in Nafion film. Ethynylferrocene **1** was prepared by the reported method [50]. CD₂Cl₂ (D, 99.8%) were purchased from Cambridge Isotope Laboratories, Inc. Tetrafluoroboric acid (54% in diethyl ether) 800172 was purchased from Merck. All further operations were performed in argon atmosphere. CH₂Cl₂ was distilled from P₂O₅ before use. High purity CO₂ (> 99.997%, 0.001% H₂O) was used as received. Aluminium oxide (neutral, 150 mesh), PPh₃, and DPPE were purchased from Merck and used as received.

High-pressure pump (Thar Technologies Inc., USA) was used and the pressure in the cell was maintained with an accuracy of at least ± 0.1 MPa. All experiments were carried out in the stainless steel reactor (10 cm³). The optical cell for the *in situ* study of solubility, in stainless steel SITEC-Sieber Engineering AG (3.3 cm³), equipped with sapphire windows, heating elements, temperature regulator TPM-10A with temperature sensor type TC.

NMR spectra were registered on a Bruker Avance-500 spectrometer at 500.13 MHz for ¹H and 125.76 MHz for ¹³C (chemical shifts are given relative to Me₄Si in both cases), 160.46 MHz for ¹¹B (relative to H₃BO₃), 202.46 MHz for ³¹P (relative to H₃PO₄), 470.59 MHz for ¹⁹F (relative to CHCl₂F), Bruker Avance-400 spectrometer at 128.38 MHz for ¹¹B (relative to H₃BO₃), in CD₂Cl₂. Chemical shifts are indicated in ppm.

X-Ray single-crystal diffraction experiments were carried out with a Bruker SMART APEX II diffractometer (graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å, ω -scan technique, T = 120 K). The APEX II software [51] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction while SHELXL [52] was applied for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed geometrically and included in the structure factors calculation in the riding motion approximation. Crystallographic data and refinement details for complexes **4** and **5** are presented in Table 1. CIFs have been deposited at the Cambridge Crystallographic Database Centre and may be obtained from <http://www.ccdc.cam.ac.uk> by citing reference numbers CCDC 1543524 and 1543523 for compounds **4** and **5** respectively.

2.1.1. Preparation of (ferrocenylethenyl)triphenylphosphonium tetrafluoroborate (1:1) (**3**)

Ethynylferrocene **1** (0.02 g, 0.1 mmol) and Nafion film 0.12 g (eq. wt. 1100; 0.11 eq. H⁺) were placed in the reaction cell as follows. Powdered **1** was poured onto the bottom of the reactor and the Nafion film placed along the wall. A glass charged with powdered PPh₃ (0.05 g, 0.20 mmol) and a magnetic stirrer is placed in the reactor. Carbon dioxide (9 MPa) was injected in the reactor at room temperature. The

Table 1

Crystal Data, Data Collection and Structure Refinement Parameters for Complexes **4** and **5**.

| Complex | 4 | 5 |
|---|--|---|
| Formula | C ₃₈ H ₃₆ B ₂ F ₈ FeP ₂ | C ₃₈ H ₃₅ BF ₄ FeOP ₂ |
| molecular wt | 784.08 | 712.26 |
| crystal size (mm) | 0.28 × 0.14 × 0.04 | 0.24 × 0.10 × 0.06 |
| crystal syst | triclinic | triclinic |
| space group | P-1 | P-1 |
| a (Å) | 9.6523(7) | 11.986(2) |
| b (Å) | 11.9840(9) | 12.102(2) |
| c (Å) | 15.6106(12) | 12.526(2) |
| α (deg) | 78.2894(16) | 87.575(4) |
| β (deg) | 79.9233(17) | 80.080(4) |
| γ (deg) | 74.1403(16) | 65.037(4) |
| V (Å ³) | 1687.1(2) | 1621.7(5) |
| Z | 2 | 2 |
| d_{calcd} (g.cm ⁻³) | 1.543 | 1.459 |
| linear absorption μ (cm ⁻¹) | 6.16 | 6.18 |
| $T_{\text{min}}/T_{\text{max}}$ | 0.899/0.976 | 0.902/0.964 |
| $2\theta_{\text{max}}$ (deg) | 60 | 60 |
| no. of unique reflns (R_{int}) | 9824 (0.0480) | 9453 (0.0829) |
| no. of obsd reflns ($I > 2\sigma(I)$) | 6942 | 6336 |
| no. of params | 460 | 424 |
| R_1 (on F for obsd reflns) ^a | 0.0539 | 0.0616 |
| wR_2 (on F^2 for all reflns) ^b | 0.1169 | 0.1353 |
| GOOF | 1.065 | 1.082 |

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2 \}^{1/2}$$

reactor was kept in a thermostat at 34 °C for 5–7 min and pressurized with CO₂ to 35 MPa at 34 °C. Stirring is then turned on. The reaction mixture was kept at these pressure and temperature for 3 h, cooled to 20 °C and slowly depressurized (30–40 min). The tawny film was removed from the reactor, rinsed with dry CH₂Cl₂ and placed in a Schlenk vessel charged with dry CH₂Cl₂ (75–100 ml). After an addition of an ether solution of HBF₄ (0.1 ml) the mixture was stirred for 12–14 h. The Nafion film gradually faded. The resulting dark yellow solution was concentrated to a minimum volume and filtered through a column charged with Al₂O₃ (0.5 × 5 cm) by the pressure of argon. The products were eluted with CH₂Cl₂ followed by the mixture CH₂Cl₂: acetone (10: 1). After evaporation of the solvent, the residue was reprecipitated from CH₂Cl₂ with hexane or diethyl ether (Et₂O) giving product **3** (0.04 g, 76%) as cherry needles.

NMR: ¹H, ¹³C, ³¹P, ¹¹B, 2D HSQC (Supplementary Date, S3-S6) [29].

2.1.2. Preparation of 2-ferrocenyl-1,1,4,4-tetraphenyl-1,4-diphosphorinium tetrafluoroborate (1:2) (**4**)

Compound **4** was prepared as described above in 2.1.1 for compound **3** from ethynylferrocene **1** (0.02 g, 0.10 mmol), Nafion film 0.12 g (eq. wt. 1100; 0.11 eq. H⁺), and DPPE (0.08 g, 0.2 mmol) wetted with dry Et₂O (~ 0.4 ml). The rape yellow oily crude product **4** was dissolved in minimum quantity of CH₂Cl₂ and rapidly filtered under argon through a column charged with Al₂O₃ (0.5 × 1 cm). The products were eluted with acetone followed by EtOH. After evaporation of the solvent, the residue was reprecipitated from CH₂Cl₂ with hexane or Et₂O giving product **4** (0.032 g, 42%) as yellow crystals.

¹H NMR (CD₂Cl₂): δ 8.14 ÷ 7.44 (m, 24H, 4C₆H₅), 4.58 (s, 1H, C₅H₄), 4.53 (m, 1H, CH-CH₂), 4.38 (s, 1H, C₅H₄), 4.36 ÷ 4.19 (m, 1H, CH-CH₂), 4.26 (s, 5H, C₅H₅), 4.22 (s, 1H, C₅H₄), 4.19 ÷ 4.05 (m, 1H, P(CH₂)₂P), 4.14 (s, 1H, C₅H₄), 3.89 (m, 1H, P(CH₂)₂P), 3.74 (m, 1H, CH-CH₂), 3.61 (m, 1H, P(CH₂)₂P), 3.40 (m, 1H, P(CH₂)₂P), ¹³C NMR JMODECHO (CD₂Cl₂): δ 136.9 (d, *n*-1C, C₆H₅, ⁴J_{C-P} = 3.8 Hz), 136.7 (*n*-1C, C₆H₅, ⁴J_{C-P} = 2.5 Hz), 136.3 (*n*-1C, C₆H₅, ⁴J_{C-P} = 3.8 Hz), 136.2 (*n*-1C, C₆H₅, ⁴J_{C-P} = 2.5 Hz), 134.0 (d, *m*-2C, C₆H₅, ³J_{C-P} = 10.1 Hz), 133.3 (d, *m*-2C, C₆H₅, ³J_{C-P} = 10.1 Hz), 132.8 (d, *m*-2C, C₆H₅, ³J_{C-P} = 11.4 Hz), 132.5 (d, *m*-2C, C₆H₅, ³J_{C-P} = 11.4 Hz), 132.0 (d, *o*-2C, C₆H₅, ²J_{C-P} = 12.6 Hz), 136.2 (d, *o*-2C, C₆H₅, ²J_{C-P} = 12.6 Hz), 130.7

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