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Novel sterically hindered ferrocenyl-phosphonium salt

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ABSTRACT

New sterically hindered ferrocenyl containing phosphonium salt was synthesized in two steps starting from ferrocene. To avoid halogen contamination di-tert-butylferrocenylphosphine was quaternized with methyl bis(trifluoromethanesulfonyl)imide directly. Obtained phosphonium salt was characterized with several physical methods.

GRAPHICAL ABSTRACT



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Introduction

Sterically hindered phosphonium salts became an important sub-class of ionic liquids over the past decade, an integral part of these industrially relevant solvents.^[1,2] Thus phosphonium salts as well as their functionalized analogs have found application as Pd nanocatalyst stabilizers^[3] in Suzuki^[4] and Sonogashira^[5] cross-coupling reactions.^[6] Moreover it was found that structure and texture of bulky phosphonium salt allow to apply it as a binder for paste electrodes to study redox properties of insoluble compounds.^[7,8] The synthesis and physicochemical properties especially redox activity of phosphonium salts containing ferrocenyl fragment are a very intriguing assignment.^[9,10] In present work synthesis of ferrocene containing salt utilized direct quaternization reaction with MeNTf₂ was discussed.

Results and discussion

Results and discussion

Di(*tert*-butyl)ferrocenylphosphine has been prepared by the most common way, namely the Fc lithiation with *tert*-butyl-lithium and subsequent reaction with di(*tert*-butyl)chlorophosphine **1**.^[11]

The starting substrate di(*tert*-butyl)chlorophosphine has been obtained by the reaction of an excess of *tert*-butylmagnesium chloride with phosphorus trichloride followed by separation of the product from the reaction mixture by distillation under reduced pressure (Scheme 1).^[12]

Lithiation with *tert*-butyllithium usually results in a mixture of mono- and 1,1-dilithidated derivatives. To avoid

formation of dilithiated compounds and to obtain single monolithium ferrocene, the reaction has been carried out in diethyl ether (Scheme 2).

An addition of *tert*-butyllithium to a solution of ferrocene and *t*-BuOK^[13] in diethyl ether results in a color change of the solution from brown to orange, indicating that the Fc-H was lithiated. Subsequent slow dropwise addition of di(*tert*butyl)chlorophosphine **1** leads to the precipitation of orange di(*tert*-butyl)ferrocenylphosphine **3**.

The desired salt was obtained by direct alkylation with MeNTf₂ in one step. Initial imide **4** was synthesized according to known method.^[9] (Scheme 3) Iodomethane was added to obtained *in situ* RTIL [Ag(MeCN)₄]₂[Ag(NTf₂)₃] at -78 °C and left stirring overnight at room temperature.

At the next step imide 4 was added to phosphine 3 dissolved in toluene (Scheme 4).

Since imide is less active than methyl iodide, the reaction mixture was stirred at $50 \,^{\circ}$ C for 12 hours. Unreacted phosphine was washed sequentially with petroleum ether and Et₂O. Solvents residue was removed *in vacuo*. Resulting product was obtained as ocher crystalline powder.

In ³¹P NMR spectrum of compound 5 (Figure S1), one signal is observed at 49.04 ppm, in the same region as the signal of bulky phosphonium salts appears.^[14] In ¹H NMR spectrum of compound 5 (Figure S2), the protons of *tert*-butyl group appear as a doublet at 1.48 ppm. The protons of the methyl group form a doublet at 2.30 ppm. The signal of protons in the unsubstituted cyclopentadienyl ring of ferrocene is present as a five-proton singlet at 4.44 ppm and two multiplets with an intensity of two protons, corresponding to the signals of the monosubstituted cyclopentadienyl fragment of ferrocene are exist at 4.67 and at 4.83 ppm.

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Scheme 1. Preparation of di(tert-butyl)chlorophosphine.



Scheme 2. Preparation of di(tert-butyl)ferrocenylphosphine 3.



Scheme 3. Synthesis of methyl bis(trifluoromethanesulfonyl)imide 4.

Electrospray ionization mass-spectrometry (ESI-MS) of phosphonium salt **5** was performed (Figure S3). The spectrum clearly revealed the peaks of cationic part and bis(trifluoromethanesulfonyl)imide anion.

The phosphonium salt 5 melts at ~146 °C with sequential decomposition that could be clearly observed from TG-DSC data (Figure S4) as well as from direct melting point measurement. Despite the presence of NTf₂-anion, compound 5 has a high melting point due to the compact structure of the cation.

Conclusions

We have successfully synthesized new di-*tert*-butyl(ferrocenyl)-methylphosphonium bis(trifluoro-methanesulfonyl)imide from phosphine and MeNTf₂ directly. Obtained compound was characterized by NMR, TG-DSC, ESI-MS.

Experimental

All the work related to the preparation of the starting substrates, the synthesis and the workup of products, was carried out in an inert atmosphere using standard Schlenk apparatus. All solvents and purchased reagents were absolute by the appropriate methods, mainly by distillation in an inert atmosphere. NMR spectra were recorded with multinuclear spectrometer Bruker AVANCE-400 (400.1 MHz (¹H), 100.6 MHz (¹³C) and 162.0 MHz (³¹P)). Chemical shifts are given in parts per million relative to SiMe₄ (¹H, internal solvent) and 85% H₃PO₄ (³¹P, external). Thermo gravimetric analysis was performed on the NETZSCH STA 449F3 with a heating rate 10 K per minute up to 400 °C in an argon atmosphere. Melting points was measured with Stuart SMP30 (Stuart, Cole-Parmer, UK). *t*-BuLi ("1.6 M solution") (by Sigma Aldrich) were used without a preliminary



Scheme 4. Synthesis of di-*tert*-butyl(ferrocenyl)methylphosphonium bis(trifluoromethanesulfonyl)imide 5.

purification. Mass Electrospray ionization mass spectrometry (ESI-MS) was performed n the AmazonX mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany). The measurements were carried out in the positive/negative ion detection mode in the m/z range from 100 to 1000. The voltage on the capillary was 140 V. Data was processed using the DataAnalysis 4.0 program (Bruker Daltonik GmbH, Bremen, Germany).

The procedure for the synthesis of di(*tert*-butyl)ferrocenylphosphine (3) In a two-necked Schlenk vessel equipped with a magnetic stirrer, ferrocene (10.3 mol, 1.923 g) and t-BuOK (1.55 mmol, 0.173 g) were placed, the mixture was dissolved in 150 ml diethyl ether. The solution was cooled down to -78 °C. A solution of t-BuLi (10.3 mmol) was added over 10-15 minutes. Stirring of the reaction mixture was carried out at -70° C. for 1 hour. An orange precipitate of di(tert-butyl) ferrocenylphosphine was formed. Next the reaction mixture was brought to 0°C and t-Bu₂PCl (5.15 mmol, 0.98 ml) was added dropwise. After the completion of the reagent adding, the cooling bath was removed, the reaction mixture was allowed to reach room temperature. After Et₂O was removed in vacuum, the residual was dissolved in 200 ml of the petroleum ether and filtered through short silica column. The solvent removal results in the dark-brown solid 2.431 g (71%). ³¹P NMR (162 MHz) δ , ppm: 28.5 (s).

The procedure for the synthesis of methyl bis(trifluoromethanesulfonyl)imide (4) 2.41 g silver nitrate (14.2 mmol, 1.11 eq.) in 4 ml acetonitrile and added to 4.09 g lithium bis(trifluoromethanesulfonyl)imide (14.2 mmol, 1.11 eq.) in 4 ml acetonitrile. The reaction mixture was stirred for 2 h at room temperature. The formation of white precipitate was observed. The solvent was removed *in vacuo*. The *in situ* generated [Ag(MeCN)₄]₂[Ag(NTf₂)₃] was cooled down to $-78 \,^{\circ}$ C and 1.82 g methyl iodide (12.8 mmol, 1.0 eq.) was added. The reaction mixture was stirred within 12 h at room temperature. The crude product was purified by vacuum distillation. Yield 2.38 g (63%) B.p. = 78-80 \,^{\circ}C/200 mm Hg.

The procedure for the synthesis of di-*tert*-butyl(ferrocenyl)methylphosphonium bis(trifluoromethanesulfonyl)imide (5) 0.69 g methyl bis(trifluoromethanesulfonyl)imide (2.32 mmol) was added to 0.731 g di(*tert*-butyl)ferrocenylphosphine (2.2 mmol) dissolved in 10 ml toluene. The reaction mixture was stirred at 50°C for 12 h. The crude product was washed with 20 ml petroleum ether twice and with 20 ml diethyl ether twice. The precipitate was filtered and the solvent residues was removed *in vacuo*. Yield 1.100 g (76%). M.p. = 146 °C. ¹H NMR (400 MHz, CDCl₃), δ , ppm: 1.48 (d, 18H,³ J_{PH} = 15.66 Hz, P(C(CH₃)₃)₂), 2.30 (d, 3H,² J_{PH} = 11.74 Hz, P-CH₃), 4.44 (s, 5H, H_{Cp}), 4.67 (s, 2H, H_{Cp}), 4.83 (s, 2H, H_{Cp}). ³¹P NMR (162 MHz, CDCl₃), δ , ppm: 49.04 (s). ESI-MS *m*/*z* 345.2 (M⁺ - H), 279.8 (M⁻).

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