

2-(Perfluoroalkyl)ethyl Triflates, Building Blocks for the Synthesis of Bis(polyfluoroalkylated) Cyclopentadienes

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Abstract: Fluorinated building blocks, 2-(perfluorohexyl)ethyl triflate (**11a**) and 2-(perfluorooctyl)ethyl triflate (**11b**) were prepared from the corresponding fluoroalkanols and triflic anhydride. Fluorinated triflates **11** were employed for the preparation of bis(polyfluoroalkylated) cyclopentadienes **9**, which are potential ligands for homogeneous catalysts used in fluoruous biphasic systems. Fluorotriflates **11** are also excellent substrates for the preparation of various polyfluorinated compounds, e.g. nitriles or azides, by nucleophilic substitution.

Key words: 2-(perfluoroalkyl)ethyl triflate, fluoroalkyl triflate, bis(polyfluoroalkylated) cyclopentadiene, fluorinated cyclopentadiene, fluorophilic ligand, ligand for fluoruous biphasic system

Homogeneous catalysis in biphasic systems containing fluoruous phase belongs to the most attractive topics in recent organofluorine chemistry.^{1,2} An essential part of these systems consists of a homogeneous catalyst with significant fluorophilic properties, which are introduced into the molecule by means of fluorophilic ligands. These catalysts found also excellent use in reactions in supercritical CO₂.³

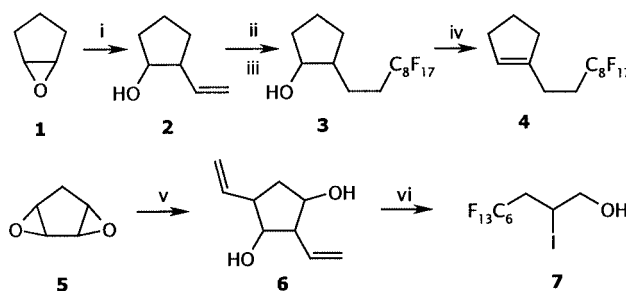
Sufficient fluorophilic properties of the catalysts are achieved provided that the overall fluorine content in the molecule is high.⁴ This results in the need of fluorophilic ligands with multiple fluorinated chain. Phosphines with multiple fluorinated chains can be synthesized relatively easily and are hence mostly used for fluorophilic catalysts.

Homogeneous catalysts with cyclopentadiene based ligands are very common and therefore it is surprising that only little attention has been paid to the synthesis of cyclopentadiene derivatives with fluorophilic properties.^{5,6} Known cyclopentadienes contain only one fluorinated chain and hence their fluorophilic properties are insufficient. We were therefore interested in developing a strategy for the synthesis of cyclopentadienes with two attached fluorinated chains.

Our first strategy for the preparation of bis(polyfluorinated) cyclopentadienes **9** started from cyclic epoxides. The epoxide ring in **1** was opened with vinylmagnesium bromide, then radical addition of a perfluoroalkyl iodide, iodide reduction and final dehydration gave **4** in 5.4% yield.⁷ Although this strategy worked well for the model compound, 6-oxabicyclo[3.1.0]hexene (cyclopentene-1,2-oxide, **1**), we obtained unexpected side-product **7**

when attempting to prepare the target fluorocyclopentadienes **9** from 3,7-dioxatricyclo[4.1.0.0^{2,4}]-heptane **5** (see Scheme 1).

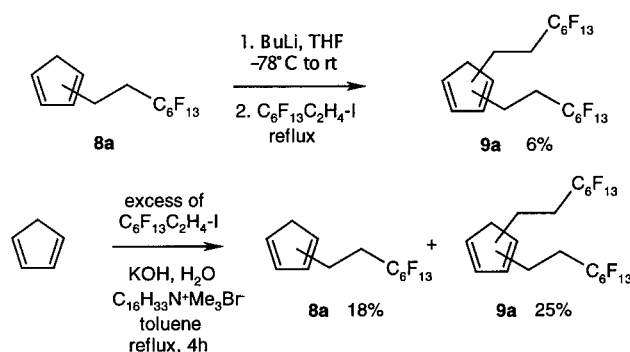
We therefore turned our attention to methods which employ reactions of cyclopentadiene based carbanions with polyfluoroalkylated electrophiles. This approach was used earlier for the preparation of cyclopentadienes substituted by one polyfluoroalkyl chain (**8**).⁶ We first prepared monopolyfluorinated cyclopentadiene **8** (mixture of 1- and 2-substituted isomers in about 1:1 ratio) according to the literature.⁶ Lithiation by BuLi and then reflux of the carbanion formed with 2-(perfluorohexyl)ethyl iodide gave the bis-polyfluoroalkylated cyclopentadiene **9** in very poor yield, mostly because of low conversion of the reaction (Scheme 2).



Scheme 1 i CH₂=CHMgBr, CuI, THF, 0 °C, 3 h, 54%; ii C₈F₁₇I, AIBN, 100 °C, 1 h, 64%; iii Bu₃SnH, AIBN, toluene, 60 °C, 4 h, 77%; iv Nafion-H[®], toluene, 100 °C, 24 h, 21%; v CH₂=CHMgBr, CuI, THF, 0 °C, 3 h, 13%; vi C₆F₁₃I, Na₂S₂O₄, H₂O/MeCN, 20 °C, 3 h, 52%.

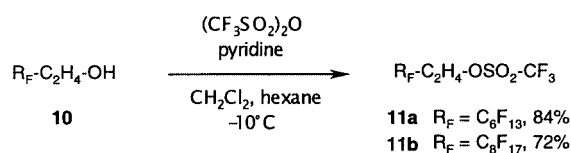
When the cyclopentadienide carbanion was formed under PTC conditions⁶ and reacted for prolonged time with an excess of 2-(perfluorohexyl)ethyl iodide, a mixture of monosubstituted and disubstituted cyclopentadienes (**8a**, **9a**) was formed in slightly better but still unacceptable yield (Scheme 2).⁸ Moreover, we were not able to prepare disubstituted cyclopentadiene **9b** with two 2-(perfluorooctyl)ethyl chains by this method. This initiated our search for fluorinated electrophiles containing a better leaving group.

To obtain fluorinated electrophiles with high reactivity, we synthesized two fluorotriflates **11**, viz. 2-(perfluorohexyl)ethyl triflate⁹ (**11a**) and 2-(perfluorooctyl)ethyl



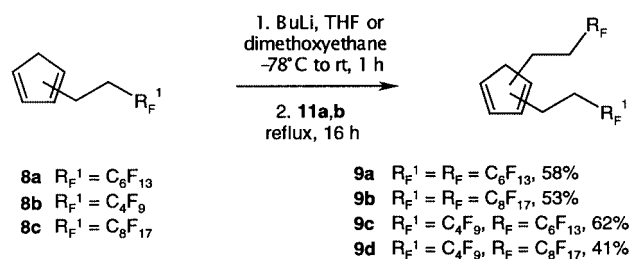
Scheme 2

triflate¹⁰ (**11b**) by reaction of triflic anhydride with the corresponding fluorinated alcohols **10**^{11,12} according to slightly modified general procedure reported by Fife et al.¹³ in good yields (Scheme 3). Analogous preparation of polyfluorinated triflates **11** appeared previously only in the patent literature¹⁴ and author claims the use of building blocks **11** for the reactions with aryllithiums.



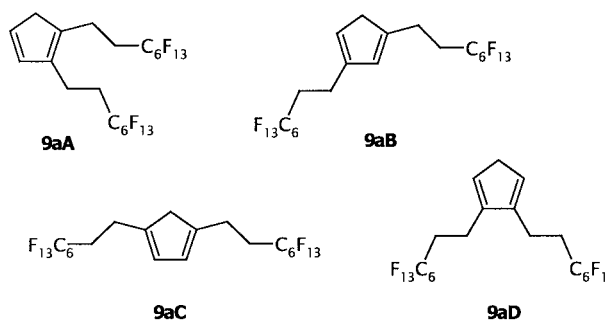
Scheme 3

Mono(polyfluoroalkylated) cyclopentadienes **8** prepared according to the literature⁶ as a mixture of 1- and 2-substituted isomers in about 1:1 ratio were lithiated by BuLi at low temperature in THF or dimethoxyethane to form the corresponding substituted cyclopentadienides, which were reacted with polyfluoroalkyl triflates **11** to afford the corresponding bis(polyfluoroalkylated) cyclopentadienes **9** in good yields (Scheme 4).¹⁵ Another advantage of this approach is that the synthesis of bis(polyfluoroalkylated) cyclopentadienes **9** with two different polyfluorinated chains is feasible. This enables fine tuning of fluorophilic properties of ligands **9**.



Scheme 4

Bis(polyfluoroalkylated) cyclopentadienes **9** synthesized by this method, as well as by the one mentioned above represent a complex mixture of isomers. Separation of this mixture to individual components is extremely difficult if feasible at all and is our main recent target. Nevertheless, in the case of cyclopentadienes substituted by two identical fluoroalkyl chains (**9a**, **9b**) we found by careful analysis of 1D and 2D NMR spectra that the mixtures consist of four regioisomers **A-D** (Figure).¹⁶⁻¹⁹ The ratio of isomers varied depending on the method employed. As an example, cyclopentadiene **9a** prepared by the PTC method contained regioisomers **A**, **B**, **C**, **D** in the 10:52:19:19 ratio, whereas cyclopentadiene **9b** prepared by the triflate method contained less of the main isomer **B** with the corresponding regioisomer ratio 18:39:19:24.



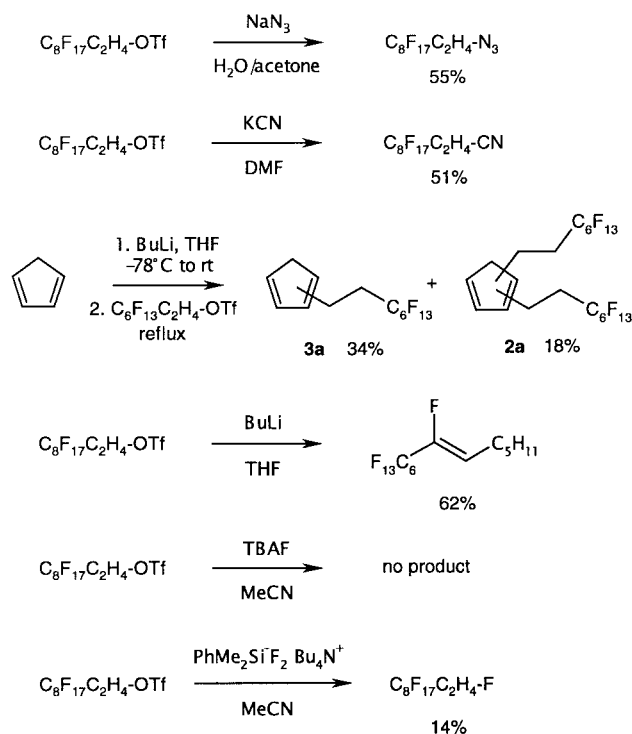
Figure

Polyfluoroalkyl triflates **11** are potentially useful compounds. With the aim to disclose the scope and limitations of their applications, we reacted 2-(perfluorooctyl)ethyl triflate (**11b**) with a series of soft and hard nucleophiles (Scheme 5). With good soft nucleophiles as sodium azide, as well as with weak soft nucleophiles as potassium cyanide or lithium cyclopentadienide, the reaction proceeded smoothly with moderate to good yields. With hard nucleophile like butyllithium, substitution was accompanied by elimination of hydrogen fluoride in contrast to reaction with softer phenyllithium reported in the patent.¹⁴ With hard and weak nucleophiles like TBAF, no products were formed. On the other hand, a softer source of fluoride anion, tetrabutylammonium difluorodimethylphenylsilylate,²⁰ afforded polyfluorodecane in a poor yield.

Polyfluoroalkyl triflates **11**, whose preparation we developed, were used by us for the efficient synthesis of various bis(polyfluoroalkylated) cyclopentadienes **9**. They can also be employed advantageously as fluorinated building blocks for the preparation of substances with polyfluorinated chain.

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Scheme 5

References and Notes

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- Formation of bis(polyfluoroalkylated) cyclopentadienes **9** in small amounts as side-products in the preparation of mono(polyfluoroalkylated) cyclopentadienes **8** by the PTC method has been reported in the literature.⁶
- NMR of 2-(perfluorohexyl)ethyl triflate (**11a**): ¹H NMR δ 2.67 (m, 2H), 4.78 (m, 2H); ¹⁹F NMR δ -75.4 (s, 3F), -81.6 (t, 2F, J = 10 Hz), -114.0 (m, 2F), -122.1 (m, 2F), -123.2 (m, 2F), -123.9 (m, 2F), -126.2 (m, 2F).
- NMR of 2-(perfluorooctyl)ethyl triflate (**11b**): ¹H NMR δ 2.68 (m, 2H), 4.79 (m, 2H); ¹⁹F NMR δ -75.1 (s, 3F), -81.3 (t, 2F, J = 10 Hz), -114.0 (m, 2F), -122.1 (m, 2F), -123.2 (m, 4F), -123.9 (m, 2F), -126.6 (m, 2F).
- We thank Elf Atochem Co. for generous gift of fluorinated iodides and alcohols.
- Preparation of 2-(perfluorooctyl)ethyl triflate (**11b**): The flask was charged with dry CH₂Cl₂, cooled to -10 °C and triflic anhydride (3.04 g, 10.7 mmol) was added to it. After 5 min, a mixture of 2-(perfluorooctyl)ethanol (**10b**, 5.00 g, 10.7 mmol), dry pyridine (0.79 g, 10 mmol), dry CH₂Cl₂ (50 mL) and dry hexane (50 mL) was slowly (40 min) introduced into the mixture while cooled and stirred. Stirring and cooling were maintained for another 40 min, followed by removal of salts by filtration and purification of the crude triflate through short column of silica (eluent: CH₂Cl₂). Removal of solvents in vacuo afforded 4.60 g of solid fluorotriflate **11b** (yield 71.6%), which was recrystallized from hexane (white crystals, m.p. 40-42 °C).
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- Preparation of bis[(2-perfluorohexyl)ethyl]cyclopentadiene (**9a**): The flask was charged with dry THF (50 mL) and [(2-perfluorohexyl)ethyl]cyclopentadiene (**8a**, 1.50 g, 3.63 mmol). The mixture was cooled while stirred to -80 °C and BuLi (2.2 mL, 3.9 mmol) was syringed to it. Stirring was continued for 15 min at -80 °C to r.t. and the mixture was cooled back to -80 °C, followed by addition of 2-(perfluorohexyl)ethyl triflate (**11a**, 2.30 g, 4.63 mmol). The mixture was then refluxed for 16 h. After removing the solvents in vacuo, bis(polyfluoroalkylated) cyclopentadiene **9a** (1.59 g, 57.7%) was obtained by column chromatography (eluent: hexane, R_F 0.9) as a yellowish oil.
- NMR of 1,2-bis[2-(perfluorohexyl)ethyl]cyclopenta-1,3-diene (**9aA**): ¹H NMR δ 2.23 (m, 4H), 2.56 (m, 4H), 2.88 (t, 2H, J = 1.2 Hz), 6.26 (d, 1H, ³J_{HH} = 5.5 Hz), 6.28 (d, 1H, ³J_{HH} = 5.5 Hz, J = 1.2 Hz); ¹³C NMR δ 17.9 (s, 1C), 21.3 (s, 1C), 30.4 (m, 2C), 43.2 (s, 1C), 108.3-121.5 (m, 12C), 131.7 (s, 1C), 133.7 (s, 1C), 138.1 (s, 1C), 143.9 (s, 1C); ¹⁹F NMR δ -81.5 (t, 6F, ³J_{FF} = 10 Hz); -115.2 (m, 4F); -122.4 (m, 4F); -123.4 (m, 4F); -124.0 (m, 4F); -126.7 (m, 4F).
- NMR of 1,3-bis[2-(perfluorohexyl)ethyl]cyclopenta-1,3-diene (**9aB**): ¹H NMR δ 2.23 (m, 4H), 2.56 (m, 4H), 2.84 (quintet, 2H, J = 1.8 Hz), 5.87 (sextet, 1H, J = 1.6 Hz), 6.04 (m, 1H); ¹³C NMR δ 20.6 (s, 1C), 21.3 (s, 1C), 30.4 (m, 2C), 42.9 (s, 1C), 108.3-121.5 (m, 12C), 125.0 (s, 1C), 129.0 (s, 1C), 143.9 (s, 1C), 147.2 (s, 1C); ¹⁹F NMR δ -81.5 (t, 6F, ³J_{FF} = 10 Hz); -115.2 (m, 4F); -122.4 (m, 4F); -123.4 (m, 4F); -124.0 (m, 4F); -126.7 (m, 4F).
- NMR of 1,4-bis[2-(perfluorohexyl)ethyl]cyclopenta-1,3-diene (**9aC**): ¹H NMR δ 2.23 (m, 4H), 2.56 (m, 4H), 2.83 (sextet, 2H, J = 1.8 Hz), 6.04 (m, 2H); ¹³C NMR δ 18.5 (s, 2C), 30.4 (m, 2C), 39.5 (s, 1C), 108.3-121.5 (m, 12C), 127.9 (s, 2C), 143.8 (s, 2C); ¹⁹F NMR δ -81.5 (t, 6F, ³J_{FF} = 10 Hz); -115.2 (m, 4F); -122.4 (m, 4F); -123.4 (m, 4F); -124.0 (m, 4F); -126.7 (m, 4F).
- NMR of 2,3-bis[2-(perfluorohexyl)ethyl]cyclopenta-1,3-diene (**9aD**): ¹H NMR δ 2.23 (m, 4H), 2.56 (m, 4H), 2.79 (t, 2H, J = 1.1 Hz), 6.02 (quintet, 2H, J = 0.9 Hz); ¹³C NMR δ 21.3 (s, 2C), 30.4 (m, 2C), 44.7 (s, 1C), 108.3-121.5 (m, 12C), 127.3 (s, 2C), 143.9 (s, 2C); ¹⁹F NMR δ -81.5 (t, 6F, ³J_{FF} = 10 Hz); -115.2 (m, 4F); -122.4 (m, 4F); -123.4 (m, 4F); -124.0 (m, 4F); -126.7 (m, 4F).
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