Pergamon

TETRAHEDRON

Tetrahedron 58 (2002) 3841–3846

Preparation of bis(polyfluoroalkyl)cyclopentadienes, new highly fluorophilic ligands for fluorous biphase catalysis

Tomáš Bříza,[a] Jaroslav Kvíčala,[a,*] Oldřich Paleta[a] and Jan Čermák[b]

[a]Department of Organic Chemistry, Institute of Chemical Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic
[b]Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, Rozvojová 135, 165 02 Prague 6, Czech Republic

Received 5 November 2001; revised 22 January 2002; accepted 30 January 2002

Abstract—Bis[2-(perfluoroalkyl)ethyl]cyclopentadienes were synthesized from lithium [2-(perfluoroalkyl)ethyl]cyclopentadienides and 2-(perfluoroalkyl)ethyl triflates as mixtures of four regioisomers, structure of which was determined by ^{1}H and ^{13}C NMR spectroscopy. 2-(Perfluoroalkyl)ethyl triflates are useful fluorinated building blocks that can be employed in the synthesis of functionalised polyfluorinated substances. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Trends towards 'green chemistry' have led to the introduction of methods with low environmental impact. Among these methods, homogeneous catalysis in biphase systems with one fluorous phase attracted attention of organofluorine chemists.[1–4] Homogeneous catalysts for fluorous biphase catalysis (FBC) possess fluorophilic properties, which are mostly provided by attached polyfluorinated ligands. Surprisingly, high solubility of fluorophilic homogeneous catalysts in supercritical CO_2 has made them perspective candidates for applications in supercritical CO_2.[5,6]

Basic structural requirement that provides sufficient fluorophilic properties of the catalysts is the overall fluorine content in the molecule, which should exceed 60%.[7,8] Attempts to provide this high fluorine content by extending the length of single fluorinated chain lead to inferior solubility in both phases employed.[8] This results in the need of fluorophilic ligands with multiple fluorinated chains. Phosphines with multiple fluorinated chains can be synthesised relatively easily and are hence mostly used for fluorophilic catalysts.[1,9–12]

Cyclopentadiene based ligands are substantial structure unit for many organometallic compounds and homogeneous catalysts,[13] but only little attention has been paid to the synthesis of cyclopentadiene derivatives with fluorophilic properties.[14,15] Reported cyclopentadienes[14,15] contain only one fluorinated chain. As a consequence, their fluorophilic properties were unsufficient and, therefore, fluorinated cyclopentadienes had to be combined with polyfluorinated phosphine ligands.[14] This stimulated our aim in the synthesis of cyclopentadienes with two attached fluorinated chains and our preliminary results were recently published.[16]

(Perfluoroalkyl)methyl triflates have been employed for the preparation of fluorophilic ligands.[9,17] 2-(Perfluoroalkyl)-ethyl triflates have been prepared by an electrochemical method.[18] Their use as a building block for the preparation of fluorinated aromatic compounds has been patented.[19]

2. Results and discussion

We decided to attach both polyfluoroalkyl groups to the cyclopentadiene ring separately in two steps. We started with the preparation of mono(polyfluoroalkylated)cyclopentadienes **1** according to Ref. 15. We employed two methods reported in Ref. 15, i.e. the reaction of 2-(perfluoroalkyl)ethyl iodides (**2**) with lithium cyclopentadienide, and the reaction of fluoroalkyl iodides **2** with cyclopentadiene (**3**) and potassium hydroxide under PTC conditions. In contrast to the original paper,[15] we were not able to achieve published high yields by the latter method, but the reaction with lithium cyclopentadienide afforded surprisingly high yields (up to 84%) of monosubstituted fluorocyclopentadienes **1**.

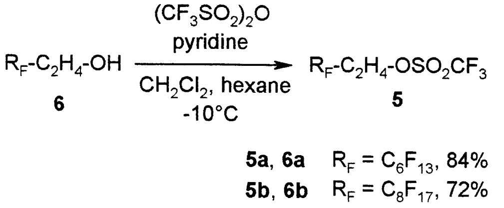
In Ref. 15, formation of bis(polyfluoroalkylated)cyclopentadienes **4** as side products in small amounts is briefly mentioned when the PTC method was employed. We therefore attempted first to prepare bis(polyfluoroalkylated)-cyclopentadienes **4** by this way and employed higher excess of fluoroalkyl iodides **2** and longer reaction times, but the yields of fluorocyclopentadienes **4** were generally poor. We

---

Keywords: fluorous; fluorophilic; fluorocyclopentadiene; bis(polyfluoroalkyl)cyclopentadiene; fluoroalkyl triflate; (perfluoroalkyl)ethyl triflate.

[*] Corresponding author. Tel.: +420-2-2435-4242; fax: +420-2-2435-4288; e-mail: kvicalaj@vscht.cz

0040–4020/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0040-4020(02)00212-0



Scheme 1.

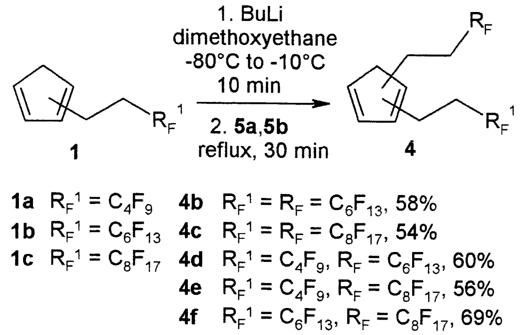
hence used the reaction under the PTC conditions for the preparation of bis(polyfluoroalkylated)cyclopentadienes **4** only before we developed the triflate strategy.

2.1. Preparation of bis[2-(perfluoroalkyl)ethyl]cyclopentadienes from 2-(perfluoroalkyl)ethyl trifluoromethanesulfonates

We successfully lithiated monosubstituted cyclopentadiene **1b** at low temperature, but reaction of anion formed with fluoroalkyl iodide **2b** afforded only low yield of the target bis(polyfluoroalkylated)cyclopentadiene **4b**. We felt that this could be caused by a low reactivity of the leaving group, iodide, attached close to the perfluorinated chain. To overcome this, various fluorinated trifluoromethanesulfonates has been successfully used,[9,17] but the use of 2-(perfluoroalkyl)ethyl triflates (**5**) appeared previously only in patent literature.[19] We prepared two fluorotriflates **5a,b** by slightly modified general procedure reported by Fife[20] from the corresponding 2-(perfluoroalkyl)ethanols **6b**, **6c** in good yields (Scheme 1).

Fluorotriflates **5**, fluorinated electrophiles of superior reactivity compared to fluoroalkyl iodides **2**, were successfully reacted with fluoroalkylated cyclopentadienides to form bis(fluoroalkylated)cyclopentadienides **4**. This confirmed that lithiation of fluorocyclopentadienes **1** proceeded without side reactions, e.g. elimination of lithium fluoride analogous to that observed in the reaction of fluorotriflate **5b** with butyllithium. In the preparation of fluorocyclopentadienes **4**, higher boiling point of the reaction mixture had to be used to guarantee sufficient conversion of the reaction. Hence, 1,2-dimethoxyethane proved to be superior solvent than diethyl ether of THF (Scheme 2).

Bis(polyfluoroalkylated)cyclopentadienes **4** were formed as a complex mixture of regioisomers. Analysis by GC revealed that four regioisomers were formed, which was confirmed by the group analysis of the mixtures by ^{1}H and ^{13}C NMR spectra. We attempted first to separate these regioisomers by column chromatography or by preparative HPLC. However, fluoro cyclopentadienes **4** are compounds of very low polarity without any functional groups and we thus could not find eluent or a mixture of eluents which could distinguish among subtle differences in molecules of individual regioisomers. Even if we tested various mixtures of unpolar hydrophilic and fluorophilic solvents, the maximum we obtained was partial enrichment of some fractions by individual isomers. Moreover, we were not able to separate the regioisomers by preparative GC, as fluoro cyclopentadienes **4** probably formed aerosols and thus, though separated on the column, could not be freezed out from the gaseous mobile phase.



Scheme 2.

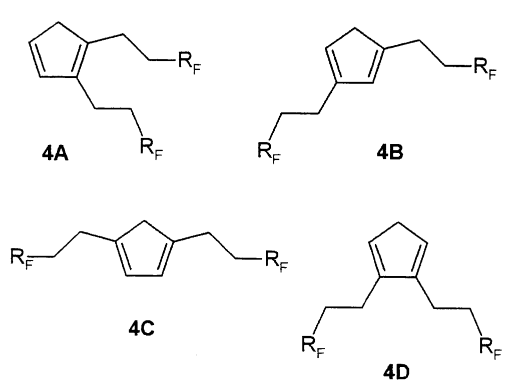
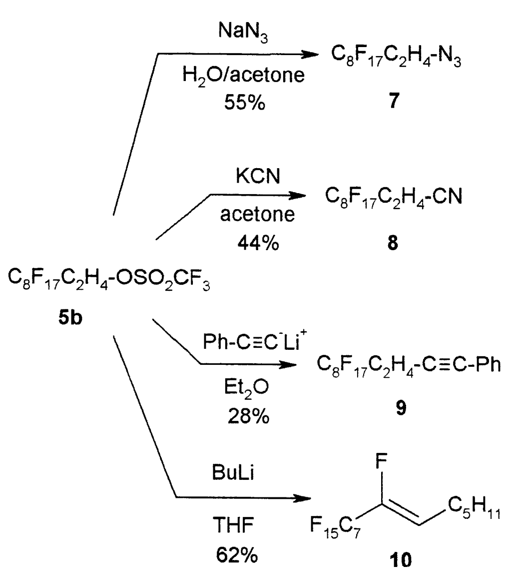


Figure 1. Regioisomers of bis(polyfluoroalkylated)cyclopentadienes **4**.

Fortunately, both methods of the preparation of fluorocyclopentadienes **4** afforded slightly different amounts of regioisomers, what along with the enrichment of some fractions from column chromatography by individual isomers served a helping hand in the determination of the regioisomer ratio, as well as their structure, by detailed analysis of the ^{1}H and ^{13}C NMR spectra.[21] No regioisomers containing fluoroalkyl substituent attached to the ring methylene carbon were formed and the four regioisomers **4A–D** have the structure depicted in Fig. 1.



Scheme 3.

2.2. Reactions of 2-(perfluoroalkyl)ethyl trifluoromethanesulfonates with other nucleophilic reagents

Fluoroalkyl triflates **5** can be used with advantage as fluorinated building blocks with improved reactivity compared to fluoroalkyl iodides **2**. With the aim to disclose scope and limitations of their use, we reacted fluoroalkyl triflate **5b** with a series of nucleophiles (Scheme 3).

Moderate to good yields of the corresponding products **7–9** were obtained by reactions of **5b** with sodium azide, potassium cyanide and lithium 2-phenylacetylide, which reflects that fluorotriflates **5** can be successfully reacted even with nucleophiles of a moderate strength. On the other hand, the reaction of fluorotriflate **5b** with hard nucleophile, butyllithium, was accompanied by the elimination of hydrogen fluoride forming unsaturated product, fluoroalkene **10**. This result shows a limitation of a syntetic use of **5**.

3. Conclusions

Reactions of lithium salts based on mono(polyfluoroalkylated)cyclopentadienes **1** with polyfluoroalkyl trifluoromethanesulfonates **5** proved to be the preferable method for the synthesis of bis(polyfluoroalkylated)cyclopentadienes **4**, which can also be prepared in inferior yields directly from cyclopentadiene (**3**) and fluoroalkyl iodides **2**. By the stepwise method, fluorocyclopentadienes **4** with two different fluoroalkyl ponytails can be formed, which enables fine tuning of the fluorophilic properties. Fluoroalkyl triflates **5** appear to be useful fluorinated building blocks that can be reacted with a wide range of electrophiles except of the hard ones, which eliminate hydrogen fluoride from the fluorinated chain.

4. Experimental

4.1. General comments

Temperature data were not corrected. ^{1}H NMR spectra were recorded with a Varian Gemini 300 HC spectrometer at 300.1 MHz and a Bruker Avance DRX 500 spectrometer at 500.1 MHz using TMS as internal standard. ^{13}C NMR spectra (at 100.6 MHz using Me_4Si as an internal standard) and ^{19}F NMR (at 376.5 MHz using $CFCl_3$ as the internal standard with upfield values designed negative) were measured with a Bruker AMX-3 400 spectrometer. FTIR spectra were recorded with a Nicolet 740 instrument. Elemental analyses were carried out at the Laboratory of Elementary Analyses of ICT Prague.

All manipulations including organometallic reagents, as well as all reactions were performed under an argon atmosphere with exclusion of moisture and atmosferic oxygen in oven-dried apparatuses. 2-(Perfluoroalkyl)ethyl iodides (**2**) and 2-(perfluoroalkyl)ethanols (**6**) were kindly gifted by Elf Atochem. Cyclopentadiene (**3**) was freshly distilled prior to use. (3,3,4,4,5,5,6,6,6-Nonafluorohexyl)cyclopentadiene (**1a**), (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)cyclopentadiene (**1b**) and (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)cyclopentadiene (**1c**) were prepared as mixtures of 1- and 2-substituted regioisomers **1A** and **B** according to Ref. 15 (methods b and c). Concentration of butyllithium solution was estimated prior to use according to Ref. 22. Dry solvents and reagents were obtained using standard procedures. Solvents were discarded from the reaction mixtures with a vacuum rotary evaporator and last traces were removed at 100 Pa. Silica (60–200 μm, Merck) was used for column chromatography. Bis(polyfluoroalkyl)cyclopentadienes slowly decompose at rt and has to be stored in a freezing chamber.

4.2. 2-(Perfluoroalkyl)ethyl triflates (5)[16]

4.2.1. 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl trifluoromethanesulfonate (5a). A flask was charged with dichloromethane (200 mL) and trifluoromethanesulfonic anhydride (23.2 g, 82.2 mmol). The mixture was cooled to −20°C while vigorously stirred and a solution of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol (**6a**, 30.0 g, 82.4 mmol) and pyridine (6.2 g, 78 mmol) in dichloromethane (80 mL) and dioxane (80 mL) was added. The mixture was then stirred at 0°C for 30 min. Salts were filtered off and solvents were removed by evaporation. Purification of the residue by column chromatography (10×4 cm, eluent dichloromethane) followed by vacuum distillation afforded fluoro triflate **5a** as a colourless liquid (34.4 g, 83.9%, bp 53–55°C/11 Pa). IR ($CHCl_3$), 1422, 1244, 1145 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ 2.67 (2H, m), 4.78 (2H, m). ^{13}C NMR ($CDCl_3$), δ 31.3 (t, $^{2}J_{CF}$=21 Hz), 67.7 (s), 107.9–119.2 (6C, m), 113.6 (q, $^{1}J_{CF}$=308 Hz). ^{19}F NMR ($CDCl_3$), δ −75.4 (3F, s), −81.6 (2F, t, J_{FF}=10 Hz), −114.0 (2F, m), −122.1 (2F, m), −123.2 (2F, m), −123.9 (2F, m), −126.2 (2F, m).

4.2.2. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl trifluoromethanesulfonate (5b). A flask was charged with dichloromethane (50 mL) and trifluoromethanesulfonic anhydride (3.04 g, 10.78 mmol). The mixture was cooled to −20°C while intensively stirred and a solution of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecan-1-ol (**6b**, 5.00 g, 10.8 mmol) and pyridine (0.76 g, 9.6 mmol) in dichloromethane (50 mL) and dioxane (50 mL) was added. The mixture was then stirred at 0°C for 30 min. Salts were filtered off and solvents were removed by evaporation. Purification of the residue by column chromatography (10×2.5 cm, eluent dichloromethane) followed by crystallisation (hexane–chloroform 20:1, −10°C) afforded fluoro triflate **5b** as a white powder (4.60 g, 72.3%, mp 40–42°C). IR ($CHCl_3$), 1422, 1245, 1145 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ 2.68 (2H, m), 4.79 (2H, m). ^{13}C NMR ($CDCl_3$), δ 31.3 (t, $^{2}J_{CF}$=21 Hz), 67.6 (s), 107.0–119.5 (8C, m), 118.6 (q, $^{1}J_{CF}$=308 Hz). ^{19}F NMR ($CDCl_3$), δ −75.1 (3F, s), −81.3 (3F, t, J_{FF}=10 Hz), −114.0 (2F, m), −122.1 (2F, m), −123.2 (6F, m), −123.9 (2F, m), −126.6 (2F, m).

4.3. Preparation of bis[2-(perfluoroalkyl)ethyl]cyclopentadienes (4)[16]

4.3.1. Bis(3,3,4,4,5,5,6,6,6-nonafluorohexyl)cyclopentadiene (4a). A three-necked flask equipped with efficient mechanical stirrer was charged with cyclopentadiene (**3**, 3.80 g, 57.5 mmol), excess of 1,1,1,2,2,3,3,4,4-nonafluoro-6-iodohexane (**2a**, 64.5 g, 172 mmol), and benzene

(120 mL). To this mixture, a solution of potassium hydroxide (108 g, 1.92 mol) and hexadecyl(trimethyl)ammonium bromide (1.0 g, 2.75 mmol) in water (120 mL) was added. This two-phase mixture was heated for 1 h to 60°C and 1 h to reflux while vigorously stirred. After cooling to room temperature, the mixture was diluted with water (200 mL/mmol of cyclopentadiene) and extracted with diethyl ether (4×150 mL). Combined organic layers were washed with saturated solution of sodium chloride (50 mL), water (150 mL) and dried over anhydrous magnesium sulfate. Solvents were removed and bis(polyfluoroalkylated)-cyclopentadiene **4a** (5.23 g, 16.3%, bp 102–122°C/360 Pa, colourless oil) was obtained as a mixture of four regioisomers **A**, **B**, **C**, **D** in the 16:52:16:16 ratio along with mono(polyfluoroalkylated)cyclopentadiene **1a** (3.39 g, 18.9%, bp 32–40°C/290 Pa) by fractional vacuum distillation. IR (CHCl$_3$), 2900, 1359, 1228, 1134 cm^{-1}. ^{1}H NMR (CHCl$_3$) regioisomer **A** (1,2-**4a**), δ 2.26 (4H, m), 2.57 (4H, m), 2.88 (2H, t, J=1.2 Hz), 6.27 (1H, d, $^{3}J_{\mathrm{HH}}$=5.5 Hz), 6.29 (1H, d, $^{3}J_{\mathrm{HH}}$=5.5 Hz, J=1.2 Hz); regioisomer **B** (1,3-**4a**), δ 2.26 (4H, m), 2.57 (4H, m), 2.85 (2H, quintet, J=1.8 Hz), 5.87 (1H, sextet, J=1.6 Hz), 6.04 (1H, m); regioisomer **C** (1,4-**4a**), δ 2.26 (4H, m), 2.57 (4H, m), 2.83 (2H, t, J=1.1 Hz), 6.02 (2H, quintet, J=0.9 Hz); regioisomer **D** (2,3-**4a**), δ 2.26 (4H, m), 2.57 (4H, m), 2.79 (2H, sextet, J=1.8 Hz), 6.04 (2H, m); ^{13}C NMR (CHCl$_3$), regioisomer **A** (1,2-**4a**), δ 17.9 (s), 21.3 (s), 30.4 (2C, m), 43.2 (s), 108.2–120.5 (8C, m), 131.7 (s), 133.7 (s), 138.1 (s), 143.9 (s); regioisomer **B** (1,3-**4a**), δ 20.5 (s), 21.3 (s), 30.4 (2C, m), 42.9 (s), 108.2–120.5 (8C, m), 125.0 (s), 129.0 (s), 143.9 (s), 147.2 (s); regioisomer **C** (1,4-**4a**), δ 21.3 (2C, s), 30.4 (2C, m), 44.7 (s), 108.2–120.5 (8C, m), 127.3 (2C, s), 143.9 (2C, s); regioisomer **D** (2,3-**4a**), δ 18.5 (2C, s), 30.4 (2C, m), 39.5 (s), 108.2–120.5 (8C, m), 127.9 (2C, s), 143.9 (2C, s). ^{19}F NMR (CDCl$_3$), δ −81.7 (6F, m), −115.4 (4F, m), −124.9 (4F, m), −126.5 (4F, m). Anal. calcd for C$_{17}$H$_{12}$F$_{18}$: C, 36.58; H, 2.15. Found: C, 37.49; H, 2.60.

4.3.2. General procedure for the preparation from fluoro triflates 5. A flask was charged with [2-(perfluoroalkyl)ethyl]cyclopentadiene (**1**) and 1,2-dimethoxyethane (50 mL/mmol of fluorocyclopentadiene **1**), cooled to −80°C and butyllithium solution was added while stirring. The mixture was heated to −10°C and stirred for 10 min. Then it was cooled again to −80°C and a solution of 2-(perfluoroalkyl)ethyl trifluoromethanesulfonate (**5**) in 1,2-dimethoxyethane (2.5 mL/mmol of fluoroalkyl triflate **5**) was dropwise added to it. The mixture was then heated to reflux for 30 min and cooled to room temperature. Solvents were removed and final product **4** was obtained by column chromatography (15× 2.5 cm, eluent hexane).

4.3.3. Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)cyclopentadiene (4b). Preparation according to procedure 4.4.1 starting from 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane (**2b**, 38.7 g, 51.8 mmol), cyclo-pentadiene (1.90 g, 28.7 mmol), hexadecyl(trimethyl)-ammonium bromide (0.50 g, 1.4 mmol) and potassium hydroxide (54.0 g, 0.96 mol) afforded bis(polyfluoroalkylated)cyclopentadiene **4b** (4.10 g, 19.0%, bp 140–175°C/400 Pa, colourless oil) as a mixture of four regioisomers **A**, **B**, **C**, **D** in the 10:52:19:19 ratio along with mono(polyfluoroalkylated)cyclopentadiene **1b** (2.70 g, 22.8%, bp 60–70°C/400 Pa) as a side-product.

Preparation according to general procedure starting from (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)cyclopentadiene (**1b**, 1.50 g, 3.63 mmol), butyllithium (1.78 M solution in hexanes, 2.2 mL, 3.90 mmol) and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl trifluoromethanesulfonate (**5a**, 2.30 g, 4.63 mmol) afforded bis(polyfluoroalkylated)cyclopentadiene **4b** (1.59 g, 58.0%, colourless oil) as a mixture of four regioisomers **A**, **B**, **C**, **D** in the 21:40:23:16 ratio. IR (neat): 2937, 1460, 1365, 1317, 1239, 1202, 1145 cm^{-1}. ^{1}H NMR (CDCl$_3$), regioisomer **A** (1,2-**4b**), δ 2.23 (4H, m), 2.56 (4H, m), 2.88 (2H, t, J=1.2 Hz), 6.26 (1H, d, $^{3}J_{\mathrm{HH}}$=5.5 Hz), 6.28 (1H, d, $^{3}J_{\mathrm{HH}}$=5.5 Hz, J=1.2 Hz); regioisomer **B** (1,3-**4b**), δ 2.23 (4H, m), 2.56 (4H, m), 2.84 (2H, quintet, J=1.8 Hz), 5.87 (1H, sextet, J=1.6 Hz), 6.04 (1H, m); regioisomer **C** (1,4-**4b**), δ 2.23 (4H, m), 2.56 (4H, m), 2.79 (2H, t, J=1.1 Hz), 6.02 (2H, quintet, J=0.9 Hz); regioisomer **D** (2,3-**4b**), δ 2.23 (4H, m), 2.56 (4H, m), 2.83 (2H, sextet, J=1.8 Hz), 6.04 (2H, m). ^{13}C NMR (CDCl$_3$), regioisomer **A** (1,2-**4b**), δ 17.9 (s), 21.3 (s), 30.4 (2C, m), 43.2 (s), 108.3–121.5 (12C, m), 131.7 (s), 133.7 (s), 138.1 (s), 143.9 (s); regioisomer **B** (1,3-**4b**), δ 20.6 (s), 21.3 (s), 30.4 (2C, m), 42.9 (s), 108.3–121.5 (12C, m), 125.0 (2C, s), 143.9 (s), 147.2 (s); regioisomer **C** (1,4-**4b**), δ 21.3 (2C, s), 30.4 (2C, m), 44.7 (s), 108.3–121.5 (12C, m), 127.3 (2C, s), 143.9 (2C, s); regioisomer **D** (2,3-**4b**), δ 18.5 (2C, s), 30.4 (2C, m), 39.5 (s), 108.3–121.5 (12C, m), 127.9 (2C, s), 143.8 (2C, s). ^{19}F NMR (CDCl$_3$), δ −81.5 (6F, t, $^{3}J_{\mathrm{FF}}$=10 Hz), −115.2 (4F, m), −122.4 (4F, m), −123.4 (4F, m), −124.0 (4F, m), −126.7 (m, 4F). Anal. calcd for C$_{21}$H$_{12}$F$_{26}$: C, 33.62; H, 1.60; Found: C, 33.80; H, 1.76.

4.3.4. Bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)cyclopentadiene (4c). Preparation according to general procedure starting from (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)cyclopentadiene (**1c**, 200 mg, 39.1 μmol), butyllithium (2.50 M solution in hexanes, 0.17 mL, 40.0 μmol) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl trifluoromethanesulfonate (**5b**, 350 mg, 58.7 μmol) afforded bis(polyfluoroalkylated)cyclopentadiene **4c** (200 mg, 53.5%, mp 64–66°C, colourless wax) as a mixture of four regioisomers **A**, **B**, **C**, **D** in the 18:39:24:19 ratio. IR (CHCl$_3$): 2900, 1451, 1203, 1145 cm^{-1}. ^{1}H NMR (CDCl$_3$) regioisomer **A** (1,2-**4c**), δ 2.31 (4H, m), 2.65 (4H, m), 2.95 (2H, t, J=1.2 Hz), 6.34 (1H, d, $^{3}J_{\mathrm{HH}}$=5.5 Hz), 6.36 (1H, d, $^{3}J_{\mathrm{HH}}$=5.5 Hz, J=1.2 Hz); regioisomer **B** (1,3-**4c**), δ 2.31 (4H, m), 2.65 (4H, m), 2.92 (2H, quintet, J=1.8 Hz), 5.94 (1H, sextet, J=1.6 Hz), 6.12 (1H, m); regioisomer **C** (1,4-**4c**), δ 2.31 (4H, m), 2.65 (4H, m), 2.90 (2H, t, J=1.1 Hz), 6.09 (2H, quintet, J=0.9 Hz); regioisomer **D** (2,3-**4c**), δ 2.31 (4H, m), 2.65 (4H, m), 2.86 (2H, sextet, J=1.8 Hz), 6.12 (2H, m); ^{13}C NMR (CDCl$_3$), regioisomer **A** (1,2-**4c**), δ 17.9 (s, CH$_2$), 21.3 (s, CH$_2$), 30.4 (2C, m), 43.3 (s), 107.7–119.1 (16C, m), 131.7 (s), 133.8 (s), 138.1 (s), 143.8 (s); regioisomer **B** (1,3-**4c**), δ 20.6 (s), 21.3 (s), 30.4 (2C, m), 43.0 (s), 107.7–119.1 (16C, m), 125.0 (s), 129.0 (s), 144.0 (s), 147.3 (s); regioisomer **C** (1,4-**4c**), δ 21.3 (2C, s), 30.4 (2C, m), 44.7 (s), 107.7–119.1 (16C, m), 127.3 (2C, s), 144.0 (2C, s); regioisomer **D** (2,3-**4c**), δ 18.5 (2C, s), 30.4 (2C, m), 39.5 (s), 107.7–119.1 (16C, m), 128.0 (2C, s), 143.9 (2C, s). ^{19}F NMR (CDCl$_3$), δ -81.7 (6F, m), -115.2 (4F, m), -122.2 (4F, m), -122.4 (8F, m), -123.2 (4F, m), -124.0 (4F, m), -126.6 (4F, m). Anal. calcd for C$_{25}$H$_{12}$F$_{34}$: C, 31.33; H, 1.25; Found: C, 31.59; H, 1.26.

4.3.5. (3,3,4,4,5,5,6,6,6-Nonafluorohexyl)(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)cyclopentadiene (4d). Preparation according to general procedure starting from (3,3,4,4,5,5,6,6,6-nonafluorohexyl)cyclopentadiene (**1a**, 500 mg, 1.60 mmol), butyllithium (2.15 M solution in hexanes, 0.82 mL, 1.77 mmol) and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl trifluoromethanesulfonate (**5a**, 954 mg, 1.92 mmol) afforded bis(polyfluoroalkylated)cyclopentadiene **4d** (630 mg, 59.8%, colourless oil) as a mixture of four regioisomers **A**, **B**, **C**, **D** in the 23:35:25:17 ratio. IR (CHCl$_3$), 2932, 1454, 1357, 1235, 1135 cm^{-1}. ^{1}H NMR (CDCl$_3$), regioisomer **A** (1,2-**4d**), δ 2.25 (4H, m), 2.55 (4H, m), 2.88 (2H, t, J=1.2 Hz), 6.27 (1H, d, $^3J_{\mathrm{HH}}$=5.5 Hz), 6.28 (1H, d, $^3J_{\mathrm{HH}}$=5.5 Hz, J=1.2 Hz); regioisomer **B** (1,3-**4d**), δ 2.25 (4H, m), 2.55 (4H, m), 2.84 (2H, quintet, J=1.8 Hz), 5.87 (1H, sextet, J=1.6 Hz), 6.04 (1H, m); regioisomer **C** (1,4-**4d**), δ 2.25 (4H, m), 2.55 (4H, m), 2.82 (2H, t, J=1.1 Hz), 6.02 (2H, quintet, J=0.9 Hz); regioisomer **D** (2,3-**4d**), δ 2.25 (4H, m), 2.55 (4H, m), 2.78 (2H, sextet, J=1.8 Hz), 6.04 (2H, m); ^{13}C NMR (CDCl$_3$), regioisomer **A** (1,2-**4d**), δ 18.1 (s), 21.4 (s), 30.4 (2C, m), 43.4 (s), 108.8–118.4 (10C, m), 131.9 (s), 133.9 (s), 138.2 (s), 144.1 (s); regioisomer **B** (1,3-**4d**), δ 20.7 (s), 21.4 (s), 30.4 (2C, m), 43.1 (s), 108.8–118.4 (10C, m), 125.2 (s), 129.2 (s), 144.1 (s), 147.4 (s); regioisomer **C** (1,4-**4d**), δ 21.4 (2C, s), 30.4 (2C, m), 44.9 (s), 108.8–118.4 (10C, m), 127.5 (s), 144.1 (s); regioisomer **D** (2,3-**4d**), δ 18.1 (2C, s), 30.4 (2C, m), 39.7 (s), 108.8–118.4 (10C, m), 128.1 (2C, s), 143.9 (2C, s). ^{19}F NMR (CDCl$_3$), δ -81.3 (3F, m), -81.6 (3F, m), -115.4 (4F, m), -122.4 (2F, m), -123.4 (2F, m), -124.0 (2F, m), -125.0 (2F, m), -126.6 (4F, m). Anal. calcd for C$_{19}$H$_{12}$F$_{22}$: C, 34.67; H, 1.82; Found: C, 35.14; H, 1.95.

4.3.6. (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)(3,3,4,4,5,5,6,6,6-nonafluorohexyl)cyclopentadiene (4e). Preparation according to general procedure starting from (3,3,4,4,5,5,6,6,6-nonafluorohexyl)cyclopentadiene (**1a**, 500 mg, 1.60 mmol), butyllithium (2.3 M solution in hexanes, 0.77 mL, 1.77 mmol) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl trifluoromethanesulfonate (**5b**, 1.146 g, 1.92 mmol) afforded bis(polyfluoroalkylated)cyclopentadiene **4e** (680 mg, 56.0%, light yellow oil) as a mixture of four regioisomers **A**, **B**, **C**, **D** in the 22:44:16:18 ratio. IR (CHCl$_3$), 2928, 1454, 1357, 1212, 1134 cm^{-1}; ^{1}H NMR (CDCl$_3$), regioisomer **A** (1,2-**4e**), δ 2.20 (4H, m), 2.54 (4H, m), 2.86 (2H, (2H, t, J=1.2 Hz), 6.24 (1H, d, $^3J_{\mathrm{HH}}$=5.5 Hz), 6.26 (1H, d, $^3J_{\mathrm{HH}}$=5.5 Hz, J=1.2 Hz); regioisomer **B** (1,3-**4e**), δ 2.20 (4H, m), 2.54 (4H, m), 2.82 (2H, quintet, J=1.8 Hz), 5.84 (1H, sextet, J=1.6 Hz), 6.02 (1H, m); regioisomer **C** (1,4-**4e**), δ 2.20 (4H, m), 2.54 (4H, m), 2.80 (2H, t, J=1.1 Hz), 5.99 (2H, m); regioisomer **D** (2,3-**4e**), δ 2.20 (4H, m), 2.54 (4H, m), 2.76 (2H, sextet, J=1.8 Hz), 6.02 (2H, m); ^{13}C NMR (CDCl$_3$), regioisomer **A** (1,2-**4e**), δ 18.0 (s, CH$_2$), 21.3 (s, CH$_2$), 30.4 (2C, m), 43.3 (s), 108.4–120.6 (12C, m), 131.8 (s), 133.8 (s), 138.2 (s), 144.1 (s); regioisomer **B** (1,3-**4e**), δ 20.6 (s), 21.3 (s), 30.4 (2C, m), 43.0 (s), 108.4–120.6 (12C, m), 125.0 (s), 129.0 (s), 144.1 (s), 147.3 (s); regioisomer **C** (1,4-**4e**), δ 21.3 (2C, s), 30.4 (2C, m), 44.8 (s), 108.4–120.6 (12C, m), 127.4 (2C, s), 143.9 (2C, s); regioisomer **D** (2,3-**4e**), δ 18.6 (2C, s), 30.4 (2C, m), 39.5 (s), 108.4–120.6 (12C, m), 128.0 (2C, s), 143.9 (2C, s); ^{19}F NMR δ (CDCl$_3$), δ -81.5 (3F, m), -81.8 (3F, m), -115.3 (4F, m), -122.2 (2F, m), -122.4 (4F, m), -123.2 (2F, m), -124.0 (2F, m), -124.9 (2F, m), -126.5 (4F, m); Anal. calcd for C$_{21}$H$_{12}$F$_{26}$: C, 33.26; H, 1.58; Found: C, 32.73; H, 1.67.

4.3.7. (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-cyclopentadiene (4f). Preparation according to general procedure starting from (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)cyclopentadiene (**1b**, 500 mg, 1.21 mmol), butyllithium (2.3 M solution in hexanes, 0.58 mL, 1.33 mmol) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl trifluoromethanesulfonate (**5b**, 1.084 g, 1.82 mmol) afforded bis(polyfluoroalkylated)cyclopentadiene **4f** (720 mg, 69.2%, light yellow oil) as a mixture of four regioisomers **A**, **B**, **C**, **D** in the 21:49:12:18 ratio. IR (CHCl$_3$), 2929, 1453, 1366, 1206, 1145 cm^{-1}. ^{1}H NMR (CDCl$_3$), regioisomer **A** (1,2-**4f**), δ 2.32 (4H, m), 2.64 (4H, m), 2.96 (2H, t, J=1.2 Hz), 6.34 (1H, d, $^3J_{\mathrm{HH}}$=5.5 Hz), 6.36 (1H, d, $^3J_{\mathrm{HH}}$=5.5 Hz, J=1.2 Hz); regioisomer **B** (1,3-**4f**), δ 2.32 (4H, m), 2.64 (4H, m), 2.92 (2H, quintet, J=1.8 Hz), 5.95 (1H, sextet, J=1.6 Hz), 6.12 (1H, m); regioisomer **C** (1,4-**4f**), δ 2.32 (4H, m), 2.64 (4H, m), 2.90 (2H, t, J=1.1 Hz), 6.09 (2H, quintet, J=0.9 Hz); regioisomer **D** (2,3-**4f**), δ 2.32 (4H, m), 2.64 (4H, m), 2.87 (2H, sextet, J=1.8 Hz), 6.12 (2H, m); ^{13}C NMR (CDCl$_3$), δ regioisomer **A** (1,2-**4f**), δ 18.0 (s, CH$_2$), 21.4 (s, CH$_2$), 30.5 (2C, m), 43.3 (s), 108.4–120.7 (14C, m), 131.8 (s), 133.8 (s), 138.2 (s), 144.0 (s); regioisomer **B** (1,3-**4f**), δ 20.6 (s, CH$_2$), 21.4 (s, CH$_2$), 30.5 (2C, m), 43.0 (s), 108.4–120.7 (14C, m), 125.1 (s), 129.0 (s), 144.0 (s), 147.2 (s); regioisomer **C** (1,4-**4f**), δ 21.3 (2C, s), 30.5 (2C, m), 44.8 (s), 108.4–120.7 (14C, m), 127.3 (2C, s), 144.0 (2C, s); regioisomer **D** (2,3-**4f**), δ 18.6 (2C, s), 30.5 (2C, m), 39.6 (s), 108.4–120.7 (14C, m), 128.0 (2C, s), 143.8 (2C, s). ^{19}F NMR (CDCl$_3$), δ -81.4 (6F, m), -115.2 (4F, m), -122.2 (2F, m), -122.4 (6F, m), -123.2 (2F, m), -123.4 (2F, m), -124.0 (4F, m), -126.7 (4F, m); Anal. calcd for C$_{23}$H$_{12}$F$_{30}$: C, 32.19; H, 1.40; Found: C, 31.69; H, 1.74.

4.4. Reactions of fluoro triflate 5b with nucleophiles

4.4.1. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylazide (7). A flask was charged with acetone (10 mL, water (5 mL), sodium azide (87 mg, 1.34 mmol) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl trifluoromethanesulfonate (**5b**, 250 mg, 0.42 mmol). The mixture was refluxed for 2 h, then cooled to room temperature, diluted with water (20 mL) and extracted with diethyl ether (3×20 mL). Combined organic layers were dried over anhydrous magnesium sulfate and solvents were removed by evaporation. Purification of the residue by column chromatography (10×2 cm, eluent hexane) afforded fluoro azide **7** as a colourless oil (112 mg, 54.6%), which gave IR and NMR spectra identical with Ref. 23.

4.4.2. 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoroundecanenitrile (8). A flask was charged with acetone (20 mL, potassium cyanide (116 mg, 1.75 mmol) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl trifluoromethanesulfonate (**2b**, 700 mg, 1.17 mmol). The mixture was refluxed overnight (16 h), then cooled to room temperature and salts were removed by filtration. Purification of the residue by column chromatography (20×2 cm, eluent hexane–dichloromethane 1:1) afforded fluoro nitrile **8** as white crystals[24] (246 mg, 44.2%, mp 64–66°C). IR (CHCl$_3$), 2362, 2219, 1260, 1173, 1039 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ 2.53 (2H, m), 2.70 (2H, t, $^3J_{HH}$=7.7 Hz). ^{13}C NMR δ (CDCl$_3$) 9.8 (s), 27.6 (t, $^2J_{CF}$=21 Hz), 116.8 (s). ^{19}F NMR (CDCl$_3$), δ −81.2 (3F, t), −114.0 (2F, m), −122.2 (2F, m), −122.4 (4F, m), −123.2 (2F, m), −124.2 (2F, m), −126.6 (2F, m). Anal. calcd for $C_{11}H_4F_{17}N$: C, 27.92 H, 0.85. Found: C, 27.65 H, 0.88.

4.4.3. 5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluoro-1-phenyldodec-1-yne (9). A flask was charged with diethylether (15 mL) and ethynylbenzene (100 mg, 0.98 mmol), the mixture was cooled to −80°C while stirred and butyllithium (2.5 M solution in hexanes, 0.43 mL, 1.08 mmol) was added. After warming to 20°C, the mixture was transferred by a syringe to a stirred solution of fluoro triflate (**2b**, 500 mg, 800 μmol) in diethyl ether (20 mL) at room temperature. The mixture was then refluxed for 3.5 h. After cooling to room temperature, water (2 mL) was added and the crude reaction mixture was extracted with water (3×30 mL). Combined organic layers were dried with anhydrous magnesium sulfate and solvents were evaporated. Purification of the residue by column chromatography (10×2.5 cm, eluent hexane) afforded fluoro ethyne **9** as white crystals (130 mg, 28.3%, mp 31–32°C). IR (CHCl$_3$), 3023, 2927, 1600, 1492, 1445, 1202, 1148 cm^{-1}. ^{1}H NMR (CDCl$_3$), δ 2.46 (2H, m), 2.75 (2H, t, $^3J_{HH}$=7.6 Hz), 7.36 (5H, m). ^{13}C NMR (CDCl$_3$), δ 11.5 (t, $^3J_{CF}$=5.6 Hz), 30.8 (t, $^2J_{CF}$=22 Hz), 81.8 (s), 86.2 (s), 107.3–120.5 (8C, m), 123.2 (s), 128.1 (s), 128.3 (s), 131.6 (s). ^{19}F NMR (CDCl$_3$), δ −81.7 (3F, m), −115.2 (2F, m), −122.2 (2F, m), −122.4 (4F, m), −123.2 (2F, m), −124.0 (2F, m), −126.6 (2F, m). Anal. calcd for $C_{18}H_9F_{17}$: C, 39.44; H, 1.64. Found: C, 39.83; H, 1.75.

4.4.4. 7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Hexadecafluorotetradec-6-ene (10). A flask was charged with THF (20 mL) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl trifluoromethanesulfonate (**2b**, 250 mg, 0.42 mmol). The mixture was cooled to −80°C and butyllithium (1.78 M, 0.35 mL, 0.63 mmol) was added. The mixture was then stirred at 0°C over 2 h, followed by removal of solvents by evaporation. Purification of the residue by column chromatography (5×2.5 cm, eluent diethyl ether) afforded fluoro alkene **10** as semi-solid crystals (126 mg, 62.2%) which gave IR and NMR spectra identical to those given in Ref. 25.

Acknowledgements

We thank the Grant Agency of the Czech Republic for financial support of this work (Grant No. 203/99/0135).

References

1. Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72–75.
2. Horváth, I. T. *Acc. Chem. Res.* **1998**, *31*, 641–650.
3. Hope, E. G.; Stuart, A. M. *J. Fluorine Chem.* **1999**, *100*, 75–83.
4. Fish, R. H. *Chem. Eur. J.* **1999**, *5*, 1677–1680.
5. Kainz, S.; Koch, D.; Baumann, W.; Leitner, W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1628–1630.
6. Koch, D.; Leitner, W. *J. Am. Chem. Soc.* **1998**, *120*, 13398–13404.
7. Barthel-Rosa, L. P.; Gladysz, J. A. *Coord. Chem. Rev.* **1999**, *190–192*, 587–605.
8. Kiss, L. E.; Kövesdi, I.; Rábai, J. *J. Fluorine Chem.* **2001**, *108*, 95–109.
9. Alvey, L. J.; Rutherford, D.; Juliette, J. J. J.; Gladysz, J. *J. Org. Chem.* **1998**, *63*, 6302–6308.
10. Bhattacharyya, P.; Gudmunsen, D.; Hope, E. G.; Kemmitt, R. D. W.; Paige, A. M.; Stuart, J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3609–3612.
11. Kainz, S.; Luo, Z.; Curran, D. P.; Leitner, W. *Synthesis* **1998**, 1425–1427.
12. Richter, B.; Spek, A. L.; van Koten, G.; Deelman, B.-J. *J. Am. Chem. Soc.* **2000**, *122*, 3945–3951.
13. Keenan, M. J. Cyclopentadiene and dicyclopentadiene. 4th ed, *Kirk-Othmer Encyclopedia of Chemical Technology*; Kroschwitz, J. I., Howe-Grant, M., Eds.; Wiley: Chichester, 1993; Vol. 7, pp 859–876.
14. Herrera, V.; de Rege, P. J. F.; Horváth, I. T.; Le Husebo, T.; Hughes, R. P. *Inorg. Chem. Commun.* **1998**, *1*, 197–199.
15. Hughes, R. P.; Trujillo, H. A. *Organometallics* **1996**, *15*, 286–294.
16. Bříza, T.; Kvíčala, J.; Mysík, P.; Paleta, O.; Čermák, J. *Synlett* **2001**, 685–687.
17. Sinou, D.; Pozzi, G.; Hope, E. G.; Stuart, A. M. *Tetrahedron Lett.* **1999**, *40*, 849–852.
18. Germain, A.; Commeyras, A. *Tetrahedron* **1981**, 487–492.
19. Iwahara, M. JP 07179384 1996; *Chem. Abstr.* **1996**, *124*, 8394.
20. Fife, W. K.; Ranganathan, P.; Zeldin, M. *J. Org. Chem.* **1990**, *55*, 5610.
21. Identification of the structure of individual regioisomers by 1D and 2D NMR methods required a lot of brain work, as well as precise NMR measurements. The details of the assignment will be given in the following paper together with the NMR analysis of regioisomers of organometallic complexes based on bis(polyfluoroalkylated)cyclopentadienes **4**.
22. Furniss, B. S.; Hammford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*; 5th ed; Wiley: New York, 1991; pp 443–444.
23. Szonyi, F.; Cambon, A. *J. Fluorine Chem.* **1989**, *42*, 59–68.
24. Ooishi, T. JP 05331127 1993; *Chem. Abstr.* **1997**, *121*, 108011.
25. Chauvin, A.; Greiner, J.; Pastor, R.; Cambon, A. *J. Fluorine Chem.* **1984**, *25*, 259–261.