Journal of Organometallic Chemistry 695 (2010) 537–545

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis and fluxional behaviour of new "heavy fluorous" cyclopentadienes

Lucie Červenková Šťastná *, Jan Čermák, Petra Cuřínová, Jan Sýkora

Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, v.v.i., Rozvojová 135, 165 02 Prague 6, Czech Republic

ARTICLE INFO

Article history:
Received 6 October 2009
Received in revised form 13 November 2009
Accepted 16 November 2009
Available online 24 November 2009

Keywords:
Heavy fluorous cyclopentadienes
Titanium cyclopentadienyl complex
Polyfluoroalkylsilanes
Fluxional behaviour
Variable temperature NMR

ABSTRACT

The new "heavy fluorous" cyclopentadienes $C_5H_{6-n}[M(C_2H_4C_6F_{13})_3]_n$ (M = Si, n = 1 (**3**); n = 2 (**4**) and M = Sn, n = 1 (**10**)) were synthesized by reaction of cyclopentadienyl lithium with $BrSi(C_2H_4C_6F_{13})_3$ (**2**) or commercial $BrSn(C_2H_4C_6F_{13})_3$. Fluorous cyclopentadienes prepared in this manner contain three or six C_6F_{13} groups, which significantly increase their solubility in perfluorinated solvents. They also provide intermediates for titanium complexes suitable for fluorous biphase catalysis. All three isomers of silylcyclopentadienes **3** and **4** were identified and fully characterized by two dimensional NMR spectroscopy, which was performed at low temperature. The allylic isomers **3a** and **4a** undergo degenerate metallotropic rearrangement. This fluxional behaviour was compared with the behaviour of previously prepared cyclopentadienes **6** and **7** ($C_5H_{6-n}[SiMe_2(C_2H_4C_8F_{17})]_n$ where n = 1, 2, respectively). The presence of allylic isomers **6a** and **7a** was further confirmed by Diels-Alder cycloaddition of the strong dienophile tetracyanoethylene (TCNE), providing compounds **8** and **9**.

1. Introduction

A number of cyclopentadienes substituted with one or two "ponytails" (fluoroalkyl chains of the formula $(CH_2)_m(CF_2)_{n-1}CF_3$ (often abbreviated $(CH_2)_mR_{fn}$)), and their complexes have been reported previously [1]. The "heavy fluorous" cyclopentadienes (with three to five $(CH_2)_mR_{f8}$ chains) were prepared by irradiation of the manganese complexes [2]. The complexes are extremely soluble in perfluorinated solvents and they are potentially suitable for fluorous biphase catalysis, especially with the respect to catalyst recycling. Another way to prepare the "heavy fluorous" cyclopentadienes is *via* substitution reactions using polyfluoroalkylsilanes [3], which have C_6F_{13} or longer chains. These silanes have been used for the synthesis of fluorinated aryl compounds [4]. The silicon atom on the aromatic ring has a positive inductive effect and reduces the strong electron-withdrawing properties of the ponytails. We have previously reported the synthesis of fluorinated silylcyclopentadienes [5] and their fluorophilic properties [6]. Synthesis of similar cyclopentadienes has been reported by van Koten et al. [7]. In these cases [5–7] the cyclopentadienes and their Ti or Zr complexes were substituted by only one ponytail on the silicon atom. According to the literature, cyclopentadienylsilanes can have a maximum of four silyl groups [8]; namely in the 2,3,5,5-positions. For further synthesis of the cyclopentadienyl complex at least one hydrogen in position 5 is needed and thus cyclopentadiene can be modified with a maximum of three silyl groups [8].

Cyclopentadienylsilanes show fluxional behaviour [9]. Metallotropic shifts take place at room temperature and prototropic shifts prevail at elevated temperature, both resulting in the interconversion of individual isomers (Si–allyl and Si–vinyl). This coalescence leads to the broadening of resonances at room temperature in the ^1H and ^{13}C NMR spectra. The ligand used can significantly affect the isomer ratio, as documented by a series of cyclopentadienylsilanes of the type $C_5H_5SiMe_{3-x}Cl_x$ [8]. The relative abundance of the vinylic isomer increases with the number of chlorine ligands or with temperature. In trimethylsilylcyclopentadiene the 1,2-prototropic shift is 10^6 times slower than the 1,2-silatropic shift [10]. The activation energy of the metallotropic shift in cyclopentadienylsilanes was determined to be 13.1–18.6 kcal/mol [11,12]. The free energy of activation of the migration process increases in the series Sn, Ge, Si, C. In comparison to silane, the cyclopentadienetrimethylstannane is a highly fluxional molecule with a free energy of activation of 7.8 kcal/mol. The migration of the trimethylstannyl group ceased at −150 °C [13].

Here we report the synthesis of new "heavy fluorous" cyclopentadienes with three fluorocarbon chains of length C_6F_{13} at a single silicon or tin atom. Further shielding of the ponytail is provided by the $-CH_2CH_2-$ spacer. The monosubstituted cyclopentadiene bears three fluoroalkyl chains and the disubstituted bears six. The preparation of these ligands always gives a mixture of isomers. They are air and moisture sensitive, but have high boiling points, making separation almost impossible. Fortunately, every isomer can be identified in low-temperature NMR spectra, even when in a mixture of mono- and disubstituted ligands. Thus, in principle, no separation is needed. The fluxional behaviour of these

* Corresponding author. Tel.: +420 220390273; fax: +420 220920661.
E-mail address: stastna@icpf.cas.cz (L. Červenková Šťastná).

0022-328X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2009.11.021

compounds is discussed, and compared with the behaviour of cyclopentadienes substituted with the $-SiMe_2(C_2H_4C_8F_{17})$ group, whose synthesis was published previously [5].

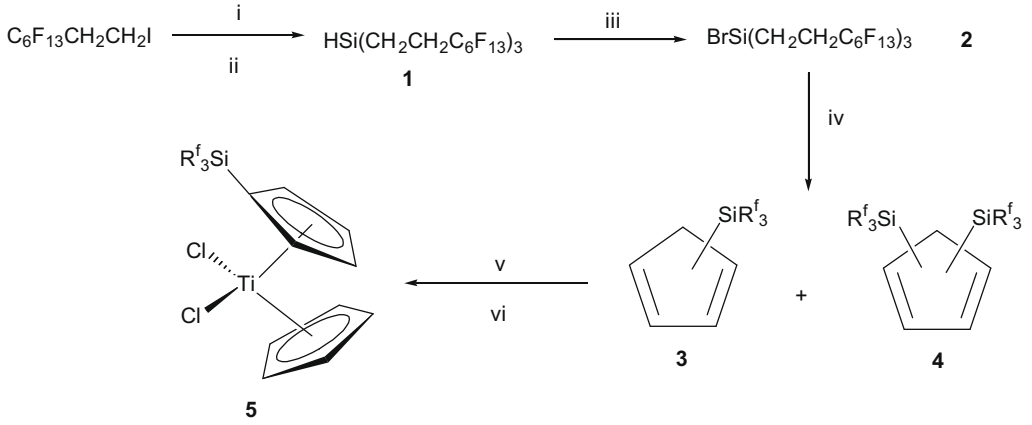
2. Results and discussion

2.1. Synthesis of polyfluoroalkylsilane

Preparation of polyfluorinated silane **1** was attempted, starting from a fluorinated Grignard reagent and according to a literature procedure [4], but with little success. The product obtained in this reaction was impure and consisted of *ca* 22% $O[Si(C_2H_4C_6F_{13})_3]_2$ and 25% dimer $C_6F_{13}C_4H_8C_6F_{13}$. The low reaction yield made further synthesis impractical. We improved the synthesis of **1** by the reaction of $C_6F_{13}C_2H_4I$ with *t*-BuLi, according to a literature procedure [14], followed by reaction with $HSiCl_3$ (Scheme 1). This method was very efficient and a 95% conversion of the organolithium intermediate was achieved. The yield of product **1** was 84%. The product contained only 11% $O[Si(C_2H_4C_6F_{13})_3]_2$. This side product was prepared independently by hydrolysis of **2** and identified by ^1H and ^{29}Si NMR spectroscopy.

2.2. Synthesis and identification of isomers of fluorinated silylcyclopentadienes

Cyclopentadienes **3** were obtained, as a mixture of the three possible isomers (Fig. 1), by the reaction of polyfluorinated bromosilane **2** and cyclopentadienyl lithium. Three isomers of a disubstituted by-product **4** (8% in total) were also obtained. All monosubstituted isomers of **3** (1-, 2- and 5-isomer) were identified *via* low temperature ^1H NMR spectroscopy (Fig. 2). The ^1H NMR measurements were performed at 0 °C because although at lower temperatures the lines were narrower an additional signal overlap occurred at 3.15 ppm (isomer **3c** and **4c**). The allylic region was crucial for isomer identification. The signals of CH or CH_2 groups were resolved from edited gHSQC spectra and the further connectivity to the vinylic protons was assigned from gCOSY spectra. The final structure of an individual isomer was proposed from proton signal integration (Table 1). This procedure revealed three isomers of **3** (as mentioned above) and three isomers of **4** (2,5-, 1,3- and 1,4-isomer) in the product mixture. The structures are shown in Fig. 1. Only disubstituted cyclopentadienes where the silyl groups are not in neighbouring positions were formed. We also propose that two silyl groups, both bearing three bulky $-CH_2CH_2C_6F_{13}$



(i) *t*-BuLi; (ii) $HSiCl_3$, (iii) Br_2, (iv) CpLi, (v) BuLi, (vi) $TiCpCl_3$; $R^f = CH_2CH_2C_6F_{13}$

Scheme 1.

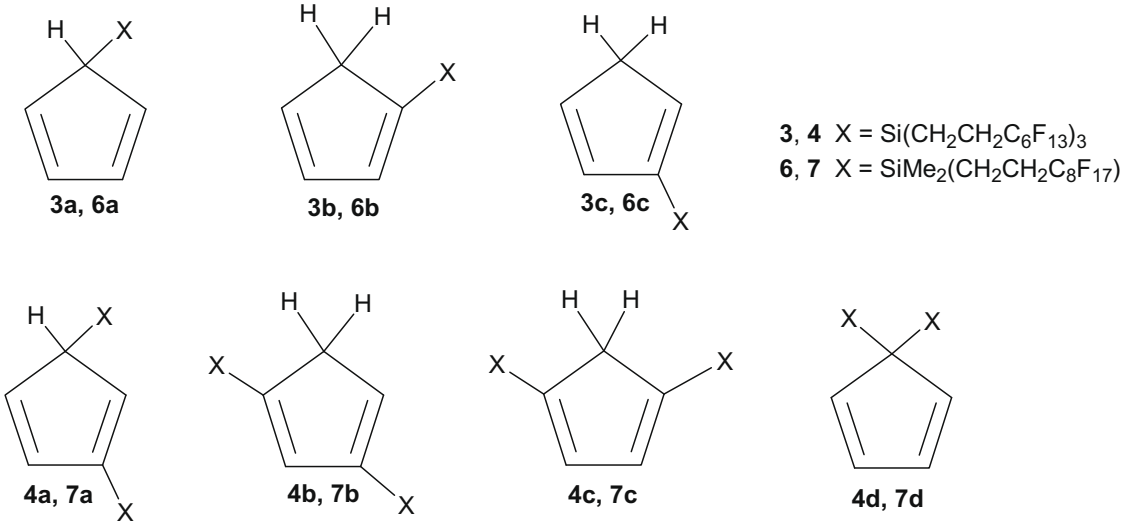


Fig. 1. Isomers of cyclopentadienes **3**, **4**, **6** and **7**.

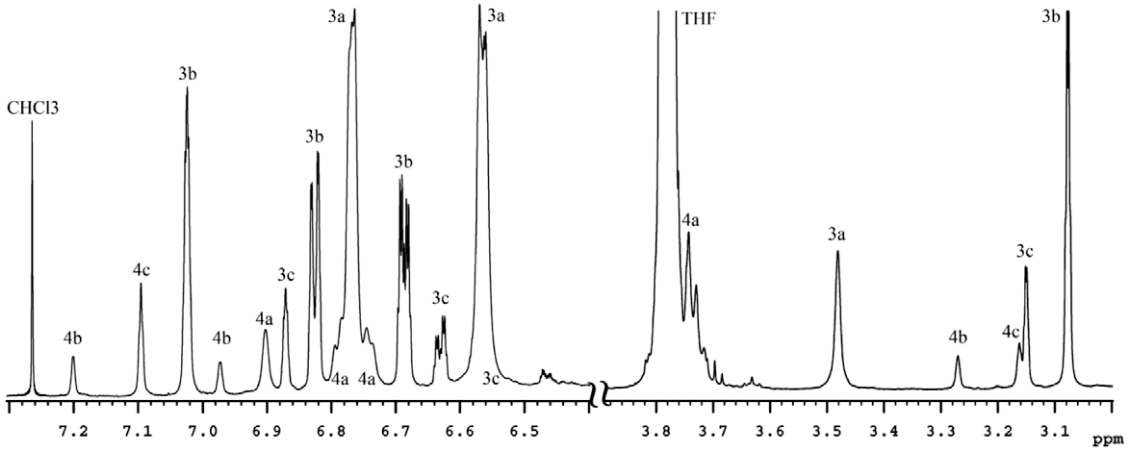


Fig. 2. ^{1}H NMR spectrum of cyclopentadienes **3** and **4** measured at 0 °C.

Table 1
Proportion of individual isomers in the mixture of compounds **3** and **4**.

	3a	3b	3c	4a	4b	4c
Integration of allylic proton signal	1	2	2	1	2	2
Integration of vinylic proton signals	2:2	1:1:1	1:1:n.r.	1:1:1	1:1	2
Proportion	40%	30%	10%	10%	5%	5%

n.r.: not resolved due to signal overlap; the signal was observed in the COSY spectrum at 6.51 ppm.

Table 2
Proportion of individual isomers in the mixture of compounds **6** and **7**.

	6a	6b	6c	7a	7b	7c	7d
Integration of allylic proton signal	1	2	2	1	2	2	–
Integration of vinylic proton signals	2:2	1:1:1	1:1:n.r.	1:1:1	1:1	2	2:2
Proportion	20%	4%	1%	25%	2%	4%	44%

n.r.: not resolved due to signal overlap; the signal was observed in the COSY spectrum at 6.51 ppm.

chains, cannot simultaneously occupy positions 5 of the cyclopentadiene ring due to steric hindrance, contrary to the situation in the other disubstituted cyclopentadiene **7**, where the main isomer is **7d** [5]. As can be seen from Fig. 2, no isomer **4d** was detected.

NMR studies revealed the composition of the mixture to be in the ratio of 4:1 for **3:4** and 9:1 for **6:7** [5]. At 0 °C the proportion of monosubstituted isomers was approximately 4:3:1 (**3a**:**3b**:**3c**) and of disubstituted isomers 1:0.5:0.5 (**4a**:**4b**:**4c**) (see Table 1). This composition was stable over the temperature range studied, 263–313 K. A 1D-NOESY experiment was used to differentiate between isomers **3b** and **3c**. In this experiment, **3b** showed the simultaneous interaction of CH_2 (in the cyclopentadiene) and one vinylic proton with the irradiated CH_2 group in the ponytail.

The most important ^{13}C signals were determined from gHMBC and gHSQC NMR spectra. The signals in the ^{29}Si NMR spectrum were assigned according to the integration of signals in the ^{1}H spectra and the characteristic chemical shift of the allylic or vinylic silicon signals. The signals of the allylic silicons were found further downfield (higher ppm).

Previously [5] we suggested that the mixture of isomers of cyclopentadiene **7** consisted of all seven possible isomers. Now, after more detailed NMR study, we report that the mixture contains four isomers of compound **7** and three isomers of monosubstituted cyclopentadiene **6** (Table 2). An attempt to separate **6** and **7** by distillation was not successful, and simply resulted in an increase in the proportion of **7** present in the mixture (Fig. 3). Other separation techniques were not attempted as **6** and **7**, like **3** and **4**, were highly air and moisture sensitive. The identification of the individual components in the mixture of cyclopentadienes **6** and **7** was performed at −5 °C. The same NMR experiments as in the case of cyclopentadiene **3** were used. The ^{29}Si resonances were

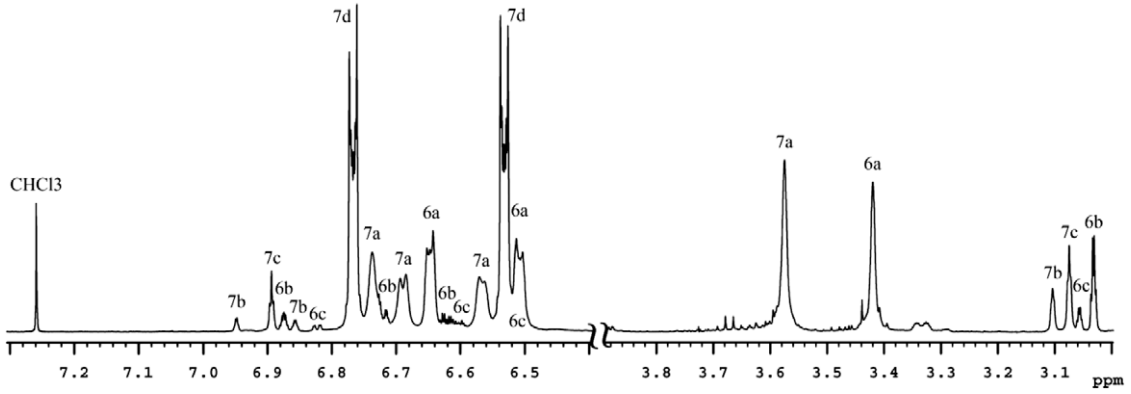


Fig. 3. ^{1}H NMR spectrum of cyclopentadiene **6** and **7** measured at −5 °C. The vertical scale of the allylic region has been doubled.

assigned only for the main isomers; the signals of **6b**, **6c** and **7b** were not assigned. Only the spectral range where the signals were found is given (see Section 4).

2.3. Fluxional behaviour of fluorinated silylcyclopentadienes

As for other monosubstituted cyclopentadienes [5,7,8], the most populated isomer **3a** (5-isomer) undergoes a degenerate metallotropic shift at a rate comparable to the NMR time-scale, which causes signal broadening at room temperature. Lowering of the temperature can slow down the metallotropic shift and cause narrowing of the NMR signals. The AA′BB′X system can initially be recognized at 273 K. A variable temperature NMR study was performed in the range 263–313 K in a sealed NMR tube; due to the insolubility of **3** in $CDCl_3$, a mixture of solvents $CDCl_3$ and $C_2F_3Cl_3$ (in the ratio 1:1) was used. The simulation of experimental spectra confirmed the 1,2-silyl shift and provided the activation parameters (Table 3). The most populated disubstituted isomer **4a** (2,5-isomer) also showed a metallotropic shift that was assigned to a degenerate 1,2-silyl shift 2,5 → 2,5′ (Fig. 4). The simulation of this behaviour relied mostly on the fitting of the separated vinyl proton at 6.9 ppm (H1). The other signals were almost useless at higher temperatures due to strong signal overlap (Fig. 5). Nevertheless, some thermodynamic data could be derived.

The allylic isomers of **6** and **7** displayed similar behaviour. A variable temperature NMR study was performed in the range 273–313 K. Lower temperatures could not be reached as the sample became inhomogeneous; a higher temperature measurement, in a sealed NMR tube, was not attempted. The narrower temperature range was found to be satisfactory for most of the compounds studied. The activation parameters were calculated only for the monosubstituted isomer **6a**, which, like **3a**, undergoes a degenerate metallotropic shift *via* a 1,2-silyl shift. Problems occurred during simulation of disubstituted isomer **7a**. The fluxional behaviour of this isomer cannot be fitted simply as a degenerate 2,5 → 2,5′ shift similar to that of **4a**, mentioned above. Furthermore, the 5,5-isomer (**7d**), which is not present in the mixture of **3** and **4,** shows a linear signal decrease with rising temperature and signal broadening (Fig. 6). Both effects indicate some additional dynamic processes. Isomer interconversion can be also observed in the ^{29}Si NMR spectra.

Table 3
Activation parameters obtained from an Eyring plot for the dynamic processes in the cyclopentadienes studied.

	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/K mol)	$\Delta G^{\ddagger}_{300}$ (kcal/mol)
3a	10.2 ± 0.2	−17.3 ± 0.4	15.4 ± 0.2
4a	11.1 ± 0.2	−13.3 ± 0.4	15.1 ± 0.2
6a	10.3 ± 0.1	−16.8 ± 0.2	15.4 ± 0.1

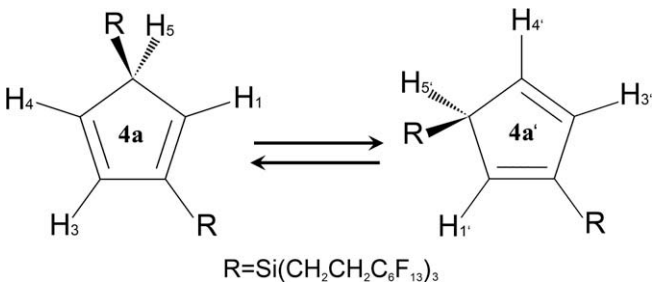


Fig. 4. Schematic depiction of the degenerate 1,2-silyl shift of **4a** (2,5 → 2,5′). H3 → H1′ (H3′ → H1) and H4 → H5′ (H4′ → H5) exchange takes place.

The ^{29}Si quantitative NMR measurements proved that the signal decrease for the 5,5-isomer over the temperature range 273–313 K is accompanied by a signal increase of a third for the allylic silicon atom in the 2,5-isomer. Simultaneously, there was an increase in the strength of the signals in the vinylic silicon region by two thirds (Fig. 7); it was not possible to accurately integrate the individual signals in this region, which is why the region was integrated as a whole. The increase in signal strength of both silicon signals in the 2,5-isomer should be equal. The discrepancy of one third can be attributed to the missing 1,5-isomer, which presents a rational step in the 5,5 → 2,5 isomer pathway [9] (Fig. 8). Nevertheless, all attempts to fit this complex dynamic behaviour in the ^1H NMR spectra using a gNMR program [15] failed.

2.4. Diels-Alder reaction of tetracyanoethylene (TCNE) with cyclopentadienes *6* and *7*

The cyclopentadienes **6** and **7** were reacted with strong dienophile TCNE at 25 °C (Scheme 2). In the case of cyclopentadiene **6**, only the product from the main isomer **6a** was obtained. In the reaction of isomers of **7** the most reactive isomer was not the most populated **7d**, but the fluxional **7a** (2,5-isomer). The reaction yield (70%) confirmed the interconversion of the 5,5-isomer **7d** into **7a**, as suggested above (Fig. 8), and hence its further reaction with TCNE. No reaction products were observed from the vinylic isomers. The Diels-Alder reactions of **6** and **7** with the strong dienophile TCNE gave only products **8** and **9**, respectively. The 2D-NOESY experiment showed the hydrogen atom H7 in the exo position (pointing towards the cyano groups) in both cases (Scheme 2).

2.5. Fluorinated cyclopentadienylstannane

Commercially available polyfluorinated bromostannane ($BrSn(CH_2CH_2C_6F_{13})_3$) was used for the synthesis of fluorinated cyclopentadiene **10** (Scheme 3). In this case, the activation energy of the 1,2-stannyl shift is very low in comparison to that of the 1,2-proton shift and thus only the highly fluxional allylic isomer can be observed under normal conditions. In the ^1H NMR spectrum of cyclopentadiene **10**, only one signal (δ = 6.19 ppm) was observed for all five ring protons at 25 °C and at −40 °C. The signal of the ring protons is accompanied by $^{117/119}Sn$ satellites showing the $^2J(^{117/119}Sn, ^1H)$ coupling constant is equal to 23 Hz.

2.7. Fluorinated dichlorotitanocene

The fluorinated cyclopentadienes **6** and **7** can be used in the preparation of dichlorotitanocene complexes, as shown previously [5,6]. These complexes are more stable than the free ligands and can be isolated more easily. The dichlorotitanocene complex of **6** ($Ti[Cp(SiMe_2(C_2H_4C_8F_{17}))]_2Cl_2$) provided a crystal structure [5].

Analogous to **6** and **7**, the cyclopentadiene **3** was used for the synthesis of the titanium(IV) complex **5**, which was synthesized from a monocyclopentadienyltrichlorotitanium(IV) complex (see Scheme 1). Reaction of the mixture of **3** and **4** gave the dichlorotitanocene complex and some impurities. The yield of complex **5** was 64%.

3. Conclusion

The new "heavy fluorous" cyclopentadienes were synthesized by the reaction of cyclopentadienyl lithium with $BrSi((CH_2)_2R_{f6})_3$. Ligands (**3**, **4**) prepared by this method contain three or six ponytails, which significantly increase their solubility in perfluorinated solvents and their usage in biphase catalysis, in contrast to those substituted by only one or two chains (**6**, **7**). The substituent has

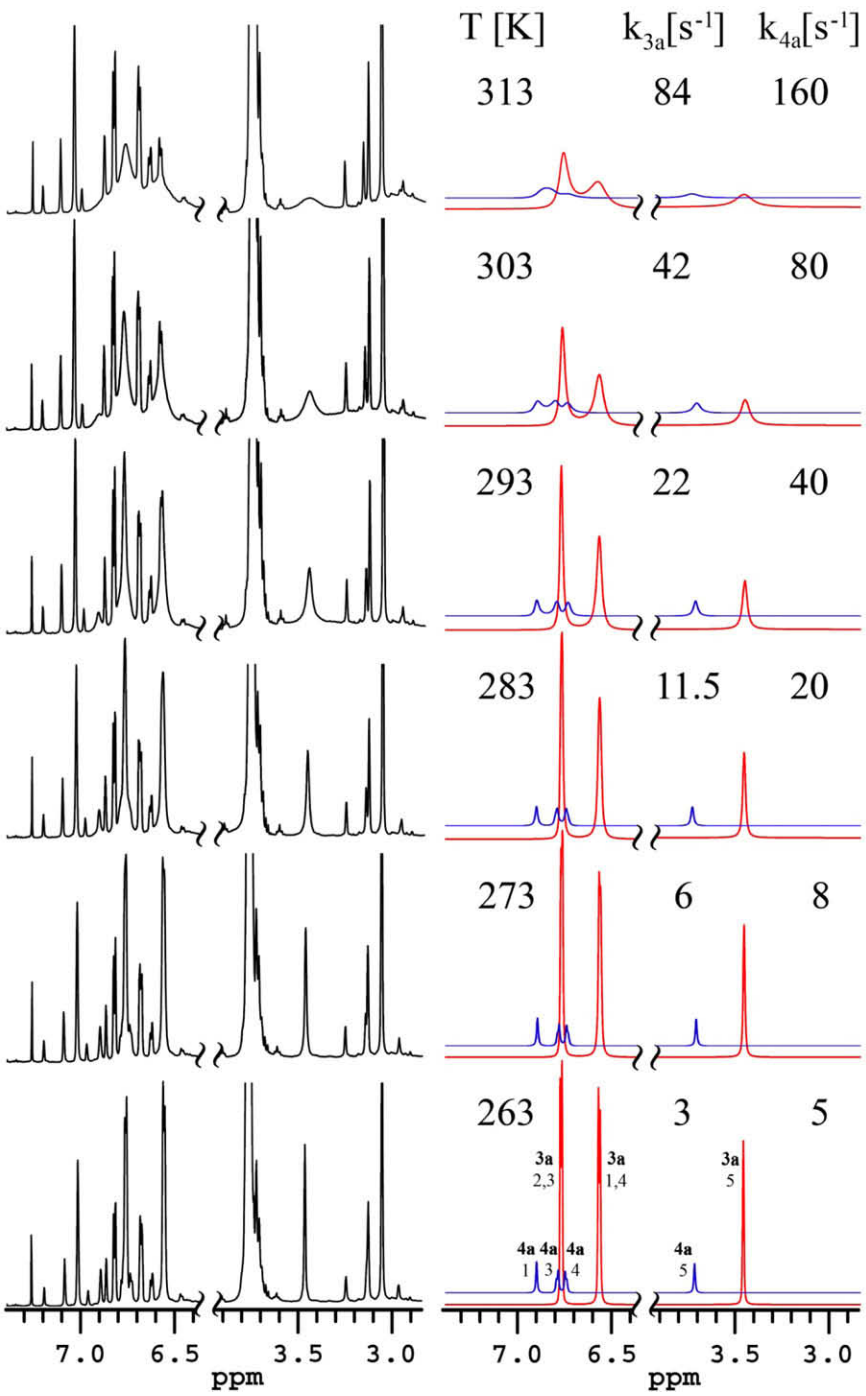


Fig. 5. Ring protons in the ^{1}H NMR spectra of the mixture of **3** and **4**; experimental (black) and simulated (red for **3a** and blue for **4a**), measured in a solvent mixture of $CDCl_3$ and $C_2F_3Cl_3$ (in the ratio 1:1) in the temperature range 263–313 K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

no effect on the fluxional behaviour of the monosubstituted cyclopentadienes **3a** and **6a**. However, the fluxional behaviour of the disubstituted cyclopentadienes shows significant differences between isomers. The $-Si((CH_2)_2R_{f6})_3$ group is such a sterically demanding substituent that it disables disubstitution of the cyclopentadiene ring in the neighbouring ring positions. Thus the 5,5-isomer (**4d**) was not detected, whilst the 5,5-isomer **7d** prevails among the isomers of **7** (T = 268 K). A degenerate 1,2-silatropic shift was observed for the 2,5-isomer (**4a**). Isomer **7d** undergoes a non-degenerate 1,2-silatropic shift and the population of **7a** increases with temperature. Moreover the presence of the 1,5-isomer was deduced.

4. Experimental

4.1. General procedures

All experiments were carried out in anhydrous conditions under an inert atmosphere of argon or nitrogen, using standard Schlenk or glove box techniques. Solvents were dried by the usual procedures, then distilled and kept under argon. $CDCl_3$, $CF_2ClCFCl_2$ and FC-84 (a commercially available fluorocarbon liquid with an average molecular weight of 388 and with a b.p. of 80 °C) were dried over molecular sieves and stored under argon. Solutions of butyllithium and *tert*-butyllithium, 3,3,4,4,5,5,6,6,7,7,8,8,8-trid-

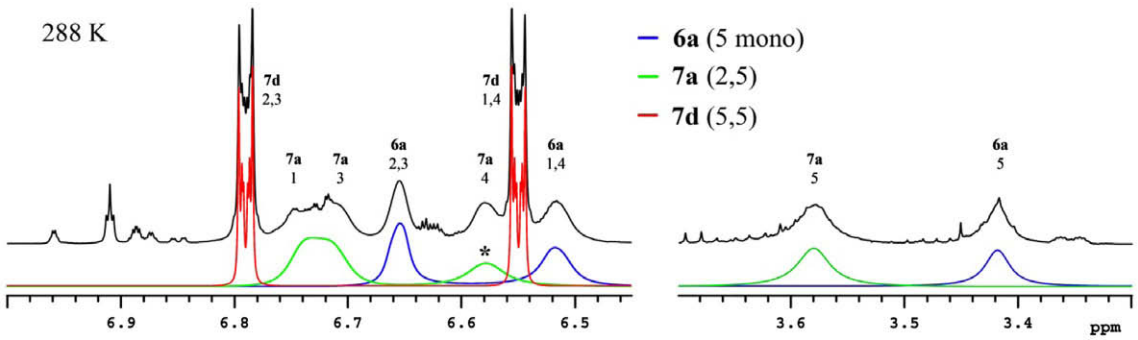


Fig. 6. Simulation of the fluxional behaviour in a mixture of **6** and **7** at 288 K; experimental (black) and simulated (blue for **6a**, green for **7a** and red for **7d**). The signal of H1 in **7a** (marked with the asterisk) reveals an exchange at half the speed of the other hydrogens in the molecule at this temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

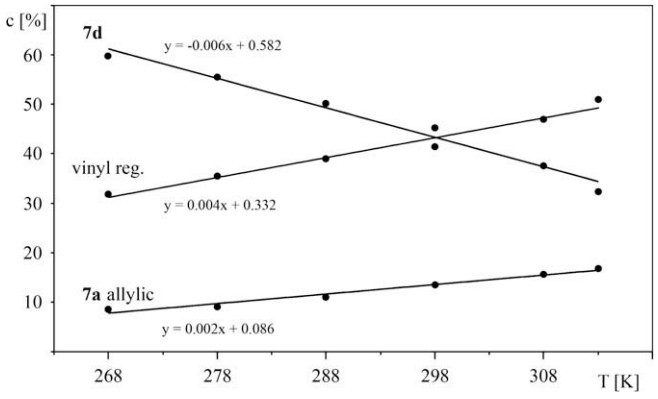


Fig. 7. Dependence of the allylic isomer ratio of **7** on temperature; taken from the quantitative ^{29}Si NMR spectra.

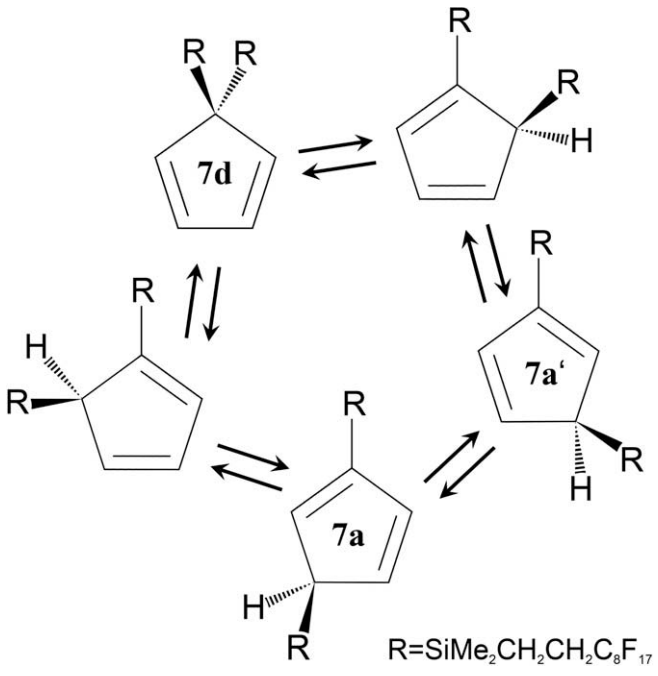
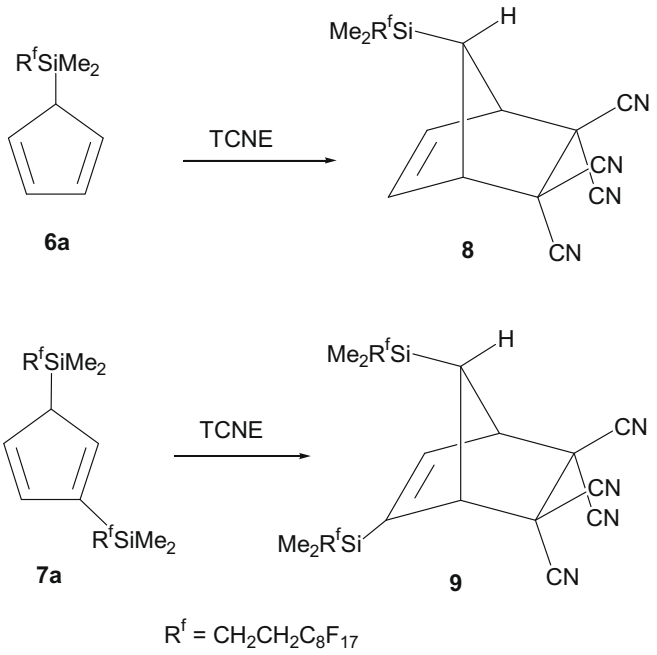
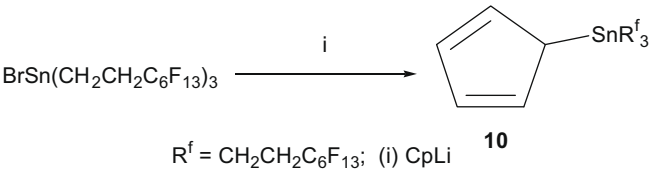


Fig. 8. Schematic depiction of the 1,2-sigmatropic shift pathway in allylic derivatives of **7**; the interconversion of 5,5- (**7d**) into 2,5- (**7a**) *via* the 1,5-isomer.

ecafluorooctyliodide, bromotris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)stannane, bromine and TCNE were obtained from commercial suppliers and used without further purification. Commercially obtained trichlorosilane was freshly distilled before use. The Cyclopentadienyltrichlorotitanium complex [16], cyclopentadienyl lithium [17], bromotris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane **2** [18], [(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilyl]cyclopentadiene **6** [5] and [bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilyl]cyclopentadiene **7** [5] were prepared according to literature methods. ^{1}H, ^{13}C {1H}, ^{119}Sn {1H} and ^{29}Si {1H} (inept technique) NMR spectra were recorded on a Varian Mercury 300 spectrometer at 300, 75, 112 and 60 MHz, respectively, in a mix-



Scheme 2.



Scheme 3.

ture of solvents $CDCl_3$ and $CF_2ClCFCl_2$ (1:1), unless otherwise stated. Variable temperature ^{1}H NMR spectroscopy was performed on a Varian Inova 500 spectrometer. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to hexamethyldisilane, except ^{119}Sn (relative to external $Sn(CH_3)_4$). The variable temperature ^{1}H NMR spectra were analyzed using a gNMR program [15]. Activation parameters were obtained from the modified Eyring equation: $\ln(k/T) = -\Delta H^{\ddagger}/RT + (23.76 + \Delta S^{\ddagger}/R)$ using least-squares fit to linear plot $\ln(k/T)$ versus $1/T$ [19]. The ^{29}Si NMR spectra for the quantitative analysis of the fluxional behaviour of **7** were measured by INEPT pulse sequence modified for the $SiMe_2(CH_2-)$ group [20].

Elemental analyses were carried out at the laboratory of elementary analysis of IOCB Prague.

4.2. Synthesis of tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (**1**)

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyliodide (6.43 g, 11.20 mmol) was dissolved in a mixture of pentane (30 mL) and diethyl ether (20 mL). The solution was stirred and cooled to −78 °C before addition of 1.7 M *t*-butyllithium in pentane (7.20 mL, 12.24 mmol). The mixture was stirred for 5 min. Freshly distilled trichlorosilane (0.36 mL, 3.55 mmol) was added and the solution was frozen immediately. The temperature was then raised to 0 °C. The reaction mixture was stirred for 1 h at 0 °C and then poured onto ice (*ca* 5.00 g) and stirred for 15 min. The resulting biphasic mixture was filtered through silica gel. The layers were separated and the aqueous phase was extracted with ethylacetate (3 × 50 mL). The combined organic phases were dried ($MgSO_4$) and evaporated to afford a yellow oil consisting of 89% product (3.36 g, 3.14 mmol) and 11% of the impurity di[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)siloxane] (0.84 g, 0.39 mmol). The yield of the silane was 84% based on the starting iodide. ^{1}H NMR (25 °C, 300 MHz): δ 0.96 (m, 6H), 2.08 (m, 6H), 3.93 (bs, 1H). ^{29}Si{1H} NMR (25 °C, 60 MHz): δ −2.39 (s, 1Si). Di[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)siloxane] ^{1}H NMR (25 °C, 300 MHz): δ 0.96 (m, 12H), 2.08 (m, 12H). ^{29}Si{1H} NMR (25 °C, 60 MHz): δ 8.12 (s, 1Si).

4.3. Synthesis of [tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]cyclopentadiene (**3**)

Cyclopentadienyl lithium (0.025 g, 0.347 mmol) was dissolved in 10 mL of THF at 0 °C. The prepared bromosilane **2** (0.403 g, 0.351 mmol) was added dropwise to the solution, stirred for 1 h at 0 °C and then allowed to warm to ambient temperature (25 °C). The colour of the reaction mixture changed to dark green, and it was stirred overnight (18 h). The solvent was removed under vacuum and then the product was extracted with fluorinated solvent FC-84. The solvent was evaporated to afford a brown oil (0.408 g) containing product **3** (0.233 g, 0.205 mmol), *bis*[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]cyclopentadiene (**4**) (0,053 g, 0,024 mmol) and impurity di[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)siloxane] (0.122 g, 0.057 mmol, 20%). The yield of the cyclopentadienes **3** and **4** was 72% based on the starting fluorinated bromosilane.

4.3.1. Isomer **3a**

^{1}H NMR (0 °C, 500 MHz): δ 0.92 (m, 6H), 2.00–2.20 (m, 6H), 3.48 (bs, 1H), 6.66 (system AA′BB′, 4H). ^{13}C{1H} NMR (0 °C, 125 MHz): δ 4.89 (bs, 3Si–*C*H$_2$), 25.28 (bt, 3CF$_2$–*C*H$_2$), 47.31 (s, 1 > *C*H), 104–120 (m, 6*C*F$_n$), 131.66 (bs, 2*C*H=), 132.94 (bs, 2*C*H=). ^{29}Si{1H} NMR (25 °C, 100 MHz): δ 5.50 (s, 1Si).

4.3.2. Isomer **3b**

^{1}H NMR (0 °C, 500 MHz): δ 0.88 (m, 6H), 2.0–2.20 (m, 6H), 3.08 (m, 2H), 6.69 (m, 1H), 6.83 (m, 1H), 7.03 (m, 1H). ^{13}C{1H} NMR (0 °C, 125 MHz): δ 1.62 (s, 3Si–*C*H$_2$), 25.28 (bt, 3CF$_2$–*C*H$_2$), 44.46 (s, 1*C*H$_2$), 104–120 (m, 6*C*F$_n$), 133.05 (s, 1*C*H=), 137.84 (s, 1 > *C*=), 139.87 (s, 1*C*H=), 146.48 (s, 1*C*H=). ^{29}Si{1H} NMR (25 °C, 100 MHz): δ −3.88 (s, 1Si).

4.3.3. Isomer **3c**

^{1}H NMR (0 °C, 500 MHz): δ 0.88 (m, 6H), 2.00–2.20 (m, 6H), 3.15 (m, 2H), 6.56 (m, 1H), 6.63 (m, 1H), 6.87 (m, 1H). ^{13}C{1H} NMR (0 °C, 125 MHz): δ 1.87 (s, 3Si–*C*H$_2$), 25.28 (bt, 3CF$_2$–*C*H$_2$), 44.31 (s, 1*C*H$_2$), 104–120 (m, 6*C*F$_n$), 133.59 (s, 1*C*H=), 135.19 (s, 1*C*H=), 147.02 (s, 1*C*H=), 138.31 (s, 1 > *C*=). ^{29}Si{1H} NMR (25 °C, 100 MHz): δ −3.77 (s, 1Si).

4.3.4. Isomer **4a**

^{1}H NMR (0 °C, 500 MHz): δ overlap signals with compound **3** (m, 12H), 2.00–2.20 (m, 12H), 3.74 (bs, 1H), 6.74 (bm, 1H), 6.79 (bm, 1H), 6.9 (bm, 1H) ^{13}C{1H} NMR (0 °C, 125 MHz): δ overlap signals with compound **3** (*C*H$_2$), 51.19 (bs, 1 > *C*H), 104–120 (m, 12*C*F$_n$), 134.11 (bs, 1*C*H=), 134.93 (bs, 1*C*H=), 144.16 (bs, 1*C*H=), not detected due to low concentration (s, 1>*C*<). ^{29}Si{1H} NMR (25 °C, 100 MHz): δ −3.66 (s, 1Si), 6.17(s, 1Si).

4.3.5. Isomer **4b**

^{1}H NMR (0 °C, 500 MHz): δ overlap signals with compound **3** (m, 12H), 2.00–2.20 (m, 12H), 3.27 (bm, 2H), 6.97 (bm, 1H), 7.20 (bm, 1H). ^{13}C{1H} NMR (0 °C, 125 MHz): δ overlap signals with compound **3** (*C*H$_2$), 48.42 (s, 1 > *C*H$_2$), 104–120 (m, 12*C*F$_n$), not detected due to low concentration (s, 1*C*H=), (s, 1*C*H=), (s, 1>*C*<). ^{29}Si{1H} NMR (25 °C, 100 MHz): δ −3.26(s, 1Si), −3.33(s, 1Si).

4.3.6. Isomer **4c**

^{1}H NMR (0 °C, 500 MHz): δ overlap signals with compound **3** (m, 12H), 2.00–2.20 (m, 12H), 3.16 (bs, 2H), 7.10 (bm, 2H). ^{13}C{1H} NMR (0 °C, 125 MHz): δ overlap signals with compound **3** (*C*H$_2$), 49.55 (bs, 1*C*H$_2$), 105–120 (m, 12*C*F$_n$), 146.07 (bs, 2*C*H=), not detected due to low concentration (s, 1>*C*<). ^{29}Si{1H} NMR (25 °C, 100 MHz): δ −3.33 (s, 2Si).

4.4. Synthesis of [{η^5-C_5H_5}{η^5-$C_5H_4Si(CH_2CH_2C_6F_{13})_3$}TiCl$_2$] (**5**)

A suspension of **3** (0.077 g, 0.070 mmol) in 15 mL of hexane was stirred and cooled to 0 °C. A 2.87 M solution of butyllithium (0.024 mL, 0.068 mmol) was added dropwise to the suspension at 0 °C. The reaction mixture was allowed to come to ambient temperature (25 °C) and stirred for 2 h. After decantation the hexane solution was separated by syringe and the residue was dried under vacuum and then dissolved in 10 mL of THF. This dark solution was added dropwise to a yellow solution of (η^5-cyclopentadienyl)trichlorotitanium(IV) complex (0.015 g, 0.068 mmol) in 10 mL of THF. The yellow reaction mixture became reddish and was stirred overnight (18 h). The solvent was evaporated and the product was extracted with 25 mL of pentane. The extract was filtered and the solvent was evaporated under vacuum. Chromatography on silica gel (diethylether/hexane, 2:1) gave complex **5** as red oil (0.057 g, 0.043 mmol, 63%). ^{1}H NMR (25 °C, 500 MHz): δ 0.81–0.87 (m, 6H), 1.8–2.0 (m, 6H), 6.61 (s, 5H), 6.67 (system AA′BB′, 4H). ^{13}C{1H} NMR (25 °C, 125 MHz): δ 3.69 (s, 3Si–*C*H$_2$), 25.86 (t, $^2J_{CF}$ = 24.1 Hz, 3CF$_2$–*C*H$_2$), 105–122 (m, 5*C*F$_2$, 1*C*F$_3$), 115.60 (s, 2*C*H=), 120.77 (s, 5*C*H=), 127.94 (s, 1 > *C*=), 131.56 (s, 2*C*H=). ^{29}Si{1H} NMR (25 °C, 100 MHz): δ −1.42 (s, Si). *Anal.* Calc. for $C_{34}H_{21}Cl_2F_{39}SiTi$: C, 31.00; H, 1.61. Found: C, 31.07; H, 1.67%.

4.5. Determination of isomers of $C_5H_5SiMe_2(CH_2CH_2C_8F_{17})$ (**6**)

Synthesis of cyclopentadiene **6** was published previously [5].

At −30 °C the spin system AA′BB′X of the ring protons of cyclopentadiene **6a** and the coupling constants were recognized: δ(A,A′) = 6.65 ppm; δ(B,B′) = 6.51 ppm; δ(X) = 3.42 ppm; $^3J_{AA'} = {}^4J_{BB'}$ = 1.8 Hz; $^3J_{AB} = {}^3J_{A'B'}$ = 4.9 Hz; $^4J_{AB'} = {}^4J_{A'B}$ = 1.5 Hz; $^4J_{AX} = {}^4J_{A'X}$ = 1.1 Hz; $^3J_{BX'} = {}^3J_{B'X}$ = 1.2 Hz. Signals of higher field BB′ belong to protons at the positions 1 and 4.

4.5.1. Isomer **6a**

^{1}H NMR ($CDCl_3$, −5 °C, 500 MHz): δ 0.02 (bs, 6H), 0.67 (m, 2H), 1.85–2.20 (m, 2H), 3.42 (bs, 1H), 6.51 (m, 2H), 6.65 (m, 2H). ^{13}C{1H} NMR ($CDCl_3$, −5 °C, 125 MHz): δ −2.36 (s, 2*C*H$_3$); 3.97 (s, Si–*C*H$_2$), 25.42 (t, $^2J_{CF}$ = 23.6 Hz, CF_2–*C*H$_2$), 50.75 (bs, 1 > *C*H), 104–120 (m, 8*C*F$_n$), 130.97 (bs, 2*C*H=), 132.78 (bs, 2*C*H=). ^{29}Si{1H} NMR ($CDCl_3$, −5 °C, 100 MHz): δ 4.18 (s, 1Si).

4.5.2. Isomer **6b**

^{1}H NMR ($CDCl_3$, −5 °C, 500 MHz): δ 0.88 (m, 2H), 1.85–2.20 (m, 2H), 3.03 (m, 2H), 6.62 (m, 1H), 6.72 (m, 1H), 6.87 (m, 1H). ^{13}C{1H} NMR ($CDCl_3$, −5 °C, 125 MHz): δ 45.15 (s, 1*C*H$_2$), 104–120 (m, 8*C*F$_n$), 133.14 (s, 1*C*H=), 138.74 (s, 1*C*H=), 143.26 (s, 1*C*H=), 144.70 (s, 1 > *C*=). ^{29}Si{1H} NMR ($CDCl_3$, −5 °C, 100 MHz): δ −7.29 to −7.39 (s, 1Si).

4.5.3. Isomer **6c**

^{1}H NMR ($CDCl_3$, −5 °C, 500 MHz): δ 1.04 (m, 2H), 1.85–2.20 (m, 2H), 3.06 (m, 2H), 6.60 (m, 1H), 6.82 (m, 2H). ^{13}C{1H} NMR ($CDCl_3$, −5 °C, 125 MHz): δ 44.07 (s, 1*C*H$_2$), 104–120 (m, 8*C*F$_n$). ^{29}Si{1H} NMR ($CDCl_3$, −5 °C, 100 MHz): δ −7.29 to −7.39 (s, 1Si).

4.6. Determination of isomers of $C_5H_4[SiMe_2(CH_2CH_2C_8F_{17})]_2$ (**7**)

Synthesis of cyclopentadiene **7** was published previously [5].

4.6.1. Isomer **7a**

^{1}H NMR ($CDCl_3$, −5 °C, 500 MHz): δ 0.12 (bs, 6H), 0.21 (bs, 6H), 0.61 (m, 2H), 0.90 (m, 2H), 1.85–2.20 (m, 4H), 3.58 (bs, 1H), 6.57 (bm, 1H), 6.69 (bm, 1H), 6.74 (bm, 1H). ^{13}C{1H} NMR ($CDCl_3$, −5 °C, 125 MHz): −3.26 (s, 2*C*H$_3$), 3.78 (s, *C*H$_2$), 5.04 (s, *C*H$_2$), 25.92 (t, $^2J_{CF}$ = 22.9 Hz, *C*H$_2$), 53.83 (bs, 1 > *C*H), 104–120 (m, 16*C*F$_n$), 133.50 (bs, 1*C*H=), 134.05 (bs, 1*C*H=), 142.90 (bs, 1*C*H=), 143.08 (s, 1>*C*<). ^{29}Si{1H} NMR ($CDCl_3$, −5 °C, 100 MHz): δ −7.43 (bs, 1Si), 4.28 (bs, 1Si).

4.6.2. Isomer **7b**

^{1}H NMR ($CDCl_3$, −5 °C, 500 MHz): 0.88 (m, 4H), 1.85–2.20 (m, 12H), 3.11 (bm, 2H), 6.86 (m, 1H), 6.95 (m, 1H). ^{13}C{1H} NMR ($CDCl_3$, −5 °C, 125 MHz): 47.86 (s, 1 > *C*H$_2$), 104–120 (m, 16*C*F$_n$), 144.16 (s, 1*C*H=), 145.43 (s, 1CH=), 149.40 (s, 1>*C*<). ^{29}Si{1H} NMR ($CDCl_3$, −5 °C, 100 MHz): δ −7.29 to −7.39 (s, 1Si), δ −7.29 to −7.39 (s, 1Si).

4.6.3. Isomer **7c**

^{1}H NMR ($CDCl_3$, −5 °C, 500 MHz): 0.88 (m, 4H), 1.85–2.20 (m, 4H), 3.07 (bm, 2H), 6.90 (bm, 2H). ^{13}C{1H} NMR ($CDCl_3$, −5 °C, 125 MHz): 48.95 (s, 1 > *C*H$_2$), 105–120 (m, 16*C*F$_n$), 143.62 (s, 2*C*H=), 150.85 (s, 2>*C*<). ^{29}Si{1H} NMR ($CDCl_3$, −5 °C, 100 MHz): δ −7.35 (s, 2Si).

4.6.4. Isomer **7d**

^{1}H NMR ($CDCl_3$, −5 °C, 500 MHz): δ 0.09 (bs, 12H), 0.46 (m, 4H), 1.74–1.85 (m, 4H), 6.53 (m, 2H), 6.77 (m, 2H). ^{13}C{1H} NMR ($CDCl_3$, −5 °C, 125 MHz): −2.18 (s, 4*C*H$_3$), 3.60 (s, 2*C*H$_2$), 26.18 (t, $^2J_{CF}$ = 22.8 Hz, *C*H$_2$), 55.88 (s, 1>*C*<); 104–120 (m, 16*C*F$_n$), 132.06 (s, 2*C*H=), 133.50 (s, 2*C*H=). ^{29}Si{1H} NMR ($CDCl_3$, −5 °C, 100 MHz): δ −0.18 (s, 2Si). The spin system AA′BB′ and coupling constants of cyclopentadiene **7d** were determined at −5 °C: δ(A,A′) = 6.77 ppm; δ(B,B′) = 6.53 ppm; $^3J_{AA'} = {}^4J_{BB'}$ = 3.5 Hz; $^3J_{AB} = {}^3J_{A'B'}$ = 5.8 Hz; $^4J_{AB'} = {}^4J_{A'B}$ = 1.2 Hz.

4.7. Synthesis of 7-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilyl-bicyclo[2.2.1]hept-5-ene-2,2,3,3-tetracarbonitrile (**8**)

A mixture of isomers of **6** (0.150 mg, 0.26 mmol) was dissolved in 5 mL of toluene before TCNE (0.033 mg, 0.26 mmol) was added. The reaction mixture was stirred for 30 h at 25 °C. Filtration and evaporation of the residual solvent gave the product as a white solid (0.11 g, 0.16 mmol, 62%). Mp: 134–139 °C. ^{1}H NMR (CD_3CN, 25 °C, 300 MHz): δ 0.06 (s, 6H), 0.80 (m, 2H), 1.79 (s, 1H), 2.05–2.19 (m, 2H), 4.27 (m, 2H), 6.63 (dd, $^3J_{HH}$ = 2.1 Hz, 2H). ^{13}C{1H} NMR (CD_3CN, 25 °C, 75 MHz): −2.75 (s, 2*C*H$_3$), 5.42 (s, *C*H$_2$), 26.22 (t, $^2J_{CF}$ = 23.3 Hz, *C*H$_2$), 49.71 (s, 1*C*H), 49.84 (s, 2>*C*<), 60.59 (s, 2*C*H), 104–120 (m, 8*C*F$_n$), 113.22 (s, 2*C*N), 114.18 (s, 2*C*N), 138.85 (s, 2*C*H=). ^{29}Si{1H} NMR (CD_3CN, 25 °C, 60 MHz): δ 3.93 (s, 1Si). *Anal.* Calc. for $C_{23}H_{15}F_{17}N_4Si$: C, 39.55; H, 2.16; N, 8.02. Found: C, 39.51; H, 2.12; N, 7.99%.

4.8. Synthesis of 5,7-bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilyl-bicyclo[2.2.1]hept-5-ene-2,2,3,3-tetracarbonitrile (**9**)

A mixture of the isomers of **7** (0.112 mg, 0.10 mmol) was dissolved in 5 mL of toluene before TCNE (0.013 mg, 0.10 mmol) was added. The reaction mixture was stirred for 30 h at 25 °C. Filtration and evaporation of the residual solvent gave the product as a light brown solid (0.082 g, 0.07 mmol, 70%). Mp: 150–155 °C. ^{1}H NMR (CD_3CN, 25 °C, 300 MHz): δ 0.11 (d, 6H), 0.35 (d, 6H), 0.75 (m, 2H), 0.99 (m, 2H), 1.87 (bs, 1H), 7.97–2.18 (m, 4H), 4.04 (m, 1H), 4.08 (m, 1H), 6.87 (m, 1H). ^{13}C{1H} NMR (CD_3CN, 25 °C, 75 MHz): −2.93 (s, *C*H$_3$), −2.80 (s, *C*H$_3$), −2.73 (s, *C*H$_3$), −2.61 (s, *C*H$_3$), 4.99 (s, *C*H$_2$), 5.20 (s, *C*H$_2$), 26.17 (t, $^2J_{CF}$ = 23.3 Hz, *C*H$_2$), 26.33(t, $^2J_{CF}$ = 23.3 Hz, *C*H$_2$), 49.32 (s, >*C*<), 49.48 (s, >*C*<), 51.04 (s, *C*H), 60.99 (s, *C*H), 63.86 (s, *C*H), 104–120 (m, 16*C*F$_n$), 113.11 (s, *C*N), 114.01 (s, *C*N), 114.30 (s, *C*N), 150.56 (s, *C*H=), 151.80 (s, >*C*=). ^{29}Si{1H} NMR (CD_3CN, 25 °C, 60 MHz): δ −4.88 (s, 1Si), 3.49 (s, 1Si). *Anal.* Calc. for $C_{35}H_{24}F_{34}N_4Si_2$: C, 34.95; H, 2.01; N, 4.66. Found: C, 34.91; H, 2.02; N, 4.69%.

4.9. Synthesis of tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) stannylcyclopentadiene (**10**)

Cyclopentadienyl lithium (0.072 g, 1.00 mmol) was dissolved in 5 mL of THF at −78 °C and was added dropwise to a solution of tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)bromostannane (1.290 g, 1.00 mmol) in 5 mL of THF at 0 °C. The reaction mixture was stirred overnight (17 h) and was then allowed to warm to ambient temperature (25 °C). The colour of the reaction mixture changed to green and then to light brown. The solvent was removed under vacuum. The product was extracted with pentane, and the solvent removed to afford the product as a brown oil (1.096 g, 0.895 mmol, 90%). ^{1}H NMR (25 °C, 500 MHz): δ 1.06 (t, $^3J_{HH}$ = 8.4 Hz, 6H), 2.31 (m, 6H), 6.19 (s, 5H). ^{13}C{1H} NMR (25 °C, 125 MHz): δ 0.15 (s, 3Sn–*C*H$_2$), 28.08 (t, $^2J_{CF}$ = 23.8 Hz, 3CF_2–*C*H$_2$), 113.43 (s, 5*C*H), 106–120 (m, 6*C*F$_n$). ^{119}Sn{1H} NMR (25 °C, 187 MHz): δ 5.87 (s, 1Sn).

Acknowledgments

This work was supported by the Grant Agency of the Academy of Science of the CR (Grant No. IAA400720706), and by the Ministry of Education of the Czech Republic (Grant No. LC06070). The authors wish to thank Dr. J. Pinkas for valuable comments and Dr. E. Munro for proof-reading.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.11.021.

References

[1] (a) R.P. Hughes, H.A. Trujillo, Organometallics 15 (1996) 286;
(b) R.P. Hughes, T. Le Husebo, A.L. Rheingold, L.M. Liable-Sands, G.P.A. Yap, Organometallics 16 (1997) 5;
(c) R.P. Hughes, S.M. Maddock, J. Am. Chem. Soc. 119 (1997) 5988;
(d) V. Herrera, P.J. F de Rege, I.T. Horváth, R.P. Hughes, Inorg. Chem. Commun. 1 (1998) 197;
(e) J. Čermák, K. Auerová, H.T.T. Nguyen, V. Blechta, P. Vojtíšek, J. Kvíčala, Collect. Czech. Chem. Commun. 66 (2001) 382;
(f) T. Bříza, J. Kvíčala, O. Paleta, J. Čermák, Tetrahedron 58 (2002) 3841;
(g) J. Kvíčala, T. Bříza, O. Paleta, K. Auerová, J. Čermák, Tetrahedron 58 (2002) 3847;
(h) D. Hazafy, M. Sobociková, P. Štěpnička, J. Ludvík, M. Kotora, J. Fluorine Chem. 124 (2003) 177;
(i) M. Sobociková, P. Štěpnička, D. Ramella, M. Kotora, Collect. Czech. Chem. Commun. 71 (2006) 190.
[2] (a) L.V. Dinh, J.A. Gladysz, Chem. Commun. (2004) 998;
(b) L.V. Dinh, J.A. Gladysz, Chem. Eur. J. 11 (2005) 7211.
[3] B. Boutevin, F. Guida-Pietrasanta, A. Ratsimihety, J. Fluorine Chem. 60 (1993) 211.
[4] B. Richter, E. de Wolf, G. Van Koten, B.-J. Deelman, J. Org. Chem. 65 (2000) 3885.
[5] J. Čermák, L. Šťastná, J. Sýkora, I. Císařová, J. Kvíčala, Organometallics 23 (2004) 2850.
[6] L. Červenková Šťastná, K. Auerová, J. Kvíčala, J. Čermák, J. Organomet. Chem. 692 (2007) 1974.
[7] P.G. Merle, V. Chéron, H. Hagen, M. Lutz, A.L. Spek, B.-J. Deelman, G. van Koten, Organometallics 24 (2005) 1620.
[8] P. Jutzi, R. Sauer, J. Organomet. Chem. 50 (1973) C29.
[9] P. Jutzi, Chem. Rev. 86 (1986) 983.
[10] S.G. McLean, W.B. Reed, Can. J. Chem. 48 (1970) 3110.
[11] B.J. Grimmond, J.Y. Corey, Organometallics 18 (1999) 4646.
[12] J. Pinkas, J. Kubišta, R. Gyepes, J. Čejka, P. Meunier, K. Mach, J. Organomet. Chem. 690 (2005) 731.
[13] A.V. Kisin, V.A. Korenevsky, N.M. Sergeyev, Yu.A. Ustynyuk, J. Organomet. Chem. 34 (1972) 93.
[14] I. Villuendas, A. Parrilla, A. Guerrero, Tetrahedron 50 (1994) 12673.
[15] P.H.M. Budzelaar, gNMR Version 5.0.6.0., NMR Simulation Program, 2005.
[16] W.A. Hermann, A. Salzer (Eds.), Synthetic Methods of Organometallic and Inorganic Chemistry, vol. 1, Georg Thieme Verlag, Stuttgart, 1996, p. 94.
[17] J.F.W. Keana, M.D. Ogan, J. Am. Chem. Soc. 108 (1986) 7951.
[18] A. Studer, D.P. Curran, Tetrahedron 53 (1997) 6681.
[19] J. Sandström, Dynamic NMR Spectroscopy, Academic Press, London, 1982.
[20] J. Schraml, Collect. Czech. Chem. Commun. 48 (1983) 3402.