

Fluorophilic properties of (perfluorooctyl)ethyldimethylsilyl substituted and tetramethyl(perfluoroalkyl) substituted cyclopentadienes and their Ti(IV), Rh(III), and Rh(I) complexes

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Abstract

Fluorous partition coefficients in perfluorohexane/toluene system for 37 fluorinated silylcyclopentadienes, titanium(IV) complexes derived from them, perfluoroalkyl substituted tetramethylcyclopentadienes, and their Rh(III) and Rh(I) complexes were determined. Specific fluorophilicity and fluorosness according to Kiss and Rábai were calculated for each compound with the help of molecular volume computed with the Gaussian program. The results show relative unimportance of fluorine content parameter for fluorophilicity as shown by a rhodium(I) complex being fluorophilic at fluorine content as low as 46.3%. As expected, fluorophilicity increased with the fluorous ponytail length and ponytail number in series of similar compounds, whereas polar M–Cl bonds were decreasing it. Fluorophilicities of tetramethyl(perfluoroalkyl)cyclopentadiene tautomers varied considerably despite only small differences in molecular volume being found. Most of the compounds were prepared previously, several new silylcyclopentadienes and titanium(IV) silylcyclopentadienyl complexes are reported here for completion.

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1. Introduction

Fluorous biphasic catalysis as a subtopic of fluorous biphasic systems (FBS) now represents one important direction in modern catalysis, the term fluorous that can be used in analogy to aqueous, being first used by Horváth and Rábai [1]. Fluorous biphasic systems combine the advantages of both homogenous and heterogeneous systems. On one hand, FBS allow maintaining homogenous reaction conditions due to the miscibility of perfluorinated solvent with organic solvent at elevated temperatures and on the other hand, they enable the simple separation of fluorinated reagent or catalyst. Recently, a new reaction protocol, fluorous catalysis without perfluorinated solvent due to temperature-dependent solubility of solid fluorous cata-

lyst in the solvent, was independently introduced by Wende and Gładysz [2] and Yamamoto et al. [3].

We are interested in fluorous cyclopentadienyl complexes due to the wide use of Cp ligands in organometallic chemistry and homogeneous catalysis. A number of fluorous cyclopentadienyl complexes with one polyfluorinated chain (ponytail) per ring have been reported previously. Hughes and Trujillo [4] prepared ferrocenes and cyclopentadienyl complexes of Re(I), Mn(I) and Co(I). Herrera et al. [5] synthesized complexes with Rh(I) while Ruwwe [6] prepared and characterized complexes of Zr(IV) in his doctoral Dissertation. In all of the above mentioned examples –CH₂CH₂– group was used as a spacer between a fluorous ponytail and a cyclopentadienyl ring for the shielding of strong electron-withdrawing properties of the ponytail. Research group of van Koten [7] published synthesis and olefin polymerization activity of fluorous zirconocene dichloride complexes, which were substituted with ponytails

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via $-\text{Si}(\text{CH}_3)_n-$ spacer. Dinh and Gladysz [8] prepared “heavy fluorous” cyclopentadienyl complexes and cyclopentadienes bearing three to five $(\text{CH}_2)_m\text{C}_8\text{F}_{17}$ ponytails.

We have recently reported the syntheses of three new types of fluorous cyclopentadienes and their transition metal complexes. The preparation of perfluoroalkyl substituted tetramethylcyclopentadienes and their complexes with Rh(III) and Rh(I) was published first [9]. The second type was represented by cyclopentadienes with two polyfluoroalkylated substituents [10], which were coordinated to Fe(II) and Rh(I) [11]. The third ligand type were cyclopentadienes containing one or two (perfluorooctyl)ethyl-dimethylsilyl groups and a trimethylsilyl or a trimethylstannyl group [12]; various substituted Ti(IV) complexes were prepared from these ligands. Here we report the synthesis of some other Ti(IV) complexes, the measurement of their fluorophilic properties together with the properties of previously prepared compounds [12] and the fluorophilic properties of perfluoroalkylated tetramethylcyclopentadienes and their rhodium complexes [9].

2. Results and discussion

2.1. Definition of fluorophilicity, methods of determination and compounds measured

Fluorous partition coefficient (P_i) quantifies the equilibrium distribution of a solute (i) between immiscible fluorous and organic phases in a defined solvent system, the $\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene mixture being the most frequently used one. The abbreviation P_i then represents a concentration ratio with the value for non-fluorous phase in the denominator. The natural logarithm of the concentration ratio, $\ln\{[c_i(\text{CF}_3\text{C}_6\text{F}_{11})]/[c_i(\text{toluene})]\}$, has been given the abbreviation f_i , for fluorophilicity. According to a definition [13], a compound is fluorophilic if its f_i value is positive. Fluorous partition coefficients for cyclopentadienes $\text{C}_5\text{H}_4(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17})(\text{SiMe}_3)$, **1**, **2** and (tetramethyl)cyclopentadienes $\text{C}_5\text{HMe}_4\text{C}_4\text{F}_9$, $\text{C}_5\text{HMe}_4\text{C}_6\text{F}_{13}$, $\text{C}_5\text{HMe}_4\text{C}_8\text{F}_{17}$, $\text{C}_5\text{HMe}_4\text{C}_{10}\text{F}_{21}$ [14] were determined by gas chromatography. Coefficients for Ti(IV), Rh(III) and Rh(I) [14] complexes were established by determination of the titanium and the rhodium content by UV spectrophotometric and AAS analyses, respectively.

Two other characteristics were calculated from the experimentally determined partition coefficients. Kiss et al. [13] defined specific fluorophilicity $f_{\text{spec}}(i)$ by Eq. (1), where the ratio of the van der Waals volumes compensates for the cavity formation energy differences in both phases caused by size

$$f_{\text{spec}}(i) = \frac{f(i)V_{\text{vdw}}(\text{CF}_3\text{C}_6\text{F}_{11})}{V_{\text{vdw}}(i)} \quad (1)$$

The fluorousness of ligands and complexes was calculated according to the definition (2) by Kiss et al. [13]. Fluorousness determines percentual likeness of a compound to perfluoro(methycyclohexane)

$$\%f_{\text{ness}}(i) = \frac{100f_{\text{spec}}(i)}{f_{\text{spec}}(\text{CF}_3\text{C}_6\text{F}_{11})} = 24.4f_{\text{spec}}(i) \quad (2)$$

Experimental and calculated values of fluorine content, fluorous partition coefficients, fluorophilicities, specific fluorophilicities and fluorousnesses of fluorinated cyclopentadienes **1–7** and their Ti(IV), Rh(III) and Rh(I) complexes **8–21** are summarized in Tables 1 and 2, respectively.

2.2. Synthesis of fluorinated silylcyclopentadienes

As shown in Scheme 1 a mixture of mono- and di-substituted cyclopentadienes **1** and **2** was used for the synthesis of mixture of trimethylstannylcyclopentadienes **22** and **23**, which were substituted with one or two fluorinated silyl substituents. The preparation of pure cyclopentadiene **22** has been published previously [12]. Similarly to compound **22**, cyclopentadiene **23** underwent degenerate metallotropic shift at a rate comparable to the NMR scale at room temperature, so that the signal of quartet carbons was broad. From the silicon NMR spectrum the coupling constants $^{29}\text{Si}-^{119}\text{Sn}$ for cyclopentadienes **22** and **23** $^2J_{\text{SiSn}} = 27.8$ Hz and $^4J_{\text{SiSn}} = 19.9$ Hz, respectively, were determined.

2.3. Synthesis of fluorinated monocyclopentadienyltitanium(IV) complexes

The method of synthesis of monocyclopentadienyltitanium(IV) complexes from trimethylstannylcyclopentadiene

Table 1
Fluorophilic properties of fluorinated cyclopentadienes^a

Compound	Fluorine content (%)	P_i	f_i	$V_{\text{vdw}}(i)$ (\AA^3)	$f_{\text{spec}}(i)$	$f_{\text{ness}}(i)$ (%)
1a ^b	56.6	6.88	1.93	438	0.82	20.0
1b ^b	56.6	6.88	1.93	433	0.85	20.8
1c ^b	56.6	6.88	1.93	421	0.83	20.2
2a ^b	60.1	16.29	2.79	745	0.70	17.0
2b ^b	60.1	16.29	2.79	750	0.69	16.9
2c ^b	60.1	16.29	2.79	770	0.67	16.5
2d ^b	60.1	16.29	2.79	810	0.64	15.6
2e ^b	60.1	16.29	2.79	797	0.65	15.9
2f ^b	60.1	16.29	2.79	733	0.71	17.3
2g ^b	60.1	16.29	2.79	767	0.68	16.5
3a ^b	50.3	1.11	0.10	535	0.04	0.9
3b ^b	50.3	1.11	0.10	551	0.04	0.9
3c ^b	50.3	1.11	0.10	543	0.04	0.9
4a ^c	50.3	0.16	-1.83	299	-1.14	-27.8
4b ^c	50.3	0.31	-1.17	302	-0.72	-17.6
5a ^c	56.1	1.40	0.34	338	0.19	4.5
5b ^c	56.1	1.06	0.06	354	0.03	0.7
5c ^c	56.1	0.79	-0.24	336	-0.13	-3.2
6a ^c	59.8	3.24	1.18	390	0.56	13.7
6b ^c	59.8	2.24	0.81	397	0.38	9.2
6c ^c	59.8	1.90	0.64	392	0.30	7.4
7b ^c	62.3	3.14	1.14	460	0.46	11.3
7c ^c	62.3	2.31	0.84	438	0.36	8.7

^a Synthesis of the compound as indicated.

^b Ref. [12].

^c Ref. [9].

Table 2
Fluorophilic properties of Ti(IV), Rh(III) and Rh(I) cyclopentadienyl complexes^a

Compound	Fluorine content (%)	P_i	f_i	$V_{vdw}(i)$ (Å ³)	$f_{spec}(i)$	$f_{ness}(i)$ (%)
8^b	44.6	0.129	-2.05	518	-0.74	-18.0
9^b	52.6	0.585	-0.54	850	-0.12	-2.9
10^b	42.9	0.103	-2.27	548	-0.77	-18.8
11^b	51.4	0.254	-1.37	881	-0.29	-7.1
12^c	39.1	0.086	-2.45	638	-0.72	-17.5
13^c	48.6	0.065	-2.73	1030	-0.49	-12.0
14^d	33.3	0.003	-5.81	669	-1.61	-39.4
15^d	40.3	0.02	-3.91	774	-0.94	-22.9
16^d	45.3	0.52	-0.65	836	-0.15	-3.5
17^d	49.1	1.42	0.35	937	0.07	1.7
18^d	34.3	0.19	-1.66	362	-0.85	-20.8
19^d	41.3	0.62	-0.48	411	-0.22	-5.3
20^d	46.3	1.51	0.41	469	0.16	4.0
21^d	50.0	2.24	0.81	506	0.30	7.2

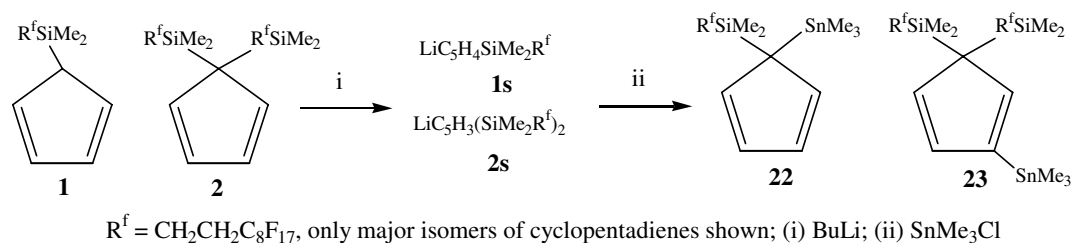
^a Synthesis of the compound as indicated.

^b This work.

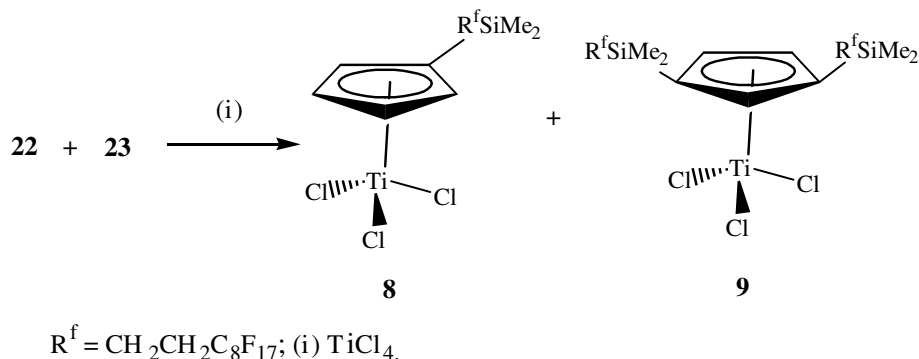
^c Ref. [12].

^d Ref. [9].

[15] was used for the preparation of complexes **8** and **9**. Scheme 2 presents the synthesis of the mixture of monocyclopentadienyltitanium(IV) complexes **8** and **9** from the mixture of cyclopentadienes **22** and **23** with titanium(IV) chloride. The product mixture was easily separated by fractional crystallization, the complex **9** crystallized at 25 °C as yellow dust with about 7% of complex **8**. Complex **8** crystallized at -30 °C, with 14% of complex **9**. The pure complex **8** have been prepared previously [12] from **22**.



Scheme 1.



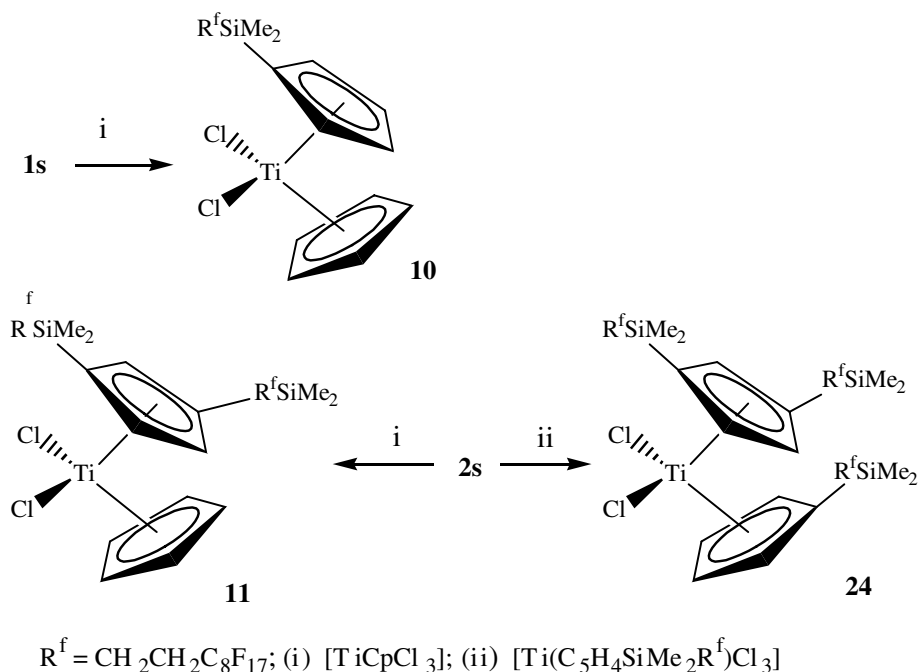
Scheme 2.

2.4. Synthesis of fluorinated dichlorotitanocenes

As shown in Scheme 3 monocyclopentadienyltitanium(IV) complexes [TiCpCl₃] and [Ti(C₅H₄SiMe₂R^f)Cl₃] reacted with lithium salts (**1s** and **2s**) of cyclopentadienes **1** and **2** to form three differently substituted dichlorotitanocenes. Complex **11** was prepared from **2s** containing 25% of cyclopentadienide **1s**. Pure complex **11** was then obtained by the fractional crystallization of the mixture of products **10** and **11**. A similar fractional crystallization like the one used for complexes **8** and **9** was used, complexes **11** (substituted with two fluorinated silyl groups) and **10** crystallized at 25 °C and -30 °C, respectively. The complex **24** substituted with three polyfluorinated ponytails has the fluorine content 55%. Behavior of complex **24** was similar to recently published complex [12], with two polyfluorinated ponytails, each on one cyclopentadienyl ring (1,1'-substitution). Both complexes were insoluble in any common organic or perfluorinated solvent at room temperature. They were soluble in the mixture of chloroform and 1,1,2-trichlorotrifluoroethane at room temperature or in 1,1,2,2-tetrachloroethane at 80 °C.

2.5. Fluorophilic properties of cyclopentadienes, Ti complexes and Rh complexes

Fluorine content over 60% is considered empirically to be a prerequisite for preferential partition into fluoruous phase, although it was realized that number, length, branching and spatial arrangement of fluoruous ponytails played an important role [16].



Scheme 3.

Several theoretical models of fluorophilicity were reported, some of them suppressing [13,17] the other stressing [18] the role of this parameter. The inspection of data in Tables 1 and 2 showed that although only two compounds (7a,b) had fluorine content higher than 60.1% quite a number of them were moderately fluorophilic, the lowest fluorine content for a fluorophilic compound from our collection being 46.3% (rhodium complex 20). On the other hand, at the comparable fluorine contents 44.6% and 48.6%, the fluorophilicities of titanium(IV) chloro complexes 8 and 13, respectively, were both below -2 . Our results therefore support, though only on a qualitative basis, the comparably lower significance of fluorine content parameter on calculated fluorophilicity reported in some models [13,17] as opposed to the model of Platts et al. [18] who consider it to be the decisive parameter.

The results further show generally detrimental effect of polar M–Cl bonds on fluorophilic properties of studied compounds. This is best demonstrated by direct comparison of Rh(III) chloro complexes with Rh(I) carbonyl complexes of the same fluororous chain length (14 vs. 18, 15 vs. 19, etc.) but also by very low fluorophilicity (10–13) and even insolubility (24) of some dichlorotitanocenes with silyl substituents.

On the other hand, the $-\text{SiMe}_2-$ spacer improved fluorophilic properties of uncomplexed cyclopentadienes even at a reduced fluorine content: the fluorophilicity of 2 was 1.3 times higher than that of $\text{C}_5\text{H}_4(\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17})_2$ ($f_i = 2.2$) published by Kvíčala et al. [11].

As expected, a steady increase of fluorophilicity with the ponytail length (e.g. in series 4a–6a, 4b–7b, 14–17, 18–21) and ponytail number (1 vs. 2) was observed if series of compounds with similar structures were compared.

It should be noted here that whereas individual values of the partition coefficient P_i could be measured for every tetramethyl(perfluoroalkyl)cyclopentadiene tautomer (4a–7c), the values for individual isomers of silylsubstituted cyclopentadienes (e.g. 2a–2g) could not be obtained due to isomerization equilibrium [12] taking place between the isomers. Nevertheless, the silylsubstituted cyclopentadiene isomers had different calculated molecular volumes, therefore they were included in Table 1 as individual compounds.

Only small differences in molecular volume were found for different tetramethyl(perfluoroalkyl)cyclopentadiene tautomers (e.g. for 6a–6c values in the range 390–397 Å³), yet their fluorophilicities varied much more (0.64–1.18). It was concluded that the differences had to be ascribed to the true differences in spatial arrangement of fluororous ponytails which in turn caused different spatial arrangement of fluororous and organic domains in these molecules. Molecular volume parameter only was not suitable to adequately describe fluorophilicity in this case which further supports importance of finding a parameter that would include differences in spatial arrangement of fluororous and organic domains in fluorophilicity models in future.

3. Conclusion

Partition coefficients and some derived values for a set of 37 moderately fluorophilic cyclopentadienes and titanium and rhodium complexes obtained from them are reported. Some of the compounds were synthesized in this work, the rest was reported recently. Contrary to some models of fluorophilicity, this work shows that the fluorine content of a compound is a comparably unimportant

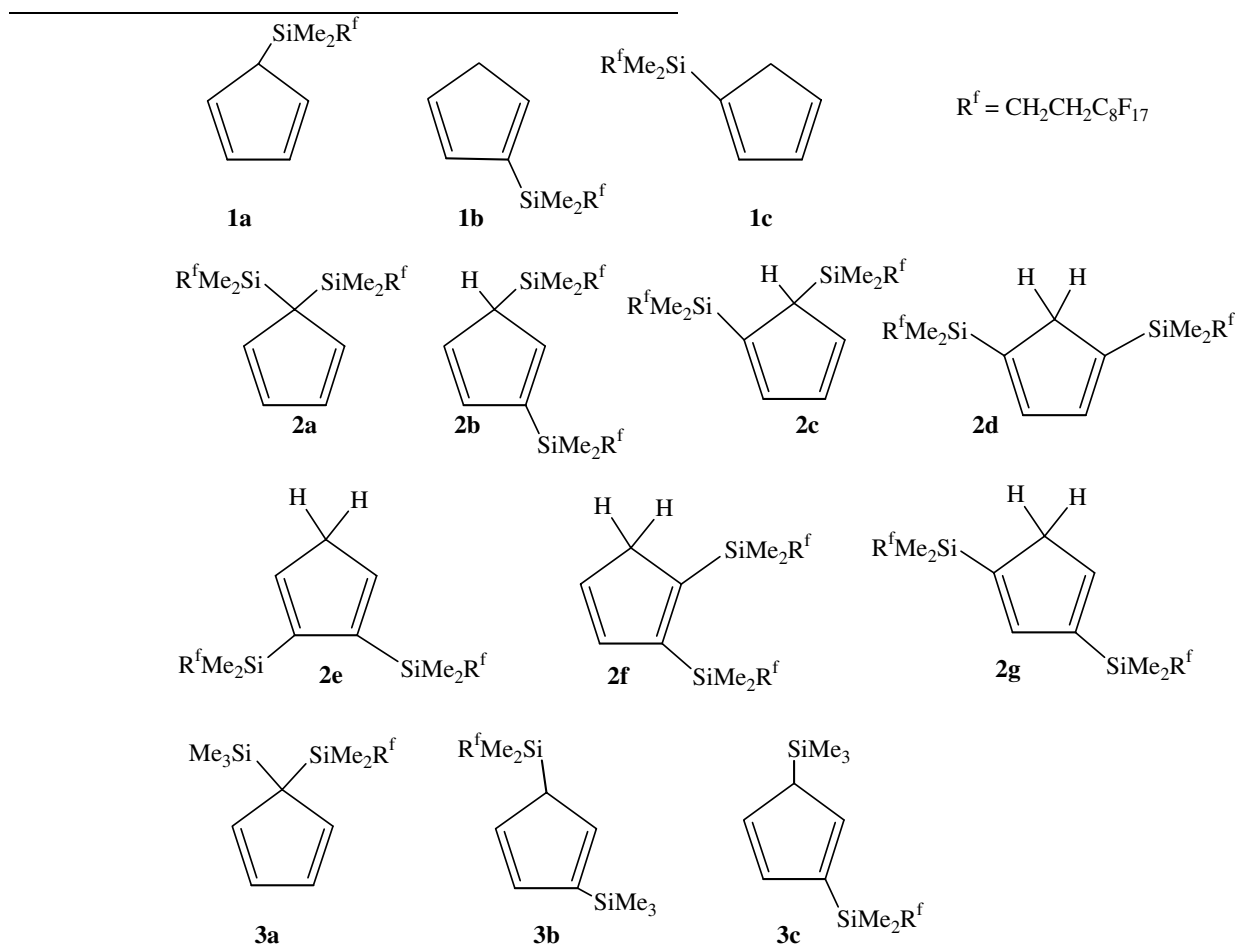
parameter since a compound with fluorine content as low as 46.3% can have a positive value of fluorophilicity.

4. Experimental

4.1. General procedures

All manipulations were carried out in an inert atmosphere of nitrogen with exclusion of moisture and atmo-

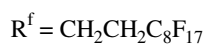
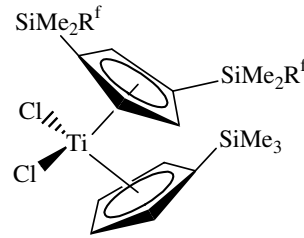
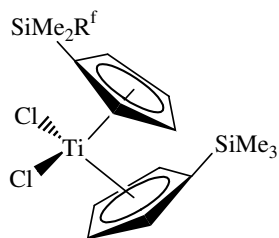
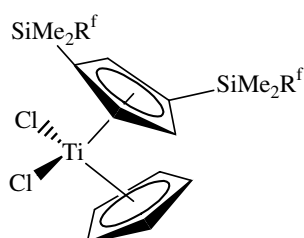
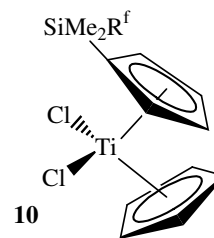
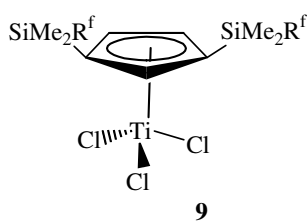
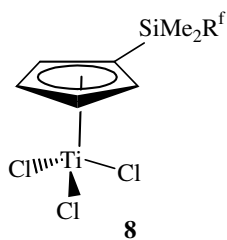
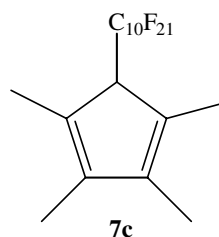
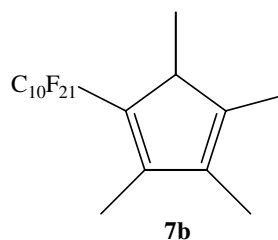
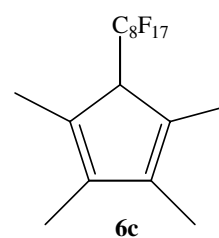
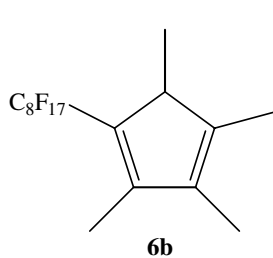
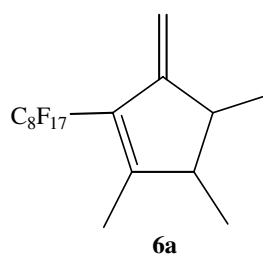
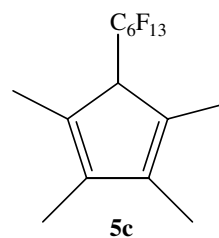
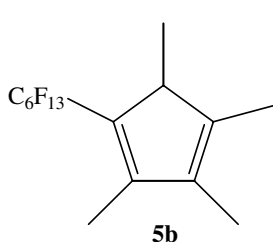
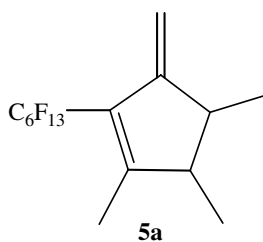
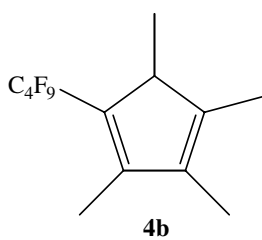
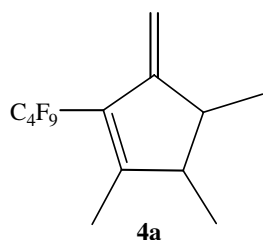
[9], $[\text{Ti}(\text{C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17})\text{Cl}_3]$ (**8**) [12], $[\text{Ti}(\text{C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17}) (\text{C}_5\text{H}_4\text{SiMe}_3\text{Cl}_2)]$ (**12**) [12], $[\text{Ti}\{\text{C}_5\text{H}_3(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17})_2\} (\text{C}_5\text{H}_4\text{SiMe}_3\text{Cl}_2)]$ (**13**) [12], $[\text{Rh}(\text{C}_5\text{Me}_4\text{C}_4\text{F}_9)\text{Cl}_2]_2$ (**14**) [9], $[\text{Rh}(\text{C}_5\text{Me}_4\text{C}_6\text{F}_{13})\text{Cl}_2]_2$ (**15**) [9], $[\text{Rh}(\text{C}_5\text{Me}_4\text{C}_8\text{F}_{17})\text{Cl}_2]_2$ (**16**) [9], $[\text{Rh}(\text{C}_5\text{Me}_4\text{C}_{10}\text{F}_{21})\text{Cl}_2]_2$ (**17**) [9], $[\text{Rh}(\text{C}_5\text{Me}_4\text{C}_4\text{F}_9)(\text{CO})_2]$ (**18**) [9], $[\text{Rh}(\text{C}_5\text{Me}_4\text{C}_6\text{F}_{13})(\text{CO})_2]$ (**19**) [9], $[\text{Rh}(\text{C}_5\text{Me}_4\text{C}_8\text{F}_{17})(\text{CO})_2]$ (**20**) [9], and $[\text{Rh}(\text{C}_5\text{Me}_4\text{C}_{10}\text{F}_{21})(\text{CO})_2]$ (**21**) [9] were prepared according to literature methods as indicated.

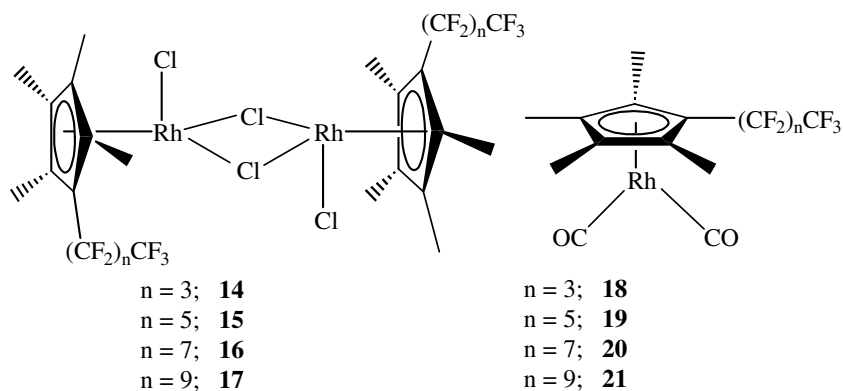


spheric oxygen using standard Schlenk techniques. Solvents were dried by usual procedures then distilled and kept under nitrogen, CDCl_3 was dried by molecular sieves and stored under nitrogen. Titanium(IV) chloride, trimethylstannyl chloride, and butyllithium were commercial products used without further purification.

Compounds $[\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3]$ [15], $\text{C}_5\text{H}_5\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17}$ (**1a–1c**) [12], $\text{C}_5\text{H}_4(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17})_2$ (**2a–2g**) [12], $\text{C}_5\text{H}_4(\text{SiMe}_3)(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17})$ (**3a–3c**) [12], $\text{C}_5\text{H}_2\text{Me}_3(\text{CH}_2)\text{C}_4\text{F}_9$ (**4a**) [9], $\text{C}_5\text{HMe}_4\text{C}_4\text{F}_9$ (**4b**) [9], $\text{C}_5\text{H}_2\text{Me}_3(\text{CH}_2)\text{C}_6\text{F}_{13}$ (**5a**) [9], $\text{C}_5\text{HMe}_4\text{C}_6\text{F}_{13}$ (**5b**, **5c**) [9], $\text{C}_5\text{H}_2\text{Me}_3(\text{CH}_2)\text{C}_8\text{F}_{17}$ (**6a**) [9], $\text{C}_5\text{HMe}_4\text{C}_8\text{F}_{17}$ (**6b**, **6c**) [9], $\text{C}_5\text{HMe}_4\text{C}_{10}\text{F}_{21}$ (**7b**, **7c**)

^1H , ^{13}C $\{^1\text{H}\}$, ^{19}F , and ^{29}Si $\{^1\text{H}\}$ (inept technique) NMR spectra were measured on a Varian Mercury 300 spectrometer at 299.98, 75.44, 282.23 and 59.60 MHz, respectively, in CDCl_3 solvent unless stated otherwise. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to hexamethyldisilane, except ^{19}F (relative to CFCl_3 , referenced to external α,α,α -trifluorotoluene at -63.29 ppm). Relaxation times of 5 s had to be used in some cases instead of the usual value of 1 s for measurement of $^{13}\text{C}\{^1\text{H}\}$ spectra to reveal broad aliphatic quaternary carbon signals. Elementary analyses were carried out at the laboratory of elementary analysis of IOCB Prague. Unfortunately, high-resolution mass spectrometry analysis





of the compounds having molecular weights of more than 640 was not available to us. GC analyses were done with a Hewlett Packard 5890 instrument. AAS measurements were carried out with GBC Avanta Summa instrument. UV spectrophotometric analyses were done with a UV spectrophotometer Hewlett Packard 8451A at 410 nm. A color complex of Ti with hydrogen peroxide was measured.

4.2. Synthesis of $C_5H_3(SiMe_2CH_2CH_2C_8F_{17})_2(SnMe_3)$ (**23**)

To a stirred solution of **2** (2.10 g, 1.95 mmol, 70%) and **1** (0.48 g, 0.84 mmol, 30%) in hexane was added dropwise 1.6 M BuLi (3.29 ml, 2.79 mmol) at 0 °C. The reaction mixture was stirred, left to warm to ambient temperature, then stirred further for 4 h. The solvent was filtered off and the white solid was dried under a vacuum to give 1.94 g (about 2.66 mmol) of the mixture of **2s** (70%) and **1s** (30%). The mixture was dissolved in 10 ml of THF and to this solution trimethylstannyl chloride (0.53 g, 2.66 mmol) was added. The reaction mixture was stirred at ambient temperature for 1 h and then heated under reflux for 4 h. The solution was evaporated to give a suspension of LiCl in the liquid product, which was then extracted into diethyl ether (20 ml) and the extract was filtered. The filtrate was evaporated to give brown oil (2.60 g, 2.49 mmol), which contains 57% of compound **23** (1.48 g, 1.37 mmol, yield 70%), 26% of **22** (0.68 g, 0.65 mmol, yield 77%) and 17% of perfluorinated siloxane (0.42 mmol). 1H NMR (25 °C): δ 0.01 (bs, 9H), 0.21 (bs, 12H), 0.65–0.71 (m, 4H), 1.78 (m, 4H), 6.66 (d, $^3J_{HH} = 1.8$ Hz, 1H), 6.66 (d, $^4J_{HH} = 1.5$ Hz, 1H), 6.70 (dd, $^3J_{HH} = 1.8$ Hz, $^4J_{HH} = 1.5$ Hz, 1H). $^{13}C\{^1H\}$ NMR (25 °C): δ -7.26 (s, Sn-CH₃), -2.57 (s, Si-CH₃), 5.65 (s, Si-CH₂), 25.79 (t, $^2J_{CF} = 23.6$ Hz, CH₂-CF₂), 100.00 (bs, $2>C<$), 104–124 (m, C₈F₁₇), 132.48 (s, 2CH=), 142.34 (s, CH=). ^{19}F NMR (25 °C): δ -126.90 (s, 2F), -123.98 (s, 2F), -123.45 (s, 2F), -122.64 (s, 6F), -117.01 (s, 2F), -81.66 (s, 3F). $^{29}Si\{^1H\}$ NMR (25 °C): δ -4.46 (s, 2Si).

4.3. Synthesis of $[\{\eta^5-C_5H_3(SiMe_2CH_2CH_2C_8F_{17})_2\}TiCl_3]$ (**9**)

The previously prepared mixture (2.6 g, 2.49 mmol) of **22**, **23** and siloxane was dissolved in 5 ml of THF and this solution was added dropwise to the solution of titanium tetrachloride (0.22 ml, 2.03 mmol) in 5 ml of toluene at room temperature. The reaction mixture was stirred overnight at room temperature and then filtered. The yellow solid was dried in a vacuum to give the complex **9** 1.17 g (0.95 mmol, yield 69%) containing 0.05 g (0.07 mmol, 6.9%) of complex **8** as an impurity. The filtrate was evaporated and the residue was extracted with 25 ml of hexane. After partial solvent evaporation a solid started to crystallize and the extract was put into a freezer (-30 °C). After 14 days the yellow-orange solid was filtered off at -30 °C and dried in a vacuum to give complex **8** 0.41 g (0.56 mmol, yield 86%) with 0.11 g (0.09 mmol, 14%) of complex **9** as an impurity. 1H NMR (25 °C): δ 0.48 (s, 12H), 1.05 (t, $^2J_{HF} = 8.6$ Hz, 4H), 1.9–2.5 (m, 4H), 7.29 (d, $^4J_{HH} = 1.8$ Hz, 2H), 7.40 (t, $^4J_{HH} = 1.8$ Hz, 1H). $^{13}C\{^1H\}$ NMR (25 °C): δ -2.73 (s, Si-CH₃), 5.81 (s, Si-CH₂), 25.62 (t, $^2J_{CF} = 24.0$ Hz, CH₂-CF₂), 107–123 (m, C₈F₁₇), 131.80 (s, CH=), 134.93 (s, CH=), 142.87 (s, $>C=$). ^{19}F NMR (25 °C): δ -126.64 (s, 2F), -123.72 (s, 2F), -123.25 (s, 2F), -122.43 (s, 6F), -116.43 (s, 2F), -81.31 (s, 3F). $^{29}Si\{^1H\}$ NMR (25 °C): δ -2.13 (s, 2Si). Anal. Calc. (Found) for C₂₉H₂₃Cl₃F₃₄Si₂Ti C, 28.37 (28.55); H, 1.89 (1.98).

4.4. Synthesis $[Ti(\eta^5-C_5H_5)(\eta^5-C_5H_4SiMe_2CH_2CH_2-C_8F_{17})Cl_2]$ (**10**)

A solution of lithium (2-perfluorooctyl)ethyldimethylsilylcyclopentadienide (0.64 g, 1.11 mmol) in 15 ml THF was added dropwise to a yellow solution of (η^5 -cyclopentadienyl)trichlorotitanium(IV) complex (0.24 g, 1.11 mmol) in 5 ml THF. The yellow reaction mixture became reddish and was stirred for 1 h at ambient temperature, then it was refluxed for 12.5 h and left to cool to room temperature. The solvent was evaporated and the product was extracted

into 25 ml of toluene. The extract was filtered and the solvent partially evaporated in vacuo. When a solid started to crystallize, the flask was put into a freezer ($-30\text{ }^{\circ}\text{C}$). After 4 days the orange-red solid was filtered off at $-30\text{ }^{\circ}\text{C}$ and dried in a vacuum to give 0.69 g of complex **7** (0.83 mmol, yield 82%). ^1H NMR (25 $^{\circ}\text{C}$): δ 0.38 (s, 6H), 1.13 (m, 2H), 1.9–2.5 (m, 2H), 6.56 (s, 5H), 6.71(AA'BB'system, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (25 $^{\circ}\text{C}$): δ -2.54 (s, Si-CH₃), 6.12 (s, Si-CH₂), 25.75 (t, $^2J_{\text{CF}} = 23.8$ Hz, CH₂-CF₂), 106–119 (m, C₈F₁₇), 119.25 (s, 2CH=), 120.23 (s, 5CH=), 129.43 (s, 2CH=), 131.03 (s, >C=). ^{19}F NMR (25 $^{\circ}\text{C}$): δ -126.58 (s, 2F), -123.62 (s, 2F), -123.19 (s, 2F), -122.35 (s, 6F), -116.28 (s, 2F), -81.27 (s, 3F). $^{29}\text{Si}\{^1\text{H}\}$ NMR (25 $^{\circ}\text{C}$): δ -2.94 (s, Si). Anal. Calc. (Found) for C₂₂H₁₉Cl₂F₁₇SiTi C, 35.08 (35.15); H, 2.54 (2.46).

4.5. Synthesis of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{CH}_2\text{-CH}_2\text{C}_8\text{F}_{17})_2\}\text{Cl}_2]$ (**11**)

The THF solution (5 ml) of a mixture (1.00 g, about 1.05 mmol) of lithium salts of **2** (0.78 mmol, about 75%) and **1** (0.27 mmol, about 25%) was added dropwise to the yellow solution of (η^5 -cyclopentadienyl)trichlorotitanium(IV) complex (0.23 g, 1.05 mmol) in 5 ml of THF. The yellow reaction mixture became reddish and was stirred for 1 h at ambient temperature then refluxed for 5.5 h and finally left to cool to room temperature. The orange-red solid precipitated after 12 h, the solid was filtered off and dried in a vacuum. Complex **11** was obtained in 56% yield (0.56 g, 0.44 mmol). The filtrate was partially concentrated and when a solid started to crystallize the flask was put into a freezer ($-30\text{ }^{\circ}\text{C}$). After 4 days an orange-red solid was filtered off at $-30\text{ }^{\circ}\text{C}$ and dried in a vacuum to give 0.20 g of complex **10** (0.25 mmol) with 14% of **11** (0.04 mmol) as an impurity. ^1H NMR (25 $^{\circ}\text{C}$): δ 0.37 (s, 12H), 0.89–0.94 (m, 4H), 1.85 (m, 4H), 6.57 (s, 5H), 6.93 (d, $^4J_{\text{HH}} = 1.8$ Hz, 2H), 7.01 (t, $^4J_{\text{HH}} = 1.8$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (25 $^{\circ}\text{C}$): δ -2.71 (s, Si-CH₃), 6.45 (s, Si-CH₂), 25.60 (t, $^2J_{\text{CF}} = 24.3$ Hz, CH₂-CF₂), 106–119 (m, C₈F₁₇), 120.58 (s, 5CH=), 130.53 (s, 2CH=), 131.49 (s, >C=), 135.58 (s, 1CH=). ^{19}F NMR (25 $^{\circ}\text{C}$): δ -126.64 (s, 2F), -123.72 (s, 2F), -123.25 (s, 2F), -122.44 (s, 6F), -116.49 (s, 2F), -81.29 (s, 3F). $^{29}\text{Si}\{^1\text{H}\}$ NMR (25 $^{\circ}\text{C}$): δ -3.16 (s, 2Si). Anal. Calc. (Found) for C₃₄H₂₈Cl₂F₃₄Si₂TiC, 32.47 (32.45); H, 2.24 (2.26).

4.6. Synthesis of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17})\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{C}_8\text{F}_{17})_2\}\text{Cl}_2]$ (**24**)

The solution of lithium (2-perfluorooctyl)ethylidimethylsilylcyclopentadienide (0.16 g, 0.28 mmol) in 10 ml THF was added dropwise to the yellow solution of complex **9** (0.34 g, 0.28 mmol) in 10 ml THF. The mixture became reddish, was stirred for 1 h at ambient temperature, then it was refluxed for 16 h and then left to cool to room temperature. The solvent was partially removed in a vacuum and when a solid started to crystallize the flask was put into a freezer

($-30\text{ }^{\circ}\text{C}$). After 5 days the resulting orange-red solid was filtered off at $-30\text{ }^{\circ}\text{C}$ and dried in a vacuum to give 0.33 g of complex **24** (0.17 mmol, yield 67%). ^1H NMR (CDCl₃ + 1,1,2-trichlorotrifluoroethane, 25 $^{\circ}\text{C}$): δ 0.36 (s, 18H), 0.89 (m, 4H), 1.00 (m, 2H), 1.82–2.12 (m, 6H), 6.57 (AA'BB'system, 4H), 6.76 (d, $^4J_{\text{HH}} = 1.8$ Hz, 2H), 6.96 (t, $^4J_{\text{HH}} = 1.8$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃ + 1,1,2-trichlorotrifluoroethane, 25 $^{\circ}\text{C}$): δ -2.23 (s, 4C, Si-CH₃), 1.03 (s, 2C, Si-CH₃), 6.25 (s, 1C, Si-CH₂), 6.59 (s, 2C, Si-CH₂), 25.94 (t, $^2J_{\text{CF}}$ not resolved, 2C, CH₂-CF₂), 26.06 (t, $^2J_{\text{CF}}$ not resolved, 1C, CH₂-CF₂), 105–119 (m, C₈F₁₇), 114.42 (s, 2CH=), 129.32 (s, 2CH=), 131.37 (s, 2 >C=), 132.90 (s, >C=), 133.96 (s, 2CH=), 137.94 (s, CH=). ^{19}F NMR (CDCl₃ + 1,1,2-trichlorotrifluoroethane, 25 $^{\circ}\text{C}$): δ -126.64 (s, 2F), -123.72 (s, 2F), -123.25 (s, 2F), -122.43 (s, 6F), -116.43 (s, 2F), -81.31 (s, 3F). $^{29}\text{Si}\{^1\text{H}\}$ NMR (CDCl₃ + 1,1,2-trichlorotrifluoroethane, 25 $^{\circ}\text{C}$): δ -3.24 (s, 2Si), -2.96 (s, 1Si). Anal. Calc. (Found) for C₄₆H₃₇Cl₂F₅₁Si₃Ti C, 31.36 (31.24); H, 2.12 (2.02).

5. Fluorous partition coefficients for fluorinated cyclopentadienes

A flask (a Schlenk flask for silylcyclopentadienes) was charged with a fluorinated cyclopentadiene (about 40 mg of silylcyclopentadienes and about 100 mg of tetramethylcyclopentadienes), CF₃C₆F₁₁ (2.00 ml) and toluene (2.00 ml), the mixture was magnetically stirred for 2 h at 25 $^{\circ}\text{C}$. After 2 h, the mixture was left standing to separate the layers, aliquots (0.50 ml) were taken from both phases. To each sample, (trifluoromethyl)benzene (5 μl for silylcyclopentadienes and 10 μl for tetramethylcyclopentadienes) and diethyl ether (0.50 ml) were added, samples were shaken and analyzed by GC.

6. Fluorous partition coefficients for fluorinated Ti(IV) complexes

A flask was charged with fluorinated Ti(IV) complex (about 0.10 g), CF₃C₆F₁₁ (2.00 ml) and toluene (2.00 ml), the mixture was magnetically stirred for 2 h at 25 $^{\circ}\text{C}$. After 2 h, the mixture was left standing to separate the layers, aliquots (0.50 ml) were filtered from both phases. The solvents were evaporated in air during 7 days. Residues were treated with 10 M H₂SO₄ (5.0 ml), the acid was removed at 530 $^{\circ}\text{C}$ and the residue dissolved in deionized water. Hydrogen peroxide (5 ml of a 3% solution) was added to the aqueous solution and titanium content was determined by spectrophotometric analysis.

7. Fluorous partition coefficients for fluorinated tetramethylcyclopentadienyl Rh(III) and Rh(I) complexes

A flask (a Schlenk flask for Rh(I) complexes) was charged with fluorinated Rh complex (about 50 mg), CF₃C₆F₁₁ (2.00 ml) and toluene (2.00 ml), the mixture was magnetically stirred for 2 h at 25 $^{\circ}\text{C}$. After 2 h, the

mixture was left standing to separate the layers, aliquots (1.50 ml) were taken from both phases. Solvents were removed by evaporation in air. Residues were treated with concentrated H₂SO₄ (0.5 ml). After removing the acid at 530 °C, residues were melted with K₂S₂O₇, cooled, treated with aqueous H₂SO₄(10%) and analyzed by AAS.

8. Calculations of specific fluorophilicity and fluorosness [13]

Specific fluorophilicity and fluorosness were calculated according to Eqs. (1) and (2). Molecular volumes of optimized molecules were calculated by Monte Carlo method with the Gaussian program [19]. Due to the known inaccuracy of the calculation (about 10%), the simplest available method was used for molecule optimization. For cyclopentadienes, semiempirical AM1 method was used for calculation of both the optimized structure and molecular volume. This method could not be used for optimization of metal complexes, therefore multilayer ONIOM method was used with the calculation of the part of the molecule containing the Cp ring(s), the metal, and the other ligands by ab initio HF/3-21G* method and the part containing fluoros ponytails by molecular mechanics (UFF). Molecular volumes of the complexes were then calculated using AM1 again. In some cases the AM1 method did not converge and ab initio HF/STO3G method had to be used. The value of molecular volume of perfluoromethylcyclohexane was calculated as 186 Å³.

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References

[1] I.T. Horváth, J. Rábai, *Science* 266 (1994) 72.

- [2] M. Wende, J.A. Gladysz, *J. Am. Chem. Soc.* 123 (2001) 11490.
- [3] K. Ishihara, S. Kondo, H. Yamamoto, *Synlett* (2001) 1371.
- [4] R.P. Hughes, H.A. Trujillo, *Organometallics* 15 (1996) 286.
- [5] V. Herrera, P.J.F. de Rege, I.T. Horváth, L.T. Husebo, R.P. Hughes, *Inorg. Chem. Commun.* 1 (1998) 197.
- [6] J. Ruwwe, Doctoral Dissertation, Westfälische Wilhelms Universität Münster 1998.
- [7] P.G. Merle, V. Chéron, H. Hagen, M. Lutz, A.L. Spek, B.-J. Deelman, G. van Koten, *Organometallics* 24 (2005) 1620.
- [8] L.V. Dinh, J.A. Gladysz, *Chem. Eur. J.* 11 (2005) 7211.
- [9] J. Čermák, K. Auerová, H.T.T. Nguyen, V. Blechta, P. Vojtíšek, J. Kvíčala, *Collect. Czech. Chem. Commun.* 66 (2001) 382.
- [10] T. Bříza, J. Kvíčala, O. Paleta, J. Čermák, *Tetrahedron* 58 (2002) 3841.
- [11] J. Kvíčala, T. Bříza, O. Paleta, K. Auerová, J. Čermák, *Tetrahedron* 58 (2002) 3847.
- [12] J. Čermák, L. Št'astná, J. Sýkora, I. Císařová, J. Kvíčala, *Organometallics* 23 (2004) 2850.
- [13] R.H. Kiss, I. Kövesdi, J. Rábai, *J. Fluorine Chem.* 108 (2001) 95.
- [14] K. Auerová, Diploma Thesis, Charles University, Department of Inorganic Chemistry, Prague, 2001.
- [15] W.A. Hermann, A. Salzer (Eds.), *Synthetic Methods of Organometallic and Inorganic Chemistry*, vol. 1, Georg Thieme Verlag, Stuttgart, 1996, p. 94.
- [16] I.T. Horváth, *Acc. Chem. Res.* 31 (1998) 641.
- [17] E. de Wolf, P. Ruelle, J. van den Broeke, B.-J. Deelman, G. van Koten, *J. Phys. Chem. B* 108 (2004) 1458.
- [18] F.T.T. Hugue, K. Jones, R.A. Saunders, J.A. Platts, *J. Fluorine Chem.* 115 (2002) 119.
- [19] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian 03*, Revision D.01, Gaussian, Inc., Wallingford, CT, 2004.