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Synthesis, fluorophilicities and regioisomer composition of ferrocenes and rhodium complexes based on bis(polyfluoroalkylated) cyclopentadienes

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Abstract—Ferrocenes and rhodium(I) carbonyl complexes were synthesized from lithium bis[2-(perfluoroalkyl)ethyl]cyclopentadienides and ferrous chloride–THF complex or tetracarbonyldichlorodirhodium. Fluorophilicities of starting bis[2-(perfluoroalkyl)ethyl]cyclopentadienes and ferrocenes made there from were determined. Four regioisomers of bis[2-(perfluoroalkyl)ethyl]cyclopentadienes, three regioisomers of the corresponding ferrocenes and two regioisomers of the corresponding rhodium complexes were identified and their ratio determined by 1D and 2D NMR spectroscopy.

1. Introduction

Organometallic complexes play a key role in homogeneous catalysis, which is essential for many industrial processes.[1,2] Attempts to reduce environmental impact of separation of catalysts from products have led recently to the introduction of biphase catalytic systems with two liquid phases.[3] A use of aqueous or hydrophilic phase as the second phase has drawbacks in low compatibility with some chemical reactions and therefore systems with second fluorous phase have been devised.[4–7]

Fluorophilic properties of organometallic complexes for fluorous biphase catalysis (FBC) depend on a number of factors, some of which have not yet been fully understood.[8] Overall content of fluorine has to exceed 60%,[8,9] but providing this by an attachment of two shorter polyfluorinated ponytails is more efficient than by using only one but long ponytail due to better solubility properties.[8,10] Due to advantageous ligand properties and easy preparation, phosphines with multiple fluorinated chains have been employed with advantage as fluorophilic ligands for FBC.[4,10–14]

Other ligands have attracted substantially less attention. Organometallic complexes containing η^5-cyclopentadienyl group belong to significant homogeneous catalysts,[15] but previously only one preparation of cyclopentadienes containing fluorinated ponytails has been reported.[16] These cyclopentadienes contain only one polyfluorinated chain and their fluorophilic properties are hence too weak.[16] Therefore, they have to be combined with fluorous phosphanes to prepare organometallic complexes for FBC.[17]

We have recently published our preliminary results concerning preparation of cyclopentadienes with two attached fluorinated ponytails[18] and full details on the preparation of bis(polyfluoroalkylated) cyclopentadienes and their regioisomer composition are presented in the preceding article in this issue.[19]

2. Results

2.1. Preparation of tetrakis[2-(perfluoroalkyl)ethyl]-ferrocenes

Stability in air and easy preparation make ferrocenes ideal organometallic complexes for the study of fluorophilic properties.[16] As ferrocenes are prepared from deprotonated cyclopentadienes, fluorinated ponytails have to contain alkylene spacer to prevent decomposition during deprotonation.[20] We therefore synthesized a series of bis[2-(perfluoroalkyl)ethyl]cyclopentadienes **1a–f** as mixtures of four regioisomers **1A–D**,[19] which composition was determined by careful analysis of NMR spectra (Section 3). Despite considerable effort we were not able to separate individual regioisomers due to very close properties and hence employed fluoro cyclopentadienes **1** as regioisomer mixtures (Fig. 1).

Keywords: fluorous; fluorophilic; fluorocyclopentadiene; bis(polyfluoroalkyl)cyclopentadiene; cyclopentadiene complex; ferrocene; rhodium complex; NMR spectroscopy.

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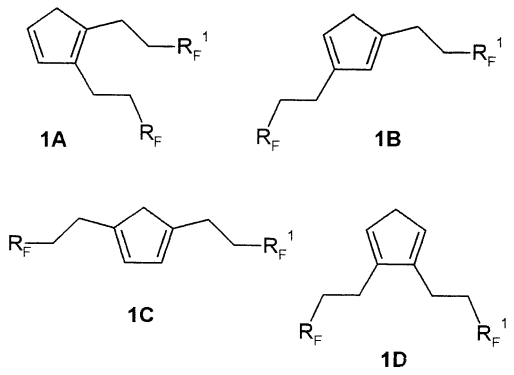
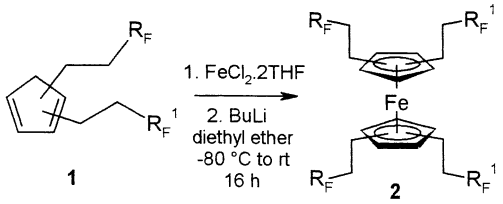


Figure 1. Regioisomers of bis(polyfluoroalkylated) cyclopentadienes **1**.



1a, **2a** $R_F = R_F^1 = C_4F_9$, 43%
1b, **2b** $R_F = R_F^1 = C_6F_{13}$, 48%
1c, **2c** $R_F = R_F^1 = C_8F_{17}$, 47%
1d, **2d** $R_F = C_4F_9$, $R_F^1 = C_6F_{13}$, 59%
1e, **2e** $R_F = C_4F_9$, $R_F^1 = C_8F_{17}$, 58%
1f, **2f** $R_F = C_6F_{13}$, $R_F^1 = C_8F_{17}$, 62%

Scheme 1.

Tetrakis(polyfluoroalkylated) ferrocenes **2a**–**f** were prepared by a reaction of $FeCl_2 \cdot 2$ THF complex with deprotonated fluorocyclopentadienes **1** in analogy to Ref. 16. Similarly to deprotonation of mono(polyfluoroalkylated) cyclopentadienes **3**,[16,19] we did not encounter any problems with deprotonation of fluorocyclopentadienes **1**, made with butyllithium at −80°C. No dehydrofluorination was observed. Tetrakis(polyfluorinated) ferrocenes **2a**–**f** were obtained in moderate to good yields as complex mixtures of regioisomers (Scheme 1).

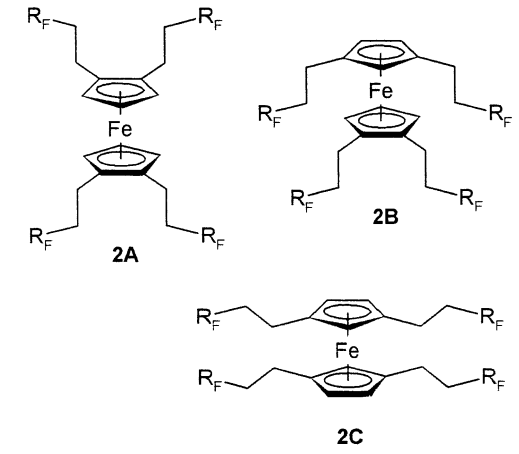
Tetrakis(polyfluoroalkylated) ferrocenes are stable and with the exception of the ferrocene with longest fluorinated ponytails, **2f**, no problems with solubility similar to that reported in Ref. 16 were met.

Ferrocenes **2a**,**b**, substituted symmetrically by two shorter fluorinated ponytails consist of three regioisomers **2A**–**C**, the structures and relative ratios of which were determined by 1D and 2D NMR spectroscopy (Fig. 2).

Unfortunately, NMR spectra of other bis(polyfluoroalkylated) ferrocenes **2c**–**f** were not so clear and did not allow to determine the ratios of the corresponding regioisomers (Section 3).

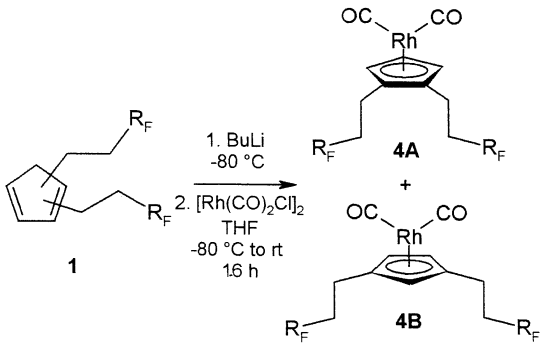
2.2. Preparation of bis[2-(perfluoroalkyl)ethyl]cyclopentadienyl(dicarbonyl)rhodium

Reaction of bis(polyfluoroalkylated) cyclopentadienes **1a**,**b** with tetracarbonyldichlorodirhodium afforded rhodium complexes **4a**,**b** in poor to moderate yields as mixtures of 1,2-disubstituted regioisomer **4A** and 1,3-disubstituted regioisomer **4B** (Scheme 2).



$R_F = C_4F_9$, **2aA**:**2aB**:**2aC** = 14:76:10
$R_F = C_6F_{13}$, **2bA**:**2bB**:**2bC** = 15:65:20

Figure 2. Regioisomers of tetrakis(polyfluoroalkylated) ferrocenes **2**.



1a, **4a** $R_F = C_4F_9$, 44%, **4aA**:**4aB** = 34:66
1b, **4b** $R_F = C_6F_{13}$, 25%, **4bA**:**4bB** = 32:68

Scheme 2.

In contrast to fluoro ferrocenes **2**, rhodium complexes **4** are not air stable and their work-up including column chromatography has to be performed under inert conditions. Even in the absence of oxygen, they are not long term stable at room temperature. Among the decomposition products (perfluoroalkyl)ethenes were detected by NMR spectroscopy. Syntheses of more stable organometallic complexes based on fluoro cyclopentadienes are in progress.

2.3. Measurements of fluorophilicities of fluorocyclopentadienes 1 and fluoroferrocenes 2

Starting experimental entry for the estimation of fluorophilic properties is fluorous partition coefficient, P_i(FBS), which is the ratio of concentrations of given fluorous compound in two particular solvents. Natural logarithm of fluorous partition coefficient for toluene and perfluoro(methylcyclohexane) as the respective solvents, measured at 25°C, is called fluorophilicity, f_i. If its value is positive, the

compound can be regarded as fluorophilic.[8] We employed gas chromatography for the estimation of fluorous partition coefficients in fluorocyclopentadienes **1**, whereas the corresponding coefficients for ferrocenes were estimated by determination of the iron content by AAS.[17] In order to compensate cavity formation energy differences in both phases caused by different size of fluorophilic molecules, we also calculated specific fluorophilicity, $f_{spec}(i)$ according to equation published by Kiss, Kövesdi and Rábai.[8]

$$f_{spec}(i) = f_i \cdot V_{vdw}(CF_3C_6F_{11})/V_{vdw}(i) \quad (1)$$

Instead of calculating molecular volumes (V_{vdw}) by the method of Bodor et al.,[8,21] we employed standard calculations of molecular volumes included into Gaussian 98.[22] Finally, we also computed *fluorousness*, $\%f_{ness}(i)$, of fluorinated cyclopentadienes **1** and fluoroferrocenes **2** with the aim to measure their percentual likeness to perfluoro-(methylcyclohexane) according to Kiss, Kövesdi and Rábai definition.[8]

$$\%f_{ness}(i) = 100f_{spec}(i)/f_{spec}(CF_3C_6F_{11}) = 24.4f_{spec}(i) \quad (2)$$

All experimental and calculated values, i.e. fluorous partition coefficients, fluorophilicities, specific fluorophilicities and fluorousnesses are listed together with the relative fluorine content for compounds **1** and **2** in Table 1.

Table 1. Fluorophilic properties of fluorocyclopentadienes **1** and fluoroferrocenes **2**

Compound	R_F	$R_F{}^1$	%F	FPC[a]	f_i[b]	$f_{spec}(i)$[c]	$\%f_{ness}$[d]
1a	C_4F_9	C_4F_9	61.3	1.2	0.2	0.08	2
1b	C_6F_{13}	C_6F_{13}	65.2	4.9	1.6	0.61	15
1c	C_8F_{17}	C_8F_{17}	67.4	8.8	2.2	0.72	18
1d	C_4F_9	C_6F_{13}	63.5	3.0	1.1	0.44	11
1e	C_4F_9	C_8F_{17}	65.2	4.6	1.5	0.56	14
1f	C_6F_{13}	C_8F_{17}	66.4	6.4	1.9	0.64	16
2a	C_4F_9	C_4F_9	58.4	10	2.3	0.48	12
2b	C_6F_{13}	C_6F_{13}	62.9	72	4.3	0.80	20
2d	C_4F_9	C_6F_{13}	61.0	17	2.8	0.56	14
2e	C_4F_9	C_8F_{17}	62.9	22	3.1	0.56	14
2f	C_6F_{13}	C_8F_{17}	64.3	22	3.1	0.52	13

[a] Fluorous partition coefficient.
[b] Fluorophilicity.
[c] Specific fluorophilicity.
[d] Fluorousness.

3. Discussion

3.1. [2-(Perfluoroalkyl)ethyl]cyclopentadienes

Bis(polyfluoroalkylated) cyclopentadienes **1** were prepared as reported in Ref. 19 from the corresponding monosubstituted cyclopentadienes **3**. These were made according to Ref. 16 and consisted of two regioisomers, 1-[2-(perfluoroalkyl)ethyl]cyclopentadiene **3A** and 2-[2-(perfluoroalkyl)-ethyl]cyclopentadiene **3B** in approximate 1:2 ratio. The major isomer was assigned in the original paper[16] as 2-isomer **3B** based on cyclopentadiene ring methylene hydrogen signals: the more upfield signal of major isomer **5B** was splitted to quartet, whereas that of isomer **3A** to sextet, which was explained to be the result of both $^3J_{HH}$ and $^4J_{HH}$ coupling.[16] However, the values of coupling constants did not exceed 2 Hz and we felt that this explanation could be erroneous due to long range coupling to fluorines. We therefore performed NOE experiment with [2-(perfluorobutyl)ethyl]cyclopentadiene **3a** and found that only irradiation of the upfield signal of the ring methylene hydrogens resulted in NOE with both methylene groups of polyfluoroalkyl ponytail (Fig. 3). Hence, this isomer has to be the 1-isomer **5A** and the original assignment based on coupling[16] was erroneous.

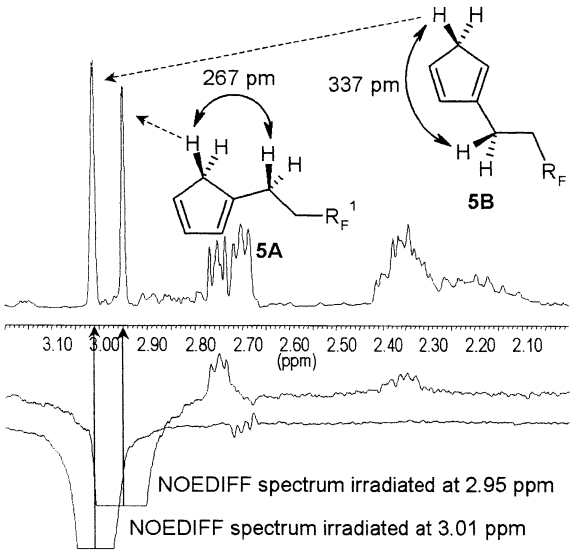


Figure 3. NOEDIFF spectra of ring methylene hydrogens of [2-(perfluorobutyl)ethyl]cyclopentadiene **5a**.

3.2. Bis[2-(perfluoroalkyl)ethyl]cyclopentadienes

Bis(polyfluoroalkylated)cyclopentadienes **1** were prepared as complex mixture of regioisomers. Crude analysis of the NMR spectra confirmed only that no regioisomer containing the ponytail attached to the saturated ring carbon was

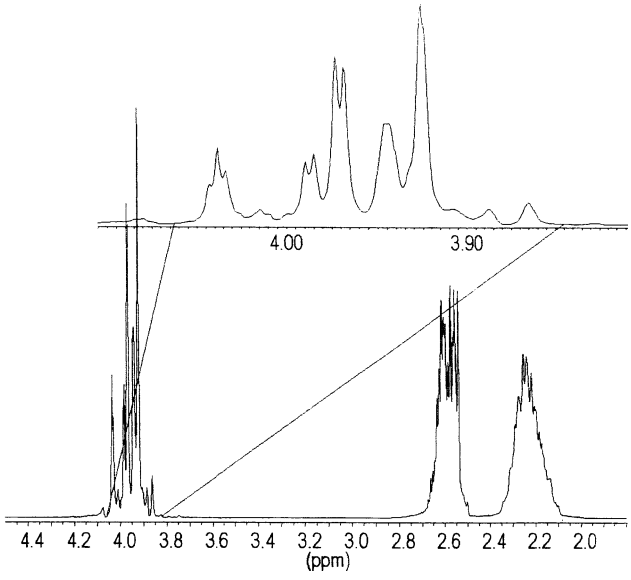


Figure 4. ^{1}H NMR spectrum of fluoroferrocene **2a**.

formed in analogy to monosubstituted cyclopentadienes **5**. Detailed inspection of their NMR spectra allowed an assignment of four remaining regioisomers **1A**–**D**. We started with the vinylic part of ^{1}H spectra and assigned first the signals of minor 1,2-isomer **1A**, which were the only signals with comparably large $^{3}J_{HH}$ coupling (5.5 Hz) and therefore a characteristic roof shape. In the ring methylene hydrogens area, four signals were detected with one signal strongly dominating over the others. As no signal of this intensity was observed in the vinylic area, it had to correspond to the remaining non-symmetrically substituted 1,3-isomer **1B**. Signals of ring methylene hydrogens of the remaining symmetrically substituted isomers **1C**,**D** have similar multiplicities and shifts to that of monosubstituted cyclopentadienes **3A**,**B** and we correspondingly assigned the upfield shift to the 1,4-isomer **1C**. Assignment of vinylic hydrogens based on integration was impeded by a coalescence of one signal of isomer **1B** with signal of isomer **1C**, but fortunately we synthesized fluorocyclopentadienes **1** by two different procedures[19] and consequently two sets of regioisomers with different regioisomer ratios were available. Signals of methylenes of fluorinated ponytails are heavily splitted and overlaid and could not be assigned to individual regioisomers. Assignment of individual carbon signals in fluorocyclopentadienes **1** was based on careful analysis of HMQC spectra and again exploited with advantage the presence of two different sets of regioisomers.

3.3. Tetrakis[2-(perfluoroalkyl)ethyl]ferrocenes

Fluoroferrocenes **2** formed from a mixture of four regioisomers of fluorocyclopentadienes **1A**–**D** should in principle consist of three regioisomers, 1,1′,2,2′-isomer **2A**, 1,1′,2,3′-isomer **2B** and 1,1′,3,3′-regioisomer **2C**. First inspection of ^{1}H NMR spectra and group analysis of signals confirmed that the products are present, but it seemed to be impossible to distinguish the individual regioisomers (Fig. 4).

Fortunately, we were able to separate partially one regioisomer from the mixture of isomers of ferrocene **2a** by precise column chromatography. This isomer was easily assigned structure **2C** based on symmetry and small J_{HH} coupling constant value (Fig. 5, upper spectrum). Right choice of the window function and the corresponding parameters in the FID of NMR spectrum of the remaining mixture revealed surprisingly more details (Fig. 5, lower spectrum), but problems with overlap of signals were solved only after COSY spectrum was taken (Fig. 5).

By this way, the ratio of regioisomers **2aA**–**aC**,**2bA**–**bC** formed could be determined. Individual signals in ^{13}C NMR spectra were then assigned with the help of HMQC spectra. Unfortunately, although the group analysis of the NMR spectrum, as well as elemental analyses confirmed unequivocally the structure of other fluoroferrocenes **2c**–**f**,

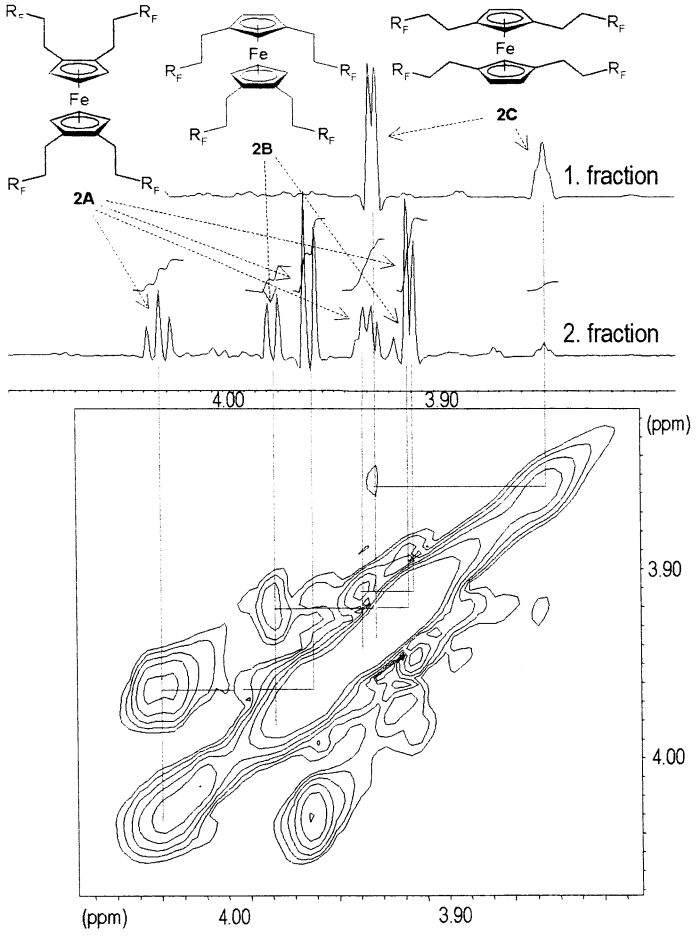


Figure 5. COSY spectrum of fluoroferrocene **2a** and assignment of regioisomers **2aA**–**aC**.

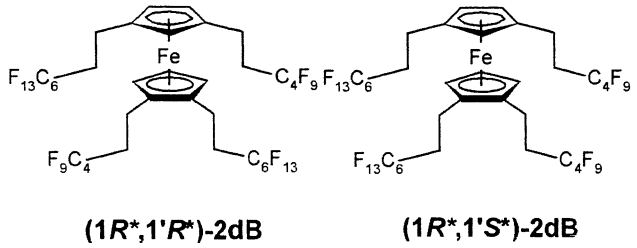


Figure 6. Diastereoisomers of regioisomer **2dB**.

we were not able to carry out for them similar analysis based on ^{1}H NMR spectra. In the case of regioisomers **2d**–**f**, we suspect that the reason for more complex shape of spectra is caused by the presence of diastereoisomers (Fig. 6), however, the complexity of spectrum of symmetric regioisomer **2c** with long fluorinated ponytails is hard to explain.

It could arise from significant rotation barriers and unsymmetrical ground state structures similar to that observed by Okuda and Herdtweck[23] for tetrakis(trimethylsilylated) ferrocenes, taking into account that the steric demand of long aliphatic chains is often underestimated.[†]

3.4. Bis[2-(perfluoroalkyl)ethyl]cyclopentadienyl-(dicarbonyl)rhodium complexes

Both regioisomers of rhodium complexes **4A**,**B** could be partially separated by column chromatography and hence no problems occurred with the assignment of individual signals in the NMR spectra to the respective regioisomers, of course, with the exception of overlaid signals (signals in ^{19}F NMR spectra, signals of methylene groups of fluorinated ponytails in ^{1}H NMR spectra, signals of fluorine-bearing carbons in ^{13}C NMR spectra).

3.5. Measurements of fluorophilic properties

Whereas fluorous partition constants of fluorocyclopentadienes **1** could be determined easily from GC analyses of the corresponding phases using appropriate internal standard in this case (trifluoromethyl)benzene, the corresponding partition constants of fluoroferrocenes **2** had to be estimated by AAS measurements of concentration of soluted ferrous ions after decomposition of evaporation residues of both phases.

Fluorophilicities of fluorinated cyclopentadienes **1** rise with the content of fluorine nearly linearly. No significant difference in fluorophilicity was observed when two medium-sized fluorinated ponytails (**1b**) were replaced by one shorter and one longer ponytail (**1e**).

Although all fluorocyclopentadienes **1** can be regarded fluorophilic, having fluorophilicity greater than zero,[8] a presence of at least one medium-length chain (C_6F_{13}) significantly improves fluorophilic properties. Better fluorophilicity is achieved in accordance with expectations when longest fluorinated ponytails are present (**1c**). In fact, only isomer **1c** showed limited solubilities in common organic solvents as chloroform.

In contrast to fluorophilic properties of fluorocyclopentadienes **1**, no similar simple patterns were observed for fluorophilicities of fluoroferrocenes **2**. Surprisingly, far higher fluorophilicity was found for fluoroferrocene **1b** with four equal medium-sized fluorinated chains and no improvement was observed when longer ponytails were used. We have a suspicion that this can have some relation to a complex shape of the NMR spectra of fluoroferrocenes **2c**–**f**. Surprising properties of these ferrocenes are the subject of our continuing intensive study. Due to low stability, we until now did not carry out the estimation of fluorophilicities of rhodium complexes **4**.

In contrast to fluorophilicity, specific fluorophilicity and related fluorousness[8] roughly correspond to the length of fluorinated ponytails used and seem to be thus the superior criterion for evaluation of fluorophilic properties. In principle, all cyclopentadienes **1** and ferrocenes **2** with at least one medium-sized (C_6F_{13}) fluorinated ponytail show high fluorophilicity, whereas their solubility in perfluorinated solvents is still good in contrast to fluorophilic monosubstituted cyclopentadienes **1** with one very long chain.[16]

4. Conclusions

Bis(polyfluoroalkylated) cyclopentadienes **1** are highly fluorophilic ligands providing that they bear at least one medium-size polyfluorinated chain. They can be lithiated at low temperatures without significant loss of hydrogen fluoride from fluorinated ponytails and can thus be used for the preparation of various fluorophilic organometallic complexes. Tetrakis(polyfluorinated) ferrocenes **2** made there from are highly fluorophilic complexes with sufficient stability, but fluorophilic carbonyl rhodium complexes slowly decompose at room temperature even when moisture and air are excluded. In contrast to monosubstituted fluorophilic ferrocenes, no limitations caused by inferior solubility in perfluorinated solvents were encountered.

5. Experimental

5.1. 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. NOE spectra were recorded with a Bruker Avance DRX 500 spectrometer. COSY and HMQC spectra were recorded 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. GC analyses were done with a Nordion Micromat MRGC412 instrument. AAS measurements were carried out with GBC Avanta Summa instrument.

All manipulations including organometallic reagents, as

[†] We thank the referee for the advice of possible sterical crowding.

well as all reactions were performed under an argon atmosphere with exclusion of moisture and atmospheric oxygen in oven-dried apparatuses. Bis(3,3,4,4,5,5,6,6,6-nonafluorohexyl)cyclopentadiene (**1a**), bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)cyclopentadiene (**1b**), bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)cyclopentadiene (**1c**), (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 (**1d**), (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 (**1e**) and (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 (**1f**) were synthesized as mixtures of four regioisomers **A**–**D** according to Ref. 19. Tetracarbonyldichlorodirhodium and anhydrous ferrous chloride were purchased from Aldrich. $FeCl_2$·2 THF complex was prepared according to Ref. 24. Concentration of butyllithium solution was estimated prior to use according to Ref. 25. 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 had to be stored in a freezing chamber.

5.2. Preparation of ferrocenes

General procedure: A flask was charged with $FeCl_2$·THF complex and diethyl ether (80 mL/mmol of $FeCl_2$ complex) was added. To this mixture, bis[2-(perfluoroalkyl)ethyl]-cyclopentadiene (**1**) was dropwise added while stirring. The mixture was cooled to −80°C and butyllithium solution was syringed into it. The mixture was allowed to warm to room temperature and stirred overnight. Solvents were removed and hexane (200 mL/mmol of $FeCl_2$ complex) was added to the dark residue. The mixture was refluxed for 10 min and filtered. Hexane was removed and purification of the residue by column chromatography (15×2 cm, eluent hexane) afforded product as a yellow oil.

5.2.1. Tetrakis(3,3,4,4,5,5,6,6,6-nonafluorohexyl)ferrocene (2a). From $FeCl_2$·2 THF complex (87 mg, 0.32 mmol), bis(3,3,4,4,5,5,6,6,6-nonafluorohexyl)cyclopentadiene (**1a**, 300 mg, 53.7 μmol) and butyllithium (2.50 M solution in hexanes, 0.32 mL, 0.81 mmol), tetrakis(polyfluoroalkylated) ferrocene **2a** (134 mg, 42.6%, clear yellow oil) was obtained as a mixture of three regioisomers **A**,**B**,**C** in the 14:76:10 ratio. IR ($CHCl_3$) 2956, 1457, 1357, 1223, 1133 cm^{-1}. ^1H NMR ($CDCl_3$) regioisomer **A** (1,1′,2,2′-**2a**), δ 2.25 (8H, m), 2.58 (8H, m), 3.92 (2H, t, $^3J_{HH}$=2.7 Hz), 3.98 (4H, d, $^3J_{HH}$=2.7 Hz); regioisomer **B** (1,1′,2,3′-**2a**), δ 2.25 (8H, m), 2.58 (8H, m), 3.92 (2H, d, $^3J_{HH}$=1.4 Hz), 3.94 (1H, t, $^3J_{HH}$=1.4 Hz), 3.96 (2H, d, $^3J_{HH}$=2.5 Hz), 4.03 (1H, t, $^3J_{HH}$=2.5 Hz); regioisomer **C** (1,1′,3,3′-**2a**), δ 2.25 (8H, m), 2.58 (8H, m), 3.86 (2H, t, $^3J_{HH}$=1.4 Hz), 3.93 (4H, d, $^3J_{HH}$=1.4 Hz). ^{13}C NMR ($CDCl_3$) regioisomer **A** (1,1′,2,2′-**2a**), δ 18.1 (4C, s), 32.4 (4C, t, $^2J_{CF}$=22 Hz), 68.4 (2C, s), 69.3 (4C, s), 84.8 (2C, s), 108.6–120.2 (16C, m); regioisomer **B** (1,1′,2,3′-**2a**), δ 18.1 (2C, s), 20.0 (2C, s), 32.4 (2C, t, $^2J_{CF}$=22 Hz), 32.7 (2C, t, $^2J_{CF}$=22 Hz), 68.0 (1C, s), 68.4 (1C, s), 69.2 (2C, s), 69.4 (2C, s), 84.8 (2C, s), 86.5 (2C, s), 108.6–120.2 (16C, m); regioisomer **C** (1,1′,3,3′-**2a**), δ 20.1 (4C, s), 32.8 (4C, t, $^2J_{CF}$=22 Hz), 69.0 (4C, s), 69.6 (2C, s), 86.7 (4C, s), 108.6–120.2 (16C, m). ^{19}F NMR ($CDCl_3$), δ −81.6 (12F, t, J_{FF}=9.8 Hz), −115.2 (8F, m), −124.9 (8F, m), −126.5 (8F, t, J_{FF}=12.8 Hz). Anal. calcd for $C_{34}H_{22}F_{36}Fe$: C, 34.90; H, 1.88. Found: C, 35.22; H, 2.08.

5.2.2. Tetrakis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)ferrocene (2b). From $FeCl_2$·2 THF complex (95 mg, 0.35 mmol), bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorohexyl)cyclopentadiene (**1b**, 440 mg, 58.0 μmol) and butyllithium (2.50 M solution in hexanes, 0.38 mL, 0.88 mmol), tetrakis(polyfluoroalkylated) ferrocene **2b** (219 mg, 48.1%, clear yellow oil) was obtained as a mixture of three regioisomers **A**,**B**,**C** in the 15:65:20 ratio. IR ($CHCl_3$) 2957, 1456, 1365, 1239, 1145 cm^{-1}. ^1H NMR ($CDCl_3$) regioisomer **A** (1,1′,2,2′-**2b**), δ 2.26 (8H, m), 2.60 (8H, m), 3.92 (2H, t, $^3J_{HH}$=2.7 Hz), 3.99 (4H, d, $^3J_{HH}$=2.7 Hz); regioisomer **B** (1,1′,2,3′-**2b**), δ 2.26 (8H, m), 2.60 (8H, m), 3.92 (2H, d, $^3J_{HH}$=1.4 Hz), 3.94 (1H, t, $^3J_{HH}$=1.4 Hz), 3.96 (2H, d, $^3J_{HH}$=2.5 Hz), 4.04 (1H, t, $^3J_{HH}$=2.5 Hz); regioisomer **C** (1,1′,3,3′-**2b**), δ 2.26 (8H, m), 2.60 (8H, m), 3.86 (2H, t, $^3J_{HH}$=1.4 Hz), 3.94 (4H, d, $^3J_{HH}$=1.4 Hz). ^{13}C NMR ($CDCl_3$) regioisomer **A** (1,1′,2,2′-**2b**), δ 18.1 (4C, s), 32.4 (4C, t, $^2J_{CF}$=22 Hz), 68.4 (2C, s), 69.3 (4C, s), 84.8 (2C, s), 108.6–120.2 (16C, m); regioisomer **B** (1,1′,2,3′-**2b**), δ 18.1 (2C, s), 20.0 (2C, s), 32.4 (2C, t, $^2J_{CF}$=22 Hz), 32.7 (2C, t, $^2J_{CF}$=22 Hz), 68.0 (1C, s), 68.4 (1C, s), 69.2 (2C, s), 69.4 (2C, s), 84.8 (2C, s), 86.5 (2C, s), 108.6–120.2 (16C, m); regioisomer **C** (1,1′,3,3′-**2b**), δ 20.1 (4C, s), 32.8 (4C, t, $^2J_{CF}$=22 Hz), 69.0 (4C, s), 69.6 (2C, s), 86.7 (4C, s), 108.6–120.2 (16C, m). ^{19}F NMR ($CDCl_3$), δ −81.5 (12F, t, J_{FF}=10 Hz), −115.0 (8F, m), −122.4 (8F, m), −123.4 (8F, m), −124.1 (8F, m), 126.7 (8F, m). Anal. calcd for $C_{42}H_{22}F_{54}Fe$: C, 31.07; H, 1.43. Found: C, 29.99; H, 1.49.

5.2.3. Tetrakis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)ferrocene (2c). From $FeCl_2$·2 THF complex (161 mg, 0.60 mmol), bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorohexyl)cyclopentadiene (**1c**, 700 mg, 73.0 μmol) and butyllithium (2.50 M solution in hexanes, 0.63 mL, 1.5 mmol), tetrakis(polyfluoroalkylated) ferrocene **2c** (340 mg, 47.2%, clear yellow oil) was obtained. IR ($CHCl_3$) 2957, 1456, 1365, 1239, 1145 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.26 (8H, m), 2.59 (8H, m), 3.87–4.06 (6H, m). ^{13}C NMR ($CDCl_3$) δ 18.2–20.2 (4C, singlets), 32.8 (4C, m), 67.9–69.5 (6C, singlets), 84.7–86.5 (4C, singlets), 108.2–120.4 (32C, m). ^{19}F NMR ($CDCl_3$), δ −81.4 (12F, t, J_{FF}=10 Hz), −115.0 (8F, m), −122.4 (24F, m), −123.3 (8F, m), −124.0 (8F, m), −126.7 (8F, m). Anal. calcd for $C_{50}H_{22}F_{68}Fe$: C, 30,48; H, 1.11. Found: C, 31.35; H, 1.18.

5.2.4. Bis(3,3,4,4,5,5,6,6,6-nonafluorohexyl)bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)ferrocene (2d). From $FeCl_2$·2 THF complex (74 mg, 0.27 mmol), (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 (**2d**, 280 mg, 42.5 μmol) and butyllithium (2.50 M solution in hexanes, 0.27 mL, 0.68 mmol), tetrakis(polyfluoroalkylated) ferrocene **2d** (171 mg, 58.7%, clear yellow oil) was obtained. IR ($CHCl_3$) 2957, 1457, 1357, 1234, 1134 cm^{-1}. ^1H NMR ($CDCl_3$), δ 2.19 (8H, m), 2.53 (8H, m), 3.79–3.97 (6H, m). ^{13}C NMR ($CDCl_3$) δ 18.1–20.0 (4C, singlets), 32.5 (4C, m), 67.9–69.3 (6C, singlets), 84.8–86.5 (4C, singlets),

108.4–118.7 (20C, m). ^{19}F NMR ($CDCl_3$), δ −81.4 (6F, m), −81.7 (6F, m), −115.0 (4F, m), −115.2 (4F, m), −122.4 (4F, m), −123.4 (4F, m), −124.1 (4F, m), −125.0 (4F, m), −126.6 (8F, m). Anal. calcd for $C_{38}H_{22}F_{44}Fe$: C, 33.31; H, 1.61. Found: C, 32.98; H, 1.69.

5.2.5. Bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)bis(3,3,4,4,5,5,6,6,6-nonafluorohexyl) ferrocene (2e). From $FeCl_2$·2 THF complex (64 mg, 0.24 mmol), (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 (**1e**, 300 mg, 39.6 μmol) and butyllithium (2.50 M solution in hexanes, 0.24 mL, 0.60 mmol), tetrakis(polyfluoroalkylated) ferrocene **2e** (179 mg, 57.6%, clear yellow oil) was obtained. IR ($CHCl_3$) 2956, 1456, 1357m, 1236, 1213, 1151, 1145 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 2.25 (8H, m), 2.59 (8H, m), 3.85–4.04 (6H, m). ^{13}C NMR ($CDCl_3$) δ 18.1–20.1 (4C, singlets), 32.8 (4C, m), 67.9–70.1 (6C, singlets), 84.6–86.9 (4C, singlets), 108.2–118.8 (24C, m). ^{19}F NMR ($CDCl_3$), δ −81.4 (6F, t, $^3J_{FF}$=10 Hz, $2CF_3$), −81.7 (6F, t, $^3J_{FF}$=10 Hz, $2CF_3$), −114.9 (4F, m, $2CF_2$), −115.3 (4F, m, $2CF_2$), −122.2 (4F, m, $2CF_2$), −122.5 (8F, m, $4CF_2$), −123.3 (4F, m, $2CF_2$), −124.0 (4F, m, $2CF_2$), −125.0 (4F, m, $2CF_2$), −126.6 (8F, m, $4CF_2$). Anal. calcd for $C_{42}H_{22}F_{52}Fe$: C, 32.12; H, 1.40. Found: C, 31.81; H, 1.46.

5.2.6. Bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9, 10,10,10-heptadecafluorodecyl)bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)ferrocene (2f). From $FeCl_2$·2 THF complex (44 mg, 0.16 mmol), (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 (**2f**, 230 mg, 26.7 μmol) and butyllithium (2.50 M solution in hexanes, 0.19 mL, 0.40 mmol), tetrakis(polyfluoroalkylated) ferrocene **2f** (146 mg, 61.5%, clear yellow oil) was obtained. IR ($CHCl_3$) 2957, 1456, 1366, 1240, 1206, 1145 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 2.25 (8H, m), 2.58 (8H, m), 3.85–4.03 (6H, m). ^{13}C NMR ($CDCl_3$), δ 18.2–20.1 (4C, singlets), 32.7 (4C, m), 67.9–69.6 (6C, singlets), 84.8–86.7 (4C, singlets), 108.3–118.6 (28C, m). ^{19}F NMR ($CDCl_3$), δ 81.4 (12F, m, $4CF_3$), −115.0 (8F, m, $4CF_2$), −122.3 (4F, m, $2CF_2$), −122.5 (12F, m, $6CF_2$), −123.3 (4F, m, $2CF_2$), −123.5 (4F, m, $2CF_2$), −124.1 (4F, m, $2CF_2$), −126.7 (8F, m, CF_2CH_2). Anal. calcd for $C_{46}H_{22}F_{60}Fe$: C, 31.21; H, 1.24. Found: C, 31.06; H, 1.43.

5.3. Preparation of rhodium complexes

General procedure: A flask was charged with bis(polyfluoroalkyl)cyclopentadiene (**1**), THF (40 mL/mmol of fluorocyclopentadiene) and cooled to −80°C. Butyllithium was syringed into the mixture while stirring, the mixture was warmed to −10°C, stirred for 10 min and cooled to −80°C, followed by addition of the solution of tetracarbonyldichlorodirhodium in THF (30 mL/mmol of rhodium complex). The mixture was then warmed to room temperature and stirred overnight (16 h). Solvents were removed and dark residue purified by column chromatography on alumina (20×2 cm, eluent hexane) under inert conditions to afford product **4** as an orange oil sensitive to air.

5.3.1. [η^5-Bis(3,3,4,4,5,5,6,6,6-nonafluorohexyl)cyclopentadienyl]dicarbonylrhodium (4a). From bis(3,3,4,4,5,5,6,6,6-nonafluorohexyl)cyclopentadiene (**1a**, 1.00 g, 1.79 mmol), butyllithium (2.50 M solution in hexanes, 0.81 mL, 0.81 mmol) and $[Rh(CO)_2Cl]_2$ (270 mg, 69.5 μmol), bis(polyfluoroalkylated) rhodium complex **4a** (567 mg, 44.2%, orange oil) was obtained as a mixture of two regioisomers **A**,**B** in the 34:66 ratio. IR ($CHCl_3$) 2046, 1981, 1224, 1134 cm^{-1}. ^{1}H NMR ($CDCl_3$) regioisomer **A** (1,2-**4a**), δ 2.34 (4H, m), 2.63 (4H, m), 5.32 (1H, t, $^3J_{HH}$=2.8 Hz), 5.39 (2H, d, $^3J_{HH}$=2.8 Hz); regioisomer **B** (1,3-**4a**), δ 2.34 (4H, m), 2.63 (4H, m), 5.37 (2H, d, $^3J_{HH}$=1.6 Hz), 5.46 (1H, t, $^3J_{HH}$=1.6 Hz). ^{13}C NMR ($CDCl_3$) regioisomer **A** (1,2-**4a**), δ 17.1 (2C, s), 33.8 (2C, m), 84.4 (d, $^1J_{CRh}$=4 Hz), 86.4 (2C, d, $^1J_{CRh}$=4 Hz), 108.1 (2C, d, $^1J_{CRh}$=33 Hz), 108.3–118.9 (8C, m), 191.0 (2C, d, $^1J_{CRh}$=84 Hz); regioisomer **B** (1,3-**4a**), δ 19.1 (2C, s), 33.8 (2C, m), 86.3 (2C, d, $^1J_{CRh}$=3 Hz), 88.1 (d, $^1J_{CRh}$=3 Hz), 108.4 (2C, d, $^1J_{CRh}$=33 Hz), 108.3–118.9 (8C, m), 191.0 (2C, d, $^1J_{CRh}$=84 Hz). ^{19}F NMR ($CDCl_3$), δ −81.6 (6F, t, J_{FF}=10 Hz), −115.2 (4F, m), −124.9 (4F, m), −126.5 (4F, m). Anal. calcd for $C_{19}H_{11}F_{18}O_2Rh$: C, 31.87; H, 1.54. Found: C, 32.34; H, 1.63.

5.3.2. [η^5-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-cyclopentadienyl]dicarbonylrhodium (4b). From bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)cyclopentadiene (**1b**, 381 mg, 502 μmol), butyllithium (2.50 M solution in hexanes, 0.24 mL, 0.20 mmol) and $[Rh(CO)_2Cl]_2$ (75 mg, 0.20 mmol), bis(polyfluoroalkylated) rhodium complex **4b** (89.3 mg, 25.2%, orange oil) was obtained as a mixture of two regioisomers **A**,**B** in the 32:68 ratio. IR ($CHCl_3$) 2048, 1983, 1239, 1145 cm^{-1}. ^{1}H NMR ($CDCl_3$) regioisomer **A** (1,2-**4b**), δ 2.24 (4H, m), 2.53 (4H, m), 5.22 (1H, t, $^3J_{HH}$=2.8 Hz), 5.30 (2H, d, $^3J_{HH}$=2.8 Hz); regioisomer **B** (1,3-**4b**), δ 2.24 (4H, m), 2.53 (4H, m), 5.27 (2H, d, $^3J_{HH}$=1.0 Hz), 5.36 (1H, t, $^3J_{HH}$=1.0 Hz). ^{13}C NMR ($CDCl_3$) regioisomer **A** (1,2-**4b**), δ 17.2 (2C, s), 34.0 (2C, m), 84.4 (d, $^1J_{CRh}$=4 Hz), 86.5 (2C, d, $^1J_{CRh}$=4 Hz), 108.1 (2C, d, $^1J_{CRh}$=33 Hz), 108.7–119.0 (12C, m), 191.0 (2C, d, $^1J_{CRh}$=84 Hz); regioisomer **B** (1,3-**4b**), δ 19.1 (2C, s), 34.0 7(2C, m), 86.4 (2C, d, $^1J_{CRh}$=3 Hz), 88.1 (d, $^1J_{CRh}$=3 Hz), 108.1 (2C, d, $^1J_{CRh}$=33 Hz), 108.7–119.0 (12C, m), 191.0 (2C, d, $^1J_{CRh}$=84 Hz). ^{19}F NMR ($CDCl_3$), δ −81.3 (6F, t, J_{FF}=10 Hz), −114.7 (4F, m), −122.4 (4F, m), −123.3 (4F, m), −124.0 (4F, m), −126.6 (4F, m). Anal. calcd for $C_{19}H_{11}F_{18}O_2Rh$: C, 30.15; H, 1.20. Found: C, 32.06; H, 1.62.

5.4. Fluorous partition coefficients

5.4.1. Fluorous partition coefficients for fluorocyclopentadienes 1 by GC. A flask was charged with perfluoro(methylcyclohexane) (2 mL), toluene (2 mL) and fluorocyclopentadiene **1** (ca. 50 mg) while stirring. The mixture was heated to 60°C over 15 min and cooled to 25°C. After 1 h 1 mL of solution was taken from each layer. To each sample, (trifluoromethyl)benzene (5 μL) and diethyl ether (1 mL) were added, samples were shaked and analyzed by GC.

5.4.2. Fluorous partition coefficients for fluoroferrocenes 2 by AAS. A flask was charged with perfluoro(methylcyclohexane) (1 mL), toluene (1 mL) and fluoroferrocene

2 (ca. 20 mg) while stirring. After 1 h, the mixture was left to separate the layers for 1.5 h, which were separated and filtered. Solvents were removed by evaporation. Residues were treated with concentrated H_2SO_4 (0.5 mL), the acid was removed at 530°C, residues were melted with $K_2S_2O_7$, cooled, triturated with water and the aqueous solutions were analyzed by AAS.

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