

(Fluoroorgano)fluoroboranes and -fluoroborates

Part 3. Polyfluoroalken-1-yldifluoroboranes

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Received 9 March 2001; accepted 16 April 2001

Dedicated to Professor Voronkov on the occasion of his 80th birthday

Abstract

Polyfluoroalken-1-yldifluoroboranes $\text{RCF}=\text{CFBF}_2$ ($\text{R} = \text{F}$, *cis*-, *trans*-Cl, *trans*- C_4F_9 , *cis*- C_2F_5 , *cis*- C_6F_{13} , *trans*- C_4H_9 , *trans*- C_6H_5) were prepared by defluoridation of the corresponding fluoroborate salts $\text{K}[\text{RCF}=\text{CFBF}_3]$ using boron trifluoride in dichloromethane or fluorotrichloromethane. The alkenylboranes were characterised by ^1H -, ^{11}B - and ^{19}F -NMR spectroscopy. Their reactivity towards ether, water and anhydrous HF was investigated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Boranes; Borates; Polyfluoroalken-1-yl boron compounds; NMR

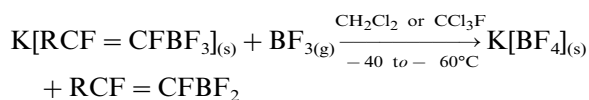
1. Introduction

Recently we have described the successful defluoridation of the potassium salts of polyfluoroaryltrifluoroborates $\text{K}[\text{C}_6\text{H}_5\text{--}_n\text{F}_n\text{BF}_3]$ ($n = 1\text{--}5$) and of perfluoroalkyltrifluoroborates $\text{K}[\text{C}_n\text{F}_{2n+1}\text{BF}_3]$ ($n = 3, 6$) under formation of the corresponding polyfluoroaryl- and perfluoroalkyldifluoroboranes using the fluoride anion acceptors BF_3 or arsenic pentafluoride [1,2]. In our previous paper [3], the synthesis of salts $\text{K}[\text{RCF}=\text{CFBF}_3]$ and their NMR and IR spectra are reported. Fluoro-containing alken-1-yldifluoroboranes are scarcely studied compounds. In 1960, trifluorovinylidifluoroborane was prepared from $\text{CF}_2=\text{CFBCl}_2$ and SbF_3 (59% yield) or from $(\text{CF}_2=\text{CF})_2\text{SnMe}_2$ and BF_3 (18% yield) [4]. Later, the difluoroboranes $\text{CF}_2=\text{C}(\text{CF}_3)\text{BF}_2$ and *cis*- $\text{BF}_2\text{CF}=\text{CFBF}_2$ were obtained by the addition of BF_3 to $\text{CF}_2=\text{C}=\text{CF}_2$ (70% yield) [5] or B_3F_5 to $\text{CF}_2=\text{CF}_2$ (yield was not given) [6]. In a preliminary communication [7], we demonstrated the principal approach to polyfluoroalken-1-yldifluoroboranes based on the defluoridation of the corresponding $\text{K}[\text{RCF}=\text{CFBF}_3]$ salts using BF_3 .

Here, we report the detailed synthesis of various difluoroboranes $\text{RCF}=\text{CFBF}_2$ ($\text{R} = \text{F}$, *cis*-, *trans*-Cl, *cis*- C_2F_5 , *cis*- C_6F_{13} , *trans*- C_4F_9 , *trans*- C_4H_9 , *trans*- C_6H_5) by defluoridation of the fluoro borate salts in an inert solvent (CH_2Cl_2 or CCl_3F), their NMR spectra as well as their reactivities towards water, ether or anhydrous HF (aHF).

2. Results and discussion

Potassium polyfluoroalken-1-yltrifluoroborates, like the salts $\text{K}[\text{C}_6\text{H}_5\text{--}_n\text{F}_n\text{BF}_3]$ and $\text{K}[\text{C}_n\text{F}_{2n+1}\text{BF}_3]$, are practically insoluble in weakly polar, weakly coordinating solvents [3]. BF_3 gas dissolves at low temperature in such solvents like CH_2Cl_2 or CCl_3F . Bubbling of BF_3 into the stirred suspension of potassium polyfluoroalken-1-yltrifluoroborate salts in CH_2Cl_2 or in CCl_3F at -40 to -60 °C led to the easy defluoridation under formation of the corresponding polyfluoroalken-1-yldifluoroboranes in high yields.



$\text{R} = \text{F}$ (1); *cis*-, *trans*-Cl (2); *cis*- C_2F_5 (3); *cis*- C_6F_{13} (4); *trans*- C_4F_9 (5); *trans*- C_4H_9 (6); *trans*- C_6H_5 (7).

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Table 1
The ^{11}B -NMR spectra of polyfluoroalken-1-yl difluoroboranes $\text{RCF}=\text{CFBF}_2^{\text{a}}$

R	$\delta(\text{B})$ (ppm)	$\tau_{1/2}$ (Hz)
F [8]	21.8 ^b	n.d.
<i>cis</i> -Cl	21.99	186
<i>cis</i> -C ₂ F ₅	20.28	106
<i>cis</i> -C ₆ F ₁₃	20.66	140
<i>trans</i> -Cl	21.10	175
<i>trans</i> -C ₄ F ₉	20.04	156
<i>trans</i> -C ₄ H ₉	21.72	160
^c	22.6	n.d.

^a Solutions in CH_2Cl_2 . Substituents R are in *cis* or *trans* positions relative to the BF_2 group.

^b In toluene- d_8 .

^c $\text{CH}_2=\text{CHBF}_2$ [9].

Defluoridation under the above conditions is neither accompanied by the migration of the $\text{C}=\text{C}$ bond into the carbon chain nor by *cis*, *trans*-isomerisation of the products.

Alkenyldifluoroboranes **1–7** are well soluble either in CH_2Cl_2 or in CCl_3F at room temperature. Compounds **4** and **5** with the perfluorinated long alkyl chain separate at lower temperature forming compact oil phases. The solutions of boranes **1–5** are stable at 20 °C over

days under a dry argon atmosphere, whereas the solutions of **6** and **7** are less stable and decompose at 20 °C within some hours to give BF_3 , *trans*- $\text{RCF}=\text{CFH}$ and additionally unrecognised fluoroorganics.

The ^{11}B -NMR spectra of the difluoroboranes **1–5** show the resonance of the boron atom at 21–22 ppm. This coincides with the previously reported ^{11}B -NMR data of $\text{CH}_2=\text{CHBF}_2$ and $\text{CH}_2=\text{CFBF}_2$ (Table 1) and is similar to those of fluoroaryldifluoroboranes [1] and perfluoroalkyldifluoroboranes [2]. In all cases, the ^{11}B -NMR signals are broad and unresolved ($\tau_{1/2} \approx 100$ –190 Hz) due to the electric quadrupole of the three-coordinated boron atom (Table 1). The ^{19}F resonances of the fluorine atoms bonded to boron are located at -80 to -88 ppm and appear broad and unresolved regardless of the temperature (-40 to $+24$ °C) (Table 2). It should be noted that replacement of the fluorine atom in the *trans*-position to the BF_2 group by the substituents $\text{R} = \text{Cl}$, C_4H_9 and C_6H_5 has no effect on the $\delta(\text{F})$ values of the fluorine atoms bonded at boron. The ^{19}F resonance of the BF_2 group in vinyl difluoroborane $\text{CH}_2=\text{CHBF}_2$ is also located in the same region at -89 ppm [11]. However, a remarkable deshielding of the fluorine atoms of the BF_2 -group is observed in the ^{19}F -NMR spectra of the difluoroboranes *cis*- $\text{RCF}=\text{CFBF}_2$ ($\text{R} = \text{Cl}$, C_2F_5 , C_6F_{13}) and *trans*-

Table 2
The ^{19}F -NMR spectra of polyfluoroalken-1-yl difluoroboranes $\text{RCF}=\text{CFBF}_2^{\text{a}}$

R	$\delta(\text{F})$ (ppm)				J (Hz)		
	F-1	F-2 <i>cis</i>	F-2 <i>trans</i>	BF_2	1,2 <i>cis</i>	2 <i>cis</i> , BF	2 <i>cis</i> ,2 <i>trans</i>
F (-40 °C)	-207.19	-98.96	-72.06	-87.06	114	24	16
F [10] ^b	-206.6	-99.8	-72.8	-86.7	114	25	18
F (24 °C) ^c	Cl	-68.04	-55.98	n.d.	–	n.d.	n.d.
F (-40 °C) ^c	Cl	-68.09	-55.79	n.d.	–	n.d.	n.d.
<i>trans</i> -Cl (24 °C)	-171.64	-97.68	–	-86.12	134	24	–
<i>trans</i> -Cl (-40 °C)	-172.26	-97.92	–	-86.50	133	27	–
F [5] ^d	CF_3 ^e	-57.3	-47.6	-82.2	–	n.d.	39.0
<i>trans</i> -C ₄ H ₉ (24 °C)	-184.86	-124.70	– ^f	-87.71	129	27	–
<i>trans</i> -C ₄ H ₉ (-20 °C)	-184.88	-124.85	– ^g	-87.63	130	n.d.	–
<i>trans</i> -C ₆ H ₅ (24 °C)	-178.88	-136.30	–	-87.00	128	n.d.	–
<i>trans</i> -C ₄ F ₉ (24 °C)	-166.57	-149.08	– ^h	-82.97	123	n.d.	–
<i>cis</i> -Cl (24 °C)	-159.59	–	-68.77	-83.12	–	–	–
<i>cis</i> -C ₆ F ₁₃ (24 °C)	-146.27	– ⁱ	-123.31	-78.98	–	–	–
<i>cis</i> -C ₂ F ₅ (24 °C)	-146.97	– ^j	-124.25	-80.36	–	–	–
<i>cis</i> - BF_2 [6]	-158	–	-158	-80.6	–	–	–

^a Solutions in CH_2Cl_2 . Fluorine atoms are in *cis* or *trans*-positions relative to the BF_2 group.

^b In CFCl_3 .

^c Derived from an admixture (9%) of $\text{K}[\text{CF}_2=\text{CClBF}_3]$.

^d Neat liquid.

^e $\delta(\text{F})$: -59.9 (CF_3); J , Hz: (2*cis*, CF_3) 22.6, J , Hz: (2*trans*, CF_3) 12.0.

^f J , Hz: (2,H-3) 25.

^g $\delta(\text{H})$: 2.61 (2 H-3), ~ 1.4 (2 CH_2), 0.86 (3 H-6).

^h $\delta(\text{F})$: -81.71 (3 F-6), -119.14 (2 F-3), -125.05 , -126.92 (2 CF_2).

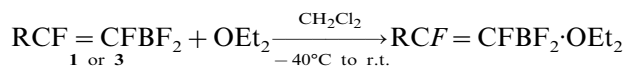
ⁱ $\delta(\text{F})$: -81.48 (3 F-8), -116.79 (2 F-3), -122.49 , -123.31 (3 CF_2), -126.68 (2 F-7).

^j $\delta(\text{F})$: -84.97 (3 F-4), -120.33 (2 F-3).

$C_4F_9CF=CFBF_2$. Similar phenomena were observed for *cis*- $BF_2CF=CFBF_2$ [6] and $CF_2=C(CF_3)BF_2$ [5]. Also the introduction of fluorine atoms in the *ortho*-positions of aryldifluoroboranes $C_6H_{5-n}F_nBF_2$ caused a similar effect [1]. It is likely, that this effect arises from an intramolecular fluorine–boron interaction.

Little information about the reactivity of fluoro-containing alkenyldifluoroboranes was known. It was reported that the interaction of borane **1** with water at room temperature resulted neither in carbon–boron nor in fluorine–boron bond cleavage but the products were not characterised. Alternatively, the quantitative protodeborylation of difluoroborane **1** took place at 120 °C (15 h) yielding trifluoroethylene [4]. The hydrolysis of compound $CF_2=C(CF_3)BF_2$ resulted in the polyfluorinated olefin $CF_2=CHCF_3$ (conditions were not reported) [5].

We have investigated the reactivity of some difluoroboranes towards water and ether and we have found that the treatment of difluoroboranes **1** and **3** with ether in CH_2Cl_2 gave as expected the etherates **8** and **9** in quantitative yield.



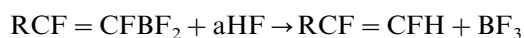
R = F (**8**); *cis*- C_2F_5 (**9**).

The coordination of diethyl ether (neutral *n*-electron donor) at the boron atom leads to a dramatic redistribution of the charge in the molecule which is reflected in the ^{19}F -NMR spectra. The spectrum of etherate **8** consists of four resonances at -94.32 (F-2*trans*), -118.82 (F-2*cis*), -199.71 (F-1) and -149.04 ($BF_2 \cdot OEt_2$) ppm [*J*, Hz: (1,2*cis*) 114, (1,2*trans*) 17, (2*cis*,2*trans*) 73, (2*cis*, $BF_2 \cdot OEt_2$) 14 and (F,B) 46]. The ^{19}F -NMR spectrum of compound **9** displays signals at -84.85 (3 F-4), -119.77 (2 F-3), -147.79 ($BF_2 \cdot OEt_2$), -137.78 and -146.49 (F-1 and F-2*trans*) ppm. A comparison of the spectra of the adducts **8** and **9** with those of the starting difluoroboranes **1** and **3** (Table 2) and those of the corresponding salts $K[RCF=CFBF_3]$ [3], demonstrates the dramatic changes when the BF_2 group [1] with the strongest σ - and π -electron accepting effect is converted to the neutral $BF_2 \cdot OEt_2$ group with a tetra coordinated boron atom or to the negatively charged BF_3^- group with the strongest σ -electron donating and negligible mesomeric effect [1].

When CH_2Cl_2 solutions of $RCF=CFBF_2$ were reacted with water at 0 °C (R = F) or at ≥ -78 °C (R = *cis*,*trans*-Cl), the formation of the anions $[RCF=CFBF_3]^-$ [3] and $[BF_4]^-$ was detected in the aqueous phase (^{19}F -NMR). No ^{19}F -NMR signals which could be attributed to the alkenes $RCF=CFH$ or the boronic acids $RCF=CFB(OH)_2$ were observed neither in the aqueous nor in the organic phase. It is known from literature [4] that difluoroboranes $RCF=CFBF_2$

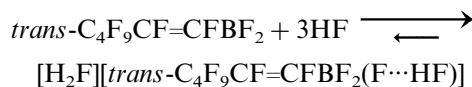
can dissolve BF_3 . We have observed BF_3 after saturation of difluoroborane solutions at -40 °C (^{19}F), but BF_3 was not detected (^{19}F) after degasing. Admixtures of BF_3 , which are still present, may be the additional source of HF during hydrolysis and responsible for the conversion of compounds **1** and **2** into $[RCF=CFBF_3]^-$ and the basis of $[BF_4]^-$ in the concurrent absence of $RCF=CFH$.

However, in anhydrous HF (aHF) the difluoroboranes **1** and **2** underwent protodeborylation and the corresponding fluoro-containing alkenes $RCF=CFH$ were formed. After shaking the $CF_2=CFBF_2$ solution in CH_2Cl_2 with aHF at -40 °C, the acidic phase contained both $CF_2=CFH$ and difluoroborane **1**. It is noteworthy to mention that the ^{19}F -NMR spectrum of the latter did not differ from that of $CF_2=CFBF_2$ in CH_2Cl_2 . This fact verifies that no significant complex formation between trifluorovinyl difluoroborane and aHF takes place. A similar picture was observed during the reaction of difluoroborane **2** with aHF.



R = F; *cis*-, *trans*-Cl.

Alternatively, the addition of aHF to a solution of *trans*- $C_4F_9CF=CFBF_2$ in CH_2Cl_2 at -20 °C followed by warming up to room temperature did not result in the protodeborylation. The ^{19}F -NMR spectrum of the acidic phase showed resonances at -79.53 (3 F-6), -115.83 (2 F-3), -122.83 , -124.50 (2 F-4 and 2 F-5), -159.83 (F-1) and -169.17 (F-2) ppm [*J*(1,2) 132 Hz], whereas the resonance of the fluorine atoms bonded to boron was not observed. The organic phase contained only traces of HF and the above-mentioned signals. This spectrum coincides with the spectrum obtained from $K[trans-C_4F_9CF=CFBF_3]$ in aHF and differs from that of the salt in MeCN [resonances at -80.41 , -115.95 , -124.12 , -125.60 , -153.06 and -177.16 ppm, respectively, and at -144.03 (BF_3^-) ppm; *J*(1,2) 130 Hz] [3]. Presumably, in aHF the formation of a complex between difluoroborane **5** (Lewis acid) and HF (F-terminus acts as Lewis base) occurred. In fact, the observed ^{19}F -NMR spectrum can present an equilibrium between the neutral difluoroborane **5**, HF and the protonated perfluoro-*trans*-hexen-1-yltrifluoroborate.



Taking into account the complex formation of **5** in aHF and the absence of a related complex of $CF_2=CFBF_2$ in aHF, the protodeborylation of difluoroboranes **1** and **2** can be described in terms of the direct attack of the proton on the carbon atom C-1 bonded to boron.

It should be noted that fluoroalkenes $RCF=CFH$ (R = F, *cis*-, *trans*-Cl) are significantly soluble in aHF

at $-40\text{ }^{\circ}\text{C}$ although their ^{19}F -NMR spectra show no protonation. For instance, the solution of $\text{CF}_2=\text{CFH}$ in aHF ($-40\text{ }^{\circ}\text{C}$) displays resonances at -99.69 (F-2*trans*), -125.98 (F-2*cis*) and -205.27 (F-1) ppm [*J*, Hz: (1,H) 70.9, (1,2*cis*) 116.7, (1,2*trans*) 33.0, (2*cis*,H) 3.4, (2*cis*,2*trans*) 88.4, (2*trans*,H) 12.6] (the positions of the fluorine atoms are with respect to the hydrogen atom). A solution of $\text{CF}_2=\text{CFH}$ in CH_2Cl_2 ($-40\text{ }^{\circ}\text{C}$) is characterised by ^{19}F resonances at -101.22 (F-2*trans*), -127.04 (F-2*cis*) and -206.27 (F-1) ppm [*J*, Hz: (1,H) 70.5, (1,2*cis*) 117.6, (1,2*trans*) 32.4, (2*cis*,H) 3.8, (2*cis*,2*trans*) 83.6, (2*trans*,H) 13.2] These spectral data coincide well with those taken from [12]. It is noteworthy, that the ^{19}F value $\delta(\text{F-1})$ of CF_2CFH given in Ref. [13] is erroneous. This wrong value is cited in the books [14,15] and the new monograph [16].

3. Experimental

NMR spectra were measured on Bruker spectrometers WP 80 SY (^1H at 80.13 MHz and ^{19}F at 75.39 MHz) and Avance DRX 500 (^1H at 500.13 MHz, ^{11}B at 160.46 MHz and ^{19}F at 470.59 MHz). Shift values were reported with respect to TMS (^1H), $\text{BF}_3\cdot\text{OEt}_2$ (^{11}B) and CCl_3F (^{19}F).

Dichloromethane, ether and CCl_3F were purified and dried by standard procedures. Hydrogen fluoride was dried by electrolysis (stainless steel cell, Ni electrodes). The preparation of salts $\text{K}[\text{RCF}=\text{CFBF}_3]$ ($\text{R} = \text{F}$, *trans*- C_4F_9 , *cis*- C_2F_5 , *cis*- C_6F_{13} , *trans*- C_4H_9 , *trans*- C_6H_5) and $\text{K}[\text{cis-}, \text{trans-ClCF}=\text{CFBF}_3]$ (contains additionally 9% of $\text{K}[\text{CF}_2=\text{CClBF}_3]$) is described in Ref. [3].

All manipulations of moisture-sensitive compounds were performed in FEP (copolymer of tetrafluoroethylene and hexafluoropropylene) equipment under a dry argon atmosphere.

3.1. Preparation of $\text{RCF}=\text{CFBF}_2$ (general procedure)

Potassium polyfluoroalken-1-yltrifluoroborate $\text{K}[\text{RCF}=\text{CFBF}_3]$ was suspended in CH_2Cl_2 or in CCl_3F at -40 to $-65\text{ }^{\circ}\text{C}$ and BF_3 (4–5 M excess) was bubbled for 20–60 min under stirring. The reaction mixture was flushed with dry argon to remove the excess of BF_3 . After centrifugation at temperatures below $-40\text{ }^{\circ}\text{C}$ ($\text{R} = \text{F}$, *cis*-, *trans*-Cl) or at $-20\text{ }^{\circ}\text{C}$ ($\text{R} = \text{trans-}\text{C}_4\text{H}_9$) or at room temperature (r.t.) ($\text{R} = \text{trans-}\text{C}_4\text{F}_9$, *cis*- C_2F_5 , *cis*- C_6F_{13} , *trans*- C_6H_5), the mother liquor was decanted, the precipitate was washed with CH_2Cl_2 , and the extract was combined with the mother liquor. Yields of difluoroboranes $\text{RCF}=\text{CFBF}_2$ were higher than 80–90% (^{19}F -NMR with the internal quantitative references $\text{CFCl}_2\text{CF}_2\text{Cl}$ or PhCF_3).

3.2. Reaction of $\text{RCF}=\text{CFBF}_2$ with ether

A solution of $\text{RCF}=\text{CFBF}_2$ ($\text{R} = \text{F}$, *cis*- C_2F_5) (0.3–0.4 mmol) in CH_2Cl_2 (0.3–0.4 ml) was cooled to $-40\text{ }^{\circ}\text{C}$ and anhydrous ether (1.7–2 M equivalents) was added. The solution was warmed to r.t. and showed the quantitative conversion of $\text{RCF}=\text{CFBF}_2$ to $\text{RCF}=\text{CFBF}_2\cdot\text{OEt}_2$ (^{19}F -NMR).

3.3. Reactions of $\text{RCF}=\text{CFBF}_2$ with water

A. Ice water (0.4 ml) was added to a solution of $\text{CF}_2=\text{CFBF}_2$ (0.42 mmol) in CH_2Cl_2 (0.48 ml) at $0\text{ }^{\circ}\text{C}$ and the mixture was shaken. The aqueous phase was decanted at $20\text{ }^{\circ}\text{C}$ and diluted with D_2O (0.3 ml). The ^{19}F -NMR spectrum showed resonances at -150.61 ppm ($[\text{H}_3\text{O}]^+ [\text{BF}_4]^-$) and at -98.53 (F-2*trans*), -123.14 (F-2*cis*), -199.00 (F-1) and -142.70 (BF_3^-) ppm [*J*, Hz: (1,2*cis*) 110, (2*cis*,2*trans*) 87, (2*cis*, BF_3) 9, (F,B) 38] ($[\text{H}_3\text{O}]^+ [\text{CF}_2=\text{CFBF}_3]^-$).

B. A solution of *cis*-, *trans*- $\text{ClCF}=\text{CFBF}_2$ (0.6 mmol) in CH_2Cl_2 (0.9 ml) was treated with aqueous acetone (0.3 ml; 0.08 mg of water) at $-78\text{ }^{\circ}\text{C}$. After warming to r.t. the organic phase contained no *cis*-, *trans*- $\text{ClCF}=\text{CFH}$ (^{19}F -NMR). An additional amount of water (0.3 ml) was added and finally the water-containing phase was decanted. Its ^{19}F -NMR spectrum showed resonances of the anions $[\text{BF}_4]^-$ (-151.07 ppm), $[\text{cis-ClCF}=\text{CFBF}_3]^-$ [-102.02 (F-2*trans*), -151.07 (F-1) and -142.61 (BF_3^-) ppm], and $[\text{trans-ClCF}=\text{CFBF}_3]^-$ [-126.80 (F-2*cis*), -162.13 (F-1) and -143.25 (BF_3^-) ppm; *J*, Hz: (1,B) 25, (1,2*cis*) 129, (2*cis*, BF_3) 9, (F,B) 40].

3.4. Reactions of $\text{RCF}=\text{CFBF}_2$ with aHF

A solution of $\text{RCF}=\text{CFBF}_2$ ($\text{R} = \text{F}$, *cis*-, *trans*-Cl, *trans*- C_4F_9) (0.2–0.4 mmol) in CH_2Cl_2 (0.3–0.8 ml) was cooled (-40 to $-50\text{ }^{\circ}\text{C}$). Cold ($-40\text{ }^{\circ}\text{C}$) aHF (0.2–0.4 ml) was added under an argon atmosphere. After repeated shaking, the acidic phase was decanted into the pre-cooled ($-40\text{ }^{\circ}\text{C}$) FEP inliner and analysed by ^{19}F -NMR spectroscopy.

Acknowledgements

We gratefully acknowledge the financial support by Deutsche Forschungsgemeinschaft, Russian Fonds of Basic Research and Fonds der Chemischen Industrie.

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