Dimethoxyhydroxycarbenium Hexafluorometallate – Synthesis, Spectroscopic Characterization and the Crystal Structure of $(MeO)_2COH^+SbF_6^-$

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Dimethyl carbonate reacts in the superacidic system HF/MF_5 (M = As, Sb) with formation of $(MeO)_2COX^+MF_6^-$ (M = As, Sb; X = H, D). $(MeO)_2COH^+SbF_6^-$ crystallizes in the orthorhombic space group $Pna2_1$ (No. 33) with $a = 9.668(2)$ Å, $b = 8.340(2)$ Å, $c = 11.135(4)$ Å and four formula units per cell. The unit cell contains $(MeO)_2COH^+$ cations of approximate C_s symmetry with an almost central trigonal planar CO_3 skeleton and C–O bond lengths in a range between 1.26(1) Å and 1.30(2) Å. The salt contains long O–H and Sb–F bond and an F···H contact of 1.62(9) Å. With regard to the formation of the salts, the reaction of dimethyl carbonate with the superacidic systems XF/MF_5 (X = H, D; M = As, Sb) is discussed and the Raman, IR, ^1H and ^{13}C NMR spectra of $(MeO)_2COX^+MF_6^-$ (M = As, Sb; X = H, D) are reported.

Introduction

The formulation of protonated compounds as reactive cationic intermediates is important for the explanation of reaction mechanisms. The evidence for such intermediates is of great importance in modern chemistry and can be used to confirm or deny known mechanisms. It has been shown that protonated compounds, for example, are not only short lived intermediates, but are even available in stabilized forms. A kinetic stabilization is possible due to protonation with superacids like HF/MF_5 or HSO_3F/MF_5 (M = As, Sb). This field of chemistry has been mainly developed by Olah, who was able to prove the existence of many protonated organic compounds in superacidic systems by NMR spectroscopy.[1–3]

In superacidic systems like FSO_3H/SbF_5 or HF/MF_5 (M = As, Sb) an extended spectrum of organic and inorganic species, for example element hydrides of group 15 and 16, can be protonated and stabilized.[4–14] Almost all known carbocations are mainly identified in solution by NMR spectroscopy. However, the crystal structures of protonated acetic acid, protonated carbonic acid and protonated formic acid have been investigated.[15–18] Attempts to isolate the H_2COH^+ cation failed because of the formation of the $(CH_2)O(CH_2)OH^+$ cation.[19] Substances with a CO_3 skeleton, such as the carbonate anion, the protonated carbonic acid or the monoperoxocarbonic acid anion are known and have been spectroscopically and structurally investigated.[17,20] In the row of the simplest mono-, di- and trioxocarbenium ions, we tried to isolate the dimethoxyhydroxycarbenium hexafluorometallates at low temperature in order to study their chemical behavior in acidic systems.

Results and Discussion

Formation of $(MeO)_2COH^+$ Salts

Protonation of dimethyl carbonate by the superacidic systems HF or DF/MF_5 (M = As, Sb) gives dimethoxyhydroxycarbenium hexafluorometallates [Equation (1)].

$$(MeO)_2CO + XF + MF_5 \rightarrow (MeO)_2COX^+MF_6^- \quad (X = H, D;\ M = As, Sb) \qquad (1)$$

The resulting colorless, moisture-sensitive salts, which are soluble in SO_2, decompose in the case of the arsenate above –38 °C, and in the case of the antimonate above –35 °C. Under inert conditions at –70 °C the salts can be stored for several weeks without decomposition. The remaining $(MeO)_2COH^+SbF_6^-$ contained crystals suitable for X-ray diffraction studies.

X-ray Crystal Structure of $(MeO)_2COH^+SbF_6^-$

Dimethoxyhydroxycarbenium hexafluoroantimonate crystallizes in the orthorhombic space group $Pna2_1$ (No. 33) with four units per cell (see Table 1).[21] Table 2 lists important bond lengths and angles and Figure 1 shows the crystal structure with atom labels. The arrangement of the $(MeO)_2COH^+SbF_6^-$ in the unit cell is shown in Figure 2. For data collection and reduction, a semiempirical correction determined from single ψ-scan data, and programs in the SHELXL package and PARST, were used.[22–25] The antimony layers were found by the Patterson method. All other atoms, including protons, were determined by difference Fourier synthesis. A final refinement with anisotropic (except H atoms) thermal parameters gave a value of $R = 0.0198$.

The CO bond lengths [1.26(1) Å, 1.274(8) Å and 1.30(2) Å] show no significant differences and can be compared to the lengths of the CO bonds in the dihydroxymethylcarbenium

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Table 1. X-ray diffraction data of $(MeO)_2COH^+SbF_6^-$

	$(CH_3O)_2COH^+SbF_6^-$
Formula mass	326.83
Space group (no.)	$Pna2_1$ (33)
Crystal system	Orthorhombic
a, Å	9.668(2)
b, Å	8.340(2)
c, Å	11.135(4)
Volume, Å^3	897.8(4)
Density (calcd.), g cm^{-3}	2.418
Z	4
Absorption coefficient, mm^{-1}	3.148
Temperature, K	173
$F(000)$	616
Wavelength, Å	0.71069
Theta range for data collection, °	3.05 to 24.93
Index ranges	$0 \le h \le 11$, $0 \le k \le 8$, $-13 \le l \le 0$
Reflections collected/independent	780
Parameters	142
Goodness-of-fit on F^2	1.134
R[a] $[I > 2\sigma(I)]$	0.02
R[a] (all data)	0.021
Largest diff. Peak and hole, e·Å^{-3}	0.875/−0.796
Refinement method	Full matrix, least-squares on F^2

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; Refinement method: full-matrix least-squares calculations based on F^2.

Table 2. Bond lengths [Å], selected angles (deg), and interionic distances (Å) for $(MeO)_2COH^+SbF_6^-$

	Length [Å]		Angle [deg]
Sb(1)–F(3)	1.919(3)	F(1)–Sb(1)–F(6)	90.2(2)
Sb(1)–F(4)	1.869(4)	F(2)–Sb(1)–F(5)	89.8(2)
Sb(1)–F(5)	1.868(4)	F(2)–Sb(1)–F(6)	92.4(2)
Sb(1)–F(6)	1.860(4)	F(6)–Sb(1)–F(5)	91.5(2)
O(1)–C(1)	1.26(1)	O(1)–C(1)–O(3)	122.8(11)
O(2)–C(1)	1.300(2)	O(1)–C(1)–O(2)	117.8(6)
O(3)–C(1)	1.274(8)	O(2)–C(1)–O(3)	119.4(8)
O(2)–C(2)	1.508(8)	C(1)–O(1)–H(1)	121(5)
O(3)–C(3)	1.48(1)	C(1)–O(2)–C(2)	117.2(5)
O(1)–H(1)	0.96(8)	C(1)–O(3)–C(3)	115.9(8)
O(1)···F(3)	2.570(6)		
F(3)···H(1)	1.68(8)		

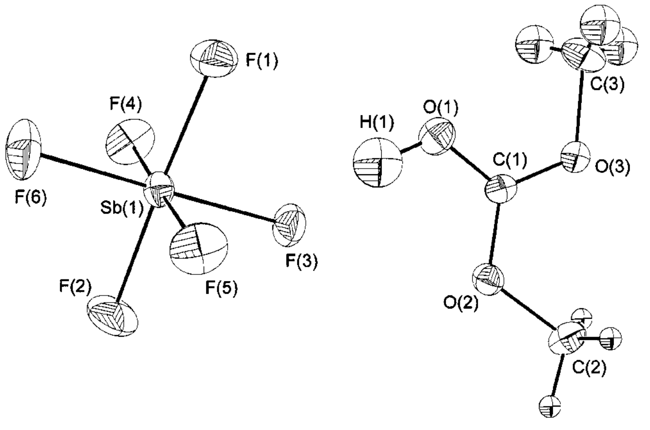

Figure 1. Projection of the asymmetric unit; thermal ellipsoids are drawn at the 50% probability level

cation and the $C(OH)_3^+$ cation as well as the almost trigonal planar CO_3 skeleton with OCO angles of 122(1)°, 117.8(6)° and 119.4(8)°.[17,18] The CO_3 skeleton geometry and the CO bond lengths, which are in a range between a single [1.508(8) Å for C(2)–O(2) and 1.48(1) Å for C(3)–O(3)] and a double CO bond [1.222(2) Å in formic acid], imply that the positive charge is delocalized. The two Me–O–C–O torsion angles [73.2(6)° and 3.1(9)°] show that the methyl groups are not located in the CO_3 plane. The O(1)···F(3) distance of 2.570(1) Å indicates a strong O(1)–H(1)···F(3) hydrogen bond,[26] which causes the Sb(1)–F(3) bond [1.919(3) Å] to be 2.7% longer than the other Sb(1)–F bonds. The maximum deviation from ideal octahedron angles in the SbF_6^- anion is 2.4°. As observed in the Raman and IR spectra the ideal octahedron structure is distorted. In the AB plane only alternating hydrogen-bonded ion pairs are formed; these planes are piled up the C axes with no contacts between adjacent planes.

Raman and IR Spectra of $(MeO)_2COX^+MF_6^-$ (X = H, D; M = As, Sb)

The infrared and Raman spectra of $(MeO)_2COD^+SbF_6^-$ are shown in Figure 3. The observed frequencies of $(MeO)_2COX^+MF_6^-$ (X = H, D; M = As, Sb) are summarized in Table 3. The assignments for the $(MeO)_2COX^+$ cation were made by a comparison with the precursor $(MeO)_2CO$ and several alkyl derivatives.[27–32] The assignments of the anions were made according to known literature data.[17,18,33]

On the condition that $(MeO)_2COX^+MF_6^-$ (X = H, D; M = As, Sb) has a C_S point symmetry, 21 (A') and 12 (A'') fundamental Raman and IR active vibrational modes are expected. Referring to the complex spectra observed, many vibrational modes are split, which could be a sign for a change to a lower symmetry in the crystal. The vibrational spectra of liquid and solid dimethyl carbonate show that, as the temperature is lowered, the observed splitting in the low-temperature spectra increases. This behavior is typical of crystal splitting in crystals of organic compounds, probably due to lattice concentration effects. The spectra become complex so that it gets difficult to assign the vibrational modes. Therefore vibrational modes are only assigned in their typical range. Without the X-ray studies and NMR spectra, the complex Raman and IR spectra could give no evidence for the existence of protonated dimethyl carbonate.

There is no denying that differences in the spectra between $(MeO)_2COH^+AsF_6^-$ and $(MeO)_2COH^+SbF_6^-$ are noticed. One possible reason for this is the crystallization in different space groups, so that varying crystalline field-splitting can be observed. Another reason might be that the influence of the anion to the vicinity of the cations differs. The measured spectra of protonated dimethyl carbonate show no further overtones, fermi resonances or combination tones in the region 1700–2900 cm^{-1}.

The antisymmetric and symmetric stretching modes of the methyl groups are observed in the region of 2960–3100 cm^{-1}. The Raman spectra of the hexafluoroantimonate anion show four different antisymmetric stretching modes at

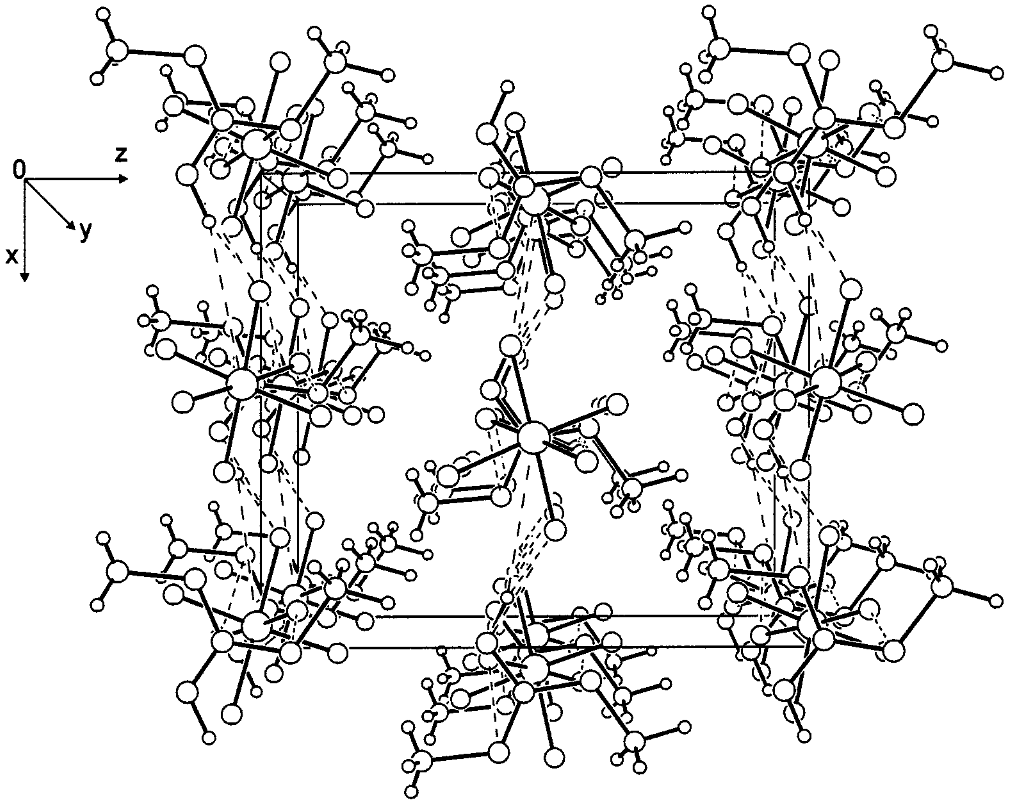

Figure 2. Projection of the $(MeO)_2COH^+SbF_6^-$ salt with contacts

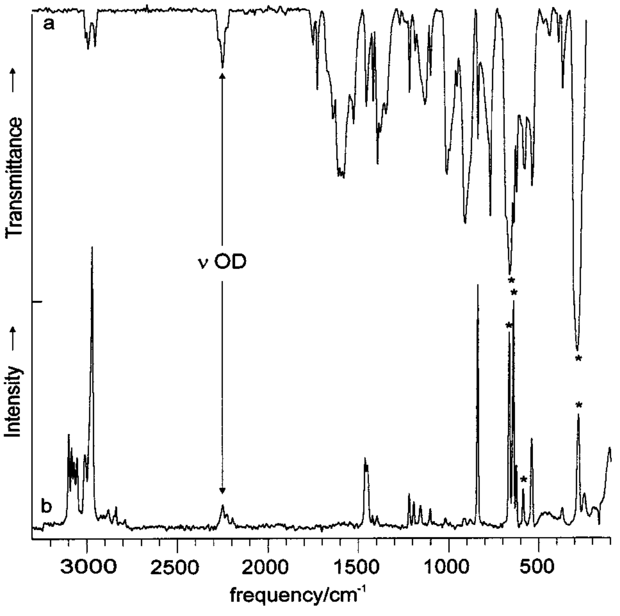

Figure 3. Infrared spectrum (trace A) and Raman spectrum (trace B) of $(MeO)_2COD^+SbF_6^-$; vibrations of the SbF_6^- anion are marked by an asterisk

3099, 3084, 3071 and 3056 cm^{-1}, but the spectra of the hexafluoroarsenate show only two modes (3090 and 3067 cm^{-1}). The same phenomenon is noticed in the area of the methyl deformation modes (1554–1349 cm^{-1}), where as many as six different frequencies are measured. Between 1220 cm^{-1} and 1153 cm^{-1} as well as between 1098 cm^{-1} and 993 cm^{-1} the rocking modes ρCH_3 are observed. A sharp Raman line and IR band is detected at 845 cm^{-1} and assigned to the CO_3 out-of-plane mode, whose position is comparable to the measured frequency in a range of 890–774 cm^{-1} for simple, complex, acidic and organic carbonate compounds.[22] The νOH absorption is observed at 3160 cm^{-1} with the H/D shifted signal at 2275 cm^{-1} (νOD) for the AsF_6^- compound and 2156 cm^{-1} for the SbF_6^- compound, which is within the expected shift range of about 900 cm^{-1}.[34]

Because of cation–anion interactions, the MF_6^- ions (M = As, Sb) do not show ideal O_h symmetry. This lowered symmetry can be seen in the spectra, where splitting of the anion vibrational modes are observed.[33]

^{1}H and ^{13}C NMR Spectra of $(MeO)_2COH^+MF_6^-$ (M = As, Sb)

The ^{1}H NMR spectra of freshly prepared $(MeO)_2COH^+MF_6^-$ (M = As, Sb) dissolved in SO_2 with TMS as external standard at –50 °C shows a singlet at $\delta = 4.59$ (AsF_6^-) and $\delta = 4.63$ (SbF_6^-) for the methyl groups and a singlet at $\delta = 11.74$ (AsF_6^-) and $\delta = 11.8$ (SbF_6^-) for the hydroxyl group. This result is comparable to the results of Olah, who observed at –80 °C a singlet at $\delta = 11.27$ for the hydroxyl group and a singlet at $\delta = 4.52$ for the methyl group.[35,36] The singlet for the proton of the hydroxyl group of the $C(OH)_3^+$ cation is detected at $\delta = 11.55$; Ramsey observed a singlet at $\delta = 4.9$ in an H_2SO_4 solution for the methyl group (Table 4).[17,37] The singlet at $\delta = 163$ in the ^{13}C NMR (^{1}H coupled) is assigned to the carbon atom of the CO_3 skeleton. In the region of $\delta = 63$ a quadruplet

Table 3. Raman and IR frequencies and their possible assignment for $(MeO)_2COX^+MF_6^-$ (X = H, D; M = As, Sb)

M = As IR	X = H Raman	M = Sb IR	X = H Raman	M = As IR	X = D Raman	M = Sb IR	X = D Raman	Possible Assignment
3162vw	3158(3)	3160vw	3158(4)					ν OH
	3090(32)	3098vw	3099(33)		3092(42)		3099(35)	ν_{as} CH_3
			3084(35)				3084(30)	ν_{as} CH_3
	3067(21)		3071(34)		3068(15)		3071(24)	ν_{as} CH_3
			3056(33)				3055(25)	ν_{as} CH_3
3038w				3047vw				ν_{as} CH_3
3016w				3019w	3016(22)	3012vw	3011(27)	ν_{as} CH_3
2990w	2986(100)			2992w	2983(100)	2994w		ν_{as} CH_3
	2977(81)	2973w	2976(100)		2968(72)	2969w	2971(100)	ν_s CH_3
				2275m	2275(8)	2256m	2251(8)	ν OD
1666vs		1660s						νCO_3
1642vs		1638s	1635(8)	1639vs		1638sh		νCO_3
				1614vs		1616s		νCO_3
						1598s		νCO_3
1585vs		1583m	1588(5)	1586vs		1585s		νCO_3
1554sh		1554m						δCH_3
			1533(6)			1529m		δCH_3
1461s	1461(18)	1458s	1464(24)	1459m	1460(30)	1460m	1463(25)	δCH_3
1446s	1453(16)		1455(18)	1447sh	1451(25)		1452(23)	δCH_3
1427s		1425s	1426(5)	1428s	1427(6)	1422m	1422(4)	δCH_3
1413s	1414(5)	1407s	1407(4)	1404s	1403(2)	1399s	1397(4)	δCH_3
		1347w	1346(6)			1349m		δCH_3
1277s		1274s		1281w		1274vw		νOCO
1219s	1221(10)	1219m	1220(13)	1220m	1221(13)	1219m	1222(12)	ρCH_3
1186s	1186(4)	1189m	1188(8)	1190w	1193(8)	1187w	1195(9)	ρCH_3
1159s	1162(5)	1153m	1159(10)		1162(8)	1157sh	1156(8)	ρCH_3
1128w		1127m		1133w		1136m		νOCO
1098vs	1098(6)	1094vs	1094(9)	1101m	1105(6)	1104m	1103(7)	ρCH_3
				1020s	1023(4)	1015vs	1019(3)	ρCH_3
993s		997m						ρCH_3
964vs	960(6)	960vs	962(8)	967m		958m		δOCO
				923vs	917(3)	915vs	918(3)	δCOD
846s	845(84)	846s	844(73)	844s	843(91)	845s	842(90)	γCO_3 out of plane
791vs		799s		796m				ρCO_3
		775s		779s	778(2)	774vs		ρCO_3
				768s				ρCO_3
632vs	631(23)	630vs	629(27)	626s	628(23)	628s	627(23)	γCO_3 in plane
608s		610s		606w				ρCO_3
			575(6)	573s				ρCO_3
565s	565(23)	563s	564(22)	568m				ρCO_3
	542(7)			547s	549(21)	544s	542(35)	τCH_3
537vs		536vs	536(19)	533vs	532(16)			τCH_3
				490s		479vw	486(4)	τCH_3
444sh		448vw	444(3)			449vw	443(5)	τCH_3
423sw				424s				τCH_3
375vs	378(23)	378m	374(4)	374sh	376(33)	374m	371(7)	τCH_3
256m		255s	252(4)	257vs				δCOC
	246(7)		242(5)		245(10)		249(12)	δCOC
202w					187(4)		196(7)	Lattice
	734(17)	664vs	665(100)		735(20)	667vs	667(73)	νMF_6^-
	721(4)		648(31)	719				νMF_6^-
701vs	702(34)	643vs	640(88)		702(48)	641vs	644(85)	νMF_6^-
	689(76)			683s	688(66)			νMF_6^-
676vs	677(50)				674(71)			νMF_6^-
593vw	595(7)		588(18)	601	598(9)	586s	586(14)	νMF_6^-
394vs	394(10)	284vs	281(37)	399	394(12)	289vs	283(41)	νMF_6^-
	366(14)				364(19)			νMF_6^-
	313(9)			318vs	311(6)			νMF_6^-

with a coupling constant of 141 Hz is observed and assigned to the methyl groups.

Experimental Section

Caution! *Avoid contact with these compounds as the hydrolysis of AsF_6^- and SbF_6^- salts forms HF, which burns the skin and causes irreparable damage. Safety precautions should be taken when using and handling these materials.*

All synthetic work and sample handling was performed by employing standard Schlenk techniques and a vacuum line (stainless steel or glass). SbF_5 (Merck) was purified by fractional distillation. The synthesis of $(MeO)_2CO$ and the drying of HF and SO_2 were carried out by known literature methods (R. Minkoite, A. Kornath, D. Savodny, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 643–644). Reactions in HF/DF were carried out in a KEL-F reactor with a KEL-F valve.[38] Infrared spectra were recorded with a Bruker IFS 113V spectrophotometer. The spectra of dry powders were obtained on a CsI plate in a cooled IR cell.[39] The Raman spectra were recorded

Table 4. ^1H and ^{13}C NMR spectroscopic data of mono-, di- and trihydroxycarbenium ions

Ion/Precursor	^1H NMR δ [ppm] –Me	–OH	^{13}C NMR δ [ppm] –Me	CO_3
$(MeO)_2CO$[d]			–55	36
$(MeO)_2COH^+$	4.9[a]			
	4.52[b]	11.27[b]		
	4.59[c]	11.74[c]	63[c]	163[c]
$MeOC(OH)_2{}^+$[c]	4.47	11.55		31[d]
		11.18		
$C(OH)_3{}^+$[e]		11.7		167
$(MeO)_2CH^+$[f]	4.54		64.5	181
$(MeO)_2C(Me)^+$[f]	4.38		67	193
$(MeO)_3C^+$[f]	4.45		68	164

[a] Ref.[27] – [b] Ref.[37] at –80 °C. – [c] Own measurements at –60 °C with TMS as external standard. – [d] In parts per million from CS_2. – [e] Ref.[17] – [f] CD_3NO_2 as standard.

with a T64000 (ISA) using a CCD detector (EEV CCD15–11) and an Ar^+ laser tube (514.5 nm) from Spectra Physics. The spectra were recorded in a glass cell cooled with liquid nitrogen. The NMR spectra were recorded with a Bruker DPX 300 spectrometer with TMS as external standard. Single crystals were placed in Lindemann capillaries in a cooled stream of dry nitrogen, and an X-ray diffraction study was carried out at –100 °C using an Enraf Nonius Mach3 automated diffractometer.

Preparation of $(MeO)_2COX^+MF_6^-$ (M = As, Sb; X = H, D): In a 50 mL KEL-F reactor, SbF_5 (1.09 g, 5 mmol) or AsF_5 (0.85 g, 5 mmol) was dissolved in HF (3 g). The solution was frozen at –196 °C and $(MeO)_2CO$ (0.45 g, 5 mmol) was added under an inert atmosphere (N_2). The mixture was warmed to –70 °C and kept for 30 minutes. The excess HF was slowly removed under dynamic vacuum at –78 °C. The reactions with DF were made analogously to the above described synthesis.

Acknowledgments

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