

Synthesis and characterization of (2,6-difluorophenyl)xenon(II) and bis(2,6-difluorophenyl)iodine(III) trifluoromethanesulfonates

Dieter Naumann*, Robert Gnann, Vasilios Padelidakis, Wieland Tyrra

Institut für Anorganische Chemie der Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany

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Abstract

The reactions of bis(2,6-difluorophenyl)iodine(III) and 2,6-difluorophenylxenon(II) tetrafluoroborates with trimethylsilyl trifluoromethanesulfonate yield the corresponding bis(2,6-difluorophenyl)iodine(III) and (2,6-difluorophenyl)xenon(II) trifluoromethanesulfonates. The products were identified by NMR and vibrational spectroscopy as well as by mass spectrometry. The cation peak of an organoxenon compound has been detected for the first time by FAB mass spectrometry.

Keywords: Synthesis; (2,6-Difluorophenyl)xenon(II) trifluoromethanesulfonate; Bis(2,6-difluorophenyl)iodine(III) trifluoromethanesulfonate; NMR spectroscopy; FAB mass spectra

1. Introduction

Since trivalent diaryliodine(III) compounds have practical application in organic synthesis due to their activity in biological and photopolymerization processes, these species are of significant interest in chemical research [1].

In the case of diaryliodine(III) trifluoromethanesulfonates in particular, several different preparative methods have been published. Iodosyl trifluoromethanesulfonate reacts with trimethylsilyl derivatives of aromatic compounds to give the corresponding diaryliodine(III) compounds [2]. Another type of reaction is based on iodosylbenzene, trifluoromethanesulfonic acid and aromatic compounds [3].

We have reported the synthesis of bis(pentafluorophenyl)iodine(III) sulfonates $[I(C_6F_5)_2][OSO_2R]$ ($R = CF_3, 2,4,6-(NO_2)_3C_6H_2$) from the reactions of iodine tris(trifluoroacetate) with pentafluorobenzene in the presence of the sulfonic acid [4].

In contrast to the chemistry of organic trivalent iodine derivatives, which originated in 1894 with Hartmann and Mayer's preparation of the (4-iodophenyl)phenyliodine(III) cation [5], arylxenon(II) salts are quite a new class of compounds [6,7]. Arylxenon(II) salts have been prepared as fluoroborates [8,9], hexa-

fluoroarsenates [10] or pentafluorobenzoates [11], but an arylxenon(II) trifluoromethanesulfonate has not been described hitherto.

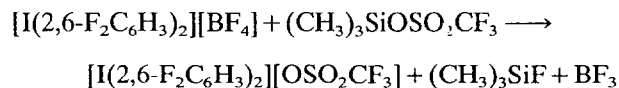
Herein we report the syntheses of $[I(2,6-F_2C_6H_3)_2][OSO_2CF_3]$ and $[Xe(2,6-F_2C_6H_3)][OSO_2CF_3]$ from the metathesis reactions of the corresponding tetrafluoroborates with $(CH_3)_3SiOSO_2CF_3$.

2. Results and discussion

Trimethylsilyl trifluoromethanesulfonate, first prepared by Schmeisser, Sartori and Lippsmeier in 1970 [12], is used in organic synthesis as a highly reactive silylating agent and a Lewis acid [13]. The conversion of fluorides into trifluoromethanesulfonates by $(CH_3)_3SiOSO_2CF_3$ was demonstrated by Banks and Sharif [14].

In continuation of our work on ligand-exchange reactions of silicon derivatives with iodine [15] and xenon [16] compounds, we applied these results to the exchange of the tetrafluoroborate anion with the CF_3SO_3 group.

The reaction of bis(2,6-difluorophenyl)iodine(III) tetrafluoroborate with $(CH_3)_3SiOSO_2CF_3$ readily yields the analogous trifluoromethanesulfonate.

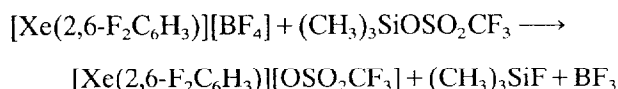


* Corresponding author.

The reaction proceeds in acetonitrile solution and can be monitored by ^{19}F NMR spectroscopy. The intensity of the $[\text{BF}_4]^-$ resonance decreases in favour of the resonances of $(\text{CH}_3)_3\text{SiF}$ and $\text{BF}_3 \cdot \text{CH}_3\text{CN}$. The exchange is complete within 48 h at -40°C . After distilling off all volatile components in vacuo, $[\text{I}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2][\text{OSO}_2\text{CF}_3]$ was obtained as an analytically pure pale yellow solid in 90% yield.

The chemical and physical properties of $[\text{I}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2][\text{OSO}_2\text{CF}_3]$ are characteristic for diaryliodine(III) salts with less nucleophilic anions. This compound is remarkably stable. In comparison with $[\text{I}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2][\text{BF}_4]$ (dec. 228°C) [17], no evidence for decomposition was found below 350°C . Thus, it was not surprising that the EI mass spectra of this derivative showed only a few peaks which could be assigned to the ions $[\text{I}(\text{C}_6\text{H}_3\text{F}_2)_2]^+$, $\text{C}_6\text{H}_3\text{F}_2\text{I}^+$, $(\text{C}_6\text{H}_3\text{F}_2)_2^+$ and $\text{C}_6\text{H}_3\text{F}_2^+$. With the exception of $(\text{C}_6\text{H}_3\text{F}_2)_2^+$, no polyaryls could be detected in contrast to the mass spectrometric decay of $[\text{I}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2][\text{BF}_4]$ [17].

The similarities between aryliodine(III) and arylxenon(II) chemistry [11,18] have encouraged us to use this reaction type for the synthesis of the first arylxenon(II) trifluoromethanesulfonate. As expected, the exchange reaction of $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)][\text{BF}_4]$ and $(\text{CH}_3)_3\text{SiOSO}_2\text{CF}_3$ proceeded in the same manner as with the iodine derivative.



The high affinity of the $(\text{CH}_3)_3\text{Si}$ group towards fluorine is very important in these reactions.

In contrast to $[\text{C}_6\text{F}_5\text{Xe}][\text{OCOC}_6\text{F}_5]$ [11], no evidence for the covalent character of the xenon–oxygen bond was found in $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)][\text{OSO}_2\text{CF}_3]$. The exceptionally high acidity of trifluoromethanesulfonic acid, accompanied by the low nucleophilic character of the anion, may be responsible for the fact that the chemical behaviour of the arylxenon(II) trifluoromethanesulfonate is similar to that of the analogous tetrafluoroborate.

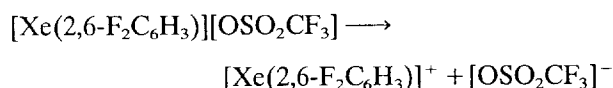
In aqueous media, $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)][\text{OSO}_2\text{CF}_3]$ is completely hydrolyzed within 12 h with $\text{C}_6\text{H}_4\text{F}_2$ and $\text{CF}_3\text{SO}_3\text{H}$ being detected as the only fluorine-containing components in the ^{19}F NMR spectrum of the reaction mixture.

$[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)][\text{OSO}_2\text{CF}_3]$ can only be dissolved in polar solvents such as CH_3CN . The chemical shift in the ^{129}Xe NMR spectrum ($\delta = 2125$ ppm, CH_3CN) is approximately the same as that measured for the tetrafluoroborate ($\delta = 2089$ ppm, $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$). The similarities in the ^{19}F and ^{13}C NMR spectra also indicate complete dissociation of both compounds in acetonitrile solution (see Table 1).

Table 1
NMR data for $[\text{XeAr}_r][\text{BF}_4]$ and $[\text{XeAr}_r][\text{OSO}_2\text{CF}_3]$ ($\text{Ar}_r = 2,6\text{-F}_2\text{C}_6\text{H}_3$, chemical shifts (δ) in ppm; coupling constants in Hz)

	$[\text{XeAr}_r][\text{BF}_4]^a$	$[\text{XeAr}_r][\text{OSO}_2\text{CF}_3]$
^1H NMR		
solvent/temp.	$\text{CD}_3\text{CN}/-30^\circ\text{C}$	$\text{CD}_3\text{CN}/21^\circ\text{C}$
$\delta(\text{H-4})$	7.9	7.8
$\delta(\text{H-3,5})$	7.4	7.3
$^3J(^{19}\text{F}-^1\text{H})$	8.0	8.3
$^{19}\text{F}\{^1\text{H}\}$ NMR		
solvent/temp.	$\text{CD}_3\text{CN}/-30^\circ\text{C}$	$\text{CH}_3\text{CN}/21^\circ\text{C}$
$\delta(\text{F-2,6})$	-99.6	-100.1
$\delta([\text{BF}_4])$	-149.7	
$\delta([\text{OSO}_2\text{CF}_3])$		-78.5
$^3J(^{129}\text{Xe}-^{19}\text{F})$	52	54
^{129}Xe NMR		
solvent/temp.	$\text{CD}_3\text{CN}/\text{CH}_2\text{Cl}_2/-30^\circ\text{C}$	$\text{CH}_3\text{CN}/21^\circ\text{C}$
$\delta(\text{Xe})$	-2089	-2125
$^3J(^{129}\text{Xe}-^{19}\text{F})$	52	54
$^{13}\text{C}\{^1\text{H}\}$ NMR		
solvent/temp.	$\text{CD}_3\text{CN}/21^\circ\text{C}$	$\text{CD}_3\text{CN}/21^\circ\text{C}$
$\delta(\text{C-1})$	88.8	89.4
$^1J(^{129}\text{Xe}-^{13}\text{C})$	99	106
$^2J(^{19}\text{F}-^{13}\text{C})$	27	26
$\delta(\text{C-2,6})$	156.8	157.5
$^1J(^{19}\text{F}-^{13}\text{C})$	258	258
$\delta(\text{C-3,5})$	115.2	115.5
$\delta(\text{C-4})$	137.8	138.4
$^3J(^{19}\text{F}-^{13}\text{C})$	9	9
$\delta(\text{CF}_3\text{SO}_3)$		121.3
$^1J(^{19}\text{F}-^{13}\text{C})$		319

^a Taken from Ref. [8].



Comparison of the vibrational frequencies of $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)][\text{OSO}_2\text{CF}_3]$ and $[\text{I}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2][\text{OSO}_2\text{CF}_3]$ shows an obvious similarity between these compounds and $[\text{I}(\text{C}_6\text{F}_5)_2][\text{OSO}_2\text{CF}_3]$ [4]. The absorption bands of the CF_3SO_3 group are more similar to those of $\text{NaOSO}_2\text{CF}_3$ than to those of $\text{I}(\text{OSO}_2\text{CF}_3)_3$ [19–21], supporting the assumption of an ionic character in the element–oxygen bonds.

Although $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)][\text{OSO}_2\text{CF}_3]$ is thermally stable up to 132°C as determined from DTA measurements, the cation peak $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)]^+$ was never detected in the EI and FI mass spectra. These methods led directly to cleavage of the xenon–carbon bond and allowed only detection of elemental xenon and $[\text{C}_6\text{H}_3\text{F}_2\text{OSO}_2\text{CF}_3]^+$ as well as fragments of this ion. In contrast to this decay, the mass spectra of the diaryliodine(III) trifluoromethanesulfonates exhibit cation peaks with a high intensity.

If FAB mass spectrometry, whose use has been also reported for quite unstable alkenyl(phenyl)- and alkynyl(phenyl)iodine(III) species [22], is used for ana-

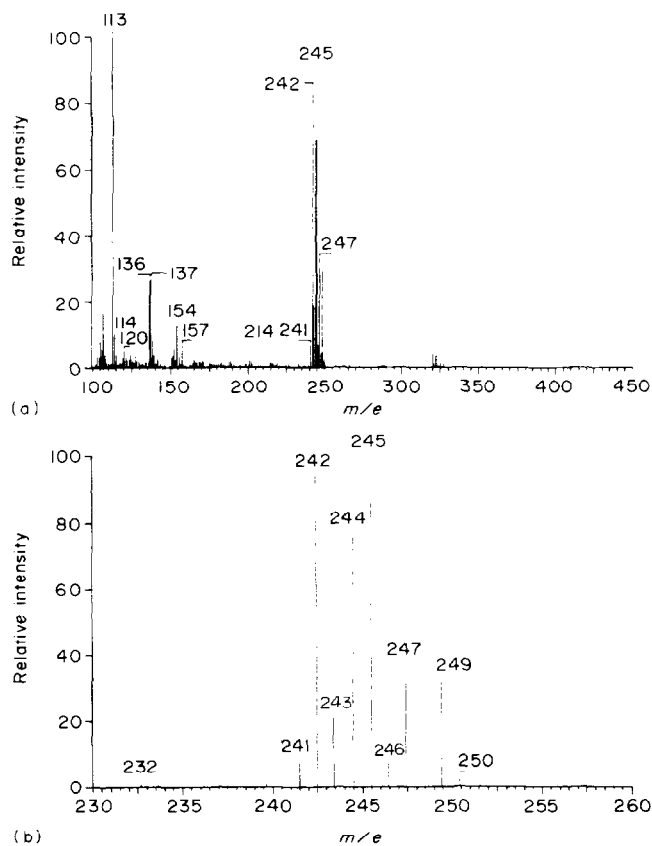


Fig. 1. FAB mass spectrum of $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)][\text{OSO}_2\text{CF}_3]$. (a) Synoptical spectrum; (b) spread region (m/e 230–260).

lyzing the 2,6-difluorophenylxenon(II) triflate, the peak corresponding to the cation $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)]^+$ can be detected with a relative intensity of 100% (after conversion of the intensity to monoisotopic relations by use of the coefficient 100/26.89) without any evidence for the formation of polyphenyls (Fig. 1). The measured isotope pattern is in agreement with that calculated.

A crystal structure analysis of $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)]\text{[OSO}_2\text{CF}_3]$ is underway.

3. Experimental details

^1H and ^{19}F NMR spectra were recorded on a Bruker FT-NMR AC 200 spectrometer at 200.1 MHz and 188.3 MHz, respectively, ^{13}C and ^{129}Xe NMR on a Bruker FT-NMR AMX 300 spectrometer at 75.5 MHz and 83.3 MHz, respectively. $(\text{CH}_3)_4\text{Si}$ (^1H , ^{13}C), CCl_3F (^{19}F) and XeF_2 (1 M solution in CH_3CN) were used as external standards. A negative chemical shift denotes a resonance occurring to low frequency (high field) of the reference substance.

Infrared spectra were recorded on a Perkin-Elmer PE 580 B spectrometer using KBr pellets and polyethylene pellets. The Raman spectra were run on a Jobin Yvon U 1000 spectrometer equipped with an Ar^+ laser (Spectra Physics) operating at 514.5 nm.

EI mass spectra were recorded on a modified Varian MAT CH5 spectrometer. The FAB mass spectrum was measured on a Varian MAT 731 spectrometer equipped with an Iontech 11 NF FAB cannon. $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)]\text{[OSO}_2\text{CF}_3]$ was dissolved in a $\text{CH}_3\text{CN}/\text{CF}_3\text{COOH}$ mixture. Elemental xenon was used as the bombarding gas (acceleration voltage, 6–8 kV), *m*-nitrobenzyl alcohol (NBA) being employed as the matrix component. Ions containing xenon refer to ^{132}Xe (natural abundance 26.89%); conversion to monoisotopic relations was achieved by use of the coefficient 100/26.89.

The DTA measurements were recorded on a Mettler TA1 thermoanalyzer.

Fluorine was analyzed as described in Ref. [23], iodine as in Ref. [24] after combustion of the sample as described in Ref. [25].

All reactions were carried out under dry nitrogen using Schlenk techniques. Solvents were purified by standard methods. $[\text{I}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2]\text{[BF}_4]$ was prepared according to Ref. [17]; $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)]\text{[BF}_4]$ according to Ref. [8a]. $(\text{CH}_3)_3\text{SiOSO}_2\text{CF}_3$ was purchased from Aldrich and used as received.

3.1. Preparation of $[\text{I}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2]\text{[OSO}_2\text{CF}_3]$

$[\text{I}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2]\text{[BF}_4]$ (1.5 g, 3.4 mmol) was dissolved in 10 ml of CH_3CN at -40°C . A solution consisting of 0.61 ml (3.4 mmol) of $(\text{CH}_3)_3\text{SiOSO}_2\text{CF}_3$ in 10 ml of CH_3CN was added dropwise. After stirring the reaction mixture for 48 h at -40°C , the solvent was distilled off at ambient temperature. Drying the residue for 2 d in vacuo led to 1.53 g (90%) of $[\text{I}(2,6\text{-F}_2\text{C}_6\text{H}_3)_2]\text{[OSO}_2\text{CF}_3]$ as a pale yellow solid. No decomposition could be observed up to 350°C .

Elemental analysis of $\text{C}_{13}\text{H}_6\text{F}_7\text{IO}_3\text{S}$ (values in parentheses are calculated): I, 26.11% (25.27%); F, 26.02% (26.48%). ^1H NMR (CD_3CN , 21°C) δ : 7.7 (m, 2H, H-4); 7.3 (m, 4H, H-3,5) ppm. ^{19}F NMR (CH_3CN , 21°C) δ : -78.5 (s, $^1J(^{19}\text{F}\text{-}^{13}\text{C})=320$ Hz, 3F, OSO_2CF_3); -95.1 (m, 4F, F-2,6) ppm. ^{13}C NMR (CD_3CN , 21°C) δ : 161.5 (dm, $^1J(^{19}\text{F}\text{-}^{13}\text{C})=255$ Hz, C-2,6); 139.3 (dm, $^1J(^{13}\text{C}\text{-}^1\text{H})=168$ Hz, C-4); 121.2 (q, $^1J(^{19}\text{F}\text{-}^{13}\text{C})=319$ Hz, OSO_2CF_3); 114.2 (dm, $^1J(^{13}\text{C}\text{-}^1\text{H})=164$ Hz, C-3,5); 91.3 (m, C-1) ppm. MS (EI, 15 eV, 120°C , m/e): 353 (45%) $[\text{I}(\text{C}_6\text{H}_3\text{F}_2)_2]^+$; 240 (100%) $[\text{I}(\text{C}_6\text{H}_3\text{F}_2)]^+$; 226 (25%) $[(\text{C}_6\text{H}_3\text{F}_2)_2]^+$; 113 (18%) $[\text{C}_6\text{H}_3\text{F}_2]^+$. Fragments with intensities less than 10% have been omitted. IR (cm^{-1}): 1595; 1585; 1470; 1445; 1265; 1245; 1180; 1080; 1035; 935; 800; 790; 770; 750; 690; 645; 580; 525. Raman (cm^{-1}): 1325; 1225; 1028; 759; 563; 383; 313; 216.

3.2. Preparation of $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)]\text{[OSO}_2\text{CF}_3]$

To a suspension of 0.2 g (0.6 mmol) of $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)]\text{[BF}_4]$ in 10 ml of CH_2Cl_2 at -20°C , was

added dropwise a solution consisting of 108 μl (0.6 mmol) of $(\text{CH}_3)_3\text{SiOSO}_2\text{CF}_3$ in 10 ml of CH_3CN . The mixture was stirred for 4 d at -20°C , then warmed up to ambient temperature and concentrated in vacuo until 2 ml of the solvent remained. After storing for several days at -25°C , colourless crystals precipitated which were filtered from the solution. After washing the crystals with cold CH_2Cl_2 , $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)][\text{OSO}_2\text{CF}_3]$ was obtained in 50% (0.12 g) yield. The purity was better than 98% as determined from the NMR spectra. The NMR data are summarized in Table 1.

MS (EI, 20 eV, 135°C , m/e): 262 (20%) $[(\text{C}_6\text{H}_3\text{F}_2)\text{OSO}_2\text{CF}_3]^+$; 198 (13%) $[(\text{C}_6\text{H}_3\text{F}_2)\text{OCF}_3]^+$; 132 (100%) $[\text{Xe}]^+$; 112 (2%) $[\text{C}_6\text{H}_2\text{F}_2]^+$. No further peaks of higher intensity than 2% were detected. MS (FAB): 245 (100%) $[\text{Xe}(2,6\text{-F}_2\text{C}_6\text{H}_3)]^+$; 154 (5%) $[\text{NBA}]^+$; 136 (8%) $[\text{NBA}-\text{H}_2\text{O}]^+$; 120 (2%) $[\text{NBA}-\text{CH}_2\text{OH}]^+$; 114 (3%) $[\text{CF}_3\text{COOH}]^+$; 113 (29%) $[\text{C}_6\text{H}_3\text{F}_2]^+$ (see Fig. 1). IR (cm^{-1}): 1610; 1588; 1300; 1239; 1175; 1155; 1023; 1009; 795; 761; 725; 635; 568; 521; 500; 370; 350; 320; 211. Raman (cm^{-1}): 1232; 1023; 762; 555; 374; 206. DTA measurement: exothermal decomposition at 132°C .

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References

- [1] G.F. Koser, in S. Patai and Z. Ruppert (eds.), *The Chemistry of Functional Groups, Suppl. D*, Wiley, New York, 1983, Chap. 18, p. 721 and Chap. 25, p. 1265.
- [2] P.J. Stang, V.V. Zhdankin and R. Tykwinski, *Tetrahedron Lett.*, 32 (1991) 7497.
- [3] T. Kitamura, I. Matsuyuki, K. Nagata, R. Furuki and H. Taniguchi, *Synthesis*, (1992) 945.
- [4] W. Tyrra, H. Butler and D. Naumann, *J. Fluorine Chem.*, 60 (1993) 79.
- [5] C. Hartmann and V. Meyer, *Ber.*, 27 (1894) 426.
- [6] D. Naumann and W. Tyrra, *J. Chem. Soc., Chem. Commun.*, (1989) 47.
- [7] H.J. Frohn and S. Jacobs, *J. Chem. Soc., Chem. Commun.*, (1989) 625.
- [8] (a) D. Naumann, H. Butler, R. Gnann and W. Tyrra, *Inorg. Chem.*, 32 (1993) 861; (b) T. Gilles, R. Gnann, D. Naumann and K.-F. Tebbe, *Acta Crystallogr.*, C50 (1994) 411; (c) H. Butler, D. Naumann and W. Tyrra, *Eur. J. Solid State Inorg. Chem.*, 29 (1992) 739.
- [9] (a) H.J. Frohn and C. Rossbach, *Z. Anorg. Allg. Chem.*, 619 (1993) 1672; (b) H.J. Frohn, S. Jakobs and C. Rossbach, *Eur. J. Solid State Inorg. Chem.*, 29 (1992) 729.
- [10] H.J. Frohn, S. Jakobs and G. Henkel, *Angew. Chem.*, 101 (1989) 1534.
- [11] H.J. Frohn, A. Klose and G. Henkel, *Angew. Chem.*, 105 (1993) 114.
- [12] M. Schmeisser, P. Sartori and B. Lippsmeier, *Chem. Ber.*, 103 (1970) 868.
- [13] See, for example, H. Emde, D. Domsch, H. Feger, U. Frick, A. Götz, H.H. Hergott, K. Hoffmann, W. Kober, K. Krägerloh, Th. Oesterle, W. Steppan, W. West and G. Siemchen, *Synthesis*, (1982) 1; H.C. Marsmann and H.G. Horn, *Z. Naturforsch., Teil B*, 27 (1972) 1448.
- [14] R.E. Banks and I. Sharif, *J. Fluorine Chem.*, 41 (1988) 297.
- [15] W. Tyrra and D. Naumann, *J. Fluorine Chem.*, 45 (1989) 401.
- [16] B. Cremer-Lober, D. Pfolk, H. Butler, R. Gnann, W. Tyrra and D. Naumann, *J. Fluorine Chem.*, 58 (1992) 245, *Xth Eur. Symp. Fluorine Chem.*, Padua, Italy, September 1992, Abstract C 18.
- [17] V. Padelidakis, W. Tyrra and D. Naumann, in preparation.
- [18] H.J. Frohn, J. Helber and A. Richter, *Chem.-Ztg.*, 107 (1983) 169.
- [19] M.G. Miles, G. Doyle, R.P. Cooney and R.S. Tobias, *Spectrochim. Acta*, A25 (1969) 1515.
- [20] J.R. Dalziel and F. Aubke, *Inorg. Chem.*, 12 (1973) 2707.
- [21] J.R. Dalziel, H.A. Carter and F. Aubke, *Inorg. Chem.*, 15 (1976) 1247.
- [22] P.J. Stang, *Angew. Chem.*, 104 (1992) 281.
- [23] A.D. Campbell and P.A. Dawson, *Mikrochim. Acta*, (1983) 489.
- [24] G. Jander and K.F. Jahr, *Massanalyse*, 2nd edn., de Gruyter, Berlin, 1959.
- [25] W. Schöniger, *Mikrochim. Acta*, (1955) 123.