J. Iran. Chem. Soc., Vol. 8, No. 4, December 2011, pp. 958-964.

JOURNAL OF THE
Iranian
Chemical Society

Synthesis and X-Ray Crystal Structure of Fluorous Imidazolium Salts

A. Moghimi[a,*], H.R. Khavassi[b], A.H. Benvidi[c], M. Vojdani[c] and N. Faghihimoghaddam[c]
[a]*Department of Chemistry, Imam Hossein University, Tehran, Iran, P.O. Box 16575-347*
[b]*Department of Chemistry, Shahid Beheshti University, Tehran, Iran*
[c]*Department of Chemistry, Islamic Azad University, North Branch, Tehran, Iran*

(Received 21 December 2010, Accepted 24 February 2011)

Synthesis of two salts involving CH_2O spacer between the imidazole nitrogen and hexafluoroisopropyl group in the fluorous imidazolium cations is reported. Such an insertion would result in the formation of α-ammonium ether. The two fluorous imidazolium salts involve one or two $-CH_2OCH(CF_3)_2$ groups attached to the imidazole nitrogen atoms. These products were synthesized from the reaction between methyimidazole and imidazole as nucleophiles and sevochlorane, $ClCH_2OCH(CF_3)_2$, as electrophile, in different molar ratios. The resulting products have been characterized by ^1H, ^{13}C, and ^{19}F NMR and FTIR spectroscopy. Also, the single crystal X-ray diffraction analysis for the symmetrically substituted imidazolium product is presented. The preliminary animal tests indicated no anesthetic property but the two tested salts were found to behave as calmative.

Keywords: Imidazole, Imidazolium, Fluorous, α-Ammonium ether, X-Ray crystal structure

INTRODUCTION

From the synthetic point of view, there are two general approaches to prepare novel 1,3-dialkylimidazolium salts. In the first approach, the alkyl group attached to the nitrogen atom of imidazole ring is modified. In the second, the anion of dialkylimidazolium salt is exchanged [1-4]. One way to apply structural modifications on dialkylimidazolium salts is to induce fluorine atom either on the cationic or anionic parts to reach fluorous imidazolium salts. An exploration of the literature indicates that the number of imidazolium-based salts containing fluoroanions is much larger since the former can be easily obtained by the anion exchange process [1,2]. Imidazolium salts containing fluoroanions such as $(FH)_nF^-$, BF_4^-, PF_6^-, $N(SO_2CF_3)_2^-$, $OSO_2CF_3^-$, AsF_6^-, SbF_6^- and NbF_6^- have been comprehensively reviewed. The synthesis of each member of fluoroalkylated imidazolium salts, on the other hand, needs its own specific strategy [3-10].

Some of the reported fluorous imidazolium cations are shown in Fig. 1. As is clear, fluoroalkyl groups are directly or indirectly, by $(CH_2)_n$ spacers, attached to one or two imidazole nitrogen atoms. A review of the fluorinated imidazolium cations revealed no report on the insertion of CH_2O spacer between the imidazole nitrogen and hexafluoroisopropyl groups. Such an insertion would result in the formation of α-ammonium ether, as shown in Fig. 2. Here, we report the first synthesis of fluorous imidazolium salts (**2**) and (**4**) involving one or two $CH_2OCH(CF_3)_2$ groups attached to the imidazole nitrogen atoms as well as the X-ray single crystal data obtained for salt (**4**). Considering the fact that $CH_2OCH(CF_3)_2$ group in the prepared salts forms the major part of the chemical structure of sevofluorane $FCH_2OCH(CF_3)_2$, a well-

*Corresponding author. E-mail: samoghimi@yahoo.com

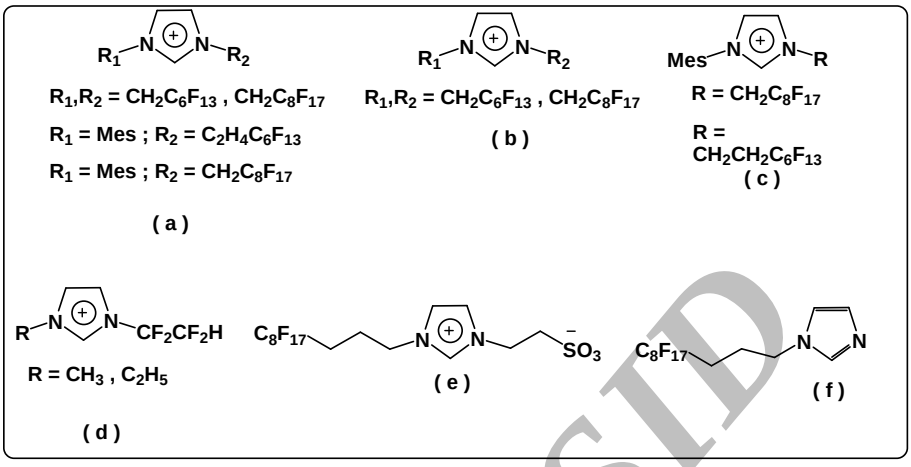


Fig. 1. Some of the selected fluorous imidazolium cations reported in the literature.

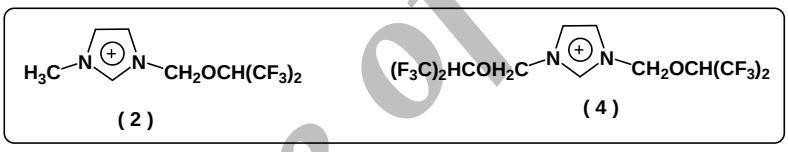


Fig. 2. Imidazolium salts reported in the current research.

known general inhalation anesthetic, the current water soluble molecules are expected to be biologically active.

EXPERIMENTAL

1,1,1,3,3,3-Hexa fluoro isopropanol (HFIP), imidazole and methyl imidazole were prepared from Merck. NMR spectra were recorded with a Brucker spectrometer (^{1}H NMR spectra at 250.13 MHz, ^{13}C NMR spectra at 62.90 MHz and ^{19}F NMR spectra at 235.13 MHz). Chemical shifts are reported on the δ scale relative to TMS. FTIR spectra were recorded on a Perkin Elmer spectrophotometer using KBr disc. Melting points were determined using Mettler.

Synthesis of 1,1,1,3,3,3-Hexafluoro(2-chloromethoxy) propane (Sevochlorane, 1)

To a 100 ml flask containing aluminum trichloride (4 g, 0.03 mol) was added cold (0 °C) HFIP (5 g, 0.03 mol) and the mixture was stirred for 1 h at 0 °C. Then, trioxane (0.89 g, 0.01 mol) was added to the reaction mixture in a single portion and the mixture was stirred while cooling at 0 °C in an ice bath for 2 h and then stirred for 3 h at RT. Afterward, water (10 g) was gradually added while vigorously stirring for 15 min. The organic phase was separated and distilled to get SVC (4.25 g) in 85% yield. ^{1}H NMR ($CDCl_3$): δ 4.66 (septet, $^3J_{FCCH}$ = 5.73 Hz, 1H), 5.56 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 72.8 (septet, $^2J_{FCC}$ = 33.4 Hz), 80 (s), 121.0 (dq, $^2J_{FC}$ = 28.31 Hz, $^3J_{FCCC}$ = 3.02 Hz). ^{19}F NMR ($CDCl_3$): δ -73.34 (d, J = 6.34 Hz, 6F).

Synthesis of 1-(1,1,1,3,3,3-Hexafluoroproisopoxy-methyl)-3-methylimidazolium Salt 2

To a sample tube (20 ml) containing methyl imidazole (0.82 g, 0.01 mol) was added SVC (2.17 g, 0.01 mol) at room temperature and the mixture was stirred for 3 days. The resulting viscose liquid was recrystallized from acetonitrile. The white crystals were obtained and washed by 2 × 2 ml diethyl ether and vacuum dried to get 2.49 g pure product **2** in 91% yield. ^{1}H NMR (DMSO+D_2O): δ 3.84 (s, 3H), 6.07 (s, 2H), 6.46 (septet, $^3J_{FCCH}$ = 6.25 Hz, 1H), 7.81 (s, 1H), 8.09 (s,

1H), 9.70 (s, 1H). ^{13}C NMR (DMSO+D_2O): δ 36.59 (s), 72.8 (septet, $^2J_{FCC}$ = 31.45 Hz), 78.4 (s), 123.8 (q, $^2J_{FC}$ = 283 Hz), 122.8 (s), 124.7 (s), 138.7 (s). ^{19}F NMR (DMSO+D_2O): δ -74.10 (d, J = 6.35 Hz, 6F). IR (neat) ν: 3178.32(s), 2728.11(s), 1585.17(s), 1560.54(s)1, 1382.76(s), 1293.29(s), 1121.24(s), 1000.56(s), 897.02(s), 870.13(s), 688.22(s).

Synthesis of Bis-1,3-(1,1,1,3,3,3-hexafluoroisopropoxymethyl)imidazolium Salt 4

Imidazolium salt **4** was prepared by two methods as follows: Method A: To a sample tube, containing imidazole (0.34 g, 0.005 mol) was added SVC (3.25 g, 0.015 mol) at room temperature and the mixture was stirred for 2 days. The resulting precipitate was filtered off and dissolved in acetonitrile (3 ml). After 1 day, the colorless crystals were obtained. The crystalline product was washed by 2 × 2 ml diethyl ether and vacuum dried to get 0.79 g pure product in 34% yield. ^{1}H NMR (DMSO+D_2O): δ 5.77 (septet, $^3J_{FCCH}$ = 5.75 Hz, 2H), 6.05 (s, 4H), 8.01 (s, 2H), 9.65 (s, 1H). ^{13}C NMR (DMSO+D_2O): δ 74.1 (septet, $^2J_{FCC}$ = 31.45 Hz), 79.4 (s), 123.4 (q, $^2J_{FC}$ = 283 Hz), 123.4 (s), 138.9 (s). ^{19}F NMR (DMSO+D_2O): δ -74.75 (d, J = 5.17 Hz, 6F). IR (neat) ν: 3079.71(s), 2905.79(s), 2739.13(s), 1559.20(s) 1407.45(s), 1110.84(s), 999.18(s), 898.01(s), 872.72(s), 688.46(s), 533.10(s).

Method B:A 50 ml round bottom flask equipped with a condenser and magnetic stirrer containing 5 ml THF was charged with imidazole (0.5 g, 7.3 mmol) and NaH (0.18 g, 7.3 mmol) and the mixture was refluxed at 70 °C for 6 h. The solvent was evaporated to get a white solid. To this was added sevochlorane (3.0 g, 13.5 mmol) and the reaction mixture was stirred at RT for 24 h. The resulting NaCl precipitate was filtered out and the filtrate was kept in a closed vial sample for 3 days to obtain 1.7 g crystalline product **4** in 67% yield. m.p.: 158-159 °C.

RESULTS AND DISCUSSION

Synthesis of 1,1,1,3,3,3-Hexafluoro(2-chloromethoxy) propane (Sevochlorane, 1)

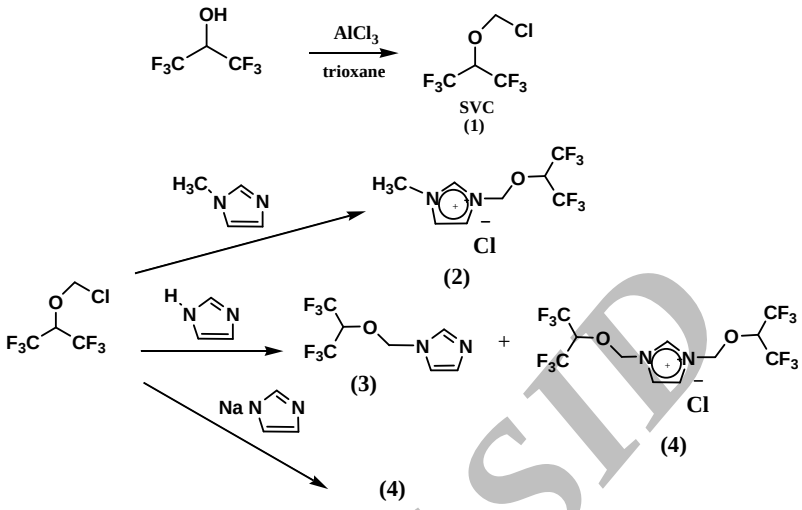
The reported procedure for the synthesis of sevochlorane (SVC) was followed with some modifications [11]. It involved one-step chloromethylation of 1,1,1,3,3,3-hexafluoro isopropanol (HFIP) using $AlCl_3$ and trioxane. The reaction temperature was kept constant at 0 °C for 2 h and then raised to room temperature. The reaction kinetics was followed by ^{1}H and ^{19}F NMR spectroscopy to optimize the reaction time. After 3 h at RT, 90% conversion was achieved and the product SVC was extracted. Since the organic phase consisted of SVC **1** and some percent of the corresponding bisacetal, the crude SVC was distilled to obtain pure SVC in 85% yield.

Synthesis of 1-(1,1,1,3,3,3-Hexafluoroisopropoxymethyl)-3-methylimidazolium Salt (2)

The solvent free reaction of equimolar amounts of methyl imidazole and SVC was followed at room temperature (Scheme 1). After two days, the single-phase reaction mixture gradually became viscose. The mixture was washed with ether to dissolve unreacted starting materials. The remaining sample was then recrystallized from acetonitrile and crystalline product, m.p.: 130-131 °C, was obtained in 91% yield. To characterize the obtained product, the corresponding ^{1}H NMR spectrum was analyzed. The presence of both imidazole ring and $CH_2OCH(CF_3)_2$ group was verified based on the known three ^{1}H peaks in the 7.8 to 10 ppm, a singlet at 3.84 ppm for methyl imidazole and more importantly a singlet at 6.07 ppm for the deshielded methylene hydrogens of $-OCH_2N^+$ and a septet at 6.46 ppm for $CH(CF_3)_2$ hydrogen. This was further confirmed by ^{13}C and ^{19}F NMR data. The expected septet peak at 72.8 ppm for CH carbon of $CH(CF_3)_2$ and a singlet at 78.4 ppm for N^+CH_2O carbon in ^{13}C NMR spectrum and a single doublet at -74.1 ppm in ^{19}F NMR spectrum further confirmed the chemical structure of imidazolium salt **2**. The observation of no more peaks in the three NMR spectra confirmed the purity of salt **2**. Contrary to 1-methyl-3-propyl imidazolium salt, the imidazolium salt **2** was not an ionic liquid.

Synthesis of Bis-1,3-(1,1,1,3,3,3-hexafluoroisopropoxymethyl)imidazolium Salt 4

Imidazolium salt **4** was prepared by two methods. In the first method, imidazole and SVC reacted at room temperature in the absence of a base. In the second, imidazole was first deprotonated by NaH and then reacted with SVC. In the first method, the 1:1 molar ratio was tried first and the reaction mixture, after being stirred for 2 days at RT, was dissolved in acetonitrile. The white crystalline precipitate filtered, dried



Scheme 1. Synthesis of imidazolium salts

and identified by NMR spectroscopy and found to be imidazolium salt **4** (4% yield). Then, the same reaction was repeated using imidazole and SVC in 1:3 molar ratio. After 24 h, a solid-liquid double-phase mixture was achieved. In order to identify the composition of the precipitate, a sample was dissolved in DMSO-d6 and analyzed by ^{1}H and ^{19}F NMR. Three species were recognized two of which showed the presence of both imidazole ring and $CH_2CH(CF_3)$ group. Accordingly, imidazolium chloride, imidazolium salts **3** and **4** were distinguished as the products. Imidazolium chloride and imidazolium salt **3** are produced as a result of HCl absorption and monoalkylation reaction while Imidazolium salt **4** is produced from the second alkylation reaction on **3**. The resulting precipitate, however, was recrystallized from acetonitrile to get imidazolium salt **4** in 34% yield. Salt **4** melts at 157-158 °C without decomposition, absorbs water rapidly, dissolves in water and DMSO, and is not soluble in chloroform and ether.

In the second method, imidazole was first deprotonated by NaH in THF followed by THF evaporation. The resulting sodium salt reacted with SVC, and NaCl precipitate was filtered out. The filtrate was kept in a closed vial sample for 3 days to obtain 1.7 g crystalline pure product **4** in higher yield, 67%. m.p.: 158-159 °C.

The characterization of imidazolium salt **4** was straightforward because of the symmetry of the molecule. The relative integration of imidazolium and CH_2 peaks in ^{1}H NMR spectrum and the existence of one septet at 5.77 ppm ($^{3}J_{FCCH}$ = 5.75 Hz, 2H) for $CH(CF_3)_2$ and a single singlet at 6.05 ppm (4H), clearly were in support of the formation of a double alkylated product **4**. Also, a doublet at 74.75 ppm (J = 5.17 Hz, 12F) in ^{19}F, a septet at 74.1 ppm ($^{2}J_{FCC}$ = 31.45 Hz) and a singlet at 79.4 ppm in ^{13}C NMR spectra clearly confirm the characterization. Single crystal structure analysis was performed on salt **4** to clarify the solid phase chemical structure.

Sevofluorane with the chemical structure $FH_2COCH(CF_3)_2$ is a known general inhalation anesthetic. This and other inhalation anesthetics have been deemed unsuitable for parenteral administration due to their low aqueous solubility, thereby making them difficult to formulate for intravenous administration. As noted earlier, structural modification of sevofluorane by replacing F with imidazolium cation was one of the goals in the current research to prepare water soluble salts containing $(CF_3)_2CHO\text{-}CH_2$ moity and to evaluate the structure and biological activities relationship. In order to evaluate the anesthetic properties of salts **2** and **4**, they were injected as intravenous aq. solutions to mice and the general behavior of the animals was followed. The preliminary tests indicated no anesthetic property. However, calmative property was noticed for both salts. The biological studies are underway in more details.

X-Ray Crystal Structure of Imidazolium Salt 4

A summary of the X-ray crystallography data for salt **4** is presented in Table 1 and the molecular structure is shown in Fig. 3. Table 2 lists bond lengths, bond angles and torsion angles. As is clear, the molecular structure consists of imidazolium cation and anionic fragment Cl^-.

CONCLUSIONS

$(CF_3)_2CH\text{-}O\text{-}CH_2Cl$ reacted with methylimidazole and imidazole in 1:1 and 2:1 mole ratio, respectively, to achieve the corresponding fluorous imidazolium chloride salts. The characterization was performed by ^1H, ^{13}C and ^{19}F NMR spectroscopy. The chemical structure of the symmetrically substituted imidazolium cation was verified by X-ray crystallography.

ACKNOWLEDGMENTS

We are grateful to Imam Hossein University for financial support.

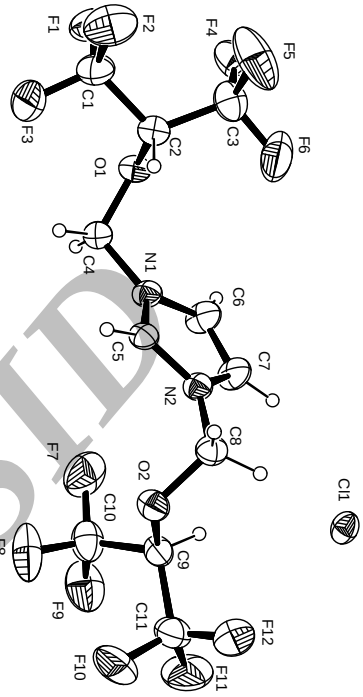


Fig. 3. ORTEP plot of imidazolium salt **4**.

Table 1. The X-Ray Crystallography Data for Imidazolium Salt **4**

Empirical formula	$C_{11}H_9N_2O_2F_{12}Cl$
Formula weight	464.65
Crystal system	Monoclinic
Space group, Z	P21/n Z = 4
Unit cell dimension	a = 10.613(10) α = 90.00˚
	b = 12.1493(8) β = 109.852(8)˚
	c = 14.1964(14) γ = 90.00˚
Unit cell volume	1726.3 A^3
Temperature (K)	298(2)
Adsorption coefficient (mm^{-1})	0.355
Calculation density (mg m^{-3})	1.788
F (0 0 0)	920
Crystal size (mm)	0.40 × 0.32 × 0.24
R value	0.0402
R_w value	0.1425
θ range for data collection (deg)	2.09 to 29.28
Limiting indices	-14 < h < 14, -16 < k < 15, -19 < l < 19
Reflection collected/unique	12361/4629 [R(int) = 0.0343]
Completeness to θ_{max}	98.2%
Goodness of fit on F^2	1.067
Final R indices[1.2sigma (1)]	R1 = 0.0611, wR2 = 0.1249

Table 2. Selected Bond Lengths (Å), Bond Angles (˚) and Torsion Angles (˚) for Imidazolium Salt **4**

C(1)-F(2)	1.315(4)	C(6)-C(7)	1.332(4)
C(1)-F(3)	1.325(4)	C(6)-N(1)	1.378(3)
C(1)-F(1)	1.328(4)	C(7)-N(2)	1.379(3)
C(1)-C(2)	1.514(4)	C(8)-O(2)	1.405(3)
C(2)-O(1)	1.407(3)	C(8)-N(2)	1.461(3)
C(2)-C(3)	1.469(4)	C(9)-O(2)	1.406(3)
C(3)-F(6)	1.313(4)	C(9)-C(11)	1.518(4)
C(3)-F(5)	1.319(4)	C(9)-C(10)	1.519(4)
C(3)-F(4)	1.328(4)	C(10)-F(8)	1.314(4)
C(4)-O(1)	1.409(3)	C(10)-F(9)	1.317(4)
C(4)-N(1)	1.456(3)	C(10)-F(7)	1.336(4)
C(5)-N(2)	1322(3)	C(11)-F(10)	1.310(4)
C(5)-N(1)	1.327(3)	C(11)-F(11)	1.321(4)
		C(11)-F(12)	1.326(4)
F(2)-C(1)-F(3)	108.6(3)		
F(2)-C(1)-F(1)	107.2(3)	O(2)-C(9)-C(10)	107.2(2)
F(3)-C(1)-F(1)	107.3(3)	C(11)-C(9)-C(10)	113.3(3)
F(2)-C(1)-C(2)	111.9(3)	F(8)-C(10)-F(9)	107.2(3)
F(3)-C(1)-C(2)	109.7(2)	F(8)-C(10)-F(7)	107.8(3)
F(1)-C(1)-C(2)	111.9(3)	F(9)-C(10)-F(7)	107.6(3)
O(1)-C(2)-C(3)	106.9(2)	F(8)-C(10)-C(9)	112.6(3)
O(1)-C(2)-C(1)	108.6(2)	F(9)-C(10)-C(9)	111.6(3)
C(3)-C(2)-C(1)	113.8(2)	F(7)-C(10)-C(9)	109.8(3)
F(6)-C(3)-F(5)	108.6(3)	F(10)-C(11)-F(11)	108.4(3)
F(6)-C(3)-F(4)	105.7(3)	F(10)-C(11)-F(12)	107.1(3)
F(5)-C(3)-F(4)	106.7(3)	F(11)-C(11)-F(12)	107.0(3)
F(6)-C(3)-C(2)	110.4(3)	F(10)-C(11)-C(9)	113.3(3)
F(5)-C(3)-C(2)	111.6(3)	F(11)-C(11)-C(9)	110.7(3)
F(4)-C(3)-C(2)	113.3(3)	F(12)-C(11)-C(9)	110.1(1)
O(1)-C(4)-N(1)	111.0(2)	C(2)-O(1)-C(4)	116.01(18)
N(2)-C(5)-N(1)	108.4(2)	C(8)-O(2)-C(9)	116.56(19)
C(7)-C(6)-N(1)	107.2(2)	C(5)-N(1)-C(6)	108.5(2)
C(6)-C(7)-N(2)	107.2(2)	C(5)-N(1)-C(4)	125.5(2)
O(2)-C(8)-N(2)	111.1(2)	C(6)-N(1)-C(4)	125.9(2)
O(2)-C(9)-C(11)	108.2(2)	C(5)-N(2)-C(7)	108.7(2)
		C(5)-N(2)-C(8)	125.1(2)
		C(7)-N(2)-C(8)	126.1(2)
F(2)-C(1)-C(2)-O(1)	-178.3(2)		
F(3)-C(1)-C(2)-O(1)	61.1(3)	O(2)-C(9)-C(11)-F(11)	-171.7(3)
F(1)-C(1)-C(2)-O(1)	-57.9(3)	C(10)-C(9)-C(11)-F(11)	69.7(4)
F(2)-C(1)-C(2)-C(3)	-59.3(3)	O(2)-C(9)-C(11)-F(12)	-5305(3)
F(3)-C(1)-C(2)-C(3)	-179.9(3)	C(10)-C(9)-C(11)-F(12)	-172.2(3)
F(1)-C(1)-C(2)-C(3)	61.1(3)	C (3)-C(2)-O(1)-C(4)	138.6(2)
O(1)-C(2)-C(3)-F(6)	-62.1(3)	C(1)-C(2)-O(1)-C(4)	-98.2(2)
C(1)-C(2)-C(3)-F(6)	178.0(3)	N(1)-C(4)-O(1)-C(2)	-77.1(3)
O(1)-C(2)-C(3)-F(5)	177.1(3)	N(2)-C(8)-O(2)-C(9)	78.3(3)
C(1)-C(2)-C(3)-F(5)	57.2(4)	C(11)-C(9)-O(2)-C(8)	113.7(2)
O(1)-C(2)-C(3)-F(4)	56.3(3)	C(10)-C(9)-O(2)-C(8)	-123.9(3)
C(2)-C(2)-C(3)-F(4)	-63.6(4)	N(2)-C(5)-N(1)-C(6)	-0.5(3)
N(1)-C(6)-C(7)-N(2)	-.08(4)	N(2)-C(5)-N(1)-C(4)	178.3(2)
O(2)-C(9)-C(10)-F(8)	-51.4(4)	C(7)-C(6)-N(1)-C(5)	0.8(3)
C(11)-C(9)-C(10)-F(8)	67.8(4)	C(7)-C(6)-N(1)-C(4)	-177.9(3)
O(2)-C(9)-C(10)-F(9)	-172.1(4)	O(1)-C(4)-N(1)-C(5)	118.5(3)
C(11)-C(9)-C(10)-F(9)	-52.9(4)	O(1)-C(4)-N(1)-C(6)	-63.0(3)
O(2)-C(9)-C(10)-F(7)	68.6(3)	N(1)-C(5)-N(2)-C(7)	0.0(3)
C(11)-C(9)-C(10)-F(7)	-172.1(3)	N(1)-C(5)-N(2)-C(8)	-175.9(2)
O(2)-C(9)-C(11)-F(10)	66.4(4)	C(6)-C(7)-N(2)-C(5)	0.5(3)
C(10)-C(9)-C(11)-F(10)	-52.3(4)	C(6)-C(7)-N(2)-C(8)	176.3(3)
		O(2)-C(8)-N(2)-C(5)	69.8(3)
		O(2)-C(8)-N(2)-C(7)	-105.3(3)

SUPPLEMENTARY DATA

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no.
CCDC 781832 for compound **4**. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB12 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.cam.ac.uk or on the web www: http://www.ccdc.cam.ac.uk.

REFERENCES

[1] K. Matsumoto, R. Hagiwara, J. Fluorine Chem. 128 (2007) 317.
[2] H. Xue, R. Verma, J.M. Shreeve, J. Fluorine Chem. 127 (2006) 159.
[3] O. Kysilka, M. Rybáčková, M. Skalický, M. Kvíčalová, J. Cvačka, J. Kvíčala, J. Fluorine Chem. 130 (2009) 929.
[4] M. Skalický, M. Rybáčková, O. Kysilka, M. Kvíčalová, J. Cvačka, J. Čejka, J. Kvíčala, J. Fluorine Chem. 130 (2009) 966.
[5] W. Shen, L.M. Wang, H. Tian, J. Tang, J.J. Yu, J. Fluorine Chem. 130 (2009) 522.
[6] Y.L. Yagupolskii, T.M. Sokolenko, K.I. Petko, L.M. Yagupolskii, J. Fluorine Chem. 126 (2005) 669.
[7] L. Xu, W. Chen, J.F. Bickley, A. Steiner, J. Xiao, J. Organomet. Chem. 598 (2000) 409.
[8] A. Furstner, L. Ackermann, B. Gabor, R. Goddard, C.W. Lehmann, R. Mynott, F. Stelzer, O.R. Thiel, Chem. Eur. J. 7 (2001) 3236.
[9] R.P. Singh, S. Manandhar, J.M. Shreeve, Tetrahedron Lett. 43 (2002) 9497.
[10] P. BonhÔte, A.P. Dias, Inorg. Chem. 35 (1996) 1168.
[11] C. Bieniarz, C. Behme, K. Ramakrishna, J. Fluorine Chem. 106 (2000) 99.