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Arsenic(III) alkoxides containing 2,2,2-trifluoroethoxy and 1,1,1,3,3,3-hexafluoroisopropoxy ligands

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Abstract

The metathesis of arsenic(III) chloride with 3 mol each of $NaOCH_2CF_3$ and $NaOCH(CF_3)_2$ in n-hexane yields $As(OR)_3$ [$R = CH_2CF_3$ and $CH(CF_3)_2$]. The reaction of $As(OR)_3$ with 1 or 2 mol of acetyl chloride in n-hexane affords $AsCl(OR)_2/AsCl_2(OR)$. All these compounds are liquids with the exception of $As(OCH_2CF_3)_3$ which is a low melting solid. Their cryoscopic molecular weights show them to be monomeric. The compounds have been characterised by elemental analysis, IR, NMR spectra and mass spectrometry. Their reaction with pyridine yields 1:1 solid adducts.

Keywords: Arsenic(III) alkoxides; Trifluoroethoxy ligands; Hexafluoroisopropoxy ligands; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

Recently, metal alkoxides have aroused renewed interest for their applications in sol–gel processes [1], as vapour-deposition reagents in the syntheses of metal oxide ceramics [2] and as polymerization catalysts [3]. The volatility and/or solubility of metal alkoxides make them good candidates for such purposes [1]. The role of fluorinated alkoxide ligands in yielding low-coordinate soluble compounds [4] may be easily understood since the fluorinated alkoxy ligands are mostly unidentate [5]. These properties may become more effective with a fluoro-alkoxy ligand having a crowded coordination sphere [6]. The ligands which belong to this class and are abundantly available are derived from 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoroisopropanol. Arsenic(III) alkoxides with these ligands have not been reported previously. We report here the synthesis and nature of arsenic(III) alkoxides containing these ligands.

2. Experimental details

2.1. Instrumentation

Details of instruments used are the same as reported previously [7].

2.2. Materials and methods

Details of the purification of the materials used and analytical methods have been outlined earlier [7,8]. C and H analyses were from the Regional Sophisticated Instrumentation Laboratory, Panjab University, Chandigarh.

Arsenic trichloride was prepared by a standard method [9].

2.2.1. Synthesis of $NaOCH_2CF_3$ and $NaOCH(CF_3)_2$

These were synthesised and purified using literature methods [10,11].

2.2.2. Synthesis of $As(OCH_2CF_3)_3$

Arsenic(III) chloride (0.92 g, 5.05 mmol) and $NaOCH_2CF_3$ (1.85 g, 15.2 mmol) were mixed and n-hexane (20 ml) and CF_3CH_2OH (1 ml) were added. The mixture was stirred for 2 h and subsequently refluxed for 1 h. Sodium chloride precipitated and the alkoxide remained in the solvent. After filtration, the filtrate was evacuated to yield a white solid which was recrystallised from 2,2,2-trifluoroethanol to afford a white powder (yield, 80%).

2.2.3. Synthesis of $As(OCH(CF_3)_2)_3$

To sodium 1,1,1,3,3,3-hexafluoroisopropoxide (2.9 g, 15.2 mmol) in 20 ml of n-hexane was added arsenic trichloride (0.9 g, 5.1 mmol). The contents were stirred for 2 h followed by refluxing for 2 h. The contents were filtered under

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Table 1
Analytical and NMR data for 2,2,2-trifluoroethoxy and 1,1,1,3,3,3-hexafluoroisopropoxy derivatives of arsenic(III) and their adducts with pyridine

Compound	M.p. (°C)	As (%)		Cl (%)		F (%)		C (%)		H (%)		NMR (δ, ppm)	
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	^{1}H	^{19}F
$As(OCH_2CF_3)_3$	62–64	19.15	20.16	–	–	44.92	45.96	18.69	19.35	1.35	1.52	4.03(q) (12 Hz)	−79.1(t) (9 Hz)
$AsCl(OCH_2CF_3)_2$ [a]	–	23.29	24.35	10.52	11.3	36.42	37.01	–	–	–	–	4.23(q) (9 Hz)	−76.1(t) (9 Hz)
$AsCl_2(OCH_2CF_3)$ [a]	–	29.21	30.73	27.90	28.36	22.12	23.36	8.79	9.8	0.72	0.82	4.3(q) (9 Hz)	−76(t) (9 Hz)
$As(OCH(CF_3)_2)_3$ [a]	–	12.01	13.02	–	–	58.23	59.37	18.62	18.75	0.42	0.50	4.76(m) (6 Hz)	−76(d) (3 Hz)
$AsCl(OCH(CF_3)_2)_2$ [a]	–	15.28	16.90	5.96	6.07	38.23	39.58	15.98	16.19	0.39	0.45	4.9(m) (3 Hz)	−75(d) (3 Hz)
$AsCl_2(OCH(CF_3)_2)$ [a]	–	29.93	29.63	21.9	22.4	35.29	36.53	11.2	11.5	0.35	0.32	4.86(m) (6 Hz)	−75(d) (3 Hz)
$As(OCH_2CF_3)_3 \cdot py$ [b]	>200	15.12	16.62	–	–	36.12	37.91	–	–	–	–	4.4(q) (9 Hz)	−78(t) (9 Hz)
$AsCl(OCH_2CF_3)_2 \cdot py$ [b]	>200	18.25	19.37	8.27	9.09	28.42	29.4	–	–	–	–	4.2(q) (9 Hz)	−75(t) (9 Hz)
$AsCl_2(OCH_2CF_3) \cdot py$ [b]	>200	22.2	23.2	19.21	21.6	18.12	17.6	–	–	–	–	4.43(q) (9 Hz)	−75(t) (9 Hz)
$As(OCH(CF_3)_2)_3 \cdot py$ [b]	>200	10.92	11.45	–	–	49.51	50.66	–	–	–	–	4.93(m) (6 Hz)	−76(d) (9 Hz)
$AsCl(OCH(CF_3)_2)_2 \cdot py$ [b]	>200	13.19	14.30	5.2	6.6	42.13	43.59	–	–	–	–	4.83(m) (6 Hz)	−76(d) (9 Hz)
$AsCl_2(OCH(CF_3)_2) \cdot py$ [b]	>200	17.95	19.1	16.19	17.9	28.01	29.10	–	–	–	–	4.23(m) (6 Hz)	−76(d) (9 Hz)

[a] Colourless liquids.
[b] White solids.

Table 2
Cryoscopic data for 2,2,2-trifluoroethoxy and 1,1,1,3,3,3-hexafluoroisopropoxy derivatives of arsenic(III)

Compound	Concentration ($\times 10^{-2}$ M)	Molecular weight	
		Experimental	Theoretical [a]
$As(OCH_2CF_3)_3$	4.5	360	372
	5.8	350	
	6.8	380	
$AsCl(OCH_2CF_3)_2$	2.5	215	308
	3.7	300	
	4.0	300	
$AsCl_2(OCH_2CF_3)$	2.1	230	244
	3.4	220	
	4.1	240	
$As(OCH(CF_3)_2)_3$	5.2	570	576
	6.2	575	
	6.9	560	
$AsCl(OCH(CF_3)_2)_2$	3.5	400	444
	4.8	420	
	6.1	430	
$AsCl_2(OCH(CF_3)_2)$	1.7	320	312
	3.2	325	
	4.2	310	

[a] For monomer.

a dry nitrogen atmosphere and the filtrate evacuated to give a colourless liquid. This liquid was washed with petroleum ether and evacuated again to afford a colourless liquid (yield, 65%).

2.2.4. Synthesis of mixed chloro-alkoxo derivatives

Reaction of $As(OR)_3$ with 1 or 2 mol of acetyl chloride [12] in n-hexane, followed by refluxing and evacuation, afforded $AsCl(OR_2)/AsCl_2(OR)$ as colourless liquids which were washed with petroleum ether and finally evacuated (yield, 60%–70%). These compounds decomposed on attempted distillation under reduced pressure.

Pyridine adducts were prepared by adding pyridine to a solution of the alkoxide in Et_2O when the solid adduct precipitated. This was filtered, washed with Et_2O and dried under vacuum.

3. Results and discussion

3.1. Synthesis and properties

Arsenic trichloride reacts with 3 equiv. of sodium 2,2,2-trifluoroethoxide in n-hexane/CF_3CH_2OH to yield a hygroscopic low-melting white solid.

$$AsCl_3 + 3NaOCH_2CF_3 \xrightarrow[-3NaCl]{} As(OCH_2CF_3)_3$$

This compound is soluble in $CHCl_3$, CH_2Cl_2, n-hexane, benzene, nitrobenzene and most donor solvents. The corresponding mixed chloro-2,2,2-trifluoroethoxy derivatives have been

Table 3
Mass ion peaks for 2,2,2-trifluoroethoxy and 1,1,1,3,3,3-hexafluoroisopropoxy derivatives or arsenic(III)

$As(OCH_2CF_3)_3$			$AsCl(OCH_2CF_3)_2$			$AsCl_2(OCH_2CF_3)$			$As(OCH(CF_3)_2)_3$			$AsCl(OCH(CF_3)_2)_2$		
m/z	R.I.[a]	Assignment	m/z	R.I.[a]	Assignment	m/z	R.I.[a]	Assignment	m/z	R.I.[a]	Assignment	m/z	R.I.[a]	Assignment
369	20	$[As(OCHCF_3)]^+$	289	100	$[AsCl(OCH_2CF_3)(OCH_2CF_2)]^+$	188	2	$[AsCl(OC(CF_2))]^+$	557	2	$[As(OCH(CF_3)_2)_2[OCH(CF_3)(CF_2)]^+$	394	100	$[AsCl(OCH(CF_3)_2]OCH(CF_3)]^+$
204	21	$[As(OCH_2CF_3)(OCH_2)]^+$	182	6	$[AsF_2(OCH_2F_2)]^+$	113	7	AsF_2^+	547	28	$[As(OCH(CF_3)_2]_2(CF_3)_2]^+$	305	2	$[AsCl(OCH(CF_3)_2]^+$
113	23	AsF_2^+	91	32	AsO^+	98	11	$OCHCF_3^+$	507	6	$[As(OCH(CF_3)_2]_2[OCH(CF_3)]$	289	54	$[AsCl(CHCF_3)(OCHCF_3)]^+$
98	100	CF_3CHO^+	75	2	As^+	97	7	$OCCF_3^+$	409	100	$[As(OCH(CF_3)_2]_2]^+$	182	8	$[AsF_2(CF_3)]^+$
77	13	$OCCF_3^+$	73	3	OF_3	92	6	$[AsOH]^+$	311	16	$[As(OCH(CF_3)_2)CF_3]^+$	150	4	$[C(CF_3)_2]^+$
70	20	HCF_3^+				91	22	AsO^+	201	17	$[As(OCH(CF_3)(CF)^+$	69	30	CF_3^+
69	18	CF_3				70	33	CHF_3^+	129	60	$AsOF_2^+$			
						69	100	CF_3^+	79	8	$OCHCF_3^+$			
						51	7	CHF_2^+	69	5	CF_3^+			

[a] R.I. = relative intensity.

prepared by reaction of 1 or 2 mol of acetyl chloride with $As(OCH_2CF_3)_3$. The compounds $AsCl(OCH_2CF_3)_2$ and $AsCl_2(OCH_2CF_3)$ are hygroscopic colourless liquids. A similar procedure was adopted for the synthesis of the corresponding 1,1,1,3,3,3-hexafluoroisopropoxy derivatives. Analytical data for all the compounds are given in Table 1.

Molecular weight determination of the compounds in benzene showed them to be monomeric (Table 2). As a consequence of electronegativity and steric effects of the ligands, association is inhibited. However, the small size of the central atom may also contribute to such a behaviour. Although antimony(V) 2,2,2-trifluoroethoxides [13] and 1,1,1,3,3,3-hexafluoroisopropoxides [7] are monomeric, the compound $Bi(OCH(CF_3)_2)_3 \cdot THF$ is a 1,1,1,3,3,3-hexafluoroisopropoxy-bridged dimer [14].

3.2. Infrared spectra

The IR spectra show a single band in the 1120–1042 cm^{-1} region where ν(C–O) of the $-OCH_2CF_3$ or $-OCH(CF_3)_2$ moieties absorb [15]. Significant information concerning the bonding situation of the alkoxy ligand can be deduced from the position and number of C–O stretching bands [16]. Terminal C–O stretching occurs generally at 1150–1050 cm^{-1} and a bridging C–O gives an absorption band at 950–1050 cm^{-1}. In the present case, only one band appears in the former region and this supports the presence of only terminal alkoxy groups. The mixed chloro-alkoxo compounds show ν(As–Cl) at 330–350 cm^{-1} [17]. There was no evidence of chlorine bridging in these compounds, as a comparison of the spectrum of $As(OCH(CF_3)_2)_3$ with the spectra of $AsCl(OCH(CF_3)_2)_2$ and $AsCl_2(OCH(CF_3)_2)$ showed no new band in the latter compounds in the 300–200 cm^{-1} spectral region where $\nu(As–Cl \rightarrow As)$ is expected to absorb [18].

3.3. Nuclear magnetic resonance spectra

^1H NMR spectra (Table 1) of the 2,2,2-trifluoroethoxy and 1,1,1,3,3,3-hexafluoroisopropoxy derivatives appear as a quartet and multiplet respectively, while their ^{19}F NMR spectra show a triplet and doublet [7,19].

3.4. Mass spectrometric studies

The mass spectra of these compounds (Table 3) show neither the mass ion peak corresponding to the molecular ion nor any peak above the monomeric species, suggesting the absence/decomposition of any dimeric complex in the vapour phase.

3.5. Reaction with pyridine

The electron-withdrawing effect of fluorine atoms is extended to As through oxygen in these compounds, thus increasing the acceptor power of the arsenic atom. In this case, a donor molecule such as pyridine may coordinate to arsenic with an expansion of the coordination number of As. Reaction of pyridine affords 1:1 adducts and the analytical and NMR details of the adducts are given in Table 1. The shifts in the characteristic vibrations in the infrared spectrum of pyridine on complex formation with the present complexes compare well with its adducts with other Lewis acids [20,21]. The value of ν(C–O) in these complexes shifts to lower frequencies by 5–10 cm^{-1}, whereas ν(As–Cl) shifts lower by 20–30 cm^{-1}.

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