Reactions of [SbR$_3$X$_2$]$_2$O with carboxylates and the crystal structures of [SbPh$_3$(O$_2$CCF$_3$)$_2$]$_2$O and [SbMe$_3$(O$_2$CCH$_3$)$_2$]$_2$O

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Abstract

Reactions of [SbPh$_3$Br]$_2$O and [SbMe$_3$Cl]$_2$O with a number of carboxylates lead to halogen substitution and formation of either [SbR$_3$(O$_2$CR′)]$_2$O or SbR$_3$(O$_2$CR′)$_2$. X-ray structures for two of the products, [SbPh$_3$(O$_2$CCF$_3$)]$_2$O and [SbMe$_3$(O$_2$CCH$_3$)]$_2$O, show that the carboxylates are unidentate. From NMR spectroscopy, the oxygen bridged compounds are hydrolysed by adventitious water giving SbR$_3$(O$_2$CR′)OH in solution but when R = phenyl the original compounds can be recovered on crystallisation. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Antimony(V); Carboxylates; Hydrolysis; Crystal structure; NMR spectra

1. Introduction

We have previously reported [1] that reactions between oxo-bridged di-antimony compounds, such as [SbPh$_3$Br]$_2$O and [SbMe$_3$Cl]$_2$O, and phosphinates and arsinates lead to products in which the new ligands also bridge between antimony centres and this paper describes similar reactions with related carboxylates.

Carboxylates are versatile ligands and although there are examples where the ligand is unidentate, for example, three of the acetate groups in SbPh(O$_2$CMe)$_4$ [2], bidentate behaviour is more often observed, especially where the central atom is coordinatively unsaturated. This is the case with the fourth, chelating, acetate in SbPh(O$_2$CMe)$_4$. Reduction of antimony Lewis acidity also leads to basically unidentate carboxylates in, for example, SbPh$_3$(O$_2$CMe)$_2$ [3] and SbPh$_3$(O$_2$CPh)$_2$ [4], but even here there are weak secondary chelating Sb...O interactions. Bridging carboxylates, on the other hand, are present in [(SbCl$_3$)$_2$(μ-O)(μ-OR^1)(μ-O$_2$CR^2)], where R^1 = H, R^2 = Me [5], CCl$_3$, Pr^i [6] and R^1 = Me, R^2 = CF$_3$, Et [7] and in the 'cage' compound, [(SbPh$_2$)$_4$(μ-O)$_4$(μ-OH)$_2$(μ-O$_2$CMe)$_2$] · HO$_2$CMe, and related molecules [8,9]; bridging trifluoroacetate groups are present in both [(SbF$_3$)$_2$(μ-O)(μ-O$_2$CCF$_3$)$_2$] and [(SbF$_4$)$_2$(μ-F)(μ-O$_2$CCF$_3$)] [10]. Antimony(III) compounds containing bridging carboxylates, include Sb(O$_2$CMe)$_3$ [11], Sb(O$_2$CCF$_3$)$_3$ [12] and SbPh$_2$(O$_2$CMe) [13].

Chelating, rather than bridging, carboxylates, however, are present in both [SbPh$_2$(O$_2$CMe)$_2$]$_2$O [8] and [SbPh$_2$(O$_2$CPh)$_2$]$_2$O [14], giving antimony atoms in seven-fold coordination. Related oxo-bridged compounds, [SbPh$_3$(O$_2$CR)]$_2$O, are also known [15] but X-ray structures are not available. Here the lower Lewis acidity from the presence of three phenyl groups may, as for SbPh$_3$(O$_2$CR)$_2$ compounds, lead to unidentate coordination and this paper describes new results in this area.
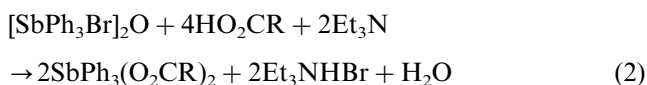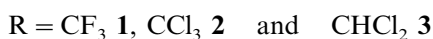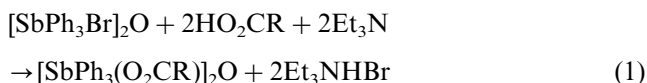
2. Results and discussion

2.1. Preparations

Three oxygen bridged bis(triphenylantimony) dicarboxylates, [SbPh$_3$(O$_2$CCF$_3$)]$_2$O **1**, [SbPh$_3$(O$_2$CCCl$_3$)]$_2$O

2 and $[SbPh_3(O_2CCHCl_2)]_2O$ **3** have been prepared by treating $[SbPh_3Br]_2O$ with the appropriate carboxylic acid in the presence of triethylamine, as described previously [15] (Eq. (1)). Related reactions with either chloroacetic acid or benzoic acid, however, led to bridge cleavage (Eq. (2)) and the products were $SbPh_3(O_2CCH_2Cl)_2$ **4** and $SbPh_3(O_2CPh)_2$ **5**, respectively. Bridge cleavage giving $SbPh_3(O_2CMe)_2$ **6** also occurred in the reaction of $[SbPh_3Br]_2O$ with 2 mol of $Ag(O_2CMe)$, but even with prolonged reaction times there was no reaction with either $Na(O_2CMe)$ or $(MeCO)_2O$.

$$[SbPh_3Br]_2O + 2HO_2CR + 2Et_3N$$
$$\rightarrow [SbPh_3(O_2CR)]_2O + 2Et_3NHBr \qquad (1)$$

$$R = CF_3 \; \textbf{1}, \quad CCl_3 \; \textbf{2} \quad and \quad CHCl_2 \; \textbf{3}$$

$$[SbPh_3Br]_2O + 4HO_2CR + 2Et_3N$$
$$\rightarrow 2SbPh_3(O_2CR)_2 + 2Et_3NHBr + H_2O \qquad (2)$$

$$R = CH_2Cl \; \textbf{4} \quad and \quad Ph \; \textbf{5}$$

Rather surprisingly, both $[SbMe_3(O_2CMe)]_2O$ **7** and $[SbMe_3(O_2CBu^t)]_2O$ **8** were obtained in good yield from $[SbMe_3Cl]_2O$ and two mols of, respectively, $Ag(O_2CMe)$ or $Na(O_2CBu^t)$ and the silver acetate reaction clearly follows a different course from that with $[SbPh_3Br]_2O$. Neither the expected substitution product nor the bridge cleavage product was obtained on treatment of $[SbMe_3Cl]_2O$ with two mols of HO_2CCF_3 in the presence of triethylamine and ^{1}H NMR spectroscopy showed the presence of a number of unidentified products.

2.2. Infrared spectroscopy

IR spectroscopy provides a method of assessing carboxylate coordination modes from the position of, and separation (Δv) between, the antisymmetric and symmetric CO_2 stretching modes. Deacon and coworkers [16] point out that for acetates and trifluoroacetates this correlation is limited to recognition of:

1. Complexes with unidentate carboxylates where $\Delta v_{unidentate} > \Delta v_{ionic}$, and;
2. Complexes with chelating or bridging carboxylates, where $\Delta v_{bridging \; or \; chelating}$ is often $< \Delta v_{ionic}$. (Δv_{ionic} values are 164 and 223 cm^{-1}, respectively, for the acetate and trifluoroacetate.)

Selected IR data for compounds **1**–**8** are summarised in Table 1 and, in cases where previous data are available, they are in good agreement [15,17]. Bands for $[SbPh_3(O_2CCF_3)]_2O$ **1** at 1714 cm^{-1} and 1437 cm^{-1} give $\Delta v = 277$ cm^{-1}, only slightly greater than the ionic value but close to that in $Sb(O_2CCF_3)_3$ (293 cm^{-1}), which is known to have effectively unidentate trifluoroacetate groups [12]. In $[(SbCl_3)_2(\mu\text{-O})(\mu\text{-OH})(\mu$-

$O_2CCF_3)]$, presumed to have symmetrically bridging trifluoroacetate groups, Δv (153 cm^{-1}) is, as expected, substantially lower [6]. It is interesting that in spite of the similarity in stoichiometry between **1** and $[SbF_3(O_2CCF_3)]_2O$ [12], the latter contains symmetrically bridging trifluoroacetate groups; this change in trifluoroacetate coordination is probably due to the increased antimony Lewis acidity from the presence of fluorines on antimony.

Δv values for compounds **2**–**8** clearly point to the presence of unidentate carboxylate groups and this has been confirmed by X-ray crystallography for two mono-antimony compounds, $SbPh_3(O_2CR)_2$ where R = Ph **5** [4] or Me **6** [3]. In each case, the solid state structure, however, includes weak secondary bonds between antimony and the double bonded oxygen of the carboxylate group. In some spectra the carboxylate bands are split, i.e. $v_{asym}(CO_2)$ for **3** and **4** and $v_{sym}(CO_2)$ for **4**, probably showing the in-phase and out-of-phase components and it is interesting that for **1**–**3** the frequency of $v_{asym}(CO_2)$ decreases with increase in pK_a of the parent carboxylic acid. All oxygen bridged compounds show a band at 710–750 cm^{-1}, assigned to Sb–O–Sb stretching.

2.3. NMR spectroscopy

The NMR behaviour of the triphenylantimony bridged compounds **1**–**3** is similar to that observed previously with $[SbPh_3Br]_2O$ and related compounds [18] in that there is ready hydrolysis by traces of moisture from the $CDCl_3$ solvent and elsewhere to give monoantimony hydroxo species, $SbPh_3(OH)(O_2CR)$, and if no precautions are taken to dry the solvent rigorously, the spectra contain signals associated with both this species (**B**) and the unhydrolysed oxygen bridged starting compound (**A**). A solution of **3**, prepared under strictly anhydrous conditions, showed only the triplet, triplet, doublet pattern of peaks for the *m*-(7.30) *p*- (7.45) and *o*- (7.60 ppm) protons of the phenyl groups of the unhydrolysed compound (**A**); the

Table 1
Selected IR bands (cm^{-1})

Compound	$v_a(CO_2)$	$v_s(CO_2)$	Δv	v(Sb–O–Sb)
$[SbPh_3(O_2CCF_3)]_2O$ **1**	1714	1437	277	742
$[SbPh_3(O_2CCCl_3)]_2O$ **2** [15]	1701	1289	412	737
$[SbPh_3(O_2CCHCl_2)]_2O$ **3**	1694/1669	1325	356	740
$SbPh_3(O_2CCH_2Cl)_2$ **4**	1672/1654	1346/1332	324	737
$SbPh_3(O_2CPh)_2$ **5**	1645	1324	321	
$SbPh_3(O_2CMe)_2$ **6** [17]	1630	1318	312	
$[SbMe_3(O_2CMe)]_2O$ **7**	1623	1374	249	710
$[SbMe_3(O_2CBu^t)]_2O$ **8**	1620	1326	294	750

dichloroacetate proton gave a singlet at 5.55 ppm. After this sample was exposed to atmospheric moisture for 24 h, additional signals appeared at 5.75 (singlet, C*H*Cl$_2$), 7.53 (multiplet, *m*- and *p*-Ph) and 8.11 (multiplet, *o*-Ph) ppm, associated with the hydrolysis product, SbPh$_3$(OH)(O$_2$CCHCl$_2$) (**B**). Similarly, under anhydrous conditions, the ^{13}C{^{1}H} spectrum of **3** showed only resonances for the non-hydrolysed compound at 67.8 (Cl$_2$*C*H), 129.3 (*m*-Ph), 131.1 (*p*-Ph), 133.7(*o*-Ph) and 138.1(*ipso*-Ph) ppm. Crystallisation of solutions containing the hydroxocompound led, as previously observed with related compounds [18], to recovery of only the oxo-bridged original, implying that hydroxo compounds are unstable in the solid state.

Solutions of **1** and **2**, prepared with no precautions against contamination by atmospheric moisture, clearly showed two sets of signals; the triplet, triplet, doublet pattern of the oxo-bridged parents (**A**) [at 7.31, 7.45 and 7.52 ppm, respectively, for **1** and 7.35, 7.48 and 7.53 ppm for **2**] and the two multiplets [at 7.53 (*m*- and *p*-Ph) and 8.06 (*o*-Ph) ppm for **1** and at 7.53 and 8.12 ppm for **2**] of the hydrolysis products, SbPh$_3$(OH)(O$_2$CR) (**B**). Again, crystallisation of NMR samples led to quantitative recovery of the original compounds. Proton spectra of SbPh$_3$(O$_2$CCH$_2$Cl)$_2$ **4**, SbPh$_3$(O$_2$CPh)$_2$ **5** and SbPh$_3$(O$_2$CMe)$_2$ **6** all showed the second order phenyl multiplets, typical of monomeric trigonal bipyramidal SbPh$_3$X$_2$ compounds.

Under strictly anhydrous conditions, the proton spectrum of [SbMe$_3$(O$_2$CMe)]$_2$O **7** showed the expected singlets at 1.62 and 1.83 ppm for, respectively, the *Me*-Sb and *Me*-CO$_2$ resonances and exposure to atmospheric moisture gave new peaks at 1.82 and 1.90 ppm, suggesting hydrolysis with the probable (unconfirmed) formation of SbMe$_3$(OH)(O$_2$CMe). In contrast to the behaviour of solutions of **1**–**3**, the parent compound was not recovered on crystallisation and hydrolysis appears to be irreversible. It is interesting to note here that stable antimony(V) hydroxo species usually require the presence of sterically demanding groups, e.g. Sb(mesityl)$_3$Br(OH) [18] and Sb(mesityl)$_3$(OH)$_2$ [19] are known, but recently a related methylantimony compound, SbMe$_3$(OH)(O$_2$PPh$_2$), has been identified [20]. The ^{13}C{^{1}H} spectrum of **7** under anhydrous conditions showed the expected signals at 14.5 (*Me*-Sb), 23.3 (*Me*-CO$_2$) and 176.4 (Me*C*O$_2$) ppm. The *Me*-Sb signal in the ^{1}H spectrum of [SbMe$_3$(O$_2$CBu^t)]$_2$O **8** under anhydrous conditions was at 1.59 ppm, with a singlet for the Bu^t protons at 1.03 ppm, while the ^{13}C{^{1}H} NMR showed singlets at 14.3 (*Me*-Sb), 27.7 (C*Me$_3$*), 39.1 (O$_2$C-*C*Me$_3$) and 183.5 (O$_2$*C*Bu^t).

2.4. Mass spectrometry

The highest mass fragment in the FAB spectrum of [SbPh$_3$(O$_2$CCHCl$_2$)]$_2$O **3** was Sb$_2$Ph$_6$O(O$_2$CCHCl$_2$)$^+$ (*m/z* 847) and a second diantimony ion at *m/z* 811 results from subsequent loss of chlorine and hydrogen giving Sb$_2$Ph$_6$O(O$_2$CCCl)$^+$. Further ions were assigned to SbPh$_3$(O$_2$CCHCl$_2$)$^+$, SbPh$_3$OH$^+$, SbPh$_2$$^+$, SbPh$^+$, SbO$_2C^+$ and the commonly observed Ph$_2$$^+$ ion.

Major fragmentation in the EI spectrum of SbPh$_3$(O$_2$CCH$_2$Cl)$_2$ **4** is via loss of carboxylate giving SbPh$_3$(O$_2$CCH$_2$Cl)$^+$ and SbPh$_2$$^+$ but loss of phenyl is much less probable. The Sb(O$_2$CCH$_2$Cl)$^+$ ion was present along with the rearrangement ion SbPh$_3$Cl$^+$. Fragmentation of SbPh$_3$(O$_2$CMe)$_2$ **6** followed a similar route.

The highest mass peak in the EI spectrum of [SbMe$_3$(O$_2$CMe)]$_2$O **7** was Sb$_2$Me$_6$O(O$_2$CMe)$^+$ (*m/z* 407) and two further diantimony fragments, Sb$_2$Me$_6$O$^+$ and Sb$_2$Me$_4$O$^+$, were also observed; other notable peaks were SbMe$_3$(O$_2$CMe)$^+$, SbMe$_3$OH$^+$, SbMeOH$^+$ and SbMe$_2$$^+$.

2.5. X-ray crystallography

Single crystal X-ray structures have been determined for [SbPh$_3$(O$_2$CCF$_3$)]$_2$O **1** and [SbMe$_3$(O$_2$CMe)]$_2$O **7**.

2.5.1. Structure of [SbPh$_3$(O$_2$CCF$_3$)]$_2$O **1**

The molecular structure of **1** is shown in Fig. 1 with selected bond lengths and angles in Table 2. The determination was not completely satisfactory as the C(3) trifluoroacetate group was disordered and could not be adequately modelled but it confirms that the trifluoroacetate groups are basically unidentate, as suggested by the IR spectrum. Unreliable bond parameters for the C(3) trifluoroacetate group have been omitted from Table 2. Antimony shows trigonal bipyramidal geometry with equatorial phenyls [Sb–C 2.100(6)–2.112(6) Å] and oxygens from the bridge and a trifluoroacetate in axial positions. Secondary bonding via the formally non-bonded oxygens is very weak [Sb(1)...O(3), Sb(2)...O(5), 3.196(4), 3.402(4) Å, respectively] and opening of one of the equatorial angles at each antimony [C(11)–Sb(1)–C(31) 128.5(2)°, C(41)–Sb(2)–C(61) 123.9(2)°] is probably as a consequence of this.

The bridging oxygen angle, 137.9(2)°, falls at the lower end of the range for compounds of this type, cf. 139.0° in [SbPh$_3$Cl]$_2$O [21], 170.2 and 176.6° in [SbPh$_3$Br]$_2$O [22] and 180° in one form of [SbPh$_3$I]$_2$O [23], and the bridge is slightly asymmetric [Sb(1)–O(1) 1.983(4), Sb(2)–O(1) 1.966(4) Å]. These distances (mean 1.975 Å) are substantially shorter than those to the carboxylate oxygens (mean 2.239 Å), which in turn are significantly longer than formal Sb–O single bonds
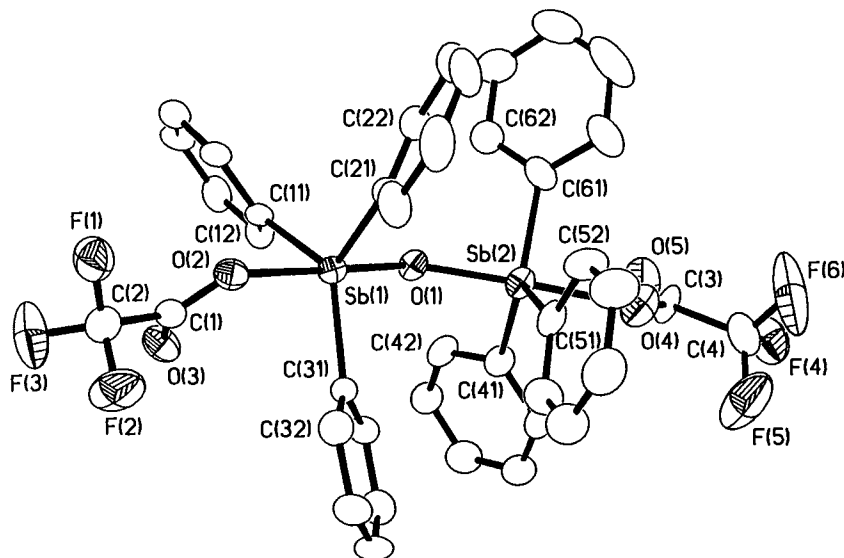
Fig. 1. Structure of [SbPh₃(O₂CCF₃)]₂O **1** showing the atom numbering scheme.

(ca. 2.03 Å) in SbPh₃(OMe)₂ [24] and Sb(mesityl)₃(OH)₂ [19]. This elongation may be a consequence of a small contribution from the ionic form, $[(SbPh_3)_2O]^{2+}$ $2[O_2CCF_3]^-$, and is supported by the fact that the phenyl groups are all bent away from the bridging oxygen (mean O(1)–Sb–C 94.1°).

This determination also confirms the structural differences between this compound and the formally similar [SbF₃(O₂CCF₃)]₂O, which contains symmetrically bridging trifluoroacetate groups and octahedral geometry at antimony [10]. The Sb–O(carboxylate) distances in the latter (2.028 and 2.107 Å) are shorter than those

in **1**, and clearly replacement of fluorine by phenyl significantly reduces antimony Lewis acidity and consequently the extent of secondary bonding.

2.5.2. Structure of [SbMe₃(O₂CMe)]₂O **7**

The molecular structure of **7** is shown in Fig. 2 with selected bond lengths and angles in Table 3. Antimony geometry is again trigonal bipyramidal and a crystallographic two-fold axis passes through the bridging oxygen. The Sb–O–Sb angle is 140.1(4)° and the bridge is necessarily symmetrical [Sb–O 1.978(2) Å]. As expected from IR spectroscopy, the acetates are near unidentate with again only weak secondary interactions (Sb...O 3.207(4) Å) with acetate C–O distances of 1.304(9) Å [C(4)–O(2)] and 1.218(8) Å [C(4)–O(3)], compared with values of 1.43 and 1.23 Å for single and double bonds, respectively.

All three equatorial angles deviate from the ideal 120° but contrary to the situation in **1**, the largest angle [C(1)–Sb(1)–C(2) 123.2(3)°] is not that associated with the secondary Sb...O interaction, which occurs between the C(2) and C(3) methyls [C(2)–Sb(1)–C(3) 122.5(3)°]. Bonds between antimony and the carboxylate are again longer (2.197(4) Å) than expected but the increase is lower than in **1** and consequently less ionic character is presumed to be present.

3. Experimental details

3.1. Preparation of [SbPh₃(O₂CCF₃)]₂O **1**

Trifluoroacetic acid (0.24 g, 2.08 mmol) was added slowly to a stirred suspension of [SbPh₃Br]₂O) [18] (0.92 g, 1.04 mmol) and toluene (25 cm³), leading to dissolu-

Table 2
Selected bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for [SbPh₃(O₂CCF₃)]₂O **1**

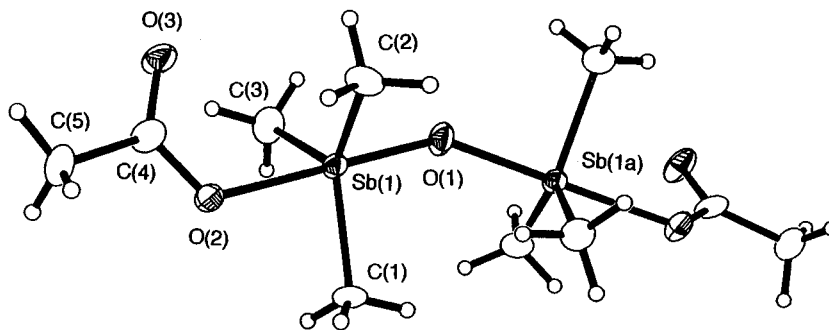|			
Sb(1)–O(1)	1.983(4)	Sb(1)–O(1)–Sb(2)	137.9(2)
Sb(1)–O(2)	2.255(4)	O(1)–Sb(1)–O(2)	179.0(1)
Sb(1)...O(3)	3.196(4)	O(1)–Sb(1)–C(11)	90.6(2)
Sb(1)–C(11)	2.109(5)	O(1)–Sb(1)–C(21)	95.7(2)
Sb(1)–C(21)	2.107(5)	O(1)–Sb(1)–C(31)	94.2(2)
Sb(1)–C(31)	2.109(5)	C(11)–Sb(1)–O(2)	88.5(2)
Sb(2)–O(1)	1.966(4)	C(21)–Sb(1)–O(2)	84.2(2)
Sb(2)–O(4)	2.222(4)	C(31)–Sb(1)–O(2)	86.7(2)
Sb(2)...O(5)	3.402(4)	C(11)–Sb(1)–C(21)	111.6(2)
Sb(2)–C(41)	2.112(6)	C(11)–Sb(1)–C(31)	128.5(2)
Sb(2)–C(51)	2.100(6)	C(21)–Sb(1)–C(31)	118.9(2)
Sb(2)–C(61)	2.108(6)	O(1)–Sb(2)–O(4)	178.8(2)
O(3)–C(1)	1.235(5)	O(1)–Sb(2)–C(41)	91.0(2)
O(2)–C(1)	1.258(5)	O(1)–Sb(2)–C(51)	100.3(2)
C(1)–C(2)	1.509(6)	O(1)–Sb(2)–C(61)	92.5(2)
C(41)–Sb(2)–O(4)	88.1(2)		
C(51)–Sb(2)–O(4)	79.5(2)		
C(61)–Sb(2)–O(4)	88.7(2)		
C(41)–Sb(2)–C(51)	119.2(2)		
C(41)–Sb(2)–C(61)	123.9(2)		
C(51)–Sb(2)–C(61)	115.1(2)		
O(3)–C(1)–O(2)	128.6(4)		

Fig. 2. Structure of [SbMe$_3$(O$_2$CCH$_3$)]$_2$O **7** showing the atom numbering scheme.

tion. Triethylamine (0.21 g, 2.08 mmol) was then added and the mixture stirred at room temperature for 16 h. Precipitated triethylammonium bromide was filtered off and evaporation of solvent in a vacuum yielded a white solid, which was recrystallised from a mixture of chloroform and hexane. Yield 0.61 g (62%). M.p. 228–230°C. ^{1}H NMR (CDCl$_3$, 250 MHz, RT) δ 7.31 (12H, t, $^3J_{HH} = 7$ Hz, *m*-Ph-**A**), 7.45 (6H, t, $^3J_{HH} = 7$ Hz, *p*-Ph-**A**); 7.52 (12H, d, $^3J_{HH} = 7$ Hz, *o*-Ph-**A**), 7.53 (18H, m, *m*- and *p*-Ph-**B**), 8.06 (12H, m, *o*-Ph-**B**), where **A** is [SbPh$_3$(O$_2$CCF$_3$)]$_2$O and **B** is SbPh$_3$(OH)(O$_2$CCF$_3$). IR (nujol mull, CsI): 1714vs, 1437s, 1393m, 1185vs, 1144s, 998w, 841w, 794w, 742vs, 721m, 691m, 456m cm^{-1}. Found: C, 50.5; H, 3.4. C$_{40}$H$_{30}$F$_6$O$_5$Sb$_2$ calc.: C, 50.7; H, 3.2%

3.2. Preparation of [SbPh$_3$(O$_2$CCCl$_3$)]$_2$O 2

[SbPh$_3$Br]$_2$O (1.00 g, 1.13 mmol) was treated with trichloroacetic acid (0.37 g, 2.27 mmol) and triethylamine (0.23 g, 2.28 mmol) in toluene (30 cm^3) and after filtration and evaporation to dryness, the remaining solid was crystallised from chloroform. Yield 0.38 g (32%). M.p. 170–174°C (177°C [15]). ^{1}H NMR (CDCl$_3$, 250 MHz, RT) δ 7.35 (12H, t, $^3J_{HH} = 7$ Hz, *m*-Ph-**A**), 7.48 (6H, t, $^3J_{HH} = 7$ Hz, *p*-Ph-**A**), 7.53 (12H, d,

Table 3
Bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for [SbMe$_3$(O$_2$CCH$_3$)]$_2$O **7**

Sb(1)–O(1)	1.978(2)	Sb(1)–O(1)–Sb(1a)	140.1(4)
Sb(1)–O(2)	2.197(4)	O(1)–Sb(1)–O(2)	179.8(2)
Sb(1)...O(3)	3.207(4)	O(1)–Sb(1)–C(1)	97.4(2)
Sb(1)–C(1)	2.104(6)	O(1)–Sb(1)–C(2)	92.4(2)
Sb(1)–C(2)	2.098(8)	O(1)–Sb(1)–C(3)	90.7(3)
Sb(1)–C(3)	2.102(7)	C(1)–Sb(1)–O(2)	82.4(2)
O(2)–C(4)	1.304(9)	C(2)–Sb(1)–O(2)	87.6(2)
O(3)–C(4)	1.218(8)	C(3)–Sb(1)–O(2)	89.5(3)
C(4)–C(5)	1.506(11)	C(1)–Sb(1)–C(2)	123.2(3)
		C(1)–Sb(1)–C(3)	113.2(3)
		C(2)–Sb(1)–C(3)	122.5(3)
		O(3)–C(4)–O(2)	124.0(7)

Sb(1a) is generated by the symmetry transformation $-x$, y, $0.5-z$.

$^3J_{HH} = 7$ Hz, *o*-Ph-**A**), 7.53 (18H, m, *m*- and *p*-Ph-**B**) 8.12 (12H, m, *o*-Ph-**B**), where **A** is [SbPh$_3$(O$_2$CCCl$_3$)]$_2$O and **B** is SbPh$_3$(OH)(O$_2$CCCl$_3$). IR (nujol mull, CsI): 1701vs, 1435s, 1289vs, 1074w, 997w, 834s, 738vs, 691vs, 454m cm^{-1}. Found: C, 46.8; H, 3.8. C$_{40}$H$_{30}$Cl$_6$O$_5$Sb$_2$ calc.: C, 45.9; H, 2.9%

3.3. Preparation of [SbPh$_3$(O$_2$CCHCl$_2$)]$_2$O 3

Similarly, dichloroacetic acid (0.36 g, 2.81 mmol), [SbPh$_3$Br]$_2$O (1.00 g, 1.13 mmol) and triethylamine (0.29 g, 2.81 mmol) in toluene (20 cm^3) gave crystals of the required compound. Yield 0.51 g (46%). M.p. 211–214°C. ^{1}H NMR (CDCl$_3$, 250 MHz, RT) δ 5.55 (2H, s, C*H*Cl$_2$-**A**), 5.75 (2H, s, C*H*Cl$_2$-**B**), 7.30(12H, t, $^3J_{HH} = 7$ Hz, *m*-Ph-**A**), 7.45 (6H, t, $^3J_{HH} = 7$ Hz, *p*-Ph-**A**), 7.60 (12H, d, $^3J_{HH} = 7$ Hz, *o*-Ph-**A**), 7.53 (18H, m, *m*- and *p*-Ph-**B**), 8.11 (12H, m, *o*-Ph-**B**), where **A** is [SbPh$_3$(O$_2$CCHCl$_2$)]$_2$O and **B** is SbPh$_3$(OH)(O$_2$CCHCl$_2$). Under strictly anhydrous conditions signals due to **A** only were observed. ^{13}C{^{1}H} NMR (CDCl$_3$, 69 MHz, RT, anhydrous, signals due to **A** only observed) δ 67.8 (Cl$_2$*C*H), 129.3 (*m*-Ph), 131.1 (*p*-Ph), 133.7 (*o*-Ph), 138.1 (*ipso*-Ph), quaternary carboxylate carbon not observed. IR (nujol mull, CsI): 1694s, 1669s, 1435s, 1325vs, 1193m, 740vs, 692s, 459s cm^{-1}. Mass spectrum (FAB), *m/z* (rel. int. (%)): 847 (Sb$_2$Ph$_6$O(O$_2$CCHCl$_2$)$^+$, 49), 811 (Sb$_2$Ph$_6$O(O$_2$CCCl)$^+$, 18), 479 (SbPh$_3$(O$_2$CCHCl$_2$)$^+$, 23), 369 (SbPh$_3$OH$^+$, 5), 275 (SbPh$_2$$^+$, 23), 198 (SbPh$^+$, 23), 154 (Ph$_2$$^+$, 100), 77 (Ph$^+$, 43). Found: C, 48.3; H, 3.3. C$_{40}$H$_{32}$Cl$_4$O$_5$Sb$_2$ calc.: C, 49.1; H, 3.3%

3.4. Reaction of [SbPh$_3$Br]$_2$O with two mols of HO$_2$CCH$_2$Cl

A stirred suspension of [SbPh$_3$Br]$_2$O (0.99 g, 1.12 mmol) and toluene (20 cm^3) was treated with chloroacetic acid (0.22 g, 2.36 mmol) giving a clear solution. Addition of triethylamine (0.24 g, 2.36 mmol) led to the immediate formation of a white precipitate. The mixture was stirred at ambient temperature for 24

h and then filtered to remove insolubles. Removal of solvent in a vacuum gave a white solid which was recrystallised from a chloroform-hexane mixture to give crystals of $SbPh_3(O_2CCH_2Cl)_2$ **4**. Yield 0.56 g (46% based on $[SbPh_3Br]_2O$). M.p. 132–135°C (132–133°C [17]). ^1H NMR (CDCl$_3$, 250 MHz, RT) δ 3.86 (4H, s, C*H*$_2$Cl), 7.55 (9H, m, *m*- and *p*-Ph), 8.03 (6H, m, *o*-Ph). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 69 MHz, RT) δ 42.5 (Cl*C*H$_2$), 129.6 (*m*-Ph), 131.7 (*p*-Ph), 133.9 (*o*-Ph), 135.8 (*ipso*-Ph), 169.9 (O$_2$*C*). IR (nujol mull, CsI): 1673w, sh, 1646vs, 1481m, 1435s, 1366m, 1332vs, 1259m, 1228w, 1073m, 1021m, 998m, 773vs, 737s, 692s, 461s, 452s cm^{-1}. Mass spectrum (EI), m/z (rel. int. (%)): 461 (SbPh$_2$(O$_2$CCH$_2$Cl)$_2^+$, 6), 445 (SbPh$_3$(O$_2$CCH$_2$Cl)$^+$, 74), 387 (SbPh$_3$Cl$^+$, 17), 275 (SbPh$_2^+$, 14), 214 (Sb(O$_2$CCH$_2$Cl)$^+$, 33), 198 (SbPh$^+$, 47), 154 (Ph$_2^+$, 100), 77 (Ph$^+$, 38). Found: C, 48.8; H, 3.5. C$_{22}$H$_{19}$Cl$_2$O$_4$Sb calc.: C, 48.9; H, 3.6%

3.5. Reaction of $[SbPh_3Br]_2O$ with two mols of HO_2CPh

As described above, $[SbPh_3Br]_2O$ (1.02 g, 1.15 mmol), benzoic acid (0.30 g, 2.42 mmol) and triethylamine (0.25 g, 2.42 mmol) were stirred in toluene (25 cm^3) and the oily residue, which remained after filtration and evaporation of the solution, was crystallised from chloroform/hexane to give $SbPh_3(O_2CPh)_2$ **5**. Yield 0.22 g (16% based on $[SbPh_3Br]_2O$). M.p. 172–175°C (176–177°C [25]). ^1H NMR (CDCl$_3$, 250 MHz, RT) δ 7.36 (4H, t, $^3J_{HH} = 7.5$ Hz, *m*-Ph-benzoate), 7.47 (2H, t, $^3J_{HH} = 7.5$ Hz, *p*-Ph-benzoate), 7.51 (9H, m, *m*- and *p*-Ph-Sb), 7.96 (4H, d, $^3J_{HH} = 7.5$ Hz, *o*-Ph-benzoate), 8.14 (6H, m, *o*-Ph-Sb). IR (nujol mull, CsI): 1645s, 1577w, 1536w, 1435s, 1324vs, 1300s, 1125w, 1068w, 1024w, 998w, 764vs, 734vs, 718s, 691s, 449s cm^{-1}. Found: C, 64.0; H, 4.1. C$_{32}$H$_{25}$O$_4$Sb calc.: C, 64.6; H, 4.2%.

3.6. Reaction of $[SbPh_3Br]_2O$ with two mols of AgO_2CMe

Silver acetate (0.33 mg, 1.97 mmol) was added to a stirring solution of $[SbPh_3Br]_2O$ (0.70 g, 0.79 mmol) in dichloromethane (30 cm^3) and the mixture was stirred in the dark under reflux for 16 h. After removal of insolubles, the solvent was evaporated to give an off-white product which was recrystallised from chloroform/hexane to give well-formed crystals of $SbPh_3(O_2CMe)_2$ **6**. Yield 0.34 g (46% based on $[SbPh_3Br]_2O$). M.p. 209–212°C (213–215°C [24]). ^1H NMR (CDCl$_3$, 250 MHz, RT) δ 1.84 (6H, s, O$_2$C*Me*), 7.49 (9H, m, *m*- and *p*-Ph), 8.01 (6H, m, *o*-Ph). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 69 MHz, RT) δ 22.1 (*C*H$_3$), 129.1 (*m*-Ph), 130.9 (*p*-Ph), 133.8 (*o*-Ph), 139.0 (*ipso*-Ph), 175.7(O$_2$*C*). IR (nujol mull, CsI): 1630s, 1318s,

1008w, 932m, 915w, 688m, 672w, 609w, 486m cm^{-1}. Mass spectrum (EI) m/z (rel. int. (%)): 411 (SbPh$_3$(O$_2$CMe)$^+$, 61), 393 (SbPh$_2$(O$_2$CMe)$_2^+$, 20), 369 (SbPh$_3$OH$^+$, 11), 352 (SbPh$_3^+$, 7), 334 (SbPh$_2$(O$_2$CMe)$^+$, 8), 275 (SbPh$_2^+$, 18), 257 (SbPh(O$_2$CMe)$^+$, 27), 215 (SbPhOH$^+$, 22), 198 (SbPh$^+$, 100), 180 (Sb(O$_2$CMe)$^+$, 35), 154 (Ph$_2^+$, 91), 77 (Ph$^+$, 41), 60 (HO$_2$CMe$^+$, 10). Found: C, 56.1; H, 4.6. C$_{22}$H$_{21}$O$_4$Sb calc.: C, 56.1; H, 4.5%

3.7. Preparation of $[SbMe_3(O_2CMe)]_2O$ **7**

All manipulations in this and the following experiment were carried out under anhydrous argon using stringent Schlenk and glovebox techniques.

A solution of $[SbMe_3Cl]_2O$ (0.67 g, 1.59 mmol) in dichloromethane (20 cm^3) was added to a suspension of silver acetate (0.58 g, 3.5 mmol) and dichloromethane (10 cm^3) in the dark. The mixture was then stirred for ca. 24 h at room temperature, after which precipitated silver salts were removed by filtration. The pale purple solution was then evaporated a give an off-white powder, which was crystallised from a dichloromethane-pentane mixture to give the required compound **7**. Yield 0.60 g (81%); m.p. 174–176°C. ^1H NMR (250 MHz, CDCl$_3$, RT) δ 1.62 (18H, s, *Me*-Sb), 1.83 (6H, s, O$_2$C*Me*). Decomposition noted after exposure to atmospheric moisture. $^{13}C\{^1H\}$ NMR (69 MHz, CDCl$_3$, RT) δ 14.5 (*Me*-Sb), 23.3 (O$_2$C*Me*), 176.4 (O$_2$*C*Me). IR (nujol mull, CsI): 1623s, 1374s, 1311s, 1097(w, br), 1015m, 925m, 851s, 710s, 658s, 577m, 527w, 493m cm^{-1}. Mass spectrum (EI), m/z (rel. int. (%)): 409 (Sb$_2$Me$_6$O(O$_2$CMe)$^+$, 3), 351 (Sb$_2$Me$_6$O$^+$, 30), 321 (Sb$_2$Me$_4$O$^+$, 18), 225 (SbMe$_3$(O$_2$CMe)$^+$, 100), 183 (SbMe$_3$OH$^+$, 49), 153 (SbMeOH$^+$, 28), 151 (SbMe$_2^+$, 23). Found: C, 25.6; H, 5.2. C$_{10}$H$_{24}$O$_5$Sb$_2$ calc.: C, 25.7; H, 5.2%.

3.8. Preparation of $[SbMe_3(O_2CBu^t)]_2O$ **8**

A solution of $[SbMe_3Cl]_2O$ (0.37 g, 0.88 mmol) in dichloromethane (20 cm^3) was added to a suspension of sodium trimethylacetate (0.22 g, 1.80 mmol) and dichloromethane (10 cm^3). After stirring at room temperature for 16 h, the mixture was filtered to give a clear solution. Evaporation of volatiles in a vacuum gave crude product which was crystallised from a mixture of toluene and hexane to give $[SbMe_3(O_2CBu^t)]_2O$ **8**. Yield 0.32 g (66%). ^1H NMR (250 MHz, CDCl$_3$, RT) δ 1.03 (18H, s, O$_2$C*Bu^t*), 1.59 (18H, s, *Me*-Sb). [Traces of the new compound SbMe$_3$(O$_2$CBu^t)$_2$ were also detected before recrystallisation, δ 1.08 (18H s, O$_2$C*Bu^t*), 1.7 (9H, s, *Me*-Sb).] $^{13}C\{^1H\}$ NMR (69 MHz, CDCl$_3$, RT) δ 14.3 (*Me*-Sb), 27.7 (C*Me$_3$*), 39.1 (*C*Me$_3$), 183.5 (O$_2$*C*Bu^t). IR (nujol mull, CsI): 1620s, 1326s, 1211s, 849w, br, 750s, 603m, 550w cm^{-1}. Mass spectrum (EI),

Table 4
Crystallographic data

Compound	1	7
Chemical formula	$C_{40}H_{30}F_6O_5Sb_2$	$C_{10}H_{24}O_5Sb_2$
Formula weight	948.1	467.8
Crystal size (mm)	$0.32 \times 0.12 \times 0.10$	$0.28 \times 0.21 \times 0.07$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	20.436(2)	14.249(3)
b (Å)	10.1755(9)	8.684(3)
c (Å)	19.518(5)	14.177(3)
β (°)	112.494(13)	114.58(2)
Volume (Å³)	3749.8(11)	1595.3(7)
Z	4	4
D_c (g cm⁻³)	1.679	1.948
Radiation (Å)	Mo–K_α (0.71069)	Mo–K_α (0.71069)
μ (cm⁻¹)	15.14	33.93
$F(000)$	1864	904
θ limits (°)	2–25	2–25
Index ranges	$-23 < h < 23$	$-15 < h < 12$
(for unique data)	$-11 < k < 11$	$-9 < k < 10$
	$-22 < l < 17$	$-12 < l < 16$
Temperature (K)	150	150
Total data collected	15116	3168
Unique data	5572	1236
R(int)	0.0884	0.1220
Structure solution	Direct methods (SHELXS-86)	Direct methods (SHELXS-86)
Refinement	Full matrix-LS on F²	Full matrix-LS on F²
Data / variables	5572/478	1204/83
Goodness of Fit (S)	0.935	1.100
Final diff. map (e Å⁻³)	+2.14, −1.15	+4.29, −2.04
R observed data [$I > 2\sigma(I)$]	0.0466	0.0609
R_w all data	0.1252	0.1464

m/z (rel. int. (%)): 303 ($Sb_2Me_3O^+$, 7), 151 ($SbMe_2^+$, 80), 121 (Sb^+, 61). Found: C, 34.1; H, 6.6. $C_{16}H_{36}O_5Sb_2$ calc.: C, 34.8; H, 6.6%.

3.9. Crystal structure determinations for [SbPh₃(O₂CCF₃)]₂O **1** and [SbMe₃(O₂CMe)]₂O **7**

Crystals of each compound suitable for X-ray crystallography were obtained by slow diffusion of hexane into concentrated chloroform solutions; crystal data and details of the structure solutions are summarised in Table 4.

In each case slightly more than one hemisphere of data was collected on a Delft Instruments FAST TV area detector diffractometer, equipped with a rotating anode FR591 generator using Mo–K_α radiation [26]. The data were corrected for Lorentz and polarisation effects. The structures were solved by direct methods (SHELXS-86) [27] and Fourier difference syntheses and

refined on F_o^2 by full matrix least squares using all unique data (SHELXL-93) [28].

The C(3) trifluoroacetate group of **1** was disordered and during refinement was restrained to have bond parameters similar to those of the C(1) group. Thermal parameters for the fluorines of the C(3) group were high and it was not to possible to model accurately the electron density in terms of alternative atom positions; bond parameters for this group are therefore not included in Table 2. The phenyl hydrogen atoms were placed at calculated positions [d(C–H) 0.95 Å] and refined with fixed isotropic thermal parameters, riding on the attached carbon atom. Hydrogen atoms in **7** were treated similarly [d(C–H) 0.98 Å].

Full details of the atomic coordinates, thermal parameters and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

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