Reactions of fluorinated acid anhydrides with metal alkoxides

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Abstract

Metal alkoxides $M(OR)_4$ (where $M = Ti$ or Zr and $R = $ methyl or ethyl) have been reacted with trifluoroacetic, trifluoromethanesulfonic and fluorosulfonic anhydrides. The methoxides yielded disubstituted derivatives in all cases, whereas the ethoxides gave different products. In this way new compounds, i.e. $Zr(OCH_3)_2(O_2CCF_3)_2$, $Ti(OCH_3)_2(O_2CCF_3)_2$, $Ti_2O(O_2CCF_3)_6$, $Zr(OCH_3)_2(O_3SCF_3)_2$, $Ti(OC_2H_5)_2(O_3SCF_3)_2$, $Zr(OCH_3)_2(O_3SF)_2$ and $Ti(OC_2H_5)_2(O_3SF)_2$, have been isolated in nearly quantitative yield. These reactions also provide an alternative route for the synthesis of previously known compounds $Zr(O_2CCF_3)_4$ and $Zr(O_3SCF_3)_4$. The products have been characterised by elemental analysis, infrared and NMR (^1H and ^{19}F) spectroscopy and molecular weight determination.

Introduction

Literature reports regarding trifluoroacetic anhydride, $(CF_3CO)_2O$ [1], and trifluoromethanesulfonic anhydride, $(CF_3SO_2)_2O$ [2, 3], and their reactions with various substrates are widespread. Fluorosulfonic anhydride, $(FSO_2)_2O$, though known for 40 years has been little investigated [4]. We have recently reported reactions of fluorosulfonic and trifluoromethanesulfonic anhydrides with titanium(IV) methoxide, $Ti(OCH_3)_4$, yielding products [5, 6] of the type $Ti(OCH_3)_2(O_3SR)_2$, where $R = F$ or CF_3. This further stimulated our interest in the reactions of these fluorinated acid anhydrides and readily available trifluoroacetic anhydride with metal alkoxides, especially methoxides and ethoxides as a means of preparing new mixed ligand derivatives with interesting structural features as well as providing a new route to the preparation of previously known/unknown completely substituted derivatives. The only known reaction of such type amongst these three anhydrides is the reaction of caesium trifluoromethoxide with $(FSO_2)_2O$ [7].

Experimental

Chemicals

Trifluoroacetic anhydride (Aldrich) and trifluoromethanesulfonic acid (Aldrich) were distilled before use. Trifluoromethanesulfonic and fluorosulfonic an-

hydrides were prepared via literature methods [8, 9] and distilled twice before use. $Ti(OCH_3)_4$ [10], $Ti(OC_2H_5)_4$ [10], $Zr(OCH_3)_4$ [11] and $Zr(OC_2H_5)_4$ [11] were prepared as described in the literature. Fluorosulfonic acid was prepared as described earlier [12]. $TiCl_4$ (Fluka) was distilled before use. The solvents were dried and distilled before use. **Caution! Fluorosulfonic anhydride is a toxic material and should be handled with care [13].**

Analytical

Sulfur and fluorine were determined as described earlier [14]. Zirconium and titanium were analysed by standard methods [15]. Carbon and hydrogen were determined microanalytically. Molecular weights were determined cryoscopically in nitrobenzene.

All manipulations, i.e. synthetic reactions and sample preparations, were carried out either in a vacuum line or under a dry nitrogen atmosphere.

Instrumentation

The IR spectra of the compounds were recorded as neat solids/Nujol/hexachlorobutadiene mulls between AgCl plates on a Perkin-Elmer PE-1430 ratio recording spectrophotometer. The ^1H and ^{19}F NMR spectra were recorded either on a JEOL FX-90Q or Varian EM-390 spectrometer operating at 90 MHz, using $CFCl_3$ and tetramethylsilane as internal references. Positive chemical shifts are downfield from the reference.

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Preparation of bis(methoxy)titanium(IV) trifluoroacetate, $Ti(OCH_3)_2(O_2CCF_3)_2$

Freshly sublimed titanium(IV) methoxide (0.42 g, 2.4 mmol) was loaded into a 50 ml Pyrex reactor fitted with a Rotaflo stopcock and then evacuated for 2 h. Excess trifluoroacetic anhydride (2.9 g, 14.1 mmol) was condensed onto it via vacuum methods. The contents were allowed to warm to room temperature and then maintained at ~35 °C for 64 h. Removal of all volatiles *in vacuo* gave bis(methoxy)titanium(IV) trifluoroacetate (0.82 g, 2.4 mmol) as a fine white solid in quantitative yield. Analysis: Calc. for $C_6H_6F_6O_6Ti$: C, 21.4; H, 1.8; F, 33.9; Ti, 14.3%. Found: C, 21.2; H, 1.6; F, 33.5; Ti, 13.5%. IR (cm^{-1})*: 1635 (s b); 1480 (ms); 1360 (w b); 1305 (w b); 1285 (sh); 1245 (w); 1200 (m b); 1155 (m b); 1065 (m); 925 (m b); 880 (sh); 850 (m); 800 (b sh); 790 (m); 660 (w); 650 (w); 605 (w); 505 (sh); 480 (b sh). ^{19}F NMR† ($C_6H_5NO_2$/CFCl$_3$) δ: -78.25 (s, CF$_3$) ppm. ^{1}H NMR ($C_6H_5NO_2$/TMS) δ: +3.86 (s, OCH$_3$) ppm. Mol. weight (nitrobenzene): Calc., 336. Found, 351.

Preparation of oxo hexa(trifluoroacetato)dititanium(IV), $Ti_2O(O_2CCF_3)_6$

Freshly distilled titanium(IV) ethoxide (0.282 g, 1.24 mmol) was reacted with trifluoroacetic anhydride (1.2 g, 5.64 mmol) in a similar fashion as above and the contents allowed to warm to room temperature over a period of 8 h. $Ti_2O(O_2CCF_3)_6$ (0.48 g, 0.59 mmol) was isolated after removal of volatiles from the pale yellow liquid *in vacuo* as a creamy shining solid in 98% yield. Analysis: Calc. for $C_{12}F_{18}O_{13}Ti_2$: C, 18.2; F, 43.3; Ti, 12.1%. Found: C, 17.9; F, 44.0; Ti, 12.3%. IR (cm^{-1}): 1795 (s); 1640 (vs b); 1470 (vs); 1410 (m); 1365 (vs); 1355 (sh); 1340 (s); 1220 (s b); 1160 (vs b); 1060 (sh); 1035 (sh); 990 (sh); 960 (m); 910 (m b); 845 (s); 805 (w b); 785 (m); 605 (m b); 525 (m). ^{19}F NMR (CH_3NO_2/CDCl$_3$/CFCl$_3$) δ: -76.4 (s, CF$_3$); -76.6 (s, CF$_3$) ppm. Mol. weight (nitrobenzene): Calc., 790. Found, 805.

Preparation of bis(ethoxy)titanium(IV) trifluoromethanesulfonate, $Ti(OC_2H_5)_2(O_3SCF_3)_2$

Trifluoromethanesulfonic anhydride (4.8 g, 16.9 mmol) was condensed via vacuum methods onto freshly sublimed titanium(IV) ethoxide (0.85 g, 3.7 mmol) in a similar reactor as described above. The contents were gradually allowed to attain a temperature of 10 °C. Drying of the contents under vacuum conditions gave the title compound as a white solid in quantitative yield (1.6 g, 3.7 mmol). Analysis: Calc. for $C_6H_{10}F_6O_8Ti$: C,

16.5; H, 2.3; F, 26.2; S, 14.7; Ti, 11.0%. Found: C, 16.3; H, 2.5; F, 25.9; S, 13.9; Ti, 11.3%. IR (cm^{-1}): 2880 (vs); 2840 (s); 2810 (sh); 2780 (m); 1465 (m); 1445 (s b); 1415 (m); 1380 (m); 1340 (vs b); 1300 (sh); 1240 (m); 1200 (s b); 1195 (sh); 1155 (m); 1140 (s b); 1110 (m); 1090 (w b); 1065 (w b); 1020 (m b); 1000 (m); 990 (w b); 965 (m b); 915 (s b); 880 (w b); 800 (m b); 790 (sh); 760 (s); 745 (sh); 730 (sh); 665 (s sh); 640 (s b); 610 (m); 590 (m); 545 (b sh); 500 (sh). ^{19}F NMR (CH_3NO_2/CFCl$_3$) δ: -80.50 (s, CF$_3$) ppm. ^{1}H NMR [$(CF_3SO_2)_2$O/TMS] δ: +4.37 (q, OCH$_2$); +1.27 (t, CH$_3$) ppm. Mol. weight (nitrobenzene): Calc., 436. Found, 450.

Preparation of bis(ethoxy)titanium(IV) fluorosulfonate, $Ti(OC_2H_5)_2(O_3SF)_2$

Freshly distilled titanium(IV) ethoxide (1.3 g, 5.70 mmol) was reacted with fluorosulfonic anhydride (4.71 g, 25.9 mmol) as above. The contents were allowed to warm slowly to 10 °C overnight and the title compound, i.e. $Ti(OC_2H_5)_2(O_3SF)_2$ (1.84 g, 5.49 mmol) was obtained in 97% yield after drying as above. Analysis: Calc. for $C_4H_{10}F_2O_8S_2Ti$: C, 14.3; H, 2.9; F, 11.3; S, 19.0; Ti, 14.3%. Found: C, 13.5; H, 2.7; F, 12.5; S, 18.7; Ti, 13.9%. IR (cm^{-1}): 2990 (vs); 2940 (m); 2910 (s sh); 2880 (s sh); 1465 (sh); 1445 (s sh); 1400 (s); 1385 (s); 1360 (m); 1350 (mw); 1310 (s b); 1190 (vs); 1150 (m); 1100 (m b); 1070 (m); 1010 (s sh); 1000 (s); 965 (m); 915 (vs b); 815 (s); 800 (s sh); 665 (m); 655 (m); 595 (m); 500 (s sh).

Preparation of bis(methoxy)zirconium(IV) trifluoroacetate, $Zr(OCH_3)_2(O_2CCF_3)_2$

$Zr(OCH_3)_2(O_2CCF_3)_2$ (1.8 g, 4.8 mmol) was obtained in quantitative yield by reacting 1.0 g (4.7 mmol) of zirconium(IV) methoxide with trifluoroacetic anhydride (4.4 g, 21.1 mmol) *in vacuo* for 12 h at ambient temperature. Analysis: Calc. for $C_6H_6F_6O_6Zr$: C, 19.0; H, 1.60; F, 30.1; Zr, 24.0%. Found: C, 18.7; H, 1.78; F, 29.8; Zr, 23.3%. IR (cm^{-1}): 2945 (m); 2925 (s); 2880 (m); 1655 (vs b); 1490 (s); 1460 (m); 1375 (s); 1365 (sh); 1340 (w); 1225 (vs b); 1170 (s b); 1022 (m b); 895 (sh); 865 (s); 800 (vs); 650 (s sh); 635 (sh); 620 (m); 600 (w); 530 (m). ^{19}F NMR (CDCl$_3$/CFCl$_3$) δ: -75.3 (s, CF$_3$) ppm. ^{1}H NMR (CDCl$_3$/TMS) δ: +3.97 (s, OCH$_3$) ppm. Mol. weight (nitrobenzene): Calc., 379. Found, 390.

Preparation of bis(methoxy)zirconium(IV) trifluoromethanesulfonate, $Zr(OCH_3)_2(O_3SCF_3)_2$

Zirconium(IV) methoxide (0.34 g, 1.6 mmol) was reacted with trifluoromethanesulfonic anhydride (1.85 g, 6.6 mmol) and the products kept at room temperature for 4 d. The contents were evacuated to yield $Zr(OCH_3)_2(O_3SCF_3)_2$ (0.68 g, 1.5 mmol) in 96% con-

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*v = very, s = strong, m = medium, w = weak, b = broad and sh = shoulder.

†s = singlet, d = doublet, t = triplet, q = quartet.

version. Analysis: Calc. for $C_4H_6F_6O_8S_2Zr$: C, 10.6; H, 1.3; F, 25.3; S, 14.2; Zr, 20.2%. Found: C, 10.2; H, 1.8; F, 25.6; S, 13.3; Zr, 21.3%. IR (cm^{-1}): 2985 (s); 2940 (m); 2845 (m); 1460 (s); 1415 (sh); 1360 (vs b); 1270 (sh); 1245 (sh); 1205 (s b); 1155 (m); 1120 (m); 1070 (m); 1030 (vs b); 920 (m); 880 (m b); 812 (m b); 770 (m); 720 (sh); 635 (vs b); 510 (m). ^{19}F NMR $(CH_3NO_2/CFCl_3)$ δ: -80.33 (s, CF$_3$) ppm. Mol. weight (nitrobenzene): Calc., 451. Found, 470.

Preparation of bis(methoxy)zirconium(IV) fluorosulfonate, $Zr(OCH_3)_2(O_3SF)_2$

$Zr(OCH_3)_2(O_3SF)_2$ (0.856 g, 2.44 mmol) was isolated in 98% yield by reacting zirconium(IV) methoxide (0.53 g, 2.48 mmol) with fluorosulfonic anhydride (1.22 g, 6.7 mmol) in vacuo for 5 d at ~ 35 °C. Analysis: Calc. for $C_2H_6F_2O_8S_2Zr$: C, 6.8; H, 1.7; F, 10.8; S, 18.2; Zr, 25.9%. Found: C, 7.0; H, 2.0; F, 10.2; S, 17.7; Zr, 25.6%. IR (cm^{-1}): 2960 (s b); 2920 (m); 2845 (m b); 1455 (s b); 1400 (vs); 1385 (m); 1320 (vs b); 1270 (m b); 1235 (sh); 1225 (m); 1200 (m b); 1165 (s); 1150 (s); 1080 (m); 970 (s); 845 (sh); 810 (vs); 765 (w). ^{19}F NMR $(CH_3NO_2/CFCl_3)$ δ: $+50$ (s, SF) ppm. Mol. weight (nitrobenzene): Calc., 351. Found, 338.

Preparation of zirconium(IV) trifluoroacetate, $Zr(O_2CCF_3)_4$ [16]

$Zr(OC_2H_5)_4$ (0.44 g, 1.6 mmol) was loaded into a Pyrex reactor fitted with a Teflon stopcock and evacuated for 2 h. Dry dichloromethane (~ 15 ml) was condensed onto it via vacuum methods followed by a slight excess of trifluoroacetic anhydride (1.63 g, 7.75 mmol). The contents were kept at 35 °C for 6 d, after which the volatiles were pumped away to yield $Zr(O_2CCF_3)_4$ as a white solid in 98% conversion (0.86 g, 1.53 mmol). Analysis: Calc. for $C_8F_{12}O_8Zr$: C, 17.7; F, 42.0; Zr, 16.8%. Found: C, 17.9; F, 42.3; Zr, 17.5%. IR (cm^{-1}): 1660 (vs b); 1500 (s); 1425 (s); 1380 (vs); 1215 (vs b); 1170 (vs b); 900 (m); 870 (s); 800 (vs); 690 (sh); 655 (m b); 620 (s); 600 (m); 530 (s); 470 (s): ^{19}F NMR $(CH_2Cl_2/CFCl_3)$ δ: -77.17 (s, CF$_3$) ppm.

Preparation of zirconium(IV) trifluoromethanesulfonate, $Zr(O_3SCF_3)_4$ [17]

Zirconium(IV) ethoxide (0.48 g, 1.8 mmol) was reacted with trifluoromethanesulfonic anhydride (2.2 g, 7.8 mmol) in vacuo and the mixture allowed to warm to room temperature slowly over a period of 2 h. The volatiles were removed after allowing the contents to react at ambient temperature for 4 d. This gave $Zr(O_3SCF_3)_4$ as a white solid in nearly quantitative yield (1.19 g, 1.7 mmol). Analysis: Calc. for $C_4F_{12}O_{12}S_4Zr$: C, 6.9; F, 33.2; S, 18.6; Zr, 13.3%. Found: C, 6.5; F, 32.9; S, 18.1; Zr, 13.2%. IR (cm^{-1}): 1465 (s sh); 1445 (s); 1370 (vs b); 1310 (w); 1235 (m); 1210
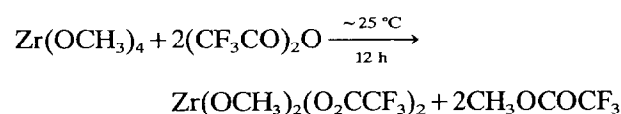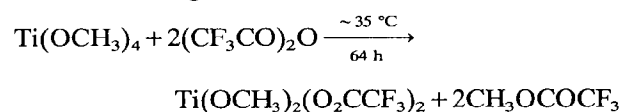
(vs); 1140 (vs); 1100 (m); 1060 (sh); 1020 (vs); 1000 (m); 980 (m); 940 (m); 870 (sh); 810 (m b); 775 (m); 765 (s); 650 (s sh); 625 (vs b); 600 (m); 500 (s). ^{19}F NMR $(CH_3NO_2/CFCl_3)$ δ: -78.5 (s, CF$_3$) ppm. Mol. weight (nitrobenzene): Calc., 687. Found, 670.

Completion of the reactions was estimated in the following manner. The volatiles were removed and the change in weight of the reactor noted from time to time. After each such measurement, the volatiles were condensed back and the reaction allowed to proceed under the stated conditions. The reaction was deemed to be complete when no further change in weight was observed.

The volatile products, ROCOCF$_3$ [18], ROSO$_2$X (X = F [19], CF$_3$ [20, 21]; R = CH$_3$, C$_2$H$_5$) were identified from their IR and NMR spectra.
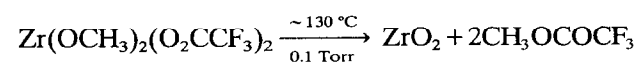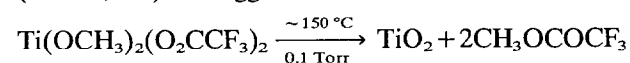
Results and discussion

Trifluoroacetic anhydride reacts with Ti(OCH$_3$)$_4$ and Zr(OCH$_3$)$_4$ to yield Ti(OCH$_3$)$_2$(O$_2$CCF$_3$)$_2$ and Zr(OCH$_3$)$_2$(O$_2$CCF$_3$)$_2$, respectively, in a clean fashion in the following manner:

$$Ti(OCH_3)_4 + 2(CF_3CO)_2O \xrightarrow[64 \text{ h}]{\sim 35 \text{ °C}}$$

$$Ti(OCH_3)_2(O_2CCF_3)_2 + 2CH_3OCOCF_3$$

$$Zr(OCH_3)_4 + 2(CF_3CO)_2O \xrightarrow[12 \text{ h}]{\sim 25 \text{ °C}}$$

$$Zr(OCH_3)_2(O_2CCF_3)_2 + 2CH_3OCOCF_3$$

Both bis(methoxy)titanium(IV) and bis(methoxy)-zirconium(IV) trifluoroacetates are white, hygroscopic solids, thermally stable up to 200 °C at atmospheric pressure under anhydrous conditions. They are both soluble in diethyl ether, nitromethane and nitrobenzene. Zr(OCH$_3$)$_2$(O$_2$CCF$_3$)$_2$ is soluble in CHCl$_3$ and CH$_2$Cl$_2$ to some extent as well.

The thermal decompositions of Ti(OCH$_3$)$_2$(O$_2$CCF$_3$)$_2$ and Zr(OCH$_3$)$_2$(O$_2$CCF$_3$)$_2$ are very interesting. Residues in both cases correspond to the formation of MO$_2$ (M = Ti, Zr) as suggested below:

$$Ti(OCH_3)_2(O_2CCF_3)_2 \xrightarrow[0.1 \text{ Torr}]{\sim 150 \text{ °C}} TiO_2 + 2CH_3OCOCF_3$$

$$Zr(OCH_3)_2(O_2CCF_3)_2 \xrightarrow[0.1 \text{ Torr}]{\sim 130 \text{ °C}} ZrO_2 + 2CH_3OCOCF_3$$

The reaction between trifluoroacetic anhydride and zirconium(IV) ethoxide produced completely substituted zirconium(IV) trifluoroacetate and this provides an alternative route for the preparation of Zr(O$_2$CCF$_3$)$_4$ [16].
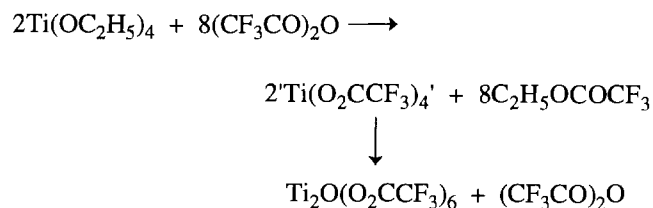
$$Zr(OC_2H_5)_4 + 4(CF_3CO)_2O \xrightarrow[6\,d]{\sim 35\,°C}$$

$$Zr(O_2CCF_3)_4 + 4C_2H_5OCOCF_3$$
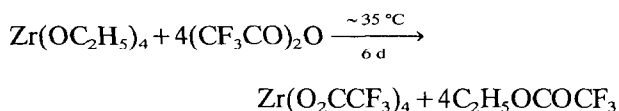
$Zr(O_2CCF_3)_4$ is a white, hygroscopic solid which does not melt or decompose up to 200 °C.

However, the reactions of trifluoroacetic anhydride with titanium(IV) ethoxide did not yield the tetrakis(trifluoroacetate) of titanium. Rather, an oxo product was obtained according to the following equation:

$$2Ti(OC_2H_5)_4 + 7(CF_3CO)_2O \xrightarrow[8\,h]{\sim 25\,°C}$$

$$Ti_2O(O_2CCF_3)_6 + 8C_2H_5OCOCF_3$$
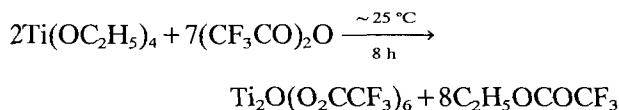
The formation of the oxo product, $Ti_2O(O_2CCF_3)_6$, may be taking place through an intermediate stage, where initially formed '$Ti(O_2CCF_3)_4$' further decomposes to the thermally more stable $Ti_2O(O_2CCF_3)_6$.

$$2Ti(OC_2H_5)_4 + 8(CF_3CO)_2O \longrightarrow$$

$$2'Ti(O_2CCF_3)_4' + 8C_2H_5OCOCF_3$$
$$\downarrow$$
$$Ti_2O(O_2CCF_3)_6 + (CF_3CO)_2O$$

$Ti_2O(O_2CCF_3)_6$ is a creamy amorphous solid (repeated attempts to obtain a powder X-ray diffraction pattern failed), soluble in nitromethane and nitrobenzene. It does not melt or decompose up to 200 °C under a dry atmosphere. Isolation of the oxo product $Ti_2O(O_2CCF_3)_6$ further supports earlier reports by various workers [22–24] that $Ti(O_2CCF_3)_4$ is not obtainable, whilst $Zr(O_2CCF_3)_4$ and $Hf(O_2CCF_3)_4$ are known. Analogous reactions of $TiCl_4$ with fatty acids yielded $Ti_2O(O_2CR)_6$ derivatives, rather than $Ti(O_2CR)_4$ [25]. The t-butyl acetate has been used to prepare tetrakis(acetates) of zirconium [26] and thorium [27] from the respective chlorides. However, reaction of t-butyl acetate with $TiCl_4$ resulted in the formation of only the oxoacetate [28] as below:

$$2TiCl_4 + 7CH_3OCOBu^t \longrightarrow$$

$$Ti_2O(O_2CCH_3)_6 + CH_3COCl + 7Bu^tCl$$
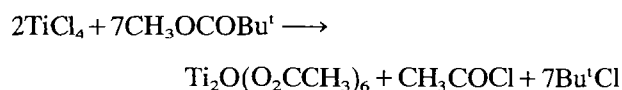
Investigations by Pande and Mehrotra [29–31] to prepare titanium tetracarboxylates by the reactions of titanium alkoxides with acetic anhydride and fatty acids always led to the isolation of the oxo product $Ti_2O(O_2CR)_6$.

The reactions of fluorosulfonic/trifluoromethanesulfonic anhydrides with titanium(IV) methoxide produce bis(methoxy)titanium(IV) fluoro/trifluoromethanesulfonates and have been described elsewhere [5, 6]. Fluorosulfonic/trifluoromethanesulfonic anhydrides react with zirconium(IV) methoxide to give partially substituted derivatives according to the following reactions:

$$Zr(OCH_3)_4 + 2(SO_2F)_2O \xrightarrow[5\,d]{\sim 35\,°C}$$

$$Zr(OCH_3)_2(O_3SF)_2 + 2CH_3OSO_2F$$

$$Zr(OCH_3)_4 + 2(SO_2CF_3)_2O \xrightarrow[4\,d]{amb.\ temp.}$$

$$Zr(OCH_3)_2(O_3SCF_3)_2 + 2CH_3OSO_2CF_3$$
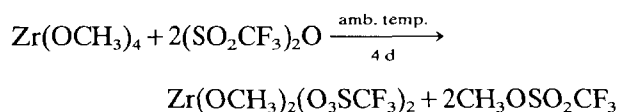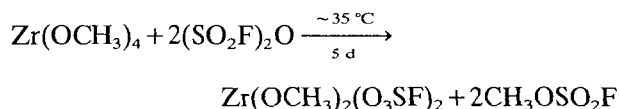
The reaction between $Ti(OC_2H_5)_4$ and $(XSO_2)_2O$ $(X = F$ or $CF_3)$ yields partially substituted derivatives in a similar fashion. Reaction above 10 °C resulted in the formation of products with erratic stoichiometries.

$$Ti(OC_2H_5)_4 + 2(XSO_2)_2O \xrightarrow[1\,d]{\sim 10\,°C}$$

$$Ti(OC_2H_5)_2(O_3SX)_2 + 2C_2H_5OSO_2X$$

$(X = F, CF_3)$
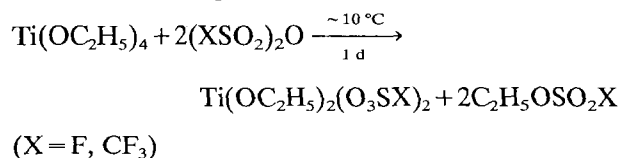
Zirconium(IV) ethoxide reacts with trifluoromethanesulfonic anhydride to give the previously known [17] zirconium(IV) trifluoromethanesulfonate and this provides an alternative route for the preparation of $Zr(O_3SCF_3)_4$:

$$Zr(OC_2H_5)_4 + 4(SO_2CF_3)_2O \xrightarrow[amb.\ temp.]{4\,d}$$

$$Zr(O_3SCF_3)_4 + 4C_2H_5OSO_2CF_3$$
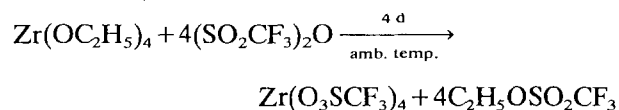
However, attempted reactions even at low temperature (0 °C) between $Zr(OC_2H_5)_4$ and $(FSO_2)_2O$ always resulted in the formation of white solids with erratic stoichiometry.

All the above-prepared fluorosulfonates and trifluoromethanesulfonates are white hygroscopic solids which did not melt or decompose up to ~ 150 °C under dry conditions. They are soluble in nitromethane and nitrobenzene, except for $Ti(OC_2H_5)_2(O_3SF)_2$ which does not dissolve in any of the non-coordinating solvents.

A comparison of the IR spectra of $Ti(OCH_3)_2(O_2CCF_3)_2$ and $Zr(OCH_3)_2(O_2CCF_3)_2$ (see Experimental section) with that of $Ti(OCH_3)_4$ [1456 (mw); 1434 (mw); 1142 (m b); 1088 (ms); 1044 (ms); 574 (m b); 460 (m); 398 (w) cm^{-1}] and $Zr(OCH_3)_4$ [1455 (ms); 1150 (s b); 1060 (m b); 960 (w b); 670 (m); 565 (m b) cm^{-1}], respectively, revealed that $Ti(OCH_3)_2(O_2CCF_3)_2$ and $Zr(OCH_3)_2(O_2CCF_3)_2$ are definite entities and do not contain unreacted metal alkoxides. The bands at 1635 and 1480 cm^{-1} in the IR spectrum of $Ti(OCH_3)_2(O_2CCF_3)_2$ and at 1655 and 1490 cm^{-1} in the IR spectrum of $Zr(OCH_3)_2(O_2CCF_3)_2$ are assigned to $\nu_{asym}CO_2$ and $\nu_{sym}CO_2$ vibrations. The magnitude of $\Delta\nu$ $(\nu_{asym}CO_2 - \nu_{sym}CO_2)$, which is of the order of 155 cm^{-1} in $Ti(OCH_3)_2(O_2CCF_3)_2$ and 165 cm^{-1} in $Zr(OCH_3)_2(O_2CCF_3)_2$, is comparable to the

values of 143 cm^{-1} in $Sb_2F_9(O_2CCF_3)$ [32] and 169 cm^{-1} in $Ag(O_2CCF_3)_2$ [33], where bridging bidentate trifluoroacetate groups have been confirmed by X-ray crystallography. The ^{19}F NMR spectra of these two derivatives exhibit a single resonance (see Experimental section), thus revealing that the two CF_3COO groups have a similar environment or are exchanging rapidly. The molecular weights of $Ti(OCH_3)_2(O_2CCF_3)_2$ and $Zr(OCH_3)_2(O_2CCF_3)_2$ in nitrobenzene demonstrate that these species are monomeric in solution.

The IR spectrum of $Ti_2O(O_2CCF_3)_6$ (see Experimental section) reveals that there are two types of trifluoroacetate groups as evidenced from the CO_2 vibrations. The bands at 1795 and 1410 cm^{-1} assignable to $\nu_{asym}CO_2$ and $\nu_{sym}CO_2$ may be attributed to a unidentate CF_3COO group since these resemble bands at 1790 and 1408 cm^{-1} in the IR spectrum of $Cs[H(O_2CCF_3)_2]$, where unidentate CF_3COO groups have been confirmed by X-ray crystallography [34]. The bands at 1640 ($\nu_{asym}CO_2$) and 1470 ($\nu_{sym}CO_2$) cm^{-1} may be attributed to bidentate bridging groups in $Ti_2O(O_2CCF_3)_6$ on the basis of bands at 1623 and 1454 cm^{-1} in the IR spectrum of $Ag(O_2CCF_3)_2$, where bidentate bridging groups have been confirmed by X-ray crystallography [33]. The ^{19}F NMR spectrum of $Ti_2O(O_2CCF_3)_6$ shows two peaks as singlets very closely spaced at -76.4 and -76.6 ppm, thus confirming that there are two different types of trifluoroacetate groups. The two signals are in the ratio 1:2, probably suggesting that two CF_3COO groups are of one type and four CF_3COO groups of another. The molecular weight of $Ti_2O(O_2CCF_3)_6$ in nitrobenzene was determined to be 805 units which matches closely with the calculated value of 790.

The various bands in the IR spectrum of $Zr(O_2CCF_3)_4$ have been listed in the Experimental section. The $\nu_{asym}CO_2$ at 1660 and $\nu_{sym}CO_2$ at 1500 cm^{-1} observed in the present work are in close agreement with previously reported values at 1660 and 1481 cm^{-1}, respectively [35]. A single resonance at -77.17 ppm in the ^{19}F NMR spectrum of $Zr(O_2CCF_3)_4$ indicates only one type of trifluoroacetate group.

The IR spectral data of $Zr(OCH_3)_2(O_3SCF_3)_2$, $Zr(OCH_3)_2(O_3SF)_2$, $Ti(OC_2H_5)_2(O_3SCF_3)_2$ and $Ti(OC_2H_5)_2(O_3SF)_2$ are listed in the Experimental section. A comparison of the IR data for these compounds with that of $Zr(OCH_3)_4$ and $Ti(OC_2H_5)_4$ confirms the distinct identity of these compounds. A perusal of the IR bands reveals [3] the reduced C_s symmetry of the SO_3X (X = F or CF_3) ligand in these compounds. The bands at 1360, 1120 and 1030 cm^{-1} in the spectrum of $Zr(OCH_3)_2(O_3SCF_3)_2$ and at 1340, 1110 and 1000 cm^{-1} in that of $Ti(OC_2H_5)_2(O_3SCF_3)_2$ may be attributed to the bridging bidentate SO_3CF_3 groups and are comparable to bands at 1358, 1105 and 1006 cm^{-1} in the

IR spectrum of $TiCl_2(O_3SCF_3)_2$, where bidentate bridging SO_3CF_3 groups have been anticipated [36]. The IR bands at 1385, 1165 and 1080 cm^{-1} for $Zr(OCH_3)_2(O_3SF)_2$ and at 1360, 1150 and 1070 cm^{-1} for $Ti(OC_2H_5)_2(O_3SF)_2$ are indicative of bridging bidentate SO_3F groups. These peaks are in close agreement [37] with the corresponding values at 1385, 1130 and 1087 cm^{-1} in the IR spectrum of $SnCl_2(O_3SF)_2$, wherein bridging bidentate fluorosulfonate groups have been suggested on the basis of ^{119}Sn Mössbauer spectroscopy [37]. The bands at 810 cm^{-1} in the IR spectrum of $Zr(OCH_3)_2(O_3SF)_2$ and at 815 cm^{-1} in that of $Ti(OC_2H_5)_2(O_3SF)_2$ are attributed to S–F stretching vibrations. Other bands in the IR spectra of these new fluorosulfonates and trifluoromethanesulfonates have not been assigned.

The ^{19}F NMR resonances of $Zr(OCH_3)_2(O_3SCF_3)_2$ and $Ti(OC_2H_5)_2(O_3SCF_3)_2$ at -80.33 and -80.5 ppm, respectively, suggest that both the trifluoromethanesulfonate groups in these compounds are in the same environment or are exchanging rapidly. The ^{19}F NMR spectrum of $Zr(OCH_3)_2(O_3SF)_2$ exhibits a single peak at $+50.0$ ppm relative to $CFCl_3$ and thus indicates the equivalence of both the SO_3F groups. $Zr(OCH_3)_2(O_3SCF_3)_2$, $Ti(OC_2H_5)_2(O_3SCF_3)_2$ and $Zr(OCH_3)_2(O_3SF)_2$ are monomeric in solution. The NMR and molecular weight data for $Ti(OC_2H_5)_2(O_3SF)_2$ could not be recorded because of the insolubility of this compound in non-coordinating solvents.

The IR spectral data for already known [17] $Zr(O_3SCF_3)_4$ are listed in the Experimental section and are not discussed here. The single resonance at -78.5 ppm in the ^{19}F NMR spectrum of $Zr(O_3SCF_3)_4$ may be attributed to the equivalence of the SO_3CF_3 groups.

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