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Communication

Flash Communication: Addition of Acid Anhydrides to Monomeric Stibine Oxides

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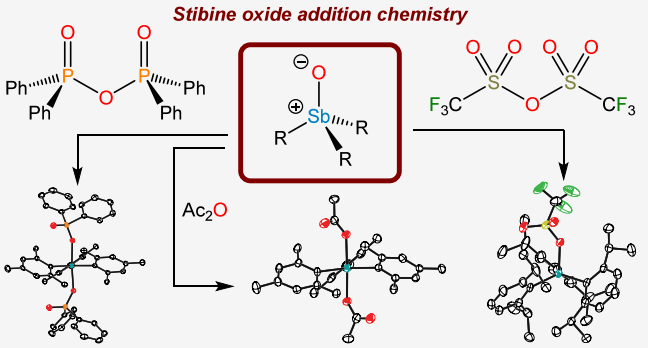
ABSTRACT: The polarized and unsaturated Sb−O bond of stibine oxides exhibits a combination of electrophilicity at the antimony atom and nucleophilicity at the oxygen atom. Here, we explore the consequent ability of Mes_3SbO compounds to undergo 1,2-addition chemistry with carboxylic, sulfonic, and phosphinic acid anhydrides to afford stiboranes of the type Mes_3SbX_2. With the bulkier stibine oxide $Dipp_3SbO$, reaction with triflic anhydride permits in situ preparation of $Dipp_3Sb(OTf)_2$, which crystallized as the stibonium triflate salt. This reactivity also enables the disaggregation of the polymeric stibine oxide $(Ph_3SbO)_n$ under mild conditions, providing an alternative synthetic route to Ph_3SbX_2 products.



With the exception of the metalloids As and Te, there is a relative dearth of isolable terminal oxo compounds of p-block metals/metalloids.[1,2] As and Te readily form terminal oxo compounds, such as arsine oxides and telluroxides,[3] which undergo addition with anhydrides. For example, Ph_2TeO heated in Ac_2O affords $Ph_2Te(OAc)_2$,[4] and Ph_3AsO heated with Tf_2O yields the disulfonate complex $Ph_3As(OTf)_2$.[5] Analysis of studies of the remaining p-block metals/metalloids is complicated by the fact that earlier work frequently depicted substances now known to be $(R_nEO)_m$ oligomers as the corresponding R_nEO monomeric species when describing their reactivity with acid anhydrides. For example, dialkyltin oxides heated in Ac_2O readily afford the dialkyltin diacetates,[6] and a brief note describes the conversion of simple inorganic salts and oxides such as $NaBiO_3$, $NaAsO_2$, Bi_2O_3, Na_2TeO_3, and I_2O_5 to trifluoroacetates via reaction with $(CF_3CO)_2O$.[7] Within group 15, the polymeric nature of unhindered stibine oxides is now well appreciated,[8−11] although reaction of these oligomers with suitably strong Lewis acids can promote disaggregation.[12−14] It has been reported that reaction of triphenylstibine oxide with Tf_2O affords $Ph_3Sb(OTf)_2$,[15] but subsequent efforts to reliably access larger quantities of this useful reagent employed salt metathesis,[16] which could suggest that there are complications that arise from using the ill-defined polymeric $(Ph_3SbO)_n$ starting material. These studies highlight that reaction with acid anhydrides can disaggregate oligomerized main-group oxides, but do not speak to the reactivity of the unsaturated $E-O_{term}$ bonds.

Recent advancements in the design of molecules kinetically stabilized against self-association/oligomerization have permitted a number of terminal oxo compounds of main-group metals/metalloids to be isolated for the first time.[17−21] Continuing in our efforts to understand the reactivity of the unsaturated Sb^+-O^- bonds in monomeric compounds of the type R_3SbO,[13,20,22−24] we explored reactions of monomeric stibine oxides with a variety of organo-oxyacid anhydrides (Scheme 1).

We previously observed clean 1,2-addition of Me_3ECl (E = group 14 element) across the stiboryl bond of Mes_3SbO,[24] and so we first investigated reactions of acid anhydrides with this monomeric stibine oxide. The stiborane $Mes_3Sb(OAc)_2$ is a known compound, previously prepared via *t*BuOOH oxidation of Mes_3Sb in an ethereal solution of AcOH.[25] We anticipated that nucleophilic attack of the stiboryl O atom of Mes_3SbO on the anhydride carbonyl of Ac_2O would install the acetyl group on the O atom of the stiboryl motif and release one equivalent of AcO^-, which would then bind to the Sb(V) center. The reaction did indeed form $Mes_3Sb(OAc)_2$,[25] which permitted us to determine its structure by single-crystal X-ray diffraction (Figure 1a). The geometry about the Sb center is trigonal bipyramidal, with the large mesityl substituents at the equatorial positions and the more apicophilic acetates at the axial positions with an O−Sb−O angle of 172.93(9)°. As expected because of the three-center-four-electron bonding along the O−Sb−O axis, the two Sb−O bond lengths of 2.111(3) and 2.112(3) Å in the product are statistically

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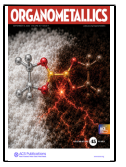

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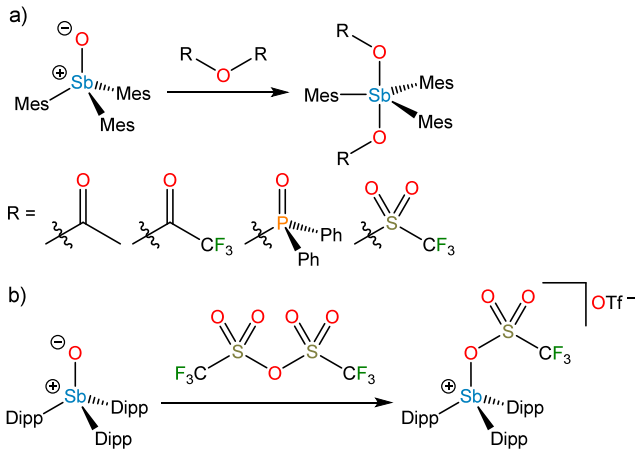
Scheme 1. Synthesis of (a) Stiboranes through the Reaction of Mes_3SbO with Various Acid Anhydrides and (b) $[Dipp_3Sb(OTf)]OTf$ through the Reaction of $Dipp_3SbO$ with Triflic Anhydride



significantly longer than the Sb−O bond length of 1.848(2) Å in free Mes_3SbO.[24]

Reaction with the even more electrophilic carboxylic acid anhydride $(CF_3CO)_2O$ proceeded analogously, affording the new compound $Mes_3Sb(O_2CCF_3)_2$. This species exhibited a single ^{19}F NMR signal at −75.7 ppm, and a single set of mesityl resonances in the ^1H and ^{13}C NMR spectra. Single-crystal X-ray diffraction revealed a trigonal bipyramidal geometry analogous to that of $Mes_3Sb(OAc)_2$ (Figure 1b). The longer Sb−O bond length of 2.1451(19) Å is consistent with this carboxylate interacting more weakly with the Sb(V) center.

The success of the reactions with carboxylic acid anhydrides led us to investigate the reaction of Mes_3SbO with the phosphinic acid anhydride $(Ph_2PO)_2O$. As with the carboxylic acid anhydrides, the addition resulted in rapid consumption of the starting materials and the clean formation of a single new product with a ^{31}P NMR signal at 19.4 ppm, which is shifted upfield from the signal of $(Ph_2PO)_2O$ at 28.1 ppm. There are, to our knowledge, no known Sb(V) complexes bearing phosphinate ligands, but this result is consistent with a final product of the form $Mes_3Sb(O_2PPh_2)_2$: the increase in shielding is consistent with the three-center-four-electron bonding interaction in the stibine oxide addition product, which concentrates charge on the axial ligands. A single-crystal X-ray diffraction study confirmed the composition of the product (Figure 1c). The Sb−O bond length was 2.1320(14) Å, the $P-O_{bridging}$ length was 1.5331(14) Å, and the $P-O_{terminal}$ length was 1.4794(15) Å. This complex makes an interesting comparison to $[Ph_3Sb(OPPh_3)_2](OTf)_2$,[16] which has Sb−O bond lengths of 2.1027(16) and 2.1001(16) Å, and $P-O_{bridging}$ lengths of 1.5242(17) and 1.5288(18) Å. The longer Sb−O bond length in $Mes_3Sb(O_2PPh_2)_2$, despite the anionic nature of the ligand, highlights the impact of the steric bulk of the mesityl substituents.

The previously reported complex $[Ph_3Sb(OPPh_3)_2](OTf)_2$ was formed from the reaction of Ph_3PO with $Ph_3Sb(OTf)_2$, which was in turn prepared from Ph_3SbCl_2 and 2 equiv of AgOTf.[16] The analogous complex $Mes_3Sb(OTf)_2$ was similarly prepared via the reaction of Mes_3SbCl_2 with AgOTf.[26] In addition to providing fundamental insight into the nature of pnictogen coordination chemistry, $Ar_3Sb(OTf)_2$ compounds have demonstrated utility as potent Lewis acids and as reagents for the oxidative formation of E−E (e.g., P−P) bonds.[16,26−28] From the reactivity described above with carboxylic and phosphinic acid anhydrides, we anticipated that reaction with a sulfonic acid anhydride would proceed readily and we did indeed observe that Tf_2O reacts with Mes_3SbO to cleanly generate $Mes_3Sb(OTf)_2$ (see Supporting Information).

In our earlier work on the addition of R_3ECl (E = group 14 element) compounds with stibine oxides, we observed a lack of reactivity with $Dipp_3SbO$, which we ascribed to the steric bulk of the Dipp groups. We suspected, however, that strongly electrophilic anhydrides might be able to overcome the effect of this steric bulk, as we have observed previously with Lewis acidic boranes.[13] Indeed, we observed that combining $Dipp_3SbO$ with the most electrophilic of the anhydrides that we had investigated above, Tf_2O, led to rapid formation of a new single product, which featured a single CH septet and a single CH_3 doublet by ^1H NMR spectroscopy. Although solutions of this product could be reliably generated *in situ*, it proved to be incredibly reactive and would decompose rapidly as evidenced by disappearance of NMR resonances and the growth of many new signals. Crystals could be grown, but if they were observed for any length of time on the microscope, a wave of decomposition/discoloration would rapidly propagate through the solid. If crystals were grown rapidly and mounted rapidly into a precooled cryostream, however, diffraction data

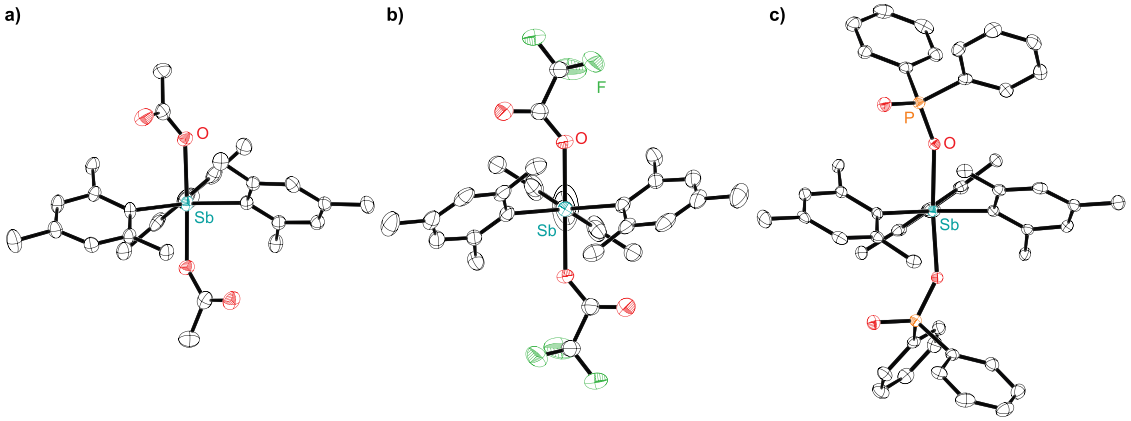


Figure 1. Molecular structures at 50% probability of (a) $Mes_3Sb(OAc)_2$, (b) $Mes_3Sb(O_2CCF_3)_2$, and (c) $Mes_3Sb(O_2PPh_2)_2$. H atoms and minor components of disorder are omitted for clarity. Color code: Sb teal, O red, F green, P orange, C black.

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suitable for structure solution could be obtained. The single-crystal X-ray diffraction experiment revealed the crystals to contain, not the neutral stiborane $Dipp_3Sb(OTf)_2$, but rather the tetrasubstituted stibonium triflate salt $[Dipp_3Sb(OTf)]OTf$ (Scheme 1b, Figure 2). The Sb−O bond length of 2.0267(18)

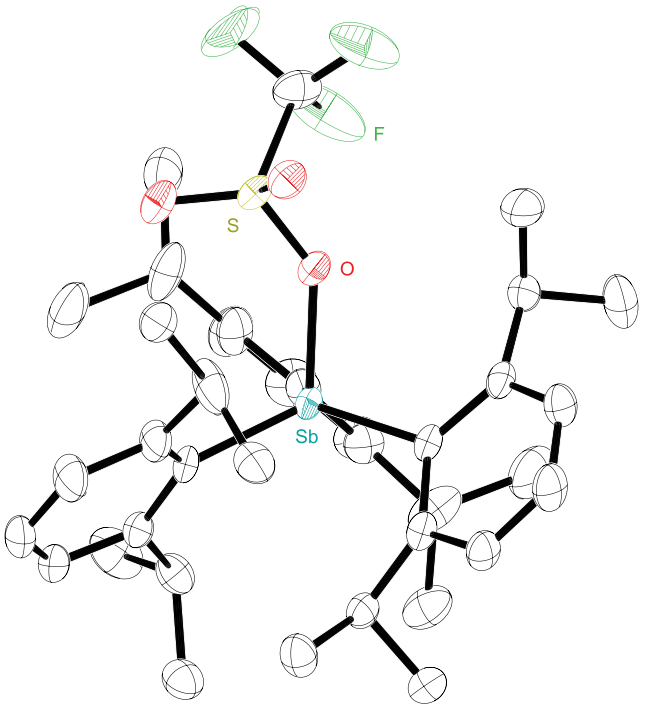

Figure 2. Molecular structure at 50% probability of $[Dipp_3Sb(OTf)]$-OTf. H atoms, minor components of disorder, and counterion are omitted for clarity. Color code: Sb teal, O red, F green, S yellow, C black.

Å is significantly shorter than the Sb−O bond lengths of 2.173(2) and 2.178(2) Å in $Mes_3Sb(OTf)_2$, which is expected because of the three-center-four-electron bonding in the latter. We believe that this stibonium salt is the species observed spectroscopically and that there is rapid exchange of the inner- and outer-sphere triflate groups. We suspect that the decomposition we observed arises from water binding to this highly electrophilic Lewis acid.

In the absence of sterically bulky substituents, stibine oxides exist as polymers, rather than discrete monomers. We observed that even an anhydride with only moderate electrophilicity, Ac_2O, was able to disaggregate $(Ph_3SbO)_n$. Stirring a suspension of this polymer in CH_2Cl_2 with an excess of Ac_2O led to the gradual consumption of the solid and the formation of $Ph_3Sb(OAc)_2$, as assessed by NMR spectroscopy (see the Supporting Information).

In summary, this work establishes monomeric stibine oxides as versatile platforms for 1,2-addition chemistry with acid anhydrides, providing new insight into the reactivity of polarized Sb−O bonds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.6c00231.

NMR spectra, crystallographic refinement tables, thermal ellipsoid plots, and powder diffractograms (PDF)

Accession Codes

Deposition Numbers 2550914−2550916 and 2550918 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

The authors declare no competing financial interest.

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