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Pnictogens

Lewis Acidity of the $SbCl_3$/*o*-chloranil System

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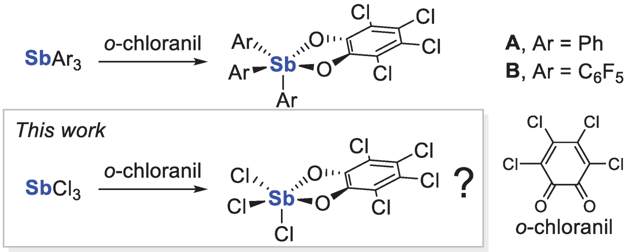
Abstract: While $SbCl_3$ is typically inert toward oxidation by *ortho*-quinones, we use *o*-chloranil to show that the outcome of such reactions may be altered by the presence of a donor such as triphenylphosphine oxide, which readily traps the $SbCl_3(cat^{Cl})$ synthon (cat^{Cl} = tetrachlorocatecholate) in the form of the corresponding adduct $Ph_3PO{\rightarrow}SbCl_3(cat^{Cl})$. The same reaction in the presence of a chloride salt affords the corresponding antimonate anion $[Cl_4Sb(cat^{Cl})]^-$. Computational studies indicate that the putative $SbCl_3(cat^{Cl})$ synthon has a higher chloride ion affinity than $SbCl_5$, suggesting significant Lewis acidity. This property is further demonstrated by the use of the $SbCl_3$/*o*-chloranil system for both THF polymerization and a Friedel–Crafts-type alkylation of benzene using 1-fluorooctane. Finally, the reaction of *E*-stilbene with *o*-chloranil in the presence of $SbCl_3$ affords the corresponding benzodioxene, suggesting that $SbCl_3$ may also operate as a redox-active catalyst.

Antimony chemistry has garnered renewed interest, particularly due to the high Lewis acidity displayed by antimony(V) compounds, as established early on by Gillespie and Olah in their independent contributions to the chemistry of antimony pentahalides for the generations of superacids[1–4] and for the activation of C–F bonds.[5–8] The pronounced acidity of antimony(V), which has been exploited for C–H bond activation chemistry,[9–11] extends to a variety of organoantimony derivatives,[12–14] some of which behave as Lewis superacids.[15,16] Lewis superacidic or not, organoantimony(V) derivatives constitute useful platforms for a number of transformations as illustrated in the literature.[12,17–30] When mildly Lewis acidic, such organoantimony species are also often water tolerant and can behave as pnictogen bond donors[31] with applications in aqueous phase catalysis,[27,32] anion capture,[33–35] and anion transport across biological-like interfaces.[36,37] A straightforward method for generating these derivatives involves the oxidation of a stibine with an *ortho*-quinone,[38,39] such as *o*-chloranil. This reaction is particularly convenient in the case of electron-rich stibines, which are readily converted into catecholatostiboranes, such as $Ph_3Sb(cat^{Cl})$ (cat^{Cl} = tetrachlorocatacholate; **A**).[40,41] More recently, we have tested the application of this approach to more electron-poor stibines such as tris(pentafluorophenyl)stibine. In 2018, we reported that the formation of $(C_6F_5)_3Sb(cat^{Cl})$ (**B**) is much slower than that of **A**, indicating the reluctance of the electron-poor antimony atom to undergo oxidation to the pentavalent state (Scheme 1).[22] Reflecting upon these results, we have now questioned whether antimony trichloride ($SbCl_3$) could be oxidized by *o*-chloranil. This investigation was motivated by the potential to generate a highly Lewis acidic antimony(V) derivative from easy-to-handle chemicals. Additionally, we hypothesized that the reluctance of electron-poor antimony(III) species to undergo oxidation may offer opportunities for oxidative addition and reductive elimination cycling at antimony, thereby opening avenues for main-group-mediated redox catalysis.

To begin this investigation, we first computed the structure of $SbCl_3(cat^{Cl})$ (**1**), the target Lewis acid. The structure of this derivative was optimized in Orca 5.0.2[42–44] using the PBEh-3c functional and the def2-mSVP basis set,[45] where it was found to adopt a square pyramidal geometry about the antimony center. A gas phase thermodynamic analysis indicated that the formation of **1** from $SbCl_3$ and *o*-chloranil is endergonic ($\Delta G = +3.0$ kcal mol^{-1}). This in silico prediction is consistent with our observation that $SbCl_3$ and *o*-chloranil do not react to form **1** in acetonitrile, chloroform, or diethyl ether (Et_2O, Figure 1). Attempts to observe **1** at −40 °C by ^{13}C NMR spectroscopy in $CDCl_3$ were also unsuccessful, with *o*-chloranil being the only detectable species. Reasoning that the addition of an exogenous Lewis base could stabilize **1** and drive the reaction, we repeated this reaction in the



Scheme 1. Oxidation of trivalent stibines to pentavalent catacholatostiboranes by *o*-chloranil and objective of the current study.

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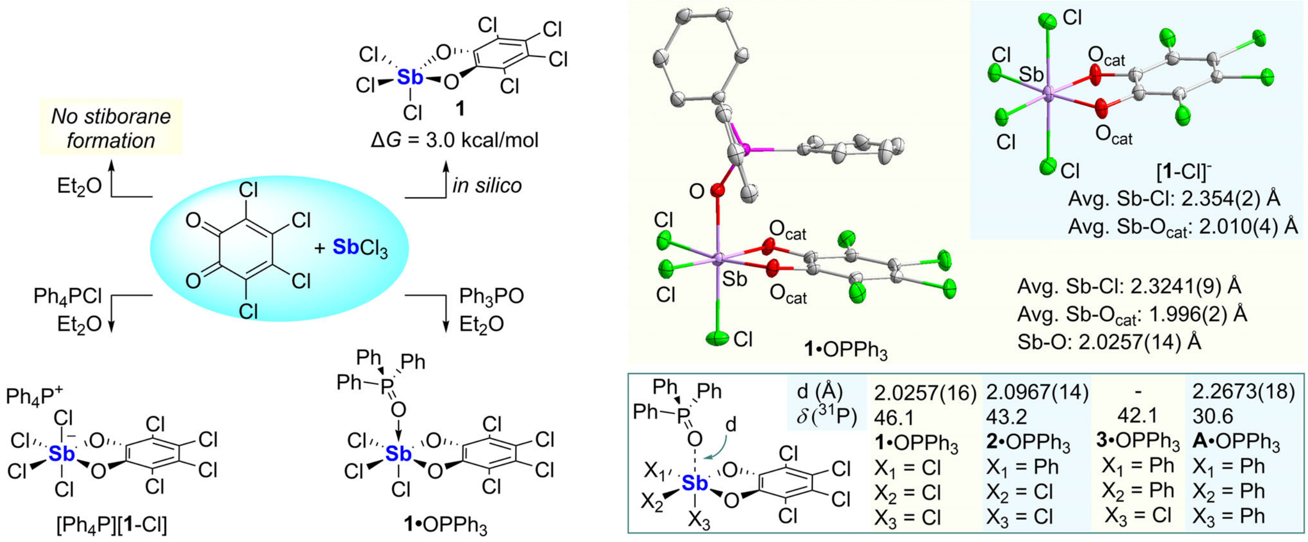


d (Å)	2.0257(16)	2.0967(14)	-	2.2673(18)
δ(^{31}P)	46.1	43.2	42.1	30.6
	1•OPPh$_3$	**2**•OPPh$_3$	**3**•OPPh$_3$	**A**•OPPh$_3$
	X$_1$ = Cl	X$_1$ = Ph	X$_1$ = Ph	X$_1$ = Ph
	X$_2$ = Cl	X$_2$ = Cl	X$_2$ = Ph	X$_2$ = Ph
	X$_3$ = Cl	X$_3$ = Cl	X$_3$ = Cl	X$_3$ = Ph

Figure 1. Left: Reactions of the SbCl$_3$/*o*-chloranil system reported in this work, yielding the isolable products [Ph$_4$P][SbCl$_4$(cat^{Cl})] ([Ph$_4$P][**1**-Cl]) and Ph$_3$PO→SbCl$_3$(cat^{Cl}) (**1**•OPPh$_3$). Right: Single crystal X-ray diffraction structures of [Ph$_4$P][**1**-Cl] and **1**•OPPh$_3$ with selected bond lengths. Counter-ion and hydrogen atoms removed for clarity. Thermal ellipsoids drawn at 50% probability level. The inset shows a summary of Sb—O bond distances and ^{31}P NMR chemical shifts for **1**•OPPh$_3$, **2**•OPPh$_3$, **3**•OPPh$_3$ and **A**•OPPh$_3$.

presence of one equivalent of [PPh$_4$][Cl] in Et$_2$O. Under these conditions, the reaction mixture rapidly lost the deep red color characteristic of *o*-chloranil. The ^{13}C NMR resonances corresponding to the oxygen-bound carbon atoms also shift downfield from 169.3 ppm for *o*-chloranil to 144.5 ppm, suggesting the reduction of the *ortho*-quinone to a catecholate. Additionally, ESI mass spectrometry identified a molecular peak consistent with an antimonate anion, [SbCl$_4$(cat^{Cl})]$^-$ ([**1**-Cl]$^-$), providing initial evidence for the addition of chloride to the antimony center (Figure 1). Carrying out the reaction using bench-top reagents afforded the same outcome.

Similar observations were made when Ph$_3$PO was used as a base. Indeed, when Ph$_3$PO was combined with SbCl$_3$ and *o*-chloranil in Et$_2$O either on the bench or under an inert atmosphere, a rapid color change was observed, indicating consumption of the quinone. The product of this reaction, which spontaneously precipitated, was isolated by filtration and identified as **1**•OPPh$_3$ (Figure 1). This adduct was first characterized by ^{31}P NMR spectroscopy, which revealed a single resonance at 46.1 ppm. This resonance is significantly shifted downfield when compared to both free Ph$_3$PO (29.1 ppm) and the Ph$_3$PO adduct of the previously reported stiborane **A** (**A**•OPPh$_3$; 30.6 ppm).[46] In fact, the observed ^{31}P NMR resonance is similar to that of Cl$_5$Sb•OPPh$_3$ (46.3 ppm), suggesting that **1** and SbCl$_5$ possess comparable Lewis acidities.[22,47]

The formation of both [Ph$_4$P][**1**-Cl] and **1**•OPPh$_3$ was confirmed by single-crystal X-ray diffraction (Figure 1). The antimony center in the antimonate [**1**-Cl]$^-$ adopts an octahedral geometry, with the catecholate oxygen atoms occupying two of the coordination sites. An octahedral geometry is also observed in **1**•OPPh$_3$, which crystallizes as the *fac*-isomer with the triphenylphosphine oxide ligand bound *trans* to a chloride ligand. The geometries of **1**•OPPh$_3$ and [**1**-Cl]$^-$ are similar, as indicated by average Sb—Cl bond distances of 2.3241(9) and 2.354(2) Å, respectively, and average Sb—O$_{cat}$ bond distances of 1.996(2) and 2.010(4) Å, respectively. Additionally, the Sb—Cl bonds in these two new species are comparable to those in the hexachloroantimonate anion (avg. 2.352(4) Å).[48] The Sb—O bond distance of 2.0257(16) Å to the oxygen atom of the phosphine oxide in **1**•OPPh$_3$ is within the expected value for a single bond based on the sum of the covalent radii of the two elements (Σr_{cov}(Sb,O) = 2.03 Å)[49] and is shorter than those found in the dication [(Ph$_3$PO)$_2$SbPh$_3$]$^{2+}$ (Sb-O = 2.11 Å).[50] Notably, it is also shorter than the Sb—O bond present in the OPPh$_3$ adduct of the previously synthesized compound **A** (Sb-O = 2.2673(18) Å). These parameters indicate the tight coordination of the phosphine oxide to the antimony center of **1**, speaking to the elevated Lewis acidity of this novel antimony(V) species. Analysis of the P—O bond supports this conclusion as it stretches from 1.484(1) Å in free Ph$_3$PO to 1.5338(14) Å in **1**•OPPh$_3$.[51] This elongated P—O bond approaches the P—O distance found in the methoxyphosphonium cation [MeOPPh$_3$]$^+$ (P-O = 1.562(1) Å).[52]

As an additional point of comparison, we were able to independently synthesize and characterize the Ph$_3$PO adducts of PhSbCl$_2$(cat) (**2**)[53] and Ph$_2$SbCl(cat) (**3**), with the latter being newly prepared in the context of this investigation (see Supporting Information). Their respective Ph$_3$PO adducts **2**•OPPh$_3$ and **3**•OPPh$_3$ were generated by the addition of a stoichiometric amount of Ph$_3$PO to solutions of the parent stiborane in dichloromethane. As expected, the ^{31}P NMR resonances of **2**•OPPh$_3$ and **3**•OPPh$_3$ (43.2 and 42.1 ppm, respectively) were between those of **1**•OPPh$_3$ and **A**•OPPh$_3$ (Figure 1). While **3**•OPPh$_3$ could not be characterized crystallographically, single crystals of **2**•OPPh$_3$ were obtained. The most salient feature in the structure of **2**•OPPh$_3$ is the length of the Sb—O bond, which stands at 2.0967(14) Å, somewhat elongated relative to **1**•$OPPh_3$ (2.0257(16) Å) but shorter than that of **A**•$OPPh_3$ (Sb-O = 2.2673(18) Å). In agreement with the intermediate Lewis acidity of **2**, we note that the P─O bond length of its triphenylphosphine oxide adduct (1.5290(14) Å) falls between that of **1**•$OPPh_3$ (1.5338(14) Å) and **A**•$OPPh_3$ (1.5022(19) Å).

The above results indicate that Lewis acid **1** can be accessed in a base-stabilized form. The characterization of its Ph_3PO adduct by ^{31}P NMR spectroscopy also suggests that its Lewis acidity is close to that of $SbCl_5$. To investigate this aspect further, we have compared its gas phase chloride ion affinity (CIA) to that of $SbCl_5$. Here, we use the CIA as defined by Erdmann and Greb, analyzing the thermodynamic parameters with trimethylsilyl chloride as a CIA benchmark.[54,55] Our results indicate that the CIA of **1** (73.6 kcal mol^{-1}) exceeds that of $SbCl_5$ (65.2 kcal mol^{-1}) by 8.4 kcal mol^{-1} in the gas phase or by 1.6 kcal mol^{-1} when solvation effects are taken into account with $CHCl_3$ as the solvent (see Supporting Information). Since the formation of **1** is endergonic due to an unfavorable entropy term, we decided to compute the free energy of the reaction in Equation 1, which afforded a value of −5.7 kcal mol^{-1} at 298 K. This computational finding indicates that the Lewis acidity of the $SbCl_3$/*o*-chloranil system toward chloride is greater than that of $SbCl_5$, suggesting the potential of such pairs to serve as precursors to Lewis superacids.[16] In fact, we have already verified that SbF_3 and *o*-chloranil react with one another in diethyl ether when in the presence of $[N^nBu_4][F]$ to afford $[N^nBu_4][SbF_4(cat^{Cl})]$, a salt isolated in an analytically pure form and characterized both structurally and spectroscopically (see Supporting Information). This reaction, although sluggish, suggests that the SbF_3/*o*-chloranil system may also be regarded as a potential SbF_5 analog.

$$[SbCl_6]^- + SbCl_3 + o\text{−chloranil} \rightarrow SbCl_5 + [\mathbf{1} - Cl]^- \qquad (1)$$

Emulating an approach recently used to investigate the acceptor properties of other antimony species,[56,57] we decided to seek further insights into the Lewis acidity of **1** by carrying out an energy decomposition analysis using the ADF program.[58] This method afforded an energy value (ΔE) of −73.9 kcal mol^{-1} for the formation of [**1**-Cl]$^-$, in good agreement with the computed CIA value of **1** (73.6 kcal mol^{-1}). This ΔE value exceeds that obtained for $SbCl_5$ (−65.8 kcal mol^{-1}), pointing to the favorable influence of the tetrachlorocatecholate ligand has on the chloride ion affinity of the antimony center. As the sum of the interaction energies (ΔE_{int}) of **1** and $SbCl_5$ differs by less than 2 kcal mol^{-1}, the larger chloride affinity of **1** can be primarily attributed to its lower strain energy (ΔE_{strain}), the energy required to distort the geometry of the free Lewis acid to the geometry it assumes in the antimonate species. Indeed, as illustrated in Figure 2, the ΔE_{strain} of **1** (13.9 kcal mol^{-1}) and that of $SbCl_5$ (20.3 kcal mol^{-1}), differ by 6.5 kcal mol^{-1}. This difference can be correlated to the distorted square pyramidal geometry computed for **1** and its resemblance to that in [**1**-Cl]$^-$. In the case of $SbCl_5$, the D_{3h} Lewis acid needs to undergo a more energetically costly reorganization to reach the C_{4v} structure it adopts in the transition state.[57,59] In the case of **1**, this distortion is facilitated by the geometrical constraints imposed by the five-membered ring formed upon coordinating the catecholate ligand to the antimony atom.

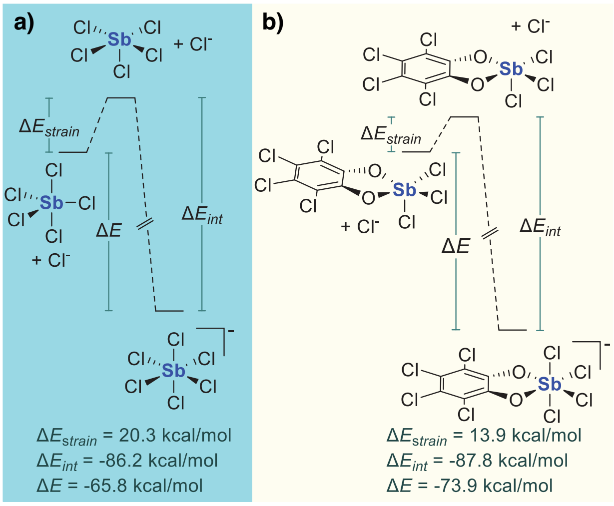
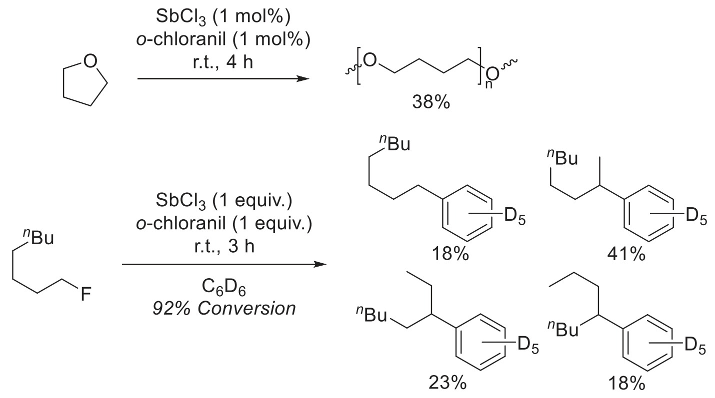


Figure 2. Energy decomposition analysis of the interaction of $SbCl_5$ (panel a) and **1** (panel b) with the chloride anion.

Encouraged by the above experimental and computational findings, we began to study the potential of $SbCl_3$/*o*-chloranil as a Lewis acid activator or catalyst. Initial evidence for the potency of this system was obtained by an investigation of its behavior in THF, a solvent that was readily polymerized by 1 mol% of $SbCl_3$/*o*-chloranil. Polymerization was confirmed by ^1H NMR spectroscopy, specifically the appearance of resonances corresponding to poly(THF), which indicated 38% conversion after 4 h (Scheme 2) and 54% conversion after 24 h by integration of the THF and poly(THF) NMR signals. In the absence of *o*-chloranil, no reaction is observed. To further exploit the Lewis acidity of $SbCl_3$/*o*-chloranil, we decided to test the ability of this system to activate C─F bonds. Toward this end, equimolar amounts of $SbCl_3$, *o*-chloranil and 1-fluorooctane were dissolved in C_6D_6. After 3 h, the ^1H NMR spectrum of the mixture indicated 92% conversion, with resonances consistent with the formation of four isomers of (phenyl-d_5)octane. Formation of these Friedel–Crafts products provides unambiguous evidence for activation of the C─F bond of 1-fluorooctane and the presence of multiple isomers suggests that there is an isomerization of the octyl cation prior to its trapping by benzene-d_6. We note that 2-(phenyl-d_5)octane is made in the highest proportion, consistent with the stability of the secondary carbocation formed by isomerization immediately after fluoride abstraction.

To further leverage the Lewis acidity of the $SbCl_3$/*o*-chloranil system, we investigated its application as a possible catalyst for the Friedel–Crafts dimerization of 1,1-diphenylethene, a reaction promoted by triarylhalostibonium cations.[60] Attempts to replicate this chemistry with $SbCl_3$/*o*-chloranil were unsuccessful. In contrast, a rapid reaction was observed when *E*-stilbene, an isomer of 1,1-diphenylethene, was employed. Analysis of this reaction indicated the formation of the *anti*- isomer of 2,3-diphenyl-5,



Scheme 2. Catalytic and stoichiometric reactivity promoted by $SbCl_3$/*o*-chloranil, including the polymerization of THF (top) and the Friedel–Crafts-type alkylation of C_6D_6 with 1-fluorooctane (bottom).

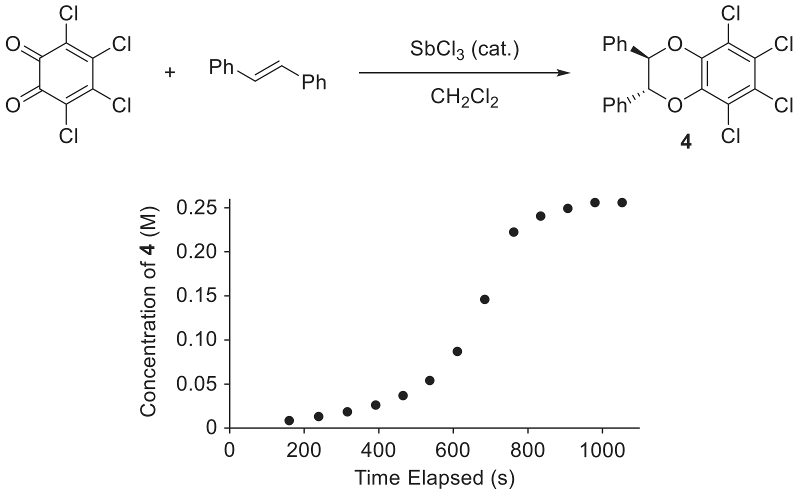


Figure 3. Top: Hetero-Diels-Alder reaction between *E*-stilbene and *o*-chloranil catalyzed by $SbCl_3$. Bottom: Concentration of **4** over time in the reaction between *o*-chloranil and *E*-stilbene catalyzed by 0.5 mol% $SbCl_3$.

6,7,8-tetrachlorobenzodioxene (**4**), as a result of a hetero-Diels-Alder reaction between *E*-stilbene and *o*-chloranil, hinting at the possible role of $SbCl_3$ as a catalyst (Figure 3). To test this hypothesis further, the reaction was repeated with a catalytic amount of $SbCl_3$ (1 mol%), leading to rapid formation of **4**. The speed at which the reaction proceeded complicated an investigation of its kinetics. Only at significantly lower catalyst loading were we able to observe product formation using ^{1}H NMR Spectroscopy. The catalytic trace in Figure 3, obtained with a loading of 0.5%, shows a relatively long induction period followed by a rapid rise in product formation. The length of this induction period increases drastically when the catalyst loading is further decreased (See Supporting Information). It is also drastically shortened at higher loadings, thereby preventing accurate monitoring of product formation. The lack of linearity in the kinetic of this reaction may indicate catalyst maturation, possibly via aggregation. In a study of olefin chlorination using $SbCl_5$, it was proposed that the antimony(V) reagent equilibrated into $[SbCl_4][SbCl_6]$ as the active species.[61,62] We propose that a similar speciation can take place in $SbCl_3$/*o*-chloranil, possibly yielding the $[SbCl_2(cat^{Cl})]$[**1**-Cl] ion pair as the active species, which would explain the observed sensitivity of the reaction progress to the concentration of $SbCl_3$. While mechanistic details are not yet available, we envision that this reaction could proceed via redox cycling at antimony, which adds *o*-chloranil and eliminates it in the presence of the olefin.

In summary, our attempts to synthesize the highly Lewis acidic stiborane $SbCl_3(cat^{Cl})$ from *o*-chloranil and $SbCl_3$ have shown that its formation is endergonic and not observed in typical solvents. The addition of a base alters this situation and readily drives the redox reaction by stabilization of the antimony(V) center, as verified by the isolation of both a phosphine oxide adduct and a tetrachloroantimonate salt. As supported by calculations, the putative stiborane, $SbCl_3(cat^{Cl})$, has a similar Lewis acidity to $SbCl_5$, a trait corroborated by the ability of the $SbCl_3$/*o*-chloranil system to polymerize THF and activate the C–F bond of fluoroalkanes. Lastly, the formation of the benzodioxene **4** in the reaction of $SbCl_3$/*o*-chloranil with *E*-stilbene raises the possibility of catalytic redox cycling at antimony. Current efforts are focused on clarifying the mechanism of this cyclization reaction.

Supporting Information

The data supporting the results reported in this article are available in the Supporting Information in the form of experimental and analytical procedures, computational details, spectra, and optimized geometries. CCDC 2430828–2430834 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre. The authors have cited additional references within the Supporting Information.[22,42–45,53–55,58,63–81]

Acknowledgements

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Antimony • Catalysis • Lewis acid • Main group • Pnictogen

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