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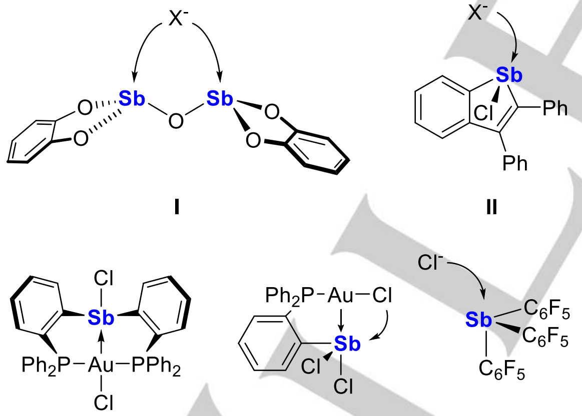
Digging the σ-hole of organoantimony Lewis acids by oxidation

Mengxi Yang, Daniel Tofan, Chang-Hong Chen, Kevin M. Jack, and François P. Gabbaï*

Abstract: The development of group 15 Lewis acids is an area of active investigation that has led to numerous advances in anion sensing and catalysis. While phosphorus has drawn considerable attention, emerging research shows that organoantimony(III) reagents may also act as potent Lewis acids. By comparing the properties of $SbPh_3$, $Sb(C_6F_5)_3$, and $SbAr^F_3$ with those of their tetrachlorocatecholate analogs $SbPh_3Cat$, $Sb(C_6F_5)_3Cat$, and $SbAr^F_3Cat$ (Cat = *o*-$O_2C_6Cl_4$, Ar^F = 3,5-$(CF_3)_2C_6H_3$), we now show that the Lewis acidity of electron deficient organoantimony(III) reagents can be readily enhanced by oxidation to the +V state as verified by binding studies, organic reaction catalysis, and computational studies. We rationalize these results by explaining that oxidation of the antimony center leads to a lowering of the accepting σ* orbital and a deeper carving of the associated σ-hole.

The chemistry of group 15 Lewis acids is experiencing a surge of activity that has led to a series of stimulating developments in the area of phosphorus-mediated catalysis.[1] Antimony derivatives, because of their intrinsically higher Lewis acidity,[2] are also drawing considerable attention both in the areas of small molecule activation and catalysis[3] as well as in anion complexation.[4] Recent efforts in the chemistry of organoantimony(III)[5] have established that derivatives such as **I**[6] and **II**[7] readily bind halide anions (Figure 1) via donation into the σ* orbital (Figure 2).[7] Based on the same principle, we also found that antimony (III) halides could serve to promote activation of transition metals either via direct interaction with the metal (**III**)[8] or anion abstraction (**IV**)[9] (Figure 1).



I **II**

III **IV** **2**

Figure 1. Selected examples of antimony(III) compounds acting as Lewis acids.

It is interesting to note that the Lewis acidity at antimony can also be imparted through the use of perfluorinated ligands. While $SbPh_3$ (**1**) does not possess any notable Lewis acidity, Matile *et al.* have shown recently that $Sb(C_6F_5)_3$ (**2**) binds chloride anions and catalyzes anion pairing reactions involving organic chlorides (Figure 1).[10] This halide binding event again illustrates the presence of low lying σ* orbitals which accept density from a donor orbital located on the incoming anion. This phenomenon can also be referred to as resulting from the presence of a so-called σ-hole,[11] a term that usually emphasizes the contribution of electrostatic forces to the interaction (Figure 2).[12] In this paper, we show that oxidation of antimony to the +V state can be used to carve the electrostatic potential profile about the antimony atom, leading to a deeper σ-hole. We also demonstrate that control over the depth of the σ-hole impacts the affinity of antimony for incoming electron-rich substrates and turns on catalysis.

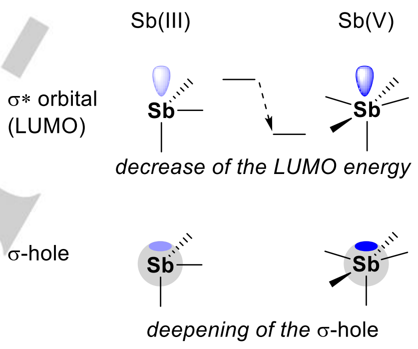


Figure 2. Orbital and electrostatic origin of the Lewis acidity in antimony derivatives. The intensification of the blue color illustrates an energy lowering in the case of the LUMO and a greater positive charge development at antimony in the case of the σ-hole.

To probe the effect of oxidation on antimony acceptors, we decided to compare the properties of $SbPh_3$ (**1**), $Sb(C_6F_5)_3$ (**2**), and $SbAr^F_3$ (**3**) with those of their tetrachlorocatecholate analogs $SbPh_3Cat$ (**4**), $Sb(C_6F_5)_3Cat$ (**5**), and $SbAr^F_3Cat$ (**6**) (Cat = *o*-$O_2C_6Cl_4$, Ar^F = 3,5-$(CF_3)_2C_6H_3$) (Figure 3). While most of these compounds have been described previously,[3c,4c,13] **6** was prepared by reaction of **3** with *o*-chloranil and its structure was verified by X-ray crystallography.[14] We note in passing that the use of the electron deficient tetrachlorocatecholate ligands in **5** and **6** is necessary to stabilize the +V oxidation state of these compounds.

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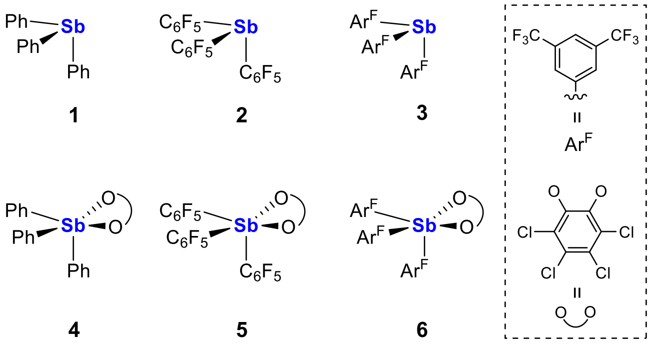

Figure 3. Antimony-based Lewis acids studied in this work.

With these compounds at our disposal, we decided to test their reactivity toward simple Lewis bases. For the purpose of this study, we chose to benchmark the Lewis acidity of these compounds against triphenylphosphine oxide, a base known to coordinate to antimony (V) compounds.[3c] Using ^{1}H and ^{19}F NMR spectroscopy, we found that **1**, **2**, and **3** do not interact to any measurable extent with Ph_3PO in $CDCl_3$. By contrast, the ^{1}H, ^{31}P and ^{19}F NMR spectra of stiboranes **4**, **5** and **6** undergo drastic changes upon addition of Ph_3PO. In the case of **4**, we observed that the 1:1 adduct $Ph_3PO\rightarrow SbPh_3Cat$ is in rapid equilibrium with **4** and Ph_3PO at NMR concentrations. Incremental addition of **4** to a solution of Ph_3PO induces a progressive downfield shift of the ^{31}P NMR resonance consistent with increasing concentrations of the 1:1 adduct. Treatment of this titration data affords a binding constant (K) of 120 ± 20 M^{-1}. (Figure 4) Unlike **4**, the fluorinated stiboranes **5** and **6** form 1:1 adducts with the Ph_3PO ($Ph_3PO\rightarrow Sb(C_6F_5)_3Cat$ and $Ph_3PO\rightarrow SbAr^F{}_3Cat$, respectively) with no evidence of dissociation or exchange at NMR concentrations. Since the ^{31}P NMR chemical shift of Ph_3PO is equal to 29.6 ppm, that measured for the adducts (41.5 ppm for **5** and 40.0 ppm for **6**) suggests a substantial polarization of the P=O functionality upon coordination to antimony. UV-vis titration experiments carried out by adding incremental amounts of Ph_3PO to $CHCl_3$ solutions of **5** or **6** afford 1:1 binding isotherms that could be fitted with K = 3 (± 0.8) × 10^4 M^{-1} for **5** and K = 3 (± 1) × 10^5 M^{-1} for **6** (Figure 4 and Figure S8). These binding constants are one to two orders of magnitude higher than that measured for **4**. This enhancement in Lewis acidity can be attributed to the fluorination of the aryl rings and their resulting electron-withdrawing properties. The higher Lewis acidity measured for **6** corroborates fluoride ion affinity (FIA) trends computed by Krossing who found that $BAr^F{}_3$ (471 kJ/mol) has a higher fluoride anion affinity than $B(C_6F_5)_3$ (444 kJ/mol).[15] Given that the ^{31}P NMR shift of $Ph_3PO\rightarrow Sb(C_6F_5)_3Cat$ is more downfield than that of $Ph_3PO\rightarrow SbAr^F{}_3Cat$, these UV-vis titration results indicate that Lewis acidity measurements based on the simple measurement of the ^{31}P NMR chemical shift of a coordinated phosphine oxide can be inaccurate.[16] A more general conclusion of these experiments is that the Lewis acidity of stibines is readily enhanced by oxidization with *ortho*-chloranil.

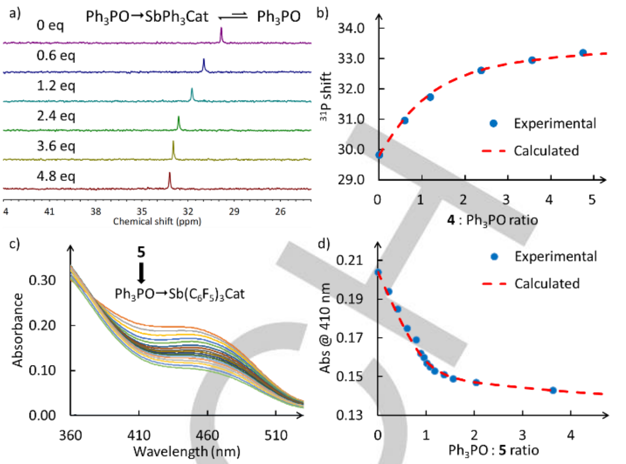

Figure 4. a) Spectral changes in the ^{31}P NMR spectra of Ph_3PO (1.47 × 10^{-2} M) in $CDCl_3$ observed upon incremental addition of $SbPh_3Cat$ (**4**). b) The experimental and the calculated 1:1 binding isotherm for **4** and Ph_3PO based on the ^{31}P NMR chemical shifts. The data were fitted with K = 120 ± 20 M^{-1}, $\delta(Ph_3PO)$ = 29.8 ppm, $\delta(Ph_3PO\rightarrow SbPh_3Cat)$ = 33.6 ppm. c) Spectral changes observed in the UV-Vis absorption spectra of $Sb(C_6F_5)_3Cat$ (**5**) (5.34 × 10^{-4} M) upon addition of Ph_3PO (5.10 × 10^{-2} M) in $CHCl_3$. d) The experimental and the calculated 1:1 binding isotherm for **5** and Ph_3PO based on the UV-vis absorbance at 410 nm. The data were fitted with K = 3 (± 0.8) × 10^4 M^{-1}, ε(**5**) = 382 $M^{-1}cm^{-1}$, $\varepsilon(Ph_3PO\rightarrow Sb(C_6F_5)_3Cat)$ = 275 $M^{-1}cm^{-1}$.

Although stibines **2** and **3** remain unchanged in the presence of Ph_3PO, formation of adducts appear to take place in hexanes, a solvent of lower polarity. Addition of stibine **2** and **3** to a solution of Ph_3PO in hexanes triggers a downfield shift of the ^{31}P NMR signal from 23.4 ppm to 28.5 ppm in the case of **2** and 28.4 ppm in the case of **3**. Crystals of $Ph_3PO\rightarrow Sb(C_6F_5)_3$ were obtained by cooling a pet ether (40-60) solution to −20°C, comfirming the molecular structure of the proposed adduct.[14] The crystal structure of $Ph_3PO\rightarrow Sb(C_6F_5)_3$ confirms the presence of an interaction between the antimony center and the oxygen of the phosphine oxide in the solid state. The oxygen atom is positioned *trans* to the C1 carbon atom (∠O1-Sb-C1 = 164.8°) suggesting alignment of an oxygen lone pair with the σ-hole or σ* orbital of the Sb-C1 bond. The Sb1-O1 distance of 2.628(4) Å is well within the sum of the van der Waals radii of the two elements (ΣR_{vdW}(Sb,O) = 3.97 Å)[17], consistent with the presence of a secondary interaction. These structural results constitute the first crystallographic verification that $Sb(C_6F_5)_3$ is a pnictogen bond donor[11b,11c] or an antimony(III) Lewis acid. These structural results are corroborated by a natural bond orbital (NBO) analysis[18] of the adduct. This analysis describes the Sb-O linkage as a lp(O)→σ*(Sb-C) donor-acceptor interaction of E_{del} = 15.6 kcal/mol (Figure 5). This adduct also appears to also be stabilized by an arene-perfluoroarene interaction involving the phenyl ring containing C31 and the pentafluorophenyl ring containing C13 and whose centroids are separated by 3.58 Å. The presence of this interaction indicates that **2** also possesses π-acidic properties.

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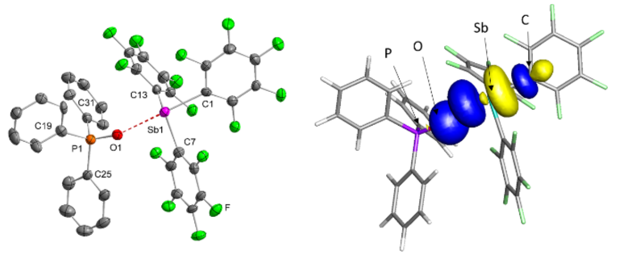


Figure 5. Left: The structure of $Ph_3PO{\rightarrow}Sb(C_6F_5)_3$ in the crystal. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sb1-O1 = 2.628(4), P1-O1-Sb1 = 161.2(2), O1-Sb1-C1 = 164.8(2). Right: Principal lp(O)→σ*(Sb-C) NBO donor-acceptor interactions found in the adduct. Isovalue = 0.05.

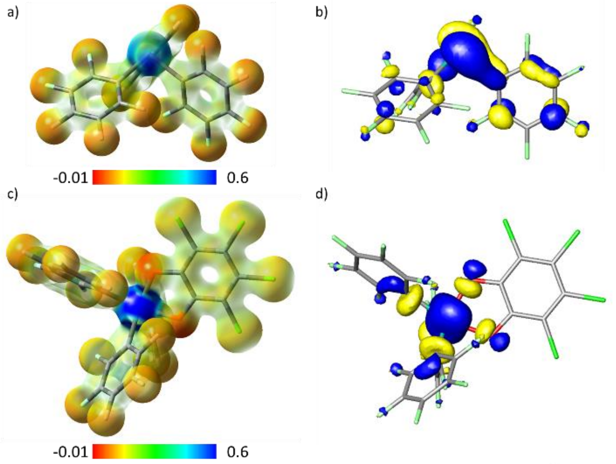


Figure 6. Electrostatic potential map (isovalue = 0.05) and LUMO contour plot (isovalue = 0.05) of **2** (a, b) and **5** (c, d).

We propose that the higher Lewis acidity observed for the stiboranes results from a deepening of the σ-hole and a lowering of the antimony-centered σ* orbitals upon oxidation of the antimony atom (Figure 2). Such effects are illustrated in Figure 6 for **2** and **5**. Comparison of the electrostatic potential maps of these two compounds show a greater development of positive character at the antimony center of **5** illustrating the above mentioned deepening of the σ-hole. We also note that while both compounds feature directional σ* orbitals, that of **5** (-2.65 eV) is significantly lower in energy than that of **2** (-1.76 eV), in line with its higher Lewis acidity. As shown in Table 1, a lowering of the LUMO energy is also observed upon conversion of **1** into **4,** and **3** into **6**. Using fluoride ion affinity (FIA) as a computational probe of Lewis acidity, our calculations reveal that oxidation of the stibines into their corresponding stiboranes raises their FIA by 110-150 kJ/mol.

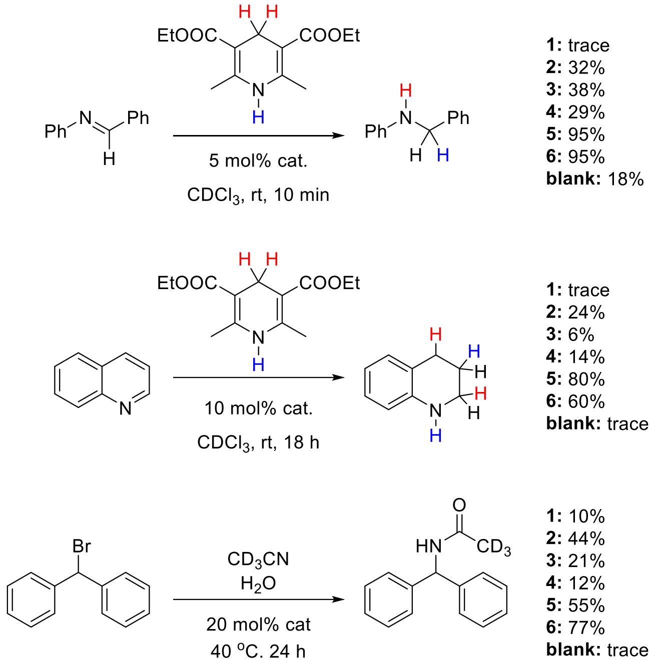
Table 1. Calculated gas phase fluoride ion affinities and LUMO energies of the Lewis acids.

Compound	FIA (kJ/mol)	LUMO (eV)
1	248	-0.55
2	374	-1.76
3	365	-1.90
4	398*	-1.62
5	485*	-2.65
6	497*	-2.68

*Isomers are present of the fluoride adducts of **4**-**6**. The values reported here are based on the most thermally stable isomer. See SI for further details.

The next step of our study was to determine whether these derivatives can be used to catalyze organic transformations, and whether the Lewis acidity trend derived from the above titration experiments and calculations could also be reflected kinetically (Scheme 1). We first tested these compounds as catalysts for the transfer hydrogenation reaction known to occur between Hantzsch ester and *N*-benzylideneaniline.[19] This reaction was carried out in $CDCl_3$, with a 5 mol% catalyst loading. We found that the most Lewis acidic perfluorinated stiboranes **5** and **6** afforded an almost quantitative yield of the amine product after 10 min while **1** was essentially inactive. The non-fluorinated stiborane **4** proved to be significantly less active than **5** and **6**, leading to a 29% yield after 10 min. This yield is in fact comparable to that obtained with the perfluorinated stibines **2** and **3**. A comparable trend was found when these antinomy derivatives were used for the hydrogenation of quinoline using Hantzsch ester, with **5** and **6** displaying the highest performance (80% and 60%, respectively). We also probed the use of these compounds as catalysts for the formation of *N*-benzhydryl acetamide by reaction of diphenylbromomethane with acetonitrile and water.[20] Consistent with the trend established in the transfer hydrogenation reactions, the perfluorinated stiboranes showed the highest activity; however, the difference in reactivity observed with the fluorinated stibines, in particular **2**, was a lot less pronounced. We also note that the reaction catalyzed by the non-fluorinated derivatives **1** and **4** showed accumulation of the hydrolysis product diphenylmethanol. Altogether, the catalytic activity of these antimony compounds correlates well with their experimentally-determined Lewis acidity as well as with the computed LUMO energy. A last important point of discussion concerns the unusually elevated activity of **2** in all three reactions, and especially in the Ritter-like reaction involving diphenylbromomethane. Given that the antimony-centered Lewis acidity in **2** is much lower than that in **5** and **6**, we believe that the commendable performance of this stibine results in part from the π-acidic properties of the C_6F_5 substituents, as seen in the structure of $Ph_3PO{\rightarrow}Sb(C_6F_5)_3$. We speculate that these π-acidic properties help acidify the electrophilic reagents involved in these reactions thus augmenting the catalytic properties of this simple fluorinated stibine.[21]

Scheme 1. Transfer hydrogenation of *N*-benzylideneaniline and quinoline, and Ritter-like reactions showing yields when compounds **1**-**6** are used as catalysts.



The results presented herein show that the Lewis acidity of pnictogen bond donor based on organoantimony is notably enhanced by oxidation to the +V state, a conclusion that parallels that drawn in the case of iodine(III) halogen bond donors.[22] Our analyses indicate that this Lewis acidity increase originates from a lowering of the antimony centered σ^* orbital as well as a deepening of the σ-hole. These two effects, which respectively capture the covalent and electrostatic nature of the interaction formed between the antimony Lewis acid and the incoming Lewis base, are manifested in the binding constants obtained when these organoantimony compounds complex with Ph_3PO. The same effects also readily enhance their catalytic properties in transfer hydrogenation and Ritter-like reactions when the antimony is in the +V state. Finally, the work described herein illustrates the duality that connects the orbital-based and σ-hole-based descriptors of Lewis acidity in a way that mirrors the continuum existing between covalent and ionic bonding extremes.

Experimental Section

The experimental procedures are provided in the Supplemental Information.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: antimony • Lewis acids • σ-hole • transfer hydrogenation • molecular recognition

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[14] CCDC 1857184 (**6**) and 1857185 ($Ph_3PO \rightarrow Sb(C_6F_5)_3$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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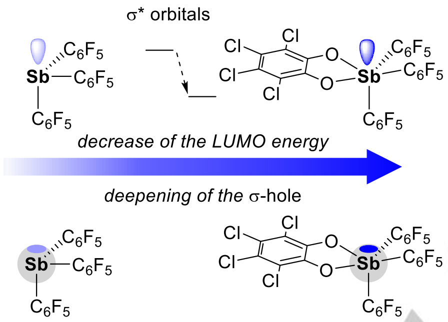
COMMUNICATION

Taking a dig at the σ-hole! Oxidation of organoantimony derivatives from the +III to the +V state leads to a more pronounced σ-hole on antimony making these main group compounds better pnictogen bond donors or better Lewis acids. These results, which can be rationalized using orbital-based arguments, define a new strategy for tuning the magnitude of pnictogen bonding with applications in catalysis.



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Digging the σ-hole of organo-antimony Lewis acids via oxidation