

PRF Grant Number: 56871

Project Title: Activation of Carbon Dioxide with Antimony Lewis Acids

Program ND

Principal Investigator: Dr. François P. Gabbaï

In this second year of the this award, we have continued to investigate the synthesis and properties of main group Lewis acids with the view of using these new derivatives for the activation of CO₂. Because none of the compounds we obtained proved to be adapted to the activation of CO₂, we chose to focus our work on other small molecules including isocyanates. As part of this effort, we have synthesized the triflate salts of a series of tetraarylstibonium cations of general formula [ArSbPh₃]⁺ with Ar = Mes (**1**⁺), *o*-(dimethylamino)phenyl (**2**⁺), and *o*-((dimethylamino)methyl)phenyl (**3**⁺) (Fig. 1).¹ When used as catalysts for the reactions of isocyanates with oxiranes, we found that the catalytic efficiencies of **2**⁺ and **3**⁺ are affected by the presence of an ancillary amino donor which quenches the Lewis acidity of the antimony center. Stibonium cations that lack an adjacent donor group proved to be more active, leading to the predominant formation of the 3,4-oxazolidinones (**A**). Out of these studies, [MesSbPh₃]⁺ emerged as the most selective catalyst, a property that is correlated to the bulk of the mesityl substituent and the sterically crowded nature of the Lewis acidic antimony center.

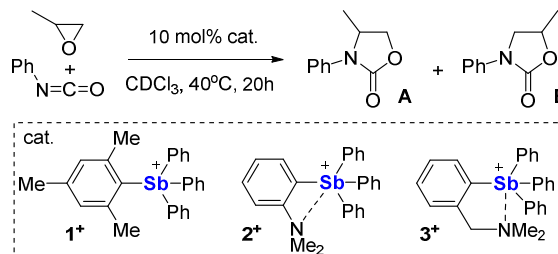


Figure 1

To more broadly probe the potential that antimony Lewis acid hold as catalysts, we decided to investigate a family of antimony (III) and antimony (V) Lewis acids bearing fluorinated aryl substituents. The objective of this study, which involved derivatives such as Sb(C₆F₅)₃ (**4**) and Sb(C₆F₅)₃(*o*-O₂C₆Cl₄) (**5**), was to assess the influence of oxidation on the Lewis acidic properties of the antimony center (Fig. 2). Computational studies showed that oxidation lowers the energy of the antimony-based accepting σ* orbital and “deepens” the associated σ-hole.² These changes are manifested experimentally by an increase in the stability constant of the Lewis adducts that these antimony derivatives form with Ph₃PO. Although the adduct formed by **4** with this phosphine oxide is labile in solution, it could be crystallized from petroleum ether solution at -20 °C. A single crystal X-ray diffraction analysis provided unambiguous evidence for the coordination of the oxygen atom to antimony, thus confirming that Sb(C₆F₅)₃ is indeed Lewis acidic (Fig. 2). To complement these studies, we have also tested the use of these fluorinated antimony compounds as catalysts for organic reactions including transfer hydrogenation and Ritter-like reactions. Again, we found that the oxidized antimony compounds are more potent catalysts, thus corroborating the results obtained in the phosphine oxide binding studies.

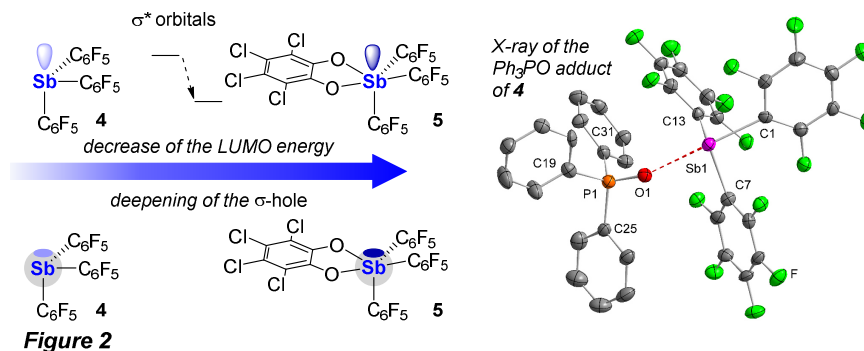


Figure 2

To understand if cooperative effects could arise when two Lewis acidic moiety are positioned in proximity to one another, we have investigated the synthesis of bifunctional antimony(V) Lewis acids.³ The scope of these studies was expanded to also include related boron-based derivatives such as 1,8-bis(dimesitylboryl)biphenylene (**6**) and 1,8-bis(dimesitylboryl)tritycene (**7**) (Fig. 3).⁴ We first surveyed

the properties of these compounds using cyclic voltammetry and single crystal X-ray diffraction, which showed that **6** is more electron deficient than **7** while also displaying a boron–boron separation (4.566(5) Å) shorter by ~ 1 Å than that in **7** (5.559(4) Å). These differences appear to dictate the coordination behavior of these two compounds. While **7** remains inert toward hydrazine, we observed that **6** forms a very stable $\mu(1,2)$ hydrazine complex which can also be obtained by phase transfer upon layering a solution of **6** with a dilute aqueous hydrazine solution. The stability of this complex is further reflected by its lack of reaction with benzaldehyde at room temperature. We have also investigated the behavior of **6** and **7** toward anions. In MeOH/CHCl₃ (1/1 vol) both compounds selectively bind cyanide to form the corresponding $\mu(1,2)$ chelate complexes with a B–C \equiv N–B bridge at their cores. Competition experiments in protic media show that the anionic cyanide complex ($[\mathbf{6}\text{-}\mu_2\text{-CN}]^-$) formed by **6** is the most stable, with no evidence of decomplexation even in the presence of B(C₆F₅)₃. These two diboranes are highly selective for the cyanide anion, at least in MeOH/CHCl₃, a medium in which no reaction is detected with the fluoride anion. However, we observed that **6** quickly underwent a base-promoted hydrolysis when mixed with TASF (tris(dimethylamino)sulfonium difluorotrimethylsilicate) in wet THF. Work-up of the product in the presence of an aluminum(III) salt as a fluoride scavenger afforded the bifunctional borane/borinic acid derivative **8** (Fig. 3).⁵ We observed that **8** readily binds a fluoride anion by formation of a unique B–F \cdots H–O–B hydrogen bond (see structure of $[\mathbf{8}\text{-F}]^-$ in Fig. 3). This hydrogen bond is characterized by a short H–F distance of 1.79(3) Å and a large coupling constant ($^1J_{\text{HF}}$) of 57.2 Hz. The magnitude of this interaction, which has also been investigated computationally, augments the fluoride anion binding properties of **8**, thus making it compatible with aqueous environments. These results also illustrate the potential that borinic acid functionalities hold as molecular recognition units for anions and electron rich substrates.

In addition to generating a total of 8 publications, this grant has benefited the education of a dynamic group of students including Chang-Hong Chen who obtained his Ph.D. in summer 2018 and who is now employed by Intel. Another student, Mengxi Yang defended her Ph.D. thesis on Oct. 12, 2018 and will graduate at the end of the term.

References

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3. Chen, C.-H.; Gabbai, F. P. "Coordination of a stibine oxide to a Lewis acidic stiborane at the upper rim of the biphenylene backbone" *Dalton Transactions* **2018**, 47, 12075-12078.
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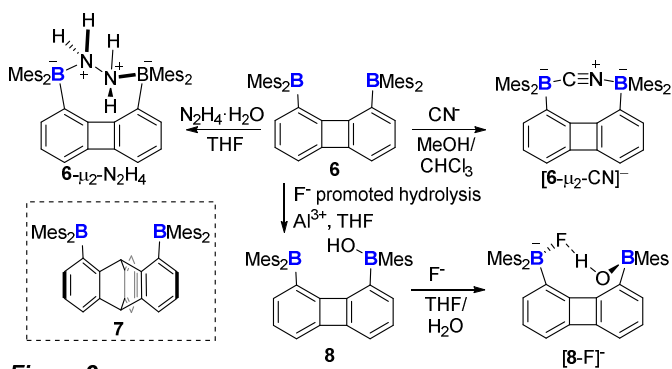


Figure 3