Main Group Oxygen-Atom Transfer Reagent: Investigating μ-Oxo-Bridged Binuclear Compounds for Catalytic Oxidation Reactions

THE UNIVERSITY OF TEXAS AT ARLINGTON

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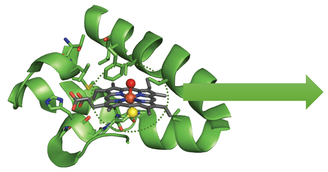
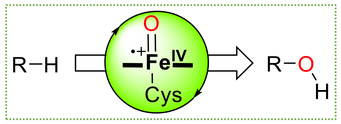
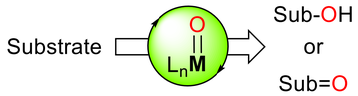
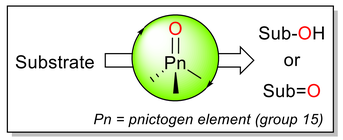
INTRODUCTION



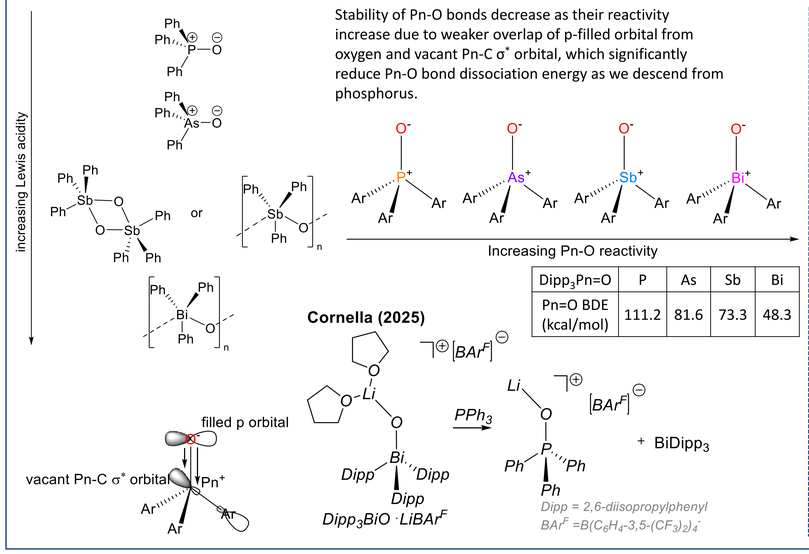




M *= V, Cr, Mn, Fe, Co, Ni, Cu, Mo, Ru, Rh ...*

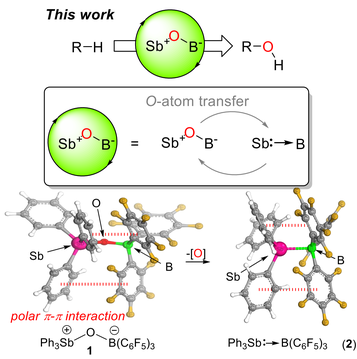


Oxygen-atom transfer is a critical process in both biological and chemical systems. Recent developments suggest that heavy pnictogen oxides such as antimony oxides can become a promising oxygen-atom transfer agent. However, monomeric Sb=O bonds present stabilization and reactivity challenges. To overcome these, bulky substituents and Lewis acids are utilized. We propose that $(C_6H_5)_3SbOB(C_6F_5)_3$ (**1**), a μ-oxo-bridge binuclear compound, can promote oxygen transfer through a Lewis pair interaction mechanism.



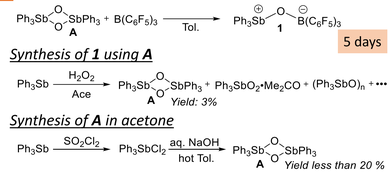
Stability of Pn-O bonds decrease as their reactivity increase due to weaker overlap of p-filled orbital from oxygen and vacant Pn-C σ* orbital, which significantly reduce Pn-O bond dissociation energy as we descend from phosphorus.

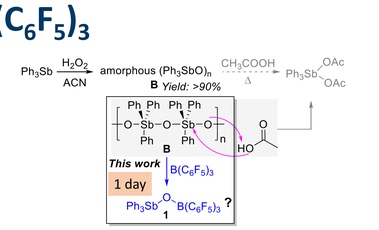
Dipp$_3$Pn=O	P	As	Sb	Bi
Pn=O BDE (kcal/mol)	111.2	81.6	73.3	48.3



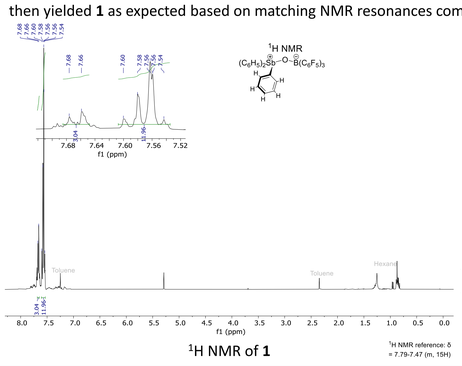
This research examines the compound's electronic structure as well as reactivity, with the focus on improving its oxygen-transfer efficiency. We evaluate its oxygen-atom transfer capability by reacting with triphenyl phosphine, while its reversible interaction with water indicates that it remains stable even in previously incompatible conditions. This flexibility creates new pathways to explore its effectiveness across diverse reaction environments.

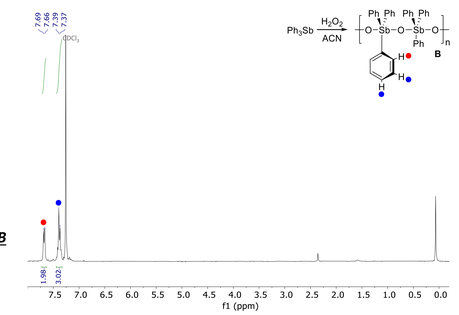
SYNTHESIS OF $Ph_3SbOB(C_6F_5)_3$





Attempts were made to obtain compound **1**. Previous studies suggested by treating **A** with BCF over 5 days, the desired product would be obtained. However, multiple efforts to synthesize **A** seemed unproductive. We hypothesized that **B** would be the perfect alternative due to similar structure. Treatment of **B** with BCF then yielded **1** as expected based on matching NMR resonances compared to previous literatures.

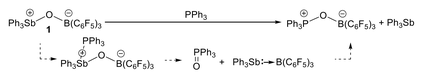


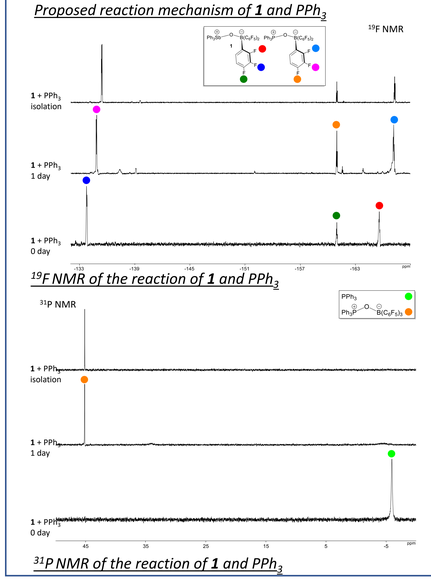


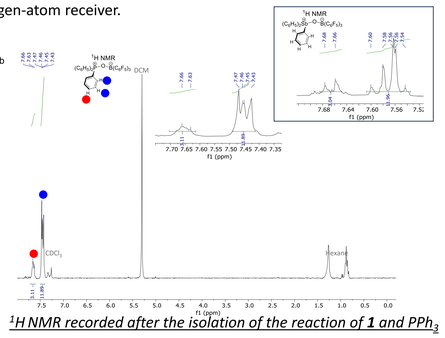
Reported crystal structure of **1** obtained from previous journal CCDC registration number 1045571

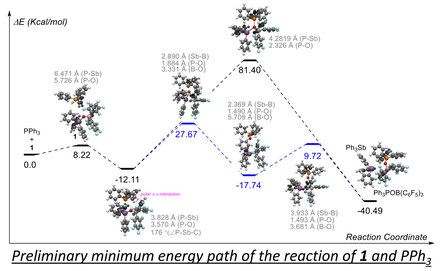
OXYGEN ATOM TRANSFER REACTIVITY

Inspired by previous literatures, attempts to replicate similar oxygen-atom transfer reactions was conducted by utilizing PPh_3 as an oxygen-atom receiver.





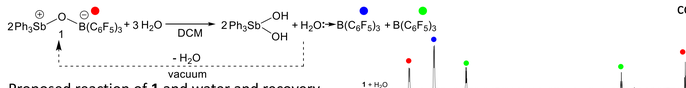


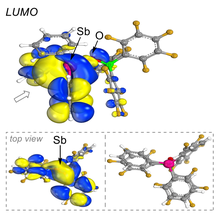


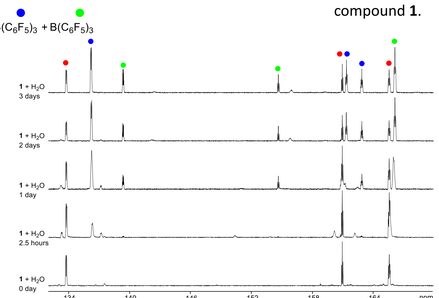
After 1 day, NMR reports suggest conversion to a new species upon treatment of **1** with PPh_3. Preliminary computational data supports the formation of a new species based on a lower energy level.

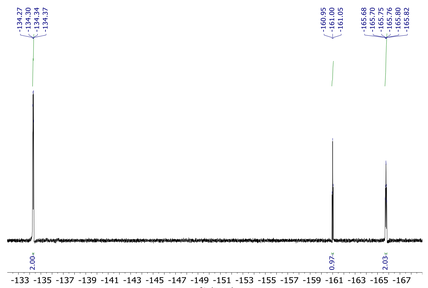
STABILITY OF $Ph_3SbOB(C_6F_5)_3$ IN WATER

Experiments were carried out to assess stability of **1** in volatile solvents, particularly water. This would further enhance our understanding on the nature of **1** as well as fully comprehend its capability. After evaporating the reaction for 4 days, a mixture of species reverted back to the original compound **1**.









Conclusion

We successfully replicated the synthesis of **1** using the amorphous triphenyl antimony oxide instead of the dimeric one. Upon acquiring it, efforts to further understand its stability in volatile environments were made. Additional studies will be instituted to reinforce our knowledge on the nature of the Sb-O-B oxo-bridge in different reacting conditions and different substrates to better the oxygen-atom transfer process. Moreover, we will also study its catalytic properties in a variety of oxidation processes.

References

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