

A Dicationic Bismuth(III) Lewis Acid: Catalytic Hydrosilylation of Olefins



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Invited for the cover of this issue is Ajay Venugopal from the Indian Institute of Science Education and Research Thiruvananthapuram. The cover image shows dication $[\text{Tp}^{\text{Me}_2\text{Bi}}]^{2+}$ catalyzing olefin hydrosilylation under mild conditions.

Is your current research mainly curiosity-driven or rather applied?

"I have no special talents. I am only passionately curious" – Albert Einstein. Yes, our research is largely curiosity-driven, but we do not shy away from the applications that show up. We explore the chemistry of reactive p-block compounds, pushing their limits of electrophilicity. Curiosity drives us to design synthetic routes to access low-coordinate electrophilic compounds. Such compounds are expected to exhibit remarkable Lewis acidic catalytic activity.

What prompted you to investigate this topic?

Bismuth, a non-hazardous element located in the neighborhood of toxic heavy elements, offers the opportunity to explore the reactivity of heavy metal cations. Our investigations on electrophilic bismuth compounds led us to quantify Lewis acidity of organobismuth cations (*Inorg. Chem.*, **2017**, 56, 9391–9395). While we could experimentally quantify Lewis acidity at a single electrophilic site, we were unable to isolate a reactive bismuth cation. Our intuition, enhanced by collaborative theoretical investigations, led us to arrive at the tridentate tris(pyrazolyl)borate ligand for trapping this bismuth cation leading to three electrophilic sites on bismuth. Lewis acids with multiple electrophilic sites are rarely isolated.

What is the most significant result of this study?

While bismuth compounds have been used in stoichiometric amounts as Lewis acids in a wide range of organic transformations, examples of highly reactive compounds that can be employed in catalytic amounts are rare. Molecular and electronic understanding of such reactive bismuth species, and hence their application in Lewis acid catalysis, is not well developed. Isolation of a tricoordinate bismuth dication with a weakly coordinating counter anion in a weakly nucleophilic solvent system is the crucial part of this study. The highly reactive bismuth dication has proved to be a good catalyst for olefin hydrosilylation.

What future opportunities do you see in the light of the results presented in this paper?

Our exploration on this bismuth dication has provided a glimpse of how "soft" bismuth can be made to exhibit hard electrophilic properties. $[\text{Tp}^{\text{Me}_2\text{Bi}}]^{2+}$, bearing di-positive charge and possessing a large vacant coordination sphere, offers an

opportunity to explore its possible role in the activation of inert chemical bonds. We see a larger picture evolving in the chemistry of main group elements, following the degree of control achieved here in stabilizing dications.

How did the collaboration on this project start?

Our collaboration with the computational group started by a chance meeting at Thiruvananthapuram airport on the September 30th, 2016. The synergy of theory and experiment has witnessed "the best of both worlds" and continues in many levels today. We express our gratitude to Manoj Vasudevan for creating the cover picture.



Front Cover
Ajay Venugopal et al.
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