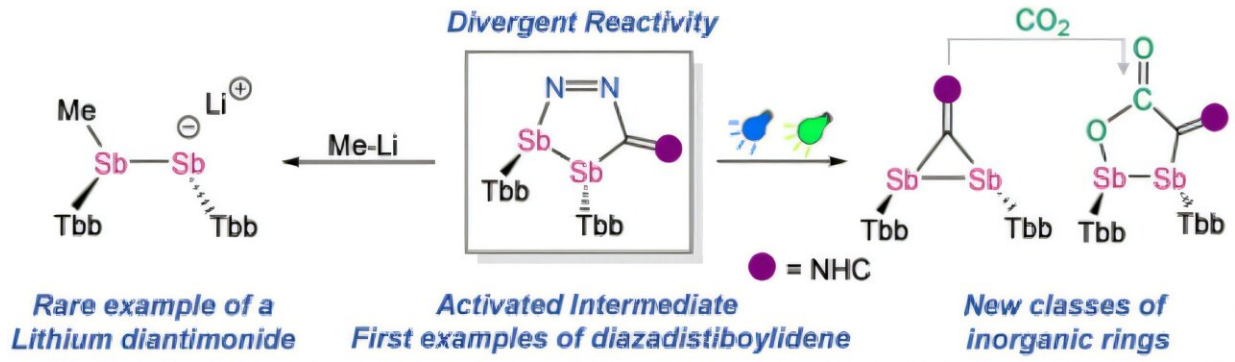
Heavy dipnictogen chemistry: Researchers create heterocycles with more than one antimony atom

January 16 2025, by Bob Yirka



Credit: *Journal of the American Chemical Society* (2025). DOI: 10.1021/jacs.4c15626

An international team of chemists has successfully created methylenedistibiranes, which are three-membered rings that have two antimony atoms and one carbon atom. In their paper published in the *Journal of the American Chemical Society*, the group describes how they were able to make the rings using just a three-step process.

Methylenedistibiranes are generally used as intermediaries due to their ability to promote selective nucleophilic substitution, resulting in the creation of diantimonyl anions. Chemists have been wanting to be able to

create them because it is difficult to use natural elements due to orbital overlap. The achievement by the team is noteworthy because making similar rings with heavier pnictogen elements like antimony and bismuth has proven to be challenging due to changes in orbital overlap trends and energies.

To create the three-membered rings, the research team first synthesized diazadistiboylidenes using [3+2]-cycloaddition between distibene and diazoolefins, which are five-membered rings that have dual antimony, nitrogen and carbon atoms. The resulting stiboylidene served as an intermediary to promote the substitution of a species with bonds formed during donation of electron pairs. The researchers note that it was a surprise to them that the reaction worked as well as it did, since there are few examples of small ring formation with more than one antimony atom.

The researchers next created a reaction between methyllithium and the diazadistiboylidenes, which resulted in the production of an Sb–Sb negatively charged ion—which they describe as a rare example of a diantimonyl anion. They then used X-ray crystallography to crystallize and then characterize the anion. That was followed by showering the resulting diazadistiboylidenes with visible-light radiation, which resulted in the creation of the three-membered-ring methylenedistibiranes.

The researchers note that once created, the methylenedistibiranes were stable, which they describe as extraordinary. They also note that one of them was found to react with carbon dioxide, resulting in the creation of a five-membered ring that had dual antimony, carbon and oxygen atoms.

They suggest their work could set the stage for the development of heavy dipnictogen chemistry, which they note shows that diazoolefins, when exposed to light can be used to create previously heavy heterocycles, and also to serve as a means for promoting CO_2 activation. The research

team plans to continue their work, looking to make rings with heavier pnictogens.

More information: Prasenjit Palui et al, Combining Distibene, Diazoolefins, and Visible Light: Synthesis and Reactivity of Inorganic Rings, *Journal of the American Chemical Society* (2025). DOI: 10.1021/jacs.4c15626