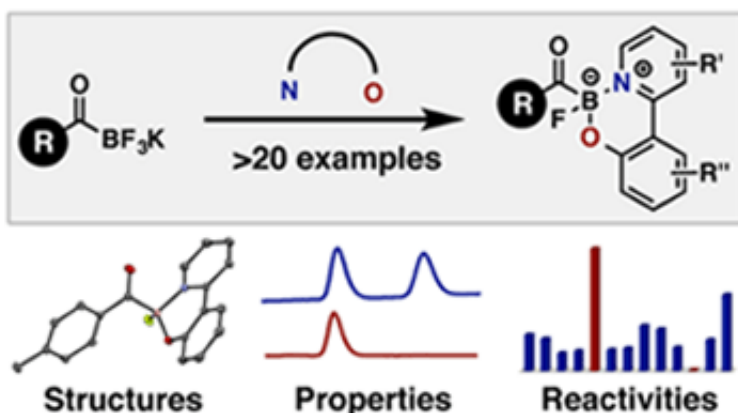


New class of monofluoro acylboronates that is stable in air and water

March 6 2015, by Heather Zeiger



(Phys.org) —Boron is the ambivert of atoms. Technically classified as a metalloid, boron can undergo organic reactions, forming covalent bonds like carbon, but it can also form ions resulting in metal-like bonds. Several studies have exploited both of these properties of boron to isolate acylborons, by coordinating the boron to a ligand, similar to a metal-ligand interaction.

Hidetoshi Noda and Jeffrey W. Bode of the Department of Chemistry and Applied Biosciences at ETH Zurich report in the *Journal of the American Chemical Society* a series of acylborons and determined a new class of bidentate ligands that when the acylborons are coordinated,

makes acylboronate compounds that are stable in air, water, and [silica gel](#). These coordinated acylboronates react with hydroxylamines more readily than their potassium acyltrifluoroborate (KAT) analogs to produce amides. Additionally, this is the first B-chiral acylboronates that are reported in the literature.

Noda and Bode began by investigating various candidates for the ligand base structure. Their goal was to find a ligand that would produce an acylboronate that was air and water stable and could be purified using silica gel. Additionally, prior studies and laboratory investigations with various ligand candidates indicated that the best ligand for stabilizing acylborons would form a six-membered ring with the [boron](#) atom. They eventually landed on a pyridine/phenol core structure.

Using X-ray crystallography, Noda and Bode confirmed that the optimum ligand for coordinating to the boron to form a monofluoro acylboronate was a ligand in which the pyridine nitrogen and the phenol oxygen coordinated with the boron to form a tetravalent, monofluoro boron species. Based on metal catalyzed reactions, they assumed that varying the substituents on the ligand would affect the reactivities and properties of the acylboronates.

They used a relatively straight-forward synthesis to form acylboronates, and found that substitution on the pyridine or on the phenol portion of the ligand affected the compound's stability.

NMR and X-ray crystallography confirmed that boron is likely tetrasubstituted in each of the acylboronate compounds. Analysis of boron's bond angles indicated sp^3 hybridization, thus making a stable tetrahedral orbital arrangement. Additionally, X-ray structure showed that the boron is chiral. Enantiomers were separated using a reverse phase HPLC column and it was determined that the enantiomers were configurationally stable. The authors report that this is the first time that

a group has reported an X-ray structure of B-chiral acylboronate.

Noda and Bode observed that despite the differing stabilities of their compounds, their various acylboronates all formed amides with an O-carbamoylhydroxylamine. However, the acylboronates had differing reactivities which was a direct consequence of the [ligand](#) structure. The different reactivities allowed the authors to deduce a reaction scheme for amide formation and deduce that the boron to nitrogen bond properties played a role in the acylboronate's reactivity.

Overall, the authors were able to synthesize a series of acylboronates using a relatively straight forward one-step synthesis from aromatic KATs that is scalable. They also identified a novel class of ligands for fine-tuning the properties and reactivities of the respective acylboronates. They were also the first to characterize B-chiral acylboronates.

More information: "Synthesis of chemically and configurationally stable monofluoro acylboronates: Effects of ligand structure on their formation, properties and reactivities", *Journal of the American Chemical Society*, [DOI: 10.1021/jacs.5b00822](https://doi.org/10.1021/jacs.5b00822)

Abstract

The recent disclosures of two classes of acylborons - potassium acyltrifluoroborates (KATs) and MIDA acylboronates - demonstrated that certain acylboron species can be both remarkably stable and uniquely reactive. Here we report new classes of ligands for acylboronates that have a significant influence on the formation, properties and reactivities of acylboronates. Our systematic investigations identified a class of neutral, monofluoroboronates that can be prepared in a one step, gram scale fashion from readily accessible KATs. These monofluoroboronates are stable to air, moisture, and silica gel chromatography and can be easily handled without any special

precautions. X-ray crystallography, NMR spectroscopy, and HPLC studies showed that they are tetravalent, configurationally stable B-chiral acylboronates. Significantly, the ligands on the boronate allow for fine-tuning of the properties and reactivity of acylboronates. In amide-forming ligation with hydroxylamines under aqueous conditions, a considerable difference in reactivity was observed as a function of ligand structure. The solid state structures suggested that subtle steric and conformational factors modulate the reactivities of the acylboronates.

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