

Polyhedral Dicarboraboranes Driven Organocatalysis

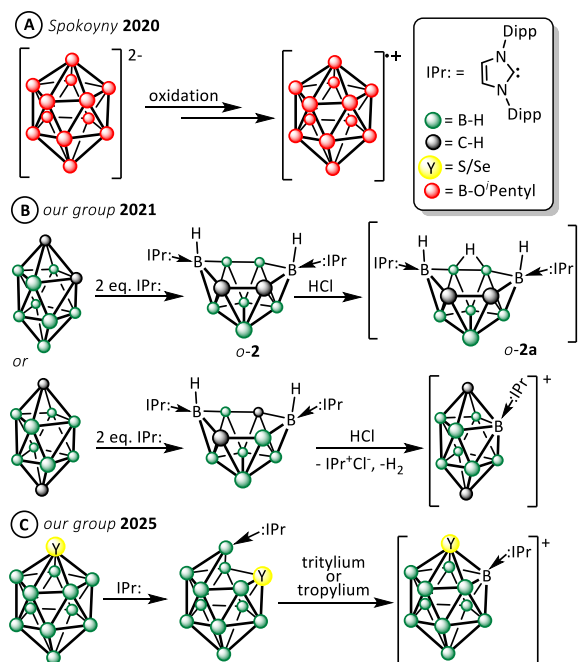
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It is extremely rare to find boron cluster compounds occupying positively charged regions within molecular structures. With few exceptions—where the positive charge resides on the organic or inorganic shell surrounding the inner (hetero)boron cluster—no examples of such cationic clusters were known before 2020, when Spokoyny's seminal report on peralkoxidated radical cation $[B_{12}(OR)_{12}]^+$ was disclosed (Scheme A). Inspired this strategy, we introduced adjacent electron density to ten-vertex dicarbaboranes or twelve-vertex chalcogena-boranes via *N*-heterocyclic-carbene coordination, followed by oxidation. The first thermally robust cationic ten-vertex dicarbaboranes (Scheme B) were synthesized through protonation of their bis-carbene adducts using HCl. In parallel, cationic twelve-vertex chalcogenaboranes (Scheme C) were obtained via protonolysis with tropylium or tritylium tetrafluoroborate, followed by *closo*-cluster formation.

The isolation of stable and easily accessible cationic ten-vertex dicarbaboranes with a *nido* structure (Scheme B – **o-2a**) inspired us to explore the reactivity arising from the virtual proximity of antagonistic hydrogen atoms. Ideally, the terminal hydrogen atom could act as a hydride donor, while the bridging hydrogen could serve as a proton source...

The adduct **o-2**, formed by the reaction of *closo*-1,2-dicarbadeceborane(10) with two equivalents of an *N*-heterocyclic carbene, exhibits superbasic properties with proton affinity surpassing that of the parent carbene. It reacts selectively with C-acids, solvents and water, with its reactivity strongly influenced by substrate *pK_a*. **o-2** facilitates various Lewis base-catalyzed transformations—including aldol condensation, the Thorpe reaction, Michael addition and Robinson annulation—with exceptional efficiency rarely observed among polyhedral (car)boranes and compounds of electropositive elements. Moreover, **o-2** effectively catalyzes conjugate additions of 4-substituted pyrazolones to electron-poor olefins, leading to the formation of new stereocenters in high yields with moderate to good diastereoselectivity. Furthermore, **o-2** promotes highly diastereoselective spirocyclization of pyrazolones with dibenzylidene-acetones, affording spiropyrazolones as single diastereomers in high yields.



Aleš Růžička is a professor of inorganic chemistry at the University of Pardubice, Czech Republic. He obtained his Ph.D. at the University of Pardubice in 2001. He spent one year of postdoctoral stay at the University of Sussex, Brighton, UK under guidance of Professor Michael F. Lappert. His research is focused on synthesis, structure and properties of species having electropositive elements decorated by strong donor ligands. In particular, his interests in main group elements such as Mg, Ca, Zn, B, Al, Si, Ge, Sn, Sb and Bi and amidinate/guanidinate ligands and carbene-related species led to findings in catalysis and material science. He published more than 420 articles in e.g., JACS, Angew. Chem. Int. Ed., Nature Communications, ACS Catalysis, which were cited almost 7 000 times. His *h*-index is 41 (based on WoS).