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Preview

The cyclotriborate trianion

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In this issue of *Chem*, Kinjo and Feng report the synthesis of a cyclotriborate trianion ($B_3R_6^{3-}$), a highly charged boron ring system with discrete two-center two-electron bonds. With three contiguous borates, the B_3^{3-} core of the feature compound defies Coulomb's law and represents the first homocyclic boron analog of the ubiquitous cyclopropane. The remarkable stability enabled full characterization and opens new vistas in the field of multiply charged boron ions.

Carbon has a ground state electronic configuration of $1s^22s^22p^2$, whereas boron, carbon's lefthand neighbor, has one electron less with a $1s^22s^22p^1$ ground state configuration. With four valence electrons, neutral carbon readily adopts sp^3 hybridization to make four bonds satisfying its octet, whereas for boron, it has a propensity for sp^2 hybridization and three bonds with a sextet. However, boron can be a chameleon with its desire to complete its octet by accepting an additional substituent to form B^- that is isoelectronic to neutral carbon. The simplest example of this relationship is CH_4 and BH_4^-, which both exhibit tetrahedral geometries but differ in charge (Figure 1A). Methane has relatively inert C−H bonds, but borohydride is a strong hydride donor. While the single central atom examples are prevalent with hydrogen or organic substituents, for higher order species, there have only been successes in diborate analogs of ethane.[1] Rings composed exclusively of borates have been elusive until the disclosure of $B_3Flr_3^{3-}$ (Flr = fluorenyl) by Kinjo and Feng.[2]

In boron chemistry, homoatomic systems readily form electron-deficient clusters rather than rings with discrete two-center two-electron bonds. The main challenge in preparing catenated borates is overcoming the repulsive forces from adjacent charged anions, which often leads to decomposition via Coulombic explosion.[3] The synthetic accomplishment of the borate analog of cyclopropane, $B_3Flr_3^{3-}$, overcomes these hurdles by a three-step route involving aluminum templating and dealumination (key step in Figure 1B). The borate units are supported by borafluorene moieties, anti-aromatic BC_4 rings that play a role in delocalizing the anionic charge away from the boron centers.[4] This clever selection enabled isolation as a potassium salt and crystallization as the crown ether encapsulated variant for full characterization and reactivity studies.

The single crystal X-ray diffraction structure revealed the homocyclic B_3-core with a near equilateral triangle akin to cyclopropanes (B–B–B bond angle range 59.1(2) to 61.6(2)°; Figure 1C). The B–B bond lengths range 1.784(6) to 1.829(6) Å, consistent with classical two-center two-electron $B(sp^3)$–$B(sp^3)$ bonds but much longer than the C–C distances in cyclopropanes (1.50 Å). There are no interactions between the potassium cations and the boron atoms. It is notable that the B–C bond of the BC_4 ring in borafluorenes is susceptible to cleavage but remains intact.[4]

The parent triatomic system, $B_3H_6^{3-}$, had been theoretically analyzed in 2012 as $Mg_3(B_3H_6)_2$, recognizing it as a potential product in the thermal decomposition of $Mg(BH_4)_2$.[5] The following year, a variant of $B_3H_6^{3-}$ bound to three iron 1,2,4-tri(*tert*-butyl)cyclopentadienyl moieties, $(Cp'FeBH_2)_3$, was isolated.[6] The authors implied that free $B_3H_6^{3-}$ is a viable metastable intermediate with predicted B–B bond lengths (1.73–1.82 Å) similar to those observed in $B_3Flr_3^{3-}$, but shorter than in the metal-coordinated $(Cp'FeBH_2)_3$ (1.873(5)–1.896(5) Å). Natural population analyses on $B_3H_6^{3-}$ indicate a negative charge on boron of −0.60, while calculations on $B_3Flr_3^{3-}$ reveal that the fluorenyl substituents delocalize the charge to give the boron atoms a charge of +0.14, accentuating the substituent stabilization.[2] Adaptive natural density partitioning, and natural bond orbital analyses, confirm the presence of three electron-precise two-center two-electron B–B σ bonds.

The isolation of $B_3Flr_3^{3-}$ presents the opportunity to explore its reactivity (Figure 1D). The team investigated reactions with trimethylamine hydrochloride, adamantyl azide, trimethylphosphine gold(I) chloride, and barium iodide. While diverse products were isolated, in all four reactions, species containing two BFlr units were obtained with the third BFlr unit eliminated, revealing the fragility of the B_3-core versus the borafluorene core. Notably, the BaI_2 reaction led to the first compound with a B–Ba bond (**1**) that had been a target for other researchers.[7] The $Me_3PAu(I)Cl$ reaction generated an $\eta^2[FlrB{=}BFlr]^{2-}$ complex featuring $Au(PMe_3)^+$ and $Au(PMe_3)_2^+$ cations above and below the π-bond (**2**). This is the first example where $[R_2B{=}BR_2]^{2-}$ ligand unit binds to two gold centers from opposite faces.[8]

The reactivity studies indicate that extrusion of a BR_2^- unit to access diboron compounds is possible. This is not the case for the reactivity of cyclopropanes but is the microscopic reverse in the cyclopropanation reaction of a carbene and an olefin. The disclosure of the cyclotriborate trianion enables future studies to determine the differences and similarities in reactivity to cyclopropanes. It will be interesting to see whether ring strain can be leveraged in 1,3-ring opening reactions as a potential route to the saturated chain, a boron analog of cyclopropane. Another interesting reaction would be

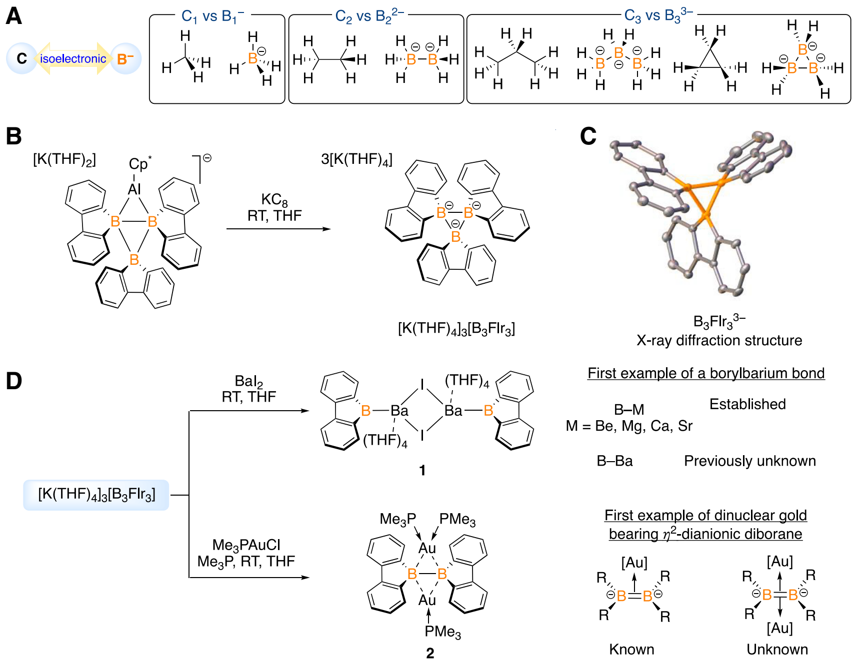

Figure 1. Chemistry of the cyclotriborate trianion

(A) Isoelectronic C_n vs. B_n^- (n = 1, 2, 3) structures.

(B) Synthesis of an isolable cyclotriborate trion, $B_3Flr_3^{3-}$: recent work by Feng and Kinjo (RT = room temperature).

(C) Single-crystal X-ray diffraction structure of $B_3Flr_3^{3-}$ (H and K atoms and THF/crown ethers coordinated to K are removed for clarity).

(D) Reactivity of $[K(THF)_4]_3[B_3Flr_3]$.

investigating whether B–B oxidative addition reactions or ring insertions are possible.

In summary, the initial report of the cyclotriborate trianion by Kinjo and Feng initiates the field of catenated borate rings. While their synthetic route is circuitous and it appears that the cyclotriborate anion was not the initial target, this is commended, as serendipitous discoveries are often the most impactful. Serendipity circumvents one of the major limitations in synthetic chemistry, the belief that unknown molecules that defy historic laws and bonding theories cannot be isolated. In this case, the cyclotriborate trianion that seemingly disobeys Coulomb's law is isolated by installing fluorenes on boron to delocalize the charge. The discovery also poses the question of whether a concise synthesis can be made for a cyclotriborate or if ring sizes greater than three borates can be accessed to generate borate analogs of cyclobutane, cyclopentane, and cyclohexane. In general, this body of work connects the fields of organoborate rings and chains to fundamental cycloalkanes and alkanes.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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