Protonolysis of the $[B(Ar_F)_4]^-$ Anion Mediated by Nucleophile/Electrophile/Water Cooperativity in a Platinum-PMe_2OH Complex

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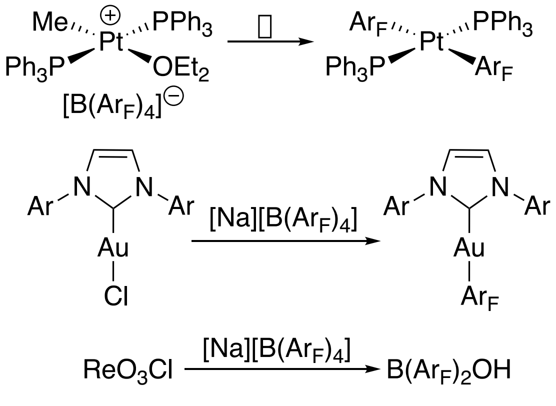
ABSTRACT: The weakly coordinating fluorinated tetraarylborate anion $[B(Ar_F)_4]^-$ (Ar_F = 3,5-$(CF_3)_2C_6H_3$), routinely used to stabilize highly electrophilic cations, is prized for its resistance to decomposition; B–C cleavage requires extremely strong acids. However, cooperation between an electrophilic Pt dication, a nucleophilic PMe_2OH ligand, and the weak acid water resulted in protonolysis of three $[B(Ar_F)_4]^-$ B–C bonds at room temperature. Treatment of $[Pt((R,R)\text{-Me-FerroLANE})(PMe_2OH)][OTf]_2$ (**2**) with water and two equiv of $[Na][B(Ar_F)_4]$ gave three equiv of the arene Ar_FH and the metallacycle $[Pt((R,R)\text{-Me-FerroLANE})(PMe_2OB(Ar_F)O)][B(Ar_F)_4]$ (**4**), via the isolated intermediate metallacycle $[Pt((R,R)\text{-Me-FerroLANE})(PMe_2OB(Ar_F)_2OH)][B(Ar_F)_4]$ (**3**).

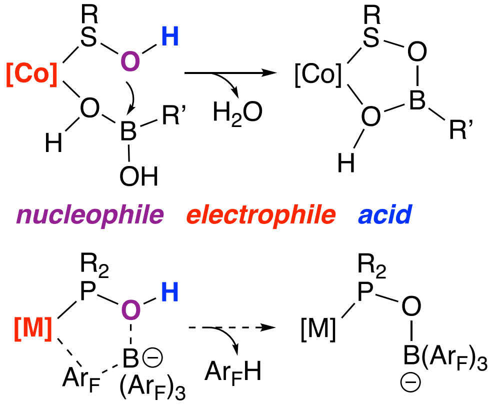
Weakly coordinating fluorinated tetraarylborate anions such as $[B(Ar_F)_4]^-$ (Ar_F = 3,5-$(CF_3)_2C_6H_3$) and $[B(C_6F_5)_4]^-$ are routinely used to stabilize highly electrophilic cations in stoichiometric reactions and in catalysis.[1] Unlike BF_4^- and BPh_4^-, which often decompose by B–F or B–C cleavage, these anions are remarkably robust.[2] For example, $[Na][B(Ar_F)_4]$ did not react with sulfuric acid in methanol even after refluxing for 7 d,[3] and although the oxonium superacid $[H(OEt_2)_2][B(Ar_F)_4]$ decomposed in CD_2Cl_2 to Ar_FH and the borane $B(Ar_F)_3$, the process was slow, with a half-life of about 20 h.[4] Electrophilic metal complexes can also break one or two B–C bonds in $[B(Ar_F)_4]^-$, as observed with platinum[5] or gold cations[6] (Scheme 1).[7] In an example with rhenium, water was proposed to be the source of the B–OH product.[8]

Scheme 1. $[B(Ar_F)_4]^-$ B–C Cleavage by Electrophilic Metal Complexes



We hypothesized that repeated B–C cleavage would occur if boron could be tethered to an electrophilic metal complex via a ligand bearing a pendant nucleophile, so that B–C activation processes would be intramolecular.[9] This strategy was inspired by the use of boronic acids as competitive inhibitors of the enzyme nitrile hydratase, where B-OH coordination to Lewis acidic Co promotes nucleophilic attack of a sulfenic acid ligand at boron and metallacycle formation with loss of water (Scheme 2).[10] The mechanistic similarity between these enzymes and synthetic nitrile hydration catalysts containing phosphinous acid (PR_2OH) ligands suggested that B–C cleavage and protonolysis of $[B(Ar_F)_4]^-$ might occur via similar nucleophile/electrophile/acid cooperation, and the anchored $B(Ar_F)_3$ group would then be available for further metal-mediated hydrolysis.[11]

Scheme 2. Proposed Mechanism of Inhibition of Nitrile Hydratase by Boronic Acids (above), and the Potential for Analogous Cooperative Reactivity by Precursors for Metal-Catalyzed Nitrile Hydration (below)



We report here that this approach led to Pt-mediated $[B(Ar_F)_4]^-$ protonolysis under mild conditions at room temperature with cleavage of three B–C bonds to yield the arene Ar_FH. NMR monitoring of these reactions and the isolation of intermediate and product metallacycles with two or one remaining B–Ar_F groups provided mechanistic information and highlighted the cooperative action of the P-O nucleophile, the Pt electrophile, and water.[12]

Sequential treatment of Pt((*R*,*R*)-Me-FerroLANE)Cl_2 with silver triflate and dimethylphosphine oxide,[13] then more AgOTf, gave formally three-coordinate dication **2** (Scheme 3), which we are investigating as a catalyst for enantioselective nitrile hydration.[14] As in related complexes, Fe→Pt donation in **2** was evident from NMR spectroscopy.[15]

Ion exchange of sparingly soluble [**2**]$[OTf]_2$ with [Li]$[B(C_6F_5)_4]$ generated the highly soluble borate salt [**2**]$[B(C_6F_5)_4]$. In contrast, treatment of [**2**]$[OTf]_2$ with two equiv of [Na]$[B(Ar_F)_4]$ resulted in formation of three equiv of the arene Ar_FH, observed by ^1H and ^{19}F NMR spectroscopy, and metallacycle **4** (Scheme 3). Adding water was not required; residual water in the solvent (CD_2Cl_2 or $C_2D_2Cl_4$) or in commercial [Na]$[B(Ar_F)_4]\bullet xH_2O$ (x ~ 2.5) was sufficient to promote this process.[16] Treatment with water, stirring the mixture, or heating accelerated the process. For example, reaction of a CH_2Cl_2 suspension of [**2**]$[OTf]_2$ with two equiv of undried [Na]$[B(Ar_F)_4]$ and 9 equiv of water at room temperature in air gave **4** after stirring overnight. Instead, drying the solvent and [Na]$[B(Ar_F)_4]$ enabled observation and isolation of an intermediate zwitterionic metallacycle **3**.[17,18]

Multinuclear NMR spectroscopy showed that complex **3** contained two inequivalent BAr_F substituents and an OH group (^1H NMR (CD_2Cl_2): δ 2.84; IR(KBr): 3579 cm^{-1}) which exchanged with D_2O,[18a] with ^{11}B NMR signals for the $[B(Ar_F)_4]^-$ anion (sharp, δ –6.6) and the metallacyclic borate (broad, δ 9.5).[19] The $^{31}P\{^1H\}$ NMR spectrum included signals for the *trans* Me-FerroLANE and PMe_2O groups (J_{PP} = 357 Hz), while the large $J_{Pt\text{-}P}$ coupling (3826 Hz) for the other Me-FerroLANE ^{31}P nucleus was consistent with the weak trans influence of the OH-B ligand.[20] Complex **3** underwent further B–C cleavage in the presence of water with formation of Ar_FH and metallacycle **4**, whose NMR and IR spectra were similar to those of **3**, but indicated that there was only one remaining B-Ar_F group and no B-OH.[21] The Ar_FBO_2 three-coordination was consistent with the ^{11}B NMR spectrum of the cation (broad, δ 32.0).[22] The structures of **3** and **4** were confirmed by X-ray crystallography (Figure 1). The PtPOBO metallacycle structure was similar in both complexes, with distorted square planar Pt, and tetrahedral and trigonal planar geometry at B in **3** and **4**, respectively (see Table S22 in the SI for selected bond lengths and angles).

Scheme 3. Pt-Mediated Protonolysis of the $[B(Ar_F)_4]^-$ Anion

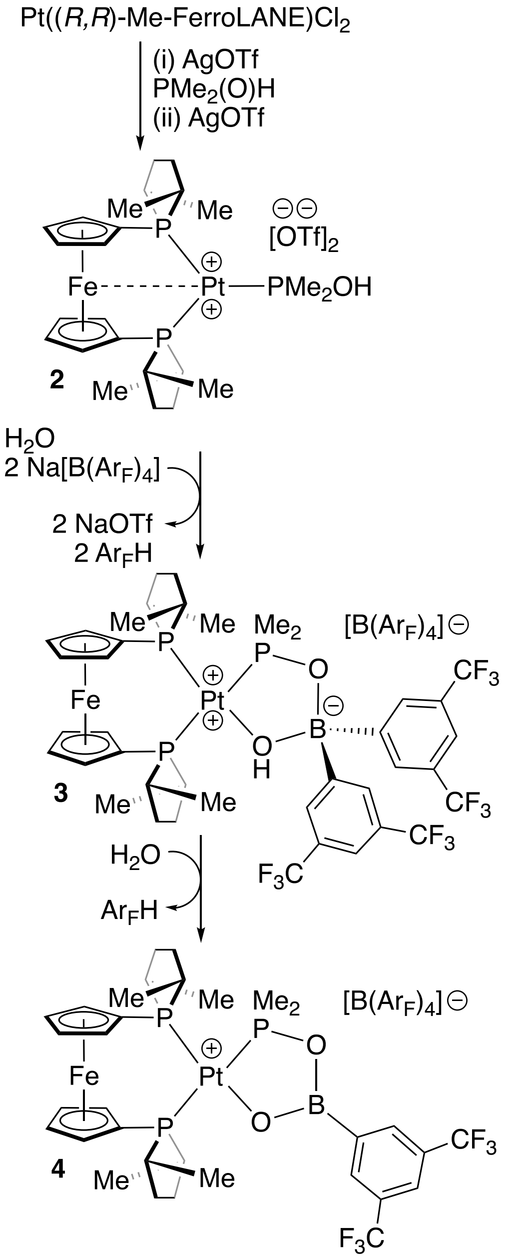
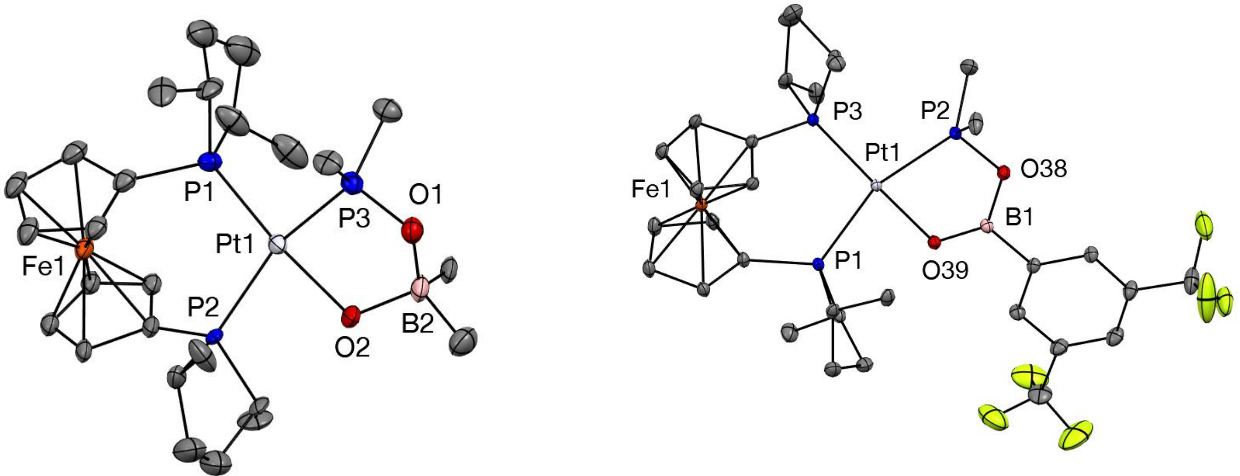
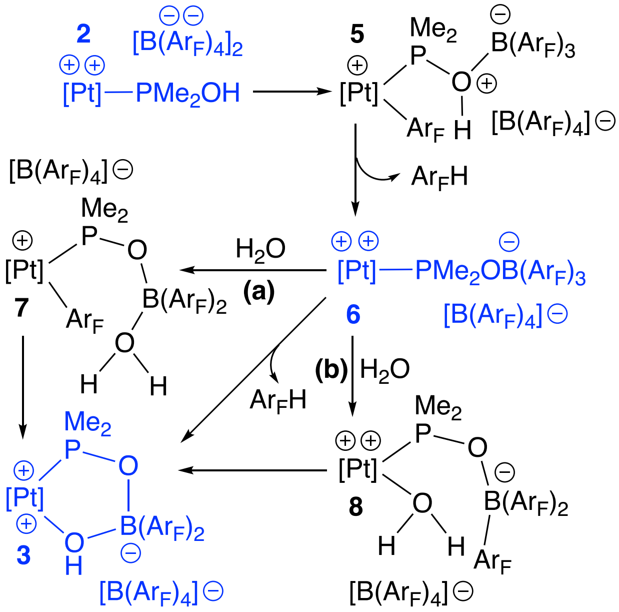


Figure 1. ORTEP diagrams of the cations in **3** (left) and **4** (right), showing only the ipso Ar_F carbons in **3**, with disorder omitted.



Scheme 4 shows a possible protonolysis mechanism for conversion of **2** to **3**, with observed or isolated species in blue and proposed intermediates in black. After triflate/borate anion exchange, B–C cleavage by dication **2**, as in Scheme 1, yields a Pt-$\mathrm{Ar_F}$ group in **5**. O-coordination of the resulting borane acidifies the P-OH group, which protonates the Pt-aryl to yield $\mathrm{Ar_FH}$ and "three-coordinate" **6**, an analog of **2** which could also be stabilized by Fe→Pt donation. Consistent with this idea, the $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum of intermediate **6**, observed under low-water conditions, was similar to that of **2**.[23] Further B–C cleavage and hydrolysis could occur by two possible cooperative mechanisms (Scheme 4): (a) transmetalation of the pendant B-$\mathrm{Ar_F}$ group to Pt, followed by protonolysis mediated by B-coordinated water in **7**,[24] or (b) B-$\mathrm{Ar_F}$ protodeboronation[25] by acidic Pt-bound H_2O in **8**.[26] Further studies will be required to investigate these possibilities, their role in conversion of **3** to **4**, and the generality of the metal-mediated borate protonolysis.

Scheme 4. Possible Mechanisms of Pt-Mediated $[\mathrm{B(Ar_F)_4}]^-$ Protonolysis of **2** to **3** via Observed Intermediate **6** (blue) and Proposed Intermediates **5** and **7-8** (black) [a]



[a] [Pt] = Pt((*R*,*R*)-Me-FerroLANE)

Although the $[\mathrm{B(Ar_F)_4}]^-$ anion is extremely resistant to protonolysis and stabilizes reactive electrophilic cations, these results show that a dicationic Pt electrophile bearing a nucleophilic P-OH group can act cooperatively with the weak acid water to cleave three B–C bonds under mild conditions at room temperature. Such cooperative reactivity of metal-hydroxyphosphine complexes is also valuable in nitrile hydration catalysis,[11] and its further development may offer a general approach to stoichiometric and catalytic activation of normally unreactive substrates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and characterization data (PDF)

X-ray crystallography data (CIF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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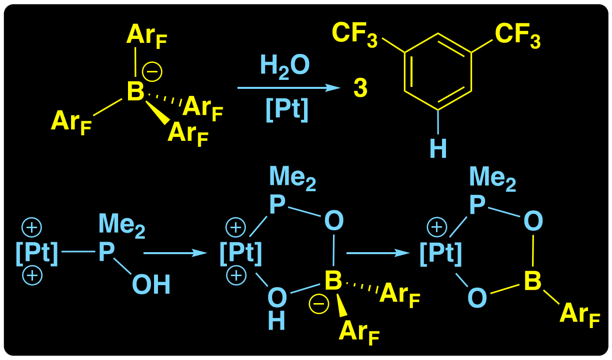

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