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Oxygenation of Organoboronic Acids by a Nonheme Iron(II) Complex: Mimicking Boronic Acid Monooxygenase Activity

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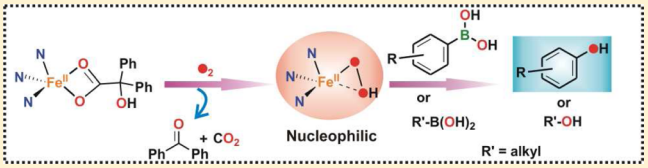
Supporting Information

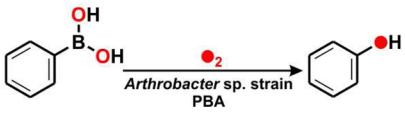
ABSTRACT: Phenolic compounds are important intermediates in the bacterial biodegradation of aromatic compounds in the soil. An *Arthrobacter sp.* strain has been shown to exhibit boronic acid monooxygenase activity through the conversion of different substituted phenylboronic acids to the corresponding phenols using dioxygen. While a number of methods have been reported to cleave the C−B bonds of organoboronic acids, there is no report on biomimetic iron complex exhibiting this activity using dioxygen as the oxidant. In that direction, we have investigated the reactivity of a nucleophilic iron−oxygen oxidant, generated upon oxidative decarboxylation of an iron(II)−benzilate complex [(Tp^{Ph2})Fe^{II}(benzilate)] (Tp^{Ph2} = hydrotris(3,5-diphenyl-pyrazol-1-yl)borate), toward organoboronic acids. The oxidant converts different aryl/alkylboronic acids to the corresponding oxygenated products with the incorporation of one oxygen atom from dioxygen. This method represents an efficient protocol for the oxygenation of boronic acids with dioxygen as the terminal oxidant.



INTRODUCTION

Microorganisms play important roles in the aerobic biodegradation of aromatic compounds.[1,2] At the initial step in the aerobic biodegradation pathway, aromatic substrates are usually activated by hydroxylation reactions. A number of metal and/or organic cofactor-dependent oxygenases carry out hydroxylation reactions using dioxygen as the oxidant.[3−5] One such hydroxylated product is phenol, an important component in the bioremediation pathway of aromatics in the soil. Phenolic compounds are the most important molecules among plant secondary metabolites and have great significance in plant development. Similarly, boron is known for its importance in many biological functions and for the growth of plants.[6] Although boron compounds are used in bacterial growth media,[7] studies on the bacterial metabolism of organoboron compounds are rare. The biological oxygenation of 2-methylcyclohexylboronic acid by the flavin-dependent cyclohexanone monooxygenase has been reported to displace a boronic acid substituent from the chiral carbon affording the corresponding alcohol with retention of absolute configuration.[8] In 2003, Wackett and co-workers reported the cleavage of the C−B bond of arylboronic acids with molecular oxygen by an *Arthrobacter nicotinovorans* strain PBA.[9] Though little is known to date about the gene(s) involved in bacterial phenylboronic acid catabolism,[10] *Arthrobacter sp.* strain PBA metabolized phenylboronic acids to the corresponding phenols with the incorporation of one oxygen atom from dioxygen (Scheme 1). The oxidation of biological arylboronic acid has been reported to follow a monooxygenase-type mechanism.[9] The boronic acid monooxygenase activity of the bacterial strain by exhibiting the C−B bond cleavage of boronic acid and concomitant formation of C−O bond without an NIH shift is an important transformation from both biological and synthetic viewpoint.

Scheme 1. Phenylboronic Acid Monooxygenase Activity by *Arthrobacter* sp. Strain PBA



Considering the importance of arylboronic acid to phenol conversion in biological and synthetic chemistry,[11] a large number of oxidation methods by using strong oxidizing agents such as hydrogen peroxide, oxone, *m*-chloroperbenzoic acid, etc. in stoichiometric amounts have been reported.[12−19] Efforts have also been devoted to develop methods with mild and environmental friendly oxidants for hydroxylation of boronic acids.[20−23] Other mild methods include copper and palladium catalyzed oxidation,[24−27] photocatalytic aerobic oxidative hydroxylation,[28,29] copper mediated electrochemical hydroxylation,[30] and oxidation by electrochemically generated superoxide anions.[31] In spite of several synthetic methodologies available for the conversion of arylboronic acids to phenols, biomimetic approaches to arylboronic acid oxygenation using metal and/or organic cofactors and O_2 remain unexplored. Recently, flavinium catalysts in the presence of a sacrificial reducing agent have been reported to catalyze the oxidative hydroxylation of arylboronic acids to phenols with molecular

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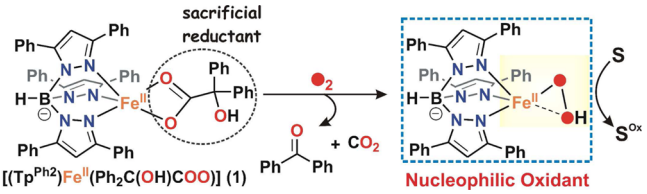
oxygen.[32] Analogous biocatalytic oxidations of C−B bonds with Baeyer−Villiger oxygenases employing the flavin cofactor have been reported,[33,34] but with the substrate scope focused on alkylboronates. In flavin-dependent monooxygenases, the reduced flavin cofactor activates dioxygen to form flavin-hydroperoxide oxidant.[35] Oxygenation reactions catalyzed by flavinium salt in the presence of sacrificial reducing agents have been reported to take place via nucleophilic hydroperoxide species.[36−39]

Similar to the reactivity observed with organic cofactor-based nucleophilic hydroperoxide, a metal-based nucleophilic O_2-derived oxidant is expected to oxygenate organoboronic acids. We have recently reported the two-electron reductive activation of dioxygen by biomimetic iron(II)-α-hydroxy acid complexes supported by a facial N_3 ligand (Tp^{Ph2} = hydrotris(3,5-diphenyl-pyrazol-1-yl)borate), where the metal-coordinated α-hydroxy acid anions acted as the sacrificial reductants.[40−42] A nucleophilic iron−oxygen oxidant thus generated exhibited oxygen-atom transfer to sulfides and olefin *cis*-dihydroxylation reactions. The oxidant was intercepted by external substrates as probes. On the basis of interception and mechanistic studies, the oxidant was proposed to be a side-on iron(II)-hydroperoxide species (Scheme 2). Since Lewis acidic boronic acids

Scheme 2. A Nucleophilic Iron−Oxygen Oxidant Intercepted in the Reaction between [(Tp^{Ph2})Fe^{II}(benzilate)] Complex and Dioxygen



are electrophilic in nature, we have investigated the efficiency of the O_2-derived nucleophilic oxidant from iron(II)-α-hydroxy acid complexes of the Tp^{Ph2} ligand for the oxygenation of aryl/alkyl boronic acids. In this article, we report the oxygenative C−B bond cleavage of aryl/alkylboronic acids by the [(Tp^{Ph2})Fe^{II}(benzilate)] (**1**) complex using O_2 as the terminal oxidant. The conversion of different substituted aryl/alkylboronic acids to the corresponding hydroxylated products by the iron complex and a mechanistic proposal of the oxidative transformation are reported in this work.

RESULTS AND DISCUSSION

Complex **1** reacts with dioxygen in benzene to undergo oxidative decarboxylation of benzilic acid to benzophenone in quantitative yield over a period of 20 min. In the reaction, hydroxylation of one of the phenyl rings of Tp^{Ph2} occurs to an extent of 90%.[40] The intraligand hydroxylation is inhibited in the presence of different external substrates, where selective oxidations of external substrates occur in preference to intraligand hydroxylation. The reaction of complex **1** with dioxygen in the presence of phenylboronic acid (5 equiv) in benzene over a period of 20 min results in the formation of a deep green solution showing a broad band at around 600 nm (Figure 1). The ESI-MS of the final oxidized solution exhibits an ion peak at m/z = 725.2 with the isotope distribution pattern calculated for [(Tp^{Ph2})Fe]$^+$ (Figure S1, Supporting Information, SI). The deep green oxidized solution shows a rhombic

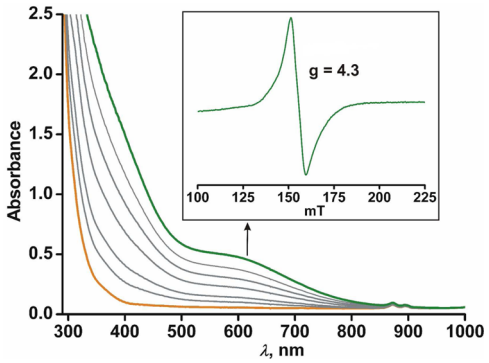


Figure 1. Optical spectral changes with time during the reaction between [(Tp^{Ph2})Fe^{II}(benzilate)] (0.4 mM in benzene) and O_2 in the presence of phenylboronic acid (5 equiv). Inset: X-band EPR spectrum of the final oxidized solution at 77 K.

signal at g = 4.3 in the X-band EPR spectrum typical of a high-spin iron(III) complex (Figure 1, inset). Thus, the iron(II)-benzilate complex is converted to an iron(III)-phenolate complex upon exposure to dioxygen in the presence of phenylboronic acid.

Analysis of the organic product by ^{1}H NMR spectroscopy after removal of the metal ion from the oxidized solution reveals the formation of phenol with 80% yield (Figure S2, SI). The GC-mass spectrum of phenol displays an ion peak at m/z = 94 (Figure 2a), which shifts two mass units higher at 96 when

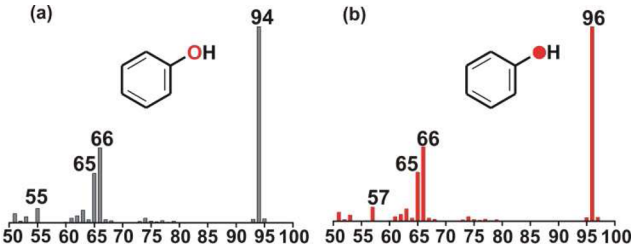


Figure 2. GC-mass spectra of phenol obtained from the reaction of **1** with phenylboronic acid in the presence of (a) $^{16}O_2$ and (b) $^{18}O_2$.

the reaction is carried out with $^{18}O_2$ (Figure 2b). In the reaction with **1**, phenylboronic acid undergoes oxidative C−B bond dissociation with concomitant formation of a C−O bond to form phenol as the only product where one oxygen atom from O_2 is incorporated into phenol. In a mixed labeling experiment with $^{16}O_2$ and $H_2{}^{18}O$, no incorporation of labeled oxygen is observed into the product. The oxidized product (phenolate) remains coordinated to the iron(III) center of the oxidized complex exhibiting a broad charge-transfer band at 600 nm. As a result, the extent of intramolecular ligand hydroxylation in the reaction of **1** with phenylboronic acid could not be quantified directly by optical spectroscopy. Therefore, with arylboronic acid substrates, the extent of intraligand hydroxylation was indirectly calculated by subtracting the percentage of oxygenated product from the percentage of intraligand hydroxylation in the absence of any substrate.

Hammett analysis is expected to provide useful information to understand the nature of the oxidant responsible for the hydroxylation of boronic acid. However, in the absence of any observable intermediate during the reaction, no absolute rate of hydroxylation of boronic acid could be obtained. But the relative rates can be calculated from product analysis of the

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competitive hydroxylation reaction of pairs of arylboronic acids. Therefore, Hammett analysis was carried out with 1:1 mixtures of phenylboronic acid and different *para*-substituted phenylboronic acids (p-X-$C_6H_4B(OH)_2$, where X = F, Cl, H, *t*Bu, OMe). A ρ value of +1.001 was obtained from the Hammett plot of the relative rates (k_{rel}) versus σ_p for p-X-$C_6H_4B(OH)_2$ (Figure 3). The result strongly indicates that the intermediate

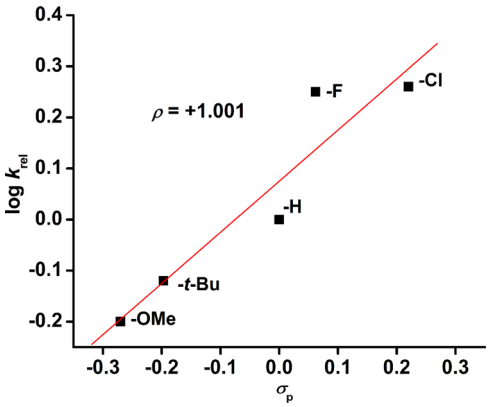


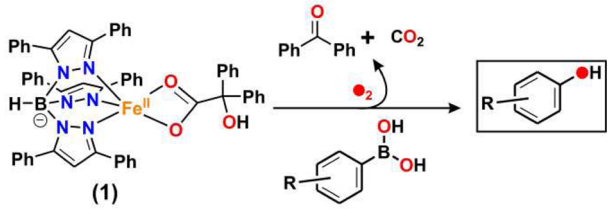
Figure 3. Hammett plot of log k_{rel} vs σ_ρ for p-X-$C_6H_4B(OH)_2$. The k_{rel} values were calculated by dividing the concentration of product from *para*-substitued phenylboronic acids by the concentration of product from phenylboronic acid.

responsible for hydroxylation of phenylboronic acid has nucleophilic character. The oxidation of arylboronic acids using oxone in aqueous acetone buffered with sodium bicarbonate has been shown to remain unaffected by the electron density of the aromatic nucleus.[13] However, the yields of phenols from the oxidation of arylboronic acids by hydroxylamine were low with substrates containing electron-withdrawing groups on the aromatic ring.[22] On the contrary, oxygenative transformation of phenylboronic acids by complex **1** affords the corresponding phenols in high yields with electron-withdrawing substituents on the phenyl ring of boronic acids. Of note, control experiments with iron(II) perchlorate only or with iron(II)-perchlorate and benzilic acid do not afford the phenol product from phenylboronic acid. The results of control experiments with simple iron salts imply the role of the supporting ligand and of the coligand (benzilate anion) in affecting biomimetic oxidation reactions by complex **1**.

Apart from different substituted phenylboronic acid, the dioxygen-derived nucleophilic oxidant from complex **1** also oxygenates other arylboronic acids (Scheme 3, Table 1). 1-Naphthylboronic acid and 2-naphthylboronic acid selectively form 1-naphthol (68%) and 2-naphthol (75%), respectively (Table 1, and Figures S3 and S4, SI). The oxygenation of aromatic boronic acid with O_2 by complex **1** therefore functionally mimics the phenylboronic acid monooxygenase activity of *Arthrobacter sp.* strain PBA (Scheme 3).

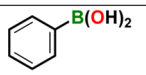
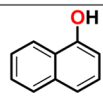
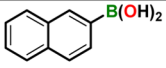
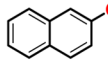
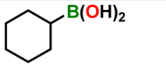
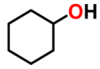
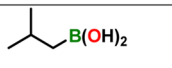
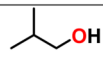
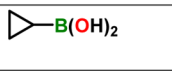
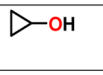
Complex **1** is also capable of converting alkylboronic acids to the corresponding hydroxylated product (Table 1). Cyclohexylboronic acid is selectively converted to cyclohexanol (Figure S5, SI). In the reaction, 60% cyclohexanol is formed, and the intramolecular ligand hydroxylation takes place to an extent of 30% (Figure S6, SI). Cyclopropylboronic acid forms cyclopropanol (37%) (Figure S7, SI), where 53% ligand hydroxylation is observed. Isobutylboronic acid affords 40% isobutanol (Figure S8, SI) along with 48% ring hydroxylated

Scheme 3. Oxygenative Conversion of Substituted Phenylboronic Acids to Phenols by Complex 1 (Bottom: Percentage Yields of Phenols from Substituted Phenylboronic Acids)



R (p-C_6H_4)	% of Phenol	R (p-C_6H_4)	% of Phenol
H	80	*t*Bu	77
F	86	OMe	72
Cl	88		

Table 1. Oxygenation of Organoboronic Acids by Complex 1[b]

Substrate	Product	% Yield	% Intra-ligand hydroxylation
Nil	-	-	90[41]
		80	10[a]
		68	22[a]
		75	15[a]
		60	30
		40	48
		37	53

[a]Calculated by subtracting the % of oxygenated product from the % of intraligand hydroxylation in the absence of any substrate. [b]Reaction conditions: 0.02 mmol of complex **1** in 10 mL O_2-saturated benzene and 0.1 mmol boronic acids; time: 20 min.

product. Therefore, hydroxylation of aryl/alkylboronic with O_2 by complex **1** represents an efficient biomimetic approach for selective oxyfunctionalization of aliphatic/aromatic substrates.

Further, the oxidations of phenylboronic acids containing reactive functional groups were studied to evaluate the chemoselectivity of the nucleophilic oxidant from complex **1** (Scheme 4). When 4-formylphenylboronic acid (5 equiv) is made to react with complex **1** and dioxygen, 4-hydroxy benzaldehyde is obtained as the major product (72%) along with a small amount (10%) of 4-carboxyphenylboronic acid (Figures S9 and S10, SI). It is therefore evident that the nucleophilic oxidant preferentially oxidizes the more electro-

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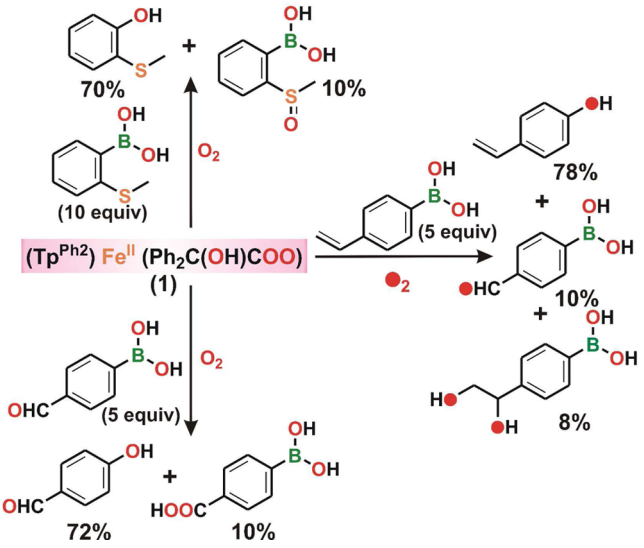
Scheme 4. Reaction of 1 with O_2 in the Presence of Different Arylboronic Acids Containing Reactive Functional Groups



philic boron center compared to the aldehydic center. The oxidant generated from **1** is known to react with benzaldehyde to afford benzoic acid and also takes part in Cannizzaro type reaction to form a mixture of benzyl alcohol and benzoic acid.[41] The metal-based oxidant oxidizes benzaldehyde to benzoic acid, and the resulting iron(II)-hydroxo species participates in a Cannizzaro reaction to convert benzaldehyde into benzyl alcohol and benzoic acid.[41] Here, the boron center is oxidized in preference to the aldehydic group, and no Cannizzaro type mechanism operates. Similarly, reaction of **1** with 1 equiv of 2-(methylthio)phenylboronic acid affords a mixture of 2-(methylthio)phenol (30%) and 2-(methylsufinyl)phenol (5%), indicating that the boron center as well as the sulfide moiety get oxidized (Figures S11 and S12, SI). With increasing concentration of the substrate, the oxo transfer reactivity to the sulfide moiety decreases (Figure S13, SI). In the presence of 10 equiv of substrate, 2-(methylthio)phenol is formed as the major product (70%) along with a minor product, 2-(methylsufinyl)-phenylboronic acid (10%) (Scheme 4, and Figures S14 and S15, SI). With an intermediate concentration (3−5 equiv) of the substrate, 2-(methylsufinyl)phenol and 2-(methylsufinyl)-phenylboronic acid are observed as minor products in addition to the major product, 2-(methylthio)phenol (Figure S13, SI). The reaction of complex **1** with thioanisole (10 equiv) has been reported to form 80% thioanisole oxide and 10% methyl phenyl sulfone. The ratio of sulfone/sulfoxide was found to be dependent on the amount of added sulfide. With 1 equiv of thioanisole, 34% sulfone was observed as the only product with no sulfoxide.[41] The results obtained with 2-(methylthio)-phenylboronic acid mirror the concentration dependent oxo transfer reactivity to sulfides by complex **1**, and the boronic acid moiety is more prone to oxidation compared to the oxo transfer reaction to a sulfide group.

The oxidant from **1** has been reported to carry out the *cis*-dihydroxylation reaction of alkenes. Unlike other alkenes, styrene affords a mixture of 1-phenylethane-1,2-diol (20%), benzaldehyde (50%), and benzoic acid (30%).[41] To compare the selectivity of the oxidant toward dihydroxylation vs boronic acid oxygenation, 4-vinyl phenylboronic acid was used as a substrate (Scheme 4). With 5 equiv of 4-vinyl phenylboronic acid, complex **1** reacts with oxygen to form a mixture of 4-vinyphenol (78%), 4-(1,2-dihydroxyethyl)phenylboronic acid (8%), and 4-formyl phenylboronic acid (10%) (Figures S16 and S17, SI). A labeling experiment with $^{18}O_2$ confirms the incorporation of a labeled oxygen atom into the oxidized products obtained from 4-vinyl phenylboronic acid. The GC-MS peak at m/z = 120 for 4-vinyphenol is shifted two mass units to m/z = 122. The mass fragment corresponding to 4-(1,2-dihydroxyethyl) phenylboronic acid at m/z = 138 is shifted by four mass units to m/z = 142. Similarly, the mass fragment for 4-formyl phenylboronic acid at m/z = 105 is shifted two units to m/z = 107 (Figure S18, SI). The data from labeling experiments thus unambiguously prove the involvement of a metal-based oxidant derived from dioxygen. The oxidant has preferential selectivity toward the nucleophilic hydroxylation of boronic acids compared to the oxo atom transfer to sulfides, dihydroxylation reaction of alkenes, and oxidation of aldehyde group.

The nucleophilic oxidant from **1** has been proposed as a side-on iron(II)-hydroperoxide species.[40,41] However, there is no direct experimental evidence for the iron(II)-hydroperoxide species. The putative iron(II)-hydroperoxide species from **1** may transform to the corresponding iron(III) species under oxidizing conditions. To test if an iron(III)-hydroperoxo species is involved in the reaction, the reaction of complex **1** with dioxygen was carried out in the presence of 10 equiv of thioanisole. The ^{1}H NMR spectrum of the final oxidized solution displayed paramagnetically shifted proton resonances typical of high-spin iron(II)-Tp^{Ph2} complexes (Figure S19, SI). Moreover the oxidized solution did not show any signal in the X-band EPR spectrum. If an iron(III)-hydroperoxide species was involved in the oxidation of substrate, the final solution after two-electron oxidation of thioanisole would show EPR signals of iron(III) products. All these results rule out the possibility of an iron(III)-hydroperoxide species as the active oxidant for the hydroxylation reaction.

From the results discussed above, a mechanism is proposed for the oxidative hydroxylation of organoboronic acids. Initially, an iron(II)-hydroperoxide species (**A**) is generated upon reductive activation of dioxygen by the iron benzilate complex (**1**). The nucleophilic iron(II)-hydroperoxide species is proposed to attack the electrophilic boron center of organo-boronic acid to form an iron(II)-peroxoborate (**B**) species (Scheme 5). The peroxo intermediate (**B**) then undergoes Baeyer−Villiger type rearrangement where migration of the aryl (or alkyl) moiety of boronic acid to the oxygen atom bonded to the iron center occurs to form the corresponding hydroxylated product (**C**), concerted with the heterolytic O−O bond cleavage of the hydroperoxide. Hydrolysis of the phenolatoborate in **C** results in the formation of phenol and boric acid. The iron(II) species (**D**) with coordinated hydroxylated product (alkoxide/phenolate) reacts with oxygen to get one-electron oxidized to form the corresponding iron(III) complex (**E**). For arylboronic acid, the green color of the final solution arises due to the phenolate coordinated iron(III) species.

CONCLUSIONS

In conclusion, we have developed an efficient protocol for selective oxygenative transformation of aryl/alkylboronic acids to the corresponding hydroxylated products by an iron(II)-benzilate complex using dioxygen as the oxidant. A dioxygen-derived nucleophilic iron−oxygen oxidant is implicated to carry out the chemoselective oxidative C−B bond cleavage of boronic acids. The reactivity of the nucleophilic iron−oxygen

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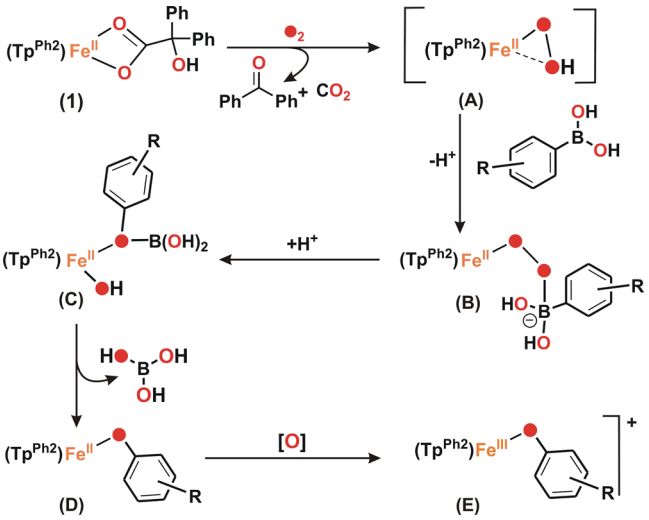
Scheme 5. Proposed Mechanism for Oxidative Hydroxylation of Boronic Acids with Dioxygen by Biomimetic Iron(II)−Benzilate Complex



oxidant has thus been harnessed in the oxidative hydroxylation of boronic acids. The reaction functionally mimics boronic acid monooxygenase activity. The oxygenative C−B bond cleavage of arylboronic acids by the iron(II) complex presented here would provide insights into the mechanism of bacterial phenylboronic acid catabolism. The relevance of this work with Flavin-dependent monooxygenases and Baeyer−Villiger monooxygenases highlights the promising aspects of nucleophilic nonheme metal-based hydroperoxides in various oxidative transformation reactions.

EXPERIMENTAL SECTION

All chemicals and reagents were obtained from commercial sources and were used without further purification unless otherwise stated. Solvents were distilled and dried before use. Preparation and handling of air-sensitive materials were carried out under an inert atmosphere in a glovebox. The ligand KTp^{Ph2} was prepared according to a procedure reported in the literature.[43] The iron(II)-benzilate complex [$(Tp^{Ph2})Fe^{II}$(benzilate)] (**1**) was synthesized according to the literature procedure.[40]

Electro-spray ionization (ESI) mass spectra were recorded with a Waters QTOF Micro YA263 instrument. Solution electronic spectra (single and time-dependent) were measured on an Agilent 8453 diode array spectrophotometer. X-band EPR measurements were performed on a JEOL JES-FA 200 instrument. All room temperature NMR spectra were collected on a Bruker Avance 500 MHz spectrometer. GC-MS measurements were carried out with a PerkinElmer Clarus 600 using Elite 5 MS (30 m × 0.25 mm × 0.25 μm) column with a maximum temperature 300 °C. Labeling experiments were carried out with $^{18}O_2$ gas (99 atom %) or H_2O^{18} (98 atom %) purchased from Icon Services Inc., USA.

Reaction of Complex 1 with O_2. The iron(II) complex (19 mg, 0.02 mmol) was dissolved in dioxygen-saturated benzene (10 mL). The solution was allowed to stir at room temperature for 20 min. After the reaction, the oxidized solution was treated with 10 mL of 3 M hydrochloric acid (HCl) solution. The organic products were then extracted with diethyl ether (3 × 15 mL), and the organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, the colorless residue was analyzed by GC-MS and ^{1}H NMR spectroscopy.

Reactions of Complex 1 with O_2 in the Presence of Organoboronic Acids. The iron(II) benzilate complex (19 mg, 0.02 mmol) was dissolved in benzene (10 mL) under a nitrogen atmosphere. To the solution was added the required equivalent of aryl/alkylboronic acid, and pure O_2 gas was purged through the solution for 2 min. The reaction solution was allowed to stir at room temperature for 20 min. After the reaction, the iron complex was decomposed by the addition of 10 mL of 3 M HCl solution. Then, organic products were extracted either with diethyl ether or with chloroform (3 × 15 mL), and the organic layer was dried over anhydrous sodium sulfate. After removal of the solvent, organic products were analyzed by GC-MS and ^{1}H NMR spectroscopy. Quantification of the oxidized organic products were performed by ^{1}H NMR spectroscopy by comparing the peak area of four aromatic ortho protons (d, 7.81 ppm) of benzophenone. For GC analyses, naphthalene was used as an internal standard, and the products were identified by comparison of their GC retention times and GC-MS with those of authentic compounds. All the products were quantified by ^{1}H NMR spectroscopy. Cyclohexanol, isobutanol, cyclopropanol, 2-(methylthio)phenol, 4-vinylphenol, 1-naphthol, and 2-naphthol were quantified by GC-MS. For Hammett analyses, the relative yields were quantified by GC-MS.

^{1}H NMR (500 MHz, $CDCl_3$, 295 K) data of the oxidized products are provided below. The spectra were compared with those of authentic compounds or with those reported in the literature.

Benzophenone: δ 7.80 (d, 4H), 7.59 (t, 2H), 7.50 (t, 4H). Phenol: δ 7.25 (t, 2H), 6.94 (t, 1H), 6.83 (d, 2H). 4-Fluoro phenol: δ 6.77 (m, 2H), 7.60 (m, 2H). 4-Chloro phenol: δ 6.77 (m, 2H) 7.19 (m, 2H). 4-*tert*-Butyl phenol: δ 7.25 (d, 2H), 6.75 (d, 2H), 2.25 (s, 9H). 4-Methoxy phenol: δ 6.78 (m, 4H), 4.47 (s, 1H), 3.77 (s, 3H). 4-Hydroxy benzaldehyde: δ 9.88 (s, 1H), 7.81 (d, 2H), 6.95 (d, 2H). 4-Carboxyphenylboronic acid: δ 8.14 (d, 2H), 7.12 (d, 2H). 2-(Methylthio)phenol: δ 6.98 (t, 1H), 7.01 (d, 1H), 7.48−7.45 (m, 2H), 2.34 (s, 3H). 2-(Methylsufinyl)phenylboronic acid: δ 7.99 (d, 1H), 7.49 (d, 1H) 7.45 (t, 1H), 7.15 (t, 1H), 2.76 (t, 3H). 2-(Methylsufinyl)phenol: δ 7.48 (d, 1H), 7.25 (m, 2H), 7.15 (d, 1H), 2.97 (3H, s). 4-Vinyphenol: δ 5.02 (d, 1H), 5.68−5.45 (m, 1H), 6.62 (dd, 1H), 6.73 (d, 2H), 7.28−7.26 (m, 2H). 4-(1,2-Dihydroxyethyl)-phenylboronic acid: δ 7.57 (d, 2H), 7.35 (d, 2H), 4.85 (m, 1H), 3.83 (m, 1H), 3.74 (m, 1H). 4-Formylphenylboronic acid: δ 7.86 (d, 2H), 8.11 (d, 2H), 10.06 (s, 1H).

Control Experiments. A mixture of $Fe(ClO_4)_2{\cdot}6H_2O$ (7.3 mg, 0.02 mmol) and phenylboronic acid (12.2 mg, 0.10 mmol) was dissolved in an oxygen saturated acetonitrile−benzene (1:5) solvent mixture (12 mL), and the solution was stirred for 20 min. In another control experiment, $Fe(ClO_4)_2{\cdot}6H_2O$ (7.3 mg, 0.02 mmol) was mixed with an equimolar amount of sodium benzilate (4.6 mg, 0.02 mmol) in an oxygen saturated acetonitrile−benzene (1:5) solvent mixture (12 mL) in the presence of 5 equiv of phenylboronic acid (12.2 mg, 0.10 mmol), and the resulting solution was stirred for 20 min. After the reaction, 10 mL of 3 M HCl solution was added to decompose the metal complex. The organic compounds were extracted with diethyl ether (3 × 15 mL), and the organic layer was dried over anhydrous sodium sulfate. In both of the experiments, no phenol formation was detected, as confirmed by GC-MS and ^{1}H NMR spectroscopy.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01198.

Spectroscopic data of oxygenated compounds (PDF)

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Notes

The authors declare no competing financial interest.

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