

# Olefin *cis*-Dihydroxylation and Aliphatic C–H Bond Oxygenation by a Dioxygen-Derived Electrophilic Iron–Oxygen Oxidant\*\*

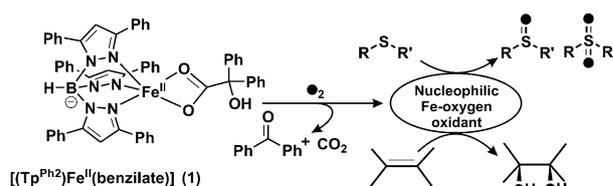
Sayanti Chatterjee and Tapan Kanti Paine\*

**Abstract:** Many iron-containing enzymes involve metal–oxygen oxidants to carry out  $O_2$ -dependent transformation reactions. However, the selective oxidation of C–H and C=C bonds by biomimetic complexes using  $O_2$  remains a major challenge in bioinspired catalysis. The reactivity of iron–oxygen oxidants generated from an  $Fe^{II}$ -benzilate complex of a facial  $N_3$  ligand were thus investigated. The complex reacted with  $O_2$  to form a nucleophilic oxidant, whereas an electrophilic oxidant, intercepted by external substrates, was generated in the presence of a Lewis acid. Based on the mechanistic studies, a nucleophilic  $Fe^{II}$ -hydroperoxo species is proposed to form from the benzilate complex, which undergoes heterolytic O–O bond cleavage in the presence of a Lewis acid to generate an  $Fe^{IV}$ -oxo-hydroxo oxidant. The electrophilic iron–oxygen oxidant selectively oxidizes sulfides to sulfoxides, alkenes to *cis*-diols, and it hydroxylates the C–H bonds of alkanes, including that of cyclohexane.

Iron-containing oxygenases activate dioxygen to catalyze a variety of biologically important oxidation reactions. In many oxygenases, high-valent iron–oxo species act as active oxidants in the oxidation reactions such as hydroxylation of aliphatic C–H bonds, *cis*-dihydroxylation/epoxidation of olefins, oxidation of sulfides, and so on.<sup>[1–4]</sup> For the reduction of dioxygen and subsequent generation of high-valent iron–oxo species, the necessary electrons are provided either by the iron center or by organic cofactors. In the heme enzymes cytochrome P450, high-valent iron–oxo oxidants oxidize strong aliphatic C–H bonds.<sup>[5–7]</sup> For Rieske dioxygenases, the nonheme enzymes involved in electrophilic *cis*-dihydroxylation of aromatic compounds, a side-on iron(III)–peroxo species has been suggested as a key oxidant in the catalytic cycle.<sup>[8–10]</sup> However, there is debate as to whether the iron(III)–(hydro)peroxo species performs *cis*-dihydroxylation or the O–O bond is cleaved to form a high-valent iron–oxo-hydroxo oxidant that carries out the *cis*-dihydroxylation reaction.<sup>[8,11,12]</sup> Although DFT calculations indicate the involvement of an iron(III)–peroxo species,<sup>[13]</sup> isotope label-

ing experiments with  $H_2^{18}O$  in the dihydroxylation by  $H_2O_2$  support the O–O bond cleavage prior to *cis*-dihydroxylation.<sup>[14]</sup>

Over the last decades, biomimetic oxidation of alkanes and alkenes by iron complexes has been extensively studied.<sup>[15–19]</sup> The presence of “ready oxidant”  $H_2O_2$  and substrates together allows the complexes to catalyze the C–H bond hydroxylation and olefin *cis*-dihydroxylation through putative high-valent iron–oxo oxidants.<sup>[17,20–23]</sup> Several iron–oxygen intermediates such as iron(III)–(hydro)peroxo and iron(IV)–oxo species have been generated through reduction of dioxygen by synthetic iron(II) complexes in the presence of electron and proton donors in stoichiometric amounts.<sup>[24–32]</sup> All these studies provide useful mechanistic information on reductive dioxygen activation by iron(II) complexes. However, examples of biomimetic iron complexes for oxidation of olefins and aliphatic substrates with dioxygen are rare.<sup>[33–36]</sup> In this endeavor, we have been exploring the dioxygen reactivity of biomimetic iron(II)– $\alpha$ -hydroxy acid complexes supported by a facial  $N_3$  ligand, hydrotris(3,5-diphenyl-pyrazol-1-yl)borate ligand ( $Tp^{Ph_2}$ ). In the complexes, the iron-coordinated  $\alpha$ -hydroxy acid (two-electron sacrificial reductant) anions provide the necessary electrons and protons for dioxygen reduction.<sup>[37,38]</sup> We have recently reported the reactivity of a nucleophilic iron–oxygen oxidant derived from  $[(Tp^{Ph_2})Fe^{II}(\text{benzilate})]$  (**1**) toward different substrates (Scheme 1). The nucleophilic oxidant has been shown to *cis*-



**Scheme 1.** A nucleophilic oxidant generated in the reaction of an iron(II)–benzilate complex of a monoanionic facial  $N_3$  ligand with  $O_2$ .

dihydroxylate alkenes with the incorporation of both the oxygen atoms of molecular oxygen into diols. The oxidant however did not exchange its oxygen atoms with water.<sup>[38]</sup>

Since high-valent electrophilic iron–oxo intermediates have been implicated as key oxidants for enzymatic and biomimetic oxidation reactions, our objectives of this work were to reverse the philicity of the nucleophilic oxidant and to evaluate the reactivity of the resulting electrophilic oxidant. Toward these objectives, we have investigated the reactivity of the oxidant from **1** in the presence of Lewis acid, because Lewis acidic metal ions are known to stabilize and modulate

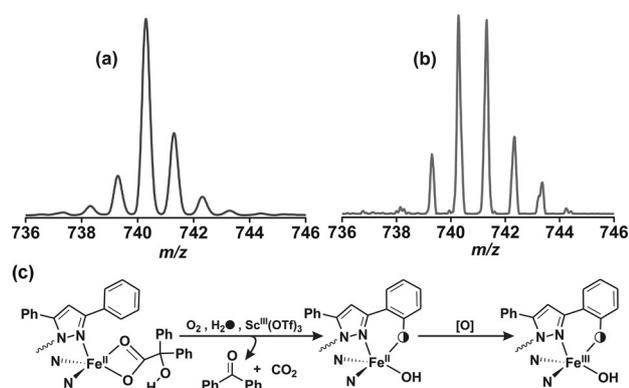
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the chemistry of metal–oxygen species.<sup>[27,30,39–44]</sup> As an outcome of our investigation, we report herein the reactivity of an electrophilic oxidant, generated from **1** in the presence of a Lewis acid, toward aliphatic and olefinic substrates. The selective oxidation of strong aliphatic C–H bonds including that of cyclohexane and *cis*-dihydroxylation of olefins by iron–oxygen oxidants generated *in situ* are presented.

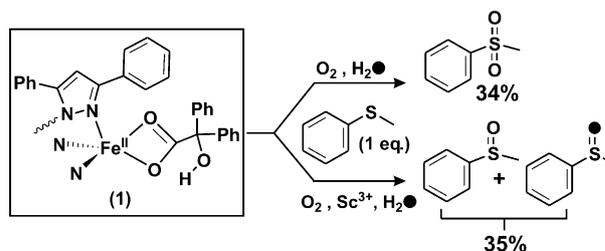
Complex **1**<sup>[37]</sup> reacts with dioxygen in the presence of an equimolar amount of Sc(OTf)<sub>3</sub> to undergo oxidative decarboxylation of benzoic acid to benzophenone in quantitative yield within 15 min. In the reaction, hydroxylation of one of the phenyl rings of Tp<sup>Ph2</sup> occurs to an extent of 90%. A mixed labeling experiment with <sup>16</sup>O<sub>2</sub> and H<sub>2</sub><sup>18</sup>O in the absence of Sc<sup>3+</sup> confirms no incorporation of labeled oxygen into the hydroxylated ligand.<sup>[38]</sup> In the presence of Sc<sup>3+</sup>, around 33% incorporation of labeled oxygen from water into the ligand takes place, as observed in the ESI-MS of the iron(III) complex [(Tp<sup>Ph2\*</sup>)Fe]<sup>+</sup> (*m/z* = 740.2) of hydroxylated ligand (Tp<sup>Ph2\*</sup>) (Figure 1).



**Figure 1.** ESI-mass spectra of the oxidized solution of **1** after the reaction a) with <sup>16</sup>O<sub>2</sub> and Sc<sup>3+</sup> and b) with <sup>16</sup>O<sub>2</sub>, H<sub>2</sub><sup>18</sup>O, and Sc<sup>3+</sup>. c) The incorporation of oxygen atom from H<sub>2</sub><sup>18</sup>O into the phenolate ring (<sup>18</sup>O shown as filled O).

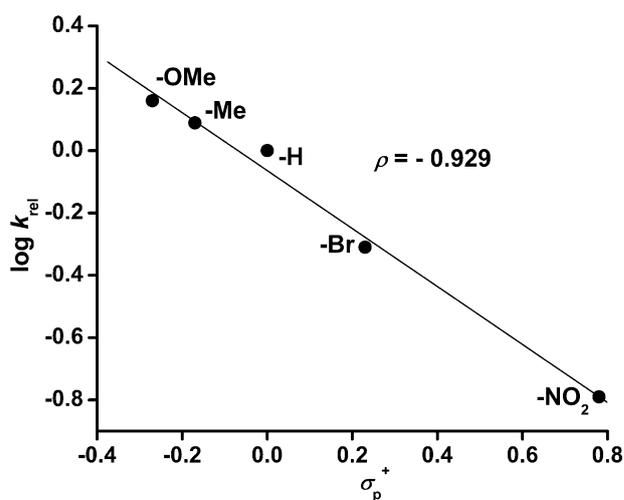
When the interception experiment with complex **1** is carried out with thioanisole and Sc<sup>3+</sup> (1 equiv each), thioanisole oxide (35%) is formed as the only product without any sulfone (Scheme 2; Supporting Information, Figure S1). In the reaction, 53% intramolecular ligand hydroxylation is estimated. This result is in contrast to the product obtained in the absence of Sc<sup>3+</sup>, where only sulfone is formed in 34% yield (Scheme 2).<sup>[38]</sup> With 10 equiv of thioanisole and one equiv of Sc<sup>3+</sup>, the yield of thioanisole oxide increases to 90% with almost no ligand hydroxylation. The ratio of sulfone to sulfoxide depends on the concentration of Sc(OTf)<sub>3</sub> added, and around one equiv of Sc<sup>3+</sup> is sufficient for complete inhibition of sulfone formation (Supporting Information, Figure S2). Other Lewis acids also control the sulfone/sulfoxide selectivity (Supporting Information, Figure S3), and unlike Sc<sup>3+</sup>, 1.7 equiv of In<sup>3+</sup>, around 2.0 equiv of Mg<sup>2+</sup> and 3.5 equiv of Na<sup>+</sup> cause complete inhibition of sulfone formation from thioanisole.

The labeling experiment for thioanisole (10 equiv) oxidation with <sup>16</sup>O<sub>2</sub> and H<sub>2</sub><sup>18</sup>O (60 equiv) in the presence of Sc<sup>3+</sup>



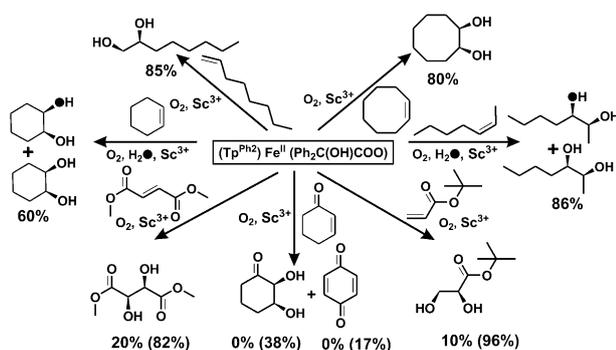
**Scheme 2.** Thioanisole-derived products obtained in the reaction of **1** with O<sub>2</sub> and H<sub>2</sub><sup>18</sup>O in the absence and presence of Sc<sup>3+</sup>.

confirms around 29% incorporation of labeled oxygen into sulfoxide (Supporting Information, Figure S4). Of note, no oxygen atom from water is incorporated into thioanisole oxide in the absence of Sc<sup>3+</sup>.<sup>[38]</sup> A control experiment with thioanisole oxide, Sc(OTf)<sub>3</sub>, and H<sub>2</sub><sup>18</sup>O in a benzene–acetonitrile solvent mixture reveals no exchange of water with sulfoxide (Experimental Section in the Supporting Information). The Lewis acid alone cannot cause the observed labeled water exchange with sulfoxide. With scandium ions, therefore, a different oxidant is generated that exchanges its oxygen atoms with water. To explore the nature of the active oxidant, Hammett analysis with different *para*-substituted thioanisoles was performed. A Hammett  $\rho$  value of  $-0.929$  confirms the electrophilic nature of the iron–oxygen oxidant generated in the presence of Lewis acid (Figure 2).

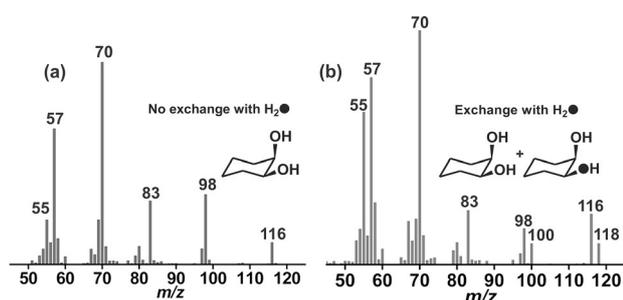


**Figure 2.** Hammett plot of  $\log k_{rel}$  vs  $\sigma_p^+$  for *p*-X-C<sub>6</sub>H<sub>4</sub>SMe obtained from the reaction of **1** with one equiv of Sc<sup>3+</sup>. The  $k_{rel}$  values were calculated by dividing the concentration of product from *para*-substituted thioanisole by the concentration of product from thioanisole.

The electrophilic iron–oxygen oxidant is able to *cis*-dihydroxylate alkenes to the corresponding *cis*-diols (Scheme 3; Supporting Information, Table S1 and Experimental Section). In the presence of 100 equiv of alkenes, the intramolecular ligand hydroxylation is completely inhibited. A labeling experiment with <sup>16</sup>O<sub>2</sub>, H<sub>2</sub><sup>18</sup>O (60 equiv), and cyclohexene in the presence of Sc<sup>3+</sup> results in the incorporation of labeled oxygen atom into the *cis*-diol product to an



**Scheme 3.** Oxidation of alkenes with  $\text{O}_2$  by complex **1** in the presence of  $\text{Sc}^{3+}$ . The values within the brackets indicate the percentage yields of *cis*-diols in the absence of  $\text{Sc}^{3+}$ .



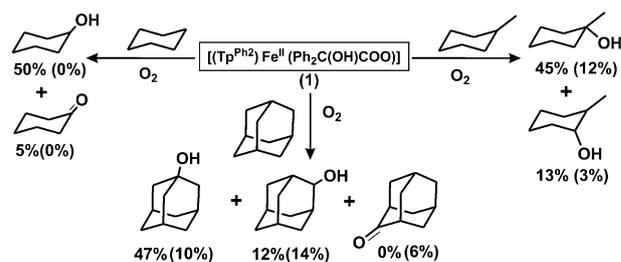
**Figure 3.** GC-mass spectra of *cis*-cyclohexane-1,2-diol obtained in the reaction of **1** with cyclohexene,  $^{16}\text{O}_2$ , and  $\text{H}_2^{18}\text{O}$  a) in the absence of  $\text{Sc}^{3+}$ , and b) in the presence of  $\text{Sc}^{3+}$ .

extent of 32% (Figure 3; Supporting Information, Table S1). Oxidations of cyclohexene with different amounts of  $\text{H}_2^{18}\text{O}$  reveal that the percentage of labeled oxygen into *cis*-diol increases linearly with the amount of added  $\text{H}_2^{18}\text{O}$  (up to 60 equiv) and then reaches at a maximum value of 32(3)% (Supporting Information, Figure S5). These results suggest the presence of a pre-equilibrium coordination of  $\text{H}_2^{18}\text{O}$  to the iron center of the active oxidant.<sup>[45]</sup> Hammett analysis with various substituted styrenes predicts a negative  $\rho$  value further confirming the electrophilic nature of the oxidant (Supporting Information, Figure S6). Thus unlike in the absence of  $\text{Sc}^{3+}$ , the oxidant formed in the presence of  $\text{Sc}^{3+}$  has electrophilic character and can exchange one of its oxygen atoms with water. The *cis*-dihydroxylation of *cis*-2-heptene with retention of stereochemistry both in the presence and absence of  $\text{Sc}^{3+}$  confirms that a metal-based oxidant is involved in the reaction through a concerted mechanism (Supporting Information, Table S1, Figures S7 and S8). While the electron-rich alkenes afford the corresponding *cis*-diols in higher yields, electron-deficient alkenes such as *tert*-butyl acrylate and dimethyl fumarate yield small percentage of diol products in the presence of  $\text{Sc}^{3+}$  (Supporting Information, Figures S9 and S10). The oxidant generated in the absence of any Lewis acid oxidizes the electron-deficient alkene 2-cyclohexenone (100 equiv) to a mixture of *cis*-2,3-dihydroxy cyclohexanone (38%) and 1,4-benzoquinone (17%) (Supporting Information, Table S1 and Figures S11 and S12).

However in the presence of  $\text{Sc}^{3+}$ , the electrophilic oxidant is unable to carry out the oxidation of alkenones.

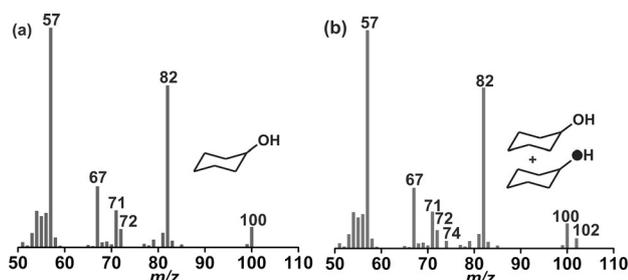
We have earlier reported that the reaction of **1** with benzaldehyde (20 equiv) yielded 75% benzoic acid and 40% benzyl alcohol. Formation of benzyl alcohol and benzoic acid suggested a Cannizzaro-type mechanism in the reaction. However, unlike the normal Cannizzaro reaction where alcohol and acid are formed in 1:1 ratio, the yield of benzoic acid was found to be higher than that of alcohol. Additional 35% benzoic acid was therefore proposed to form via oxidation of benzaldehyde by the nucleophilic metal-based oxidant.<sup>[38]</sup> On the contrary, the electrophilic oxidant generated with  $\text{Sc}^{3+}$  cannot oxidize benzaldehyde to benzoic acid but can participate in a normal Cannizzaro-type reaction to form benzoic acid and benzyl alcohol in 1:1 ratio with an overall yield of 80% (Supporting Information, Figure S13). To carry out the Cannizzaro reaction, the oxidant must have a metal-coordinated hydroxo group. This was further verified by the reaction of  $[(\text{Tp}^{\text{Ph}_2})\text{Fe}^{\text{II}}(\text{BF})]$  complex<sup>[46]</sup> with 20 equiv of 4-bromobenzaldehyde, where 4-bromobenzoic acid was not detected. A putative  $S=2$  iron(IV)-oxo species from  $[(\text{Tp}^{\text{Ph}_2})\text{Fe}^{\text{II}}(\text{BF})]$  and  $\text{O}_2$  has been reported to carry out various oxidation reactions<sup>[47]</sup> including the oxidation of cyclohexane and *n*-butane,<sup>[48]</sup> but the oxidant cannot oxidize aldehyde to carboxylic acid (Supporting Information, Figure S14). These results suggest that the nature of electrophilic oxidant from **1** is different than that from  $[(\text{Tp}^{\text{Ph}_2})\text{Fe}^{\text{II}}(\text{BF})]$ .

The nucleophilic oxidant is not efficient to cleave the C–H bond of cyclohexane (C–H bond dissociation energy = 99.5 kcal mol<sup>-1</sup>), but the electrophilic oxidant is powerful enough to oxygenate the strong C–H bond of cyclohexane. The electrophilic oxidant oxygenates cyclohexane to form about 50% cyclohexanol and 5% cyclohexanone. Although the oxidation of cyclohexane has been reported by synthetic iron(IV)-oxo complexes,<sup>[49]</sup> the oxygenation of cyclohexane with high alcohol/ketone selectivity (A/K = 10) by an  $\text{O}_2$ -derived oxidant is unprecedented (Scheme 4 and Figure 4a;



**Scheme 4.** Aliphatic C–H bond oxygenation by complex **1** with  $\text{O}_2$  in the presence of  $\text{Sc}^{3+}$ . The values within the brackets indicate the percentage yields of oxidation products in the absence of  $\text{Sc}^{3+}$ .

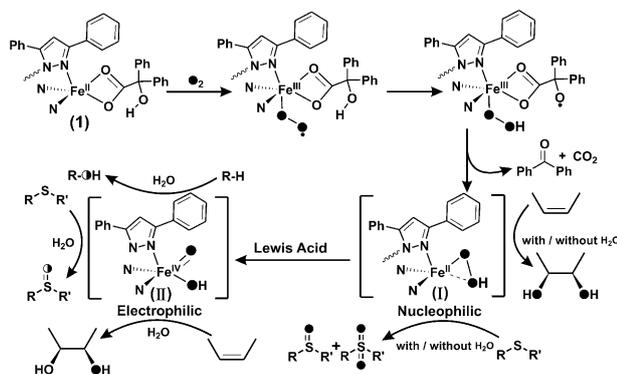
Supporting Information, Figure S15). The electrophilic oxidant exchanges one of its oxygen atoms with water present in the reaction medium, which is evident from the incorporation of around 27% of labeled oxygen atom from  $\text{H}_2^{18}\text{O}$  into cyclohexanol (Figure 4b). Substrate with relatively weak C–H bond such as methylcyclohexane (C–H bond dissociation energy = 94.3 kcal mol<sup>-1</sup>) can be oxygenated in the presence



**Figure 4.** GC-mass spectra of cyclohexanol formed in the reaction of **1** with a)  $^{16}\text{O}_2$  in the presence of  $\text{Sc}^{3+}$  and b)  $^{16}\text{O}_2$  and  $\text{H}_2^{18}\text{O}$  in the presence of  $\text{Sc}^{3+}$ .

and in the absence of  $\text{Sc}^{3+}$ . The nucleophilic oxidant oxidizes methylcyclohexane, affording 1-methylcyclohexanol (12%) and 2-methylcyclohexanol (3%) with only 15% conversion. The electrophilic oxidant, in contrast, preferentially activates the tertiary C–H bond of methylcyclohexane to form 1-methylcyclohexanol (45%) along with a small amount (13%) of 2-methylcyclohexanol (Scheme 4; Supporting Information, Figure S16). Similarly, the C–H bond of adamantane can be activated by the nucleophilic as well as by the electrophilic oxidant, but the extent of oxidation of adamantane by the electrophilic oxidant is higher where selectively 1-adamantanol (47%) and 2-adamantanol (12%) are formed (Scheme 4; Supporting Information, Figures S17 and S18). The normalized  $3^\circ/2^\circ$  C–H bond selectivity is a clear indication of a metal-based oxidation reaction.

Based on the experimental results, we propose that a nucleophilic iron(II)–hydroperoxo species (**I**) is formed upon two-electron reductive activation of dioxygen and concomitant decarboxylation of benzoic acid to benzophenone (Scheme 5). DFT calculations earlier predicted a lower



**Scheme 5.** Proposed mechanism for the formation of  $\text{O}_2$ -derived iron-oxygen oxidants in the reductive activation of dioxygen by an iron(II)–benzilate complex.

energy barrier for the heterolytic O–O bond cleavage of iron(II)–hydroperoxide compared to that of iron(III)–hydroperoxide species.<sup>[50]</sup> The presence of protic acid has been reported to lower the energy barrier even more.<sup>[51]</sup> In the same line, Lewis acid is expected to lower the O–O bond cleavage energy barrier. Since the electrophilic oxidant from

complex **1** is able to *cis*-dihydroxylate alkenes to diols with partial incorporation of oxygen atom from water and can participate in a Cannizzaro reaction, the oxidant is proposed to be an iron(IV)–oxo–hydroxo species (**III**) with the oxo and hydroxo groups disposed *cis* to each other. The high-valent iron–oxo species can exchange its oxygen atoms with water and carries out the oxidation of external substrates (Scheme 5). The heterolytic O–O bond cleavage reaction of peroxide to generate iron(IV)–oxo species with the present system is reminiscent of isopenicillin N synthase (IPNS).<sup>[52,53]</sup> Example of such intermediate in enzymatic or model systems is rare. An iron(II)–(alkyl)hydroperoxo species, obtained by one-electron reduction of the iron(III)–peroxo precursor, has been reported to undergo heterolytic O–O bond cleavage to generate an iron(IV)–oxo species.<sup>[54]</sup> The iron(II) complex reported here reductively activates dioxygen to form an iron–oxo oxidant via Lewis acid mediated O–O heterolysis of an iron(II)–hydroperoxide species.

In conclusion, a nucleophilic iron–oxygen oxidant is proposed to form in the reaction of an iron(II)–benzilate complex with dioxygen, which undergoes heterolytic O–O bond cleavage in the presence of a Lewis acid to generate an electrophilic iron–oxygen oxidant. The reversal of philicity of the nucleophilic oxidant mediated by Lewis acids is a unique result which sheds light on the nature of key oxidants involved in  $\text{O}_2$ -dependent transformation reactions. The electrophilic iron–oxygen oxidant from the complex, yet unobserved for spectroscopic characterization, was intercepted by external substrates as probes that were intermolecularly oxidized. The electrophilic oxidant performs *cis*-dihydroxylation of alkenes and hydroxylation of strong C–H bonds of aliphatic substrates including that of cyclohexane with high alcohol/ketone selectivity. The oxidant exchanges its oxygen atoms with water. On the basis of interception and mechanistic studies, an iron(IV)–oxo–hydroxo species is proposed as the active oxidant that exhibits electrophilic behavior. The versatile reactivity of the oxidant presented here would provide useful information toward the development of bioinspired oxidation catalyst for olefin *cis*-dihydroxylation and aliphatic C–H cleavage reaction using dioxygen. Further studies in that direction are being performed in our laboratory.

**Keywords:** dioxygen · electrophilic oxidants · iron · Lewis acids · oxidation

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