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Reductive Cleavage of Dioxygen Mediated by a Lewis Superacidic Bis(borane)

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Léon Escomel, Laure Vendier, David Gatineau, Florian Molton, Carole Duboc, Marcello Gennari,* and Antoine Simonneau*



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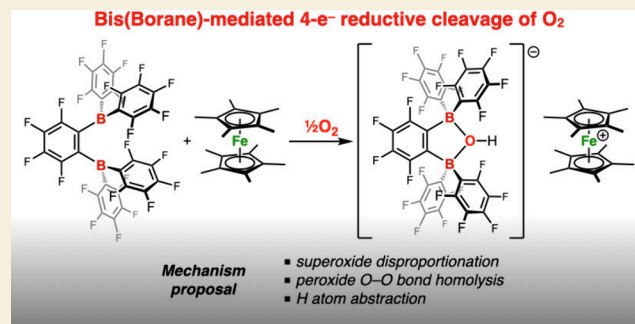
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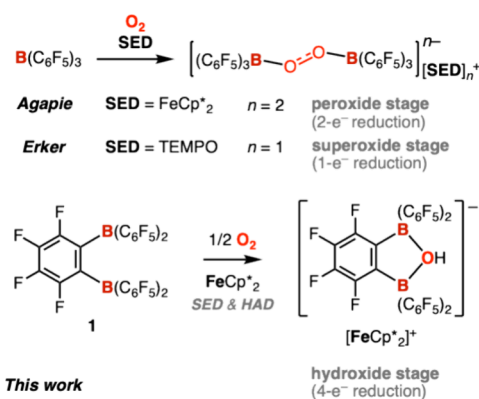
Supporting Information

ABSTRACT: The bis(borane) *o*-{(C_6F_5)₂B}₂C₆F₄ (**1**) reacts with dioxygen in the presence of decamethylferrocene (FeCp*₂, Cp* = pentamethylcyclopentadienyl) to deliver the salt [(μ -OH)-*o*-{B(C_6F_5)₂}₂C₆F₄][FeCp*₂] (**2**) featuring a hydroxide sequestered by the two adjacent boron atoms. Mechanistic investigations of this formal 4-electron reduction of O₂ suggest that it goes through the formation of a superoxide adduct [1-O₂]⁻, which evolves through disproportionation into O₂ and a peroxy-adduct [1-O₂]²⁻. Upon coordination of another equivalent of **1**, the thus-generated 4-fold boron-sequestered peroxide {[1]₂-O₂}²⁻ undergoes homolytic O–O bond cleavage to yield a pair of oxyl radicals [1-O•]⁻. These highly reactive intermediates subsequently perform hydrogen atom abstraction to lead to the hydroxide salt **2**. Our observations point to FeCp*₂ being the H atom purveyor in this final step.

KEYWORDS: boron, dioxygen, Lewis acids, metallocenes, superoxide, peroxide, oxyl radical, hydrogen atom abstraction



Scheme 1. Boron Lewis Acid Mediated O₂ Reduction with Single Electron Donors (SED)^a



^aHAD = hydrogen atom donor.

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In recent years, small molecule activation has grown as a central theme in main group chemistry,¹ driven by a quest to explore alternatives to transition metals.² Frustrated Lewis pairs (FLP) are a prominent example that emerged from this research field.³ If most of the FLP chemistry can be rationalized through ionic mechanisms, it has been demonstrated that a number of FLP-mediated activations of small molecules can proceed via radical pathways involving LA^{-•}/LB^{+•} systems and/or homolytic bond cleavages.⁴ The recent rise of the Frustrated Radical Pairs (FRP)⁵ chemistry has motivated the exploration of controlled electron delivery to small molecules with the assistance of Lewis acids.⁶ In particular, strong B- and Al-based Lewis acids have been shown to mediate O₂ reduction (Scheme 1), a process currently scrutinized for fuel cell and energy storage technologies and largely relying on the use of metal catalysts.⁷ Henthorn and Agapie showed that a 1:1 solution of B(C₆F₅)₃ and the single-electron donor (SED) FeCp*₂ (Cp* = pentamethylcyclopentadienyl), when exposed to 1 atm of O₂, yields the peroxide dianion sequestered by two borane units.^{6a} Later, employing TEMPO as the 1-e⁻ reductant, the Erker group was able to trap the superoxide intermediate.^{6b} The Stephan group explored the influence of the Lewis SuperAcid (LSA) Al(C₆F₅)₃ on O₂ reduction and was able to isolate, albeit in low yield, an O₂ cleavage product featuring an Al₄O₂

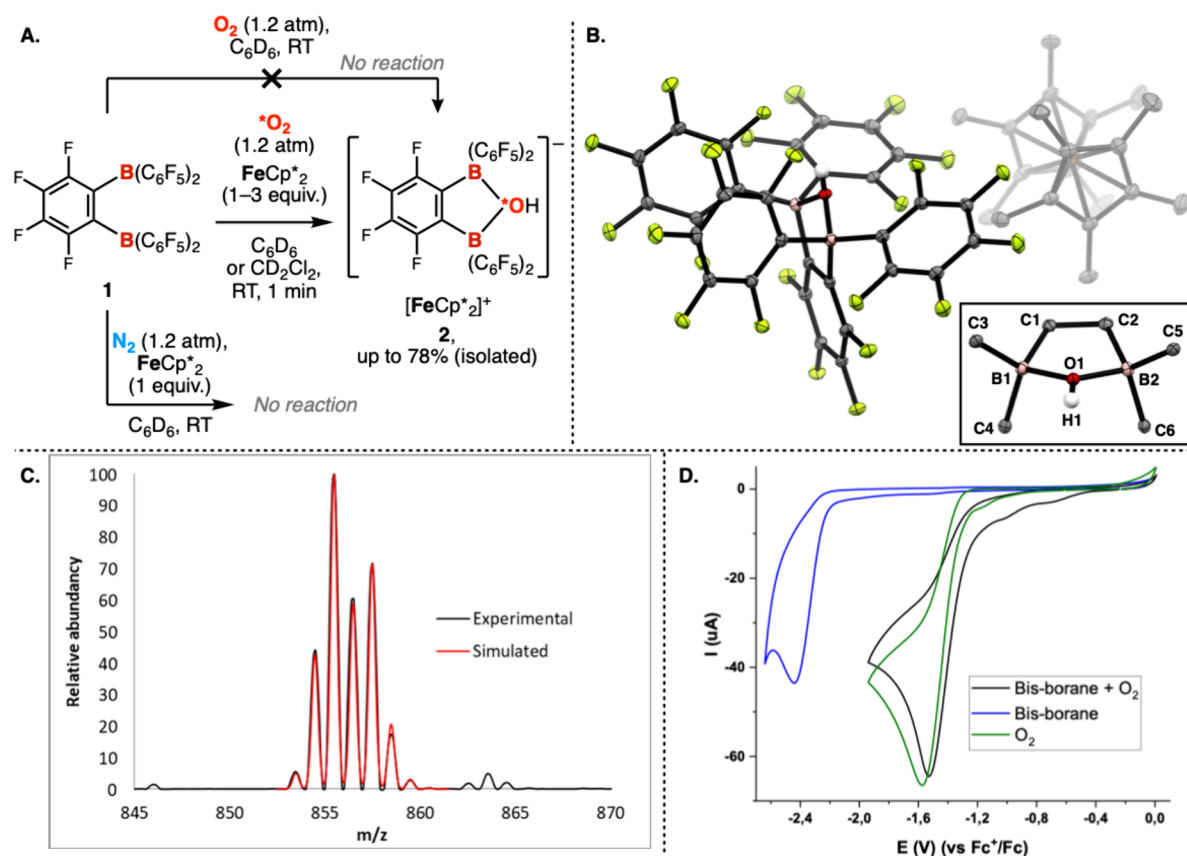


Figure 1. (A) Reactivity of **1** with O_2 in the presence of FeCp^*_2 and control experiments showing absence of reactivity without FeCp^*_2 or O_2 . $^*\text{O}$ can be either ^{16}O or ^{18}O . (B) Solid-state structure of **2** with magnification of the five-membered ring (box). Ellipsoids are represented with 30% probability. For clarity, only one of the two molecules found in the asymmetric unit ($Z' = 2$) is depicted, hydrogen atoms except H1 have been omitted, and the $\text{FeCp}^*_2^+$ cation has been shaded in the background. (C) Experimental mass spectrum (black, ESI, negative mode) obtained after performing the reaction under $^{18}\text{O}_2$, and simulated spectrum (red) of the ion $[\text{1-OH}]^-$ following an $^{18}\text{O}/^{16}\text{O}$ isotopic distribution of 40/60. (D) Cyclic voltammograms (CH_2Cl_2 , 1 M $[\text{N}(\text{nBu})_4]\text{BPh}_4$), scanning toward cathodic potentials of **1** (blue), and an O_2 -saturated solution in the presence (black) and absence (green) of **1**.

core (not shown).^{6c} These few studies demonstrate the pivotal role of the LA in facilitating O_2 activation and find an echo in catalysis and energy storage: Lewis acidic metal ions,⁸ main group species⁹ or H-bond donors¹⁰ were shown to be instrumental for enzymatic^{9a,10c} or bioinspired and artificial^{8b-f,9,10a,b,d,e} O_2 reduction,¹¹ as well as in the development of metal-air batteries.^{9a}

Recently, our group explored Piers' bis(borane) o - $\{(\text{C}_6\text{F}_5)_2\text{B}\}_2\text{C}_6\text{F}_4$ **1**¹² in the context of N_2 activation.¹³ The present article describes the reactivity of **1** with O_2 in the presence of an SED, enabling its formal 4-e^- reduction (Scheme 1). In this reaction, the chelating effect of **1** was shown to be pivotal in triggering O-O bond cleavage, followed by a Hydrogen Atom Abstraction (HAA) step, unveiling a new mode of metal-free O_2 activation.^{6a-c,14}

Treatment of **1** with decamethylferrocene (FeCp^*_2) under an O_2 atmosphere ($P_{\text{O}_2} \approx 1.2$ atm) in C_6D_6 or CD_2Cl_2 at room temperature (RT) under ambient light or in the dark results in a rapid color change from yellow-orange to deep green, in agreement with the formation of the decamethylferrocenium cation ($\text{FeCp}^*_2^+$, Figure 1A). Monitoring the reaction by UV-visible spectroscopy (Figure S13) shows the progressive increase of the $\text{FeCp}^*_2^+$ band at $\lambda = 780$ nm. ^1H NMR spectroscopy in CD_2Cl_2 reveals the expected resonance of the $\text{FeCp}^*_2^+$ methyl groups at -37.8 ppm, as well as the appearance of a broad signal at $\delta = 5.2$ ppm, attributed to a

boron-coordinated OH group (Figure S1). The ^{19}F NMR spectrum exhibits five signals (two resonances for the C_6F_4 bridge and three for the C_6F_5 groups), suggesting the formation of a symmetrical bis(borane) product **2** (Figure S2). The single resonance at $\delta = 1.6$ ppm in the ^{11}B NMR spectrum also points to an equivalent environment around the two boron nuclei (Figure S3). These NMR data are comparable to those of the $[1,2\text{-}\{(\text{C}_6\text{F}_5)_2(\mu\text{-OH})\text{B}(\text{C}_6\text{F}_5)_2\}\text{-C}_6\text{F}_4][\text{K}(18\text{-c-6})]$ derivative prepared from **1** and KOH .¹² Definitive attribution of **2** to $[1,2\text{-}\{(\text{C}_6\text{F}_5)_2(\mu\text{-OH})\text{B}(\text{C}_6\text{F}_5)_2\}\text{-C}_6\text{F}_4][\text{FeCp}^*_2]$ came by X-ray diffraction (XRD) analysis of single crystals grown from a saturated benzene solution (Figure 1B and Tables S1,2). In the solid state, the bis(borane) moiety shows pseudotetrahedral boron centers ($\tau_4^{15} = 66.8 \pm 0.8$) equidistant to the O atom of the sequestered hydroxide ($\text{B1-O1} = 1.57$ Å, $\text{B2-O1} = 1.55$ Å). These values match with B-O distances in the closely related $[\text{B}(\text{C}_6\text{F}_5)_3(\mu\text{-OH})\text{B}(\text{C}_6\text{F}_5)_3]^-$ anion.^{6a,c,d} The 5-membered ring escapes planarity as the OH caps the B_2C_2 plane with a dihedral angle of 29.7° , similar to other structures of bis(borane)-sequestered anions.¹⁶

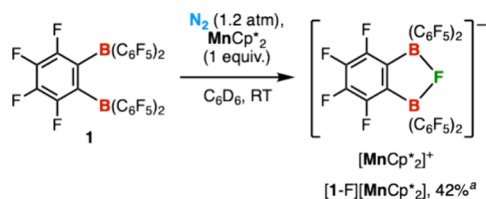
We proved that the oxygen atom in **2** originates from O_2 by ^{18}O labeling experiments coupled with electrospray ionization mass spectrometry (ESI-MS). Exposition of a CH_2Cl_2 solution of **1** and FeCp^*_2 under 1 atm of $^{18}\text{O}_2$ for a few minutes revealed the formation of **2** with an isotopic distribution $^{18}\text{O}_2$

($m/z = 857.5$)/ $^{16}\text{O}_2$ ($m/z = 855.5$) of 40/60 (Figure 1C). When the control experiment is carried out under $^{16}\text{O}_2$, a 0/100 ratio is found (Figure S15). We attributed the only partial ^{18}O incorporation to unavoidable $^{16}\text{O}_2$ contamination.

Consistent with the observations of the Agapie^{6a} and Stephan^{6c} groups with $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Al}(\text{C}_6\text{F}_5)_3$, respectively, the exposure of a C_6D_6 solution of **1** under an O_2 atmosphere does not trigger any appreciable reaction. Similarly, treating **1** with FeCp^*_2 under an N_2 atmosphere at ambient temperature also results in no reaction (Figure 1A). In the attempt to gain insights into the reaction mechanism, we started by evaluating the redox properties of **1**. Cyclic voltammetry (CV) recorded on a 1 mM CH_2Cl_2 solution shows an irreversible reduction wave at -2.44 V vs. $\text{FeCp}_2^+/\text{FeCp}_2$ (Figure 1D), a reduction potential that is more negative than that of $\text{B}(\text{C}_6\text{F}_5)_3$ ($E_{\text{pc}} = -1.97$ V).¹⁷ Based on CV, the quantitative formation of the $\mathbf{1}^{\bullet-}$ radical anion by an outer-sphere electron transfer from the FeCp_2^* reductant ($E_{1/2} = -0.59$ V vs. $\text{FeCp}_2^+/\text{FeCp}_2$) thus appears thermodynamically unrealistic. Therefore, Lewis acid **1**, $\text{FeCp}^*_2^+/\text{FeCp}^*_2$ and $\text{O}_2/\text{O}_2^{\bullet-}$ all have mismatched redox couples.

Different reactions were tested to probe the mechanism and understand how **2** can be generated under these experimental conditions. First, we evidenced that the radical anion $\mathbf{1}^{\bullet-}$ can be generated upon the reaction between **1** and a metallocene characterized by a mismatched reduction potential, namely MnCp^*_2 ($E_{1/2} = -1.02$ V vs. $\text{FeCp}_2^+/\text{FeCp}_2$). Instantaneous reaction occurs, leading to a mixture of compounds, with the fluoride salt $[\mathbf{1-F}][\text{MnCp}^*_2]$ as the major component (ca. 42% NMR conversion, Scheme 2 and Figure S6). Akin to $\text{B}(\text{C}_6\text{F}_5)_3^{\bullet-}$, $\mathbf{1}^{\bullet-}$ is highly unstable, in particular toward halide abstraction.¹⁹

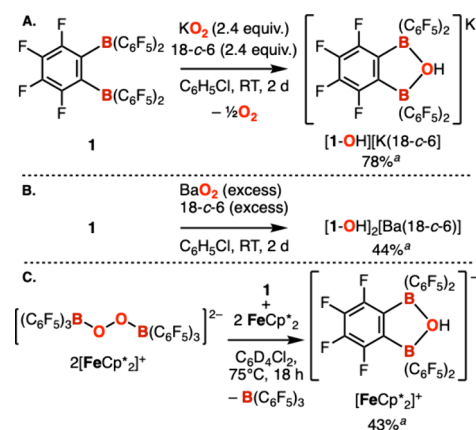
Scheme 2. Reaction of **1** with MnCp^*_2 under N_2



^aNMR conversion.

We next set out to evaluate the reactivity of **1** with the superoxide anion. The CVs of an O_2 -saturated CH_2Cl_2 solution, both in the absence and presence of **1**, show that the $\text{O}_2 \rightarrow \text{O}_2^{\bullet-}$ redox system is slightly anodically shifted by 60 mV upon the addition of **1** ($E_{\text{pc}} = -1.52$ V vs. $E_{\text{pc}} = -1.58$ V, respectively). This shift is consistent with a chemically coupled electron transfer (EC) mechanism involving a direct interaction between the superoxide anion and **1**. To confirm this observation, we investigated the reaction between **1** and KO_2 in the presence of the crown ether 18-*c*-6. In CH_2Cl_2 , the formation of two major anionic species, $[\mathbf{1-OH}]^-$ and $[\mathbf{1-Cl}]^-$,^{16b} was evidenced by ^{19}F NMR spectroscopy (Figures S7, S8). The generation of the latter is suppressed when the reaction is carried out in chlorobenzene with excess KO_2 (Scheme 3A and Figure S9), producing mainly $[\mathbf{1-OH}]^-$. Its formation confirms that **1** reacts with the superoxide anion to enter on the same type of reactivity as with O_2 . Besides, since $[\mathbf{1-OH}]^-$ is produced in the absence of an electron donor, disproportionation of the superoxide species $[\mathbf{1-O}_2]^-$ to

Scheme 3. Reactions between **1** and Superoxide or Peroxide Sources

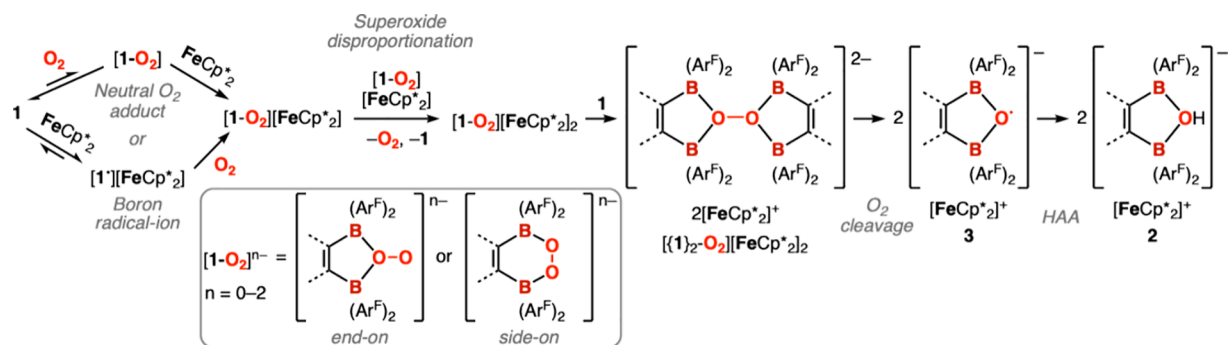


^aEstimated yields on the basis of ^{19}F NMR.

generate **1**, O_2 and $[\mathbf{1-O}_2]^{2-}$ (or from $\{[\mathbf{1}]_2\text{-O}_2\}^-$ to $\{[\mathbf{1}]_2\text{-O}_2\}^{2-}$) is proposed to occur. This is confirmed by the reaction of **1** with 0.5 equiv of KO_2 that converts only half of **1** into **2**, as determined by ^{19}F NMR (Figure S10). Zheng et al. have also reported that the related LA $\text{B}(\text{C}_6\text{F}_5)_3$ catalyzes the disproportionation of the superoxide intermediate generated from the electrochemical reduction of O_2 .^{10a}

The reactions of **1** with either BaO_2 in the presence of 18-*c*-6 in chlorobenzene (Scheme 3B) or the boron peroxide $\{[\text{B}(\text{C}_6\text{F}_5)_3]_2\text{-O}_2\}[\text{FeCp}^*_2]$ ^{6a} and two equivalents of FeCp^*_2 (Scheme 3C) lead to the hydroxide anion product, strongly supporting that **2** is formed through O–O bond cleavage of the peroxide adduct $\{[\mathbf{1}]_2\text{-O}_2\}^{2-}$ (Figures S11, S12). The instability of the latter toward O–O bond scission, compared to $\{[\text{B}(\text{C}_6\text{F}_5)_3]_2\text{-O}_2\}^{2-}$,^{6a} can be rationalized by the “chelation” of the oxygen atoms by **1**, which weakens the O–O bond to yield a pair of transient bis(borane)-sequestered oxyl radical $[\mathbf{1-O}^{\bullet}]^-$ (**3**). A subsequent H atom abstraction (HAA) step is then necessary to afford **2**, as proposed in the case of group 13 elements-bound oxyl radicals postulated in the context of N_2O activation.^{6d,20} Given that in fully deuterated solvents, no D incorporation into the OH fragment is observed, FeCp^*_2 or the crown ether, in the case of the reactions with KO_2 or BaO_2 , corresponds to the potential H^{\bullet} source. Although no byproduct supporting this hypothesis was isolated,²¹ this assumption is corroborated by significantly higher yields and selectivity observed in the presence of an excess of FeCp^*_2 (3 equiv) in the reaction of **1** with O_2 . Importantly, when FeCp_2 is used instead of FeCp^*_2 , quick and quantitative formation of FeCp_2^+ is observed. However, the ^{19}F NMR spectrum of the crude reaction mixture reveals an unselective outcome with no evidence of the signature of the bridging hydroxide adduct (Figure S5), as expected from the high C–H Bond Dissociation Energy (BDE) of ferrocene (118 kcal/mol).²²

Based on the experiments described above, a full mechanism for the O_2 reduction process is proposed in Scheme 4. The first step to generate $[\mathbf{1-O}_2]^-$ can proceed through different pathways, and the current data do not provide a definitive conclusion on how the initial electron transfer occurs. The fast reactivity observed between **1** and MnCp^*_2 , a better reductant than FeCp^*_2 but still more than 1.4 V away from the reduction potential of **1**, suggests that electron transfer from the metallocene to the bis-borane might be driven by follow-up

Scheme 4. Proposed Mechanism to Explain the Formation of Hydroxide 2 from 1, O₂ and FeCp*₂^a

reactions leading to the formation of strong bonds, e.g. B–F in the case of MnCp*₂ or B–O in the case of O₂ + FeCp*₂. An alternative scenario would involve a loosely bound 1–O₂ adduct accepting one electron from FeCp*₂. A similar mechanism was proposed for the O₂ activation by an Al(C₆F₅)₃/FeCp*₂ system, on the basis of DFT calculation.^{6c} The last hypothesis suggests that the first step follows a low-energy “Lewis acid-coupled electron transfer”^{11c} mechanistic pattern reminiscent of proton-coupled electron transfer (PCET), with the formation of an elusive complex involving all three protagonists (electron source, Lewis acid, and substrate to be activated). The resulting 1-bound superoxide species [1–O₂][–] is then proposed to disproportionate into O₂ and the peroxide adduct [1–O₂]^{2–}, as suggested by the reaction of 1 and KO₂. O₂ binding to the two boron atoms can be either end-on or side-on, although the former mode is necessary to ensure coordination of a second equivalent of 1 that is required for O–O bond cleavage occurring in [(1)₂O₂]^{2–}.²³ This yields two units of bis-borane-sequestered oxyl radical 3, which subsequently perform HAA, presumably from the C–H bond of FeCp*₂. The formation of two strong B–O bonds is proposed as the driving force behind the entire process.

To the best of our knowledge, the reactivity of 1 with O₂ represents the first example of a boron Lewis acid-assisted reductive cleavage of O₂, arising from the pivotal “chelating” effect of 1 and leading to an isolatable bis(borane)-hydroxide species through the formal 4-e[–] reduction of O₂. The proposed homolytic O–O bond cleavage with the transient generation of oxyl radicals parallels the chemistry of a certain class of oxygenases (and their bioinspired models).²⁴ The soluble methane monooxygenase (sMMO)²⁵ achieves the 4-e[–] reductive bond homolysis of O₂ at an Fe₂ core, affording two Fe(IV)=O units capable of C–H activation of methane, while Fe-bound oxyl radicals are proposed as key intermediates in other oxygenases.²⁶ Our work highlights the effect of chelating strong Lewis acids in electron delivery to small molecules and FRP chemistry. This strategy is currently further explored in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacsau.5c00516>.

Experimental methods; key spectroscopic and analytical data (PDF)

Crystal data (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

Marcello Gennari – Univ. Grenoble Alpes, CNRS UMR 5250, DCM, F-38000 Grenoble, France; orcid.org/0000-0001-5205-1123; Email: marcello.gennari@univ-grenoble-alpes.fr

Antoine Simonneau – LCC–CNRS, Université de Toulouse, CNRS, UPS, F-31077 cedex 4 Toulouse, France; orcid.org/0000-0003-4612-284X; Email: antoine.simonneau@lcc-toulouse.fr

Authors

Léon Escomel – LCC–CNRS, Université de Toulouse, CNRS, UPS, F-31077 cedex 4 Toulouse, France

Laure Vendier – LCC–CNRS, Université de Toulouse, CNRS, UPS, F-31077 cedex 4 Toulouse, France

David Gatineau – Univ. Grenoble Alpes, CNRS UMR 5250, DCM, F-38000 Grenoble, France

Florian Molton – Univ. Grenoble Alpes, CNRS UMR 5250, DCM, F-38000 Grenoble, France

Carole Duboc – Univ. Grenoble Alpes, CNRS UMR 5250, DCM, F-38000 Grenoble, France; orcid.org/0000-0002-9415-198X

Complete contact information is available at: <https://pubs.acs.org/10.1021/jacsau.5c00516>

Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Léon Escomel** data curation, formal analysis, investigation, methodology, writing - original draft, writing - review & editing; **Laure Vendier** data curation; **David Gatineau** data curation, formal analysis, methodology; **Florian Molton** data curation, formal analysis, investigation, methodology; **Marcello Gennari** funding acquisition, investigation, methodology, project administration, supervision, validation, writing - original draft, writing - review & editing; **Antoine Simonneau** conceptualization, funding acquisition, methodology, project administration, resources, supervision, validation, writing - original draft, writing - review & editing.

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Notes

The authors declare no competing financial interest.

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