Hydrocarbon Oxidation by an Exposed, Multiply Bonded Iron(III) Oxo Complex

Juan A. Valdez-Moreira, Daniel M. Beagan, Hao Yang, Joshua Telser, Brian M. Hoffman, Maren Pink, Veronica Carta, and Jeremy M. Smith*

ABSTRACT: The iron oxo unit, [Fe\(\text{III} \equiv \text{O}\)]\(^{+}\) is a critical intermediate in biological oxidation reactions. While its higher oxidation states are well studied, relatively little is known about the least-oxidized form [Fe\(\text{III} \equiv \text{O}\)]\(^{+}\). Here, the thermally stable complex PhB(AdIm)\(_3\)Fe\(\text{III} \equiv \text{O}\) has been structurally, spectroscopically, and computationally characterized as a bona fide iron(III) oxo. An unusually short Fe–O bond length is consistent with iron–oxygen multiple bond character and is supported by electronic structure calculations. The complex is thermally stable yet is able to perform hydrocarbon oxidations, facilitating both C–O bond formation and dehydrogenation reactions.

Iron(IV) oxo species, [Fe\(\text{IV} \equiv \text{O}\)]\(^{2+}\), are key intermediates in biological C–H oxidation reactions catalyzed by nonheme iron-containing oxygenases.\(^{1,2}\) Studies of model compounds reveal that hydrocarbon oxidation is initiated by hydrogen atom transfer (HAT) to the oxo ligand, generating the corresponding iron(III) hydroxide, [Fe\(\text{III} \equiv \text{OH}\)]\(^{2+}\).\(^{3,6}\) While hydrogen atom transfer in these reactions usually occurs by a concerted mechanism, for certain substrates a stepwise pathway has also been proposed.\(^{8,9}\) Specifically, initial electron transfer provides an [Fe\(\text{III} \equiv \text{O}\)]\(^{+}\) intermediate, followed by proton transfer to yield the hydroxide.

Little is known about the [Fe\(\text{III} \equiv \text{O}\)]\(^{+}\) unit, although iron(III) oxo species have been characterized in the gas phase\(^{10}\) and implicated as reaction intermediates in solution.\(^{11}\) A handful of iron(III) oxo complexes have been structurally characterized, but it is notable that these all feature second-coordination sphere hydrogen-bond donors that stabilize and shield the oxo ligand.\(^{12-14}\) thereby masking its reactivity.

Here, we report the synthesis and characterization of an iron(III) oxo complex that is devoid of second-coordination sphere hydrogen-bond donors. Structural characterization by single-crystal X-ray diffraction, combined with the electronic structure calculations, confirms iron–oxygen multiple bond character, while multiple spectroscopic methods establish a low-spin (\(S = 1/2\)) iron(III) formulation. This exposed [Fe\(\text{III} \equiv \text{O}\)]\(^{+}\) is reactive in oxo transfer and hydrocarbon oxidation reactions, including toluene hydroxylation and ethylbenzene dehydrogenation. Similar transformations are catalyzed by certain nonheme iron(II) and 2-oxoglutarate-dependent oxygenases, including in DNA alklation repair and antibiotic biosynthesis, albeit with the more highly oxidized [Fe\(\text{IV} \equiv \text{O}\)]\(^{2+}\) intermediate.\(^{15,16}\)

Reaction of the previously reported high-spin (\(S = 3/2\)) iron(I) dinitrogen complex PhB(AdIm)\(_3\)Fe-N\(_2\) (1)\(^{17}\) with equimolar N-methylmorpholine N-oxide (or pyridine-N-oxide) provides the purple iron(III) oxo complex PhB(AdIm)\(_3\)Fe\(\text{III} \equiv \text{O}\) (2) in moderate isolated yield (Scheme 1). The molecular structure of 2 has been determined by single-crystal X-ray diffraction, revealing a trigonally symmetric (\(C_3v\) symmetry) complex in which the iron oxo linkage lies on the molecular 3-fold axis (B–Fe–O angle = 178.15(9)\(^\circ\)) (Figure 1a). The complex is notable for an Fe–O distance (1.633(3) Å) that is shorter than all other iron oxo complexes characterized by XRD, regardless of oxidation state.\(^{18}\) The coordination sphere of iron is completed by three short Fe–C distances (1.933(2)–1.952(3) Å), with the iron atom roughly 1.1 Å

Scheme 1. Synthesis of Iron(III) Oxo Complex 2

\(\text{PhB}(\text{AdIm})_3\text{Fe}\equiv\text{O}\) (2)

\(\text{PhB}(\text{AdIm})_3\text{Fe}-\text{N}_2\) (1)

\(\text{PhB}(\text{AdIm})_3\text{Fe}\equiv\text{O}\) (2)
out of the plane defined by the three carbon donor atoms. A space-filling diagram reveals that the oxo ligand is accessible to substrates, lying within a pocket created by the three adamantyl groups of the tris(carbene)borate ligand (Figure 1b).

Significantly, there is no hydrogen bond to the oxo ligand in 2 (all O−H distances > 2.5 Å). This is in contrast to other structurally characterized Fe(III) oxo complexes, wherein second-coordination sphere hydrogen-bonding interactions (e.g., O−H distances = 1.7−1.8 Å) are critical to stabilizing this unit. As a result, the structural metrics of 2 differ from those for previously reported Fe(III) oxo complexes, with an Fe−O bond distance that is more than 0.2 Å shorter than in [(H$_2$buea)FeO]$_2$ (1.813(3) Å), $^{13}$ [N(afaCy)$_3$FeO]$^+$ (1.806(1) Å),$^{15}$ and [LFe$_3$O(PzNHtBu)$_3$FeO]$^+$ (1.817(2) Å).$^{14}$

In combination with the results of electronic structure calculations (see below), a strong band at 858 cm$^{-1}$ in the IR spectrum has been assigned to the Fe−O stretching frequency (Figure S10). This frequency is greater than that of the 100−200 cm$^{-1}$ Fe−O stretching frequency of other mononuclear iron(III) oxo complexes, wherein significant iron−oxygen multiple bond character in 2 is evident from slow relaxation at low temperature, which is often observed in half-integer spin (Kramers) complexes. The $^{57}$Fe Mössbauer spectral parameters of 2 are distinct from those of other iron(III) oxo complexes, namely, [(H$_2$buea)FeO]$_2$ (δ = 0.30 mm s$^{-1}$; $\Delta E_Q$ = 0.71 mm s$^{-1}$ at 77 K)$^{12}$ and [N(afaCy)$_3$FeO]$^+$ (two species observed in the solid state, δ = 0.31 mm s$^{-1}$; $\Delta E_Q$ = −1.1 mm s$^{-1}$ and δ = 0.31 mm s$^{-1}$; $\Delta E_Q$ = −2.1 mm s$^{-1}$ at 6 K)$^{16,17}$). The spectral parameters for 2 are also different from the iron(III) oxo site in the tetranuclear complex [LFe$_3$O(PzNHtBu)$_3$FeO]$^+$ (δ = 0.43 mm s$^{-1}$; $\Delta E_Q$ = 3.04 mm s$^{-1}$ at 80 K)$^{18,19}$). However, the Mössbauer parameters of 2 are similar to those reported for structurally related low-spin (S = 1/2) Fe(III) imido complex PhB(AdIm)$_3$FeOH (δ = −0.11 mm s$^{-1}$; $\Delta E_Q$ = 1.65 mm s$^{-1}$ at 78 K),$^{20}$ suggesting a similar electronic structure.

ENDOR spectra of 2 show signals from $^{1}$H, $^{11}$B, and $^{14}$N magnetically coupled to the paramagnetic [Fe$^{III}$=O]$^+$ center (Figures 2c and S19). The pulsed 35 GHz $^{1}$B ENDOR$^{3}$ spectrum at g$_{\parallel}$ (g$_{\perp}$) shows well-resolved hyperfine and quadrupole splitting (Figure 2c, top), and simulation of the field-dependent $^{11}$B ENDOR pattern (Figure S20) yields hyperfine and quadrupole tensors: A($^{11}$B) = [1.0, 1.6, 3.1] MHz, P($^{11}$B) = [−0.11, −0.07, +0.18] MHz. The quadrupole tensor frame is coaxial with the g-tensor frame, with the
maximum component directed along \( g_5 = g_8 \). As this component must lie closely along the \( C_3 \) axis of the trigonally symmetric boron atom, this indicates that \( g_5 \) also lies along the \( C_3 \) axis of 2, as is the case for the \( S = 1/2 \) iron(V) nitride complex, \([\text{PhB}(\text{BuIm})_2\text{Fe}≡\text{N}]^-\). \(^{24}\) The 35 GHz pulsed ENDOR spectrum collected at \( g_5 \) further shows \(^{14}\)N hyperfine coupling from two sets of nitrogen atoms, Figure 2c, bottom. Simulation of the field-dependent \(^{14}\)N ENDOR pattern is shown in Figure S21. As supported by DFT computations, the larger coupling is assigned to the three symmetry-equivalent \( N \) atoms and the smaller to the three \( N \) atoms (Figure S25, Table S4).

DFT calculations reproduce the observed doublet (\( S = 1/2 \)) ground spin state. Geometry optimization of this state (B3LYP/def2-svp) gives structural parameters in good agreement with those observed by single-crystal X-ray diffraction, whereas the optimized structures for the quartet (\( S = 3/2 \)) and sextet (\( S = 5/2 \)) states provide significantly longer iron–oxygen and iron–carbon bond distances (Table S1). The electronic structure of the doublet state was determined from a single-point calculation at a higher level of theory (B3LYP/def2-TZVP/def2-TZVPP), revealing significant Fe–O multiple bond character, as inferred from the structural and vibrational data (see above). The singly occupied molecular orbital (SOMO) is the \( \pi^* \) antibonding combination of an iron-based orbital of \( 3d_{xz}/4p_z \) parentage (\( z \) along the 3-fold symmetry axis) and the oxygen \( 2p_z \) orbital (Figure 3a), which partially offsets bonding by the filled Fe–O \( \sigma \) orbital (SOMO-2, Figure S23). Strong \( \pi \) bonding is provided by two doubly-occupied orbitals that are largely the perpendicular \( \pi \)-bonding combinations of Fe \( 3d_{yz}/3d_{zx} \) and O \( 2p_y/2p_x \) (SOMO-2 and SOMO-3), whereas the antibonding combinations are unoccupied (SOMO+1 and SOMO+2). This iron–oxygen multiple bond character is supported by the results of a natural bond orbital (NBO) analysis, which provides an Fe–O bond order of 2.5, decreased from a triple-bond value of 3 by the odd electron in the antibonding SOMO (Wiberg bond index \( 1.50 \)). The computations further indicate that the bond is polarized toward the oxygen atom and show that the majority of the spin density is located on iron (Löwdin spin density 0.813) but with a non-negligible amount on the oxo ligand (Löwdin spin density 0.151), as shown in Figure 3b. The computations give hyperfine couplings/spin densities of the carbene ligand atoms consistent with experiment (Table S4). A similar spin delocalization is observed for \( S = 1/2 \) Fe(V) oxo complexes, but with the unpaired electron housed in an Fe–O \( \pi^* \) orbital. \(^{25}\)

Although the oxo ligand 2 is buried in the pocket created by the adamantyl groups, it is nonetheless accessible along the trigonal axis (Figure 1c). Notably, 2 extracts an H atom from toluene, in so doing forming both the high-spin (\( S = 2 \)) iron(II) hydroxide complex PhB(AdIm)\(_2\)FeOH (3), and the high-spin Fe(II) benzoxo complex PhB(AdIm)\(_2\)Fe-OCH\(_2\)Ph (4), with the two complexes formed in the ratio 3:4 (1:0.65) (Scheme 2).

Scheme 2. Reaction of 2 with Toluene to Give 3 and 4

![Scheme 2](image)

Figure 3. Results of electronic structure calculations for 2, as determined by DFT (B3LYP/def2-TZVP/def2-TZVPP). Hydrogen atoms omitted for clarity. (a) Natural orbital representation for the SOMO, isodensity shown at 0.07; (b) spin density, isodensity shown at 0.01.

Figure 4. X-ray crystal structures of (a) 3; and (b) 4. Thermal ellipsoids shown at 50% probability; hydrogen atoms are omitted, tris(carbene)borate ligands are shown as lines, carbon, iron, nitrogen, and oxygen atoms are shown as black, orange, blue, and red ellipsoids, respectively.

The structure of 3 contains the same iron coordination environment as in 2 (Figure 4a). The Fe(II)–O (1.876(6) \( \text{Å} \)) and Fe–C bonds (2.09(1)–2.112(9) \( \text{Å} \)) of 3 are longer than the respective distances in 2 but are similar to those observed in other high-spin Fe(II) tris(carbene)borate complexes.\(^{17,26}\) The hydroxide ligand proton was located in the Fourier difference map and confirmed by a sharp infrared band at 3669 \( \text{cm}^{-1} \) that is assigned to the O–H stretch. The complex has been characterized by other spectroscopic methods, all of which are compatible with the structural formulation (see Supporting Information).

Complex 4 has also been characterized by single-crystal X-ray diffraction (Figure 4b). It is likely formed by a “non-rebound” mechanism in which the benzyl radical product from the reaction of 2 with toluene is trapped by an additional equivalent of 2.\(^{27}\) No kinetic isotope effect is observed for the rate of reactions of 2 with toluene and toluene-\( d_6 \).

The reactivity of 2 toward toluene is consistent with the computed O–H BDFE for hydroxide complex 3. Specifically, the gas phase BDFE\(_{\text{OH}}\) = 82 kcal/mol, suggesting thronemal hydrogen atom transfer from toluene (gas phase BDFE\(_{\text{CH}}\) = 81.6 kcal/mol) to \( 2.\)\(^{18,25}\) The iron oxo complex 2 has a significantly greater driving force for HAT than does \([\text{H}_2\text{buea})\text{FeO}\]\(^{17-}\) (BDFE\(_{\text{OH}}\) = 64 kcal/mol for \([\text{H}_2\text{buea})\text{FeOH}\])\(^{29,30}\) consistent with the hypothesis that the
reactivity of the oxo ligand is attenuated by second-coordination sphere hydrogen-bond donors.

Uniquely for a molecular iron complex in any oxidation state, 2 also facilitates hydrocarbon dehydrogenation, a reaction carried out by an \([Fe^{IV}=O]^{2+}\) intermediate in some iron(II) and 2-oxoglutarate-dependent oxygenases. Specifi-
cally, 2 reacts with equimolar ethylbenzene to provide the hydroxide complex 3 along with 0.5 equiv of styrene (Scheme 3), which was characterized by \(^1\)H NMR spectroscopy and GC/MS. Complex 2 can also carry out two-electron oxygen atom transfer chemistry, as evidenced by its ability to catalytically oxidize \(\text{PPh}_2\text{Me}\) to the phosphine oxide, \(\text{O}=\text{PPh}_3\text{Me}\); however, oxygen atom transfer from 2 to styrene to form styrene oxide is not observed.

In conclusion, the extremely bulky tris(carbene)borate ligand supports an isolable \([\text{Fe}^{III}=\text{O}]^{4-}\) fragment without the presence of stabilizing, but deactivating, hydrogen-bond donors, in contrast to previously characterized complexes. This unmasks the inherent reactivity of this fragment, which is demonstrated by its distinctive ability to oxidize hydrocarbons.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.1c00890.

Full experimental and computational details (PDF)

Coordinates for the optimized structures of 2 (\(S = 1/2, 3/2, 5/2\)) and 3 (XYZ)

Accession Codes

CCDC 2094972–2094974 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

### AUTHOR INFORMATION

**Corresponding Author**

Jeremy M. Smith — Department of Chemistry, Indiana University, Bloomington, Indiana 47405, United States; orcid.org/0000-0002-3206-4725; Email: smith962@indiana.edu

**Authors**

Juan A. Valdez-Moreira — Department of Chemistry, Indiana University, Bloomington, Indiana 47405, United States

Daniel M. Beagan — Department of Chemistry, Indiana University, Bloomington, Indiana 47405, United States

Hao Yang — Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0001-7229-0957

Joshua Telser — Department of Biological, Physical and Health Sciences, Roosevelt University, Chicago, Illinois 60605, United States; orcid.org/0000-0003-3307-2556

Brian M. Hoffman — Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-3100-0746

Maren Pink — Department of Chemistry, Indiana University, Bloomington, Indiana 47405, United States

Veronica Carta — Department of Chemistry, Indiana University, Bloomington, Indiana 47405, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acscentsci.1c00890

#### Notes

The authors declare no competing financial interest.

Computationally optimized structures as well as raw Mössbauer and EPR data have been deposited at IU Data CORE and are freely available (DOI: 10.5967/66dp-0171).

### ACKNOWLEDGMENTS

We thank Prof. Liang Deng and Yiming Fan (SIOC) for an initial sample of iron starting material. Funding from the NSF is gratefully acknowledged by J.A.V.-M. and J.M.S. (CHE-1900020) and by B.M.H. (MCB-1908587). This material is also based upon work supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0019342 (to B.M.H.). Support for the acquisition of the Bruker Venture D8 diffractometer through the Major Scientific Research Equipment Fund from the President of Indiana University and the Office of the Vice President for Research is gratefully acknowledged. NSF’s ChemMatCARS Sector 15 is supported by the NSF Divisions of Chemistry (CHE) and Materials Research (DMR), under Grant Number CHE-1834750. Use of the Advanced Photon Source, an Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory, was supported by DOE under Contract No. DE-AC02-06CH11357.

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■ NOTE ADDED AFTER ASAP PUBLICATION

Published ASAP on September 23, 2021; Figure 1 revised September 24, 2021 to correct production error.