

A New Fe^{III}-oxo That Challenges the Status QuoCite This: *ACS Cent. Sci.* 2021, 7, 1608–1610

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An Fe^{III}-oxo supported by a tris(carbene)borate ligand features strong metal–oxygen multiple bonding yet has hydrocarbon oxidation activity.

The diverse reactivity of Fe-oxidases and -oxygenases toward hydrocarbons ensues from the Fe^{IV} and Fe^V oxo intermediates generated in these enzymes. Consequently, researchers have pursued the synthesis of these high-valent compounds in synthetic systems; by now, numerous examples are known, in both high- and low-spin states.¹ The high oxidation states of the group 8 transition metal ion allow a good balance between oxo stability and reactivity. Representing a major advancement in oxo chemistry, Valdez-Moreira et al. have now generated a unique Fe^{III}-oxo complex, PhB(AdIm)₃Fe=O, based on the tris(carbene)-borate ligand.² The complex is a rare example of a mid-valent iron-oxo complex. More importantly, it is the only isolated complex of this class with strong metal-oxo multiple bonding (bond order = 2.5) yet exhibits unprecedented reactivity.

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The ability of PhB(AdIm)₃Fe=O to support a multiply bonded oxo species despite the lower Fe³⁺ oxidation state is largely a consequence of the pseudo-tetrahedral geometry enforced by the tris(carbene)borate ligand. Metal-oxo bonding in tetragonal complexes is governed by the rules of the “Oxo

Wall”:⁵ only one low lying d_{xy} orbital is of nonbonding character in C_{4v} symmetry (Figure 1), such that generally only complexes with fewer than four d-electrons (e.g., Fe^{IV} centers) can support a M-oxo bond order ≥ 2. A doubly bonded iron-oxo is in principle feasible for Fe^{III} complexes that possess quartet ground states. Such species have indeed been observed and spectroscopically characterized, albeit only in the gas phase.³ The situation for trigonal bipyramidal compounds is more stringent. The lowest lying d-orbitals are the d_{xz}- and d_{yz}-based M-oxo π* orbitals (Figure 1). Population of these molecular orbitals by even a single electron already weakens the metal–oxo interaction. Several groups have nonetheless successfully isolated Fe^{III}-oxo compounds in this coordination geometry by using a clever strategy that exploits second-sphere interactions. Amine groups in the ligand periphery of these complexes—which include [Fe^{III}{H₃buea}(O)]²⁻ (depicted in Figure 1),⁴ [N(afa^{Cy})₃Fe(O)]⁺,⁶ and a terminal Fe^{III}-oxo of the (tertbutylamino)pyrazolate based Fe₄ cluster⁷—engage in H-bonding with the oxygen atom, thereby shielding and stabilizing the singly bonded Fe–O species, perhaps too much. Despite the long Fe–O distances, and a confirmed high-spin configuration for [Fe^{III}{H₃buea}(O)]²⁻, the reactivity of these compounds is rather limited.

Pseudo-tetrahedral geometries, on the other hand, readily enable M=O multiple bonding with d electron configurations of up to d⁶.

Published: October 12, 2021



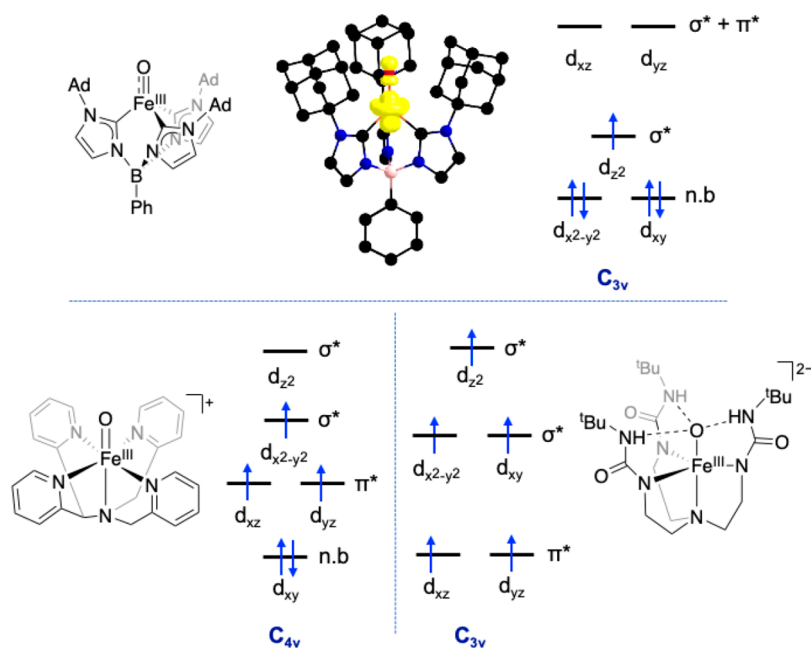


Figure 1. Examples of Fe^{III}-oxo complexes in pseudo-tetrahedral (top; reproduced from ref 2. Copyright 2021 The Authors. Published by American Chemical Society);² tetragonal (bottom left),³ and trigonal bipyramidal (bottom right)⁴ geometries, along with simplified qualitative d-orbital splitting diagrams.

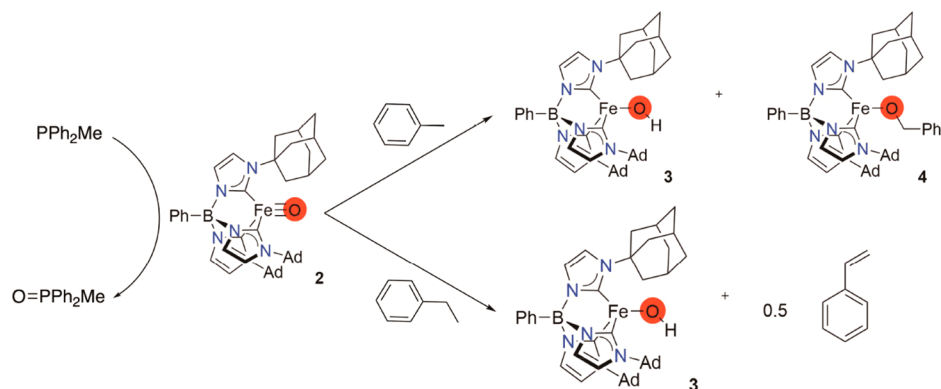


Figure 2. Reactions performed by PhB(AdIm)₃Fe=O. Reproduced from ref 2. Copyright 2021 The Authors. Published by American Chemical Society.

Pseudo-tetrahedral geometries, on the other hand, readily enable M=O multiple bonding with d electron configurations of up to d⁶. This arises because the lowest energy d-orbitals in C_{3v} symmetric four-coordinate compounds are largely nonbonding (Figure 1). In fact, Fe^{III}- as well as Co^{III}-imides—which are isoelectronic with oxos—based on tris(phosphino)-, tris(pyrazolyl)-, and tris(carbene)-borate ligands have been known for quite some time.⁸ However, the analogous L₃Fe^{III}-oxos have been elusive, until now. PhB(AdIm)₃Fe=O has an S = 1/2 configuration and, consequently, a remarkably short Fe–O distance of 1.633(2) Å,² even in comparison to known Fe(IV) complexes (1.65–1.68 Å).¹ The reactivity of PhB(AdIm)₃Fe=O is thus particularly striking. The complex can carry out hydrogen atom abstraction, O atom transfer, as well as the dehydrogenation of ethylbenzene, as otherwise only available to Fe^{IV}-oxo species.

The authors attribute the reactivity to a so-called “unmasking” of the oxo, due to the absence of the H-bonding interactions that are present among other Fe^{III}-oxo complexes.

The authors attribute the reactivity to a so-called “unmasking” of the oxo, due to the absence of the H-bonding interactions that are present among other Fe^{III}-oxo complexes. However, the structure shows that the adamantyl groups of the tris(carbene)borate ligand encapsulate the oxygen atom. Perhaps these units are the goldilocks of side groups: just right, i.e., bulky enough to protect the oxo and enable its formation while still allowing substrate access. However, in contrast to the wealth of spectroscopic information and

structure function studies that are available for Fe^{IV}-oxo species, the factors that underpin the activity of PhB-(AdIm)₃Fe=O are still to be determined. Likewise, it remains to be seen how ligand variations might alter the reactivity and properties of related mid-valent oxo complexes. The work by the Smith group will certainly foster the discovery of further examples and reveals that such compounds could have significant, and surprising, activity.

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<https://pubs.acs.org/10.1021/acscentsci.1c01184>

Notes

The author declares no competing financial interest.

REFERENCES

- (1) Larson, V. A.; Battistella, B.; Ray, K.; Lehnert, N.; Nam, W. Iron and manganese oxo complexes, oxo wall and beyond. *Nat. Rev. Chem.* **2020**, *4*, 404–419.
- (2) Valdez-Moreira, J. A.; Beagan, D. M.; Yang, H.; Telser, J.; Hoffman, B. M.; Pink, M.; Carta, V.; Smith, J. M. Hydrocarbon Oxidation by an Exposed, Multiply Bonded Iron(III) Oxo Complex. *ACS Cent. Sci.* **2021**. DOI: [10.1021/acscentsci.1c00890](https://doi.org/10.1021/acscentsci.1c00890).
- (3) Andris, E.; Navratil, R.; Jasik, J.; Puri, M.; Costas, M.; Que, L.; Roithova, J. Trapping Iron(III)-Oxo Species at the Boundary of the “Oxo Wall”: Insights into the Nature of the Fe(III)-O Bond. *J. Am. Chem. Soc.* **2018**, *140*, 14391–14400.
- (4) MacBeth, C. E.; Golombek, A. P.; Young, V. G., Jr.; Yang, C.; Kuczera, K.; Hendrich, M. P.; Borovik, A. S. O₂ Activation by Nonheme Iron Complexes: A Monomeric Fe(III)-Oxo Complex Derived From O₂. *Science* **2000**, *289*, 938–941.
- (5) Winkler, J. R.; Gray, H. B. Electronic Structures of Oxo-Metal Ions. *Struct. Bonding (Berlin, Ger.)* **2011**, *142*, 17–28.
- (6) Matson, E. M.; Park, Y. J.; Fout, A. R. Facile Nitrite Reduction in a Non-heme Iron System: Formation of an Iron(III)-Oxo. *J. Am. Chem. Soc.* **2014**, *136*, 17398–17401.
- (7) Reed, C. J.; Agapie, T. A Terminal FeIII-Oxo in a Tetranuclear Cluster: Effects of Distal Metal Centers on Structure and Reactivity. *J. Am. Chem. Soc.* **2019**, *141*, 9479–9484.
- (8) Saouma, C. T.; Peters, J. C. M≡E and M = E Complexes of Iron and Cobalt that Emphasize Three-fold Symmetry (E = O, N, NR). *Coord. Chem. Rev.* **2011**, *255*, 920–937.