Dioxygen Reactivity of Biomimetic Fe(II) Complexes with Noninnocent Catecholate, $\alpha$-Aminophenolate, and $\alpha$-Phenylenediamine Ligands

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Dioxygen Reactivity of Biomimetic Fe(II) Complexes with Noninnocent Catecholate, o-Aminophenolate, and o-Phenylenediamine Ligands

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ABSTRACT: This study describes the O2 reactivity of a series of high-spin mononuclear Fe(II) complexes each containing the facially coordinating tris(4,5-diphenyl-1-methylimidazol-2-yl)phosphine (Ph2TIP) ligand and one of the following bidentate, redox-active ligands: 4-tert-butylicatecholate ([BuCatH]), 4,6-di-tert-butyl-2-amino-phenolato ([Bu2APH]), or 4-tert-butyl-1,2-phenylenediamine ([BuPDA]). The preparation and X-ray structural characterization of [Fe3+(Ph2TIP)(BuCatH)]OTf, [Fe2+(Ph2TIP)(Bu2APD)](OTf)2, [Fe2+(Bu2PDA)]OTf, and [Fe2+(Ph2TIP)(Bu2APH)]OTf [2]OTf was reported in our previous paper [Bittner et al., Chem.—Eur. J. 2013, 19, 9686–9698]. These complexes mimic the substrate-bound active sites of nonheme iron dioxygenases, which catalyze the oxidative ring-cleavage of aromatic substrates like catechols and aminophenols. Each complex is oxidized in the presence of O2, and the geometric and electronic structures of the resulting complexes were examined with spectroscopic (absorption, EPR, Mössbauer, resonant Raman) and density functional theory (DFT) methods. Complex [3]OTf reacts rapidly with O2 to yield the ferric-catecholate species [Fe3+(Ph2TIP)(BuCat)]+ (3m+), which undergoes further oxidation to generate an extradiol cleavage product. In contrast, complex [4]2+ experiences a two-electron (2e−) ligand-based oxidation to give [Fe2+(Ph2TIP)(BuPDA)](OTf)2 (4a+), where DIBQ is o-diaminobenzoquinone. The reaction of [2] with O2 is also a 2e− process, yet in this case both the Fe center and [Bu2AP] ligand are oxidized; the resulting complex (2m+ is best described as [Fe3+(Ph2TIP)(Bu2ISQ)]+, where ISQ is o-iminobenzoquinone. Thus, the oxidized complexes display a remarkable continuum of electronic structures ranging from [Fe3+(L2−)]+ (3m+) to [Fe3+(L+)]2+ (2m+) to [Fe2+(L2)]2+ (4m+). Notably, the O2 reaction rates vary by a factor of 105 across the series, following the order [3] > [2] > [4]2+, even though the complexes have similar structures and Fe3+/2+ redox potentials. To account for the kinetic data, we examined the relative abilities of the title complexes to bind O2 and participate in H-atom transfer reactions. We conclude that the trend in O2 reactivity can be rationalized by accounting for the role of proton transfer(s) in the overall reaction.

1. INTRODUCTION

Catechols and their nitrogen-containing analogs (o-aminophenols and o-phenylenediamines; see Scheme 1) are well-established members of the “o-phenylene family” of redox noninnocent ligands.1−18 One-electron oxidation of these bidentate ligands provides the corresponding (di)(imino)-semiquinone radicals, and two-electron oxidation yields the closed-shell (di)(imino)benzoquinones. Complexes that combine the noninnocent ligands in Scheme 1 with redox-active metal center(s) often possess ambiguous electronic structures, since multiple assignments of ligand and metal oxidation states are possible. Thus, careful examination with a variety of experimental and computational methods is usually required to obtain accurate electronic-structure descriptions.19−23

While the role of o-phenylene ligands in electron-transfer series has been studied extensively, their ability to facilitate proton-coupled electron transfers (PCETs) in transition-metal complexes has received less attention. As shown in Scheme 1, the free compounds are able to donate a total of two protons (2H+) and two electrons (2e−) in various combinations.
Coordination to a redox-active metal center is expected to perturb the chemical and electronic properties of these ligands, resulting in complexes with rich and unpredictable PCET landscapes. Such complexes may find applications in chemical processes that require multiple proton and electron transfers, including energy-related reactions like water oxidation, hydrogen production, and nitrogen fixation.\textsuperscript{24–29} For instance, an iron complex with \(\alpha\)-phenylenediamine ligands was recently shown to undergo photochemical H\(_2\)-evolution via PCET steps.\textsuperscript{30} Similarly, Heyduk et al. have found that zirconium(IV) complexes with noninnocent bis(2-phenolate)amide ligands react with O\(_2\) to yield \(\text{[Zr}^{4+}\text{(Ph}2\text{TIP)}\text{]}\) species—a process that requires donation of 1H\(^+\) and 2e\(^-\) from each ligand.\textsuperscript{31}

Our interest in noninnocent ligands stems from efforts to prepare synthetic mimics of nonheme iron dioxygenases. These enzymes carry out the oxidative ring-cleavage of aromatic substrates (catechols, aminophenols, and hydroquinones), and the catalytic cycles are thought to involve formation of a ferrous-(substrate radical) intermediate.\textsuperscript{32–35} The high-spin ferrous centers of 1 and 2\textsuperscript{+} are bound to the 2-amino-4,6-di-\(\text{Bu}\)naphtalene \((\text{Bu}2\text{APH})\) “substrate,” and the enzymatic coordination replication is achieved using a facially coordinating N3 supporting ligand: hydrotris(3,5-diphenylpyrazol-1-yl)boration \((\text{Ph}2\text{Tp})\) in the case of 1 and tris(4,5-diphenyl-1-methylimidazo-2-yl)phosphine \((\text{Ph}2\text{TIP})\) in 2\textsuperscript{+} OTf (see Scheme 2). These complexes were shown to engage in ligand-based H-atom transfer (HAT) reactions to yield novel species containing an Fe(II) center coordinated to an iminobenzosemiquinonate \((\text{Bu}2\text{r-ISQ})\) radical, thus providing synthetic precursors for the putative Fe(II)/ISQ intermediate of the enzyme. The Fe(II)/ISQ complexes can be further oxidized by one electron, although it has proven difficult to determine whether this process is ligand- or iron-based. Detailed crystallographic, spectroscopic, and computational analyses suggest that the fully oxidized species have intermediate electronic configurations between the Fe\(^{3+}\)–\(\text{Bu}2\text{r-ISQ}\) and Fe\(^{4+}\)–\(\text{Bu}2\text{1BQ}\) limits,\textsuperscript{37} where \(\text{Bu}2\text{1BQ}\) is iminobenzosemiquinone with tert-butyl substituents in the 4- and 6-positions.

In this Manuscript, we expanded upon our previous studies by preparing mononiron(II) \(\text{Ph}2\text{TIP}\)-based complexes with ligands derived from catechol and \(\alpha\)-phenylenediamine. Like the \(\alpha\)-aminophenolate studies described above, we began with the synthesis and X-ray structural characterization of nonnuclear, high-spin Fe(II) complexes, each containing a bidentate ligand capable of both proton and electron transfer. The catecholate complex \(3\text{OTf}\) was prepared using 4-tert-butylcatechol \((\text{Bu}2\text{CatH})\) and the \(\text{Ph}2\text{TIP}\) supporting ligand (Scheme 2). The \(\alpha\)-phenylenediamine complex \(4\text{OTf}\), has the overall formulation of \([\text{Fe}^{(\text{Bu}2\text{TIP})}(\text{MeCN})_3]\text{OTf}\), where \(\text{Bu}2\text{PDA}\) is 4-tert-buty1,1,2-phenylenediamine. Each of the three Fe(II) complexes \(\{2\text{+}\},\{3\text{+}\}\) and \(\{4\text{+}\}\) is air-sensitive, and the products of the O\(_2\) reactions have been characterized with spectroscopic (ultraviolet–visible (UV–vis) absorption, electron paramagnetic resonance (EPR), Mössbauer, resonance Raman) and computational (density functional theory (DFT)) methods. These studies revealed that the identity of the ligand controls whether the O\(_2\)-driven oxidation is an Fe- or ligand-based process (or a combination of both). In addition, O\(_2\) reaction rates vary by greater than 5 orders of magnitude across the series, despite the fact that the overall structures of the Fe(II) complexes are quite similar. Thus, this unique series of complexes has provided a valuable framework for exploring the relationship between ligand-based PCET chemistry and the O\(_2\) reactivity of Fe complexes. The implications of these results for the O\(_2\) activation mechanisms of the ring-cleaving dioxygenases are also discussed.

### 2. EXPERIMENTAL SECTION

**Materials.** Reagents and solvents were purchased from commercial sources and were used as received, unless otherwise noted. Air-sensitive materials were synthesized and handled under inert atmosphere using a Vacuum Atmospheres Omni-Lab glovebox. The \(\text{Ph}2\text{TIP}\)\textsuperscript{38} and \(\text{Ph}2\text{APH}\)\textsuperscript{39} ligands and the 2,4,6-tri-\(\text{Bu}\)-tert-buty1phenoxyl radical \((\text{TTBP})\) were prepared according to literature procedures. Synthetic procedures for complexes \([\text{Fe}^{(\text{Ph}2\text{TIP})}(\text{MeCN})_3]\text{OTf}\),\textsuperscript{38} \(\text{Bu}2\text{PDA}\) and \(\{2\text{+}\}\text{OTf}\) were published previously by our group.

**Physical Methods.** Elemental analyses were performed at Midwest Microlab, LLC in Indianapolis, IN. UV–vis absorption spectra were measured with an Agilent 8453 diode array spectrometer equipped with a cryostat from Unisoku Scientific Instruments (Osaka, Japan). Fourier-transform infrared (FTIR) spectra of solid samples were obtained with a Thermo Scientific Nicolet iS5 FTIR spectrometer equipped with the iD3 attenuated total reflectance accessory. \(\text{H}\) and \(\text{F}\) NMR spectra were recorded at room temperature with a Varian 400 MHz spectrometer. \(\text{F}\) NMR spectra were referenced to the benzo trifluoride peak at \(-63.7\) ppm. Mass spectra were collected using an Agilent 6890 gas chromatography–mass spectrometer (GC–MS) with a HP-5 (5% phenylmethylpolysiloxane) column. Cyclic voltammetric (CV) measurements were conducted in the glovebox with an epsilon EC potentiostat (iBAS) at a scan rate of 100 mV/s. Cyclic voltametric (CV) measurements were conducted in the glovebox with an epsilon EC potentiostat (iBAS) at a scan rate of 100 mV/s. EPR experiments were performed using a Bruker ELEXSYS E600 featuring an ER441DM cavity that resonates at 9.63 GHz, an Oxford Instruments ITC503 temperature controller, and an ESR-900 He flow cryostat. The program EasySpin\textsuperscript{41} was used to simulate and fit experimental spectra. Resonance Raman (rR) spectra were measured with excitation from either a Coherent I-305 Ar+ laser (488.0 nm) or I-
The DCE solvate is only partially (80%) populated. The ethereal solvate is only partially (78%) populated.

302C Kr* laser (647.1 nm) with ~30 mW of power at the sample. The scattered light was collected using a 135° backscattering arrangement, dispersed by an Acton Research triple monochromator equipped with a 1200 grooves/mm grating and detected with a Princeton Instruments Spec X 100BR CCD camera. Spectra were accumulated by an Acton Research triple monochromator equipped with a 0.04 T permanent magnet, maintaining temperatures between 5 and 300 K. Mössbauer spectra were recorded on a closed-cycle refrigeration spectrometer, model CCR4K, equipped with a 0.04 T permanent magnet, maintaining temperatures between S and 300 K. Mössbauer spectra were analyzed using the software WMOSS (Thomas Kent, SeeCo.us, Edina, Minnesota). The samples consisted of solid powders or crystalline material suspended in nujol, placed in Delrin 1.00 mL cups, and then frozen in liquid nitrogen. The [Fe(Ph2TIP)(MeCN)3](OTf)2 sample was prepared from material crystallized from a mixture of 1,2-dichloroethane (DCE) and Et2O. The air-oxidized sample obtained by either slow dissolution of Et2O into a concentrated MeCN solution or pentane layering of a DCE solution containing 1 equiv of Fe(II) starting complexes with O2. The isomer shifts are quoted at 5 K.

| Table 1. Summary of X-ray Crystallographic Data Collection and Structure Refinement |
|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
|                          | [3](OTf)2DCE             | [4](OTf)(BPh4)3·DCE·C6H52FeN8O6PS | [5](MeCN)(OTf)2·MeCN·Et2O     | [6](OTf)·1SC5H5Cl2  |
| empirical formula         | C60H55Cl5F6FeN8O6PS      | C60H55Cl5F6FeN8O6PS      | C60H55Cl5F6FeN8O6PS      | C60H55Cl5F6FeN8O6PS      |
| formula weight            | 1298.85                  | 1590.34                  | 1388.96                  | 1200.28                  |
| crystal system            | monoclinic               | monoclinic               | monoclinic               | monoclinic               |
| space group               | P21                     | P21/n                    | P1                      | P1                      |
| a, Å                     | 21.4928 (2)              | 21.4928 (2)              | 21.4928 (2)              | 21.4928 (2)              |
| b, Å                     | 18.3202 (4)              | 18.3202 (4)              | 18.3202 (4)              | 18.3202 (4)              |
| c, Å                     | 17.9588 (3)              | 17.9588 (3)              | 17.9588 (3)              | 17.9588 (3)              |
| α, deg                   | 90                      | 90                      | 88.192 (2)               | 97.790 (1)               |
| β, deg                   | 90.1428 (9)              | 90.1428 (9)              | 90.1428 (9)              | 90.1428 (9)              |
| γ, deg                   | 90                      | 90                      | 90.1428 (9)              | 90.1428 (9)              |
| V, Å3                    | 8006.8 (3)               | 8006.8 (3)               | 8006.8 (3)               | 8006.8 (3)               |
| Z                        | 4                       | 4                       | 4                       | 4                       |
| Dm, g/cm³                | 1.399                    | 1.399                    | 1.376                    | 1.429                    |
| μ, mm⁻¹                  | 1.5418                   | 0.7107                   | 0.7107                   | 1.5418                   |
| θ range, deg             | 6 to 148                 | 6 to 148                 | 6 to 147                 | 6 to 147                 |
| reflections collected    | 60 871                   | 77 363                   | 74 982                   | 74 982                   |
| independent              | 23 500                   | 19 234                   | 19 234                   | 19 234                   |
| reflections [Ra = 0.0372] | [Ra = 0.0348]            | [Ra = 0.0372]            | [Ra = 0.0348]            | [Ra = 0.0372]            |
| data/restraints/parameters | 23 500/7/1532           | 19 234/67/1058           | 16 362/7/898             | 21 895/129/1607          |
| GOF (on P)               | 1.041                    | 1.051                    | 1.050                    | 1.074                    |
| R1(r2/R2) (I > 2σ(I))²   | 0.0390/0.1022            | 0.0962/0.2182            | 0.0470/0.1170            | 0.0425/0.1169            |
| R1(r2/R2) (all data)²   | 0.0395/0.1028            | 0.1280/0.2375            | 0.0589/0.1253            | 0.0478/0.1215            |

Footnotes: 42 Low-field (0.04 T) variable temperature (5–200 K)

Footnotes: 43ters [Ra = 0.0372] [Ra = 0.0348] [Ra = 0.0372] [Ra = 0.0348] [Ra = 0.0372]

Footnotes: 44 X-ray crystallographic parameters are provided in Table 1, and experimental details are available in the CIFs.

Footnotes: 45 X-ray crystallographic parameters are provided in Table 1, and experimental details are available in the CIFs.

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Dioxygen Reactivity Studies. Oxygenation studies were performed by injecting anaerobic solutions of the Fe(II) complex into O2-saturated solutions of CH2Cl2 at the desired temperature. Elemental analysis calculations were performed by injecting anaerobic solutions of the Fe(II) complex into O2-saturated solutions of CH2Cl2 at the desired temperature. Elemental analysis calculations were performed by injecting anaerobic solutions of the Fe(II) complex into O2-saturated solutions of CH2Cl2 at the desired temperature.

DFT Computations. DFT calculations were performed using the ORCA 2.9 software package developed by Dr. F. Neese (MPI for Chemical Energy Conversion). Calculations involving 4'-enabled Hückel's three-parameter hybrid functional for exchange along with the Lee–Yang–Parr correlation functional (B3LYP). These calculations utilized Ahlrichs' valence triple-ζ basis set (TZV) and auxiliary basis set in conjunction with polarization functions on all atoms. The geometry-optimized model of the Fe(II) complex with bidentate tert-butyl substituents of the bidentate ligand were replaced with Me groups. Geometry optimizations were performed for the Fe(II) precursors, [Fe/O2] adducts, and O2 under tight convergence criteria, and the resulting models were used to obtain gas-phase vibrational and thermodynamic data. Solvent effects were calculated using the conductor-like screening model (COSMO) with a dielectric constant (ε) of 9.08 for CH2Cl2. The “spin-flip” feature of ORCA was employed to generate [Fe/O2] wave functions for S1 = 2 and 1 states.

3. RESULTS AND ANALYSIS

3.A. Synthesis, X-ray Structures, and Electrochemical Properties. Reaction of [Fe(Tpp-TIP)(MeCN)](OTf)2 with iBuCatOH or iBuPDA in THF generated the [PPh3-based complexes [3]OTf and [4](OTf)2], respectively; the synthesis of [3]' also required 1 equiv of NaBPh₄. Yellow crystals of [3]OTf were grown by layering a DCE solution with hexane. Recrystallization of [4](OTf)2 by slow diffusion of Et2O into a DCE solution provided colorless and analytically pure material that was used in subsequent reactivity and spectroscopic studies. Crystals for X-ray diffraction (XRD) analysis were obtained by either (i) slow diffusion of Et2O into a concentrated MeCN solution of [4](OTf)2 or (ii) pentane layering of a DCE solution. In the latter case, the resulting crystals diffracted poorly due to extensive disorder of the triphenylphosphine counteranions. However, by adding 1 equiv of NaBPh₄ to the DCE solution, we were able to grow well-diffracting crystals with an overall composition of [4](OTf)(BPh₄).

As shown in Figure 1, the X-ray structure of [3]OTf features a five-coordinate (5C) Fe(II) complex with bidentate monoanionic catecholate and facially coordinating PPh3-TIP ligands. The [3]OTf unit cell contains two symmetrically independent complexes, and metric parameters for both are provided in Table 2. The Fe(II) coordination geometry is trigonal-bipyramidal for one cation (r = 0.70) and distorted square-pyramidal (r = 0.24) for the other. The crystallographic data provide solid evidence that the catecholate ligand is monoanionic. First, there is a significant difference in the lengths of the O1–C49 and O2–C50 bonds (1.39 and 1.33 Å, respectively). Second, the iBuCatH ligand binds asymmetrically with Fe1–O1 bond distances that are ~0.30 Å longer than the corresponding Fe1–O2 bonds. The protonated donor is weakly bound with an Fe1–O1 distance of 2.23 ± 0.01 Å, while the anionic donor exhibits a shorter Fe1–O2 distance of 1.92 ±

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“The [3]OTf·2DCE structure contains two symmetry-independent complexes per unit cell. Parameters are provided for both structures. “The [5]OTf·1.5CH2Cl2 structure contains two symmetry-independent complexes per unit cell. Since the structures are nearly identical, parameters are only provided for one complex. “See reference 69 for definition of the r value.

0.01 Å (Table 2). Such bond distances are generally similar to those observed in the four previously reported Fe(II) complexes with monoanionic catecholate ligands.35,70–72 The triflate counteranion forms a hydrogen bond with the hydroxyl group of the °HCatH ligand, consistent with the O1--O3(Trf) distance of ~2.67 Å. The average Fe–N bond distance is 2.150 Å, similar to the corresponding distances measured for the °HAPH-based complex (2)35 and indicative of a high-spin, pentacoordinate Fe(II) complex.72 Consistent with this fact, the 1H NMR spectrum displays paramagnetically shifted peaks ranging from 65 to ~30 ppm (Supporting Information, Figure S1).

The two X-ray structures of complex [4]2+ shown in Figure 2 reflect the different conditions under which the crystals were generated (vide supra). Crystals grown in a DCE/pentane mixture contain a 5C dicatonic Fe complex associated with one OTf and one BPh4 counteranion, in addition to DCE and pentane solvent molecules (Table 1). The coordination environment of the Fe(II) center is intermediate between square-planar and trigonal-bipyramidal (r = 0.45; Table 2). In contrast, the structure arising from crystals grown in MeCN/ Et2O features a six-coordinate (6C) Fe(II) center bound to a solvent-derived MeCN ligand in addition to °H2TIP and °H2PDA (Figure 2). The increase in coordination number lengthens the average Fe–Ndp, bond distance from 2.13 Å in [4]2+ to 2.19 Å in [4]MeCN).35 The °H2PDA ligand binds symmetrically in the 6C structure (Fe–Ndp, distance of 2.24(1) Å), while the Fe1–N7/N8 distances differ by 0.093 Å in the 5C structure. The observed Fe–N bond lengths indicate that the Fe(II) centers are high-spin in both structures. This conclusion is supported by the corresponding 1H NMR spectrum (Supporting Information, Figure S1) and the measured magnetic moment of 5.48 μB in CH2Cl2. The neutral charge of the °H2PDA ligands is confirmed by the presence of N–C bond lengths of 1.45(1) Å, typical of aryl amines (anilide anions, in contrast, exhibit N–C bond distances of ~1.39 Å). In both structures, the °H2PDA ring tilts out of the plane formed by the N7–Fe1–N8 chelate by ~23°, and each triflate is hydrogen-bonded to an amino group of °H2PDA.
As described below, the noninnocent nature of the o-phenylene ligands plays an important role in the reactions of the corresponding Fe(II) complexes with O₂. To highlight this phenomenon, we prepared a "control" φH₂TIP-based Fe(II) complex with a completely innocent ligand (i.e., one incapable of transferring either protons or electrons). For this purpose we selected 2-methoxy-5-methylphenolate (Me₂MP; Scheme 2); this ligand is structurally similar to an(Me₂CatH, yet the second O-donor is methylated instead of protonated. Complex [Fe²⁺(φH₂TIP)(Me₂MP)]OTf, [5]OTf, was prepared in a manner similar to [3]OTf, and light green crystals were obtained by layering a CH₂Cl₂ solution with hexanes. The resulting structure reveals a 5C, high-spin Fe(II) center bound to phiH₂TIP and Me₂MP in a distorted trigonal-bipyramidal geometry (Supporting Information, Figure S2). Importantly, the Fe–O/N bond distances measured for [5]⁺ are very similar to those found for [3]⁺ (Table 2); like an(Me₂Cat, the Me₂MP ligand binds in an asymmetric manner, with Fe–O distances of 1.92 and 2.23 Å. Thus, the overall structure of [5]⁺ closely resembles those in the φ-phenylene series. However, methylation of the –OH donor eliminates the possibility of ligand-based electron transfer (ET) and proton transfer (PT), and this change causes the O₂ reactivities of [3]⁺ and [5]⁺ to diverge in dramatic fashion (vide infra).

Voltammetric studies of the Fe(II) complexes were conducted in CH₂Cl₂ at a scan rate of 100 mV/s with 0.1 M (NBu₄)PF₆, as the supporting electrolyte; redox potentials were referenced to ferrocenium/ferrocene (Fc⁺/0). The CV of the catecholate complex [3]⁺ displays an irreversible anodic wave at +740 mV (Figure 3) and a quasi-reversible couple with E₁/₂ = −30 mV (peak-to-peak separation, ΔE, of 120 mV). Complex [5]⁺ exhibits a quasi-reversible event at nearly the same potential (−10 mV, ΔE = 145 mV), consistent with the structural similarity between [3]⁺ and [5]⁺ noted above. In our previous electrochemical studies of high-spin SC Fe(II) complexes withTp or TIP ligands, the Fe²⁺/Fe³⁺ couple generally appears within 300 mV of the Fc⁺/0 reference.37,73,74 Thus, it is reasonable to assign the first oxidations of [3]⁺ and [5]²⁺ to the Fe²⁺/Fe³⁺ couple.

By comparison, the cyclic voltammogram of the phenylenediamine complex [4]OTf, is less well-defined, but two events are clearly evident at +70 and 560 mV in the corresponding square-wave voltammogram (dashed line in Figure 3). We attribute the low-potential peak to the Fe²⁺/Fe³⁺ couple, which appears ~100 mV higher than the corresponding potentials for [3]⁺ and [5]⁺. This anodic shift is likely due to the neutral charge of an(PDA compared to the monoanionic an(Me₂CatH and Me₂MP ligands. The high-potential redox events for [3]⁺ and [4]²⁺ arise from oxidation of the catecholate or phenylenediamine ligand, respectively. This assignment is consistent with a previous study by Lever et al., which found that the PDA ligand is oxidized at +500 mV when bound to a Ru(II) center.73 Both redox events are irreversible for [4]⁺; indeed, the electrochemical behavior of [4]²⁺ resembles those reported previously for the o-aminophenolate complex 1, which likewise exhibits an irreversible anodic wave near 0 mV, likely due to an ET–PT process.37 For reasons that are not clear to us, complex [2]OTf failed to exhibit well-defined electrochemical features; however, on the basis of prior results,73 the Fe²⁺/Fe³⁺ potential of [2]OTf is likely ~150 mV more positive than the corresponding potential of 1.

3.B. Reaction with Dioxygen. Pale yellow solutions of [3]OTf in CH₂Cl₂ undergo rapid color change upon exposure to air, yielding the blue-green chromophore 3ox. The corresponding electronic absorption spectrum, shown in Figure 4, consists of two broad bands at 700 and 905 nm with ε-values of ~1100 M⁻¹ cm⁻¹. These spectral features are characteristic of ferric-catecholate(2−) complexes and arise from an(Me₂Cat→ Fe(III) ligand-to-metal charge transfer (LMCT) transitions.51,71,72 The EPR spectrum of 3ox displays two S = 5/2 signals with E/D values of 0.14 and 0.25 (Supporting Information, Figure S3), consistent with the presence of a high-spin Fe(III) center. In addition, the Mössbauer (MB) spectrum of 3ox reveals two quadrupole doublets with isomer shifts (δ) near 0.5 mm/s, typical of high-spin ferric ions (Table 3 and Supporting Information, Figure S4). The doublets have different splittings (ΔE₉) of 0.82 and 1.24 mm/s. The heterogeneity in E/D and ΔE₉ values likely arises from different orientations of the an(Me₂Cat ligand in the oxidized complex, similar to the situation observed in the solid state for [3]OTf. Collectively, the spectroscopic data indicate that 3ox has the formula of [Fe³⁺(φH₂TIP)(an(Me₂Cat)]OTf.

In the presence of air, the distinctive absorption bands of 3ox exhibit first-order decay with a half-life (t₁/₂) of 6300 s, eventually yielding a nearly featureless spectrum. Previous studies of related complexes indicate that this decomposition corresponds to oxidation of the catecholate ligand via one (or more) of the pathways shown in Scheme 3.39,73,74 To determine reaction products, the final mixture was analyzed after treatment with acid and extraction into organic solvent (MeCN/Et₂O). The extradiol cleavage products, 4-tert-butyl-2-pyrone and 5-tert-butyl-2-pyrone, are generated in a 40:60 ratio with an overall yield of ~30%, as determined by ¹H NMR. These compounds were also observed using GC-MS, although the isomers are indistinguishable by this technique. When the

Figure 3. Cyclic voltammograms for [3]OTf (top, black), [5]OTf (middle, red), and [4]OTf (bottom, gray) collected in CH₂Cl₂ with 0.1 M (NBu₄)PF₆ as the supporting electrolyte and a scan rate of 100 mV/s. The corresponding square-wave voltammogram (dashed line) is also shown for [4]OTf. In all cases the voltammogram was initiated by the anodic sweep.
were collected at intervals of 1, 20, and 440 s, respectively. Each reaction was performed with $^{18}$O$_2$, the ion signal arising from the extradiol products shifted upward by two mass units, providing conclusive evidence for incorporation of one O atom from O$_2$ (Supporting Information, Figure S5). The 3$^{ox}$ reactivity conforms to the previously established pattern that iron(III)-catecholate complexes with facial, tridentate supporting ligands yield primarily extradiol products, while those with tetridentate ligands provide intradiol products.\textsuperscript{50,51,77,78}

Interestingly, while [3]$^+$ converts to 3$^{ox}$ in a matter of seconds upon exposure to O$_2$, complex [5]$^+$ is relatively stable in the presence of air. As shown in Supporting Information, Figure S6, the $^1$H NMR spectrum of [5]$^+$ in CD$_2$Cl$_2$ features paramagnetically shifted peaks at 58 and $\sim$10 ppm that arise from the Me$_2$MP ligand. These peaks display only modest decreases in intensity (relative to an internal standard) after exposure to O$_2$ for several days, indicating that the geometric and electronic structures of [5]$^+$ remain essentially intact in aerobic solution. UV–vis absorption spectra of [5]$^+$ in O$_2$-saturated CH$_2$Cl$_2$ were collected over a span of 24 h (Supporting Information, Figure S7). These data revealed a gradual increase of absorption intensity in the 500–900 nm region, which corresponds to formation of the ferric complex, [Fe$^{3+}$($\text{Ph}_2$TIP)/($\text{Me}_2$MP)]$^2+$ (5$^{ox}$). The absorption spectrum of 5$^{ox}$ was measured independently by treating [5]$^+$ with 1 equiv of an acetylferrocenium salt (Supporting Information, Figure S7). On the basis of these results, the conversion of [5]$^+$ to 5$^{ox}$ is only 20% complete after 24 h. The stark contrast in O$_2$ reactivities between [3]$^+$ and [5]$^+$ is remarkable given that the two complexes possess very similar geometric structures and Fe$^{3+}$/2+ redox potentials.

As shown in Figure 4, reaction of the o-aminophenolate complex [2]OTf with O$_2$ at room temperature generates a green chromophore (2$^{ox}$) with absorption peaks at 790 and 420 nm. This spectrum is essentially identical to the one previously obtained by treating [2]OTf with 2 equiv of a one-electron oxidant (e.g., AgOTf).\textsuperscript{37} Thus, it is reasonable to assume that 2$^{ox}$ corresponds to [Fe$^{3+}$($\text{Ph}_2$TIP)/($\text{Me}_2$MP)]$^2+$, where the electronic structure can be described as either Fe$^{3+}$-$^{18}$O$_2$TSQ or Fe$^{2+}$-$^{18}$O$_2$IBQ (vide supra). These results indicate that O$_2$ is capable of extracting two electrons from [2]$^+$, whereas initial exposure of [3]$^+$ to O$_2$ involves only one-electron oxidation of the complex. In both reactions, the ET process is associated with loss of a proton from the bidentate ligand. Similar to 3$^{ox}$, complex 2$^{ox}$ undergoes decomposition in the presence of O$_2$, albeit at a much slower rate ($t_{1/2}$ $\approx$ 18 h).

The o-phenylenediamine complex [4](OTf)$_2$ is comparatively less reactive toward O$_2$, requiring days (instead of minutes or hours) for complete oxidation. The resulting complex, 4$^{ox}$, displays an intense absorption band with $\lambda_{\text{max}}$ = 715 nm ($\varepsilon$ = 4300 M$^{-1}$ cm$^{-1}$) and a weaker feature at $\sim$500 nm (Figure 4). This deep-green species is air-stable at room temperature, allowing for crystallization from a MeCN/Et$_2$O mixture. Unfortunately, extensive disorder within the crystal has prevented the collection of a high-resolution structure. The crude crystallographic data indicate that 4$^{ox}$ carries a +2 charge, based on the number of counteranions present. The complex is SC with the tBuPDA-derived ligand bound in a bidentate manner, although sizable uncertainties in metric parameters preclude reliable evaluation of Fe or ligand oxidation states. Solutions of 4$^{ox}$ are EPR silent with room-temperature magnetic moments of 5.14 $\mu_B$, indicative of a S = 2 paramagnet. Since it was not possible to obtain a suitable X-ray crystal structure of 4$^{ox}$, we employed spectroscopic and computational

Figure 4. Time-resolved absorption spectra for the reaction of [3]OTf (top), [2]OTf (middle), and [4]OTf (bottom) with O$_2$; spectra were collected at intervals of 1, 20, and 1440 s, respectively. Each reaction was performed at room-temperature in O$_2$-saturated CH$_2$Cl$_2$ ([O$_2$] = 5.8 mM). The path length of the cuvette was 1.0 cm.

Table 3. Experimental Mössbauer Parameters

<table>
<thead>
<tr>
<th>complex</th>
<th>isomer shift ($\delta$) nm/ s</th>
<th>quadrupole splitting ($\Delta E_Q$) mm/s</th>
<th>reference</th>
</tr>
</thead>
<tbody>
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<td>1.06</td>
<td>2.52</td>
<td>32</td>
</tr>
<tr>
<td>[2]OTf</td>
<td>1.06 (70%)/1.14 (30%)</td>
<td>2.08/2.93</td>
<td>32</td>
</tr>
<tr>
<td>2$^{ox}$</td>
<td>0.64</td>
<td>1.94</td>
<td>32</td>
</tr>
<tr>
<td>[3]OTf</td>
<td>1.08</td>
<td>2.05</td>
<td>this work</td>
</tr>
<tr>
<td>3$^{ox}$</td>
<td>0.53/0.50</td>
<td>0.82/1.24</td>
<td>this work</td>
</tr>
<tr>
<td>[4]OTf</td>
<td>1.04 (75%)/1.05 (25%)</td>
<td>3.13/2.53</td>
<td>this work</td>
</tr>
<tr>
<td>4$^{ox}$</td>
<td>1.03 (40%)/1.18 (35%)</td>
<td>1.98/3.24</td>
<td>this work</td>
</tr>
</tbody>
</table>

*The remaining intensity (25%) arises from the starting material, [4]OTf$_2$.*

Scheme 3

reaction was performed with $^{18}$O$_2$, the ion signal arising from the extradiol products shifted upward by two mass units, providing conclusive evidence for incorporation of one O atom from O$_2$ (Supporting Information, Figure S5). The 3$^{ox}$ reactivity conforms to the previously established pattern that iron(III)-catecholate complexes with facial, tridentate supporting ligands yield primarily extradiol products, while those with tetridentate ligands provide intradiol products.\textsuperscript{50,51,77,78}
techniques to gain insight into its geometric and electronic structures, as described in the following section.

3.C. Spectroscopic and Computational Studies of 4ox.

3.C.i. Mössbauer Experiments. Low-temperature (5 K) MB spectra of [4](OTf)2 collected before and after exposure to O2 are shown in Figure 5. The parameters obtained from fitting the data are provided in Table 3. The major component (75%) of the [4](OTf)2 spectrum is a quadrupole doublet with an isomer shift (δ) of 1.04 mm/s and large splitting (ΔEQ) of 3.1 mm/s. A minor feature (25%) is also evident with δ- and ΔEQ-values of 1.05 and 2.5 mm/s, respectively. Both signals are characteristic of nonheme high-spin Fe(II) centers with N/O of 1.05 and 2.5 mm/s, respectively. Both signals are exposed to O2 for 20 h, new features arising from (benzosemiquinone radical or (diimino)benzoquinone neutral; thus, two possibilities exist: (diimino)-

The short N–C bond distances of 1.29 Å and “four long/two short” pattern of C–C bonds in the N,N-ligand are well-established characteristics of DIBQ units. Mulliken populations revealed that spin-density is found almost exclusively on the Fe center (3.88 e spins), while the bidentate ligand is largely devoid of unpaired spin. The most relevant molecular orbital (MO) for evaluating the 4ox-DFT electronic configuration is the highest-occupied (HO) spin-down (β) MO, shown in Figure 6. The character of this MO is 74% Fe character, with electron density mainly found in a 3d orbital that bisects the N7–Fe1–N8 angle. Thus, there is only modest transfer of electron density from the Fe(II) center to the DIBQ ligand, in agreement with the MB data presented above.

To aid in band assignments, the absorption spectrum of 4ox-DFT was calculated using TD-DFT. As shown in Supporting Information, Figure S8, the computed spectrum exhibits two bands at 635 and 460 nm (ε = 5.4 and 2.2 M−1 cm−1, respectively) that correspond to features in the experimental spectrum. The higher-energy band arises primarily from a π-π* transition, as revealed in the electron
density difference map (EDDM; Supporting Information, Figure S8). In contrast, the intense near-IR (NIR) band corresponds to an Fe(II)$\rightarrow^{3}$$\pi^{*}$-DIBQ MLCT transition localized on the N7→Fe1–N8 unit.

3.C.iii. Resonance Raman Experiments. The electronic structure of the $^{3}$$\pi^{*}$ PDA-derived ligand in 4$^{\text{ax}}$ was further examined using resonance Raman (rR) spectroscopy. Since the complex exhibits a pair of prominent absorption bands, data were collected with two wavelengths of excitation ($\lambda_{\text{ex}}$: 647.1 nm from a Kr$^{+}$ laser was used to probe the NIR feature that arises from a MLCT transition, while 488.0 nm light from an Ar$^{+}$ laser was selected to resonate with the $^{3}$$\pi^{*}$-DIBQ-based $\pi$→$\pi^{*}$ transition. The composite spectrum, shown in Figure 7, was obtained by irradiating frozen samples of 4$^{\text{ax}}$ in CD$_2$Cl$_2$. In some samples, the bidentate N,N-ligand was labeled with the $^{15}$N isotope at the 2-position to aid in peak assignments.

The low-frequency region of the 4$^{\text{ax}}$ spectrum features two intense peaks at 557 and 601 cm$^{-1}$ with $^{15}$N isotope shifts of 2 and 8 cm$^{-1}$, respectively (Figure 7). The 601 cm$^{-1}$ peak is attributed to the breathing mode of the DIBQ ligand. Frequencies (in cm$^{-1}$) are provided for select peaks in the NA spectra, and the corresponding $^{14}$N→$^{15}$N shifts are shown in parentheses. Peaks marked with an asterisk (*) arise from frozen solvent.

Prior rR studies of metal-dioxolene complexes indicate that these peaks correspond to modes that couple $\nu$(N–C) and $\nu$(C–C) motions within the bidentate N,N-ligand. On the basis of its large $^{15}$N isotope shift (8 cm$^{-1}$), the experimental peak at 1384 cm$^{-1}$ matches the DFT-computed mode at 1372 cm$^{-1}$, which has primarily $\nu$(N–C) character (calculated $^{15}$N isotope shift of 7 cm$^{-1}$; Supporting Information, Figure S9). The peaks at 1413 and 1453 cm$^{-1}$ then correspond to $\nu$(C–C) motions of the $^{3}$$\pi^{*}$ DIBQ ring with only minor amounts of $\nu$(N–C) character. Similarly, Lever and co-workers recently published the crystal structure and rR spectrum of [Ru$^{3+}$Cl$_2$(NH$_3$)$_2$(DIBQ)]$, where DIBQ is unsubstituted (diminio)-benzoquinone.86 This complex displays three peaks between 1400 and 1500 cm$^{-1}$ that the authors attribute to stretching modes of the DIBQ ligand. The presence of resonance-enhanced peaks at similar frequencies in the 4$^{\text{ax}}$ spectrum provides further evidence that this complex contains a $^{3}$$\pi^{*}$-DIBQ ligand.

3.D. Kinetic Analysis of O$_2$ Reactivity. Kinetic studies were generally conducted in O$_2$-saturated CH$_2$Cl$_2$ solutions ([O$_2$] = 5.8 mM at 20 °C$^{41,42}$), and rates were measured by monitoring the growth of absorption features associated with the X$^+$ species. To ensure a large excess of O$_2$, concentrations of the Fe(II) complexes never exceeded 1.0 mM. For the reactions of [2]$^{3+}$ and [3]$^{3+}$ with O$_2$, initial rates increased linearly with Fe and O$_2$ concentrations, indicating that the reactions are first-order in both reactants (Supporting Information, Figures S10 and S11). Interestingly, while the [4]$^{2+} +$ O$_2$ reaction is also first-order in Fe concentration, the reaction rate displays only minor variations as [O$_2$] increases from 0.2 to 5.4 mM (Supporting Information, Figure S11). This zero-order [O$_2$] dependence indicates that O$_2$ binding is not the rate-limiting step in the conversion of [4]$^{2+}$→[4]$^{4+}$.

As shown in Figure 8, the reaction of [3]OTf with O$_2$ at ambient temperature proceeds via pseudo-first-order kinetics with a rate constant (k$_r$) of 0.67(5) s$^{-1}$. The formation of 2$^{\text{ox}}$ and 4$^{\text{ax}}$ under the same conditions is more complex, however, as indicated by the “S-shaped” kinetic traces (Figure 8). This behavior suggests that these species are generated via multistep mechanisms involving both ET and PT—a common occurrence for reactions that require net hydride (2$^{\text{ax}}$) or H$_2$ transfer (4$^{\text{ax}}$).77,86 Because of this mechanistic complexity, k$_r$ values for the reactions of O$_2$ with [2]$^{3+}$ and [4]$^{2+}$ were measured using the initial rates approach. Interestingly, the rates of formation span more than 5 orders of magnitude, with k$_r$ values of 0.67(5) (3$^{\text{ax}}$), 1.3(2) × 10$^{-3}$ (2$^{\text{ax}}$), and 4(2) × 10$^{-6}$ s$^{-1}$ (4$^{\text{ax}}$) in O$_2$-saturated CH$_2$Cl$_2$ at room temperature. We also measured an initial rate of 5 × 10$^{-6}$ s$^{-1}$ for the one-electron oxidation of [5]$^{2+}$ to 5$^{4+}$ (Supporting Information, Figure S7). Thus, despite similar structures, the complexes examined here differ dramatically in their O$_2$ reactivities.

Activation parameters for the [2]OTf + O$_2$ reaction were determined by measuring rates at temperatures between 22 and $\sim 30$ °C. The linear Eyring plot (Supporting Information, Figure S12) indicates an activation enthalpy ($\Delta H^\ddagger$) of 12(2) kcal·mol$^{-1}$ and a large negative activation entropy ($\Delta S^\ddagger$) of $\sim$22(5) cal·mol$^{-1}$·K$^{-1}$. Such values are similar to parameters obtained for similar Fe/O$_2$ adducts$^{46,89}$ and are consistent with an associative reaction involving O$_2$ binding to the Fe center as the rate-determining step.

3.E. Reaction with H-Atom Acceptors. In previous sections, we demonstrated that formation of the oxidized species 2$^{\text{ax}}$–4$^{\text{ax}}$ under aerobic conditions requires both electron
and proton transfers from the parent complexes, although the rates of O2 reaction vary by a factor of 10^5 across the series. Thus, it is plausible that the O2 activation mechanisms involve a combination of electron and proton transfer from the complexes to either dioxygen or superoxide. We therefore examined the reactivity of the title complexes with two well-established H-atom acceptors: TEMPO\(^+\) and 2,4,6-tri-tert-butylphenoxyl radical (TTBP\(^+\)). Both reagents exhibit a strong propensity to react via PCET mechanisms, but TTBP\(^+\) is a much more effective H-atom abstractor than TEMPO\(^+\), as indicated by the bond dissociation free energies (BDFE) of the resulting H–O bonds (BDFE = 77.1 and 66.5 kcal/mol, respectively, in MeCN).\(^90\)

Treatment of [3]\(^+\) with either TEMPO\(^+\) or TTBP\(^+\) yields a blue-green species with absorption features identical to those observed for 3\(^+\) (Supporting Information, Figure S13). Given the formulation of 3\(^+\) as [Fe\(^{3+}\)(Cat)(Ph2TIP)]\(^+\), this reaction is classified as "separated PCET" because the electron and proton originate from different units of the [3]\(^+\) complex, namely, the Fe(II) center and CatH ligand. While complexes [2]\(^+\) and [4]\(^+\) are inert toward TEMPO\(^+\), both react rapidly with TTBP\(^+\). As described in a previous manuscript,\(^37\) TTBP\(^+\) removes a hydrogen atom from the (Ph2APH ligand of [2] to generate the corresponding Fe(II)–(Ph2ISQ complex. Complex [4]\(^+\) reacts with 2 equiv of TTBP\(^+\) to provide a species with spectral features that are similar to those of 4\(^+\), although not identical (Supporting Information, Figure S14). This chromophore is evident by UV–vis spectroscopy even when a single equivalent of TTBP\(^+\) is added; this result suggests that the species generated by removal of one H-atom from [4]\(^+\) undergoes disproportionation to yield the starting complex and a 4\(^+\)-like species.

It is noteworthy that [3]\(^+\) is the only complex in the series capable of donating a H-atom to TEMPO\(^+\), indicating that the [3\(^+\)-H] bond is very weak (BDFE < 66 kcal/mol). Bordwell and Mayer have demonstrated that the BDFE the X–H bond formed in a 1H\(^+\)/1e\(^−\) PCET reaction (i.e., X\(^+\) + H\(^+\) + e\(^−\) → X–H) is given by the following equation:

\[
\text{BDFE}(X - H) = 1.37pK_a + 23.06E^0 + C_{G,solv}
\]

where \(C_{G,solv}\) is a solvent-dependent constant.\(^90,91\) In our case, the relevant parameters are the \(E^0\) values of the starting Fe(II) complexes and the p\(K_a\) values of the one-electron oxidized species. The complexes examined here exhibit greater variability in ligand acidities than in redox potentials. As described above, initial redox potentials differ by ~100 mV across the series, accounting for a modest shift of ~2.5 kcal/mol in BDFE. In contrast, the p\(K_a\) values of aromatic amines are generally ~12 units higher than the corresponding phenols—a shift of 14 kcal/mol in BDFE.\(^90,92,93\) Thus, while the differences in redox potential cannot be ignored, the weaker H-atom donating ability of complexes [2]\(^+\) and [4]\(^+\) compared to [3]\(^+\) is largely due to the greater acidity of the (Ph2CatH ligand relative to (Ph2APH and (Ph2pDA).

These results have mechanistic implications for the O2 reactivity of the complexes examined here. The strength of the [3\(^+\)-H] bond is comparable to that of perhydroxyl radical (HO\(_2\)\(^•\)), which is the product of HAT and O2 (BDFE of HO\(_2\)\(^•\) ≈ 60 kcal/mol).\(^90\) Therefore, complex [3]\(^+\) may be able to react directly with O2 via 1H\(^+\)/1e\(^−\) PCET without prior formation of a ferric-superoxo intermediate. By contrast, complexes [2]\(^+\) and [4]\(^+\) cannot participate in HAT reactions with O2 due to the greater strength of their N–H bonds. For these complexes, O2 activation likely requires initial ET from Fe(II)→O2 followed by oxidation of the ligand via concerted (or stepwise) electron and proton transfers. These mechanistic scenarios are considered further in the Discussion section.

3. F. Computational Studies of O2 Reactivity. The thermodynamics of O2 binding were examined with DFT calculations. A previous study by Schenk et al. found that hybrid functionals with a reduced amount (~10%) of Hartree–Fock (HF) exchange are most reliable for evaluating the \(E^0\) values of the ferrous (Fe(II)) and ferric (Fe(III)) oxidation states.\(^94\) We therefore employed the PBE functional with 10% HF exchange to calculate geometries and thermodynamic parameters for O2, the Fe(II) precursors, and the 6C [Fe/O2] adducts. Since exchange interactions between the unpaired electrons of Fe and O2 give rise to three possible spin states (\(S_{\text{free}} = 1, 2, 3\)), it was necessary to optimize three models for each [Fe/O2] species. The resulting \(S = 2\) [Fe/O2] structures are shown in Figure 9. (Supporting Information, Tables S1–S3 provide metric parameters for each model.) The [4/O2]\(^+\) adduct is dissociative on the \(S = 3\) surface, with calculations invariably converging to structures with very long Fe–O distances (>3.75 Å). In all other cases, O2 coordinates in a bent conformation with Fe–O–O angles between 120 and 140° and Fe–O–Fe distances ranging from 1.95 to 2.18 Å. The O2 ligand can adopt two possible orientations depending on whether the O–
O vector is pointed toward (T) or away (A) from the bidentate ligand. The two orientations are approximately isoenergetic with differences less than the estimated error of the calculations (±2 kcal/mol). In the remainder of this Paper, only the T isomers of the [Fe/O2] adducts are discussed, since these models are more relevant from a mechanistic standpoint.

Table 4 summarizes the computed thermodynamic parameters for the eight Fe(II) + O2 → [Fe/O2] reactions considered here. While the enthalpic contributions (∆HfO2 + ∆Solv) are slightly favorable in most instances, all of the reactions are endergonic (∆G = +7.0–13.0 kcal/mol) due to large and unfavorable entropic effects. A similar pattern has been observed in DFT studies of O2 binding to nonheme Fe(II) enzymes, where the calculated ∆G values range between +8 and 12 kcal/mol. To understand why the O2 binding reactions are decidedly “uphill,” it is instructive to examine the computed properties of the O–O bonds in the [Fe/O2] intermediates. Superoxide ligands typically exhibit O–O bond distances near 1.3 Å and ν(O–O) frequencies between 1050 and 1200 cm⁻¹. In contrast, our DFT-generated [Fe/O2] models have short O–O distances of 1.25 ± 0.02 Å and ν(O–O) frequencies greater than 1250 cm⁻¹ (Table 4), indicating that there is only partial charge transfer from Fe(II) to the O2 ligand. The weakness of the Fe–O2 interactions is also reflected in the low ν(Fe–O) frequencies, which range between 230 to 370 cm⁻¹.

On the basis of the DFT calculations, complex [2]+ has the greatest affinity for O2, followed in the series by [3]+ and [4]2+ (Table 4). This trend correlates with the relative donor strengths of the bidentate ligands (APH+ > CatH+ > PDA) because formation of the Fe–O2 bond requires transfer of electron density from an Fe d orbital to an empty O2 π* orbital. However, our DFT results appear to contradict the kinetic studies reported above, which found that [3]+ is significantly more reactive than [2]+ toward O2. Possible explanations for this discrepancy are provided in the following section.

4. DISCUSSION

In this Manuscript, we described the O2 reactivity of mononiron(II) complexes bound to three types of o-phenylene ligands (Schemes 1 and 2). The complexes resemble the substrate-bound intermediates of nonheme Fe(II) dioxygenases that catalyze the oxidative ring-cleavage of aromatic substrates. The PchTIP supporting ligand mimics the facial triad of protein ligands in the active site and the substrate ligands each coordinate in a bidentate manner, resulting in SC Fe(II) complexes capable of O2 binding. In an earlier study, we demonstrated that one- and two-electron oxidation of the PchAPH-based complex [2]OTf yields species containing (imino)benzosemiquinone ligands. Like aminophenolates, catecholates and phenylendiamines can serve as redox-active ligands, although the ease of oxidation of the free ligands increases across the series CatH2 < APH2 < PDA. We therefore synthesized and structurally characterized the homologous complexes [3]OTf and [4]2OTf to better understand the role of redox-active ligands in modulating the O2 reactivity of Fe complexes. The ligands are capable of donating protons as well as electrons, but the acidities run counter to the redox potentials. In other words, the most acidic ligand (PHCatH2) is the hardest to oxidize, while the most reducing ligand (PDA) is the least acidic. This interplay between ET and PT capabilities influences the rates of the O2 reactions as well as the identities of the oxidized products.

Despite similar overall structures, the three Fe(II) complexes in this study display remarkable diversity in their O2 reactivities, as summarized in Scheme 4. The differences concern both the total number of electrons transferred in the reaction (1e⁻ or 2e⁻) and the source of these electrons (iron and/or ligand). The resulting X⁺⁺ species have been characterized by various spectroscopic (UV–vis, EPR, MB, rR) and computational (DFT) methods. These results indicate that the [3]+ ↔ 3ox conversion is an Fe-based 1e⁻ process, while the [4]2+ ↔ 4ox reaction involves 2e⁻ oxidation of the ligand only. The [2]+ ↔ 2ox reaction occupies an intermediate position, since substantial


<table>
<thead>
<tr>
<th>reactants</th>
<th>spin (S_m)</th>
<th>∆HfO2</th>
<th>∆S</th>
<th>∆Solv</th>
<th>∆G</th>
<th>r(O–O) (Å)</th>
<th>ν(O–O) (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[3]+ + O2</td>
<td>S = 3</td>
<td>−0.5</td>
<td>−11.9</td>
<td>−0.1</td>
<td>+11.3</td>
<td>1.25</td>
<td>1287</td>
</tr>
<tr>
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<td>−0.2</td>
<td>−12.2</td>
<td>−1.1</td>
<td>+10.9</td>
<td>1.27</td>
<td>1260</td>
</tr>
<tr>
<td></td>
<td>S = 1</td>
<td>−1.6</td>
<td>−11.7</td>
<td>+0.2</td>
<td>+10.3</td>
<td>1.25</td>
<td>1287</td>
</tr>
<tr>
<td></td>
<td>[2]+ + O2</td>
<td>S = 3</td>
<td>−2.0</td>
<td>−10.0</td>
<td>−1.1</td>
<td>+6.9</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>S = 2</td>
<td>−1.4</td>
<td>−10.9</td>
<td>−1.7</td>
<td>+7.8</td>
<td>1.27</td>
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<tr>
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<td>−2.9</td>
<td>−11.3</td>
<td>−0.2</td>
<td>+8.3</td>
<td>1.25</td>
<td>1303</td>
</tr>
<tr>
<td>[4]2+ + O2</td>
<td>S = 2</td>
<td>+4.0</td>
<td>−11.3</td>
<td>−2.3</td>
<td>+13.0</td>
<td>1.25</td>
<td>1328</td>
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<tr>
<td></td>
<td>S = 1</td>
<td>−1.8</td>
<td>−12.2</td>
<td>+0.4</td>
<td>+10.8</td>
<td>1.23</td>
<td>1406</td>
</tr>
</tbody>
</table>

All energies in kcal/mol. Enthalpies of solution were calculated using COSMO. ∆G = ∆HfO2 + ∆Solv − T∆S

electron density is lost from both the Fe center and tBu2AP ligand. This continuum in electronic structures is evident in the isomer shifts (δ) of the Xox species (Table 3), which range from 0.50 (3ox, Fe3+) to 0.64 (2ox, Fe2.5+) to ~1.1 (4ox, Fe3+) mm/s. In addition, each of the three possible o-phenylene oxidation states (aromatic, semiquinone, benzoquinone; Scheme 1) is represented in the Xox series. Thus, the [Fe2+[Ph2TIP](o-phenylene)] framework supports a wide spectrum of redox and O2 chemistry.

Our kinetic analysis revealed that O2 reaction rates vary by a factor of 105 across the series, following the order [3]+ > [2]+ > [4]. It is somewhat counterintuitive that this order is inversely related to the electron-donating abilities of the free ligands. Moreover, these rates fail to correlate adequately with Fe2+/3+ redox potentials, all of which fall within a 100 mV range near 0 V (vs Fe+/0). Finally, if one assumes that formation of the Fe/O2 adduct is the rate-determining step, then our DFT calculations of O2-binding affinities indicate that [2]+ should be more reactive than [3]+, even though the kinetic data indicate that the reverse is true.

We believe these conflicting results can be reconciled by considering the role of PT in the O2 reaction. The fact that [3] undergoes HAT with TEMPO—a very weak H-atom acceptor—suggests that ET and PT processes are tightly coupled in the [3]+ + O2 reaction. A likely mechanism involves concerted transfer of 1e− and 1H+ to O2 as it approaches the Fe center. In contrast, the intrinsically lower acidity of aromatic amines (relative to phenols) prevents PT in the initial interaction of O2 with [2]+ and [4]. Deprotonation of these ligands in the course of the O2 reaction likely requires complete oxidation of the Fe center to lower the pKa of the amino group(s). Thus, these complexes cannot avoid the thermodynamically uphill ET from Fe(II) to O2, yet once the ferric complex is generated, proton loss to superoxide or bulk solvent would be feasible, as indicated by the CV data (vide supra). Importantly, deprotonation destabilizes the redox-active MOs of the ligand, making it possible for O2 to extract a second electron, thus generating the final 2ox and 4ox products. Thus, we propose that the [2]+→2ox conversion proceeds via a stepwise ET–PT–ET mechanism, although PT may be coupled with the second ET in a HAT reaction. This mechanism follows the one established by Paine et al. for the oxidation of [Fe2+(L)(tBu2AP)]+ in the presence of O2 (where L is the tris(2-pyridyldithio)methanido anion).

The enormous contrast between the O2 reactivities of [3]+ and [5]+ provides the clearest evidence for the decisive role of PT in determining reaction rates of the o-phenylene complexes. These two complexes have nearly identical coordination geometries and Fe3+/2+ redox potentials; however, replacing the –OH group of tBuCatH with the –OCH3 donor of Me2MP decreases the O2 reaction rate by 5 orders of magnitude. Indeed, complex [5]+ is quite stable in the presence of air, even though slow oxidation to the ferric analog (5ox) is observed over the course of days. These results provide further confirmation that the one-electron oxidation of high-spin Fe(II) centers by O2 is an unfavorable process, but the overall reaction barrier can be lowered substantially if the ET is coupled with PT (in either a stepwise or concerted manner).

The 3ox intermediate reacts further with O2 to yield products arising from extradiol ring cleavage. Previous studies have proposed a mechanism that involves direct reaction of the [Fe3+(Cat)]+ unit with O2 to form a ferric-alkylperoxo species, followed by rearrangement to the corresponding lactone (Scheme 5a). In contrast, 2ox and 4ox are relatively air-

Scheme 5

![Scheme 5](image-url)
to a \([\text{Fe}^{II}(\text{ISQ})]\) intermediate. This difference in electronic structure apparently controls subsequent reactivity, with the latter species undergoing simple 1e\(^{-}\) oxidation and the former direct addition of O\(_2\).

The results presented here highlight the mechanistic sophistication of the ring-cleaving dioxygenases. Scheme 5b provides a condensed version of the canonical enzymatic mechanism. A recent DFT study by Christian et al. of extradiol catechol dioxygenases has emphasized the role of the conserved second-sphere histidine residue in the PT steps that occur after O\(_2\) binding.\(^{20}\) This residue first deprotonates the substrate ligand, resulting in an imidazolium group that stabilizes the superoxide ligand through H-bonding interactions. The proton is eventually returned to the O\(_2\) unit after formation of the bridging alkylperoxo intermediate (Scheme 5b). Thus, the enzyme carefully “manages” the PT events to promote O\(_2\) activation and discourage the autoxidation processes observed in our models. Indeed, studies of homoprotocatechuate 2,3-dioxygenase (HPCD) have demonstrated that if the His200 residue is mutated to Ala, the enzyme generates quinone and H\(_2\)O\(_2\) instead of the ring-cleaved products.\(^{101}\) Therefore, the critical difference between the ring-cleaving dioxygenases and the synthetic models reported here (and elsewhere) is the ability to coordinate PT with O\(_2\) activation.

It is noteworthy that none of the synthetic dioxygenase models prepared to date follow the enzymatic mechanism in proceeding through an Fe/O\(_2\) adduct. Even for those complexes that carry out ligand cleavage, like \([3]\)OTf, the first step always involves 1e\(^{-}\) oxidation to the ferric complex -\(\text{Fe}^{III}\) −O\(_2\) to O\(_2\)\(^{−}\); however, in the case of \([3]\)OTf, the PCET reaction does not lead to formation of the Fe(II)-alkylperoxo intermediate (as in the enzyme) because the resulting superoxide moiety has been deactivated through protonation. By coupling O\(_2\) binding with PT to a second-sphere His residue, the dioxygenases reap the energetic benefits of PCET while avoiding the pitfall that has plagued synthetic models. Future modeling efforts should therefore be directed toward the generation of complexes capable of mimicking the enzyme’s exquisite control of PT reactions.

**ASSOCIATED CONTENT**

1H NMR spectra of the Fe(II) complexes, crystallographic structure of \([5]\)OTf, EPR and Mössbauer data for \([3]\)OTf and \([2]\)OTf; results from TD-DFT and frequency calculations of \([4]\)OTf; plots of initial rates versus Fe(II) and O\(_2\) concentrations, Eyring plot for the reaction of \([2]\)OTf with O\(_2\), absorption spectra of the reactions of \([3]\)OTf and \([4]\)OTf; with organic radicals, metric parameters for DFT-optimized models, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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**Supporting Information**

\(\text{[^{1}]}\) NMR spectra of the Fe(II) complexes, crystallographic structure of \([5]\)OTf, EPR and Mössbauer data for \([3]\)OTf and \([2]\)OTf; results from TD-DFT and frequency calculations of \([4]\)OTf; plots of initial rates versus Fe(II) and O\(_2\) concentrations, Eyring plot for the reaction of \([2]\)OTf with O\(_2\), absorption spectra of the reactions of \([3]\)OTf and \([4]\)OTf; with organic radicals, metric parameters for DFT-optimized models, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.
The weaker acidity of aryl amines relative to phenols and catechols. The corresponding Fe(II) complex containing the monoanionic form of BuCatH. Thus, the corresponding Fe(II) CT transition is shifted to higher energy and exists entirely in the UV region, resulting in a colorless complex.

Because of its fast nature, it was not possible to measure the reaction. Therefore, it was not possible to generate an Fe(II) complex containing the monoanionic form of BuCatH. Thus, the corresponding Fe(II) CT transition is shifted to higher energy and exists entirely in the UV region, resulting in a colorless complex.

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