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Photoinduced O₂-Dependent Stepwise Oxidative Deglycation of a Nonheme Iron(III) ComplexChristina Wegeberg,^{†,‡} Víctor M. Fernández-Alvarez,[§] Adiran de Aguirre,[§] Cathrine Frandsen,^{||} Wesley R. Browne,[‡] Feliu Maseras,^{§,⊥} and Christine J. McKenzie^{*,†,||}[†]Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark[‡]Molecular Inorganic Chemistry, Stratingh Institute for Chemistry, Faculty of Science and Engineering, University of Groningen, Nijenborgh 4, AG Groningen 9747, The Netherlands[§]Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Avda. Països Catalans, 16, 43007 Tarragona, Catalonia, Spain^{||}Department of Physics, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark[⊥]Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain

Supporting Information

ABSTRACT: The iron(III) complex [Fe(tpena)]²⁺ (tpena = *N,N,N'*-tris(2-pyridylmethyl)ethylendiamine-*N'*-acetate) undergoes irreversible O₂-dependent *N*-demethylcarboxylation to afford [Fe^{II}(SBPy₃)(MeCN)]²⁺ (SBPy₃ = *N,N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-alimine), when irradiated with near-UV light. The loss of a mass equivalent to the glycyl group in a process involving consecutive C–C and C–N cleavages is documented by the measurement of the sequential production of CO₂ and formaldehyde, respectively. Time-resolved UV–vis absorption, Mössbauer, EPR, and Raman spectroscopy have allowed the spectroscopic characterization of two iron-based intermediates along the pathway. The first of these, proposed to be a low-spin iron(II)-radical ligand complex, reacts with O₂ in the rate-determining step to produce a putative alkylperoxide complex. DFT calculations suggest that this evolves into an Fe(IV)-oxo species, which can abstract a hydrogen atom from a *cis* methylene group of the ligand to give the second spectroscopically identified intermediate, a high-spin iron(III)-hydroxide of the product oxidized ligand, [Fe^{III}(OH)(SBPy₃)]²⁺. Reduction and exchange of the cohydroxo/water ligand produces the crystallographically characterized products [Fe^{II}(SBPy₃)(X)]^{2+/3+}, X = MeCN, [Zn(tpena)]⁺.

INTRODUCTION

Photosensitive iron(III)-carboxylato complexes are well-known in coordination and bioinorganic chemistry.^{1–5} Iron(III) complexes of simple organic acids like oxalate, malonate, citrate, and tartrate are activated by UV and blue light,^{4,6–8} which promotes inner-sphere electron transfer from the carboxylato donor to the iron(III) ion. The resultant carboxylate radical collapses with concurrent reduction of iron(III) to iron(II) and decarboxylation (Figure 1a).^{6,9–12} This process is exploited by plants to avoid iron chlorosis (iron deficiency). Chelators such as citrate or malate bind sparingly soluble iron(III) from the soil and carry it as water-soluble iron(III) complexes from the roots to the plant tips where it is efficiently photoreduced by sunlight, releasing iron(II) to the leaves.^{13,14} Siderophores released by marine bacteria for combatting the low iron bioavailability in the oceans contain an α -hydroxy carboxylate group, and akin to the aforemen-

tioned examples, photomediated cleavage of their iron(III) complexes renders the bioavailable iron.^{15,16} One example is vibrioferrin¹⁷ (Figure 1b) found in several species of marine bacteria. Peculiarly, vibrioferrin complexes bind iron(III) relatively weakly as compared to most siderophores, probably due to the lack of a sixth donor to complete a preferred octahedral coordination geometry.¹⁸ The decarboxylated derivative has affinity for neither iron(II) nor iron(III), and consequently more bioavailable forms of iron are released to the shared iron pool for bacteria and algae.¹⁹ The oxidized photoproducts of the marine siderophores aquachelin²⁰ and aerobactin^{21,22} can coordinate iron(III), however, with a lower binding affinity than the initial complexes. This is important for cell recognition and iron release functions, because these

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Figure 1. (a) Photolysis of iron(III)-carboxylates and (b) sunlight-mediated photoactivation of the siderophore vibrioferrin.⁶

product complexes transport iron(III) into the cell.^{15,16} The photoactivated decarboxylation mechanism is used also for the citrate-based siderophore petrobactin^{23,24} in pathogenic bacteria. In this case, the photoproduct shows a higher affinity for iron(III) than does the parent complex, and both petrobactin and its photoproduct bind iron(III) with a higher affinity than does the iron transport protein transferrin,¹² consequently supplying the iron needed for the survival of the bacteria. Although not reported to be light-dependent, decarboxylation of an iron-coordinated carboxylate group also plays a crucial role in the mechanism of the α -ketoglutarate-dependent nonheme iron oxygenases such as prolyl-4-hydroxylase required for collagen synthesis and AlkB used in the repair of alkylated DNA and RNA.^{25–28}

The light-catalyzed irreversible ligand oxidation we describe herein for the iron(III) complex, [Fe(tpena)]²⁺ (tpena = *N,N,N'*-tris(2-pyridylmethyl)ethylenediamine-*N'*-acetate), models the sunlight-induced decarboxylation of iron(III) coordinated carboxylates in biology. We show that this process occurs in a stepwise fashion by monitoring the small molecule consumption and production. Additionally, we spectroscopically characterize two intermediate iron-based transients on the linear pathway. One activates dioxygen. Ironically, given the photochemistry with consequent O₂ reactivity described here, [Fe^{III}(tpena)]²⁺ is in fact an effective and robust catalyst for the oxidation of organic substrates by PhIO under nonaqueous solutions, in air.^{29,30} This is because transient coordination of this particular terminal oxidant protects the complex from photodegradation and O₂ reactions. Similarly, in water Fe(IV) oxo derivatives, [Fe^{IV}(O)(tpenaH)]²⁺/[Fe^{IV}(O)(tpena)]⁺ can be generated electrochemically, and these aggressively oxidize external substrates without ligand self-decay,^{31,32} again, even in the presence of light and air. In this case, water-derived coligands endow ligand/complex stability. The wide range of distinct and mutually exclusive biomimetic reactivities for this rare carboxylato-containing nonheme iron system illustrates the multifarious roles Fe-carboxylato moieties can adopt in nature for electronic tuning and reactivity. Despite importance in biological systems, this moiety is conspicuous in its absence in reactivity models for nonheme iron.

While sunlight is recognized as a well-known promoter for iron release by siderophores and other small biological chelators, our work implies that it is remiss not to also consider O₂ as a potentially important reagent in these processes. Although the light-induced mobilization of iron is

essential to many plants and microorganisms, the stepwise decomposition of glycol ligands that often occurs in such processes has until now not been explored rigorously.

RESULTS AND DISCUSSION

O₂ and Light-Dependent Oxidative C–N Cleavage.

Air equilibrated acetonitrile solutions of [Fe(tpena)]²⁺, which are exposed to ambient light, turn deep pink over days to weeks (λ_{max} at 382 and 555 nm). The process is accelerated at elevated temperatures to reach completion within hours. The pink solutions yield crystals of the dark purple iron(II) complex of the pentadentate Schiff base *N,N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-alimine (SBPy3), [Fe(SBPy3)(MeCN)](ClO₄)₂ (Figures 2 and 3a). Typically these are mixed with brown crystals of the starting material [Fe₂(μ -O)(tpenaH)₂](ClO₄)₄·2H₂O. Figure 2 illustrates a rationalization for this: the equilibrium (a) lies in favor of the starting material at some point during the reaction. On one occasion, a filtrate that had been left standing in a sunny fume hood for a week after isolation of [Fe₂(μ -O)(tpenaH)₂](ClO₄)₄·2H₂O synthesized by iron(III) metathesis with Zn₂(tpena)Cl₃³³ produced also purple crystals. These proved to be the related heteroleptic dimetallic [Fe(SBPy3)Zn(tpena)]₂(ClO₄)₆(H₂O)₃, Figure 3b. Thus, when bound to iron(III) as a hexadentate ligand, the tpena is susceptible to cleavage of the C–N group of the glycine arm and desaturation of the C–N bond of the 2-pyridylmethylenamine group attached to the same tertiary amine nitrogen atom. Evidenced by isolation of [Fe(SBPy3)Zn(tpena)]³⁺, it can be ascertained that tpena is not susceptible to this light-driven modification when bound to zinc(II). Both structurally characterized product complexes contain 6-coordinated iron(II) with the coordination sphere completed by either an acetonitrile molecule or a nonbonded carbonyl oxygen of tpena in [Fe(SBPy3)(MeCN)]²⁺ and [Fe(SBPy3)Zn(tpena)]³⁺, respectively. SBPy3 is a known ligand, which can be deliberately synthesized by (the more sensible approach of) Schiff base condensation of 2-pyridinecarboxaldehyde and (2-aminoethyl)bis(2-pyridylmethyl)amine, and a handful of iron complexes of SBPy3 have been reported.^{34–36} That the terminal oxidant for the conversion of the iron(III) complex of tpena to an iron(II) complex of SBPy3 is O₂ was established by control experiments in the presence and absence of air or pure O₂. The reaction also requires light, confirmed by the

Figure 2. Formation of an iron(II) complex of SBPy3 $[\text{Fe}(\text{SBPy}_3)(\text{X})]^{n+}$ ($n = 2$ for $\text{X} = \text{MeCN}$, $n = 3$ for $[\text{Zn}(\text{tpena})]^{+}$) via one or both of the *facial* or *meridional* diastereoisomers of $[\text{Fe}(\text{tpena})]^{2+}$. Fascinatingly, these mononuclear iron(III) complexes show a low-spin ($S = 1/2$) and a high-spin ($S = 5/2$) ground state, respectively.²⁹ The solid-state starting material is the “hemihydrate” oxo-bridged $[\text{Fe}_2(\mu\text{-O})(\text{tpenaH})_2]^{4+}$, which undergoes (a) reversible dehydration to form $[\text{Fe}(\text{tpena})]^{2+}$ when dissolved. Thus, *fac-}[\text{Fe}(\text{tpena})]^{2+} and *mer-}[\text{Fe}(\text{tpena})]^{2+} are interconvertible via $[\text{Fe}_2(\mu\text{-O})(\text{tpenaH})_2]^{4+}$. The cascade of reactions, oxidative deglycation and C–N oxidation of tpena to give the Fe(II) complex of SBPy3, starts with either (b) *fac-}[\text{Fe}(\text{tpena})]^{2+} or (c) *mer-}[\text{Fe}(\text{tpena})]^{2+}. The loss of $\text{C}_2\text{H}_3\text{O}_2$ is stepwise in one-carbon atom unit.****

stability of $[\text{Fe}(\text{tpena})]^{2+}$ over extended periods in the dark (Figure S1).

The UV/vis absorption spectrum of $[\text{Fe}(\text{tpena})]^{2+}$, derived from the dehydration over ca. 10 min on dissolution of the hemihydrate solid-state starting compound $[\text{Fe}_2(\mu\text{-O})(\text{tpenaH})_2](\text{ClO}_4)_4$, is shown in Figure 4 (green to blue). This process (Figure 2, step a) is manifested by a color change of the solution from yellow-brown to red-orange and resolution of the absorption at 360 nm.²⁹ Interconversion of the *fac-* and *mer-}[\text{Fe}(\text{tpena})]^{2+} diastereoisomers (Figure 2a) is feasible by dissociation and inversion of the amine group of the tridentate methylpyridine-glycine arm via $[\text{Fe}_2(\mu\text{-O})(\text{tpenaH})_2]^{4+}$ as an intermediate. Thus, both the dehydration of $[\text{Fe}_2(\mu\text{-O})(\text{tpenaH})_2]^{4+}$ and the interconversion are dependent on the presence of adventitious water (1.5 equiv of water per $[\text{Fe}(\text{tpena})]^{2+}$ is supplied by the hydrated solid $[\text{Fe}_2(\mu\text{-O})(\text{tpenaH})_2](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$). The rate of the dehydration reaction is affected by the concentration of water in the acetonitrile (Figure S2), and concentrations of water exceeding 5% v/v do not produce sufficient amounts of $[\text{Fe}(\text{tpena})]^{2+}$ for observation of the light-induced reactions described below. Efforts to introduce dehydrating agents to more fully cleave the diiron starting material were unsuccessful. The starting $[\text{Fe}_2(\mu\text{-O})(\text{tpenaH})_2]^{4+}$ is not susceptible to light-induced decom-*

Figure 3. Single-crystal X-ray structures of the cations of (a) $[\text{Fe}(\text{SBPy}_3)(\text{MeCN})](\text{ClO}_4)_2$ and (b) $[\text{Fe}(\text{SBPy}_3)\text{Zn}(\text{tpena})]_2(\text{ClO}_4)_6(\text{H}_2\text{O})_3$.

Figure 4. UV-vis absorption spectrum of initial $[\text{Fe}_2\text{O}(\text{tpenaH})_2]^{4+}$ (0.05 mM, green) and $[\text{Fe}^{\text{III}}(\text{tpena})]^{2+}$ after 10 min of dehydration (blue), and the photoproduct $[\text{Fe}^{\text{II}}(\text{SBPy}_3)(\text{MeCN})]^{2+}$ (pink) in air equilibrated acetonitrile under ambient conditions. One scan per minute during the dehydration.

position. Under ambient lighting, $[\text{Fe}^{\text{II}}(\text{SBPy}_3)(\text{MeCN})]^{2+}$ dominates UV-vis spectra after a few days.

Mössbauer spectra (Figure 5, Table 1, and Tables S4 and S5) were recorded on frozen aliquots of a solution of ^{57}Fe - $[\text{Fe}_2(\mu\text{-O})(\text{tpenaH})_2](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$ dissolved in air equilibrated acetonitrile and kept under ambient conditions.

Figure 5. Mössbauer spectra (80 K) recorded during the photo-oxidative conversion of the $^{57}\text{Fe}(\text{III})$ complex of tpena to the $^{57}\text{Fe}(\text{II})$ complex of SBPy3 in air equilibrated acetonitrile. $[^{57}\text{Fe}] = 2.5 \text{ mM}$. O_2 was not excluded during sample preparation. The spectra were recorded after (a) 30 s, (b) 10 min, (c) 3 days at rt, and (d) a final solution equivalent to the pink UV-vis trace in Figure 4 was produced by subsequent heating. Color code: $[\text{Fe}_2\text{O}(\text{tpenaH})_2]^{4+}$, green; $\text{fac-}[\text{Fe}(\text{tpena})]^{2+}$, blue; $\text{mer-}[\text{Fe}(\text{tpena})]^{2+}$, red; $[\text{Fe}(\text{SBPy3})(\text{MeCN})]^{2+}$, pink; and a light-induced iron(II) species A in orange.

Samples were collected at intervals of 30 s, 10 min, and 3 d. Finally, the solution was heated to drive the reaction to completion. $[\text{Fe}_2(\mu\text{-O})(\text{tpenaH})_2]^{4+}$ (55%) and $\text{fac-}[\text{Fe}(\text{tpena})]^{2+}$ (45%) are the major species in the initial spectrum after 30 s, Figure 5a. After 10 min, $\text{fac-}[\text{Fe}(\text{tpena})]^{2+}$ dominates (77%), and $[\text{Fe}_2(\mu\text{-O})(\text{tpenaH})_2]^{4+}$ (8%) and $\text{mer-}[\text{Fe}(\text{tpena})]^{2+}$ (15%) are minor species, Figure 5b. After 3 days (Figure 5c), the starting complexes $\text{fac-}[\text{Fe}(\text{tpena})]^{2+}$ (42%) and $[\text{Fe}_2(\mu\text{-O})(\text{tpenaH})_2]^{4+}$ (28%) are present along with the product $[\text{Fe}(\text{SBPy3})(\text{MeCN})]^{2+}$ (28%). In addition, a minor but significant, sharp singlet at $\delta = 0.48 \text{ mm s}^{-1}$ with an intensity of 2% can be fitted. This signal is associated with a photoinduced transient (A, see below). The Mössbauer spectrum of the final dark pink solution (Figure 5d) shows signals for the product $[\text{Fe}^{\text{II}}(\text{SBPy3})(\text{MeCN})]^{2+}$ (83%) and the starting oxo-bridged complex $[\text{Fe}_2(\mu\text{-O})(\text{tpenaH})_2]^{4+}$ (17%). Neither $\text{fac-}[\text{Fe}(\text{tpena})]^{2+}$ nor $\text{mer-}[\text{Fe}(\text{tpena})]^{2+}$ is present, suggesting that one or both of these monomeric species are the direct precursor(s) of $[\text{Fe}^{\text{II}}(\text{SBPy3})(\text{MeCN})]^{2+}$.

Photoinduction of Transient Intermediates A and B and Their Spectroscopic Characterization. Irradiation of air-equilibrated acetonitrile solutions comprising predominantly $[\text{Fe}(\text{tpena})]^{2+}$ with visible ($\lambda = 405\text{--}532 \text{ nm}$) or near UV light ($\lambda = 355\text{--}366 \text{ nm}$) results in the formation of higher concentrations of the yellow intermediate A, which shows an absorption band at $\lambda_{\text{max}} 384 \text{ nm}$, Figure 6a. The appearance of A is faster, when irradiated at 355 nm as compared to irradiation at 405 nm (Figure S3). The rate of photoconversion changes throughout the reaction (indicated by the slopes in Figure 6a). This rate is dependent on the concentration of $[\text{Fe}(\text{tpena})]^{2+}$. In the beginning of the reaction, this photoactive monomeric species is available, but as it is consumed, the kinetics of the equilibrium between the hemihydrate oxo bridged complex and $[\text{Fe}(\text{tpena})]^{2+}$ becomes rate-limiting; less monomeric iron complex is present. The 384 nm absorption for A persists for hours at room temperature, in air, after discontinuation of irradiation. However, over this time the band decreases in intensity. This occurs concurrently with an increase in the absorption at 555 nm due to the final product $[\text{Fe}^{\text{II}}(\text{SBPy3})(\text{MeCN})]^{2+}$. The rate of appearance of the absorption bands due to $[\text{Fe}^{\text{II}}(\text{SBPy3})(\text{MeCN})]^{2+}$ is not affected by the power and wavelength of the light source that had been used to induce the formation of A, suggesting that the conversion of A to $[\text{Fe}^{\text{II}}(\text{SBPy3})(\text{MeCN})]^{2+}$ includes the rate-determining step. Irradiation of acetonitrile solutions of $[\text{Fe}(\text{tpena})]^{2+}$ in the absence of O_2 shows that the photo-activated step is not oxygen-dependent, because A forms to the same extent and at the same rate as it does in the presence of O_2 . If the deoxygenated solution is sealed for a further 2 d, the characteristic absorption bands of $[\text{Fe}^{\text{II}}(\text{SBPy3})(\text{MeCN})]^{2+}$ do not appear. However, on exposure to air/ O_2 , the conversion is initiated and the absorbance at 555 nm due to $[\text{Fe}^{\text{II}}(\text{SBPy3})(\text{MeCN})]^{2+}$ grows in. These observations confirm that A is a transient precursor capable of reacting with O_2 .

The Mössbauer spectra of an irradiated solution containing 57-iron labeled $[\text{Fe}^{\text{III}}(\text{tpena})]^{2+}$ (Figure 6b and Table S5) are dramatically changed as compared to the series of spectra in Figure 5. This shows a dominant singlet (72%) with the same characteristics ($\delta = 0.45 \text{ mm s}^{-1}$) as the minor species, which had been fitted in the Mössbauer spectrum recorded on a mixture trapped along the reaction pathway, Figure 5c. This signal, which is associated with transient A, is consistent with an isotropic electronic structure around the iron atom: either

Table 1. Spectroscopic Assignments for Starting Complexes, Product, and Transient Species^a

	UV-vis	Mössbauer		EPR	<i>S</i> _{Fe}	Raman
	λ_{max} [nm]	δ [mm s ⁻¹]	ΔE_Q [mm s ⁻¹]	<i>g</i> ^b		ν [cm ⁻¹]
[Fe ^{III} O(tpenaH) ₂] ⁴⁺		0.43	1.63	silent	5/2	830 ^c
<i>mer</i> -[Fe ^{III} (tpena)] ²⁺	360	0.31	singlet	4.20	5/2	<i>d</i>
<i>fac</i> -[Fe ^{III} (tpena)] ²⁺		0.16	2.17	2.74, 2.29, 1.68	1/2	<i>d</i>
[Fe ^{II} (SBPy3)(MeCN)] ²⁺	382, 555	0.34	0.67	silent	0	628, 656, 706, 1004, 1080
A	384	0.45	singlet	silent	0	654, 840, 1061
B	<i>e</i>	0.44	1.15	4.25	5/2	<i>f</i>

^aAll values are obtained from samples prepared in MeCN. ^b*g*^{eff} values are denoted for *S* = 5/2. ^c $\nu_{\text{Fe-O-Fe}}$ obtained from the solid-state spectrum of [Fe₂O(tpenaH)₂](ClO₄)₄. ^dMeasurement not possible due to photochemistry initiated by the excitation laser. ^eDeconvolution impossible. ^fNo associated signal detected.

an iron(II) *S* = 0 or an iron(III) *S* = 5/2. Additionally, this spectrum made it possible to deconvolute and identify a significant spectral area of a second transient species **B** (doublet, δ = 0.44 mm s⁻¹, ΔE_Q = 1.15 mm s⁻¹, 12%, colored purple in Figure 6b,c). The spectral area of **B** increased from 12% to 27%, when the same sample was recollected after it had stood for 2 h after irradiation (in ambient light at rt), while the spectral area of **A** had decreased from 72% to 47%. The doublet associated with [Fe(SBPy3)(MeCN)]²⁺ accounts for 10% of the iron content in this second spectrum (Figure 6c). The observations suggest that **A** reacts directly with oxygen and that the transient **B** is the next relatively thermally stable transient along the pathway to the isolated [Fe(SBPy3)(MeCN)]²⁺ (Figure S4). As for all of the other Mössbauer spectra, a component of the starting material [Fe₂(μ-O)(tpenaH)₂]⁴⁺ (16%) remains unconverted, confirming that this complex is neither light nor O₂ sensitive. The overlapping signals due to *fac*-[Fe(tpena)]²⁺ (*S* = 1/2) and *mer*-[Fe(tpena)]²⁺ (*S* = 5/2), which are observed in nonirradiated acetonitrile solutions, have both disappeared.

The EPR spectrum (Figure S5) recorded on a solution analogous to those used for the Mössbauer spectroscopy in Figure 6b,c shows a low intensity signal at *g* = 4.25. This correlates with the doublet (colored purple, Figure 6c) due to the transient species **B** and can be confidently assigned to a mononuclear high-spin (*S* = 5/2) iron(III) complex. Thus, EPR silence is associated with the three remaining species in the Mössbauer spectra in Figure 6b,c. This is expected for the starting material [Fe₂(μ-O)(tpenaH)₂]⁴⁺ due to the strong antiferromagnetic coupling of the high-spin Fe(III) ions mediated by the μ-oxo ligand, and the end product, [Fe(SBPy3)(MeCN)]²⁺, a *S* = 0 iron(II) species. This means that the transient **A** is likely to be an iron(II) species (*S* = 0). Consistently, the ¹H NMR spectrum of an irradiated MeCN-*d*₃ solution of [Fe(tpena)]²⁺ (Figure S6) shows distinct and sharp peaks in the δ_H = 0–10 ppm region. However, broad paramagnetically shifted peaks at δ_H = 17.1, 16.4, 15.6, 13.3, and 10.8 ppm are observed. These are associated with the HS Fe(III) transient **B** and/or a localized organic radical, vide infra. For reference, the ¹H NMR spectrum of solutions of [Fe(tpena)]²⁺ in MeCN-*d*₃ before irradiation displays broad peaks at δ_H = 20.0, 17.6, 9.58, 3.08, -0.62, -2.95, -4.19, and -11.4 ppm, which disappear completely upon irradiation. When an equilibrated acetonitrile solution containing [Fe(tpena)]²⁺ is irradiated at 355 nm during the course of acquisition of resonance Raman spectra (Figure 7) in the absence of O₂, the light-induced reaction is immediately initiated, and several vibrational bands, that can be associated with **A**, appear. The bands increase in intensity over time. The

bands at 654, 840, and 1061 cm⁻¹ together with bands at 1227, 1289, 1569, and 1610 cm⁻¹ due to the pyridyl groups are resonantly enhanced. On subsequent exposure to O₂, these bands disappear as the bands for [Fe(SBPy3)(MeCN)]²⁺ grow in (628, 656, 706, 1004, 1080, 1156, 1158, 1211, 1261, 1299, 1551, 1570, and 1665 cm⁻¹). The Raman spectra show no signals that can be associated with the transient **B**.

Detection of Sequential One-Carbon Atom Products.

The loss of the glycyl arm from tpena and ultimate formation of SBPy3 is a mass loss equivalent to C₂H₃O₂. This can be envisaged to occur through the loss of both C atoms simultaneously or by a stepwise mechanism where each C atom is lost during consecutive C–C and C–N cleavages. Thus, one- or two-carbon atom molecules are the potential products, that is, CO₂, methanol, formaldehyde, formic, and acetic acid. Head space FTIR spectroscopy shows that CO₂ is released immediately upon commencement of irradiation (Figure 8). After 1 h of irradiation, 0.8 equiv of CO₂ is detected. This is interpreted as the release of one CO₂ from [Fe(tpena)]²⁺ and consistent with the carboxylato group being its source.

ESI–MS (Figure S7) on solutions of [Fe^{III}(tpena)]²⁺ shows a base peak (100%) at *m/z* = 446.123 corresponding to [Fe^{II}(tpena)]⁺. This peak decreased to 6% of the base peak in the spectrum of an irradiated solution (1 h, 365 LED), and new peaks appear for the product related ion [Fe^{II}(tpena-CHCOO)(ClO₄)]⁺ (*m/z* = 488.034 (34%) calcd for C₂₀H₂₂ClFeN₅O₄, *m/z* = 488.078) and ions in which the tpena has been either decarboxylated or deglycinated; that is, *m/z* = 518.084 (24%) can be assigned to [Fe^{III}(OH)(tpena-CO₂)(ClO₄)]⁺ (calcd C₂₁H₂₅ClFeN₅O₅, *m/z* = 518.089), and *m/z* = 388.118 can be assigned to [Fe^{II}(tpena-CH₂COO)]⁺ (C₂₀H₂FeN₅, calcd *m/z* = 388.122).

A signal at 9.60 ppm in the ¹H NMR spectra of the irradiated solution of [Fe(tpena)]²⁺ solution (Figure S6) is consistent with the formation of formaldehyde.³⁷ Its production was confirmed and quantified using a colorimetric approach (the Hantzsch reaction³⁸). The quantification was performed under aerobic conditions on a 1.5 mM [Fe(tpena)]²⁺ solution, which is well below the saturation level of O₂ in MeCN (~2.5 mM^{39,40}). The solution was irradiated for 2.5 h to ensure that the production of CO₂ had ceased. Simultaneous monitoring gave a total release of 1.1 mM of CO₂ and 0.9 mM CH₂O from the same solution (Figure S8), indicating that a 1:1 ratio of CO₂ and CH₂O evolves from reactions in MeCN concurrently producing [Fe(SBPy3)(MeCN)]²⁺ from [Fe(tpena)]²⁺. A 60% conversion is measured. That full conversion has not occurred is consistent with the speciation in the Mössbauer spectrum in Figure Sd

Figure 6. (a) $[\text{Fe}(\text{tpena})]^{2+}$ (0.1 mM) in MeCN before (blue) and after irradiation with 365 nm LED lamp (orange). Inset: Time trace of the growth of the 384 nm absorbance. The rates of photo conversion were determined to be 1.3 and 0.058 ms^{-1} (red and green slopes, respectively). (b) Mössbauer spectrum (80 K) recorded on an acetonitrile solution of ^{57}Fe - $[\text{Fe}(\text{tpena})]^{2+}$ (2 mM) after 1 h of exposure to a 365 LED lamp at room temperature showing formation of two new species A and B in orange and purple, respectively. $[\text{Fe}_2\text{O}(\text{tpenaH})_2]^{4+}$ is shown in green. (c) The spectrum of the same sample as that shown in (b) was recollected after 2 h standing at room temperature. The fraction of the light-induced species (orange) has decreased, and the final product of $[\text{Fe}(\text{SBPy3})(\text{MeCN})]^{2+}$ (pink) is now present.

where the starting material $[\text{Fe}_2(\mu\text{-O})(\text{tpenaH})_2]^{4+}$ is still present at the end of the reaction, and the spectrum in Figure 6b, which shows that the photoinduced transient species A

Figure 7. Resonance Raman spectra (λ_{exc} 355 nm at rt). $[\text{Fe}(\text{SBPy3})(\text{MeCN})]^{2+}$ in acetonitrile (0.1 mM, pink), initial spectrum of $[\text{Fe}(\text{tpena})]^{2+}$ (0.5 mM) in acetonitrile in the absence of O_2 (blue, measured as fast as possible with a shutter to block laser except during spectral acquisition) and after in situ irradiation at 355 nm (orange). All spectra are normalized to the solvent band at 918 cm^{-1} ; * = solvent bands from acetonitrile, and the band at 890 cm^{-1} is associated with acidic acid contamination from the acetonitrile.

Figure 8. Time-resolved head space FTIR spectra following the growth of the bands at 2337 and 2360 cm^{-1} due to gaseous CO_2 evolution occurring when a solution of $[\text{Fe}(\text{tpena})]^{2+}$ (2.1 mM) is irradiated at 365 nm (LED). Blue: Initial spectrum before irradiation. Gray: After 30 s of irradiation. Orange: After 1 h irradiation followed by 15 min without radiation so that the solution could cool and the bands due to MeCN vapor at 2293 and 2252 cm^{-1} settle.

only represents 72% of the iron in this sample. The extent of conversion is due to the concentration of adventitious water (which will change during the progress of the reaction). In summary and supported by the simplicity of the evolving iron speciation as evidenced by Mössbauer spectroscopy, the sequential loss, and the detection of equimolar amounts of evolved CO_2 and CH_2O , must mean they derive from the most obvious source, the glycol group.

Proposed Structures of Transients A and B. The results above show that CO_2 is released to give the transient A, which then reacts with O_2 with subsequent CH_2O release after which transient B is detected concurrently with $[\text{Fe}(\text{SBPy3})(\text{MeCN})]^{2+}$ production. Significantly, the color of the solution has not reached maximum possible intensity of the $[\text{Fe}$

(SBPy3)(MeCN)]²⁺ associated bands after release of all possible CH₂O. This suggests that the final step, conversion of **B** to [Fe(SBPy3)(MeCN)]²⁺, is rate limiting, and that **B** is an iron complex of SBPy3, but not [Fe(SBPy3)(MeCN)]²⁺. The combination of spectroscopic techniques shows that the transient mononuclear species **A** and **B** are a low-spin iron(II) and a high-spin iron(III), respectively. A mechanism proposed in Figure 9 is consistent with all of this information. Here, **A** is

Figure 9. Proposed mechanism based on the sequence of CO₂ and CH₂O release, the reaction with O₂, and the proposed structures of transients **A** and **B**.

an iron(II) complex of decarboxylated tpena, and **B** is an iron(III)-hydroxo complex of SBPy3. Admittedly, complex **A** is unusual, if not unrealistic. The chemical structure depicted should be taken only as a simple and unified representation. In this, the ligand is shown as a radical species in an iron(II) complex. Many resonance structures, conformers, and derivatives can be envisaged (see examples in Figures S9 and S10); however, without further information, it is meaningless to favor a specific structure. The putative intervening cyclic iron(III)-alkylperoxido complex is obtained by an O₂ insertion between the iron(II) and radical methylene C atom of **A**. This species undergoes rapid rearrangement to extrude CH₂O and produce transient **B**, [Fe^{III}(OH)(SBPy3)]²⁺. The presumably more stable condensed hemihydrate of this complex, [Fe^{III}₂(μ-O)(SBPy3)₂]⁴⁺, has been structurally characterized, so this assignment seems entirely reasonable. It is expected to be reduced easily on protonation.³⁴

Reaction Mechanism. DFT calculations are an established tool for the elucidation of reactivity involving iron complexes,⁴¹ and we have used this approach to derive a proposal based on light-induced initial CO₂ departure with subsequent O₂ activation. Unless otherwise indicated, the calculated energies are free energies, including zero-point energy, entropic corrections, solvation, and dispersion. Full details are supplied in the Computational Details. The calculations indicate that the two experimentally determined potential starting points for the photochemical process, high-spin (sextet) *mer*-[Fe(tpena)]²⁺ and low-spin (doublet) *fac*-[Fe(tpena)]²⁺, have similar energies. These data are consistent with similarity of the Fe^{III}/Fe^{II} redox potentials for the *fac* and *mer* isomers.⁴² The *mer* isomer is calculated to be 0.7 kcal mol⁻¹ more stable than the *fac* isomer, which is well within the 2 kcal mol⁻¹ uncertainty in calculated absolute stabilities. Consistently, both species are experimentally observed as mixtures in solution (Figure 5b) and the solid state.²⁹ Mössbauer spectroscopy has shown that the *fac* isomer is present in

higher concentrations, and, possibly coincidentally, this is the isomer that we have been able to isolate as crystals for use in X-ray structural characterization.²⁹ DFT calculations indicate that both isomers are close in energy to the parent dimetallic complex [Fe₂(μ-O)(tpenaH)₂]⁴⁺ (1.4 kcal mol⁻¹ above the *fac* isomer), which also suggests that the three species should be easily accessible in reaction media as described in Figure 2a, and this is indeed observed. We evaluated the vertical absorption spectra of both *fac* and *mer* isomers with TD-DFT (see the Supporting Information for further details). The major *fac* isomer has no meaningful active band in the near-UV or visible range. In contrast, the *mer* isomer shows a charge transfer band with maximum absorption at 377 nm. Hence, we postulate that the reaction proceeds through the *mer* isomer. The key orbitals in the absorption band are shown in Figure 10. It corresponds to a transition of a β electron of the lone

Figure 10. Molecular orbitals involved in the key excitation in *mer*-[Fe(tpena)]²⁺.

pair on the nitrogen associated with the glycyl arm of the ligand to one of the semioccupied d orbitals of Fe. The electron transfer results in reduction of the Fe(III) to Fe(II). The spin in the excited sextet state is located mostly in the iron center (4 electrons) and one of the nitrogens (1 electron). The radical character of the nitrogen is partially delocalized toward the carboxylate. Geometry relaxation of the excited state within the TD-DFT approach showed an elongation of the Fe–N distance in the glycyl arm, and to a lesser extent of the Fe–O distance, before it eventually failed due to intrusion of inactive transitions (more details in the Supporting Information).

Our interpretation is that the electron transfer from the ligand to the metal leads to a rearrangement where the carboxylic group loses its anionic character, thus becoming less coordinating, and the attached nitrogen group becomes a planar sp² center. It is not possible to study the intersystem crossings (ISC) that can produce this excited state within the TD-DFT approach, and other multireference treatments such as CASPT2 or NEVPT2 would be prohibitively expensive. We consider nevertheless that the results above strongly suggest that the natural evolution for this system, once the carboxylate group has lost one electron and has therefore become noncoordinating, is the loss of carbon dioxide. Our DFT calculations cannot predict the landing spin state of the relaxation, and because of this we computed the full energy profile leading to products for doublet, quartet, and sextet spin

Figure 11. Free energy profile of the reaction starting from $\text{mer-[Fe(tpena)]}^{2+}$. Experimentally reported intermediates A (equivalent to $^2\mathbf{1}$) and B (equivalent to $^6\mathbf{6}$) are highlighted by circles, as well as the observed reactant and product, $\text{mer-[Fe(tpena)]}^{2+}$ and $\mathbf{17}$, respectively. Energies in kcal mol^{-1} .

states (see the [Supporting Information](#)). Figure 11 presents our postulated evolution upon comparison of the computed profiles with available experimental data on the two detected intermediates A and B. According to Mössbauer spectroscopy (Figure 6), species A, resulting from carbon dioxide loss, must be a doublet, $^2\mathbf{1}$ ($S = 0$, Fe(II) + radical ligand). We depict intermediate $^2\mathbf{1}$ with a radical located in the N-CH_2 arm. Moreover, the identification of species A as a doublet is in agreement with the DFT values for the calculated Mössbauer spectrum (Table S8). The experimental value for the isomer shift (0.45 mm s^{-1}) is much closer to that computed for $^2\mathbf{1}$ (0.43 mm s^{-1}) than to those computed for $^4\mathbf{1}$ (0.79 mm s^{-1}) or $^6\mathbf{1}$ (0.78 mm s^{-1}).

Dioxygen then approaches $\mathbf{1}$, forming a weak adduct $\mathbf{2}$ (not shown in the Figure 11), which evolves to an alkylperoxo species $\mathbf{23}$. Intermediate $\mathbf{23}$ moves toward products through cleavage of the O-O bond in $^2\text{TS1}$. The subsequent intermediate $\mathbf{24}$ contains a terminal CH_2O group with radical character on the oxygen. This terminal group can be released as formaldehyde with a barrier of 15.2 kcal/mol through transition state $^2\text{TS2}$. The structures of $^2\text{TS1}$ and $^2\text{TS2}$, shown in Figure S14, present the expected features with a large elongation ($1.89 \text{ \AA}$) of the O-O bond being cleaved in $^2\text{TS1}$ and a similar elongation ($1.89 \text{ \AA}$) of the N-C bond being cleaved in $^2\text{TS2}$. An alternative path through direct abstraction of the benzylic hydrogen by the oxo group was found to be higher in energy (see Figure S15). The resulting iron(IV) oxo complex of an aminyl radical ligand, $^2\mathbf{5}$, can easily undergo intramolecular proton transfer to reach the very stable $[\text{Fe}^{\text{III}}(\text{OH})(\text{SBPy3})]^{2+}$ complex ($\mathbf{6}$). This complex would in principle be in the doublet state ($^2\mathbf{6}$). However, it will likely evolve to the most stable sextet spin state $^6\mathbf{6}$, which could thus be assigned to transient B. DFT calculations of the Mössbauer

spectra (Table S8) also point to this spin assignment, because the experimental values for quadrupole splitting and isomer shift (1.15 and 0.44 mm s^{-1} , respectively) are much closer to the computed values for $^6\mathbf{6}$ (1.56 , 0.38) than to those for $^4\mathbf{6}$ (2.30 , 0.36) or $^2\mathbf{6}$ (1.88 , 0.17). Complex $^6\mathbf{6}$ can then interact with the solvent (MeCN) to release water and form $[\text{Fe}(\text{SBPy3})(\text{MeCN})]^{2+}$ ($\mathbf{17}$).

Iron(III)hydroxo complexes are relatively reactive; however, several have been well characterized.^{43–51} The final step, where $^6\mathbf{6}$ is reduced with MeCN as the hydrogen atom/electron source, is quite endergonic (by $15.1 \text{ kcal mol}^{-1}$), because of the presumed formation of a $(\text{NCCH}_2)^{\bullet}$ radical in our computational model. A $E^{\text{ox}} = 1.01 \text{ V}$ vs SCE in MeCN has been measured³⁴ for $[\text{Fe}(\text{SBPy3})(\text{MeCN})]^{2+}$, and this can certainly rationalize the facile reduction of its iron(III) congener. This ease of reduction is similar to most iron(III) complexes with closely related neutral polypyridyl ligands.⁴⁹ In fact, the previously reported cation in $[\text{Fe}^{\text{II}}(\text{SBPy3})(\text{MeCN})](\text{BF}_4)_2$ is prepared by exactly this pathway: spontaneous reduction of an iron(III) parent complex, $[\text{Fe}^{\text{III}}(\text{SBPy3})(\text{DMF})](\text{BF}_4)_3$, by its dissolution in MeCN.³⁴

We admit that the free energy profile in Figure 11 is only a plausible reaction path, because there is some isomeric complexity and because there may be a number of crossing points between the different spin states that are not fully analyzed. Moreover, an alternative path could be built for the *fac* isomer of the reactant, but this depends on an initial conversion of the doublet ground state to a sextet, which can absorb (see the [Supporting Information](#)). We ruled out this option as unnecessarily complicated, and because we considered it would not add new chemical insight. In our view, the key result is the finding of at least one path that leads from the photoexcited reactant toward the isolated product.

Comparison of the free energy profile with the spectroscopic data obtained during the light-induced formation of $[\text{Fe}(\text{tpena})]^{2+}$ to $[\text{Fe}(\text{SBPy3})(\text{MeCN})]^{2+}$ (Table 1) indicates that the species **21** and **6** are likely to be the two transient species A and B, respectively, observed with Mössbauer spectroscopy in Figure 6b and c (orange and purple traces, respectively).

CONCLUSION

Monocarboxylato coordination is an important motif in O_2 activating nonheme iron enzymes, and the light-induced reactions described here are important for modeling iron mobilization in aqueous environments by small biomolecules like citrate and siderophores. We speculate that the reactivity may be pertinent for elucidating the light induction of the cleavage of nitrosyl from the protected resting state of nonheme nitrile hydratase.^{52,53} In this context, tautomeric structures involving the noninnocent NO ligand and the iron cofactor could be considered analogously to the electronic communication between the noninnocent glycol donor and iron in the tpena-based system.

The sequential CO_2 and formaldehyde loss from the glycol arm-containing complex $[\text{Fe}(\text{tpena})]^{2+}$ has been monitored and quantified, and this accords fully with the proposed stepwise mechanism. The first step is light-dependent and induces the release of CO_2 to form the yellow species A ($\lambda_{\text{max}} = 384 \text{ nm}$) with a transient band in the Mössbauer spectra consistent with a low-spin Fe(II) complex ($\delta = 0.45 \text{ mm s}^{-1}$). At this point, the ligand contains a carbon-based radical allowing for an insertion reaction of O_2 to produce an iron(III)-alkylperoxide. DFT calculations suggest ensuing O–O cleavage to give an iron(IV)oxo complex. H atom abstraction by this species and formaldehyde release produce the second transient species B proposed to be $[\text{Fe}^{\text{III}}(\text{OH})(\text{SBPy3})]^{2+}$, the oxidized precursor for the isolable $[\text{Fe}^{\text{II}}(\text{SBPy3})(\text{X})]^{n+}$; ($n = 2$ for $\text{X} = \text{MeCN}$, $n = 3$ for $[\text{Zn}(\text{tpena})]^{+}$).

It is remarkable that the decomposition of the tpena ligand has not been observed in water under ambient conditions. This is due to the stability of the hemihydrate, oxo-bridged speciation, and, surprisingly, in view of the light-induced O_2 oxidation described here, tpena is even resistant to oxidative degradation in the presence of large excesses of PhIO. The combination of these observations demonstrates how significant environment is for the chemistry of nonheme iron model compounds containing the biologically germane single carboxylate donor. In summary, we have documented an elegant way of exposing a latent O_2 activating iron site by decarboxylation.

EXPERIMENTAL SECTION

Materials and Preparation. N,N,N' -Tris-2-picolylethylenediamine- N' -acetic acid (tpenaH)⁵⁴ and $[(\text{tpenaH})\text{Fe}-\text{O}-\text{Fe}(\text{tpenaH})](\text{ClO}_4)_4(\text{H}_2\text{O})_2$ ^{31,33} were prepared as described previously. All other chemicals were purchased from Sigma-Aldrich without further purification. O_2 was removed from MeCN with the freeze–pump–thaw method.

Perchlorate salts of metal complexes are potentially explosive and should be handled with caution in small quantities.

$[\text{Fe}(\text{SBPy3})(\text{MeCN})](\text{ClO}_4)_2$. $[\text{Fe}_2(\mu-\text{O})(\text{tpenaH})_2](\text{ClO}_4)_4(\text{H}_2\text{O})_2$ (200 mg, 0.15 mmol) was dissolved in acetonitrile (300 mL), and the solution was kept at 50°C for 7 days. The solution was evaporated and dissolved in acetonitrile (5 mL). After 2 weeks, a small amount of brown $[(\text{tpenaH})\text{Fe}-\text{O}-\text{Fe}(\text{tpenaH})](\text{ClO}_4)_4(\text{H}_2\text{O})$ (25 mg) was removed by gravity filtration, and 1

mL of the clear dark purple supernatant solution was layered with diethyl ether. Dark purple, almost black needles of $[\text{Fe}(\text{MeCN})(\text{SBPy3})](\text{ClO}_4)_2$ (ca. 20 mg by crystal picking, 11%) formed within a few days, along with further $[(\text{tpenaH})\text{Fe}-\text{O}-\text{Fe}(\text{tpenaH})](\text{ClO}_4)_4(\text{H}_2\text{O})_2$ as a brown precipitate (ca. 60 mg). The reaction was not optimized for good yield. ^1H NMR (d_3 - CD_3CN) $\delta = 9.32$ (s, 1H, $\text{N}=\text{CH}$), 9.00 (d, 1H, $J = 5.6 \text{ Hz}$), 8.34 (d, 1H, $J = 7.6 \text{ Hz}$), 8.27 (td, 1H, $J = 7.6, 1.2 \text{ Hz}$), 7.85 (dd, 1H, $J = 5.6, 1.2 \text{ Hz}$), 7.82 (qd, 2H, $J = 7.6, 1.2 \text{ Hz}$), 7.45 (d, 2H, $J = 7.6 \text{ Hz}$), 7.11 (t, 2H, $J = 6.4 \text{ Hz}$), 6.59 (d, 2H, $J = 5.6 \text{ Hz}$), 4.97 (d, 2H, $J = 16.4, \text{CH}_2$), 4.75 (d, 2H, $J = 16.4, \text{CH}_2$), 3.81 (td, 2H, $J = 6.8, 1.6 \text{ Hz}$), 3.22 (t, 2H, $J = 6.0 \text{ Hz}$), and 1.94 (s, 3H, CH_3CN) ppm. ^{13}C NMR (d_3 - CD_3CN) $\delta = 169.8, 165.2, 162.1, 157.7, 154.1, 139.3, 138.8, 129.6, 128.3, 126.1, 122.8, 67.9, 64.9, 57.4$ ppm. UV–vis in MeCN: λ_{max} 382 and 555 nm.

$[\text{Fe}(\text{SBPy3})\text{Zn}(\text{tpena})_2](\text{ClO}_4)_6(\text{H}_2\text{O})_3$. $\text{Zn}_2(\text{tpena})\text{Cl}_3$ ²³ (7.24 g, 11.5 mmol) was dissolved in boiling H_2O , and $\text{Fe}(\text{ClO}_4)_3$ (3.21 g, 8.6 mmol) was added. The vial was left in the fume cupboard for a week in direct sunlight, whereupon deep purple crystals formed together with the bulk product $[\text{Fe}_2\text{O}(\text{tpenaH})_2](\text{ClO}_4)_4$ as a brown powder (75% yield). The purple crystals were isolated by vacuum filtration and washed with H_2O to give a product of 88 mg (0.4%). The reaction was not optimized for good yield. Anal. Calcd for $\text{C}_{84}\text{H}_{96}\text{Cl}_6\text{Fe}_2\text{N}_{20}\text{O}_{31}\text{Zn}_2$ 2336.95 g mol^{-1} : C, 43.17; H, 4.14; N, 11.99. Found: C, 42.92; H, 4.03; N, 11.71. ^1H NMR (400.12 MHz, MeCN- d_3) $\delta = 9.34$ (1H, d, $J = 4.80$), 8.67 (1H, d, $J = 4.40 \text{ Hz}$), 8.45 (1H, s), 8.34 (1H, s), 8.29 (1H, td, $J = 8.0, 1.6 \text{ Hz}$), 8.15 (1H, t, $J = 7.2 \text{ Hz}$), 8.03 (1H, t, $J = 7.2 \text{ Hz}$), 7.96 (3H, m), 7.89–7.80 (4H, m), 7.67 (1H, t, $J = 6.40 \text{ Hz}$), 7.56–7.44 (4H, m), 7.37 (2H, d, $J = 8.00 \text{ Hz}$), 7.24 (4H, m), 4.16–3.99 (6H, m), 3.54–3.35 (6H, m), 3.17–2.93 (5H, m), 2.74 (2H, t, $J = 6.00 \text{ Hz}$), 2.64–2.47 (2H, m). UV–vis in MeCN: λ_{max} 382 (1485) and 555 (1010) nm. ESI–MS (pos. mode, MeCN): found (calcd) $m/z = 193.553$ (193.557, $[\text{Fe}(\text{tpena})]^{2+}$, $\text{C}_{20}\text{H}_{21}\text{FeN}_5$, 1%), 197.555 (197.554, $[\text{Zn}(\text{SBPy3})]^{2+}$, $\text{C}_{20}\text{H}_{21}\text{N}_5\text{Zn}$, 5%), 227.561 (227.564, $[\text{Zn}(\text{tpenaH})]^{2+}$, $\text{C}_{22}\text{H}_{25}\text{N}_5\text{O}_2\text{Zn}$, 2%), 454.112 (454.122, $[\text{Zn}(\text{tpena})]^{+}$, $\text{C}_{22}\text{H}_{24}\text{N}_5\text{O}_2\text{Zn}$, 100%), 494.046 (494.057, $[\text{Zn}(\text{SBPy3})](\text{ClO}_4)^{+}$, $\text{C}_{20}\text{H}_{21}\text{ClN}_5\text{O}_4\text{Zn}$, 8%), and 554.062 (554.078, $[\text{Zn}(\text{tpenaH})](\text{ClO}_4)^{+}$, $\text{C}_{22}\text{H}_{25}\text{ClN}_5\text{O}_6\text{Zn}$, 1%). ATR-IR: 1602 (m), 1308 (w), 1075 (s), 765 (s), 722 (w), 621 (m).

Instrumentation and Methods. UV–vis spectra were recorded in 1 cm quartz cuvettes on either an Agilent 8453 or a Specord600 (AnalytikJena) spectrophotometer at $20 \pm 2^\circ\text{C}$. Raman spectra were recorded in 1 cm quartz cuvettes using λ_{exc} 355 nm at room temperature as described earlier.⁵⁵ Data were recorded and processed using Solis (Andor Technology) with spectral calibration performed using the Raman spectrum of MeCN/toluene (50:50 v/v). Baseline correction was performed for all spectra, and they were normalized to the solvent band of MeCN at 918 cm^{-1} . EPR spectra (X-band) were recorded on a Bruker EMX Plus CW spectrometer on frozen solutions at 100 K. ^1H NMR (400.12 MHz) and ^{13}C NMR (100.61 MHz) spectra were recorded on a Bruker Avance III 400 spectrometer at ambient temperature. Chemical shifts (δ) are denoted relative to the residual solvent peak (d_3 -MeCN: $\delta_{\text{H}} = 1.94 \text{ ppm}$, $\delta_{\text{C}} = 1.32 \text{ ppm}$). Mössbauer spectra were obtained with conventional constant acceleration spectrometers with sources of ^{57}Co in rhodium foil. The spectra were collected at 80 K by using a closed cycle helium refrigerator from APD Cryogenics. Isomer shifts are given relative to that of α -Fe at 295 K. Electrospray ionization (ESI) mass spectra were recorded in high-resolution positive mode on a Bruker microTOF-QII mass spectrometer. Irradiation of $[\text{Fe}(\text{tpena})]^{2+}$ solutions was performed with one of the following: 355 nm laser (7 mW), 365 nm (LED, M365FP1, 1200 mA, Thorlabs), 405 (LED, Thorlabs), or 405 laser (45 mW, ONDAX LM-405). Head-space FTIR spectra were recorded in sealed 1 cm quartz cuvettes on a JASCO FT/IR-4600 spectrometer with a resolution of 8 cm^{-1} . The concentration of CO_2 released was quantified on the basis of standard solutions of Na_2CO_3 as previously described.⁴² Single-crystal X-ray diffraction data for $[\text{Fe}(\text{SBPy3})(\text{MeCN})](\text{ClO}_4)_2$ were collected using a Bruker-Nonius X8 APEX-II CCD instrument at 150 K (Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), graphite monochromated fine-focused sealed tube). Structure solution was carried out with SIR-92 and refined with

SHELXL-97. Multiscan absorption correction was applied. Hydrogen atoms were placed at calculated positions and allowed to ride on their carrier atoms with isotropic displacement parameters $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$. Oxygen atoms of one of the perchlorates were modeled over two positions. X-ray crystal diffraction data of $[\text{Fe}(\text{SBPy}3)\text{Zn}(\text{tpena})_2(\text{ClO}_4)_6(\text{H}_2\text{O})_3]$ were collected at 100(2) K on a Synergy, Dualflex, AtlasS2 diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) and the CrysAlis PRO 1.171.38.43 suite. The structure was solved by dual space methods (SHELXT) and refined on F^2 using all of the reflections (SHELXL-2016). All of the non-hydrogen atoms were refined using anisotropic atomic displacement parameters, and hydrogen atoms were inserted at calculated positions using a riding model.

Computational Details. All calculations were carried using Gaussian 09 D01 software.⁵⁶ The selected level of theory for ground-state calculations was the B3LYP-D3 functional.^{57–60} It was chosen after benchmarking comparisons with other functionals (M06, PBE0-D3, ω B97X-D, M06-L, and OPBE) reported in the Supporting Information. The qualitative validity of the B3LYP-D3 results was further confirmed by recalculation of selected structures in the free energy profile with M06-L and OPBE, also reported in the Supporting Information. TD-DFT calculations were performed using the CAM-B3LYP functional, which is specifically designed for excited states.⁶¹ The LANL2TZ(f) basis set was used for Fe,^{62–64} and the 6-31+G* set was used for light atoms.^{65–67} Geometry optimizations were carried out without symmetry constraints, and frequency calculations were performed on all optimized geometries to identify minima and transition states. Solvent contributions were added via the SMD model (acetonitrile $\epsilon = 35.688$).⁶⁸ All reported energies are free energies at 298 K and 1 atm. The Mössbauer parameters were calculated using the ORCA package⁶⁹ (version 4.0). The functional and solvation were the same as described above for the geometry optimization, and the basis set was modified to CP(PPP) for iron plus def2-TZVPP for other atoms, which is deemed as more appropriate for this type of calculations.^{70–72} The computed isomer shifts (δ) were obtained using a fitted linear equation $\delta = \alpha(\rho - C) + \beta$.⁷³ A data set collection of computational results is available in the IoChem-BD repository,⁷⁴ and can be accessed via <https://doi.org/10.19061/iochem-bd-1-102>.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b07455.

X-ray crystallographic data for $[\text{Fe}(\text{SBPy}3)(\text{MeCN})](\text{ClO}_4)_2$ (CIF)

X-ray crystallographic data for $[\text{Fe}(\text{SBPy}3)\text{Zn}(\text{tpena})_2(\text{ClO}_4)_6(\text{H}_2\text{O})_3]$ (CIF)

Tables of crystallographic and structural details, time-resolved UV–vis, laser power dependence, EPR spectra, calibration for CO_2 detection, DFT benchmarking, complete free energy profiles, TD-DFT results, computed Mössbauer results, and Cartesian coordinates for all computed species (PDF)

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Notes

The authors declare no competing financial interest.

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