Green-Light-Driven Fe(III)(btz)₃ Photocatalysis in the Radical Cationic [4+2] Cycloaddition Reaction

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igcap ince the advent of photochemistry, there has been a Significant push to replace the photoredox catalysts containing Ru and Ir with those with earth-abundant and sustainable metals; metals such as Cr, Mn, Fe, Co, Ni, and Cu are particularly attractive in the first-row transition metals.¹ In classical octahedral polypyridine complexes, Ru^{II} and Ir^{III} complexes with the 4d⁶ and 5d⁶ valence electron configurations mainly exhibited photoactive properties in the metal-to-ligand charge-transfer (MLCT) excited states. The analogous MLCT luminescence from 3d⁶ Fe^{II}-polypyridine complexes has been considered attractive; however, the more contracted 3d orbitals of the Fe^{II} complex effected a ligand field substantially weaker than those of the 4d or 5d orbitals.² Weaker ligand fields on 3d metal complexes feature numerous metal-centered (MC) excited states, which allow a cascade of nonradiative relaxation processes, precluding their use as photocatalysts.

Nevertheless, several studies have been conducted on photoredox reactions using Fe^{II}-polypyridine complexes. Two pioneer reactions of enantioselective alkylation by Cozzi³ and carbazole synthesis by Collins⁴ involved visiblelight irradiation of $Fe^{II}(bpy)_3$ and $Fe^{II}(phen)_3$ catalysts. These complexes, including the recently disclosed Fe^{II}(phen) nitrate,⁵ were oxidatively quenched to afford the required singleelectron reduction of organohalide substrates and oxygen (Figure 1A). As a method for destabilizing MC states and including strong ligand fields, the electron-rich ligands, such as strongly σ -donating N-heterocyclic carbene (NHC) and also strongly π -accepting mesoionic carbene (MIC) ligands, were introduced by Wärnmark in the noble low-spin d⁵ Fe^{III} complex $[Fe(btz)_3]^{3+}$ and $[Fe(phtmeimb)_2]^+$ {btz = 3,3'dimethyl-1,1'-bis(p-tolyl)-4,4'-bis(1,2,3-triazol-5-ylidene), and phtmeimb = phenyl[tris(3-methylimidazol-1-ylidene)]borate}.⁶ These Fe^{III} complexes suppress deactivation processes sufficiently to realize excited-state lifetimes (100 ps and 1.96 ns, respectively) and room-temperature photoluminescence from the doublet ligand-to-metal charge-transfer (²LMCT) state, which is rarely expected for low-spin d⁵ metal complexes. Troian-Gautier remarkably enabled the benchmarking of the dehalogenation reaction using the [Fe-(phtmeimb)₂]⁺ complex;⁷ however, to the best of our knowledge, no useful C–C bond formation in Fe^{III}–MIC photocatalysis has been investigated.⁸

As in our previous reports on non-irradiative $Fe^{III}(phen)_3$ catalysis,⁹ most reactants of the radical cationic [4+2] cycloadditions were anethole derivatives (1,2-disubstituted alkenes), affording the stable radical cation intermediates. However, the use of terminal styrenes as alkene substrates requires the different oxidative approaches, due to their relatively high oxidation potentials ($E_{ox} = 1.3-1.7$ V vs SCE). To date, terminal styrenes have been oxidized by organo-photocatalysts, *p*-OMeTPT ($E*_{red} = 1.84$ V vs SCE)¹⁰ or Mes-Acr⁺ ($E*_{red} = 2.18$ V vs SCE),^{11,12} to afford various C–C bond formation reactions, with the requirements of either an electron relay mediator or oxidants. This work demonstrates the first green-light-driven Fe photoredox system using the Wärnmark Fe^{III}–MIC catalyst with a terminal styrene in radical cationic cycloaddition reactions.

 $Fe^{III}(btz)_3$ exhibited strong visible-light absorption with peak wavelengths of 528 and 558 nm, which enabled the radical cationic [4+2] cycloaddition reaction of 4-methoxy styrene

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A. Polypyridine- vs carbene-based Fe photoredox catalysis

Figure 1. Iron(II) and iron(III) photoredox catalysis.

(1a) and 2,3-dimethylbuta-1,3-diene (2a) under green LED irradiation ($\lambda_{max} = 525$ nm) (Table 1). To our delight, cycloadduct 3aa was produced in a promising yield (47%), along with dioxane 4aa, cyclobutane 5a, and tetrahydronaphthalene 6a, indicating that the Fe^{III} complex acted as a single electron oxidant and selectively oxidized the 4-methoxy styrene to a radical cation species, resulting in these homodimerization products (5a and 6a). Control experiments confirmed that both the iron catalyst and visible light are critical for this transformation (entry 2). To further prohibit the formation of dimerization products, 1a was added slowly over 18 h, and the use of an aromatic co-solvent, toluene, increased the reaction efficiency through the stabilization of the radical cation intermediate (entries 3 and 4).¹³ Similar to Yoon's report on counteranion dependence in photocatalysis, noncoordinating counteranions accelerated the photoredox transformation, and 2 mol % NaBArF₂₄ {sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate} was determined to be the optimal additive among the various fluorinated borates (entries 5-8).¹⁴ While cycloaddition with NaBArF24 proceeded with a comparatively improved reaction rate, reactions with Bu₄NOTs and Bu₄NClO₄ resulted only in the recovery of 4-methoxy styrene in 64% and 72% yields, respectively, without any cycloadduct **3aa**, implying a correlation between the reaction rate and the

noncoordinating properties of the counteranions.¹⁵ Performing the reaction under argon not only inhibited the formation of **4aa** but also decreased the efficiency of the entire reaction (entry 9), while aerobic conditions were found to be beneficial.

With these results in hand, the scope of the radical cation [4+2] cycloaddition reaction was investigated (Scheme 1). The scale of reaction with 1.0 mmol of 1a was tested, and the resulting efficiency was maintained at 77% yield. The methoxy substituent on the benzene of the styrene could be replaced with various alkoxy substituents, including allyloxy, fused tetrahydrofuranyl, and silyloxy groups (3ba-3ha), which implies the necessity of an electron-donating group on the benzene, similar to other results involving anethole radical cation intermediates. Pleasingly, the cyclization of styrenes containing amido substituents took place smoothly to afford cyclohexene products 3ia and 3ja. Phenyl (3ka) or naphthyl (3la) groups did not influence the product outcomes, while the thiophene heteroaromatic group (3ma) led to moderate reactivity accompanied by the dioxane side product (4ma, 24%) as a result of a [2+2+2] cyclooxygenation reaction.¹⁶ Employing isoprene 2b in lieu of 2,3-dimethylbutadiene 2a provided a moderate yield of cyclohexene 3mb accompanied by dioxane byproduct 4mb in a decreased yield of 8%. Importantly, the exclusive formation of a 1,4-disubstituted

10^d

NaBArF₂₄ (2.0)

6/-

Table 1. Optimization of the Reaction Conditions for Radical Cationic [4+2] Cycloaddition^a

DCE/toluene (9:1)



^{*a*} For the reaction, **1a** (0.1 mmol) and an additive in a solvent (0.5 mL) were slowly added to a solution of **2a** (1.0 mmol) and Fe(btz)₃(PF₆)₃ in a solvent (0.4 mL) over time in parentheses via a syringe pump under irradiation with two 18 W green LEDs. Isolated yield. ^{*b*}No Fe(btz)₃(PF₆)₃ or in the dark. ^{*c*}Under Ar. ^{*d*}**2a** (0.5 mmol).

8 (6)

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Figure 2. (a) UV-vis absorption spectra recorded during continuous photoirradiation under a green LED (525 nm) of an Ar-saturated CH₃CN containing $Fe^{III}(btz)_3$ and **1a**. (b) X-Band EPR spectra of an Ar-saturated DCE containing $Fe^{III}(btz)_3$ and **1a** before (black) and after (red) photoirradiation for 1 h. The red arrow indicates the reduction of $Fe^{III}(btz)_3$ during photoirradiation. (c) Light on/off experiments.

cyclohexene (3mb, 3ab, and 3ac) as a single regioisomer was a feature of this synthetic route with isoprene (2b) and myrcene (2c). Various cyclic and acyclic dienes were all found to be suitable substrates, generating tetrasubstituted and trisubstituted cyclohexenes 3ad-3af as 1:1-3:1 diastereomeric mixtures albeit with moderate selectivity. Subjecting 2phenylbutadiene 2g to the cation radical cyclization cleanly provided 1,4-diphenylcyclohexene derivatives.¹⁷ It is noteworthy that the excited Fe^{III}(btz)₃ selectively oxidized methoxy styrene 1a in the presence of 2-phenylbutadiene 2g, which also contains a styrene moiety. The structure of 3ag was confirmed by X-ray analysis, and varying substituents on each phenyl ring furnished desired tetrahydro-terphenyl adducts (3bg-3bj) in great yield and moderate regioselective ratios. In the M06-2X density functional theory calculations of the reaction yielding 1,4-diphenylcyclohexene 3ag and the 1,5-diphenylcyclohexene regioisomer (3ag') in a 9:1 ratio, the preferred pre-reaction complex of 1a^{•+} and 2g showed a shorter distance between C1 and C6 (2.89 Å), while the corresponding distance between

C4 and C6 in the regioisomer is 3.32 Å (Figure S11). The transition state [A-TS(3ag)] toward C1–C6 bond formation exhibited a structure involving $\pi - \pi$ stacking interactions between the two phenyl substituents, which was extended to an elaborate overlap between the ene and diene, rendering the lower transition-state energy. The addition to 2-phenylpenta-1,3-diene 2k afforded a diastereomeric mixture of cyclohexene **3ak**, one of which was structurally identified. Reactions with α methyl- and β -methyl-substituted styrenes (10 and 1p, respectively) were also examined, but reaction with anethole 1p required an increased amount of both the Fe catalyst and the NaBArF₂₄ additive in the TFE co-solvent.¹⁸ Finally, the prospect of developing a late-stage cyclization was explored by employing biobased alkene compounds. A lithocholic acid derivative, flavanol derivatives, and a vinylated tocopherol derivative were also employed to react with dimethyl and phenylbutadiene to afford 3qa, 3ra, and 3sg, respectively, demonstrating the versatility of this green-light-driven cyclization to afford various privileged scaffolds.

Scheme 1. Fe^{III}(btz)₃ Photocatalysis in Radical Cationic [4+2] Cycloaddition^a



^{*a*}For the reaction, **1a** (0.1 mmol) and NaBArF₂₄ (2 mol %) in a solvent (0.5 mL) were slowly added to a solution of **2a** (1.0 mmol) and Fe(btz)₃(PF₆)₃ (1 mol %) in a solvent (0.4 mL) upon irradiation under two 18 W green LEDs. ^{*b*}With 1 mmol of **1a**. ^{*c*}With 2 mol % Fe(btz)₃(PF₆)₃ and 4 mol % NaBArF₂₄. ^{*d*}With 3 mmol of **2a** or **2b**. ^{*e*}With 4 mol % Fe(btz)₃(PF₆)₃ and 8 mol % NaBArF₂₄ in a 4:1 DCE/TFE mixture.



Figure 3. Proposed catalytic cycle for Fe(III) photocatalysis.

The initiation step is proposed to be a selective electron transfer between the excited $Fe^{III}(btz)_3$ complex and the

terminal styrene, and the photoinduced electron transfer is exoergic as inferred from the excited-state reduction potential of Fe(III)*/Fe(II) (1.94 V vs SCE) and the oxidation potential of styrene (1.27 V vs SCE).¹⁹ The UV-vis absorption spectrum obtained for a solution of Fe^{III}(btz)₃ (1.0 mM) and 1a (0.10 M) exhibited a strong absorption band with peak wavelengths of 528 and 558 nm, which gradually disappeared after photoirradiation due to the formation of the $Fe^{II}(btz)_3$ species (Figure 2a), showing broad intense bands at 446 and 688 nm. The X-band EPR spectrum of $Fe^{III}(btz)_3$ (1 mM) and 1a (0.10 M) revealed the presence of an octahedral low-spin d⁵ Fe^{III} species with g values of 1.94 and 2.32. Photoirradiation reduced the EPR signature due to oneelectron reduction of Fe^{III}(btz)₃ into a diamagnetic low-spin d⁶ Fe^{II} species by the dienophile (Figure 2b). Light control experiments by gradually extending the irradiation time (1, 3, and 5 h) and the measured quantum yield ($\Phi = 0.49$) revealed that the alternative radical chain pathway is likely to be inefficient (Figure 2c).²⁰

On the basis of these observations, we propose a reaction mechanism involving an initial electron transfer from styrene (1a) to the photoexcited Fe^{III} complex (Figure 3). The resultant styrene radical cation undergoes addition and cyclization reactions with the diene to produce the corresponding cyclohexene radical cation (3aa⁺), which is subsequently reduced by the Fe^{II} species. The higher yield of 3aa observed under normal air conditions might involve the generation of singlet oxygen by energy transfer from the photoexcited Fe^{III}(btz)₃ complex.^{6a,21} The O₂⁻⁻ generated from ¹O₂ is expected to afford a single electron to 3aa⁺ to afford the desired product.

In summary, the green-light-driven radical cation cycloaddition triggered by the $[Fe^{III}(btz)_3]$ complex was successfully developed. The LMCT excitation and reductive quenching process enables the generation of a terminal alkene radical cation that reacts with electron-rich dienes providing a variety of 1,4-disubstituted and multisubstituted cyclohexenes that would be difficult to prepare via conventional Diels–Alder approaches. This system, which does not require any sacrificial reagent or inert conditions, can also be applied to the late-stage functionalization of biobased styrenes and is expected to promote new protocols in Fe photocatalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.2c01779.

Experimental details, NMR spectra, crystallographic methods, and coordinates of computational output files (PDF)

Accession Codes

CCDC 2153834–2153835 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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