

Photocatalysis

Combined Photoredox and Iron Catalysis for the Cyclotrimerization of Alkynes

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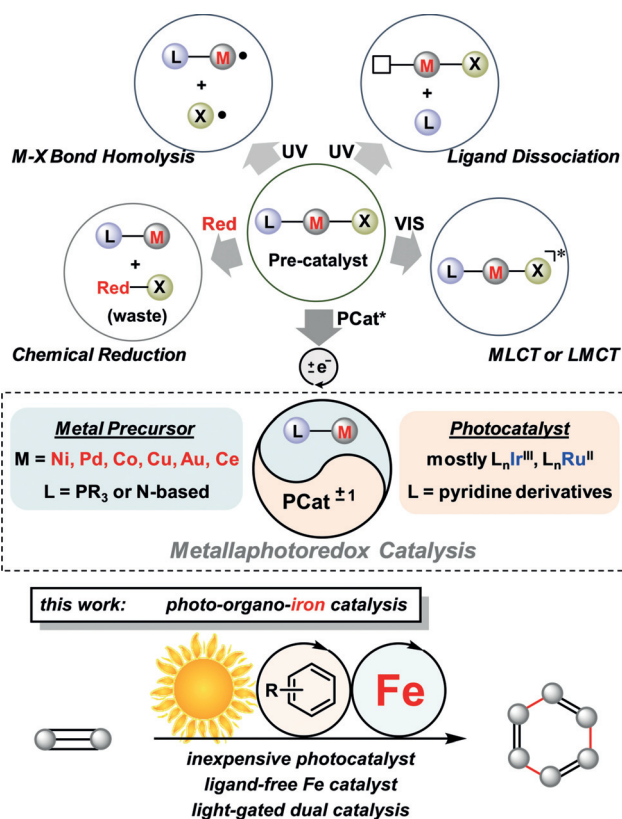
In memory of Professor Erwin Weiss, a pioneer of modern organometallic chemistry

Abstract: Successful combinations of visible-light photocatalysis with metal catalysis have recently enabled the development of hitherto unknown chemical reactions. Dual mechanisms from merging metal-free photocatalysts and earth-abundant metal catalysts are still in their infancy. We report a photo-organometal-catalyzed cyclotrimerization of alkynes by photoredox activation of a ligand-free Fe catalyst. The reaction operates under very mild conditions (visible light, 20°C, 1 h) with 1–2 mol% loading of the three catalysts (dye, amine, FeCl₂).

The merging of visible-light-driven photocatalysis with transition-metal catalysis constitutes a highly versatile approach to sophisticated organic transformations. Such approaches benefit from the bond-activation and bond-formation events in the coordination sphere of the metal catalyst and the distinct reactivity patterns of photoactivated species and open-shell intermediates.^[1,2] Although several protocols involve the direct irradiation of metal complexes by UV/Vis light, the spatial separation of photocatalyst and metal-catalyst centers may enable more diverse mechanistic scenarios and facilitate reaction optimization and selectivity control. The general modes of photoactivation of metal complexes involve ligand dissociation, M–X homolysis (mostly by UV irradiation),^[3–5] excitation of metal-to-ligand or ligand-to-metal charge-transfer bands (MLCT, LMCT),^[5–9]

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and single-electron transfer (SET) reactions in the presence of suitable redox partners (Scheme 1, top).^[1,2] The successful merging of visible-light excitation and one-electron redox processes with conventional organometallic reaction mechanisms has very recently enabled the development of hitherto unknown chemical transformations.^[1,2] This rapidly emerging field of metalla-photoredox catalysis has so far mostly been realized with pyridine complexes of Ru and Ir as photoredox catalysts and late-transition-metal complexes as chemical co-catalysts (Co, Ni, Pd, Cu, Au with phosphine, bipyridine, N-heterocyclic carbene, or amine ligands, Scheme 1).^[1,10–13] The utilization of earth-abundant 3d metals as visible-light photocatalysts has gained great interest, but is generally hampered by exceptionally short lifetimes owing to low-lying metal-centered electronic states.^[6,7,14] We wished to challenge this



Scheme 1. General strategies for photo- and chemical activation of metal precatalysts (top), and dual photo-organometal catalysis described in this work (bottom).

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established paradigm and surmised that a sustainable yet effective catalytic system would be composed of: i) an inexpensive, easily available metal-free photoredox catalyst, ii) an inexpensive and non-toxic earth-abundant metal catalyst that operates iii) in the absence of complex ligands under^[15] iv) mild conditions (i.e. visible light, room temperature). Herein, we report the first combination of a visible-light-driven photoredox activation of simple ferrous salts^[16] with an Fe-catalyzed cyclotrimerization reaction that operates under mild conditions.

The transition-metal-catalyzed cyclotrimerization of alkynes is a highly atom-efficient, redox-neutral reaction that builds modular complexity and enables rapid access to polyfunctional arenes. The search for sustainable catalysts led to the development of Fe-catalyzed protocols that required the handling of sensitive Fe complexes, ligands, and reductants.^[17–21] We aimed for the development of operationally facile conditions that would allow the in situ generation of the low-valent catalyst by visible-light-mediated photocatalytic reduction of a commercial and stable Fe salt in the presence of a stable and inexpensive reductant. Our initial investigation involved the inexpensive organic dye 9,10-diphenylanthracene (DPA), which is a highly under-utilized photoredox catalyst. The strong reducing power of its excited state ($E_{1/2}(\text{DPA}^+/\text{DPA}^* = -1.77 \text{ V})$ and its ground-state radical anion ($E_{1/2}(\text{DPA}/\text{DPA}^{\cdot-} = -1.94 \text{ V})$)^[22,23] should enable the metal-centered reduction of simple, ligand-free ferrous and ferric salts such as FeCl_2 ($E_{\text{red}} = -1.3 \text{ V}$ versus SCE).^[24,25] We probed this hypothesis in the context of the Fe-catalyzed cyclotrimerization of alkynes, a reaction that does not operate in the presence of simple ferrous and ferric salts, but requires precatalyst reduction to a low-valent state by an equimolar reductant.^[18–21] To our delight, the simple three-component catalyst comprising 9,10-diphenylanthracene (DPA) as the photocatalyst, FeCl_2 as the cyclotrimerization precatalyst, and diisopropylethylamine (DIPEA) as the catalytic reductant afforded quantitative yields of the cyclotrimerization of phenylacetylene (*r.r.* > 20:1) under visible-light irradiation (entry 1, Table 1). The optimized conditions involved very low catalyst loadings (0.4 mol% DPA, 1 mol% FeCl_2 , 2 mol% DIPEA) and irradiation in the visible range at 395–410 nm with a blue LED in acetonitrile solution for 30 min.^[26] A set of control experiments documented the crucial role of all components (entry 7). Alternative amines, iron precursors, and photocatalysts fared much poorer (entries 2–6). The precatalysts FeBr_2 , $\text{FeCl}_2(\text{thf})_{1.5}$, and $\text{FeCl}_2(\text{MeCN})_{1.4}$ ^[27] gave similar results to FeCl_2 , whereas $\text{Fe}(\text{OAc})_2$, $\text{Fe}(\text{acac})_2$, and FeCl_3 were inactive.^[26] A catalytic system adopted from a recent cobalt-catalyzed reaction gave only moderate activity and selectivity (entry 4).^[12] The merits of this catalytic alkyne cyclotrimerization are the very low catalyst loadings and mild conditions (r.t., visible light, 30 min), the high regioselectivity in favor of the unsymmetrical trimer 1,2,4-triphenylbenzene, and the use of visible light. The optimized conditions were then applied to a diverse set of alkynes bearing aryl and alkyl carbon chains and various functional groups (Scheme 2). The mild conditions tolerated F, Cl, Br, CF_3 , ester, cyclopropyl, boryl, silyl, and thiophenyl substituents. Generally, very high regioselectiv-

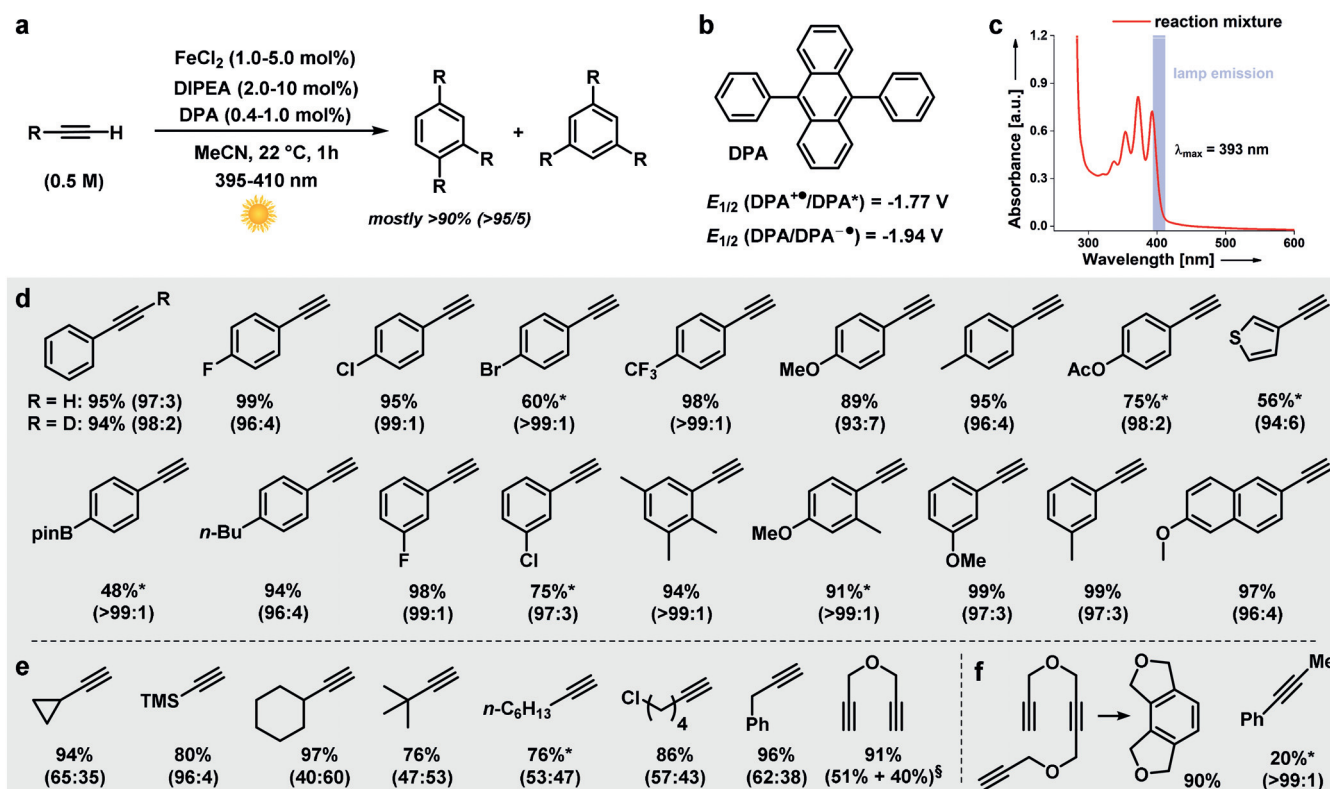
Table 1: Optimization of reaction conditions.

Entry	Deviations from the conditions shown	Yield [%] ^[a]
1	–	100 (100) ^[b]
2	2.5 mol% FeCl_2 , 5.0 mol% diisopropylamine	39 (39)
3	2.5 mol% FeCl_3 , 7.5 mol% DIPEA	0 (0)
4	5 mol% $[\text{FeCl}_2(\text{thf})_{1.5}/2\text{PCy}_3]$, 5 mol% DPA, 50 mol% DIPEA, 0.2 mmol PhCCH, 3 h, 365 nm	43 (82)
5	2.5 mol% FeCl_2 , 5.0 mol% DIPEA, 0.04 mol% anthracene, 365 nm	13 (17)
6 ^[c]	alternative photocatalysts: Eosin Y, Rhodamine 6G, Fluorescein, 9,10-dicyanoanthracene, $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, $[\text{Ir}(\text{ppy})_3]$	< 5 (< 5) each
7 ^[d]	no FeCl_2 , or no DPA, or no DIPEA, or dark reaction	< 2 (< 9) each reaction

[a] Overall GC yields of both isomers (conversions in parentheses) were determined by quantitative GC-FID versus internal *n*-pentadecane; yield of minor 1,3,5-isomer < 5%; FeCl_2 (> 99.99%) was used. [b] 95% yield of isolated product. [c] 5 mol% FeCl_2 , 10 mol% DIPEA, 5 mol% photocatalyst, 0.2 mmol phenylacetylene, 15 h; LED was chosen to match dye absorption. [d] 18 h.

ities of mostly > 19:1 (1,2,4- versus 1,3,5-trimer) were observed with arylacetylenes (Scheme 2d).^[28] Amine, aldehyde, carboxamide, and pyridine functions inhibited the catalytic reaction. Full incorporation of all three deuterium atoms into the resultant arene was observed upon reaction of 2-deutero-phenylacetylene. Alkylacetylenes exhibited very good reactivities, albeit with lower regiocontrol (Scheme 2e). The general procedure enabled intramolecular cyclizations with 1, ω -diynes (see Scheme 2e,f). Cyclotrimerization of internal alkynes showed low reactivities, whereas a triyne containing an internal alkyne gave excellent conversion (Scheme 2f).

Key mechanistic experiments were also performed. IR spectroscopic studies with $\text{FeCl}_2(\text{MeCN})_{1.4}$ showed no band shifting on addition of DIPEA or phenylacetylene individually, whereas complete consumption of $\text{FeCl}_2(\text{MeCN})_{1.4}$ occurred in the presence of both DIPEA (2 equiv) and phenylacetylene (2 equiv). The resultant IR spectrum of the light-brown mixture exhibited no $\nu_{\text{C}=\text{C}}$ bands of hypothetical σ -alkynyliron species.^[29,30] We cannot exclude the formation of (π -alkyne)iron complexes that would exhibit a bathochromic shift (and lower intensity bands) owing to strong back-bonding or the presence of polynuclear alkyne complexes.^[30,1] The potential formation of $[\text{FeCl}_2\text{L}_x(\pi\text{-PhCCH})_y]_n$ ^[32] complexes is in accordance with the observed full conversion of $\text{FeCl}_2(\text{MeCN})_{1.4}$ in the presence of amine and alkyne (no alkyne deprotonation) and the slight shift of the ^1H NMR signal of $\equiv\text{CH}$ upon addition of DIPEA to $\text{FeCl}_2(\text{MeCN})_{1.4}$ and phenylacetylene.^[26] DIPEA may assist the substitution of the strongly coordinating CH_3CN . UV/Vis studies also supported the notion that in the absence of the photocatalyst DPA no active Fe catalyst is formed before or after irradiation. Cyclic voltammetry studies of the reaction



Scheme 2. a) General conditions of the photo/iron-catalyzed cyclotrimerization. b) The organic photocatalyst DPA and its reduction potentials versus SCE in acetonitrile. c) UV/Vis spectrum of the (diluted) reaction mixture. d) Reaction scope of (functionalized) aryl acetylenes. e) Scope of alkyl acetylenes. f) Further alkyne substrates. Yields of isolated products are given (* denotes NMR yield); ratios of trisubstituted 1,2,4- versus 1,3,5-regioisomers are given in parentheses; [§][2+2+2]-derived dimer + trimer.^[26]

mixture containing $\text{FeCl}_2(\text{MeCN})_{1,4}$, DIPEA (2.0 equiv), and phenylacetylene (20 equiv) clearly documented the Fe-centered reduction at -1.3 V (versus SCE) that is well within the thermodynamic regime of the reduction potential of the photocatalyst (-1.9 V).^[26] The lifetime of the excited singlet state $^1\text{DPA}^*$ was determined by time-resolved fluorescence spectroscopy (6 ns).^[22] Stern–Volmer quenching of $^1\text{DPA}^*$ with DIPEA gave a rate constant of $k_q(\text{S}_1) = 8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at the diffusion limit that accounts for the maximum rate of the SET if radical-ion-pair formation ($\text{DIPEA}^{\bullet+}/\text{DPA}^{\bullet-}$) was perfectly efficient (Figure 1a and b).^[26] The formation of $\text{DPA}^{\bullet-}$ in presence of DIPEA and light was confirmed by transient absorption spectroscopy (bands at 565, 610, and 670 nm, see Figure 1c).^[26,33] According to laser flash photolysis (Figure 1d), this highly reducing radical anion is quenched by $\text{FeCl}_2(\text{MeCN})_{1,4}$ and thus enables regeneration of ground-state DPA to complete the photocatalytic cycle. It is important to note that the photocatalytic reduction of $\text{FeCl}_2(\text{MeCN})_{1,4}$ with DPA and DIPEA followed by alkyne addition in the dark did not generate an active catalyst for the “dark” cyclotrimerization. This result led us to conclude that (alkyne)iron complexes may play a crucial role as catalyst intermediates. Quenching studies further documented that $\text{FeCl}_2(\text{MeCN})_{1,4}$ and phenylacetylene individually do not interact with the excited photocatalyst and neither have an influence on its quenching by DIPEA. The overall mechanism is not one of photoinitiated Fe catalysis, but rather appears to

involve a dual mode of visible-light-mediated activation. Beside the photocatalytic reduction of the Fe^{II} precatalyst, the Fe-catalyzed cyclotrimerization also is light-gated and requires visible-light irradiation (Figure 2, bottom). Very low conversions were observed in the dark ($<1\%$ per min), whereas rapid conversions were recorded in light (up to 22% per min).^[8,26] There is no thermal background reaction because dark reactions at 80°C did not result in cyclotrimerization. The highly effective steady-state fluorescence quenching of DPA by a catalytic cyclotrimerization reaction mixture prepared by chemical “dark” reduction ($\text{FeCl}_2/\text{DIBAL-H}/\text{phenylacetylene} = 1:2:40$)^[24,34] may be indicative of an effective energy transfer [$k_q(\text{S}_1) = 4.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$] from excited DPA^* ($E_{\text{triplet}} = 1.77 \text{ eV}$)^[23] to a low-valent Fe species, which accounts for the observed light-gated conversion after the active cyclotrimerization catalyst has formed in the photoredox-catalytic event.^[26] In the absence of other suitable ligands, the alkyne substrates, as well as the resultant arenes, constitute competent ligands for the stabilization of low-valent Fe complexes.^[19,20] Indeed, UV/Vis monitoring of a reaction mixture showed two new weak bands at 305 and 325 nm after irradiation (see Figure S22). The same absorption bands were present in the active “dark” system $\text{FeCl}_2/\text{DIBAL-H}/\text{PhC}_2\text{H}$ (1:2:40)^[34] and correlate well with the LMCT of the known $[(\eta^6\text{-mesitylene})_2\text{Fe}]X_2$ ($X = \text{PF}_6$).^[35] We, therefore, speculate that in this metalla-photoredox catalysis only a photoexcited $[\text{Fe}^n(\text{arene})X_n]^*$ complex can undergo

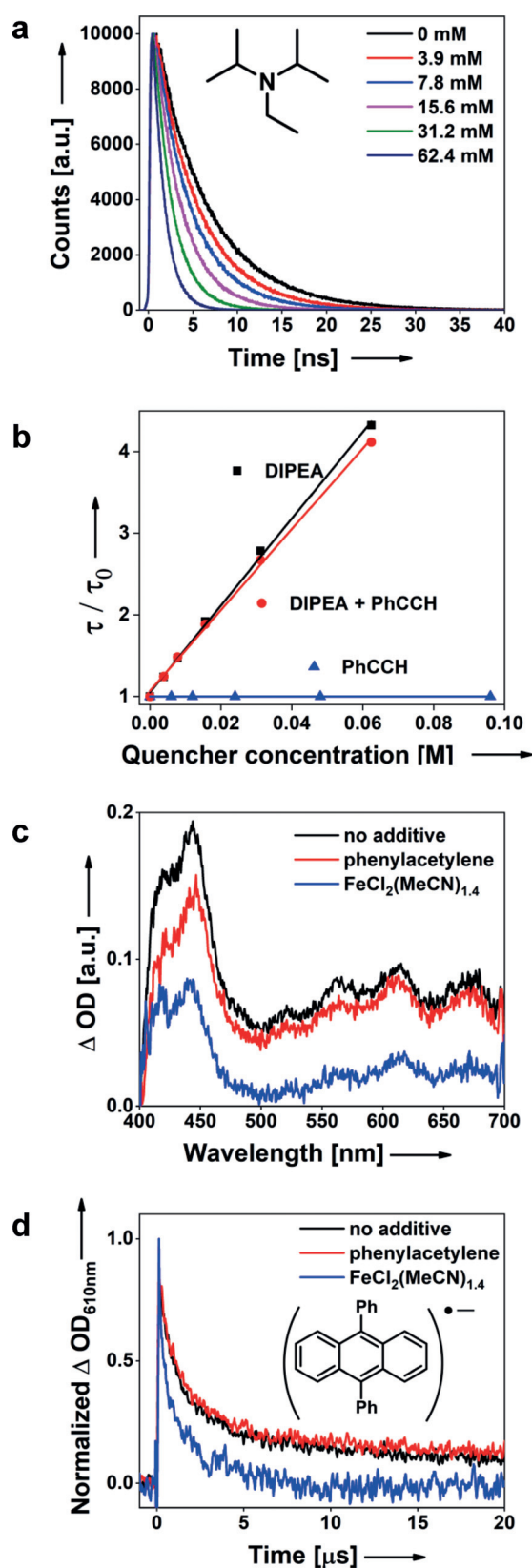


Figure 1. a) Fluorescence quenching of DPA^* by DIPEA; b) Stern–Volmer plots of amine and alkyne quench of the photocatalyst; c) Transient absorption of $DPA^{\bullet-}$ in the absence/presence of quenchers; d) Decay of $DPA^{\bullet-}$ at 610 nm monitored by laser flash photolysis.^[26]

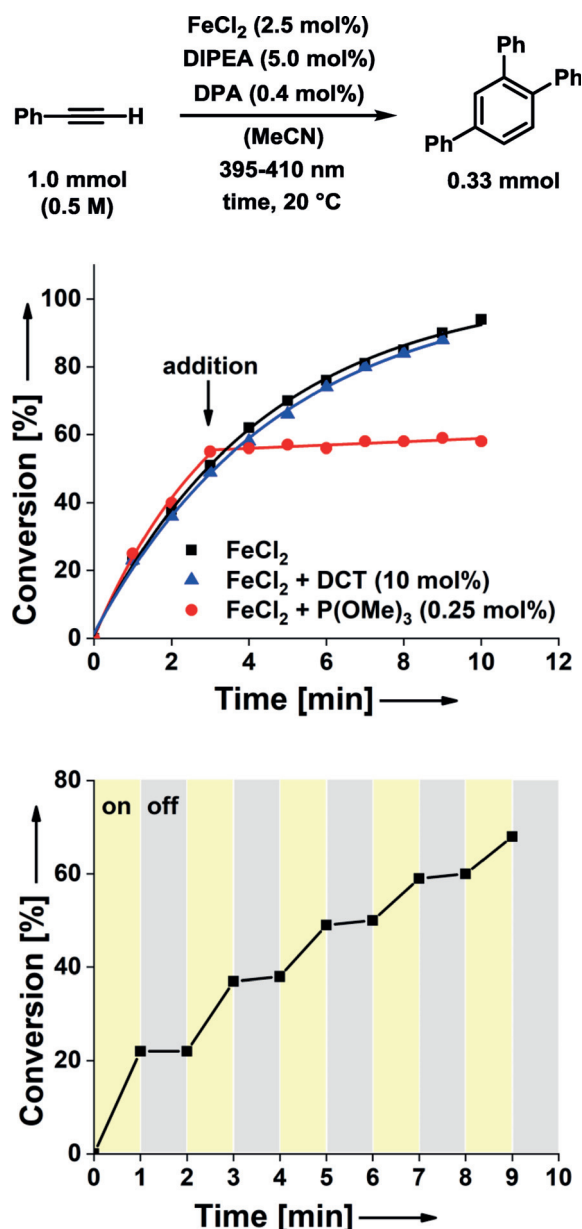
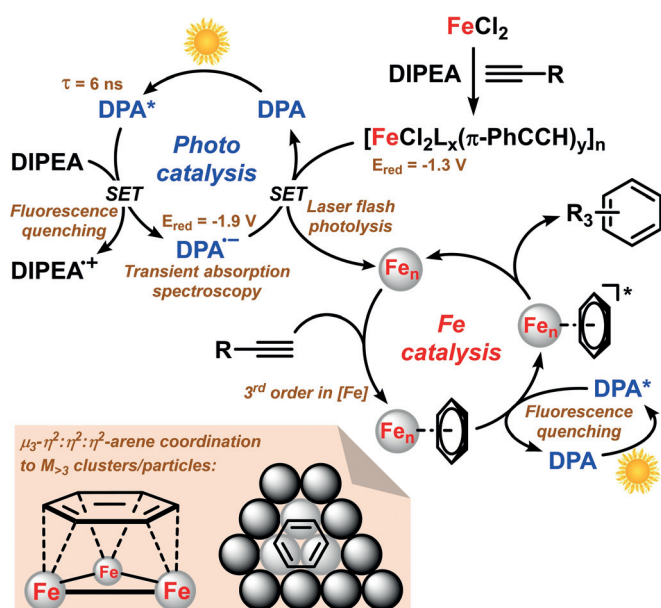


Figure 2. Poisoning studies with addition of catalyst poisons after 3 min (top). Analysis of reaction progress, including alternating light-on/off phases (bottom).^[26]

facile arene dissociation to regenerate the active cyclotrimerization catalyst. Arene dissociations from Fe complexes were reported to be accelerated by light irradiation and the presence of donor solvents.^[35,36] The latter effect is supported by the poor catalytic activity in solvents other than MeCN (i.e. DMF, THF).^[26] Light acceleration was also observed when employing Fe^0 catalysts prepared from the chemical reduction of $FeCl_2$ with DIBAL-H (95% after 15 h versus 44% in the dark)^[26,34] However, this photo effect was much lower as observed under the standard photo-organometallic catalysis conditions. Kinetic studies were performed to determine reaction orders and catalyst topology.^[26] The overall reaction displayed a reaction order of 0 in [DIPEA] and [DPA], respectively, which is also mirrored by their very high

quenching rate constant.^[26] Phenylacetylene concentrations showed an order of 0.5, whereas third-order kinetics were recorded for $[\text{FeCl}_2]$.^[26] Please note that facial μ_3 -coordination of arenes is well documented for trinuclear clusters and particles.^[39] Kinetic poisoning supported the operation of heterotopic Fe catalysts (Figure 2, top): Addition of sub-stoichiometric trimethylphosphite $[\text{P}(\text{OMe})_3, 0.1 \text{ equiv per Fe atom}]$ led to complete inhibition of catalytic turnover,^[37] whereas $\text{P}(\text{OMe})_3$ did not quench the photocatalyst. The presence of the selective homotopic catalyst poison dibenzo- $[a,e]$ cyclooctatetraene (DCT) did not affect the cyclotrimerization rate.^[38] Variations of light intensity showed that the reaction operates in the regime of photonic saturation under standard conditions, but is first order for low light intensities. This finding is in full accordance with the notion of a light-mediated catalyst formation (initiation) and a second photo-reaction that is turnover limiting once sufficient Fe catalyst has formed (Scheme 3).^[26]



Scheme 3. Proposed dual photo-organo-iron catalysis mechanism.

In conclusion, we have developed the first dual-catalytic protocol that combines organic photoredox catalysis and ligand-free Fe catalysis for synthetic applications. A low molecular weight, inexpensive, and photostable organic dye enabled the photocatalytic reduction of commercial FeCl_2 under visible-light irradiation. The subsequent Fe-catalyzed cyclization proceeds under mild conditions with high regio-control to give trisubstituted benzenes. The overall photo-reaction is light-gated and not photoinitiated. Mechanistic studies supported the notion of an amine-mediated photo-reduction of FeCl_2 by the excited radical anion of the dye and the operation of a heterotopic Fe catalyst that undergoes light-mediated arene dissociation. This successful merger of organic photoredox catalysis with low-valent base-metal catalysis employing both simple and inexpensive catalysts can serve as a versatile platform for related transformations.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkynes · cycloaddition · iron · photocatalysis · synthetic methods

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