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Combined Photoredox and Iron Catalysis for the Cyclotrimerization of Alkynes

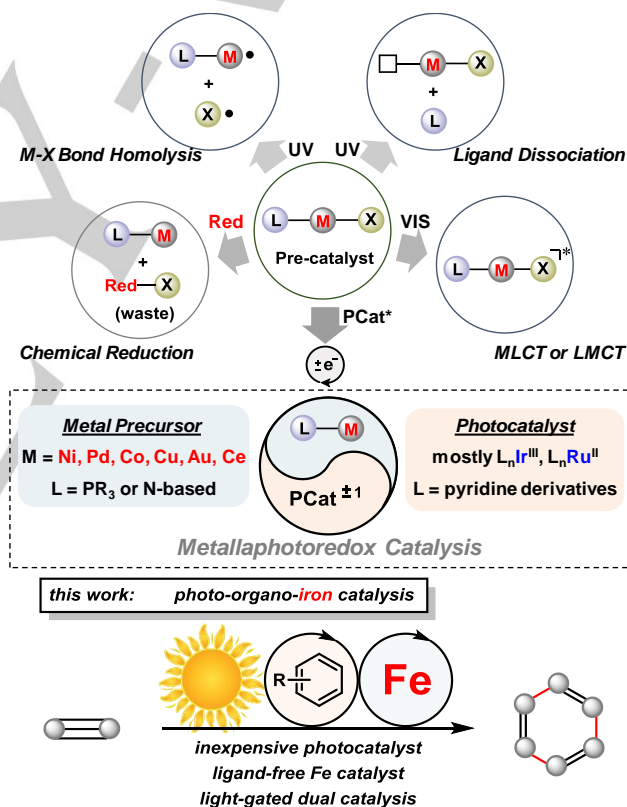
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Dedicated to Prof. Erwin Weiss†, a pioneer of modern organometallic chemistry

Abstract: Successful combinations of visible light photocatalysis with metal catalysis have recently enabled the development of hitherto unknown chemical reactions. Dual mechanisms by merging metal-free photocatalysts and earth-abundant metal catalysts are still in their infancy. We report a photo-organo-iron-catalyzed cyclotrimerization of alkynes via photoredox-activation of a ligand-free Fe catalyst. The reaction operates under very mild conditions (Vis 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 manifold of bond activation and formation events in the coordination sphere of the metal catalyst and the distinct reactivity patterns of photo-activated species and open-shell intermediates.^{[1],[2]} While several protocols involve the direct irradiation of metal complexes by UV-Vis light, the spatial separation of photo-catalyst and metal-catalyst centers may enable more diverse mechanistic scenarios and facilitate reaction optimization and selectivity control. The general modes of photo-activation 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]} 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 metallaphotoredox catalysis has so far mostly been realized with pyridine-complexes of Ru and Ir as photo-redox 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 due to low-lying metal-centered electronic states.^{[6],[7],[14]}

We wished to challenge this 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.* Vis light, room temperature). Here, we report the first combination of a visible light-driven photoredox-activation of simple ferrous salts^[16] with an Fe-catalyzed cyclotrimerization that operates under mild conditions.



Scheme 1. General strategies for photo/chemical activation of metal pre-catalysts (top), and dual photo-organo-iron catalysis of this work (bottom).

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 which required the handling of sensitive Fe complexes, ligands, and reductants.^{[17]-[21]} We aimed at the development of operationally facile conditions that would allow the in situ generation of the low-valent catalyst by visible light

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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 ($E_{1/2}(\text{DPA}^{*\bullet}/\text{DPA}^* = -1.77 \text{ V})$ and its ground-state radical anion ($E_{1/2}(\text{DPA}/\text{DPA}^{\bullet-} = -1.94 \text{ V})$)^{[22],[23]} should enable the metal-centered reduction of simple, ligand-free ferrous and ferric salts such as FeCl_2 ($E_{\text{red}} = -1.3 \text{ V vs. SCE}$).^{[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 pre-catalyst 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 photocatalyst, FeCl_2 as cyclotrimerization pre-catalyst, and diisopropylethylamine (DIPEA) as 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 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 pre-catalysts FeBr_2 , $\text{FeCl}_2(\text{thf})_{1.5}$, and $\text{FeCl}_2(\text{MeCN})_{1.4}$ ^[27] gave similar results as 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 favour 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 regioselectivities of mostly >19/1 (1,2,4- vs. 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-deuterio-phenylacetylene. Alkylacetylenes exhibited very good reactivities, albeit with lower regiocontrol (Scheme 2e). The general procedure enabled intramolecular cyclizations with 1, ω -diynes (see Schemes 2e and 2f). Cyclotrimerization of internal alkynes showed low reactivities, whereas a triyne containing an internal alkyne gave excellent conversion (Scheme 2f).

Key mechanistic experiments were performed. IR spectroscopic studies with $\text{FeCl}_2(\text{MeCN})_{1.4}$ showed no band shifting by addition of DIPEA or phenylacetylene, respectively, while 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 $\nu_{\text{C}\equiv\text{C}}$ 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) due to strong back-

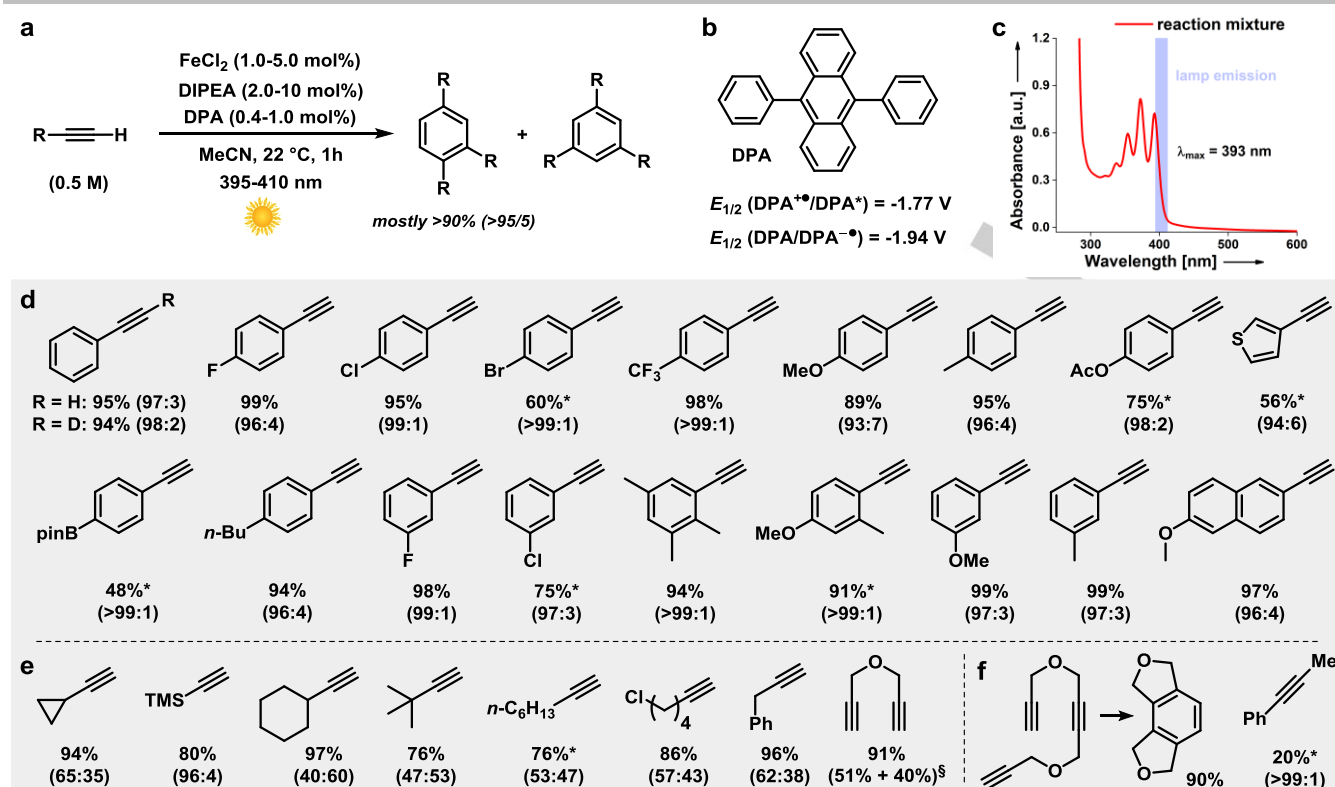
Table 1. Optimization of reaction conditions.

Entry	Deviations from the conditions above	Yield in [%] ^[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% $[\text{FeCl}_2(\text{thf})_{1.5}/\text{PCy}_3]$, 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

^[a] Overall GC yields of both isomers (conversions in parentheses) were determined by quantitative GC-FID vs. internal *n*-pentadecane; yield of minor 1,3,5-isomer <5%; FeCl_2 (>99.99%) was used. ^[b] 95% isolated yield. ^[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.

bonding or the presence of polynuclear alkyne complexes.^{[30],[31]} 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 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 (vs SCE) that is well within the thermodynamic regime of the photocatalyst's reduction potential of -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 $k_q(\text{S}_1) = 8.8 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$ at the diffusion limit which 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 1b).^[26] The formation of $\text{DPA}^{\bullet-}$ in presence of DIPEA and light was confirmed by transient absorption spectroscopy (bands at 565 nm, 610 nm, 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

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Scheme 2. a) General conditions of the photo/iron-catalyzed cyclotrimerization. b) The organic photocatalyst DPA and its reduction potentials vs. 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. Isolated yields are given (* denotes NMR yield); ratios of trisubstituted 1,2,4- vs. 1,3,5-regioisomers are given in parentheses; [§] [2+2+2]-derived dimer + trimer.^[26]

ground-state-DPA to close 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, which 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, respectively, do not interact with the excited photo-catalyst and neither have an influence on its quenching by DIPEA. The overall mechanism is not a photoinitiated Fe catalysis but rather appears to involve a dual mode of visible light-mediated activation. Beside the photo-catalytic reduction of the Fe(II) pre-catalyst, 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), while rapid conversions were recorded in light (up to 22% per min).^{[8],[26]} There is no thermal background reaction, as 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 ($k_q(S_1) = 4.8 \cdot 10^{10} \text{ M}^{-1}\text{s}^{-1}$) 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 $[\eta^6\text{-mesitylene}]_2\text{Fe}[\text{X}]_2$ ($\text{X} = \text{PF}_6$).^[35] We therefore speculate that in this metalla-photo-redox catalysis only a photo-excited $[\text{Fe}^n(\text{arene})_n]^*$ complex can undergo 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 vs. 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 toxicity.^[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 $\frac{1}{2}$, while 3rd 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 equiv. per Fe) 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

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In conclusion, we have developed the first dual catalytic protocol combining organic photoredox catalysis and ligand-free Fe catalysis for synthetic applications. A low-molecular weight, inexpensive and photostable organic dye enabled the photo-catalytic reduction of commercial FeCl₂ under visible light irradiation. The subsequent Fe-catalyzed cyclization proceeds under mild conditions with high regiocontrol to give trisubstituted benzenes. The overall photoreaction is light-gated and not photo-initiated. Mechanistic studies supported the notion of an amine-mediated photo-reduction of FeCl₂ 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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Keywords: photocatalysis • alkynes • iron • cycloaddition

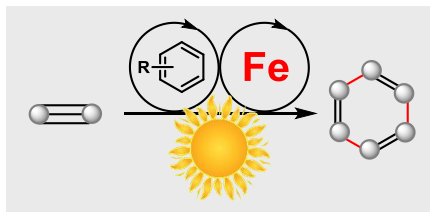
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A photo-organo-iron-catalyzed cyclotrimerization of alkynes has been developed that involves photo-redox-activation of a most simple iron catalyst. The reaction operates under very mild conditions (Vis light, 20°C, 1 h) with 1-2 mol% loading of the triple catalyst system organic dye/amine/FeCl₂.



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Combined Photoredox and Iron
Catalysis for the Cyclotrimerization of
Alkynes

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