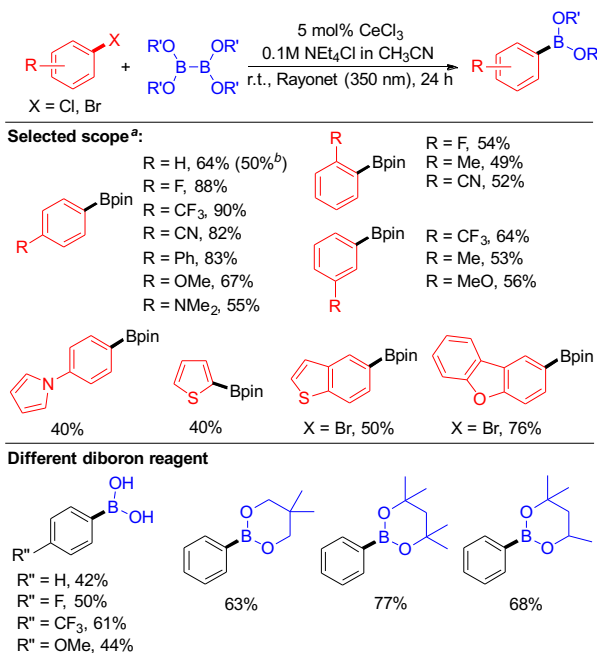


1. PRF# 56128-ND3
2. Cheap and Efficient Cerium Photosensitizers: Toward Excited State Metalloradicals for New Reactivity
3. Eric J. Schelter, University of Pennsylvania

Cerium(III) cations, with their single 4f electron, have simple, well-defined electronic structures featuring 3F_4 ground states. The luminescence of Ce^{3+} cations originates from 5d \rightarrow 4f transitions, distinctly different than other Ln $^{3+}$ cations where 4f \rightarrow 4f electronic transitions underlie their optical properties. The luminescence of cerium(III) complexes is a direct indication of long-lived excited state, that is more prone to engage in electron transfer. We have performed structural, spectroscopic, computational, and reactivity studies to demonstrate that luminescent Ce(III) guanidinate–amide complexes can mediate photocatalytic C(sp 2)–C(sp 2) bond forming reactions.¹ We have also performed photophysical and photochemical studies on a series of mixed-ligand Ce(III) guanidinate–amide and guanidinate–aryloxy complexes to establish structure–property relationship for Ce(III) photocatalysts.² The low excited-state reduction potentials ($E_{1/2}^+ \approx -2.1 \sim -2.9$ V versus Cp $_2$ Fe $^{0/+}$) and relatively fast quenching rates ($k_q = \sim 10^9$ M $^{-1}$ s $^{-1}$) toward aryl halides enabled the Ce(III) guanidinate–amide complexes to participate in photocatalytic C(sp 2)–C(sp 2) bond forming reactions through either inner-sphere or outer-sphere SET processes. Moreover, we found that the hexachloroacetate(III) anion, [Ce $^{\text{III}}$ Cl $_6$] $^-$, was a potent photoreductant in acetonitrile solution with an estimated excited-state reduction potential of -3.45 V versus Cp $_2$ Fe $^{0/+}$.³ This [Ce $^{\text{III}}$ Cl $_6$] $^-$ redox partner can also act as a potent photo-oxidant through a presumably long-lived chloride-to-cerium(IV) charge transfer excited state ($\epsilon = \sim 6000$ M $^{-1}$ cm $^{-1}$), that was used to turnover photocatalytic dechlorination reactions.

Scheme 1. Photoinduced Borylation of Aryl Halides by [Ce $^{\text{III}}$ Cl $_6$] $^-$.

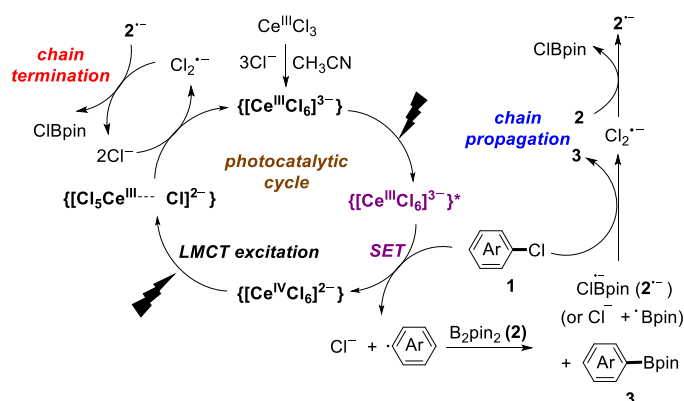


^aChloroarenes were used unless specified otherwise.^b2.7 g scale.

More recently, we demonstrated the photoinduced carbon(sp 2)–heteroatom bond forming reaction by [Ce $^{\text{III}}$ Cl $_6$] $^-$, a Miyaura borylation.⁴ This was the first use of a rare earth photoreductant into photoinduced sp 2 carbon–heteroatom bond forming reactions. We have applied our optimized borylation conditions to a variety of aryl/heteroaryl chlorides and bromides and diboron reagents, and found a broad substrate

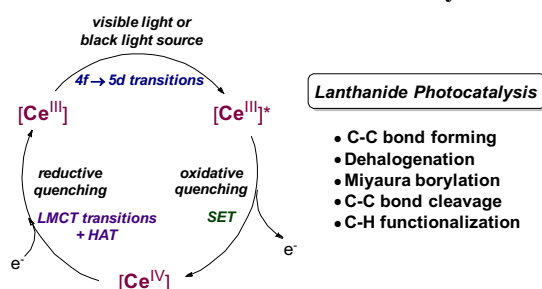
scope. Moreover, gram-scale reactions could be carried out by our system and afforded 2.7 g products. A one-pot sequential borylation and subsequent Pd-catalysed cross coupling reaction was also accomplished. Mechanistic studies were conducted to support our proposed photoinduced SET radical mechanism. The key mechanistic steps are: (1) a two-photon process (one photon for the reductive side, one for the oxidative) is operative for $[\text{Ce}^{\text{III}}\text{Cl}_6]^{3-}$. The Ce^{IV} intermediate was excited by LMCT excitation, and was reduced by an inner-sphere chloride ligand. The Cl^\cdot produced from this photochemical step, from reaction with excess Cl^- , was, in turn, quenched by ClBpin^- . And (2), a radical-chain mechanism is operative for $[\text{Ce}^{\text{III}}\text{Cl}_6]^{3-}$. This situation probably explains the shorter reaction time (24 h) using $[\text{Ce}^{\text{III}}\text{Cl}_6]^{3-}$ compared to that using $\text{Ce}(\text{III})$ guanidinate-amide photocatalysts (6 days).

Scheme 2. Proposed Mechanism.



Finally, we have summarized our recent contributions to launch the rational design and strategic applications of lanthanide photoredox catalysis into an Account article.⁵ The knowledge obtained from these studies will in term aid our design of new cerium(III) photosensitizers for photoluminescent materials with targeted properties and unknown photoredox catalysis. Overall, replacing the Ru/Ir metal photocatalysts by earth-abundant lanthanide metals is an attractive goal considering both economic and environmental benefits. This project has launched a new research direction in my group that has new secured secondary funding. A student was trained in inorganic and organic chemistry and obtained a postdoc position at a national lab.

Scheme 3. Lanthanide Photocatalysis.



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